Organic complexation in the geosphere for SR PSU

Summary

Organic ligands co-migrating from the SFR repository have the potential to significantly reduce the sorptive retention of certain radionuclides in the geosphere. While it is possible to make scoping calculations to identify which nuclides are most strongly affected and calculate approximate sorption reduction factors for use in transport calculations, there is significant uncertainty surrounding both the predicted magnitude of Kd modification and the geosphere pH buffering and dilution scenarios used as a basis for such calculations. The loss of barrier function (CCR-B2) case, however, represents a worst-case scenario for impact of organic complexation on radionuclide migration as it assumes zero sorption in the geosphere for all safety assessment relevant radionuclides even though this is likely to be highly over-conservative. The results of this calculation case documented in the radionuclide transport and dose calculation report (TR-14-09) indicate that the total loss of sorptive retardation in the geosphere has very little effect on the peak dose. This is because the main dose contributors in both the main calculation cases and the CCR-B2 calculation case are Mo-93 and C-14, which are not assumed to sorb anyway. The extent of radionuclide complexation in the geosphere by organic ligands therefore is not deemed a significant source of uncertainty for the SR-PSU safety case and can be assumed to be reasonably covered by the CCR-B2 calculation case study without the need for explicit modelling of these processes in detail. A possible complication, however, is that the CCR-B2 calculation case assumes loss of barrier function in the geosphere only, while the gravel backfill surrounding the repository retains its barrier function since it is deemed to be part of the near-field. This may not be fully conservative since loss of barrier function in the geosphere related to the presence of organic ligands might also be reasonably expected to have a deleterious impact on backfill sorption as well. As already indicated, however, this will have no impact on the main dose contributors which are assumed to be non-sorbing.

1   Background

This PM is a brief account of the impact of organic complexing agents from the SFR repository on the transport of radionuclides in the geosphere.

In previous safety assessments, the impact of organic ligands on geosphere sorption processes was neglected since uncertainties arising due to possible binding of nuclides were deemed to be already covered by pessimistic case calculations for loss of barrier function in the bedrock (i.e. no sorption in the bedrock). This was the argumentation used in Project SAFE (SKB 2001) to justify non-inclusion of organic complexation directly in the geosphere migration calculations. In SAR-08, the same reasoning was applied and a pessimistic case neglecting geosphere sorption was included (Thomson et al. 2008). A scenario of loss of barrier function in the bedrock was also included in SR-PSU assessment (SKB 2015) and fulfils the same purpose as in previous safety assessments regarding the possibility of sorptive reduction due to organic ligand binding.

In the SR-PSU safety assessment, the lowest element-specific rock matrix K_d values amongst the different choices given in Crawford (2013) for different representative groundwater types, were selected for use in radionuclide transport calculations (SKB 14a, b, 2015). Exceptions were elements and redox states deemed to exhibit sensitivity to pH and redox conditions (Np(IV), Pu(III/IV), Sn(IV), and U(IV)). For these elements where high pH conditions were judged to give deviating sorptive retention, K_d values for pH levels less than 10 were selected. This choice was based on the premise that high pH conditions were

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reasoned to be spatially limited to the immediate vicinity of the geosphere and unlikely to persist along migration paths to the surface.

In SR-PSU, however, the neutralisation of a high pH cement leachate plume was not modelled either in the hydrochemistry report (Auqué et al. 2013), or in the other supporting reports for the repository- and vault-scale hydrogeological descriptions (Abarca et al. 2013, 2014). Despite this, it is expected that high pH cement leachate will be effectively neutralised by mixing with unaffected groundwater along flowpaths in the geosphere within a short distance from the repository. Since the assumption of total loss of sorptive retardation in the geosphere is likely to be over-conservative, in the present work we have therefore sought to quantify the reduction of sorptivity that might reasonably be anticipated for key radioelements along flowpaths where dilution and neutralisation of leachate are considered to occur concurrently.

1.1 The calculation of sorption reduction factors

The report by Ochs et al. (2014) summarises the mechanisms and approach used to quantify the reduction in sorption caused by radionuclide binding with organic ligands in cementitious systems. The method is broadly the same as that discussed previously by Van Loon and Glaus (1998) and involves the calculation of sorption reduction factors (SRF's) which are used to modify recommended reference K_d values for sorption in the absence of such ligands. The sorption reduction factor is simply defined as the ratio of total radionuclide concentration and the sum of non-organic complexed species:

$$F_R = \frac{\sum \text{all species}}{\sum \text{non-organic complexed species}} = \frac{C_T}{C_T - C_{Org}} \tag{1}$$

Here, it is noted that the sorption reduction factor (SRF) is defined as the symbol F_R for simplicity and in keeping with mathematical naming conventions. Under the assumption that the sorption partitioning coefficient (K_d value) is proportional to the total concentration of dissolved nuclide, the SRF can also be defined in terms of the ratio of K_d in the absence (K_d), and presence (K_d^*) of an organic ligand:

$$F_R = \frac{K_d}{K_d^*} \tag{2}$$

The appropriate K_d value for use in transport calculations where organic ligands are present is thus given by:

$$K_d^* = \frac{K_d}{F_R} \tag{3}$$

In Crawford (2013), a correction factor approach is used to extrapolate K_d values recommended for a defined reference groundwater composition to differing in-situ groundwater compositions. The chemistry correction factor, f_{chem} is defined as:

$$f_{chem} = \frac{K_d}{K_d^0} \tag{4}$$

Where K_d^0 is the recommended value at the reference groundwater composition. If the chemistry correction factor is combined with the sorption reduction factor for organic ligand complexation, a total correction factor can be defined as:

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$$f_{tot} = \frac{f_{chem}}{F_R} \tag{5}$$

And thus:

$$K_d^* = \left(\frac{f_{chem}}{F_R} \right) K_d^0 = f_{tot} K_d^0 \tag{6}$$

2 Complexation of radionuclides in the geosphere with organic ligands

The calculation of sorption reduction factors for the geosphere is different to that for the near-field owing to the presence of large amounts of cementitious materials in the near-field. This has two effects: firstly, the pH at which radionuclide binding occurs is relatively constant at the level of the near-field cementitious porewater. Although this is dependent on the stage of cement degradation which varies over time, for all practical purposes, near-field leachate compositions are approximately static relative to the large compositional changes expected along migration paths in the geosphere. Secondly, in the near-field the concentration of organic ligands can be assumed to be approximately constant at a level defined either by the availability of organic ligands in the different waste packages or at a level determined by solubility limitations and sorption effects. For the waste packages and near-field zones it is therefore often sufficient to establish a single value for the sorption reduction factor that is conservatively fixed at a given level for the duration of the safety assessment time period under consideration.

In SR-PSU, sorption reduction factors for the repository were derived conservatively for organic ligands exceeding the no-effect concentration levels established in Ochs et al. (2014). In the radionuclide transport calculations made for SR-PSU, the SRF values were taken directly from the recommended data set (SKB 2014a, Tables 7-11a to 7-11c) assuming the maximum feasible concentration levels of organic ligands estimated by Keith-Roach et al. (2014) as a worst case scenario. The SRF values were applied to the recommended reference K_d values for concrete and bentonite/bentonite sand mixtures in the scenario for high concentration of complexing agents (scenario CCL_CA) described in SKB (2015). In this scenario, SRF values were applied only to near-field objects and rock matrix and crushed rock backfill were consequently assumed to be unaffected.

Along migration paths through the crushed rock backfill and geosphere, the concentration of organic ligands and pH will vary owing to hydrodynamic in-mixing with unaffected groundwater. In this work, the trend in groundwater composition is assumed to follow the same pattern as that outlined in Crawford (2013). The composition of the groundwater is thus assumed to be determined by the mixing fraction of cement-leachate and unaffected groundwater in a two end-member mixing calculation with the assumed presence of several mineral phases in equilibrium. The end-member corresponding to the unaffected groundwater was assumed to be the representative brackish-saline composition for temperate conditions defined by Auqué et al. (2013). The cement-leachate affected groundwater was modelled by superimposing portlandite, $Ca(OH)_2$ equilibrium on the reference groundwater without detailed consideration of cement porewater chemistry (forthwith this is referred to as the "OPC leachate"). Although this is a very simplified representation it was deemed in Crawford (2013) to be sufficient for making K_d scoping calculations in support of the geosphere K_d data recommendation.

A ferric hydroxide phase using the calibrated equilibrium constant derived by Banwart (1999) was assumed to be always present for both end-members and mixed groundwater while quartz, calcite, brucite and pyrite were permitted to precipitate if oversaturated. To quantify the impact of phosphate

complexation, hydroxyapatite was also assumed to be present to fix the dissolved concentration of phosphate. The general trend of bulk groundwater composition is shown in Figure 1 and Figure 2 as a function of cement leachate (OPC) mixing fraction. As can be seen from the curves, the transition from relatively unaffected to high pH conditions occurs over a short range of mixing fractions at around 3-5% OPC leachate (i.e. 95-97% diluted). Furthermore, the pH discontinuity is such that we can reasonably speak of a portion of the flowpath that is greater than, and respectively lower than pH 10 when discussing the groundwater chemistry.
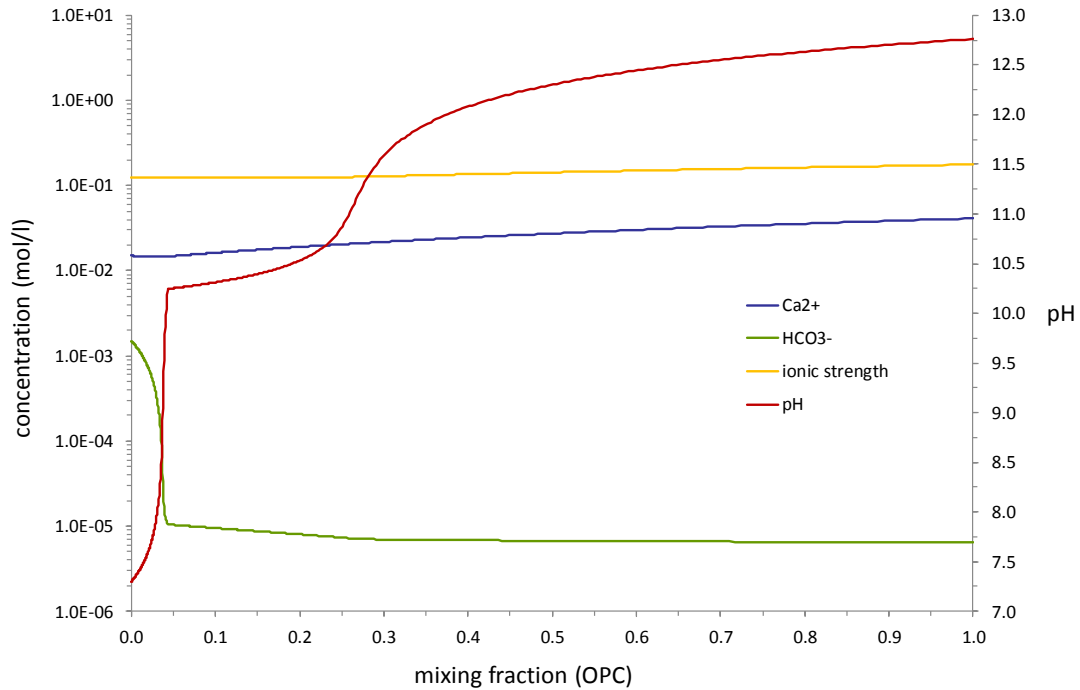
Figure 1. *Trend in bulk groundwater composition and pH as a function of cement leachate mixing fraction (OPC) assuming mixing of unaffected brackish-saline groundwater with Portlandite equilibrated brackish-saline groundwater.*

Figure 2. *Trend in Eh (mV) and pH as a function of cement leachate mixing fraction (OPC) assuming mixing of unaffected brackish-saline groundwater with Portlandite equilibrated brackish-saline groundwater.*
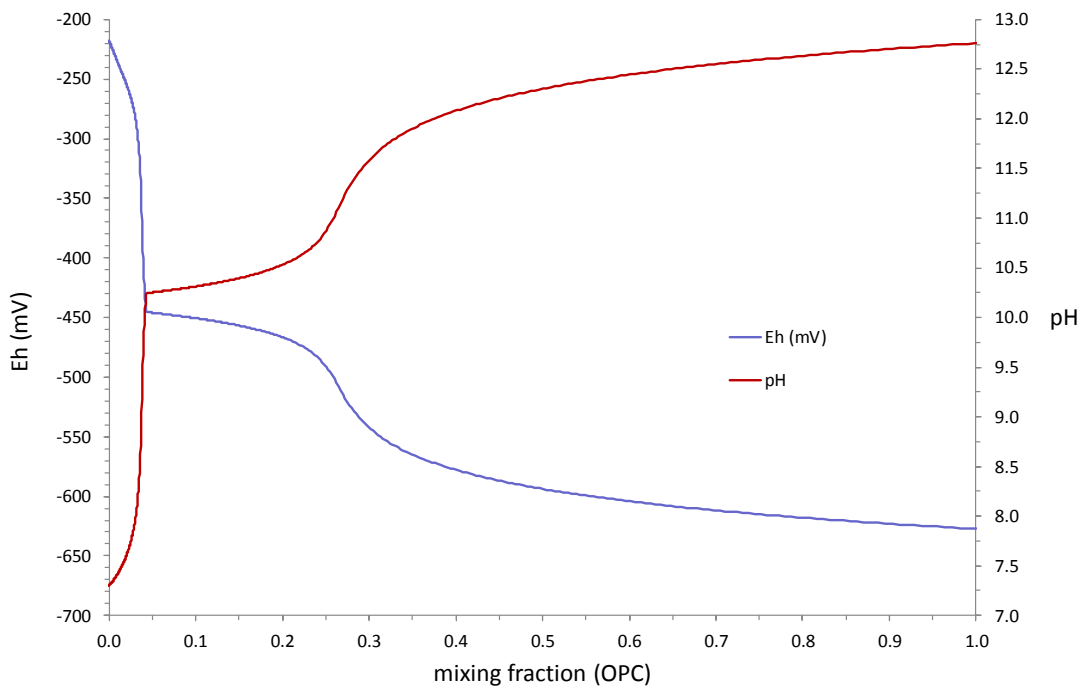
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2.1 Simultaneous simulation of sorption and organic ligand binding

In the calculations for the present analysis, this mixing model was extended to include organic ligands present in the OPC leachate at various source concentration levels spanning from 10^{-6} M up to around the maximum ligand concentrations given in Keith-Roach et al. (2014). The concentration of the organic ligand is therefore conceptualised to scale linearly from zero in unaffected groundwater (infinite dilution) up to the defined source concentration at an OPC leachate mixing fraction of unity. For these calculations, the ThermoChimie thermodynamic database (TDB) was used for simulations since the database includes the most important recognised reactions for radioelement-organic ligand binding (Giffaut et al. 2014). Some additional radioelement-ligand binding reactions not present in the TDB were included in the calculations based on thermodynamic data estimated in Ochs et al. (2014). Mechanistic sorption reactions were also included in the simulations to ascertain the theoretical impact of variable pH and Eh on the magnitude of sorption. The underlying mechanistic models for each radioelement were the same as previously used in support of the geosphere K_d data recommendation (surface complexation and cation exchange) with the addition of Cd and Pb which were not modelled in the original analysis.

The sorption reduction factor was calculated as a function of OPC mixing fraction using equation 1 and 2 independently for picomolar concentrations of radionuclide (10^{-12} M) and an excess of organic ligand ($10^{-6} – 10^{-2}$ M). This was partly intended as an internal check on the assumption that the SRF can be applied as a post simulation correction factor for the K_d value computed for reference groundwater conditions using a mechanistic sorption model. Although there are minor deviations at higher ligand concentrations owing to side reactions of the organic ligand with other groundwater components (affecting pH), the results were found to be sufficiently similar for all radioelement-ligand combinations tested that the assumption can be assumed to be valid. The main purpose of including mechanistic sorption reactions, however, was to obtain a simultaneous account of K_d variability arising due to the combined impact of groundwater compositional changes as well as organic ligand concentration during mixing dilution.

Although not all radioelement-ligand combinations could be assessed owing to a lack of thermodynamic data, enough combinations were studied that more general conclusions can be drawn for the safety assessment based on the same argumentation used for the near-field organic ligand binding processes (SKB 2014a). The actual combinations tested are listed in Table 1. Simulations were made for each radioelement-ligand combination at four to six different source ligand concentrations levels dependent on the relevant upper limit of organic ligand concentration as indicated in Table1 which are based on the values given in Keith-Roach et al. (2014). The organic ligands considered were isosaccharinic acid (ISA), nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), gluconate, citrate, and oxalate. In total, 102 separate simulations each containing 1000 realisations were made to ascertain the impact of variable pH and ligand concentration on the SRF and K_d value.

Table 1. Case studies considered in the present work for different radioelement-ligand combinations. Combinations for which thermodynamic data exist in ThermoChimie TDB are labelled "yes" while combinations lacking thermodynamic data are labelled "n/a" (not available). Yellow shaded entries correspond to simulated combinations. Yellow shaded entries also labelled "n/a" use estimated thermodynamic data, while green shaded entries indicate non-simulated combinations for which estimated data are available (Ochs et al. 2014). Red shaded entries indicate combinations for which thermodynamic data are not presently available and thus are not possible to quantify. The maximum feasible source concentration of each organic ligand is given at the top of the table.

	ISA	NTA	EDTA	Gluconate	Citrate	Oxalate
Element	$1.2 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$9.8 \cdot 10^{-3}$	$1.0 \cdot 10^{-5}$
Am	yes	yes	yes	yes	yes	yes
Cd	n/a	n/a	n/a	n/a	n/a	n/a
Ni	yes	yes	yes	n/a	yes	yes
Np	yes	yes	yes	yes	yes	yes
Pb	n/a	n/a	n/a	n/a	n/a	n/a
Pu	yes	yes	yes	yes	n/a	yes
Sr	n/a	yes	yes	n/a	yes	yes
Th	yes	yes	yes	yes	yes	yes
U	yes	yes	yes	yes	yes	yes

For some radionuclides, significant increases in K_d are anticipated at high pH levels whereas others are expected to exhibit decreases in K_d. Since the concentration of carbonate is relatively low at high pH conditions by way of the assumed calcite equilibrium, the variation of K_d at high pH for surface complexing solutes is thought to be largely due to competitive binding between aqueous phase hydrolysis reactions and the analogous binding reactions for the radioelement with hydroxyl groups on mineral surfaces. The resultant K_d value is then found to be dependent upon whichever of these processes dominates. Solutes whose sorptivity is dominated by cation exchange, on the other hand, are expected to only exhibit minor changes in sorptivity since the ionic strength hardly varies as a function of groundwater mixing and dilution in the geosphere for the modelled pH buffering process. Changes in sorptivity for these solutes are then mostly governed by small variations in speciation over the pH range investigated rather than competitive binding processes.

It should be noted that there is considerable uncertainty in the description of surface complexation sorption both in this work as well as in the modelling made in support of the K_d recommendations detailed in Crawford (2013). It is based on the assumed geochemical analogy between illite and biotite which is thought to be the dominant sorbing phase for many radioelements in granitic rock. The underlying sorption model is the same as that for Na-illite described by Bradbury and Baeyens (2009a, b). While many of the surface binding reactions are taken directly without alteration from the reference, some of the surface complexation reactions in this work that were not fitted in the original reference are assigned equilibrium constants from the linear free energy relation derived in the reference. While this is consistent with the conceptualisation of surface complexation in the reference, the absence of corroborating data for these surface binding reactions represents a significant source of uncertainty for the K_d predictions. This is of particular consequence for the assumed surface complexation reactions of U(IV), Np(IV), and Pu(III/IV) which were not parametrised in the reference. The predictions of sorptive variability for these elements and redox states must therefore be considered highly speculative and uncertain.

If complexation with organic ligands is also included in the calculation, there is additional competition for radioelement binding that depends on the concentration of the ligand. The prevailing pH also has an impact on this process since the optimal pH level for maximal binding of a radioelement is not necessarily at the pH of OPC leachate (pH $\approx$ 12.75). For NTA, EDTA, citrate, and oxalate the pH level associated with the strongest relative radioelement binding is typically much closer to that of unaffected groundwater. This must also be considered together with the degree of dilution of the organic ligand which is assumed to be proportional to the OPC mixing fraction.

The presence of an organic ligand always has either a negligible or a negative effect on K_d (i.e. K_d is reduced, never increases) in the modelled process. For some radioelements where increased sorption is expected at high pH, organic complexation either offsets some of the increase or gives rise to a decrease in the overall K_d value relative to that predicted for unaffected groundwater. In other cases, the K_d is expected to decrease significantly at high pH and the organic ligand complexation does little to change this. For organic ligands with optimal binding pH below that of OPC leachate, there is a maximum impact on K_d at some intermediate pH level on the mixing curve. For the most part, however, the sorption model predicts a decrease in K_d either at the pH of OPC leachate or at the optimal pH level for most radioelement-ligand combinations.

2.2 Impact on far-field migration calculations

The following flowpath averaging heuristic rule is given in Crawford (2013) for the impact of leachate dilution and pH buffering on K_d values in the geosphere surrounding the SFR repository:

$$\bar{K}_d \approx K_d^A \left(1 - \frac{x}{L}\right) + K_d^B \left(\frac{x}{L}\right) \tag{7}$$

Where, $\bar{K}_d$ is the flowpath average value, K_d^A is the value at the reference groundwater composition, K_d^B is the value at high pH, and the ratio x/L is the fraction of the migration path affected by high pH conditions (assumed to be pH > 10). Equation 7 assumes implicitly that the hydrodynamic transport resistance (F-factor) varies linearly along a flowpath. In other cases, the ratio x/L in equation 7 should be replaced with the F-factor weighted flowpath length fraction. In hydrogeological simulations, however, the F-factor rarely varies linearly along a flowpath and it is much more common for the bulk of the F-factor to be accumulated over short distances in the rock representing what could be termed radionuclide migration "pinch-points". The flowpath averaged K_d value then depends strongly on the pH conditions representative of the parts of the flowpath where the bulk of the hydrodynamic resistance is encountered. Equation 7 is only an approximation, however, based on the idea that the pH typically undergoes a rapid transition from strongly basic (pH > 10) to "normal" groundwater pH levels over a short distance as indicated by the sharp change in pH in Figure 1 and Figure 2 at an OPC mixing fraction just short of 5% (i.e. 95% dilution).

The actual dilution and pH buffering along individual migration paths was not studied in SR-PSU so it is not possible to say with a high degree of confidence how the flowpath average K_d should vary along flowpaths leading to the biosphere. Given the relatively (hydraulically) transmissive nature of the bedrock surrounding the SFR repository, however, and the presence of gravel backfill which functions as a hydraulic cage, we would expect dilution of OPC leachate to occur very close to the repository and the bulk of the geosphere should be relatively unaffected by high pH conditions.

Owing to the strongly non-linear variation of pH as a function of mixing fraction this assumption appears justifiable for the impact of pH in the absence of organic complexation. This is illustrated for the case of Am(III) in Figure where the blue coloured curve indicates the K_d value relative to the reference groundwater as a function of OPC mixing fraction in the absence of organic ligand (in this case, ISA). Although Am(III) is a less important dose determining nuclide, it is used here illustratively since its chemistry is relatively well understood.

As can be seen from the figure, there is a sharp jump in K_d at about 5% OPC leachate corresponding to the strong uptick in pH at the same mixing fraction as shown in Figure. When considering the impact of ISA complexation, the SRF varies more evenly (red curve) as a function of mixing fraction than the direct impact of pH on Am surface complexation. The optimal binding pH for ISA complexation of Am is slightly less than that of undiluted OPC leachate (pH ≈ 12.25), although the net effect of decreasing pH and ISA dilution means that there is little effect on K_d once the OPC fraction falls much below 5% (orange

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curve). If most of the dilution is deemed to occur in the immediate vicinity of the repository before the bulk of the hydrodynamic resistance is encountered in the geosphere, then very little impact of organic complexation is expected.
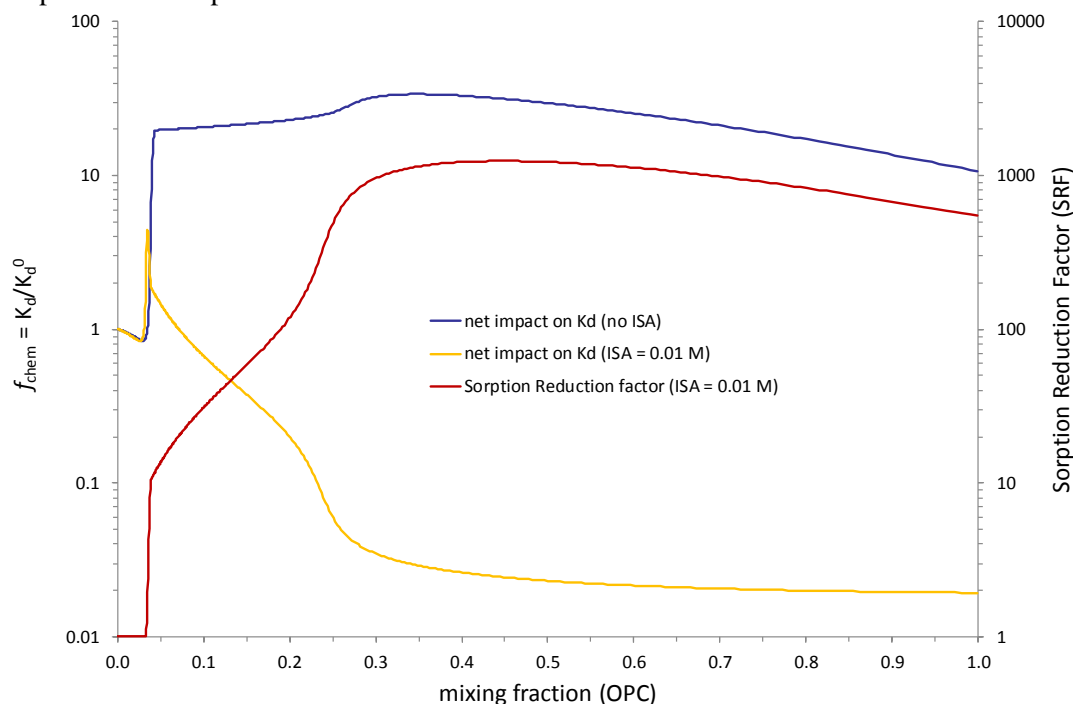
Figure 3.   Relative K_d variation predicted for Am(III) sorption in the presence (orange curve) and absence (blue curve) of ISA along a migration path plotted as a function of cement leachate (OPC) mixing fraction. The sorption reduction factor, SRF (red curve) is also plotted as a function of mixing fraction for reference purposes.

The corresponding results for sorption of Th are shown in Figure 4 and Figure 5. In this case, however, Th(IV) binds very strongly in solution with ISA which strongly offsets the increase in K_d at high pH which would be predicted in the absence of ISA. Here, the effect of ISA complexation persists to a much lower OPC mixing fraction (< 0.01%) than that for Am(III) which means that much more effective dilution is required to mitigate the impact of ISA complexation in the case of Th(IV) than for Am(III). In this case too, however, provided the bulk of the dilution and pH buffering occurs very close to the repository, we would not expect a large impact on K_d values.

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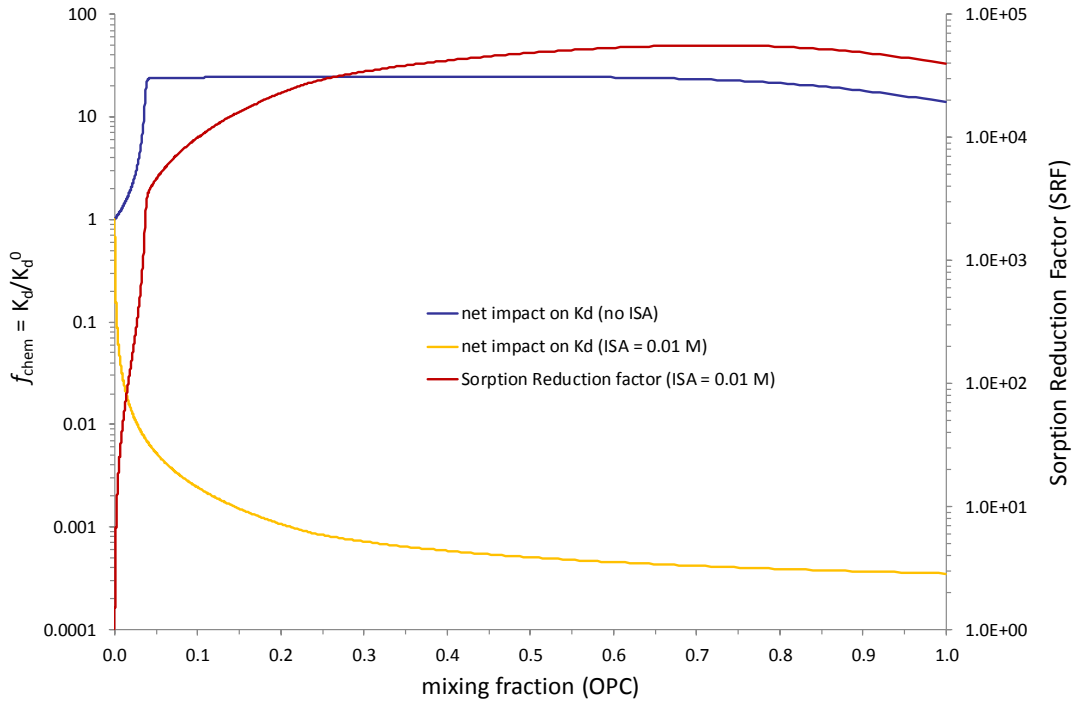Organic complexation in the geosphere for SR PSU

Figure 4. *Relative K_d variation predicted for Th(IV) sorption in the presence (orange curve) and absence (blue curve) of ISA along a migration path plotted as a function of cement leachate (OPC) mixing fraction. The sorption reduction factor, SRF (red curve) is also plotted as a function of mixing fraction for reference.*
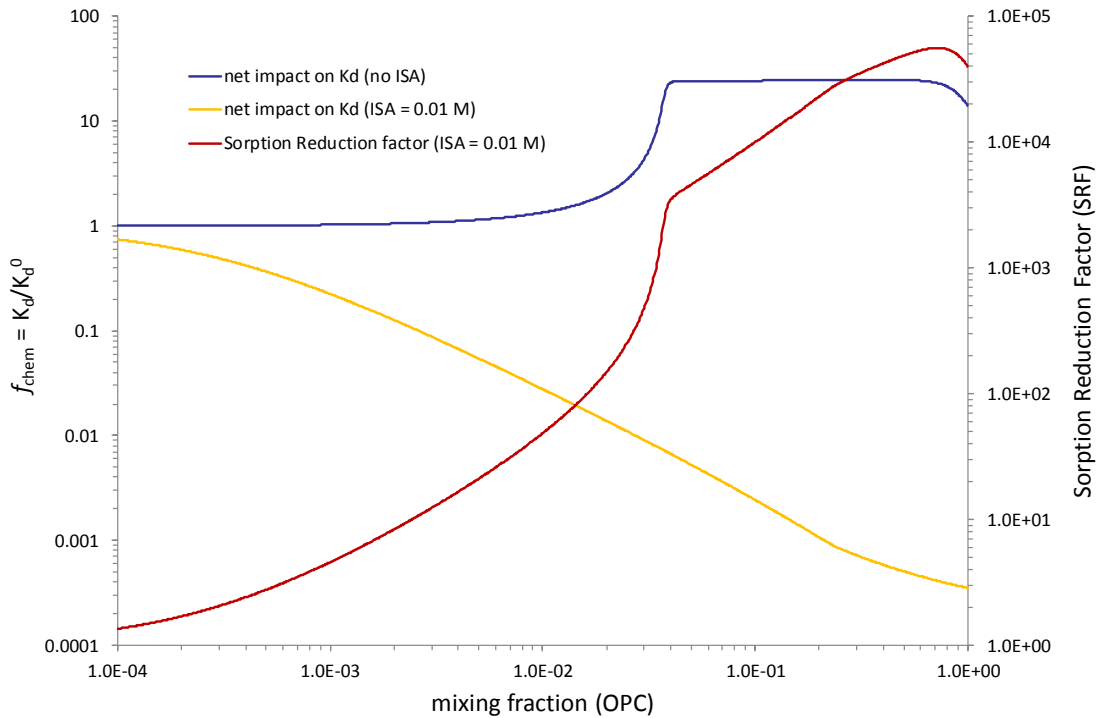

Figure 5. *Same as previous plot although with log scale for OPC mixing fraction to highlight detail at low OPC mixing fractions. Strong complexation of Th(IV) with ISA persists to very low mixing fractions (< 0.01%).*

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The simulations for Gluconate show a similar overall effect to that for ISA, although the maximum feasible concentration is about an order of magnitude less than that of ISA. Other organic ligands, however, are present at much lower maximum concentrations and have smaller impacts on the calculated sorption reduction factor. For Am(III) and Th(IV) the impact of these organic ligands for the most part does not quite offset the increase in K_d predicted for high pH conditions and therefore can be largely neglected. Am(III) binding by NTA deviates, however, in that complexation is relatively weak above pH 11 although increases significantly at lower pH levels. The sorption reduction factor here is strongly dependent on the interplay between the approach to optimal pH for binding and dilution as shown in Figure 6 and Figure 7. The corresponding case for binding of Th(IV) with NTA is shown in Figure 8 and indicates much weaker binding than that for Am(III).

Figure 6. *Relative K_d variation predicted for Am(III) sorption in the presence (orange curve) and absence (blue curve) of NTA along a migration path plotted as a function of cement leachate (OPC) mixing fraction. The sorption reduction factor, SRF (red curve) is also plotted as a function of mixing fraction for reference purposes.*

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Figure 7.   Same as pervious plot although with log scale for OPC mixing fraction. NTA complexation with Am(III) is relatively weak at the pH of unbuffered OPC leachate, although strengthens significantly at mixing fractions below 30% and persists to very low mixing fractions (< 0.01%).
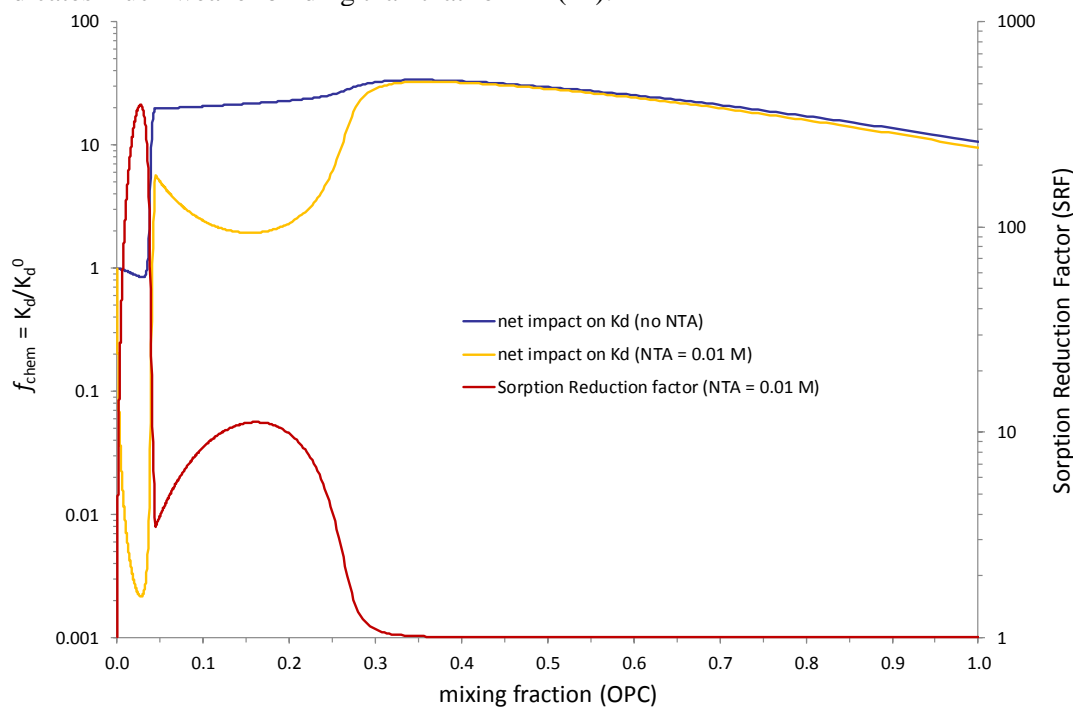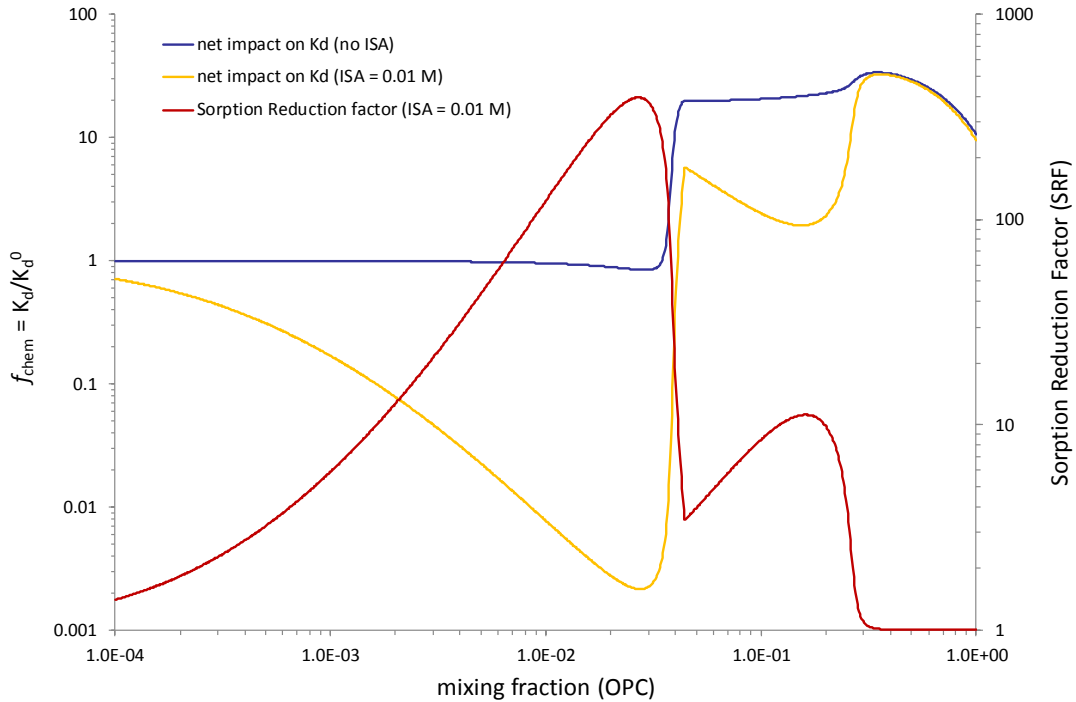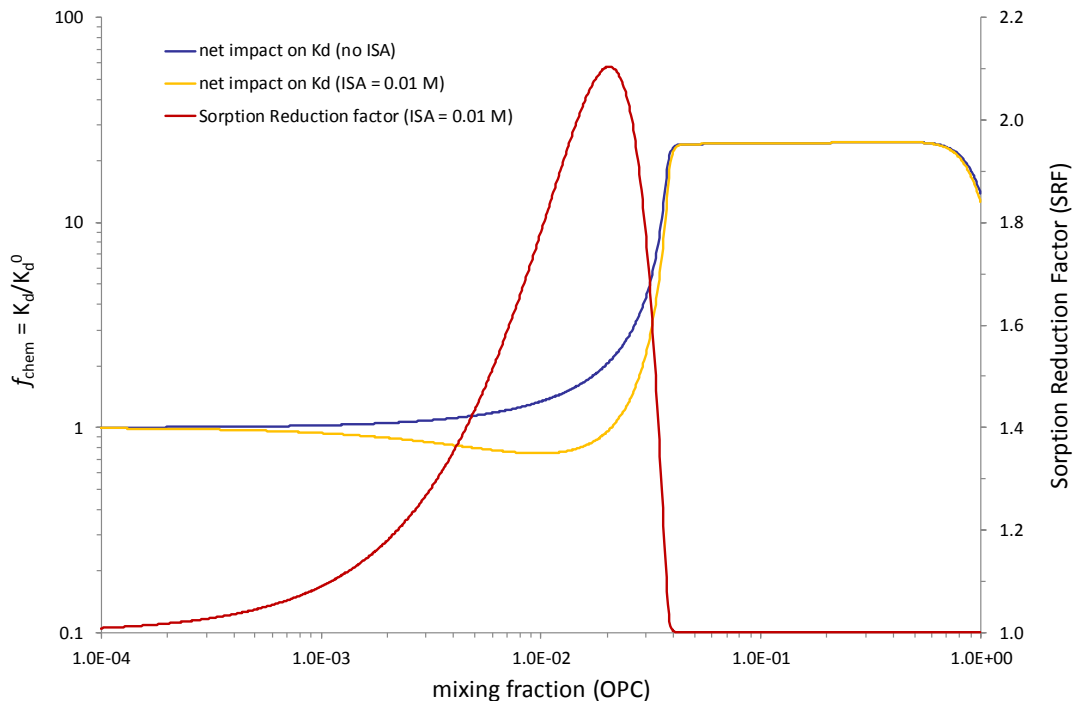

Figure 8.   Relative K_d variation predicted for Th(IV) sorption in the presence (orange curve) and absence (blue curve) of NTA along a migration path plotted as a function of cement leachate (OPC) mixing fraction. The sorption reduction factor, SRF (red curve) is also plotted as a function of mixing fraction for reference purposes. Th(IV) is only weakly complexed by NTA and very little impact on K_d is expected.

For the NTA complexation, the optimum pH for binding of Am(III) and Th(IV) is in the range 7.6 – 7.8 which is dependent on the interplay between the equilibrium for the complexation reactions and the dilution of the OPC leachate. If the NTA calculation is made assuming a constant concentration of undiluted NTA (i.e. modelled as a simple pH titration process without ligand dilution), then the sorption

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reduction factor is found to increase greatly with decreasing pH approaching that of the unaffected brackish-saline groundwater as shown in Figure 9.
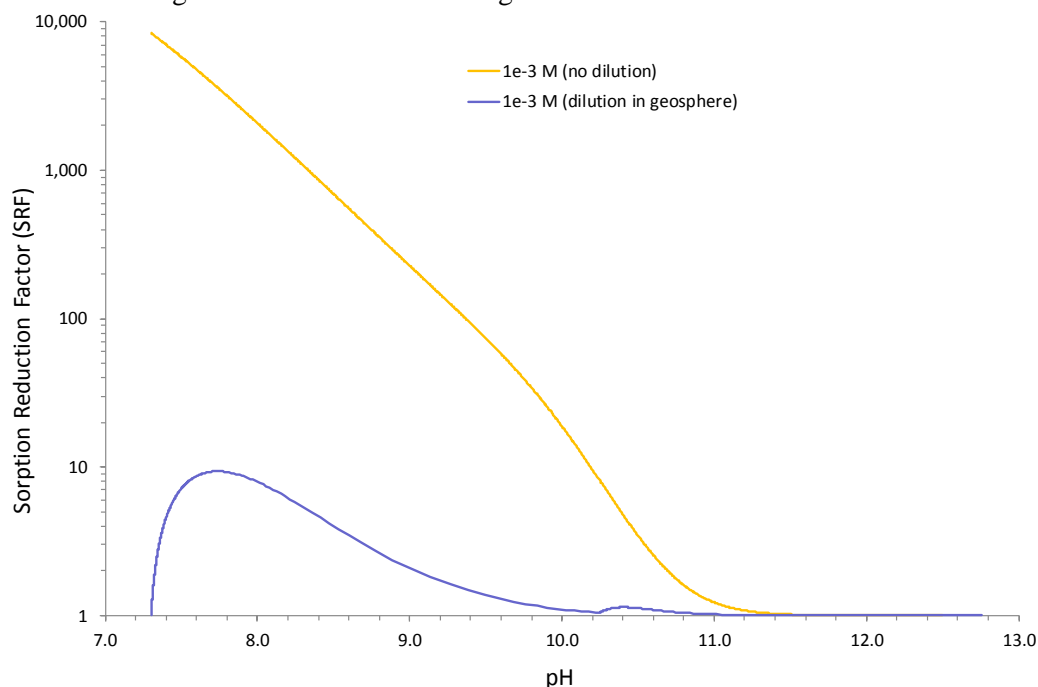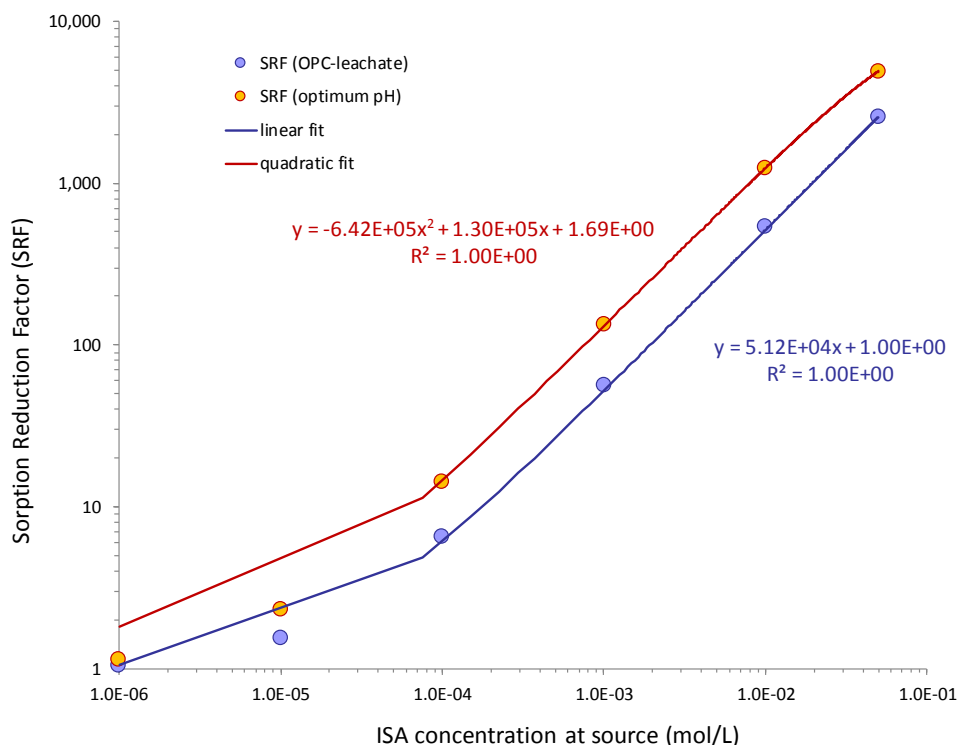

Figure 9.   Sorption reduction factor (SRF) for Am(III) binding with 0.001 M NTA plotted as a function of pH assuming no dilution in the geosphere (orange curve) and for the case of pH buffering by mixing dilution of OPC leachate (blue curve).

One interesting result of the simulations is that NTA is predicted to have a greater impact than EDTA for the sorption of both Am(III) and Th(IV) even though EDTA theoretically should bind more strongly. This is largely because of the presence of dissolved Fe which strongly competes with the simulated radioelements for binding of EDTA. In the absence of dissolved Fe, however, EDTA is found to bind these radioelements more strongly than NTA as would be normally expected. Since equilibrium with an effectively unlimited pool of ferric hydroxide mineral is assumed in the simulations, Fe dissolves and reduces the availability of free EDTA for binding with Am(III) and Th(IV) giving a much-reduced impact on the calculated sorption reduction factor.

One of the main results of the work was that the dissolved concentration of radioelement had very little effect on the calculated SRF provided the organic ligand was present at a significantly higher concentration. It was also found that the SRF at both the pH of unbuffered OPC leachate and at the optimal pH could be simply correlated with the initial organic ligand concentration at source. In most cases a linear or quadratic equation with a fixed intercept of unity at zero organic ligand concentration was sufficient to predict the magnitude of the SRF. An example for Am(III) complexation with ISA is shown in Figure 10.

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The chart contains the following annotations:

Legend:
- SRF (OPC-leachate)
- SRF (optimum pH)
- linear fit
- quadratic fit

$y = -6.42E+05x^2 + 1.30E+05x + 1.69E+00$
$R^2 = 1.00E+00$

$y = 5.12E+04x + 1.00E+00$
$R^2 = 1.00E+00$

Y-axis: Sorption Reduction Factor (SRF)
X-axis: ISA concentration at source (mol/L)

Figure 10. Sorption reduction factor (SRF) for Am(III) binding plotted as a function of ISA concentration at source at the pH of unbuffered OPC leachate (blue curve) and at the optimal radioelement binding pH 12.22 – 12.30 (red curve). Fitted curves are also shown for both data sets.

Similar correlations were developed for all radioelement-ligand concentrations and used to calculate the SRF values given in Table 2 for undiluted OPC leachate (pH ≈ 12.76) and in Table 3 at the pH of optimum (i.e. maximum) radioelement-ligand binding. The optimal binding pH level is given in Table 4 for each radioelement-ligand combination.

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Table 2.   Sorption reduction factors (SRF) predicted from the correlations developed for each radioelement-organic ligand combination at the pH of unbuffered OPC leachate and maximum feasible ligand concentration (at source) as given in the top row of the table.

	ISA	NTA	EDTA	Gluconate	Citrate	Oxalate
Element	$1.2 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$9.8 \cdot 10^{-3}$	$1.0 \cdot 10^{-5}$
Am	620	1.0	1.0	6,800	1.0	1.0
Cd	2.5	n/a	n/a	n/a	n/a	n/a
Ni	20	n/a	n/a	n/a	n/a	n/a
Np	330	n/a	n/a	n/a	n/a	n/a
Pb	1.7	n/a	n/a	n/a	n/a	n/a
Pu	112,000	n/a	n/a	n/a	n/a	n/a
Sr	1.0	n/a	n/a	n/a	n/a	n/a
Th	49,700	1.0	1.0	90,000	1.0	1.0
U	39	n/a	n/a	n/a	n/a	n/a

Table 3.   Sorption reduction factors (SRF) predicted from the correlations developed for each radioelement-organic ligand combination at the optimal binding pH and maximum feasible ligand concentration (at source) as given in the top row of the table.

	ISA	NTA	EDTA	Gluconate	Citrate	Oxalate
Element	$1.2 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$9.8 \cdot 10^{-3}$	$1.0 \cdot 10^{-5}$
Am	1,500	1,670	1.1	16,300	1.3	1.0
Cd	2.5	n/a	n/a	n/a	n/a	n/a
Ni	20	n/a	n/a	n/a	n/a	n/a
Np	330	n/a	n/a	n/a	n/a	n/a
Pb	410	n/a	n/a	n/a	n/a	n/a
Pu	112,000	n/a	n/a	n/a	n/a	n/a
Sr	1.0	n/a	n/a	n/a	n/a	n/a
Th	66,100	3.3	1.0	12,800	1.0	1.0
U	39	n/a	n/a	n/a	n/a	n/a

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Organic complexation in the geosphere for SR PSU

Table 4.   Optimal pH at level of maximum ligand binding for each radioelement-organic ligand combination assuming simultaneous pH buffering and dilution of organic ligand in the geosphere.

	ISA	NTA	EDTA	Gluconate	Citrate	Oxalate
Am	12.25	7.78	10.36	12.23	8.77	7.64
Cd	12.76	n/a	n/a	n/a	n/a	n/a
Ni	12.76	n/a	n/a	n/a	n/a	n/a
Np	12.75	n/a	n/a	n/a	n/a	n/a
Pb	10.53	n/a	n/a	n/a	n/a	n/a
Pu	12.76	n/a	n/a	n/a	n/a	n/a
Sr	n/a	n/a	n/a	n/a	n/a	n/a
Th	12.57	7.60	7.68	12.56	8.4	7.38
U	12.76	n/a	n/a	n/a	n/a	n/a

3   Conclusions

As can be seen from the analysis in the previous sections, the impact of organic ligand complexation on migration of radioelements from the SFR repository is difficult to account for in a robust fashion. This is partly due to the uncertainties involved in quantitatively predicting changes in geosphere sorption at high pH levels and partly to do with the difficulty involved in defining a robust scenario for the spatial and temporal development of high pH plume and its mitigation by dilution with unaffected groundwater in the geosphere. There are, however, three key processes that must be considered simultaneously to properly quantify the impact of organic complexation in the geosphere:

- The surface complexation sorption of radionuclides is influenced by elevated pH conditions. Some nuclides are relatively unaffected, some exhibit strong increases in K_d, whereas others exhibit significantly decreased K_d values. The variation of groundwater chemistry along a migration path (due to pH buffering caused by mixing with unaffected groundwater) therefore has a strong impact on the flowpath average K_d value that is appropriate for use in radionuclide transport modelling;
- The presence of organic ligands decreases the sorption of certain radionuclides. The impact on K_d is quantified using a sorption reduction factor (SRF) which is strongly correlated with organic ligand concentration. Dilution of the ligand concentration along migration paths by mixing with unaffected groundwater must therefore be considered to make accurate predictions of the SRF;
- The variation of groundwater pH along a migration path alters the strength of organic ligand complexation. The "optimal" pH for most efficient binding of radionuclides with organic ligands varies by radionuclide and ligand type and frequently differs from that obtained at the pH of undiluted OPC cement leachate.

The net impact of these three processes on sorption K_d values is highly dependent on the scenario of high pH plume development and must be considered on an individual basis for each radioelement-ligand combination. Unfortunately, not all safety assessment relevant radionuclides have well quantified thermodynamic data for organic ligand complexation, so in many cases conservative assumptions of strong binding or geochemical analogies must be invoked. For some radionuclides that are sensitive to pH and redox conditions, it is not clear whether K_d values should increase greatly, or be strongly diminished at high pH owing to a lack of relevant measurement data and consequential uncertainties in surface complexation model parameterisation.

Owing to these uncertainties it is difficult to formulate a suitably accurate deterministic case for geosphere radionuclide migration with organic ligand complexation given the available data. In SR-PSU, however, the loss of barrier function case CCR-B2 (no sorption in the bedrock) represents an absolute worst-case

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scenario for the uncertain impact of elevated pH conditions and organic ligand complexation in the geosphere (backfill excluded). The consequences of this calculation case for the safety assessment are discussed more thoroughly in the radionuclide transport and dose calculation report (SKB 2015), although the dose consequences barely differ from the main calculation cases (i.e. CCM-TR and CCM-EP) as indicated in Figure 10-1 of that report. This is because the main dose contributors are still Mo-93 and C-14 in the CCR-B2 calculation case of which are not assumed to sorb anyway. There is a slightly larger contribution from U-238 and U-235 in this calculation case, although it is relatively minor. The extent of radionuclide complexation in the geosphere by organic ligands therefore is not deemed a significant source of uncertainty for the SR-PSU safety case and can be assumed to be reasonably covered by the CCR-B2 calculation case study without the need for explicit modelling of these processes in detail.

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