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Technical Note

2012:63

Review of Radionuclide Sorption on Bentonite and Forsmark Bedrock Material

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SSM perspektiv

Bakgrund

Strålsäkerhetsmyndigheten (SSM) granskar Svensk Kärnbränslehantering AB:s (SKB) ansökningar enligt lagen (1984:3) om kärnteknisk verksamhet om uppförande, innehav och drift av ett slutförvar för använt kärnbränsle och av en inkapslingsanläggning. Som en del i granskningen ger SSM konsulter uppdrag för att inhämta information i avgränsade frågor. I SSM:s Technical note-serie rapporteras resultaten från dessa konsultuppdrag.

Projektets syfte

Målsättningen med detta uppdrag är att granska SKB:s val av Kd-värden i säkerhetsanalysen SR-Site för bentonitlera och berg. Aspekter som kan vara betydelsefulla att inkludera innefattar kvalitet av experimentella mätningar, liksom representativitet av data med beaktande av geokemiska och mineralogiska egenskaper hos Forsmarksberget, och mineralogisk sammansättning av bentonitlera. SKB:s hantering av osäkerheter skall också granskas. Det bör beaktas huruvida SKB:s val av Kd-värden är försvarbara antingen med utgångspunkt från konservatism (dvs. baserat på pessimistiska antaganden) eller med utgångspunkt från realism.

Sammanfattning

Denna rapport granskar sorption-data för bentonit och berg vilka har använts i säkerhetsanalysen SR-Site. Det kan konstateras att härledningen av Kd-värden har gjorts på ett systematiskt sätt och att presentationen av resultat är uttömmande. Kontroller visar att härledning och överföring av resultat kan betraktas som spårbar. Det finns dock vissa angelägenheter som behöver särskilt beaktas, till exempel de som kopplar till intervallet av betingelser som använts i experimenten, kontroll av pH-värden under experimenten samt det faktum att data delvis baserats på kemiska analogier.

De härledda Kd-värdena måste generellt betraktas som låga, och detta kan resultera i en ”sammansatt försiktighet”. Variabilitet och osäkerhet har inkorporerats i härledda parameterfördelningar, men det finns lite användning av kemisk modellering eller expert bedömningar för att underbygga detta.

De härledda sorptionsparametrarna för bentonitlera är omfattande men detta arbete behöver uppdateras för att kunna beakta nya experimentella data som publicerats efter år 2004, liksom uppdateringar av termodynamiska databaser. Dessutom har ingen hänsyn tagits till den geokemiska utvecklingen av bentonit och hur detta kan påverka sorption av radionuklider. Till sist, det finns inga omfattande känslighetsanalyser som kan illusterara betydelsen av val av Kd-värden i relation till sönderfallskedjor och kombinationer av närområdes- och bergparametrar.

Projektinformation

Kontaktperson på SSM: Bo Strömberg
Diarienummer ramavtal: SSM2011-4266
Diarienummer avrop: SSM2012-143
Aktivitetsnummer: 3030007-4032

SSM perspective

Background

The Swedish Radiation Safety Authority (SSM) reviews the Swedish Nuclear Fuel Company's (SKB) applications under the Act on Nuclear Activities (SFS 1984:3) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation facility. As part of the review, SSM commissions consultants to carry out work in order to obtain information on specific issues. The results from the consultants' tasks are reported in SSM's Technical Note series.

Objectives of the project

The objective of this assignment is to review SKB's selection of bentonite and bedrock Kd-values for the SR-Site safety assessment. Aspects that may be important to cover include quality of referenced experimental measurements, as well as representativity of data considering geochemical and mineralogical conditions in Forsmark bedrock, and mineralogical composition of bentonite clay. SKB's handling and analysis of uncertainties shall also be reviewed. It should be considered whether or not SKB's selections of Kd-values are defensible based on either conservatism or realism.

Summary

This report review sorption data for bentonite and bedrock materials which has been used in the SR-Site safety assessment. It can be concluded that the derivation Kd-values has been done in a systematic manner and that the presentation of the results is comprehensive. Checking the audit trail of derived data suggests that traceability is robust. Concerns nevertheless need consideration, for instance in relation to the range of conditions considered during the experiments, pH control during the experiments and the fact that some data are being based on chemical analogues.

The derived Kd-values are generally on the low end and this may result in "compounded cautiousness". Variability and uncertainty are incorporated in the derived parameter distributions, but there is little use of supporting chemical modeling or expert elicitation.

The derivation of sorption parameters for bentonite is comprehensive but this work requires updating to reflect new experimental data published since 2004 and updates in supporting thermodynamic databases. Furthermore, there is no consideration of the geochemical evolution of bentonite and how that might affect radionuclide sorption. Finally, there is no comprehensive sensitivity analysis which may illustrate the importance of Kd-value selection in relation to decay chains, and combinations of near-field and geosphere parameters.

Project information

Contact person at SSM: Bo Strömberg
Framework agreement number: SSM2011-4266
Call-off request number: SSM2012-143
Activity number: 3030007-4032

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Contents

1. Introduction

The safety assessment SR-Site by the Swedish Nuclear Fuel and Waste Management Company (SKB) will be reviewed by SSM in a stepwise and iterative fashion. The first step is called the Initial Review. The overall goal of the Initial Review Phase is to achieve a broad coverage of SR-Site and its supporting references, in particular identify the need for complementary information and clarifications to be delivered by SKB.

This document reviews SKB's use of radionuclide sorption parameters in the SR-Site safety assessment. Guidance from SSM [1] is that the review should consider the:

- Completeness of the safety assessment
- Scientific soundness and quality of the SR-Site
- Adequacy of relevant models, data and safety functions
- Handling of uncertainties
- Safety significance (although this will be more elaborately dealt with during the Main Review Phase)
- Quality in terms of transparency and traceability of information in SR-Site and in the associated references.

To elucidate the responses to these topics, the following issues were addressed with respect to SKB's documentation:

1. Appropriate use of site specific data;
2. Use of literature values and chemical analogues;
3. Clarity and transparency in the use of references and their use in deriving sorption parameters;
4. Use of modelling and understanding of sorption mechanisms to underpin the choice of sorption parameters;
5. The range of chemical and mineralogical conditions and the appropriateness of the selected sorption parameters to represent sorption across this range; and
6. The treatment of uncertainty and variation.

Additionally, this review is guided by Swedish Regulations. For instance the Swedish Radiation Safety Authority's General Recommendations concerning the Application of the Regulations concerning Safety in connection with the Disposal of Nuclear Material and Nuclear Waste (SSMFS 2008:21) [2] includes:

"The assumptions and calculation models used should be carefully selected with respect to the principle that the application and the selection should be justified through a discussion of alternatives and with reference to scientific data. In cases where there is doubt as to a suitable model, several models should be used to illustrate the impact of the uncertainty involved in the choice of model." And

"The validity of assumptions used, such as models and parameter values, should be supported, for example through the citing of references to scientific literature, special investigations and research results, laboratory experiments on different scales, field experiments and studies of natural phenomena (natural analogues)."

Specifically concerning sorption, this review has followed the process concerning the derivation of sorption parameters for use in assessment calculations. The review is structured to consider sorption onto bedrock and bentonite in turn, focussing on the clarity of the derivation processes, the use of appropriate underpinning data and the presentation of the data in a clear and concise manner.

Appendix 1 outlines the documents that have been reviewed. Appendix 2 outlines the need for complimentary information from SKB. Appendix 3 lists review topics that might be considered by SSM for the next phase of the review of SR-Site.

2. Technical Review

2.1. Introduction

This section focuses on the technical aspects of the derivation of appropriate sorption parameters for both the geosphere bedrock system and the near-field bentonite system. Given that the approaches to both systems are very different (and in fact notably different in terms of information available), each system is examined in turn.

2.2. Bedrock Sorption

2.2.1. Sorption Processes

The migration of radionuclides in groundwater will be retarded in the subsurface environment by the interaction of dissolved aqueous ions and the mineral surfaces of the geological material through which the groundwater flow. These interactions can take a number of physico-chemical forms, including surface-precipitation, incorporation into the mineral structures and sorption onto mineral surfaces. In common with most repository safety cases, only sorption is considered within assessment calculations. Sorption, which can be defined as the accumulation of matter at the interface between the solid surface and the aqueous phase, includes ion-exchange, where the interaction is controlled primarily by electrostatic attraction onto fixed charged sites, and surface complexation onto variable charge sites. When combined with advective and diffusive transport, sorption processes result in a net retardation of a chemical substance relative to a conservative non-sorbing tracer in the aqueous phase.

Consequently, sorption processes represent the major process in which the geosphere can act as a barrier to radionuclide migration from the repository to the available environment or biosphere. Therefore, the selection of appropriate sorption parameters is crucial for assessment calculations.

The derivation of appropriate sorption parameters for bedrock geology is detailed in a comprehensive and well presented by report by Crawford [3]. As described in [3], “sorption is used strictly to refer to adsorptive interaction with mineral surfaces by way of electrostatic and covalent chemical bonding”.

At the molecular scale, sorption processes can be very complex and [3] provides a comprehensive overview of these mechanisms and different ways of representing radionuclide sorption in mathematical models, including isotherms, ion exchange models and surface complexation models. By necessity the representation of sorption processes within models involves the use of simplifications and assumptions. The most commonly used method to represent sorption within an assessment level model is the specification of a distribution coefficient, or K_d, for each element of interest. This is the approach utilised by SKB [3].

K_d is a term that is based on thermodynamic principles such as instantaneous sorption, reversibility and a linear relationship between the amount of solute on the solid phase and the concentration of the solute in solution. It is not always possible to demonstrate these criteria, particularly in natural systems. The sorption of any particular radionuclide is also dependent on mineralogy, the accessible sorptive surface area, groundwater composition and the concentration of the radionuclide itself. Therefore, the use of a single K_d to represent sorption is a simplification, associated with numerous assumptions and caveats.

Nevertheless, the use of K_ds in assessment calculations is considered appropriate. Firstly, the likely concentrations of radionuclides in groundwater are likely to be low enough that linear sorption is an appropriate assumption (e.g. see Figure 1). Secondly, the use of a linear parameter such as K_d is simpler to implement in assessment calculations than models that depend non-linearly on, for example, variations in groundwater chemistry. As is also correctly noted in [3], the use of more complex sorption models does not necessarily lead to more accurate representations of sorption, particularly as these models require significant data which may be difficult to obtain or applied to real situations.

As noted by Crawford [3, page 39], "a powerful argument for the use of the constant K_d in safety assessment is that a large amount of the uncertainty relating to the magnitude of sorption is concentrated into a single variable, the applicability of which can be (at least partially) assessed independently of its implementation in a transport simulation code". While this is undoubtedly true, there is a danger of concentrating too much reliance on variability in one parameter without considering the physico-chemical processes that control this variability. This is discussed in subsequent sections.

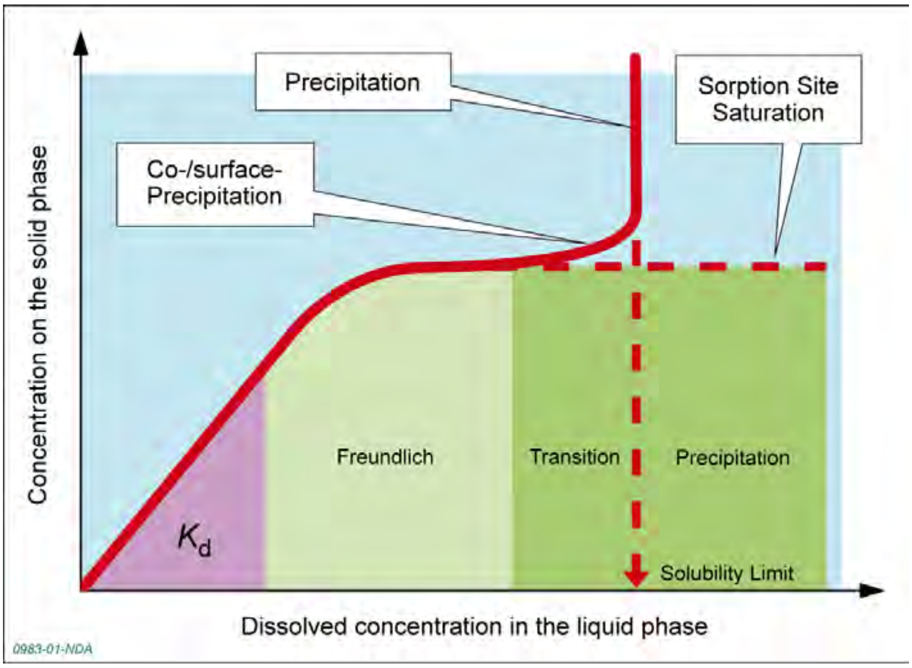


Figure 1: Relationship between radionuclide concentrations in solution and in the solid phase [4]

2.2.2. General Approach to Derivation of K_d Values

The derivation of appropriate K_d values is described in some detail in Crawford [3]. The approach is extremely systematic and is based on taking experimental data and applying various correction factors to account for variations in the solid phases used in the experiments and also to extrapolate the data to the "real" intact rock situation, in an attempt to reconcile the issues associated with the use of crushed rock in laboratory experiments.

The correction factors, or transfer factors (after [5]), used in the data compilation were:

- f_A - A surface area normalisation transfer factor accounting for the difference in sorptive surface area amongst different size fractions used in laboratory investigations, allowing data obtained for different size fractions to be converted into a mutually compatible form that can then be pooled before extrapolation to in situ conditions.
- f_m - A mechanical damage transfer factor which accounts for differences between the sorptive surface area of the reference size fraction of crushed rock and undisturbed rock in situ.
- f_{cec} - A transfer factor which accounts for differences between the cation exchange capacity (CEC) of the site specific rock type and that used in laboratory experiments.
- f_{chem} - A transfer factor which accounts for differences between the groundwater chemistry under application conditions in situ and that used in laboratory investigations.

This leads to the derivation of a recommended site-specific sorption parameter through the following expressions:

$R_d^0 = R_d \cdot f_A$
$K_d^0 = R_d^0 \cdot f_m \cdot f_{cec}$
$K_d = K_d^0 \otimes f_{chem}$

Where:

- R_d is the sorption parameter measured in the laboratory (e.g. using crushed rock of a particular particle size)
- R_d^0 is the surface area normalised sorption parameter for a specific crushed rock reference size fraction
- K_d^0 is the recommended, site specific sorption parameter for sorption on intact rock in situ, applicable to the actual groundwater composition used in the laboratory
- K_d is the recommended site specific sorption parameter for sorption on intact rock in situ, corrected for groundwaters that differ in composition in the experimental systems.

A key underpinning of this approach is the use of a “reference rock”, in this case a rock of granite to granodiorite composition, metamorphic, medium-grained, with the SKB rock code of 101057. This rock type is deemed to be the dominant rock within the candidate rock volume [6] and, it is stated, the majority of the site specific sorption experiments have been undertaken using this rock [3, p55], although this latter point is not clearly demonstrated in the documentation.

Although the mineral properties of rock 101057 are important, they are not clearly tabulated within the sorption derivation report. This reviewer finally found these in a previous report by Crawford [7], summarised below and in Figure 2.

- 28.46% Quartz
- 27-41% plagioclase
- 0.2 – 36% K-Feldspar
- 0.8-8.2% biotite
- CEC ~1 cmoles/kg

The arguments presented in [3] would have been greatly facilitated had this, and more, information regarding the composition of this rock been discussed and presented within the report.

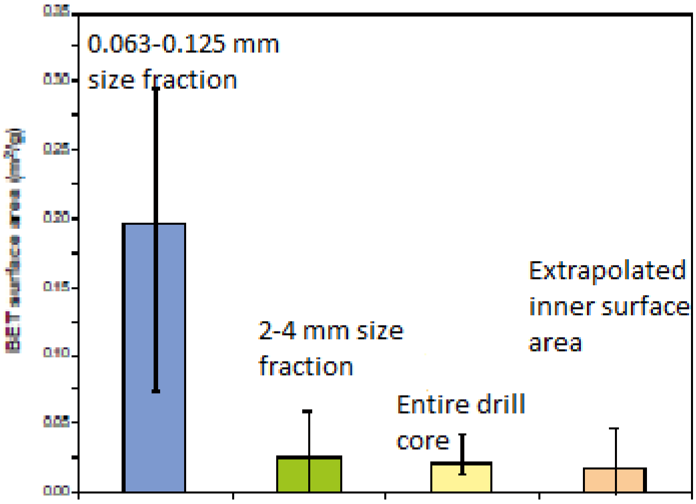


Figure 2: Comparison between the results of the total number of BET surface area [m2/g] measurement of the 101057 rock type.

The application of this methodology is applied systematically by Crawford [3] for all the radionuclides deemed of importance to the safety case. The methodology represents a good approach to, in particular, extrapolate experimental data (obtained through measuring sorption onto crushed rock samples) to the intact rock that will be encountered in the sub-surface at Forsmark.

However, a number of issues are raised by this approach.

Firstly, the factor f_{chem} is in fact rarely used in derivation process, and is generally only applied when a simple ion exchange mechanism for sorption is assumed and the impact of variations in salinity on sorption can be made. For other radionuclides, statements such as (for Americium) are used – "since there are no thermodynamic or empirical models of acceptable accuracy which could be used to describe Am sorption on granite rock, all uncertainty relating to variable or uncertain groundwater composition is assumed to be internalised in the aggregate data set combining K_d data for all groundwater compositions" [3, p151]. This has some truth but there have been considerable advances made in the use of thermodynamic models to support performance assessment calculations [10, 11,12]. Although these models have their limitations in terms of predicting K_d values *ab initio*, their use can be invaluable in informing the choice of K_ds and in particular variability to changes in chemistry. It might be expected that greater use of these models could usefully underpin the SR-Site K_d database.

It is also noticeable that, in contrast to other safety cases, there is no use of expert elicitation in the sorption derivation process, which may allow the impact of varying geochemistry to be assessed [e.g. 13, 14].

Secondly, the derivation process leads almost inevitably to low values of K_d, which may be deemed a cautious approach (as acknowledged in [3]). However, it should be borne in mind that low K_ds are not necessarily "cautious" or "conservative", particularly with regard to decay chains where a high retardation of a parent (and thus a higher concentration of daughters) may be a more conservative approach.

The low values of K_d arise firstly because of the methodology, which, through the application of transfer factors, reduces the value of the K_d from the measured experimental values. Whilst this may be deemed appropriate when considering intact versus crushed rock, the impact of the methodology is quite marked.

As an example, uranium has a derived K_d of:

Best estimate	$1.06 \cdot 10^{-4}$ m^3 kg^{-1}
Lower	$5.53 \cdot 10^{-6}$ m^3 kg^{-1}
Higher	$2.05 \cdot 10^{-3}$ m^3 kg^{-1}

The best estimate value is a low value, and could be almost considered to be non-sorbing. By comparison, the current best estimate for U(VI) sorption onto sandstone in the UK programme is $3.2 \cdot 10^{-2}$ m^3 kg^{-1} [4].

Figure 3 shows the measured values for sorption onto rock type 101057, i.e. the reference rock type. Despite being the reference rock type, the derived K_ds are significantly lower than those measured in experimental systems. The higher value of the distribution is approximately equal to the measured values whereas the best estimate is actually nearly two orders of magnitude lower than the measured values.

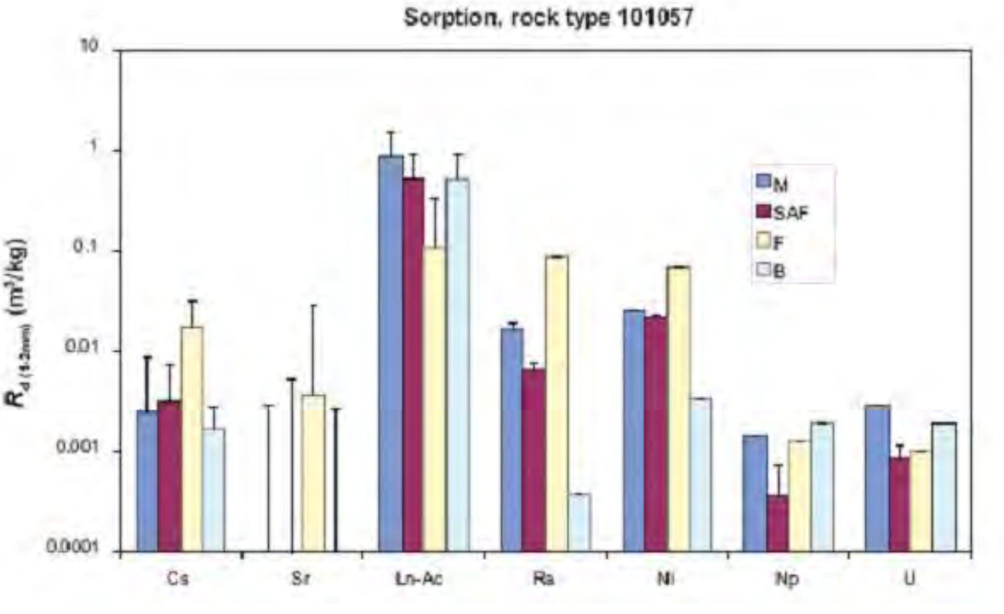


Figure 3: Measured sorption parameters for rock 101057 [7]

A second reason why K_d values are low is that the K_d derivation process considers only sorption onto the bulk mineralogy of the rock and additional retardation of radionuclide transport in fracture coatings has not been quantified. These fracture coatings, including clay minerals (e.g. chlorite, smectite, illite), metal oxide, barite and calcite, would be expected to be significant sorbers of radionuclides. In particular, the co-precipitation of radium with barite has been demonstrated to be a process actually occurring at the site [e.g. 3, 8], and given the importance of radium to overall safety assessment [9] this process should have been considered. The argument in [3] that there is difficulty in quantifying the amount of these fracture minerals along an entire migration path is undoubtedly true. However, a number of experimental measurements have been undertaken on fracture material and it would seem to be an omission not to have included these measurements in the derivation process, perhaps through an expert elicitation process.

A final point regarding the derivation process is the transparency of the experimental sorption data used. Assessment of the methodology would be much easier if the experimental data were tabulated. Instead, a sometimes tortuous audit trail is required to find the experimental data (to for example [15]).

2.2.3. Experimental Data

Experimental K_d data was taken from a mixture of sources including the Forsmark and Laxemar site investigations and literature data. These have been supplemented by use of chemical analogues when appropriate.

A reasonably large number of site specific experimental measurements have been used and utilised by Crawford [3] and these are listed below. However, it is acknowledged that the high numbers of experimental measurements may be misleading: replicates, experiments with different contact times and different particle sizes are included in this number.

- Forsmark
    - Cs, Sr, and Am/Eu 950 data points each, crushed rock samples from eight different borehole sections featuring three distinct rock types.
    - Ni, Ra, Np(V), and U(VI) 200 data points each, crushed rock samples from two borehole sections representing a single rock type.
- Laxemar
    - Cs, Sr, and Am/Eu 1,038 data points each crushed rock samples from five different borehole sections featuring four distinct rock types.
    - Ni, Ra, Np(V), and U(VI), 100 data points each, crushed rock samples from one borehole section representing a single rock type.

This review has not looked in detail at the experimental methodology, although this appears to be well documented in underlying references [e.g. 15] (although tracing back to these references is not always easy).

The main issue associated with the experimental data is that of pH drift during the experiments, and this is acknowledged by Crawford [3]. Figure 4 shows the pH drift for a number of site specific experiments, carried out over 180 days. The triangles in the graph show the initial pH in each experiment, the circles show the pH measured at various intervals during the experiment.

It can be seen that pH drift by nearly two pH units. This has been explained as CO_2 outgassing, which seems a reasonable explanation. However, the pH drift raises questions of the validity of the experimental data – the pH drift takes the experimental data out of the range observed in natural groundwaters (the shaded areas of Figure 4).

Variations in pH can have profound effects on sorption. For example, Figure 5 shows the percentage uranium sorption onto haematite as a function of pH.

The pH drift also means that interpreting experimental data in terms of contact time is also difficult. Figure 6 shows the sorption of americium as a function of contact time. The variations observed could be due to contact time or the pH drift in the experiments. This uncertainty is acknowledged in [3]: “Owing to large uncertainties concerning the interpretation of time dependencies in the laboratory data, no attempt has been made to model or filter the data with regard to sorption contact time”

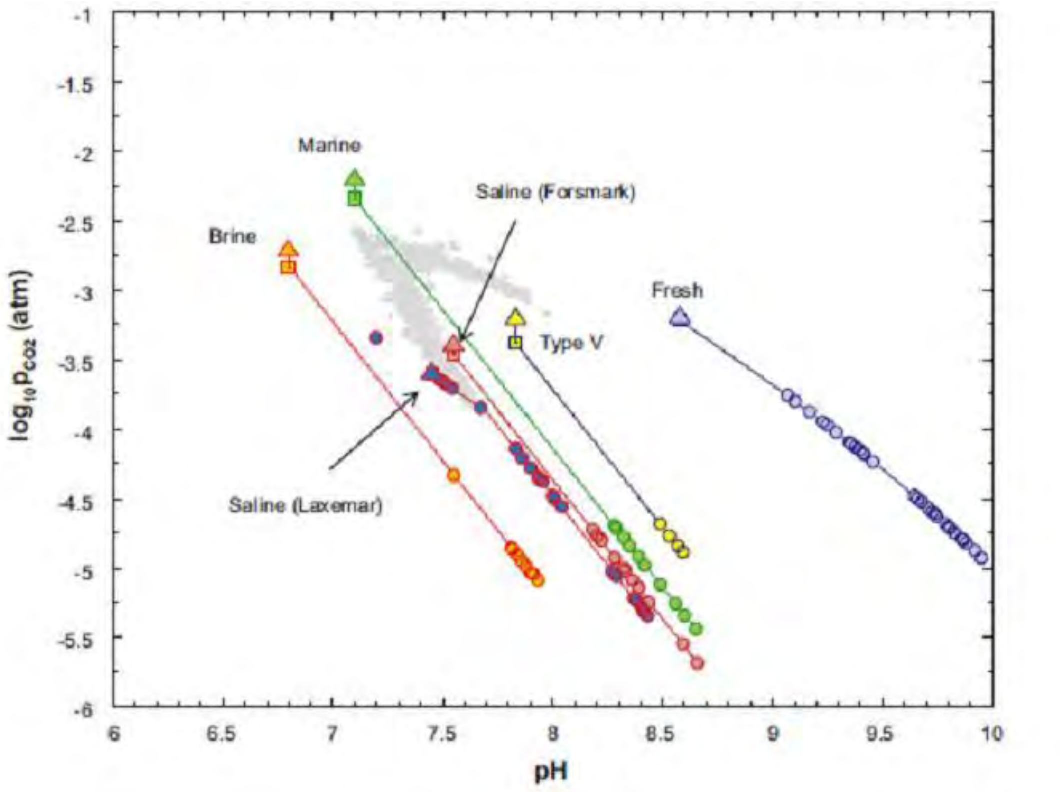


Figure 4: pH drift in site specific experiments (from [3]).

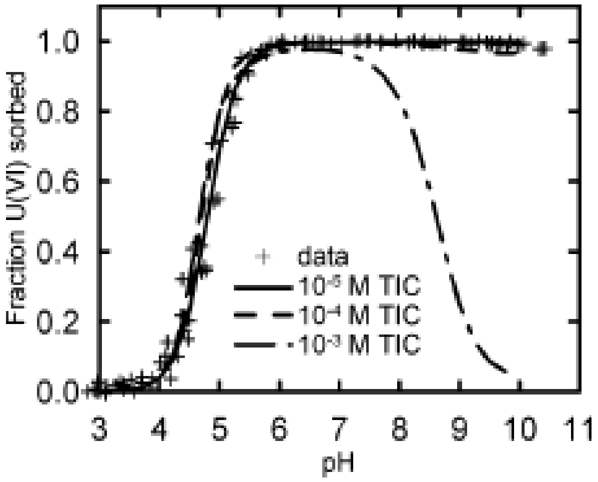


Figure 5: Uranium sorption onto haematite as a function of pH (from [16])

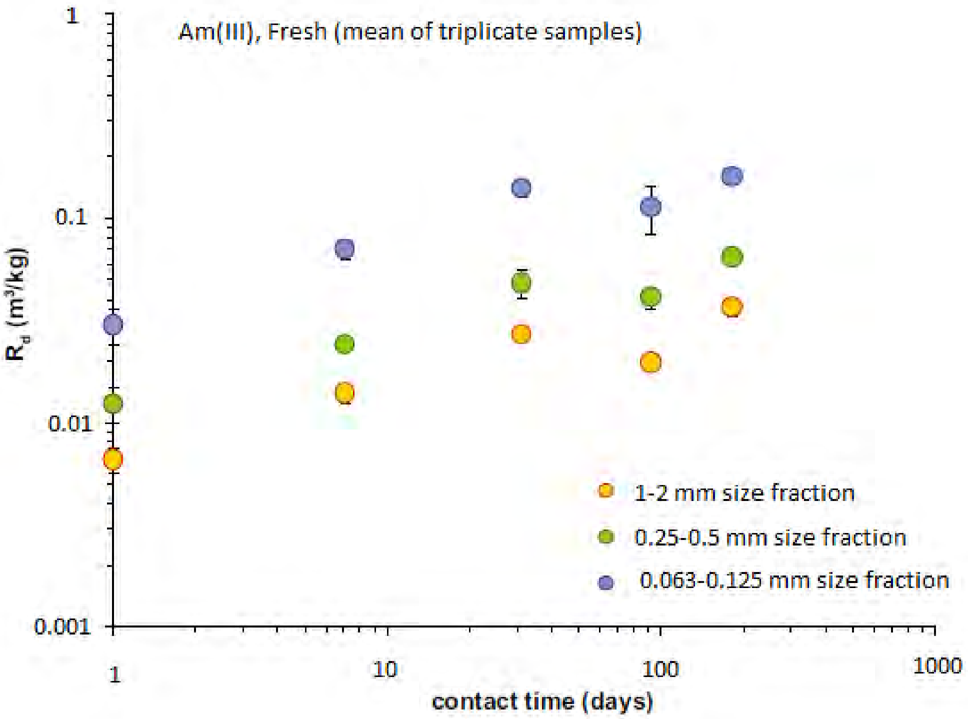


Figure 6: Sorption of americium as a function of time (from [3])

The second source of uncertainty in the experimental data is the use of analogues. Crawford presents a good section on the selection of appropriate analogues and this is summarised in Table 1.

Table 1: Analogues used in sorption parameter derivation (from [3])

Analogue species	Representing
Cs(I)	Ag(I)
Am(III)/Eu(III)	Ho(III), Sm(III), Pu(III), Ac(III), Cm(III)
Ni(II)	Cd(II)
Pu(IV)	Np(IV), U(IV), Th(IV), Zr(IV). Sn(IV), Tc(IV)
Non sorbing	Cl(-I), I(-I), C(IV,-IV), Tc(VII), Mo(IV)

Of particular note is the use of Pu(IV) as an analogue for all +4 species. It is not clear that this results in realistic K_ds. For example, Table 2 shows that for a recent derivation of K_ds for sandstone, the values vary by two orders of magnitude. Although, sandstone has different mineralogy than the granitic rocks considered here, the considerable variation in K_d values for the +4 species would be expected to be mirrored for the Forsmark system.

The second uncertainty regarding this use of the Pu analogue is the experimental data itself. The data is non-site specific and there is some uncertainty as to whether the plutonium is present as Pu(III) or Pu(IV), or both.

Therefore, the choice of K_d for important species such as uranium and thorium is based on non-site specific literature values for plutonium, with associated uncertainties as to the redox state of plutonium. It is surprising that there have been no site specific measurements of these radionuclides.

Table 2: Comparison between radionuclide (IV) sorption parameters (m^3/kg)

	This work [3]	Sandstone [4]
Th	$5.29 \cdot 10^{-2}$	$3.5 \cdot 10^{-1}$
U(IV)	$5.29 \cdot 10^{-2}$	$2.2 \cdot 10^{1}$
Np(IV)	$5.29 \cdot 10^{-2}$	1.0
Pu(IV)	$5.29 \cdot 10^{-2}$	$1.0 \cdot 10^{1}$
Tc(IV)	$5.29 \cdot 10^{-2}$	1.0

2.3. Bentonite Sorption

2.3.1. Overview

The selection of appropriate sorption parameters in SR-Site is predominantly taken from Ochs and Talerico [17], although a significant discussion of sorption processes is presented in [18] and the main data report [6] contains some discussion. The report by Ochs and Talerico also describes the derivation of diffusivity and porosity in bentonite, but the focus of this review is the derivation of sorption parameters.

As for the bedrock sorption case, it is assumed that sorption can be represented by a single K_d, with all the associated assumptions of linearity and equilibrium behaviour. Again, this is considered an appropriate approach.

2.3.2. Data derivation approach

The main issue associated with deriving K_d values appropriate to the compacted bentonite system is the transfer of information of laboratory experiments. This is for two principal reasons:

1. For practicality, most sorption measurements are carried out in dilute suspensions of bentonite (or montmorillonite, the principal component of bentonite).

2. It is not clear what is the pore water composition of compacted bentonite - it is extremely difficult to obtain pore solutions from compacted systems.

A third issue, although not connected to the transfer of experimental data, is the long term evolution of bentonite as a function of temperature, physical changes and changes due to incoming groundwater chemistry.

In terms of point 1, Ochs and Talerico assume that the sorptive properties of compacted bentonite and bentonite in suspension are identical. Data from [5] is quoted, where measured surface areas are similar for loose and compacted MX-80 bentonite. Note that this is the same reference used by Crawford [3] in applying transfer factors for data from crushed rock to intact rock. Therefore, it is assumed that data from batch sorption experiments can be taken from the literature and used in the derivation of appropriate K_d values for compacted systems. The approach employed in this report is to take data from the literature and apply “conversion factors”, an approach similar to that employed by Bradbury and Baeyens [19, 20].

Point 2 is approached through the application of thermodynamic models to derive a suitable porewater composition, taken into account variations in groundwater chemistry and the mineralogy and surface properties of bentonite. Ochs and Talerico consider that the accurate representation of porewater chemistry is crucial to the derivation of an appropriate K_d database, and variation in porewater chemistry is more significant than the differences in mineralogical properties of bentonites. The derivation of porewater chemistry is discussed below.

The conversion factors used to convert literature experimental data into more site specific data take the form of:

- Sorption capacity/CEC – to convert the CEC of the experimental system to the reference MX-80 bentonite system
- pH – to convert data from experiments with pH values outside the range considered suitable for site specific purposes
- Speciation – takes into account differences in the competition for the radionuclide by dissolved ligands

Of these, the CEC conversion factor is the more readily applied. The pH and speciation conversion factors are more complex and require more insight into the chemistry of each individual radionuclide. To facilitate this, there is some use of available thermodynamic models, particularly for nickel and caesium. It is clear however, that significant advances in thermodynamic modelling have been made since the publication of this report (2004) and it would be recommended that these should be examined and utilised in updating the K_ds, particularly for those radionuclides exhibiting complex chemistry (e.g. the actinides).

The application of the methodology described above is clearly presented and all decision points are fully discussed. The age of the report notwithstanding, the derived K_ds have been utilised in the recent generic performance assessments for the UK repository programme [4]. This is likely to represent both an endorsement of the overall approach but also a reflection that an update of the database is overdue.

2.3.3. Porewater chemistry

As discussed above, it is considered that variations in sorption are mainly due to differences in the aqueous rather than the solid phase, therefore there is a focus on an accurate characterisation of bentonite porewaters under site specific conditions.

Thermodynamic modelling was used to predict porewaters, using a reference groundwater system and variations to include a non-saline groundwater and a hypothetical groundwater with the salinity of seawater. The model considered the reactions of these groundwater systems with a reference MX-80 bentonite, considering ion exchange and surface complexation reactions [21 – note this reference is absent in the reference list, the actual reference is assumed by this reviewer to relate to this publication], under both closed and open CO_2 conditions. Alternative bentonite compositions where the bentonite has been completely converted to Ca-bentonite and where the bentonite has been depleted of soluble impurities (e.g. NaCl, KCl, gypsum) were also considered.

Table 3 shows the calculated porewater compositions for these variants. It can be seen that carbonate shows significant variation, depending on whether the system is open or closed with respect to CO_2. In contrast, the major ions, such Na, Cl, SO_4 show little variation when different groundwater chemistries are used. The major variation can be seen when considering a system where bentonite has completed converted to Ca-bentonite, with calcium in porewater being two orders of magnitude higher when compared to the concentration in the reference MX-80 bentonite.

These porewaters are subsequently used in conjunction with the conversion factors described above to derive suitable K_d values, although it is not clear that the porewater within the Ca-bentonite system is used.

Several issues are associated with these calculations of porewater:

1. There are some discrepancies between MX-80 bentonite composition in this derivation and that quoted in TR-10-15 [22]. It is not clear what impact this would have.

2. Given the age of the report, the thermodynamic data used in the report is unlikely to be consistent with other thermodynamic modelling with the SR-Site project (e.g. [23]) The modelling results are reported without reporting the aqueous thermodynamic data.

3. The representation of other evolutionary process, such as the conversion of smectite to illite, is not considered.

4. The reference groundwater is reported as “the saline Beberg water”. It is not clear whether this remains a representative groundwater in the SR-Site project

Table 3a: Calculated pore-water composition reflecting variation of groundwater chemistry (salinity) and CO_2 conditions [17]

	Saline- GW (SGW)			High-saline GW		Non-saline GW	
	RPWC mol/L	RPW mol/L	RPWA mol/L	HSPWC mol/L	HSPW mol/L	NSPWC mol/L	NSPW mol/L
Na^+	2.4725E-01	2.5667E-01	2.6321E-01	5.9590E-01	6.1173E-01	1.8395E-01	1.8754E-01
K^+	5.2934E-04	5.5048E-04	5.6468E-04	1.1175E-03	1.1504E-03	3.9292E-04	4.0114E-04
Ca^{2+}	1.5339E-02	1.4423E-02	1.7035E-02	4.6500E-02	5.0364E-02	1.0379E-02	1.0506E-02
Mg^{2+}	3.9366E-03	4.0783E-03	4.2111E-03	1.2613E-02	1.3048E-02	2.6241E-03	2.6303E-03
CO_3^{2-}	1.2514E-02	1.4778E-03	5.0248E-04	7.1539E-03	8.9140E-04	1.6700E-02	1.9614E-03
H^+	-2.6478E-03	-4.5512E-02	-6.0509E-02	-1.8369E-03	-4.1198E-02	-1.6294E-03	-4.5456E-02
Cl^-	1.6035E-01	1.6035E-01	1.6035E-01	6.5965E-01	6.5965E-01	1.9595E-02	1.9595E-02
SO_4^{2-}	4.7764E-02	4.3614E-02	4.1297E-02	1.8510E-02	1.7321E-02	7.7756E-02	7.2520E-02
$H_2SiO_4^{2-}$	1.0524E-02	1.0805E-04	1.1395E-04	1.0537E-04	1.0826E-04	1.0525E-04	1.0828E-04
SOH	8.5704E-02	8.5704E-02	8.5704E-02	8.5704E-02	8.5704E-02	8.5704E-02	8.5704E-02
LAX	3.3087E+00	3.3087E+00	3.3087E+00	3.3087E+00	3.3087E+00	3.3087E+00	3.3087E+00
pH	6.593	7.377	7.81	6.329	7.046	6.72	7.555
pCO_2	-0.98	-2.6	-3.496	-1.118	-2.6	-0.95	-2.6
	closed	open	open	closed	open	closed	open
solids	quartz calcite gypsum	quartz calcite gypsum	quartz calcite gypsum	quartz calcite gypsum	quartz calcite gypsum	quartz calcite gypsum	quartz calcite gypsum
Ionic strength	0.29311	0.29046	0.29159	0.74481	0.75992	0.23259	0.2211

Table 3b: Calculated pore-water composition reflecting variation of MX-80 bentonite properties [17]

	No impurities		Ca-bentonite	
	RPW-NI-C mol/L	RPW-NI mol/L	RPW-Ca-C mol/L	RPW-Ca mol/L
Na^+	1.6469E-01	1.6461E-01	8.5803E-03	8.9927E-03
K^+	3.4396E-04	3.4425E-04	2.0993E-05	2.2062E-05
Ca^{2+}	3.8587E-03	3.86560E-03	1.4324E+00	1.0089E-01
Mg^{2+}	1.1500E-03	1.1475E-03	2.8445E-04	3.1249E-04
CO_3^{2-}	-8.6071E-03	2.0846E-04	3.7754E-03	6.5913E-04
H^+	-8.3083E-03	-9.3018E-03	-4.2198E-03	-3.1236E-02
Cl^-	1.5570E-01	1.5570E-01	1.6035E-01	1.6035E-01
SO_4^{2-}	3.8500E-03	3.8499E-03	8.6803E-03	8.3750E-03
$H_2SiO_4^{2-}$	1.0494E-04	1.0494E-04	1.0477E-04	1.493E-04
SOH	8.5704E-02	8.5704E-02	8.5704E-02	8.5704E-02
LAX	3.3087E+00	3.3087E+00	3.3087E+00	3.3087E+00
pH	6.352	6.358	6.321	6.907
pCO_2	-2.029	-2.6	-1.383	-2.6
	closed	open	closed	open
solids	quartz	quartz	quartz calcite gypsum	quartz calcite gypsum
Ionic strength	0.1756	0.1754	0.2634	0.28275

2.3.4. Experimental data

The database compilation deliberately set out to use only systematic sets of high quality data. Where possible data obtained from MX-80 bentonite experiments was used, although other bentonites were considered, as well as data from experiments with montmorillonite. Consequently, the quantity of experimental data is relatively low and only includes:

- Am
- Cs (plus thermodynamic modelling)
- Pb
- Np(V)
- Ni (plus thermodynamic modelling)
- Se
- Th
- U(VI)

The details of these experimental data sets are well presented and calculation associated with the application of the various correction factors is clear and complete (within Appendices E and F).

Chemical analogues or assumptions of zero sorption are applied for other radionuclides. Significantly, thorium is used as an analogue for U(IV), Np(IV), Pu(IV), Sn(IV), Tc(IV). As discussed earlier, this represents a significant assumption.

Again the age of the document needs to be raised. Clearly there have been numerous experimental examinations of the sorption behaviour of radionuclides in contact with bentonite and it would be appropriate to consider these in deriving new sorption parameters for SR-Site or at the very least assess the significance of new data compared to the derived K_ds.

It is instructive to examine the values of the derived K_d values. Table 4 shows the K_d values for sorption onto MX-80 bentonite for selected radionuclides. The figures in parenthesis show where the values have been changed slightly in the main data report [6], to reflect slight changes in bentonite composition; this change is slight although the details of the calculations are not easily found within the documentation. The data in the table shows that there is only a small predicted impact from variations in groundwater chemistry.

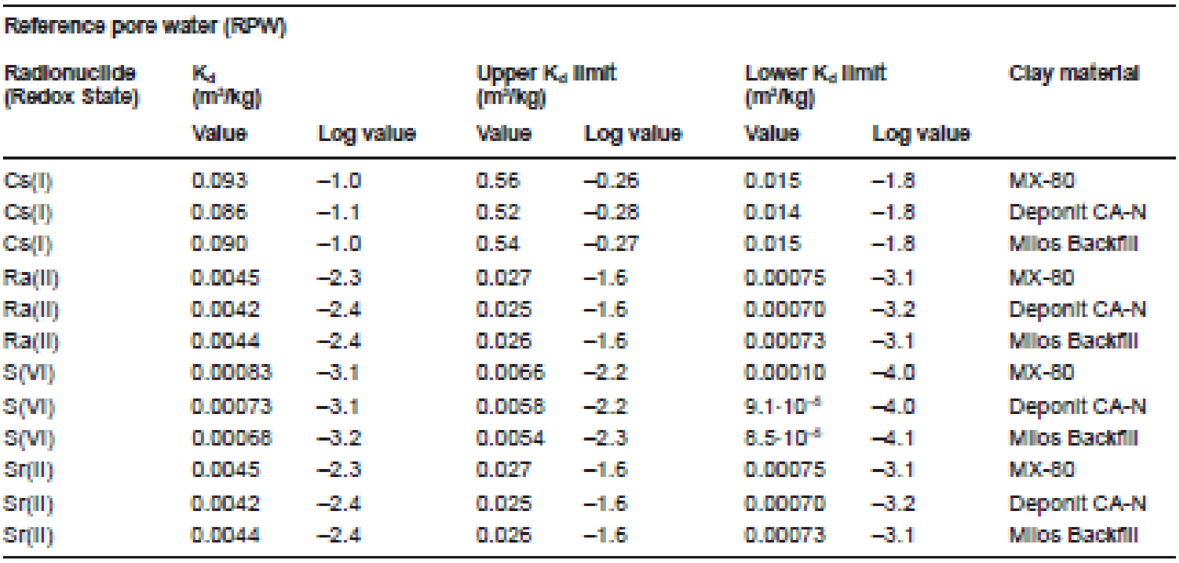
Table 4: Derived K_d values for selected radionuclides (m^3/kg)

	Reference Porewater	Reference porewater with closed CO_2	Highly saline porewater
Cs	0.11 (0.093)	0.10	0.03 (0.031)
Np(IV), Pu(IV), U(IV), Th(IV)	63	40	40
Sr(II), Ra(II)	0.005 (0.0045)	0.005	0.001 (0.0011)
U(VI)	3	14	3

2.3.5 Long term evolution of bentonite

The derivation of K_ds for compacted bentonite only considers variations due to porewater chemistry or differences in mineralogy between different bentonites, as they are emplaced. For example, Table 5 [6] shows the extremely slight variation in K_d due to the small differences in composition of MX-80, Deponit CA-N and Milos Backfill.

Table 5: Recommended Kd values for CEC sensitive elements for the reference buffer and backfill materials (m^3/kg) [6]



Reference pore water (RPW)

Radionuclide (Redox State)	K_d (m^3/kg)		Upper K_d limit (m^3/kg)		Lower K_d limit (m^3/kg)		Clay material
	Value	Log value	Value	Log value	Value	Log value	
Cs(I)	0.093	–1.0	0.56	–0.26	0.015	–1.8	MX-80
Cs(I)	0.086	–1.1	0.52	–0.28	0.014	–1.8	Deponit CA-N
Cs(I)	0.090	–1.0	0.54	–0.27	0.015	–1.8	Milos Backfill
Ra(II)	0.0045	–2.3	0.027	–1.6	0.00075	–3.1	MX-80
Ra(II)	0.0042	–2.4	0.025	–1.6	0.00070	–3.2	Deponit CA-N
Ra(II)	0.0044	–2.4	0.026	–1.6	0.00073	–3.1	Milos Backfill
S(VI)	0.00083	–3.1	0.0066	–2.2	0.00010	–4.0	MX-80
S(VI)	0.00073	–3.1	0.0058	–2.2	$9.1 \cdot 10^{-5}$	–4.0	Deponit CA-N
S(VI)	0.00068	–3.2	0.0054	–2.3	$8.5 \cdot 10^{-5}$	–4.1	Milos Backfill
Sr(II)	0.0045	–2.3	0.027	–1.6	0.00075	–3.1	MX-80
Sr(II)	0.0042	–2.4	0.025	–1.6	0.00070	–3.2	Deponit CA-N
Sr(II)	0.0044	–2.4	0.026	–1.6	0.00073	–3.1	Milos Backfill

This lack of variation is due to the small differences in mineralogy (e.g. 87% in MX-80 and 81% in Deponit CA-N) and in particular the dominance of montmorillonite/smectite in terms of sorption. The long term evolution of bentonite is not considered in the derivation of K_ds. This long term evolution could be:

- Conversion into Ca-montmorillonite. Although considered in terms of pore water composition, the impact on sorption does not appear to have been considered.

- Interactions with iron from corrosion processes in the near-field leading to the formation of Fe-montmorillonite or the replacement of smectite with non-swelling clays such as chamosite.

- Illitisation. When exposed to pressure and temperature, smectites transform into more stable silicate phases, such as illite [24]. Use in assessment calculations

Although some modelling of these processes appears to have been done [18], the impact on sorption has not been assessed.

2.4. Application in assessment calculations

K_ds for use in the assessment calculations are tabulated in the main data report [6] and these correspond exactly with the values derived by Crawford [3], indicating that this part of the audit trail is robust. Similarly, data is reported that is consistent with [17] for bentonite, although some values have been modified to reflect differences in bentonite properties to that assumed in [17].

Performance assessment calculations are described in [9], in particular, for sorption, in Section 13.5. From this, it is clear that Ra-226 dominates dose and that the dose has some sensitivity to the K_d for Ra. It is not clear, however, whether sensitivity analyses have been undertaken on the combination of Th and Ra K_d values (for both geosphere and near-field parameters) .

3. Main Review Findings

The main findings of this review are listed below:

1. The derivation of bedrock K_ds has been done in a systematic and comprehensive manner, with the general assumptions of “Kd” – linearity, equilibrium etc. being reasonable for safety assessment calculations. The main sorption report is well written and generally presented in a full and complete way.
2. Derived data has been transferred to the main data report successfully and the audit trail appears robust.
3. Some concerns about the underpinning experimental data, especially with regard to control of pH conditions and the range of conditions considered in the experiments. There is a lack of data for many key radionuclides, which has meant the extensive use of chemical analogues.
4. The derived K_d values are low, and there is a concern that there is the potential for “compounded cautiousness” in the approach. The lack of consideration of fracture minerals also leads to K_d values perhaps being lower than expected.
5. Variability and uncertainty is encompassed within the distributions of the parameters. There is little use of chemical modelling or expert elicitation processes to underpin understanding of the sources of variability in sorption.
6. The derivation of sorption parameters for bentonite is comprehensive but requires updating to reflect new experimental data recorded since the publication of the database (2004). The age of the database may also mean that thermodynamic data is not consistent with that used more recently in other SR-Site report.
7. The impact of the evolution of bentonite on sorption has not been considered and again the consistency with other geochemical models needs to be addressed
8. The details of any sensitivity studies concerning the sorption of key radionuclides, in particular decay chains and combinations of both near field and geosphere parameters, are not apparent.

4. Recommendations to SSM

A summary of the recommendations to SSM are as follows:

1. Review in detail the results of sensitivity analyses, in particular the combination of K_ds in decay changes and in bentonite and bedrock. If this has not been done, SSM should request further sensitivity analyses should be undertaken. The results of these sensitivity analyses will determine, to a large extent, the priority of the other recommendations listed below.
2. This review has not examined in detail how the underpinning sorption experimental data has been transferred through the K_d derivation process. These calculations should be made visible to SSM and spot checks undertaken to assess their accuracy.
3. A detailed review of the experimental methodology underpinning these data reviews has not been done. In particular, the impact of pH drift should be examined, with those experimental points that lie outside the natural pH range potentially being screened out of the K_d derivation process
4. SSM could consider the impact of an alternative approach to the derivation of K_ds, that takes into account fracture materials and/or chemical variations
5. The bentonite sorption database should be updated or at least reviewed in the context of more recent experimental data. Additionally, the consistency of the modelling approach and underpinning thermodynamic data should be assessed against other thermodynamic modelling undertaken as part of SR-Site.
6. The impact of the evolution of the bentonite buffer should be assessed with regard to sorption and radionuclide migration.

5. References

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APPENDIX 1

Coverage of SKB reports

Table 6: SKB reports reviewed during this study

Reviewed report	Reviewed sections	Comments
SKB (2011). Main report of the SR-Site project. SKB TR-11-01	Section 13.5.11	Use of sorption in assessment calculations
SKB (2010). Data report for the safety assessment SR-Site. SKB TR-10-52.	Section 5.3 and Section 6.8	The audit trial for sorption data.
Crawford J. (2010). Bedrock Kd data and uncertainty assessment for application in SR-Site geosphere transport calculations. SKB R-10-48	All	Derivation of K_d values
Ochs, M and Talerico, C. 2004, Data and uncertainty assessment. Migration parameters for the bentonite buffer in the KBS-3 concept SKB TR-04-18	All	Derivation of K_d values
SKB (2010) TR-10-47 Buffer, backfill and closure report for the safety assessment SR-Site	Sections 3.6, 4.5, 5.5, 6.5, 7.5, 8.5, 9.5	Properties of bentonite
Crawford, J. 2008. Bedrock transport properties Forsmark: Site descriptive modelling SDM-Site Forsmark. SKB R-08-48.	Read but not reviewed	Underlying data for Crawford (2010)
Selnert, E., Byegård, J., and Widestrand, H. 2008 Forsmark site investigation. Laboratory measurements within the site investigation programme for the transport properties of the rock. Final report SKB P-07-139	Read but not reviewed	Underlying data for Crawford (2010)

APPENDIX 2

Suggested needs for complementary information from SKB

1. SKB should make available all relevant sensitivity analyses relating to radionuclide sorption, in particular those looking at decay chains and combined bentonite and bedrock K_d studies
2. SKB should have provide access to geochemical models, modelling codes, input files and supporting databases used by SKB, to enable, if required, detailed checks to be performed, and sensitivity analyses to be undertaken and alternative models to be created. This should include the geochemical models for bentonite evolution and the calculations relating to the derivation of bedrock K_ds

APPENDIX 3

Suggested review topics for SSM

1. If not already performed by SKB (or at insufficient detail), sensitivity calculations should be performed to examine radionuclide sorption, including sorption within decay chains and combined bentonite and bedrock K_d studies
2. A review of the data used to compile the bedrock K_d database
3. Thermodynamic modelling to examine sorption in both bentonite and bedrock, to underpin the choice of K_d values used in SR-Site. This should include an examination of the role of fracture materials in influencing sorption in the far field
4. An assessment of the bentonite sorption database in the light of new experimental data and updates to thermodynamic data. Consistency with the data and approaches used within the geochemical modelling of bentonite evolution and overall EBS evolution should also be included

2012:63

The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 270 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.

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