

Memorandum: Retardation of radionuclide transport in cement affected groundwater – response to the request by SSM for supplementary information on retention of radionuclides (SSM2011-2426-110), item 1

James Crawford – Kemakta Konsult AB

2013-12-02

Innehåll

1	Introduction	3
2	SSM's request for supplementary information, item 1	4
2.1	The request – item 1	4
2.2	The reasons behind the request – item 1	4
2.3	SKB's interpretation of the request, item 1	4
3	Influence of elevated pH conditions on K_d values.....	6
3.1	Handling of groundwater chemistry variation and uncertainty in SR-Site	6
3.2	Groundwater chemistry at specific canister locations associated with radionuclide release	10
3.2.1	On the prediction of future groundwater states at specific locations	10
3.2.2	Possible impact of high pH leachate on groundwater compositional ranges	13
3.3	Mechanistic modelling of K_d variations associated with high pH conditions.....	19
3.3.1	Overview of modelling approach.....	19
3.3.2	Qualitative modelling in support of geosphere K_d recommendation at high pH.....	24
4	Conclusions	35
	References	37

1 Introduction

This memorandum deals with the request for additional information by SSM (SSM2011-2426-110) concerning the impact of alkaline leachate from cementitious materials used in the KBS-3 repository on the retardation of radionuclides in the geosphere. Scoping calculations to assess the likelihood of altered K_d for surface complexing radionuclides are made using a simplified single-site surface complexation model and groundwater compositions typical of the Forsmark site. Scoping calculations for cation exchanging radionuclides are assessed separately using the same model as used previously in the SR-Site K_d data report (Crawford 2010).

The surface complexation model assumes a geochemical analogy between the clay mineral illite and biotite which is thought to dominate sorption of radionuclides in granitic rock under normal pH conditions. Although a number of other groundwater ligands are important for radionuclide speciation, the behaviour at high pH is highly dependent on the competition between surface complexation binding reactions and analogous aqueous phase hydrolysis reactions which reduce the free concentration of the migrating nuclide. Whether an increase or decrease in K_d is expected at high pH relative to unaltered groundwater pH depends to a large extent on the number and type of surface complexes formed and the corresponding aqueous phase reactions recognised by the thermodynamic database used for calculations. For redox sensitive solutes, the situation is further complicated by transitions between redox forms which may be more or less sorbing than the redox state predominant in unaffected groundwater.

It is found that some radionuclides might experience a strong decrease in sorptivity relative to that for the reference state (unaffected groundwater), whereas others may experience a much increased sorptivity. The impact of either reduced or increased K_d in a limited zone of altered pH must be considered both in the context of the flowpath average for the actual migrating nuclide as well as possible effects on daughter nuclides in radioactive decay chains which may sorb more or less strongly than the parent nuclide. This also requires consideration of how much the near field source term in the transport calculations dominates the far-field dose rates of daughter nuclides. In this memorandum, the background groundwater chemistry at the release locations associated with canister failure is discussed and how an alkaline (high pH) plume would most likely impact on predicted far-field dose rates in the radionuclide transport calculations described previously in SKB (2010c).

2 SSM's request for supplementary information, item 1

Below, the relevant paragraphs in (SSM2011-2426-110) concerning item 1 are displayed. The request is first shown, followed by SSM's reasoning behind the request. The request for supplementary information is in Swedish and this text has been reproduced below, as shown in italic. In addition, translations of the paragraphs to English are provided. At the end of this chapter, a summary is given of SKB's interpretation of the requests.

2.1 The request – item 1

- "1. SSM anser att SKB bör redovisa hur tillförda konstruktionsmaterial som cement påverkar retardationen av radionuklider i geosfären"*

This translates to:

"SSM considers that SKB should produce an analysis of how construction materials such as cement influence the retardation of radionuclides in the geosphere"

2.2 The reasons behind the request – item 1

- "1. SKB:s hantering av retardation i geosfären karaktäriseras av ett förenklat angreppssätt där osäkerheter i den grundvattenkemiska utvecklingen implicit beaktas vid urval av K_d -värden för radionuklider (Crawford 2010), vilket diskuteras i samband med utvecklingen av grundvattnets salthalt och Eh. Delar av geosfären kan dock få ett väsentligt förändrat pH-värde i förhållande till platsundersökningsdata pga. tillförsel av stora mängder cement i slutförvaret som bergförstärkningar och tillverkning av pluggar (Bath 2012). Detta i förhållande till ursprungstillståndet förändrade förhållande kan bestå under lång tid då cementfaserna gradvis degraderas. SSM önskar att SKB redovisar hur tillförda konstruktionsmaterial som cement påverkar retardationen av radionuklider i geosfären."*

This translates to:

"SKB's handling of retardation in the geosphere is characterised by a simplified approach whereby uncertainties in the chemical evolution of groundwater are implicitly considered in the derivation of K_d values for radionuclides (Crawford 2010), which is discussed in the context of the salinity and Eh of the groundwater. Parts of the geosphere, however, may experience a profoundly altered pH level relative to the site investigation data owing to the use of large quantities of cement in the repository including rock reinforcements and plugs (Bath 2012). This altered state relative to the initial conditions can persist for very long periods as the cement phases slowly degrade. SSM requests that SKB explains how the presence of construction materials such as cement might affect retardation of radionuclides in the geosphere."

2.3 SKB's interpretation of the request, item 1

SKB makes the interpretation that the request in item 1 focuses upon whether the assignment of K_d values for the ranges of groundwater chemistry assumed in SR-Site is

conservative with regard to the possible influence of high pH conditions which may arise due to degradation of cementitious materials of construction and rock sealants. In this context, it is requested that SKB demonstrates that the possible changes in K_d which such processes imply do not have a deleterious impact on the predicted transport retardation of radionuclides released from a damaged canister.

3 Influence of elevated pH conditions on K_d values

In the following sections, the spatially and temporally variable groundwater chemistry predicted for the Forsmark site is examined in the context of radionuclide retardation processes and how these conditions might be expected to vary during a glacial cycle. How uncertainties related to groundwater composition were handled in SR-Site is discussed and the predicted groundwater composition at locations associated with actual canister failure in the central corrosion case are compared with the reference groundwater types assumed as a basis for the original data recommendations in the SR-Site K_d data report (Crawford 2010). Using a number of different groundwater compositions as initial reference states, qualitative calculations are then made to assess the likely impact of high pH conditions on K_d values for important radionuclides and how this might influence far-field dose rates relative to the central corrosion case discussed in SKB (2010c).

3.1 Handling of groundwater chemistry variation and uncertainty in SR-Site

In SR-Site, approximate corrections were made for deviations between laboratory conditions under which sorption data were obtained and in-situ conditions considered relevant for safety assessment. This included corrections for deviations in reactive surface area of mineral phases, differences in bulk mineralogy and, in a small number of cases where deemed feasible to do so, corrections for deviations in the application groundwater composition relative to groundwater types used in the laboratory investigations.

Owing to the absence of a suitably reliable mechanistic model for sorption of surface complexing solutes in association with granitic rock it was deemed only feasible to address the impact of evolving groundwater chemistry for the sorption of the cation exchanging solutes Cs(I), Sr(II), and Ra(II) where clear differences in sorptivity related to ionic strength were expected. For this purpose, a single site cation exchange model developed previously by Byegård et al. (1995, 1998) was used to calculate correction factors relative to an assumed reference groundwater composition.

The impact of groundwater composition on the sorption of Ni(II) was also evaluated since laboratory measurement data obtained during the site investigations and from literature sources indicated a clear correlation of sorptivity with ionic strength. Since the sorption of Ni(II) exhibits features of both cation exchange and surface complexation mechanisms, this was done in a semi-empirical fashion based on linear regression of measured K_d values with the ionic strength of contact solutions used in the laboratory studies. For the circumneutral to weakly alkaline pH ranges represented in the experimental data, the apparent impact of ionic strength on Ni(II) sorption may be directly related to ionic strength via a cation exchange mechanism, although it could equally well be an indirect impact of hydrolysis given that pH was approximately correlated with ionic strength for the groundwater types used in the laboratory studies. The use of an empirical regression model therefore captures the correct empirical trend of the site specific compositional data regardless of whether the true correlating variable

was pH (surface complexation), or ionic strength (cation exchange), or a mixture of both.

Since the K_d data recommendation for SR-Site was made some time prior to the safety assessment calculations of canister failure and subsequent radionuclide migration, it was not deemed feasible to track groundwater chemistry on the level of individual migration paths. Instead, it was necessary to consider projected statistical variations in groundwater chemistry throughout the entire repository volume based on the hydrochemical simulations detailed in Salas et al. (2010). For the chemistry correction factors (f_{chem}) used to predict K_d changes for the solutes Cs(I), Sr(II), Ra(II), and Ni(II) this implied treating the spatial variability of groundwater chemistry as a probability density function (pdf) describing compositional uncertainty (this is discussed in more detail in Section 3.3.1).

Since the pdf describing the spatial variability of f_{chem} is not necessarily lognormally distributed, the correction factor must be applied by convolution of the pdf for f_{chem} with the corresponding pdf describing uncertainty of the reference K_d value. In SR-Site, the convolution of uncertainty distributions was achieved by simple Monte-Carlo sampling from the associated pdf's. The assumed reference groundwater was the Forsmark Saline, Type III groundwater originally used in the laboratory investigations (see Table 1). This was deemed to be the most representative site specific groundwater for the current situation at the Forsmark site and is based on a water sample taken from borehole KFM03 in the length interval 639-646 m (Byegård et al. 2008).

Table 1. Groundwater compositions used in sorption studies for Forsmark and Laxemar site investigations. The compositions (mg/l) are based on groundwater sampled in specific intervals of the indicated boreholes and are deemed to be approximately representative of the main groundwater classes characteristic of each site.

Name	Type I	Type II	Type IIIa	Type IIIb	Type IV	Type V
Type	Fresh	Marine	Saline (Fm)	Saline (Lx)	Brine	Brackish
Borehole	HSH02	KFM02A	KFM03	KSH01A	KLX02	KLX04
Interval	0-200m	509-516m	639-646m	558-565m	1383-1392m	510-515m
Li ⁺	0.016	0.051	0.028	0.58	4.85	0.0152
Na ⁺	127	2 120	1 690	3 230	7450	691
K ⁺	2.16	33.3	14.2	12.4	32.6	3.19
Rb ⁺	(0.0252) ^A	0.0628	0.0393	0.0424	0.178	0.0424
Cs ⁺	(1.17×10 ⁻³) ^A	1.79×10 ⁻³	7.09×10 ⁻⁴	1.37×10 ⁻³	0.0186	1.37×10 ⁻³
NH ₄ ⁺	(0.0947) ^A	0.04	0.204	0.04	0.56	0.0319
Mg ²⁺	1.43	232	52.7	44.7	1.2	6.9
Ca ²⁺	5.21	934	1 470	2 190	14 800	234
Sr ²⁺	0.0695	7.95	16.9	32.2	253	4.67
Ba ²⁺	(1.29) ^A	0.188	0.0907	0.188	0.024	0.188
Fe ²⁺	(0.364) ^C	1.20	0.233	0.686	3.45	0.09
Mn ²⁺	0.02	2.12	0.318	0.46	1.11	0.109
F ⁻	3.03	0.9	0.204	0.967	(1.6) ^D	2.7
Cl ⁻	21.5	5 150	5 190	8 800	36 800	1 480
Br ⁻	(0.2) ^B	22	38.9	71	509	13.4
SO ₄ ²⁻	8.56	510	195	221	1 210	104
Si(tot)	6.56	5.2	6.28	4.7	2.6	6.63
HCO ₃ ⁻	252	124	21.9	12	42	51.4
S ²⁻	(0.01) ^B	0.05	0.0295	0.05	0.05	6.0×10 ⁻³
pH	8.58	7.1	7.55	7.45	6.8	7.83

- A) No measurements available, data imported from borehole KSH01.
- B) Based on detection limit.
- C) Based on the Fe-tot measurement.
- D) No measurements available, data imported from borehole KLX02.

As noted in Crawford (2010), treating a temporal-spatial variability as a statistical uncertainty in this fashion is not strictly correct as some parts of the geosphere may experience profound changes in groundwater composition over time, whereas other parts of the geosphere may hardly change at all. In fact, owing to the low connectivity and transmissivity of flow bearing structures in the repository volume, most of the temporal changes in composition occur in isolated regions which are not representative of the bulk of the repository volume. Using compositional statistics based on the entire repository volume to estimate correction factors therefore implies an f_{chem} distribution with a relatively constant central moment although with long tails evolving over time.

For SR-Site, the groundwater situation corresponding to the temperate time domain was considered to be most relevant for biosphere dose calculations since it is during this part of the glacial cycle that landscape dose factors are highest. Transport calculations based on this part of the glacial cycle will therefore conservatively overestimate radiological risk. In the hydrochemical calculations made by Salas et al. (2010), the temperate time domain is characterised by an initially saline dominated groundwater situation freshening over time due to meteoric infiltration. In the hydrochemical calculations, statistics of groundwater compositional parameters were compiled for times corresponding to 2 ka, 3 ka, 5 ka, and 9 ka from the initial state as indicated by the scheme depicted in Figure 1.

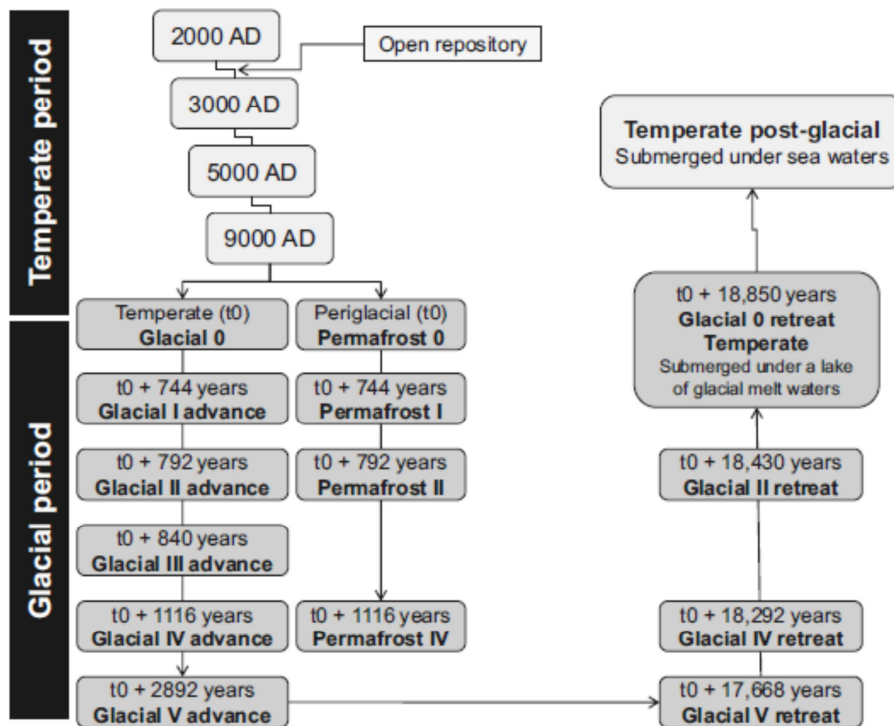


Figure 1 Overall scheme for the sequence of climatic and hydrological periods modelled in Salas et al. (2010) for the hydrogeochemical evolution of the Forsmark site.

For Cs(I), Sr(II), Ra(II), and Ni(II) the mean of the resultant pdf for K_d under the site specific groundwater compositions at different times during the temperate domain were only slightly shifted relative to the reference composition, although with increased statistical dispersion owing to the long tails of the pdf associated with f_{chem} . For the

cation exchanging solutes this was still deemed conservative since the evolution during the temperate time domain is towards lower ionic strength conditions thus implying stronger sorption (i.e higher K_d values) for these solutes over time. The f_{chem} correction factor therefore underestimates the extent of the K_d change in a conservative fashion for dose dominating migration flowpaths featuring low hydrodynamic transport resistance and high flow.

For the main surface complexing radionuclides considered in SR-Site, the situation was less clear with regard to chemical correction factors since the temporal trend could, at least in some cases, be inferred to be in the direction of decreasing sorptivity over time (i.e lower K_d values). This is largely due to the lower pH and higher carbonate levels associated with the meteoric component of the groundwater composition (this is discussed in more detail in Section 3.3).

Indeed, the site investigation data for Forsmark and Laxemar suggest a slightly reduced K_d value for Am(III)/Eu(III) in Fresh groundwater relative to Saline groundwater, possibly owing to the impact of carbonate complexation. The effect, however, was deemed to be weak relative to the overall data variability/uncertainty and could not be accurately related to solution composition. This was partly due to a drift in contact solution pH by about 1-1.5 pH units during the course of the laboratory experiments. The drift in pH was ascertained by post-mortem measurements involving a small number of control samples at the conclusion of the experiments, although these could not be linked to individual K_d measurements.

It was hypothesised that the pH drift might be related to CO_2 degassing of contact water in the gloveboxes used for the experiments, although the boundary conditions for this process were considered too uncertain to be used as a basis for quantitative estimation of chemistry correction factors. Re-equilibration of the carbonate concentration in the sample vessels to a lower partial pressure of CO_2 in the gloveboxes is now considered the most likely explanation since the same drift was observed for blank groundwater samples not in contact with geological materials. There were also other apparent data inconsistencies that made it difficult to argue for different K_d values in contact with different groundwater compositions. Principally this concerns the Marine groundwater type which exhibited inconsistent behaviour relative to the other groundwater types (see e.g. Figure D-3, pp 151 in Crawford 2010). For this reason, data for the Am(III)/Eu(III) analogue system were pooled over all contact solution compositions and assumed to represent an overall uncertainty distribution arising due to groundwater compositional uncertainty.

An additional complicating factor in the analysis was the existence of a time dependency in the laboratory sorption data for different crushed and sieved size fractions that could not be simply explained in terms of a single rate diffusive uptake. Although this could conceivably have been related to the pH drift of the contact solutions, it is considered likely that the bulk of the CO_2 degassing should have occurred prior to the addition of the radionuclide spike. The crushed rock samples had been pre-equilibrated with synthetic groundwater for a period of 89 days (with 10 water changes during the first 36 days) prior to spiking with the radionuclide tracer which should have provided ample time for sample degassing.

A very similar time-dependency was also noted for the cation exchanging solutes Cs(I), Sr(II), and Ra(II) which should not be affected by changes in pH or carbonate concentration to anywhere near the same extent as for the surface complexing solutes Am(III)/Eu(III), U(VI), and Np(V). The time dependent behaviour, although significant,

was deemed to be a minor component of the overall data variability/uncertainty and therefore the surface area corrected data sets were additionally pooled over all contact times without filtering with regard to particle size or contact time.

Recommended K_d values derived from literature data sources for surface complexing solutes were generally for water compositions that differed both from the site-specific compositions predicted by Salas et al. (2010) and those used in the SDM-Site laboratory programme. In these cases as well, since there was no acceptably reliable model (thermodynamic or empirical) that could account for uncertainty relating to groundwater composition, the only option was to pool data for all available water compositions assuming that all related uncertainties were implicitly internalised in the pooled data sets. Although not by any means ideal, the assumption was deemed to be nevertheless reasonable in the absence of more detailed data. This may be considered to be a source of bias that is very difficult to account for at the present time and will only become properly resolved when more detailed experimental data and surface complexation models of acceptable reliability become available for granitic rock types.

3.2 Groundwater chemistry at specific canister locations associated with radionuclide release

Since K_d data recommendations for SR-Site were made many months prior to the safety assessment calculations involving buffer erosion and corrosion of copper canisters, it was not possible to consider groundwater chemistry at specific release locations. Since this information is now available it is possible to revisit the particle tracking calculations and ascertain qualitatively whether the recommended K_d data values might still be considered conservative for radionuclide migration modelling.

The following sections deal with groundwater chemistry at a sample of the release locations calculated in SR-Site. The discussion has been restricted to the first 10 deposition holes associated with failure for 10 realisations of the semi-correlated DFN model in the central corrosion case as documented in Table 4-3 of the radionuclide transport report, TR-10-50 (SKB 2010c). Unless otherwise stated, all hydrogeochemical calculations presented in this document were made using PHREEQC v2.0 (Parkhurst and Appelo 1999) together with the SKB thermodynamic database (Duro et al. 2006), SKB-TDB (SKBdoc 1261302 ver 3.0).

3.2.1 On the prediction of future groundwater states at specific locations

It is very difficult to predict groundwater compositions at specific locations in the repository volume over 100,000 years into the future which is the earliest time at which a number of deposition canisters are probabilistically estimated to fail and begin releasing radionuclides. Furthermore, it must also be considered that the particular locations and local groundwater compositions associated with each of these failed canisters represents only a sampling of particular realisations of the underlying hydrogeological and hydrogeochemical models.

In the Climate Report for SR-Site, TR-10-49 (SKB 2010a), the reference glacial cycle of 120 ka duration is assumed to repeat a number of times up until the end of the one million year time perspective of the safety assessment reference evolution (SKB 2011). The timing and duration of the various time domains is shown in Figure 2 which is reproduced from the Climate Report (SKB 2010a).

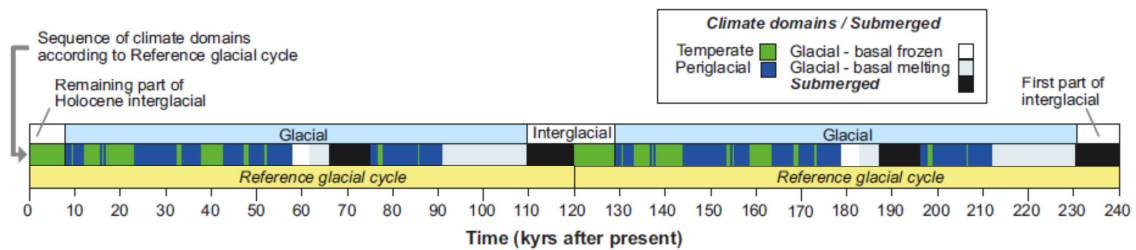


Figure 2 Evolution of climate at Forsmark for the coming 240 ka using repetitions of the reference glacial cycle. The figure illustrates how the reference glacial cycle is repeated in order to finally cover the 1 million year time perspective of the SR-Site reference evolution (see SKB 2011). The resulting duration of the locally defined interglacial periods is approximately 19 ka. For roughly half of that interglacial time, the Forsmark site is submerged under the Baltic water level. This figure is reproduced from Figure 4-35, pp 207 in TR-10-49 (SKB 2010a).

At the time of first canister failure in the deterministic calculations for the central corrosion case (SKB 2010c), the repository is expected to be fully submerged under the Baltic. The hydrogeological and hydrogeochemical configuration at this time would be reminiscent of the initial conditions assumed in the temperate time domain modelling for the present interglacial. At repository depth this would imply a predominantly glacial meltwater composition mixed with a smaller fraction of an old meteoric-glacial component (see Figure 3-63, pp 97, in Follin et al. 2007). At this time the Baltic water is most likely to be in the form of a ice meltwater lake rather than the marine/brackish composition existing today. Although this particular configuration is highly scenario specific, it is deemed nonetheless to be a reasonable starting point for a general discussion of post canister failure groundwater evolution during an approximately representative temperate time domain.

Starting from this configuration in the deterministic central corrosion case, the near field release rates are dominated by an instantaneous pulse release of moderately sorbing and non-sorbing nuclides, followed by an extended pulse (~1 ka duration) of radionuclides associated with the corrosion release fraction, and finally a sustained long-term release also including more strongly sorbing nuclides. The long-term release predicted in the radionuclide Transport Report (SKB 2010c) continues at least up until the 1 million year mark as shown in Figure 4-3, pp 64 of that report. The evolution of the geosphere during the time period subsequent to the canister failure is assumed to approximately follow the same pattern as interpreted to have occurred during the Holocene. As noted in SKB (2010c), the highest landscape dose factors are typically associated with temperate conditions when humans may be exposed to radionuclides that have accumulated in a wetland converted to arable land and when contaminated well water is utilised by humans and livestock. The groundwater situation existing during the temperate time domain is therefore considered most relevant for the radionuclide migration calculations.

Figure 3 shows the evolving groundwater composition at the location corresponding to the first canister failure together with the SDM-Site groundwater types given in Table 1. As can be seen from Figure 3, the groundwater at this location is initially close to the Forsmark Saline groundwater composition chosen as the reference groundwater for calculations. Of the first 10 failed canisters, four are within 20-30 m of the first failed canister position and therefore exhibit roughly the same temporal chemistry trend as that indicated in Figure 3. The other deposition holes are separated by larger distances and exhibit slightly different trends although the overall pattern is broadly similar.

It should be noted that since the first canister failure is expected at 114.5 ka in the deterministic case, it is difficult to strictly relate the glacial temporal evolution at this time with the reference glacial cycle since the compositional trends will not necessarily repeat in exactly the same way in each cycle. In spite of this, it is expected that the predicted groundwater compositions are still representative of the expected groundwater evolution and may be considered reasonable. The key issue here, however, is not the exact placement of canisters, but the fact that a broadly similar hydrogeochemical evolution may be expected at any release location associated with canister failure since such locations will be located in relatively high flow regions of the geosphere also associated with low hydrodynamic transport resistance.

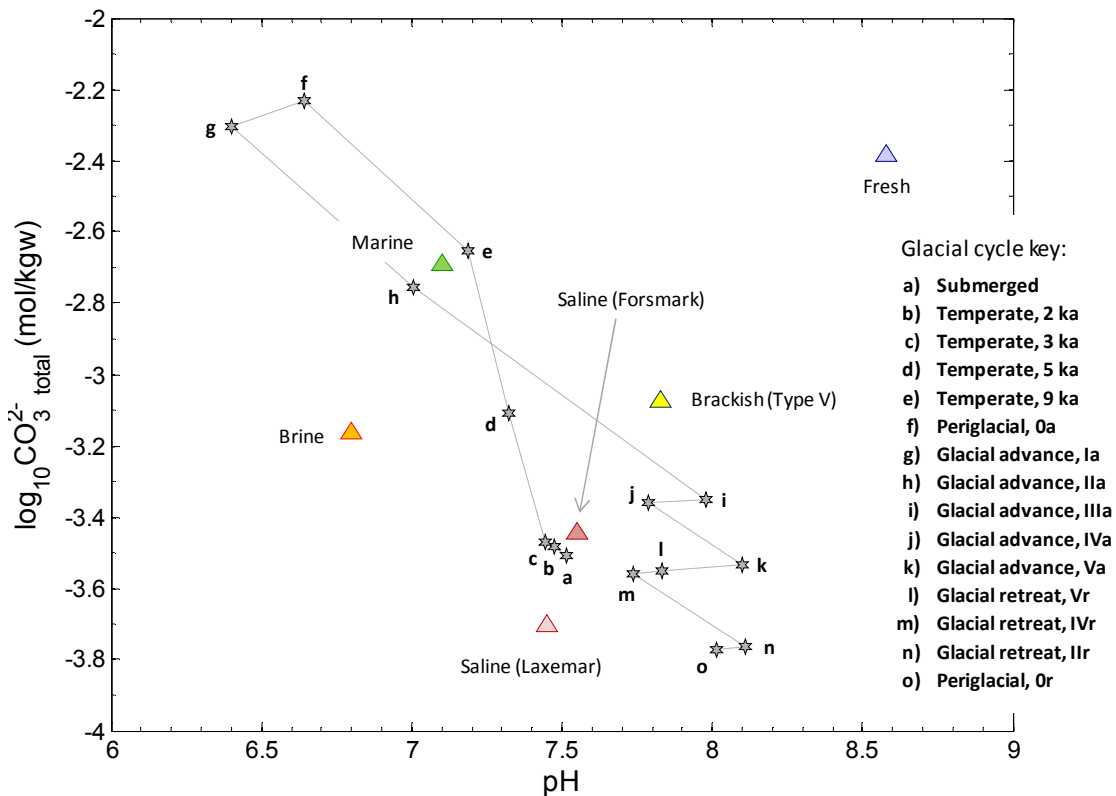


Figure 3 Groundwater composition (total carbonate vs. pH) at the location associated with first canister failure at 114.5 ka (hexagrams) compared with the groundwater types defined for the site descriptive modelling laboratory investigations (triangles). The groundwater composition is expected to evolve over the reference glacial cycle as indicated in the figure as calculated by Salas et al. (2010).

While the control volume surrounding the repository within which groundwater chemistry is reported by Salas et al. (2010) has a horizontal footprint of approximate size 2.3×2.7 km, it only extends vertically by 20 m up and down from -470 m elevation. Although there are some exceptions, most of the migration flowpaths identified by particle tracking follow a principally vertical trajectory from individual canister release locations to the biosphere. This means that it is only possible to track flowpath chemistry for a maximum of perhaps a few tens of meters depending on the particle trajectory. Over such short distances, groundwater compositions do not appear to change significantly along the studied pathlines. This is likely to be because there is very little retardation associated with the transport of the major groundwater components for the F-factors typical of canister failure locations. Any spatial changes in chemistry which do occur can therefore probably be interpreted as being due to

hydrodynamic mixing between adjacent flowpaths in the hydrogeochemical modelling. The changes in composition along the flowpaths, however, appear to be sufficiently small that the chemistry at the release location can be considered to be approximately representative of at least the first 10-20 m of a migration path and therefore detailed tracking of flowpath chemistry does not give much additional useful information from the available data.

3.2.2 Possible impact of high pH leachate on groundwater compositional ranges

In the safety assessment for the SFR repository at Forsmark currently in preparation, the impact of high pH leachate from ordinary Portland cement (OPC) and concrete materials of construction has been a major factor of significance. The calculations made in support of the K_d data recommendation (Crawford 2013b) in the SR-PSU safety assessment explicitly include scoping calculations of pH buffering resulting from OPC leachate mixing with unaffected groundwater. For this reason, the current analysis builds in large part on the work done in support of the SR-PSU K_d data recommendation. A comparison of the “type” groundwaters considered in SR-PSU (Auqué and Gimeno 2013) and the reference saline composition for SR-Site is given in Table 2.

Table 2 Composition of SR-Site reference saline groundwater (Crawford 2010) and representative compositions defined by for different time domains in the SR-PSU safety assessment (Auqué and Gimeno 2013).

	SR-Site	SR-PSU			
	Forsmark Saline reference composition	Temperate saline	Early Periglacial (20-40 ka)	Late Periglacial (extended global warming, > 40 ka)	Glacial-derived
pH	7.55	7.3	7.4	7.6	9.3
Eh (mV)	n/a*	-225	-210	-250	+400
Cl (mg/L)	5 150	3 500	190	90	0.5
SO ₄ ²⁻ (mg/L)	195	350	50	40	0.5
HCO ₃ ⁻ (mg/L)	21.9	90	300	200	22.7
Na (mg/L)	1 690	1 500	180	110	0.17
K (mg/L)	14.2	20	5	3	0.4
Ca (mg/L)	1 470	600	50	30	6.8
Mg (mg/L)	52.7	150	12	6	0.1
SiO ₂ (mg/L)	6.28	11	12	10	12.8

* The redox potential of the SR-Site reference groundwater was not stipulated in the original type groundwater compositions defined by Byegård et al. (2008).

As can be seen from Table 2 there are some key differences between the groundwater types considered in SR-PSU and the reference groundwater for SR-Site. The SR-PSU groundwaters are generally less saline than the SR-Site reference composition, being more meteoric in character with lower Ca concentrations, higher Na/Ca ratios, and much higher carbonate content. Although these are quite significant differences, the general pattern of pH buffering should be relatively similar for SR-Site groundwaters associated with failed canisters.

Figure 4 shows the composition (total carbonate vs. pH) of the SDM-Site groundwater types and those assumed in the SR-PSU hydrogeochemical modelling. Also shown are the mixing trends obtained when each of the SR-PSU groundwater types are mixed with

an OPC leachate of simplified composition (obtained by imposing Portlandite equilibrium on each groundwater type). For comparative purposes, the compositional drift of the groundwaters used in the SDM-Site laboratory experiments has also been plotted for each of the SDM-Site groundwater types where the pH change is interpreted as due to re-equilibration with a lower CO₂ partial pressure in the experimental glove boxes (for more details, see Crawford 2010). It is useful to note that the compositional trends associated with groundwater mixing with the simplified OPC leachate follow a similar pattern to that obtained by lowering the equilibrium pCO₂. This, however, is not unexpected since both processes are mutually correlated by the underlying assumption of calcite equilibrium in the calculations.

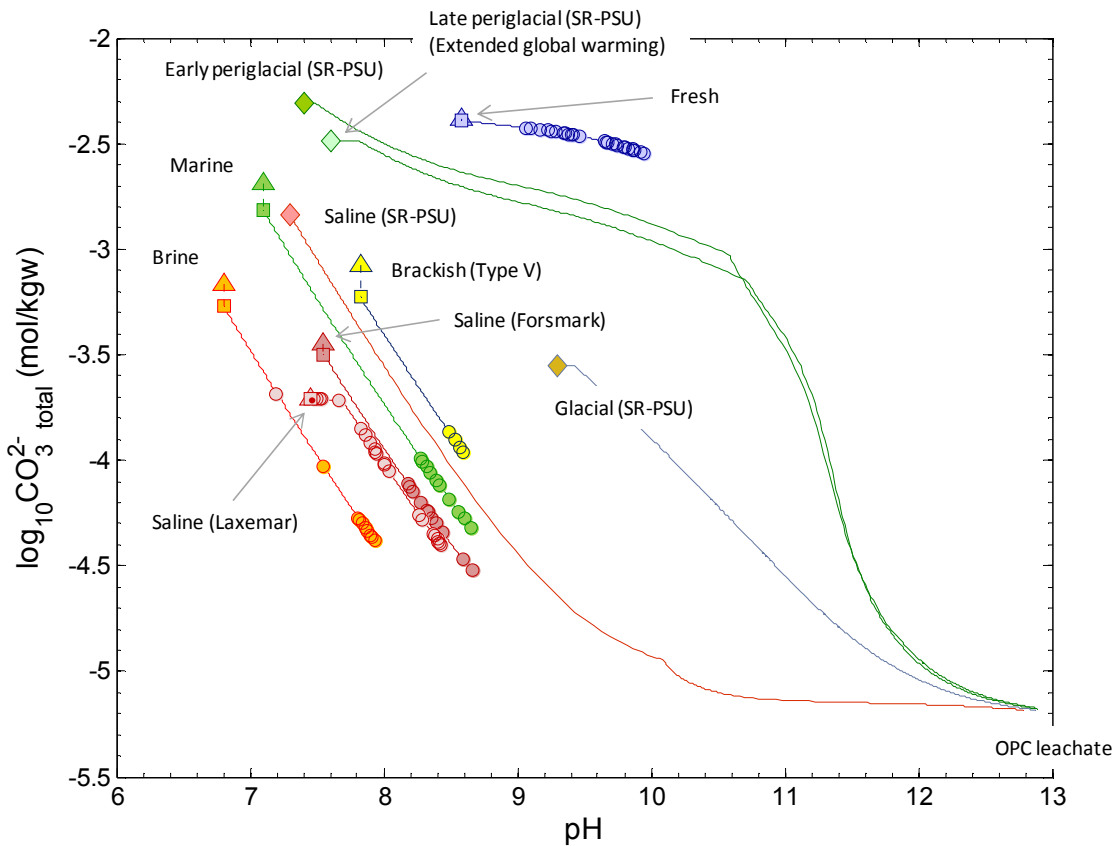


Figure 4 Comparison of groundwater compositions (total carbonate vs. pH) defined for use in the SDM-Site laboratory investigations (triangles) with compositions of “type” groundwaters assumed in the SR-PSU safety assessment (diamonds). The compositional drift of the groundwaters used in the SDM-Site laboratory investigations is indicated by circular markers and assumes degassing to a lower pCO₂ is responsible for the observed pH drift (Crawford 2010). The square markers represent the composition of the SDM-Site groundwaters upon re-equilibration of the specified compositions from Table 1 using PHREEQC (assuming an ambient laboratory temperature of 22°C). SR-PSU type groundwaters are calculated for an assumed in-situ temperature of 15°C (Crawford 2013b). The compositional trend related to mixing of the SR-PSU type groundwaters and OPC leachate is also shown.

In the SFR repository for low and medium level waste, which is the focus of the SR-PSU safety assessment, large amounts of ordinary Portland cement (OPC) are used both in the concrete structures of the repository itself as well as for the cement grout used to seal fracture intersecting tunnels. Ordinary Portland cement is strongly alkaline with a porewater pH typically equal to or exceeding 12.5. An important difference

between the radionuclide migration scenarios envisaged for SR-Site and SR-PSU is that only cement materials with a lower initial porewater pH (i.e. $\text{pH} \leq 11$) are to be used in the KBS-3 repository below the level of the top sealing (SKB 2010b). This is mainly to avoid potentially destabilising zeolitisation reactions of the bentonite buffer which might occur under high pH conditions.

It is suggested in Salas et al. (2010) that grouting materials might have the largest impact on geosphere hydrogeochemical conditions owing to their extensive use throughout the repository deposition tunnels and since they are used to seal flow-bearing fractures. Low alkalinity grouting materials such as Silica Sol (a suspension of nano-particulate silica particles) are not expected to influence groundwater compositions and therefore can be neglected over safety assessment timescales. Cement based grouts, on the other hand, may give rise to an alkaline plume that could potentially have a large impact on downstream groundwater chemical compositions. The alkaline components of cement grout porewater, principally Ca^{2+} in a long time perspective, will diffuse out of the grout into the flowing water and effect an increase in pH.

The spatial persistence of the high pH plume depends on the rate at which aquifer minerals react to buffer the alkaline leachate as well as the extent of hydrodynamic mixing with unaffected groundwater downstream. If there is a large inventory of grout, the plume may attain a steady state configuration for a long period of time. Eventually, however, the alkalinity of the grout will be slowly depleted and the grout itself will slowly evolve a different solid phase and porewater composition. If the contact surface area between the grout and flowing water is small, the rate of alkaline depletion may be slow and exhibit characteristics of a shrinking core type process (e.g. Levenspiel 1972).

The porewater pH of fresh OPC grout may initially be as high as pH 13, although after leaching of easily soluble alkali hydroxides of Na and K, this quickly stabilizes around 12.5 when Portlandite ($\text{Ca}(\text{OH})_2$) equilibrium can be assumed to dominate. The pH control by Portlandite equilibrium, however, is only a pseudo-stationary state and there is a gradual evolution of different calcium-silicate-hydrate (CSH) gel and crystalline phases over time that exert control over the porewater pH levels. As the compositional evolution progresses, the porewater pH gradually trends to successively lower levels until it reaches a final pH somewhere between 9 and 10, approximately representative of calcite equilibrium. If there is a large inventory of cement and low rate of alkalinity depletion, grout porewater pH levels ≥ 10 could persist up to 100 ka and possibly longer (see, e.g. Höglund 2013, Sidborn et al. 2012). It should be noted, however, that grout with high porewater pH levels still existing at this time will also most likely be associated with low permeable structures that are not typical of the radionuclide release locations featuring relatively high flow and poor hydrodynamic transport resistance. This is because any cementitious materials residing in release flowpaths are likely to have significantly degraded by this point.

The temporal persistence of a plume of elevated pH downstream from a cement grouted fracture depends both on the flow-wetted surface area of partially degraded grout in contact with groundwater and the rate of flow of that water past the grouted section of the fracture. The alkaline components of grout porewater will be depleted more rapidly in fast flowing groundwater than very slow flowing groundwater. If kinetic dissolution reactions of fracture minerals and rock matrix are neglected, then pH buffering of the OPC leachate will depend largely on hydrodynamic mixing processes downstream from the grouted section. For the purpose of scoping calculations, neglect of kinetic

reactions of aquifer minerals with OPC leachate is not important since the net impact on pH buffering and its concomitant effect on groundwater carbonate levels by way of calcite equilibrium should be qualitatively similar to the case of aqueous phase buffering by hydrodynamic mixing with unaffected groundwater (Crawford 2013b).

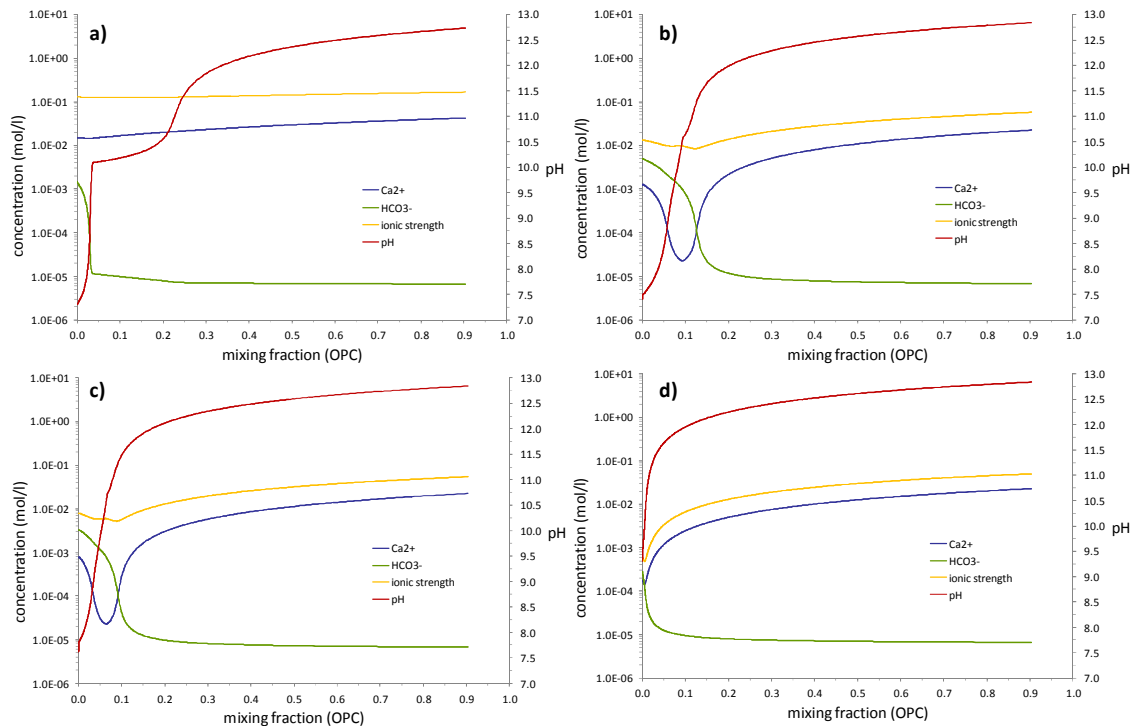


Figure 5 Trends in groundwater composition (total concentrations, ionic strength, and pH) as a function of mixing fraction for mixing of Portlandite equilibrated groundwater with unaffected groundwater. Plots are shown for a) Temperate Saline, b) Early Periglacial, c) Late Periglacial, and d) Glacial derived groundwater.

Figure 5 shows the trends of groundwater chemical composition for mixing of the simplified OPC leachate (Portlandite equilibrated groundwater), with un-affected groundwater as might occur along a migration path due to hydrodynamic mixing. These are the same calculations as presented in Crawford (2013b) in support of the SR-PSU geosphere K_d data recommendation. The corresponding trend in redox potential, Eh (mV) is plotted in Figure 6 together with pH as a function of mixing fraction for the four different groundwater types. The calculations assume $Fe^{2+}/Fe(OH)_3$ redox control based on the Banwart (1999) calibration for the Temperate Saline and both Periglacial groundwater types. The dilute composition of the Glacial derived groundwater, however, is poorly poised and it is very difficult to obtain reliable numerical convergence in mixing calculations using the $Fe^{2+}/Fe(OH)_3$ redox system. In this case, an $O_{2(g)}$ partial pressure of 1.6×10^{-19} atm. was specified instead to give the initial Eh of roughly +400 mV as specified for the Glacial derived groundwater in Table 2.

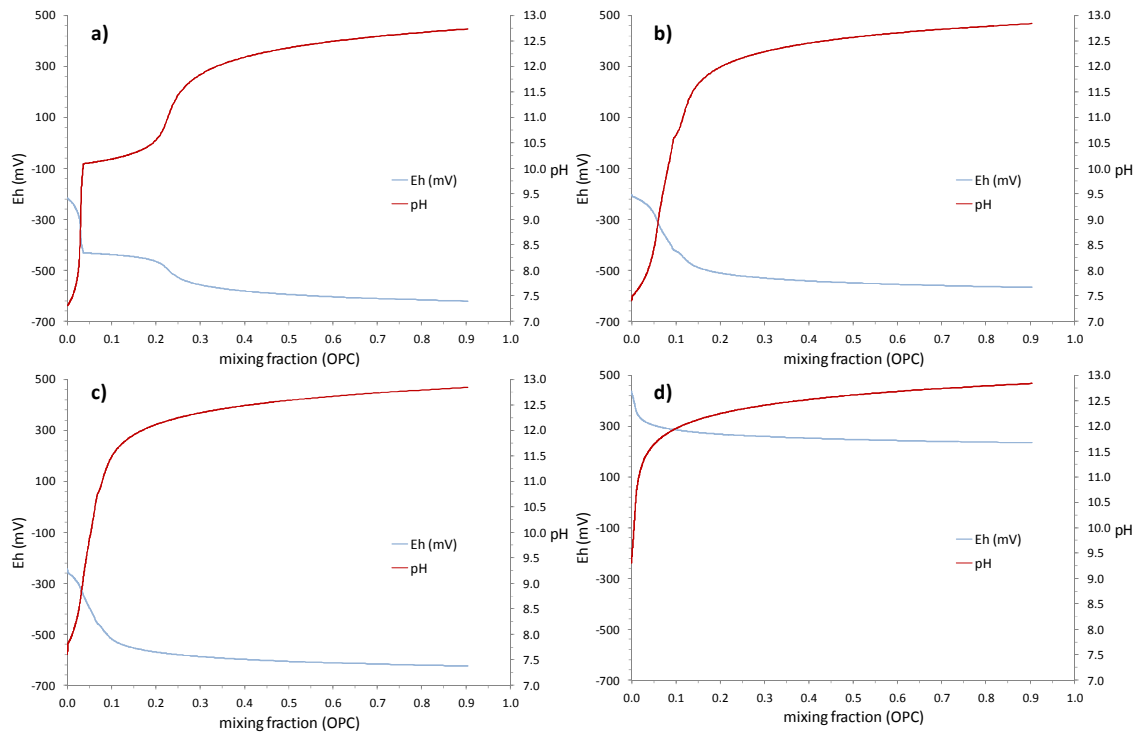


Figure 6 Trends in groundwater composition (Eh and pH) as a function of mixing fraction for mixing of Portlandite equilibrated groundwater with un-affected groundwater. Plots are shown for a) Temperate saline, b) Early Periglacial, c) Late Periglacial, and d) Glacial derived groundwater.

It should be clearly noted that the scoping calculations presented here which are based on groundwater mixing with non-aged OPC leachate (pH 12.5), must be regarded as an unlikely scenario for the conditions expected in the deep KBS-3 repository given that only low pH cement based materials are to be used. At the time of first canister failure at 114.5 ka, high pH porewater conditions may be considered extremely unlikely along dose-dominating migration flowpaths to the biosphere. Although the calculated examples are unlikely, the modelling exercise nevertheless highlights some important features of the process that are relevant to the discussion of possible impacts on geosphere K_d values.

Most importantly, the scoping calculations demonstrate that groundwater mixed with OPC leachate quickly attains a high pH at very low mixing fractions on the order of 5-20% OPC leachate (depending on the initial groundwater composition). When the pH is elevated by this process, carbonate concentrations are low owing to calcite equilibrium in the presence of high Ca^{2+} concentrations. At the same time, the redox potential decreases significantly owing to the impact of pH on $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3$ redox control. The results also demonstrate that the transition from high to low pH conditions occurs over a relatively narrow range of mixing fractions. As discussed in Crawford (2013b), if there is an approximately linear, or stepwise linear variation in the equivalent mixing fraction along a migration path, one would expect a relatively sharp transition between high pH and normal groundwater pH conditions as a function of distance. In such a case it is not unreasonable to speak in terms of a high pH (i.e. $\text{pH} \geq 10$) affected part of the geosphere and a part of the geosphere that is relatively unaffected.

Based on this idea, the net impact of an alkaline plume on radionuclide migration can be understood in a simplified fashion by consideration of the fractional flowpath length

associated with high- respectively low-pH conditions. For transport of a nuclide that is predominantly source determined (i.e. insignificant production by in-growth along a migration path), one could approximately define the flowpath average K_d as:

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

Where, K_d^A is the average K_d value for the part of the geosphere unaffected by alkaline leachate (i.e. the “reference groundwater”), K_d^B is the average K_d value for the high pH region, and x/L is the fraction of the flowpath length featuring high pH conditions (here arbitrarily defined as $\text{pH} \geq 10$). If K_d^B is much less than K_d^A , then this can be simplified even further to:

$$\bar{K}_d \approx K_d^A \left(1 - \frac{x}{L}\right) \quad (K_d^B \ll K_d^A) \quad (2)$$

Put simply, if the alkaline plume affects say, half the length of a migration path, and the K_d at high pH is known to be significantly reduced, then the flowpath average K_d should be roughly half the reference K_d value. If the difference between the limiting K_d values is sufficiently large, the actual value of reduced K_d at high pH does not have a large impact on the estimated flowpath average and the nuclide can be considered to be, for all practical purposes, non-sorbing in the alkaline affected region as per equation 2.

In the opposite situation, however, where the K_d increases at high pH, a significant K_d uncertainty remains with regards to the correct magnitude of the flowpath average. For nuclides that terminate a decay chain or have daughter nuclides with similar sorption characteristics, it may be conservative to neglect any increases in K_d if this cannot be adequately quantified. In situations where the nuclide is part of a decay chain with less strongly sorbing daughters, however, it might be necessary to perform sensitivity analyses to assess the likely impact of the uncertainty (say, assuming a K_d in the high pH region on the order of 10-100 times that for the reference groundwater).

It can be noted that equation 1 and 2 assume a constant proportionality between flowpath length and total flowpath hydrodynamic transport resistance (F-factor). Although this is sufficient for a simplified discussion of alkaline plume impact on radionuclide transport, it would be strictly more accurate to discuss flowpath averaging of K_d values in terms of the proportioning of hydrodynamic transport resistance along the flowpath instead of physical length. For the purpose of the present hypothetical discussion, however, this distinction may be neglected.

Although it appears highly unlikely that an alkaline plume would persist for long distances along a migration path over timescales exceeding 100 ka, any impact that significantly reduces the mobility of a decay chain member might still have radiological consequences for the transport of less strongly sorbing daughter nuclides since the effectively immobile parent nuclide would then constitute a much larger source of daughter activity by in-growth along the migration path. This, however, must also be considered against the fact that many of the more strongly sorbing parent nuclides (chiefly actinides) are already relatively immobile at source owing to solubility constraints and any additional retardation effect due to high pH conditions in the

immediate vicinity of the release location may not have a large net impact on biosphere dose rates if there is a large inventory of the nuclide in the leaking canister.

3.3 Mechanistic modelling of K_d variations associated with high pH conditions

Although (as already noted) there is no generalized thermodynamic sorption model of sufficient reliability that can be used to directly predict K_d values for surface complexing solutes in granitic rock, in the work performed for SR-PSU (Crawford 2013b) it was assumed that examination of results for simplified single mineral systems might be able to illuminate some of the more important effects of groundwater composition on sorption in a relative sense and help guide selection of appropriate K_d values for strongly alkaline conditions.

Given the complexity of supporting modelling calculations necessary to properly ascertain the impact of high pH conditions on K_d values for key nuclides and the time frame available, the following discussions are based largely upon the work documented in Crawford (2013b) for the SR-PSU safety assessment. Although the calculations are focused towards somewhat different conditions, the underlying principles and approximations used in this work can also be used to inform the present discussion relating to SR-Site radionuclide migration processes.

It should also be noted clearly that the deployment of thermodynamic sorption models in the selection and recommendation of K_d data for safety assessment in complex geological repository systems is still not a mature process and understanding is rapidly evolving. Even the state of the art guidance document (NEA 2012) recently produced within the OECD-NEA Sorption Project Phase III, stops short of recommending the use of thermodynamic sorption models in anything but a supporting role for this purpose. The following discussions concerning extrapolation to groundwater compositions for which there are no relevant empirical data must therefore be understood as being highly speculative and not well covered in the existing peer-reviewed literature. Much of the new material presented here, including that developed within the EU FP7-CROCK project (Crystalline Retention Processes in Rock) was also not available at the time of preparation of the original K_d data report for SR-Site, which must be acknowledged as being a feature of the ongoing developmental process.

3.3.1 Overview of modelling approach

There are two distinct modelling strategies used for applying surface complexation modelling (SCM) to complex environmental substrates such as granitic rock. The first, referred to as the generalised composite (GC) modelling approach attempts to model the composite mineral system based on the assumption of one, or more generic binding site types without consideration of the detailed properties of the mineral surfaces upon which sorption is occurring. The second, referred to as the component additivity (CA) approach involves careful consideration of the identity and proportion of total reactive surface area of individual minerals comprising the rock and combining separate SCM's for pure mineral phases from the literature under the assumption of linear additivity of resultant sorption. Both approaches are described in some detail in the review by Goldberg et al. (2007) and in the results of OECD-NEA Sorption Project (NEA 2005, 2012).

A notable difference between the two approaches is that the first involves fitting of an assumed model to measurement data, whereas the second is largely predictive in nature since it is not conditioned on the actual measurement data for the composite material.

Each approach has advantages and disadvantages. The first approach is appealing owing to its relative simplicity and since a good fit can often be found which interpolates measurement data reasonably well, although such models may not extrapolate well outside of their range of calibration. The second approach is arguably more mechanistically correct and since there is no direct calibration to measurement data the resulting models make testable, although not always accurate, predictions.

In the approach to K_d data recommendation adopted in SR-Site, the use of chemistry transfer factors (also referred to as correction factors) is proposed to extrapolate K_d values measured at a given groundwater reference composition to scenario- and site-specific groundwater compositions. The chemistry transfer factor, f_{chem} is defined simply as the ratio of the K_d value *expected* under application conditions and the corresponding value *expected* for the reference groundwater composition:

$$f_{chem} = K_{d(calc)} / K_{d(calc)}^0 \quad (3)$$

In the method description given in Crawford (2010), it is proposed that chemistry transfer factors be calculated theoretically if sufficiently robust empirical or thermodynamic models of sorption are available. The appropriate K_d value for the site specific conditions is then given by:

$$K_d = f_{chem} \cdot K_d^0 \quad (4)$$

Where K_d^0 is an empirically measured value representative of the reference groundwater composition. Usually the measured value of K_d^0 is subject to additional data uncertainties, so is defined as a probability density function (pdf). Since the future groundwater composition at any given location in the geosphere cannot be known to a high degree of certainty, the transfer factor is also treated as a probability density. The resulting pdf for the K_d obtained by convolution of the individual pdf's associated with K_d^0 and f_{chem} may then be interpreted as the conditional probability of K_d marginalized over the phase space of the uncertain groundwater composition.

Although in the SR-Site data recommendation, mechanistically calculated f_{chem} probability distributions were only actually used for the cation exchanging solutes Cs(I), Sr(II), and Ra(II) a relevant question to ask is why use such an approach when K_d values could, in principle, be calculated directly using the component additive approach without making any reference to chemistry correction factors? The main reason for the use of chemistry transfer factors is that it is usually not possible to specify key parameters of mechanistic models to the degree of accuracy necessary to give a reliable estimate of the K_d value in an *absolute* sense, although such models might still provide a mechanistically plausible account of *relative* sorptive variation. Here, the core assumption is that uncertain parameters in some situations might be partially normalizable (i.e. the unknown quantity proportionally affects both the numerator and denominator of equation 3 and therefore cancels out when calculating the ratio). Such parameters would typically include sorptive surface area, binding site density, and cation exchange capacity, although in certain situations might also encompass intrinsic surface reactive properties of particular mineral phases in the site specific rock.

In addition to this, it can be argued that an empirically measured data point for a given set of conditions will always be a better estimator of true behaviour *for those exact conditions* than a theoretical model which is, by necessity, always a simplified representation of the system in question. The use of a chemistry transfer factor that

adequately captures the main features of relative sorptive variation together with an accurate central estimate of K_d for a known and well-defined groundwater chemical composition should then always outperform direct theoretical estimates of K_d made using a model with highly uncertain parameterization.

In the cation exchange modelling used in the original SR-Site data recommendation, for example, it was not possible to specify the CEC of the rock matrix to an acceptable degree of precision which would have permitted estimation of K_d values directly. For cation exchange, the dominant mineral phases for sorption in granitic rock are expected to be biotite and its alteration product chlorite on account of their high cation exchange capacity relative to other minerals in the rock matrix. Since a single mineral can (i.e. biotite or chlorite), in most cases, be assumed to dominate cation exchange, normalizability was deemed a reasonable assumption for the sorption of Cs(I), Sr(II), Ra(II) in Forsmark metagranite thus permitting the use of a theoretically estimated pdf for f_{chem} . In this case f_{chem} was calculated using a simple, single site cation exchange model described by Byegård et al. (1995, 1998) and the projected groundwater compositions reported by Salas et al. (2010).

In the SR-Site data compilation, the theoretical calculation of f_{chem} also considered underlying uncertainties of the individual selectivity coefficients in the cation exchange model by propagating them stochastically in the analysis from their implied uncertainty distributions. The f_{chem} distribution calculated in this manner is therefore marginalized not only over the uncertain groundwater chemistry phase space, but over the uncertain, underlying thermodynamic constants as well. Handling uncertainties in this fashion provides a natural way of aggregating uncertainties from different sources into the final overall estimate of the pdf describing K_d under site specific conditions.

Although the above is deemed to be reasonable for systems where a single mineral can be demonstrated to dominate sorption, things are not quite as simple for surface complexing solutes in composite mineral systems such as granite. In granitic rock, a number of different mineral surfaces may contribute in part to the overall sorption that can be measured macroscopically. When component additivity models are used to predict sorption in such systems, it is not uncommon for theoretically derived K_d values to differ significantly to what is measured empirically. Reasons for this given in NEA (2012) include porewater compositional disequilibrium, occlusion of mineral surfaces in the rock matrix by adjacent mineral grains, surface modification by adsorbed groundwater components (chiefly Si and Al), and electrostatic effects in narrow pore spaces.

Given the compact nature of the pore spaces characterizing crystalline rock matrices, the apportioning of surface area between different mineral phases is not straightforward, particularly if mineral grains possess very different crystal sizes and habits which typically is the case. Since surface area estimates of individual mineral surfaces are not directly accessible in experiments it is usually necessary to base calculations on weighted fractions of the bulk specific surface area as measured using the BET method, or similar. Weighting fractions are difficult to assign since reported surface areas of pure minerals reported in the literature are not likely to be representative of those residing in the rock, nor will the appropriate reactive surface area necessarily be linearly related to the mineral volume fraction in the rock in any simple fashion. Furthermore, binding constants derived in laboratory investigation and reported in the literature are frequently derived for pure mineral phases that may (or, may not) have very different surface reactive properties to the natural mineral crystals residing in a complex, natural

rock matrix material. Given these uncertainties it is not altogether unexpected that component additivity models often fail to predict the correct magnitude of sorption.

If all sorbing minerals behaved similarly (i.e. similar relative changes in sorptivity) with respect to altered pH this might not be a big issue since a bulk correction factor could always be introduced to rescale the estimated K_d to an appropriate magnitude corresponding to empirical measurement data. Unfortunately, this is not the case and different minerals may dominate sorption characteristics at different pH levels in a way that does not permit simple rescaling in this fashion. For this reason, an accurate account of the relative proportions of different reactive surfaces is central to the fitness of a component additive model to reproduce macroscopic sorption behaviour. More generally, this is also why correction of laboratory K_d values with regard to bulk surface area increase due to crushing and grinding is a very blunt instrument that may lead to over-correction for mechanical damage effects relative to intact, in-situ rock.

In the EU FP7-CROCK project (<http://www.crockproject.eu/>), a hybrid approach combining features of both generalized composite and component additive methods was proposed that was intended for use in conjunction with crystalline rock where customary methods used to fit sorption models might not be feasible (Crawford 2013a). Although the proposed hybrid technique is speculative and still in an early stage of development, there are a number of general features of the modelling approach are informative and relevant to the present discussion.

The concept relies to a large extent upon the hypothesized existence of linear free energy relations (LFER's) between aqueous phase hydrolysis reactions of specific radionuclides and corresponding surface binding reactions. Such relations are well-established in the scientific literature (e.g. NEA 2012, Stumm and Morgan 1996) and have been used previously to estimate sorption binding constants for solutes where no experimental data exist (e.g. Bradbury and Baeyens 2009a, b, Dzombak and Morel 1990, Karamalidis and Dzombak 2010).

Figure 7 shows theoretically calculated sorption edges (K_d vs pH) for Eu(III) using binding constants derived from LFER's reported in the literature for specific mineral surfaces in a carbonate free, 1:1 symmetric electrolyte solution. This illustrates some important qualitative features of sorption in composite mineral systems. Although the full details of these scoping calculations are not strictly important for the present discussion, the reader is referred to Crawford (2013a) for additional details. The main feature of relevance is that for a given solute undergoing sorption, the different mineral surfaces exhibit different relative sorption characteristics with regard to impact of increasing pH. In the present example, the relative magnitude of sorption for Eu(III) on silica is predicted to increase monotonically with increasing pH relative to that observed at pH 8, whereas for illite, hydrous ferric oxide, and gibbsite the sorption is predicted to reach an optimum level at some pH in the circumneutral to mildly alkaline range and then decline with increasing pH.

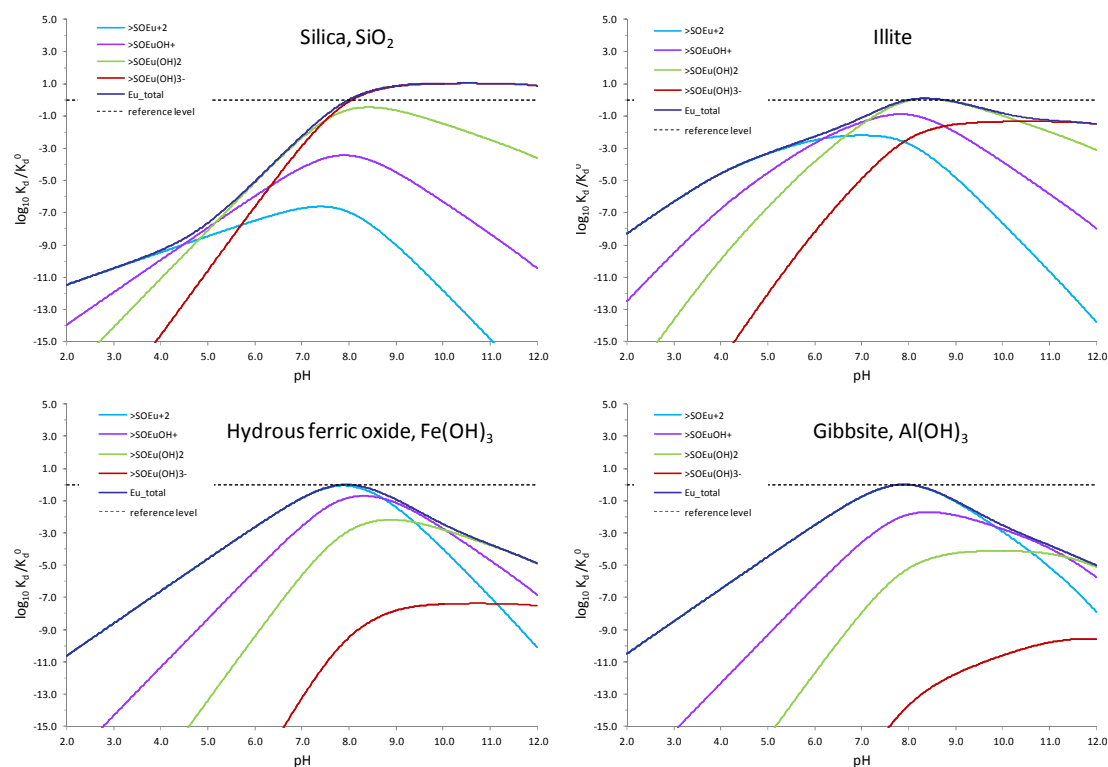


Figure 7 Theoretically calculated total relative sorption of Eu(III) and surface speciation as a function of pH on various minerals in a simple 1:1 electrolyte (0.1 M) background solution (no CO₂). The scoping simulations made using Phreeqc consider successive monodentate surface binding reactions corresponding to aqueous phase hydrolysis reactions recognised in the SKB-TDB (SKBdoc 1261302 ver 3.0) and slope factors (*m*) corresponding to linear free-energy relations (LFER's) reported in the literature for silica (*m* ≈ 0.60), illite (*m* = 0.83), hydrous ferric oxide (*m* = 1.17), and gibbsite (*m* = 1.32). The sorption data in each curve are normalised with respect to the calculated *K_d* at pH 8 as a common reference point and electrostatics have been neglected.

Similar behaviour is observed for a number of divalent, trivalent, and tetravalent cations and is related to competition between reactions involving surface binding sites and the corresponding aqueous phase hydrolysis reactions. The exact trend for each cation, however, varies depending on the particular hydrolysis reactions recognised in the thermodynamic database (TDB) used for the calculations and which surface complexation reactions are permitted. For cations that have several hydrolysis steps, the absence or presence of the higher reaction steps and values of associated reaction constants can have an overwhelming influence on whether the predicted *K_d* increases, reaches a plateau, or decreases at high pH. This typically can mean a difference of several orders of magnitude in the predicted *K_d* at pH 12 in the case of Eu(III). Not all mineral surfaces are equally sensitive to this uncertainty, however, as can be readily appreciated from Figure 7.

This relative sorptive trend can also be shown to be systematically related to the underlying LFER for each mineral surface. Importantly, it is the slope of the LFER that is of most importance for the shape of the sorption edge for a given solute in association with each binding site type. This is because the intercept of the LFER merely functions as a scaling factor to shift the sorption edge up or down (all binding reactions being affected equally), whereas the slope of the LFER alters the relative importance of successive surface species and thus modifies the shape. Although the absolute

contribution of each mineral surface to the overall sorption magnitude depends on the LFER intercept, the relative variation as a function of pH for each surface type is determined entirely by the LFER slope. This, of course, assumes that more than one surface species forms, which may not always be true so this must be dealt with on a case by case basis and ideally should be informed by spectroscopic measurement data.

Exploratory modelling indicates that mineral surfaces with larger slope factors such as ferric oxides might be associated with diminished relative cation sorption at high pH (in the absence of CO₂), whereas minerals with low slope factors such as quartz exhibit increased relative sorption at high pH. Minerals with middling slope factors, on the other hand, exhibit sorption behaviour that is somewhere in between these extremes. This implies that if more than one mineral contributes in a non-negligible way to the overall sorption in a mixture it is of great importance to accurately assess the proportion of each contributing reactive surface if one wishes to extrapolate to pH levels where there is no experimental data. The situation is complicated greatly, however, by the presence of CO₂ which can also reduce radionuclide sorption at higher pH levels due to competitive binding by carbonate ligands. Although neglected in these calculations, dissolved carbonate can also form ternary surface complexes with a number of actinides and lanthanides which further complicates matters (e.g. Marques Fernandes et al. 2008, 2010, Stumpf et al. 2002). In the case of groundwater mixing with OPC leachate in an otherwise closed system, however, carbonate concentrations are typically much lower at high pH levels owing to calcite equilibrium.

In granitic rock types, biotite is frequently cited as being the dominant sorptive mineral (e.g. NEA 2012) whereas quartz and other framework silicate minerals are often considered to only contribute in small part to the bulk sorptivity. Although an LFER is not available for biotite, it shares many crystallographic features with illite which may be considered to be a reasonable geochemical analogue. Unfortunately, empirical support for the assumption that biotite dominates sorptivity is not unequivocal, particularly in the case of actinides. In Kienzler et al. (2009), for example, Am was found to sorb inhomogeneously on all mineral surfaces with no correlation to biotite content. In other studies, e.g. Allard et al. (1985), Anderson et al. (2007), Beall et al. (1980) and Ittner et al. (1982) a relative preference for sorptive association with biotite has been identified. As might be inferred from the previous paragraphs, the relative contribution of different mineral surfaces to the overall sorptivity in granitic rock may vary non-trivially as a function of pH. The apparent inconsistency of empirical data could therefore potentially be a signature feature that might have been overlooked in autoradiographic attribution studies involving granitic rock.

As can be readily appreciated from the above, there are a great number of uncertainties that are difficult to quantify if one wishes to extrapolate K_d values to high pH levels. Since the hybrid component additivity model for Forsmark metagranite described in Crawford (2013a) is highly speculative and still in a early stage of development, a much simplified approach was therefore adopted for the corresponding SR-PSU data recommendation (Crawford 2013b). This is discussed in the following section.

3.3.2 Qualitative modelling in support of geosphere K_d recommendation at high pH

If biotite is assumed to be the dominant sorbing mineral and sorption in association with quartz and feldspar minerals is neglected, this might imply under-prediction of K_d at high pH levels for certain nuclide cations (i.e. based on the discussion in the previous section). For many radionuclides this could be considered a conservative assumption,

although for some decay chain members the impact of this might need to be addressed by additional sensitivity calculations in migration calculations. As noted in Section 3.2.2, however, this must also be considered in the light of the mobility of the parent nuclide at source which may have extremely limited solubility. In such cases, the presence of a zone of increased retardation close to the canister release location may not have a large impact on far-field dose rates since the inventory in the canister will still dominate as a source term for the less strongly sorbing daughter nuclides in the decay chain that are potentially affected.

Following this reasoning, Crawford (2013b) assumed that biotite was the dominant sorbing mineral in Forsmark metagranite and that the non-electrostatic surface complexation model for illite developed by Bradbury and Baeyens (2009a, b) could be used as an approximate geochemical analogue for biotite (henceforth, the BB09 model). All calculations were made assuming picomole radionuclide concentrations together with a much larger abundance of binding sites to ensure sorption linearity and so that the nuclide itself would not exert an influence on the bulk composition of the contacting solution.

It must be remembered that such simulations can only be considered to give very rough indications of possible (or, at least feasible) trends since the contact water compositions and the pre-conditioned state of the illite upon which the literature model is calibrated are quite different from the physicochemical conditions under present consideration. At the very least, the surface complexation model for illite is conditioned on experimental data for a symmetric 1:1 electrolyte (NaClO_4) and it is not clear how well this might extrapolate to mixed electrolyte systems such as the site specific groundwaters. Furthermore, at pH levels above about 11 the instability of silicate mineral surfaces makes predictions of sorptive chemistry even more uncertain.

Cation Exchangers

For the cation exchanging solutes Cs(I), Sr(II), and Ra(II) the same cation exchange model as used previously in Crawford (2010) was adopted although using the groundwater compositions estimated for the SR-PSU specific conditions and assuming mixing with OPC leachate. Although there is some variation in K_d over the range of compositional variability implied by mixing with OPC (see ionic strength variation in Figure 5), the changes are sufficiently small relative to the uncertainty of the calculations that K_d values can be reasonably assumed to be unaltered by high pH conditions. Although increased hydrolysis of these cations at high pH could conceivably reduce sorptivity, this effect was found to be insignificant. Since the principle radioisotopes of Cs and Sr do not participate in decay chains, neglect of the slightly increased K_d values predicted for high pH may be considered a conservative assumption. The transport calculations in the SR-Site radionuclide Transport Report (SKB 2010c) do not consider many of the much shorter lived daughter nuclides subsequent to ^{226}Ra (with the exception of ^{210}Pb), so the K_d value in that case can also be conservatively assumed to be unaltered by high pH conditions. The safety of this assumption for ^{210}Pb far-field dose rates, however, may need to be confirmed by transport calculations considering the decay chain subsequent to ^{226}Ra .

Non Redox-Sensitive Surface Complexers

Only a small subset of representative surface complexing nuclides were examined with respect to the influence of high pH conditions in the SR-PSU data recommendation (Crawford 2013b). For the radioelements considered to be insensitive to redox

conditions this included Am(III), Ni(II), and Sn(IV). As in SR-Site, Am(III) was assumed to be a geochemical analogue for all other trivalent actinides and lanthanides.

Calculations made using the BB09 model for Am(III) and the SR-PSU groundwater compositions indicated that K_d values at $\text{pH} \geq 10$ could be larger by as much as 10-100 times (or more) than the corresponding values calculated for the reference groundwater used in the calculation (pH 7-8). For the fission product isotopes of Eu, Ho, and Sm that have no daughter nuclides, the neglect of increased K_d in response to high pH conditions can be assumed to be conservative in transport calculations.

Of the decay chain isotopes, Am and Cm are potentially problematic since they reside high up in the $4n$ (^{248}Cm), $4n+1$ (^{245}Cm , ^{241}Am), $4n+2$ (^{246}Cm), and $4n+3$ (^{247}Cm , ^{243}Am) decay chains. None of these, however, appear as important contributors to the near-field dose equivalent source term (Figure 4-2, p 64) for the central corrosion case in the radionuclide transport report for SR-Site (SKB 2010c) and therefore it is difficult to see any significant increase in K_d for the geosphere having a large impact on far-field dose rates via daughter nuclides (although ^{243}Am does make a non-negligible contribution in the initial advection case).

The ^{227}Ac nuclide from the $4n+3$ decay chain features as an important dose contributor in the near-field source term in the central corrosion case on account of its short half-life (22 y). An increase in K_d for this trivalent nuclide will have little effect since all daughter nuclides decay rapidly and their dose contribution is already included in that for ^{227}Ac by way of assumed secular equilibrium in the landscape dose factor for this nuclide.

The K_d for Sn(IV) is expected to decrease by a factor of as much as 1000 at high pH according to the BB09 model owing to particularly strong aqueous phase hydrolysis which appears to overwhelm surface binding reactions. In this case, even if sorption is assumed to be negligible in the high pH region of the geosphere, the flowpath average K_d should only decrease slightly relative to the reference case of no alkaline plume provided the affected region of the geosphere is limited to, at most a few tens of meters. Although the ^{126}Sn activation product is a non-negligible contributor to the near-field source term, the impact on overall far-field dose rates should be limited.

Sorption of Th(IV) was not modeled in Crawford (2013b) since it was not considered to be an important nuclide for SR-PSU. Based on its known hydrolysis behaviour, however, similar behaviour is expected for Th(IV) as for the trivalent radioelements. This is also supported by sorption edge data reported by Bradbury and Baeyens (2005) for Montmorillonite which shows strong sorption throughout the entire alkaline pH range. Sorption of Th(IV) is already expected to be very strong at the reference groundwater composition and it is also highly immobile at source due to solubility limitations, so no net impact on far-field dose rates via in-growth of various daughter nuclides is expected.

Nb(V) and Zr(IV) were not modeled in Crawford (2013b) although supporting data reported for Finnish granite in contact with cement equilibrated groundwater suggested substantially increased K_d relative to normal groundwater pH levels. This appears to be at odds with modelling work reported by Ervanne et al. (2013) which suggests decreased sorption of Nb(V) at high pH levels, similar to what is expected for Sn(IV). Since the radioisotopes ^{94}Nb or ^{93}Zr are not decay chain members, only a significant decrease in K_d at high pH is likely to have an influence on far-field dose rates. As discussed previously in the case of Sn(IV), provided the alkaline leachate affected region of the geosphere is spatially limited, any additional contribution to the far-field

dose rate is likely to be small relative to the main dose determining nuclides (^{226}Ra , ^{79}Se , ^{129}I , ^{237}Np).

Although Pa can exist in both the tetravalent and pentavalent state, the Pa(V) form is considered relevant for SR-Site groundwater compositions and is not considered to be particularly redox sensitive. Sorption of Pa(V) was not modeled either in Crawford, 2013b) since it was not considered to be an important nuclide for SR-PSU. The ^{231}Pa isotope has a long half-life of 30 ka, resides in the $4n+3$ decay chain, and decays to ^{227}Ac (see discussion above). The sorption of Pa(V) is expected to be relatively strong, although the modelling work reported by Ervanne et al. (2013) suggests possibly decreased sorption at high pH levels. A slightly decreased flowpath average K_d for Pa(V) may give slightly elevated far-field dose rates attributable to ^{231}Pa , although slightly offset by a decrease in the dose rate contribution by ^{227}Ac . Any additional contribution to the far-field dose rate, however, is likely to be small relative to the main dose determining nuclides (^{226}Ra , ^{79}Se , ^{129}I , ^{237}Np).

Redox-Sensitive Surface Complexers

Since the groundwater compositions were defined for “type” groundwaters by Auqué and Gimeno (2013) rather than for detailed tabulated compositions as in Salas et al. (2010), the SR-PSU data recommendation (Crawford 2013b) suggested the most likely redox state for each groundwater type as specified. In the SR-Site K_d data compilation (Crawford 2010), recommended values (Table 6-1, pp 100-101) were given for all relevant redox states without specifying which should be used in transport calculations. The reason for this was that there was such a wide variation in calculated pH, Eh, and pCO_2 values throughout the repository control volume (Salas et al. 2010) that it was deemed not possible to give an unequivocal recommendation of the appropriate redox state for all canister positions. The redox uncertainty arising due to variable local conditions was handled on a case by case basis in the appendices to Crawford (2010) for the redox sensitive radioelements Np, Pu, Tc, and U. On the basis of these scoping calculations it was proposed that Np(IV), Pu(III/IV), and Tc(IV) redox states could be generally assumed for the deep repository environment. For U, on the other hand, it was not possible to always guarantee fully reducing conditions since both U(IV) and U(VI) were possible depending on local chemical compositions.

Modelling sorption response to elevated pH levels is difficult for redox sensitive species if thermodynamic transitions between redox states are permitted. This is not typically a problem in laboratory investigations since steps are often taken to ensure a well-defined redox state representing either strongly reducing or oxic conditions. If sorption reactions for different redox states are modeled in parallel and redox equilibrium is allowed, it is sometimes possible for different redox states to predominate in the aqueous and sorbed phases. In the calculations made by Crawford (2013b) surface reactions for all relevant redox states were included simultaneously to allow transitions between redox states to occur where thermodynamically possible. Although this is mechanistically reasonable and fully consistent with underlying mass action relations describing equilibrium in the system, the various modelling simplifications and data uncertainties can give rise to apparent inconsistencies that need to be dealt with.

In the calculations made by Crawford (2013b), for example, counterintuitive results were sometimes obtained when comparing outcomes for different groundwater types. The K_d predicted by the BB09 model for Glacial groundwater at pH 10.5-11.5, for example, is about 40 times larger than the K_d predicted for Saline groundwater at pH 7.3. The predominant sorbing species in the Saline groundwater is U(IV), whereas

for the Glacial groundwater, the U(VI) form is predominant. The fact that U(IV) is implicitly predicted to have a lower K_d than U(VI) in this calculation is difficult to reconcile with the heuristic rule that the hexavalent redox state is typically more mobile than the tetravalent state in natural systems.

In the SR-Site data compilation (Crawford 2010) the recommended K_d for U(IV) is roughly 500 times larger than that for U(VI), a relative variation deemed not unreasonable over a wide range of relevant groundwater compositions. Since a geochemical analogy with Th(IV) is typically invoked, the sorption of U(IV) is usually not thought to decrease at high pH levels as predicted here by the BB09 model. Database thermodynamic constants for Th(IV) hydrolysis reactions, however, differ significantly from U(IV), Np(IV), and Pu(IV). Hydrolyzed forms of Th(IV) generally have significantly reduced stability relative to the other tetravalent actinides and thus competitive binding of Th(IV) in aqueous hydrolyzed forms at high pH seems to be not as effective as for U(IV), Np(IV), or Pu(IV).

Obviously it is much easier to speak in terms of relative sorptive variation as a function of pH when there is only one relevant redox state and where there is a well-defined reference K_d value for a given groundwater composition. Predictions of relative sorptivity made for systems where two or more redox states can potentially co-exist are sometimes not consistent with empirically established relative sorptivities based on laboratory or literature data. Such differences cannot be simply eliminated by rescaling reference K_d values using a chemistry transfer factor since the relative inconsistencies remain. This is difficult to rectify given the current state of the art in sorption modelling and the recognised uncertainties of the qualitative model predictions used in support of the data recommendation.

In the SR-PSU K_d recommendation (Crawford 2013b) this was handled in a semi-qualitative fashion to retain consistency with the underlying data recommendation for oxidized and reduced states. The applied heuristic rule was based upon the assumption that the K_d for what is normally considered to be the more strongly sorbing redox state should never be less than the K_d for the less strongly sorbing redox state at the pH of the reference groundwater. If, for example, the K_d for U(IV) at high pH was predicted to be less than that for U(VI) at the reference groundwater pH level, then the value for U(VI) should be used instead for U(IV). In this fashion, U(IV) is always assigned a K_d value that is equal to, or higher than that for U(VI) where the recommended U(VI) value given in Crawford (2010) is taken to be a reasonable lower limit. Given the underlying uncertainties inherent in the calculations, this should be regarded as only a very approximate way of handling the apparent data inconsistency and may need to be revised in future safety assessments.

Np was found to behave in a relatively simple fashion for the groundwater compositions modeled in Crawford (2013b) with Np(IV) surface speciation dominating for all non-Glacial groundwater compositions. Nevertheless, the K_d values predicted for high pH conditions were significantly lower than the limiting value for Np(V) given in Crawford (2010). The ^{237}Np nuclide is relatively important for the central corrosion case in the radionuclide transport report for SR-Site on account of its long half-life (2 Ma). It is one of the dominant nuclides for the near field source term and far-field dose rates as can be seen from Figure 4-2 and Figure 4-3 in the radionuclide transport report (SKB 2010c). ^{237}Np is the nuclide with the longest half-life in the $4n+1$ decay chain and a decrease in K_d in the vicinity of a canister breach could potentially give elevated far-field dose rates. As discussed previously, however, the flowpath average K_d should only decrease

slightly relative to the reference case of no alkaline plume provided the affected region of the geosphere is of limited spatial extent.

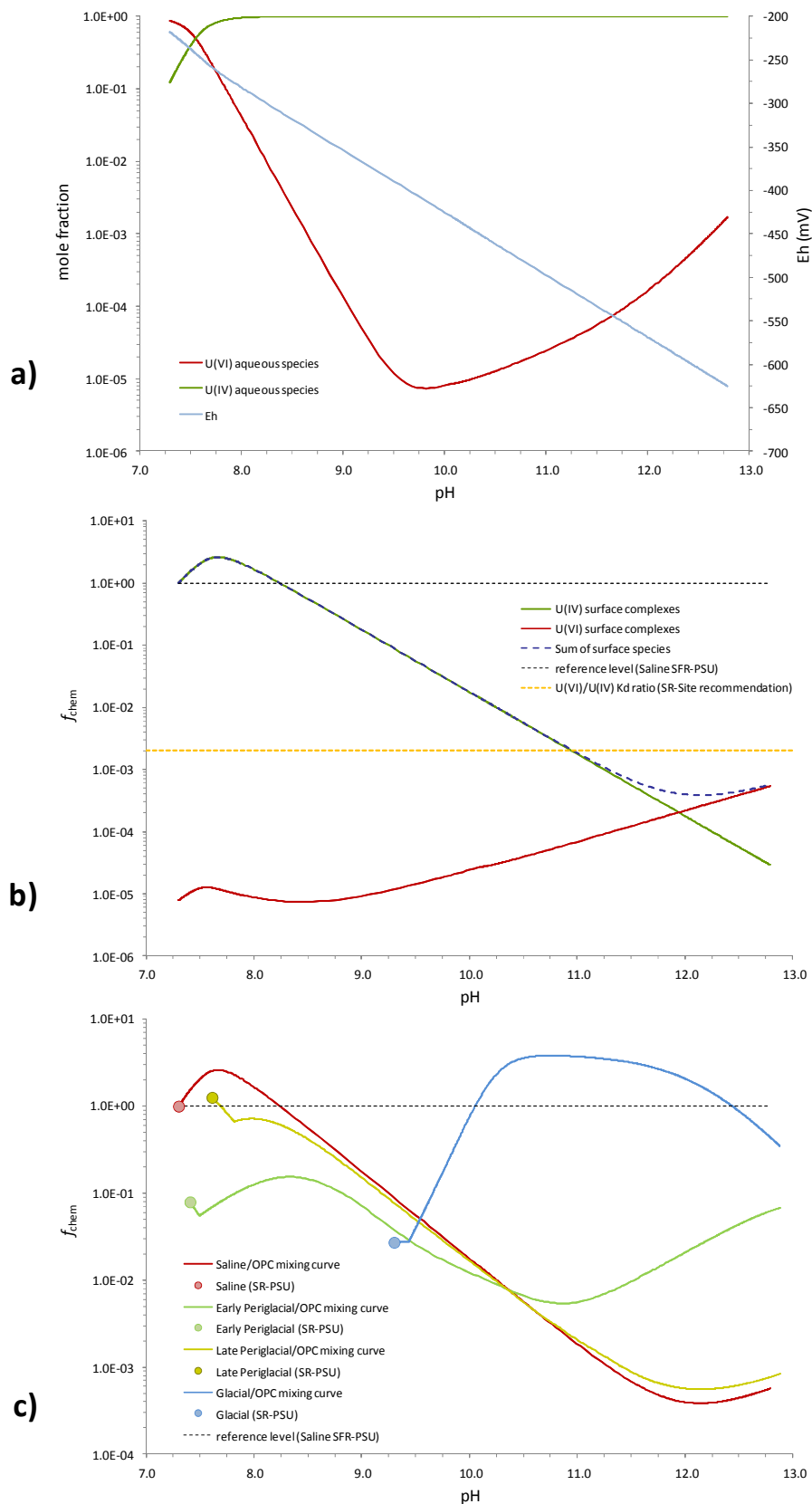


Figure 8 Theoretical variation in U redox speciation and sorption as a function of pH for site specific groundwater mixed with OPC leachate predicted by PhreeqC using the BB09 model. Panels show a) aqueous phase redox speciation for the reference Saline groundwater (SR-PSU), b) contribution of sorbed redox states to overall K_d relative to reference groundwater, c) relative variation in overall K_d predicted for different groundwater types.

Figure 8 shows the sorption behaviour predicted for U as a function of pH changes arising due to mixing of initially unaffected groundwater with the simple OPC leachate composition (portlandite equilibrated groundwater). As can be seen clearly from Figure 8a and Figure 8b, the prediction of U sorption chemistry is significantly complicated by redox transitions. For the reference Saline groundwater defined for SR-PSU, the aqueous phase speciation is initially dominated by U(VI), although U(IV) surface species make the largest contribution to the overall K_d value. The BB09 model predicts a large decrease in K_d at elevated pH levels and at $\text{pH} \approx 12$, U(VI) surface complexes are expected to dominate sorptivity, while U(IV) is the predominant redox state in the aqueous phase. As can be clearly seen from Figure 8b, at high pH the K_d for the tetravalent state is predicted to be lower than the SR-Site recommended value for U(VI).

The Early and Late Periglacial groundwater types exhibit qualitatively similar behaviour to the Saline groundwater type. For the glacial groundwater, however, U(VI) dominates both the aqueous phase redox speciation and that of the sorbed phase. An apparent inconsistency here is that U(VI) is predicted to have a higher K_d in the Glacial groundwater at high pH than the reference K_d for U(IV) in Saline groundwater. To avoid this inconsistency, the K_d for high pH conditions in SR-PSU ($\text{pH} \geq 10$) was set to the SR-Site recommended value for U(VI) for all non-Glacial groundwater types. For the Glacial groundwater, the SR-Site recommended value for U(VI) was deemed applicable for all pH levels and the relative increase in K_d predicted for high pH was neglected.

The appropriate redox state for U was already identified as an uncertainty in the radionuclide transport report (SKB 2010c) and separate case studies were therefore made assuming K_d for U(VI) and U(IV) redox predominance along migration paths. It was suspected that the high K_d values associated with U(IV) sorption would be a conservative choice since the larger inventory of ^{238}U sorbed along migration paths would give higher far-field dose rates via in-growth of the ^{226}Ra daughter nuclide in the $4n+2$ decay chain. The case study detailed in Section 4.5.4 (pp 80-81) of the radionuclide transport report (SKB 2010c) suggested, however, that when U(VI) redox speciation is assumed the dose rates attributable to the various U isotopes increase slightly, although there is very little impact on daughter nuclides relative to the assumption of U(IV) redox speciation. This is because the large inventory of U isotopes in the canister tends to dominate as a near-field source term for the daughter nuclides in all situations. Small changes in the relative in-growth of U daughters along the migration path due to altered U sorptivity appear to be overwhelmed by the source term and very little impact is therefore predicted.

Figure 9 shows the corresponding data for Pu sorption. Prediction of the relative sorptivity of Pu at high pH is even more convoluted than for U owing to the extremely complex redox behaviour of Pu. As discussed in Crawford (2010), Pu can exist in as many as four different oxidation states in groundwater (i.e. +III, +IV, +V, +VI). It is also possible for multiple redox states to coexist in nearly equimolar concentrations due to redox disproportionation reactions. For the reference Saline groundwater type defined for SR-PSU, the aqueous phase speciation and the sorbed phase is initially dominated by Pu(III) with a small contribution from Pu(IV) while the other redox states are effectively absent. At higher pH levels, there is a transition to predominantly Pu(IV) aqueous phase speciation (Figure 9a), although Pu(III) surface species still make the largest contribution (Figure 9b) to the overall K_d value over most of the pH range studied. It can also be noted that the K_d predicted for the high pH range is significantly

lower than the values used in the SR-Site transport calculations as indicated by the broken lines in Figure 9b.

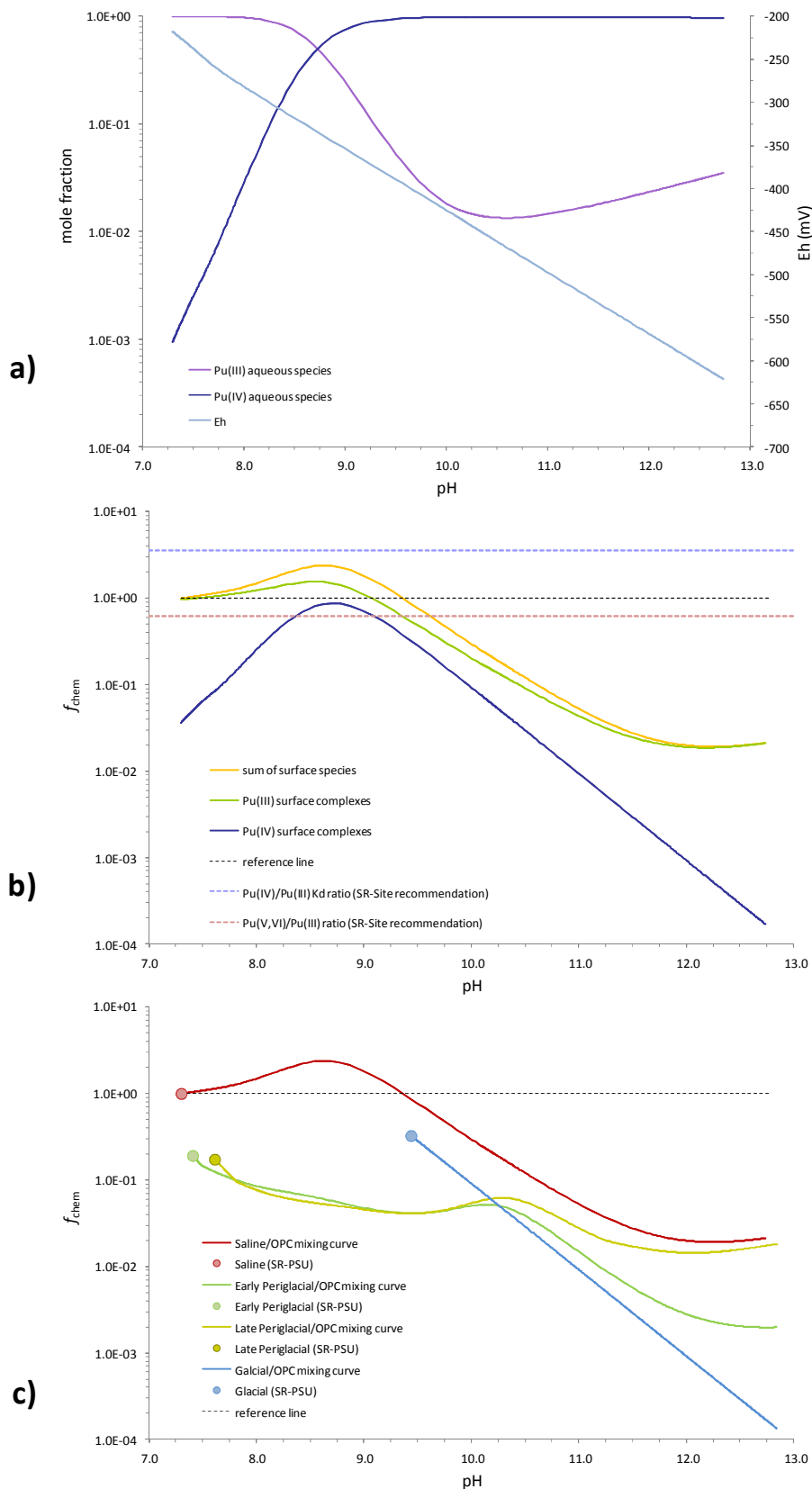


Figure 9 Theoretical variation in Pu redox speciation and sorption as a function of pH for site specific groundwater mixed with OPC leachate predicted by PhreeqC using the BB09 model. Panels show a) aqueous phase redox speciation for the reference Saline groundwater (SR-PSU), b) contribution of sorbed redox states to overall K_d relative to reference groundwater, c) relative variation in overall K_d predicted for different groundwater types.

The Early- and Late Periglacial groundwater types exhibit qualitatively similar behaviour to the Saline groundwater, although Pu(IV) surface species tend to dominate sorption in the pH interval 8-10. For the Glacial groundwater, Pu(IV) dominates both aqueous phase speciation and sorption over the entire pH range although with a smallish contribution from Pu(V).

In the SR-Site data recommendation it was argued Pu(IV) should sorb more strongly than Pu(III) on account of its higher first hydrolysis constant which implies a numerically larger intrinsic binding constant for the first surface complexation reaction of Pu(IV). Similar reasoning was also given by Choppin et al. (1997) and Choppin (2003) based on consideration of the strong hydrolysis of Pu(IV) and the low solubility product of Pu(OH)₄. As noted previously in the case of Sn(IV) and Th(IV), however, the strong aqueous phase hydrolysis of the tetravalent state appears to overwhelm the surface binding reactions which leads to a prediction of Pu(III) being the predominant surface species instead. This is the opposite behaviour to what would be expected on the basis of considering intrinsic binding constants in isolation. As can be seen from Figure 9b, the relatively greater sorptivity of Pu(III) relative to Pu(IV) predicted by the modelling conflicts with the recommendation in Crawford (2010) where the K_d to be used for Pu(IV) in transport calculations is roughly 3.6 times greater than that for Pu(III).

Since it was not clear how best to handle this apparent inconsistency it was recommended in Crawford (2013b) that the K_d value assigned in SR-Site for Pu(III) be assumed for both Pu(III) and Pu(IV) sorption in all non-OPC affected groundwater types. Since the calculations consistently predicted a significantly reduced K_d at high pH levels it was recommended that the K_d be reduced by a factor of 1 000 at pH \geq 10. This reduction factor is arbitrary, although provided the high pH region of the flowpath is restricted to at most a few tens of metres, the impact of this assumption on the flowpath average K_d should be negligible. The impact of much reduced K_d for Pu in a limited zone near the canister release location would give very slightly increased far-field dose rates of ²³⁹Pu (4n+3 decay chain) and ²⁴²Pu (4n+2 decay chain). Since there is already a large inventory of Pu in the spent fuel canister, however, any change in the K_d status of Pu along a migration path should not have a large impact on the far-field dose rates of daughter nuclides owing to the dominant source term (i.e. a similar impact is expected for Pu as previously shown in the case of U).

4 Conclusions

A groundwater mixing model for neutralisation of high pH leachate from ordinary Portland cement (OPC) has been combined with a simplified model of sorption (cation exchange and surface complexation) to investigate the possible consequences of a zone of increased pH in the vicinity of leaking canisters identified in the central corrosion case of the SR-Site transport modelling report (SKB 2010c). The sorption of cation exchangers was simulated using the simplified single site model developed by Byegård et al. (1995, 1998) and used previously in Crawford (2010). Since there is currently no surface complexation model of acceptable accuracy for prediction of sorption in granitic rock systems, the analysis is based on purely qualitative calculations using a simplified “toy model” based on a single mineral phase assumed to dominate sorption. The calculation approach assumes illite as an approximate geochemical analogue for biotite, which has been identified as a possibly dominant mineral phase for sorption of a range of radionuclides considered relevant for safety assessment. Binding constants for the surface complexation reactions were based on data given in Bradbury and Baeyens (2009a, b).

The calculations for cation exchanging radionuclides suggest only minor impacts due to the presence of OPC leachate and K_d values used in transport calculations can be reasonably assumed to be unaltered by high pH conditions. Calculations made using the surface complexation model, on the other hand, suggest a range of different behaviours for redox sensitive and non-redox sensitive radionuclides which may include very much decreased K_d values at high pH as well as increased K_d values relative to unaffected groundwater. In the case where K_d values are greatly reduced in the zone of high pH, the flowpath average K_d should not be greatly affected provided the high pH zone does not extend for more than a few tens of metres from the canister release location. In the case of a significantly increased K_d at high pH, the decreased mobility of some actinides may result in increased far field dose rates of some long lived daughter nuclides that are only weakly retarded in the geosphere (i.e. due to increased in-growth of daughter nuclides along the flowpath). Since many of the actinides that might be associated with substantially increased K_d in the high pH region have relatively high inventories at the source location, any increase in production of daughter nuclides along the migration path should only have a very minor impact given that the near-field source term for these nuclides would still most likely dominate the far-field dose rates.

Although dose effects due to altered in-growth rates within radionuclide decay chains have only been dealt with in a very rudimentary and qualitative manner, only minor changes in far-field dose rates are expected. These changes are also likely to be small relative to the major dose determining nuclides which should be relatively unchanged. The conclusion that the presence of cement in the repository has only a small impact on radionuclide retardation is further supported by the following

1. Canister failures are expected only after about one hundred thousand years and then only at high flow locations. It is quite unlikely that elevated pH conditions would persist at such locations so long after repository closure (see Section 3.2.2).
2. The overall impact of radionuclide retention in the geosphere is a small reduction in dose for the case study where Th sorption in the near field is

disregarded; see, for example, Figure 13-39 (near-field releases) and 13-40 (far-field releases) of SKB (2011). In that particular case study, while the dose rate attributable to ^{229}Th and ^{230}Th increase slightly due to a lower flowpath average K_d , the dose rate for ^{226}Ra decreases by a greater amount. Similar impacts are therefore expected for other $4n+2$ decay chain actinides associated with a decrease in K_d in the vicinity of a canister. The possibility of increased K_d in the vicinity of a canister is approximately covered by the case study including solubility limits in the near-field, which is also shown in Figures 13-39 and 13-40 of SKB (2011). In that particular case study, total doses are relatively unchanged. Both of these taken together put a bound on the possible extent of the impact of pH on radionuclide retention in the geosphere.

References

- Allard B, Ittner T, Torstenfelt B, 1985.** Migration of trace elements into water-exposed natural fissure surfaces of granitic rock. *Chemical Geology* 49, 31–42.
- Anderson E B, Rogozin Y M, Smirnova E A, Bryzgalova R V, Andreeva N R, Malimonova S I, Shabalev S I, Fujiwara A, Tochiyaama O, 2007.** Sorption-barrier properties of granitoids and andesite-basaltic metavolcanites with respect to Am(III) and Pu(IV): 1. Absorption of Am and Pu from groundwater on monolithic samples of granitoids and andesite-basaltic metavolcanites. *Radiochemistry* 49, 305–312.
- Auqué L, Gimeno M J, 2013.** Proposed composition of groundwater for SFR and its extension, during different climatic cases, SR-PSU. SKB R-13-16, Svensk kärnbränslehantering AB, in print.
- Banwart S A, 1999.** Reduction of iron(III) minerals by natural organic matter in groundwater. *Geochimica et Cosmochimica Acta* 63, 2919–2928.
- Bath A, 2012.** Groundwater chemistry in SKB's safety assessment SR-Site: initial review. Technical Note 2013:32, Swedish Radiation Safety Authority.
- Beall G W, O'Kelley G D, Allard B, 1980.** An autoradiographic study of actinide sorption on climax stock granite. ORNL-5617, Oak Ridge National Laboratory, U.S. Department of Energy.
- Bradbury M H, Baeyens B, 2005.** Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides. *Geochimica et Cosmochimica Acta* 69, 875–892.
- Bradbury M, Baeyens B, 2009a.** Sorption modelling on illite Part I: Titration measurements and the sorption of Ni, Co, Eu and Sn. *Geochimica et Cosmochimica Acta* 73, 990–1003.
- Bradbury M, Baeyens B, 2009b.** Sorption modelling on illite. Part II: Actinide sorption and linear free energy relationships. *Geochimica et Cosmochimica Acta* 73, 1004–1013.
- Byegård J, Skarnemark G, Skålberg M, 1995.** The use of some ion-exchange sorbing tracer cations in in-situ experiments in high saline groundwaters. In Murakami T, Ewing R C (eds). *Scientific basis for nuclear waste management XVIII: symposium held in Kyoto, Japan, 23–27 October 1994*. Pittsburgh, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 353), 1077–1084.
- Byegård J, Johansson H, Skålberg M, Tullborg E-L, 1998.** The interaction of sorbing and non-sorbing tracers with different Äspö rock types. Sorption and diffusion experiments in the laboratory scale. SKB TR-98-18, Svensk Kärnbränslehantering AB.
- Byegård J, Selnert E, Tullborg E-L, 2008.** Bedrock transport properties. Data evaluation and retardation model. Site descriptive modelling, SDM-Site Forsmark. SKB R-08-98, Svensk Kärnbränslehantering AB.

- Choppin G R, 2003.** Actinide speciation in the environment. *Radiochimica Acta* 91, 645–650.
- Choppin G R, Bond A H, Hromadka P M, 1997.** Redox speciation of plutonium. *Journal of Radioanalytical and Nuclear Chemistry* 219, 203–210.
- Crawford J, 2010.** Bedrock K_d data and uncertainty assessment for application in SR-Site geosphere transport calculations SKB R-10-48, Svensk Kärnbränslehantering AB.
- Crawford J, 2013a.** Approaches to modelling surface complexation sorption on complex geological materials with limited data. In Rabung T, García D, Montoya V, Molinero J (eds). Final Workshop of the Collaborative Project “Crystalline ROCK Retention Processes” (7th EC FP CP CROCK). Karlsruhe: KIT Scientific Publishing, 91–97.
- Crawford J, 2013b.** Quantification of rock matrix K_d data and uncertainties for SR-PSU. SKB R-13-38, Svensk Kärnbränslehantering AB, in print.
- Duro L, Grivé M, Cera E, Domènech C, Bruno J, 2006.** Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment. SKB TR-06-17, Svensk Kärnbränslehantering AB.
- Dzombak D, Morel F, 1990.** Surface complexation modelling: Hydrous ferric oxide. New York: Wiley.
- Ervanne H, Puukko E, Hakanen M, 2013.** Modeling of sorption of Eu, Mo, Nb, Ni, Pa, Se, Sn, Th, and U on kaolinite and illite in Olkiluoto groundwater simulants. Posiva Working Report 2013-31, Posiva Oy, Finland.
- Follin S, Johansson P-O, Hartley L, Jackson P, Roberts D, Marsic N, 2007.** Hydrogeological conceptual model development and numerical modelling using ConnectFlow, Forsmark modelling stage 2.2 SKB R-07-49, Svensk Kärnbränslehantering AB.
- Goldberg S, Criscenti L J, Turner D R, Davis J A, Cantrell K J, 2007.** Adsorption–desorption processes in subsurface reactive transport modeling. *Vadose Zone Journal* 6, 407–435.
- Höglund L-O, 2013.** The impact of concrete degradation on the BMA barrier functions. SKB R-13-40, Svensk Kärnbränslehantering AB, in print.
- Ittner T, Torstenfelt B, Allard B, 1982.** Migration of the fission products strontium, technetium, iodine, cesium and the actinides neptunium, plutonium, americium in granitic rock. SKB TR 88-02, Svensk Kärnbränslehantering AB.
- Karamalidis A K, Dzombak D A, 2010.** Surface complexation modelling: Gibbsite. New York: Wiley.
- Kienzler B, Vejmelka P, Römer J, Schild D, Jansson M, 2009.** Actinide migration in fractures of granite host rock: laboratory and in-situ investigations. *Nuclear Technology* 165, 223–240.
- Levenspiel O, 1972.** Chemical reaction engineering. 2nd ed. New York: Wiley.

Marques Fernandes M, Baeyens B, Bradbury M H, 2008. The influence of carbonate complexation on lanthanide/actinide sorption on montmorillonite. *Radiochimica Acta* 96, 691–697.

Marques Fernandes M, Stumpf T, Baeyens B, Walther C, Bradbury M H, 2010. Spectroscopic identification of ternary Cm–carbonate surface complexes. *Environmental Science & Technology* 44, 921–927.

NEA, 2005. NEA Sorption Project Phase II. Interpretation and prediction of radionuclide sorption onto substrates relevant for radioactive disposal using thermodynamic sorption models. NEA Report 5992, Organisation for Economic Co-operation and Development, Nuclear Energy Agency.

NEA, 2012. Thermodynamic sorption modelling in support of radioactive waste disposal safety cases. NEA Sorption Project Phase III. NEA Report 6914, Organisation for Economic Co-operation and Development, Nuclear Energy Agency.

Parkhurst D L, Appelo C A J, 1999. User's guide to PHREEQC (version 2): a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Denver, Colorado.

Salas J, Gimeno M J, Auqué L F, Molinero J, Gómez J, Juárez I, 2010. SR-Site – hydrogeochemical evolution of the Forsmark site. SKB TR-10-58, Svensk Kärnbränslehantering AB.

Sidborn M, Marsic N, Crawford J, Joyce S, Hartley L, Idiart A, de Vries L M, Maia F, Molinero J, Svensson U, Vidstrand P, Alexander R, 2012. Potential alkaline conditions for deposition holes of a repository in Forsmark as a consequence of OPC grouting. SKB R-12-17, Svensk Kärnbränslehantering AB, in print.

SKB, 2010a. Climate and climate related issues for the safety assessment SR-Site. SKB TR-10-49, Svensk Kärnbränslehantering AB.

SKB, 2010b. Design, production and initial state of the closure. SKB TR-10-17, Svensk Kärnbränslehantering AB.

SKB, 2010c. Radionuclide transport report for the safety assessment SR-Site. SKB TR-10-50, Svensk Kärnbränslehantering AB.

SKB, 2011. Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project. SKB TR-11-01, Svensk Kärnbränslehantering AB.

Stumm W, Morgan J J, 1996. Aquatic chemistry: chemical equilibria and rates in natural waters. 3rd ed. New York: Wiley.

Stumpf T, Bauer A, Coppin F, Fanghänel T, Kim J-I, 2002. Inner-sphere, outer-sphere and ternary surface complexes: a TRLFS study of the sorption process of Eu(III) onto smectite and kaolinite. *Radiochimica Acta* 90, 345–349.