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SR-Can

Data and uncertainty assessment

Migration parameters for the bentonite buffer in the KBS-3 concept

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August 2004

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Abstract

SKB is currently preparing license applications related to the deep repository for spent nuclear fuel and an encapsulation plant. The present report is one of several specific data reports feeding into the interim reporting for the latter application; it is concerned with the derivation and recommendation of radionuclide migration input parameters for a MX-80 bentonite buffer to PA models. Recommended values for the following parameters as well as the associated uncertainties are derived and documented for a total of 38 elements and oxidation states:

- diffusion-available porosity (ε),
- effective diffusivity (D_e),
- distribution coefficient (K_d).

Because of the conditional nature of these parameters, particularly of K_d, they were derived specifically for the conditions expected to be relevant for PA consequence calculations. K_d values were generally evaluated for the specific porewater composition and solid/water ratio representative for MX-80 compacted to 1,590 kg/m^3. Because of the highly conditional nature of K_d, this was done for several porewater compositions which reflect possible variations in geochemical boundary conditions. D_e and ε were derived as a function of density. Parameter derivation was based on systematic datasets available in the literature and/or on thermodynamic models. Associated uncertainties were assessed for a given set of PA conditions and as a function of variability in these conditions.

In a final step, apparent diffusivity (D_a) values were calculated from the recommended parameters and compared with independent experimental measurements to arrive at self-consistent sets of migration parameters.

Sammanfattning

SKB förbereder för tillfället en ansökan för en inkapslingsanläggning för använt kärnbränsle. Den här rapporten är en i mängden av de rapporter som levererar specifika data för säkerhetsredovisningen som ingår i ansökan. Den behandlar framtagning av och urval av transportparametrar för radionuklider i en buffert av MX-80 bentonit. Rekommenderade värden för följande parametrar tillsammans med tillhörande osäkerheter har tagits fram och dokumenterats för 38 grundämnen och oxidationstal:

- porositet (tillgänglig för diffusion) (ε),
- effektiv diffusivitet (D_e),
- distributionskoefficienter (K_d).

På grund av det sätt som dessa parametrar styrs av omgivningsfaktorer, särskilt K_d, har de bestämts specifikt för de förhållanden som förväntas vara relevanta för konsekvensberäkningar i säkerhetsredovisningen. K_d värden har normalt bestämts från givna porvattensammansättningar och fast fas/vätska förhållanden vilka är representativa för MX-80 kompakterad till 1 590 kg/m^3. För K_d har detta gjorts för ett flertal porvattensammansättningar för att reflektera variationer is de geokemiska randvillkoren. D_e och ε har tagits fram som en funktion av densitet. Parametervalet har baserats på systematiska publicerade datasammanställningar och/eller på termodynamiska modeller. Osäkerheterna i parametrarna har bedömts för givna förhållanden/randvillor från säkerhetsredovisningen och presenteras som en funktion av variabiliteten i dessa förhållanden.

Slutligen har den apparenta diffusiviteten (D_a) beräknats med de framtagna parametrarna och jämförts med oberoende experimentella resultat för att testa att parametrarna är internt konsistenta.

Extended Summary and road map

Introduction

SKB, the Swedish Nuclear Fuel and Waste Management Co, is currently preparing license applications to locate, build and operate i) the deep repository for spent nuclear fuel and ii) an encapsulation plant in which the spent fuel will be emplaced in canisters to be deposited in the deep repository.

Two safety reports will be produced within the next five years; one for the application to build an encapsulation plant, SR-Can, and one for the application to build the repository, SR-Site. The present report is one of several specific data reports feeding into the SR-Can Interim Report. The SR-Can Interim Report will be produced after an initial phase of the SR-Can project, with the main purpose of demonstrating the adopted methodology. Specific data reports are being prepared in cases where uncertainties of input data to safety assessment (consequence) calculations will have a decisive influence on safety related output uncertainty. The parameter and uncertainty estimates given in the specific data reports will also be compiled and further assessed in a SR-Can Data Report.

Content and organisation of the present report

The present specific data report is concerned with the derivation and recommendation of the radionuclide migration parameters for a MX-80 bentonite buffer with a dry density of 1,590 kg/m^3. Recommended values for the following parameters as well as the associated uncertainties are derived and documented for each relevant element:

- diffusion-available porosity (ε),
- effective diffusivity (D_e),
- distribution coefficient (K_d).

The report follows the general outline developed by SKB for the SR-Can interim reporting and is organised as follows:

- The derivation of recommended data and uncertainties is presented in the central chapter of the report, chapter 5, and are summarised in chapter 6.
- General discussions on data sources used and treatment of uncertainties are given in chapters 3 and 4.
- Detailed data derivation tables as well as background information on system characteristics and models used are given in the appendix.
- Chapters 1 and 2 provide a general introduction and explain the purpose of the present report in SR-Can.

The purpose of the present report is the derivation of input data for PA models. Accordingly, brief reviews of the literature are provided to the degree deemed necessary for supporting data selection, but no general review of the literature is provided. Similarly, arguments are provided why certain pieces of the literature were selected as source data base; but reasons for rejection are not discussed for each study that was considered unreliable or otherwise too limited.

A brief discussion on general aspects of sorption and diffusion processes are given in the SR-Can Process Report /SKB, 2004/, including brief discussions of conceptual uncertainties. It is recommended to consult the pertinent sections of the process report.

Approach to the derivation of data and uncertainties

General framework and scope

The present migration parameters, in particular K_d, are conditional in nature. Therefore, they were derived specifically for the conditions expected to be relevant for PA calculations. The underlying premise for the direct use of conditional parameters in consequence calculations is that conditions in parameter derivation and application are consistent. Significant discrepancies would require the re-derivation of the migration parameters.

In principle, this situation could be resolved by directly including sorption/diffusion processes in the model used for consequence calculations, which would require a THMC model approach. However, in addition to the great difficulties still associated with fully coupling THM processes on one and C processes on the other hand, the present state of the art of quantifying radionuclide sorption and diffusion in compacted bentonite does not render this a realistic option to date. For example, reliable and sufficiently constrained thermodynamic sorption models are available for very few relevant radionuclides only, the limiting factor being the lack of sorption data as function of conditions that is needed to parameterise such models. Further, the application of a thermodynamic sorption model requires a reliable standard thermodynamic database, and this prerequisite is not given for a number of radionuclides.

General approach for deriving migration parameters

To arrive at consistent sets of migration parameters, D_e, ε and K_d were first derived independently. In a second step, apparent diffusivity (D_a) values were calculated from these parameters and compared with independent experimental data. Specifically:

- Diffusion-available porosity was viewed as a physical parameter for a given bentonite and density, except for anions.
  - For anions, this parameter was evaluated together with D_e to ensure a consistent treatment of anion exclusion (see below).
  - For neutral and cationic species, ε was calculated as a function of dry and specific density of the bentonite
- Effective diffusivities were derived for non-sorbing anions, Cs, and HTO:
  - D_e for non-sorbing anions was derived on the basis of i) experimental data recorded as a function of density for several bentonite-water systems and ii) electrical double layer calculations. To take anion exclusion into account, a reduction factor for ε was derived from independent studies. The plausibility of the selected D_e and ε values was verified by comparisons with independent experimental D_a values for a range of dry densities.
  - For Cs, a higher value for D_e was selected than in case of all other elements, in combination with the physical porosity, indicating enhanced cation diffusion. Evaluations based on experimental data recorded as a function of density as well as on electrical double layer calculations confirmed this effect. The plausibility of the selected D_e and ε values was again verified by comparisons with independent experimental D_a values for a range of dry densities. As Cs sorbs on bentonite, this comparison had to include K_d (see below) as well.

  - Because of the lack of element-specific data for most radionuclides, D_e values for all other elements were represented by D_e for HTO and the physical porosity. As most radionuclides exist as a mixture of positively, negatively and uncharged species under the relevant conditions, HTO was considered to represent average diffusion properties adequately. D_e for HTO was derived as a function of density from experimental data. D_a values were calculated from these data and the recommended K_d values (see below) to evaluate the self-consistency of all selected parameters.

- Distribution coefficients (K_d) were generally evaluated for the specific porewater composition and solid/water ratio representative for MX-80 compacted to 1,590 kg/m^3. Because of the highly conditional nature of K_d, this was done for several porewater compositions which reflect possible variations in geochemical boundary conditions (groundwater and bentonite composition, pCO_2). Wherever possible, derivation of K_d was based on i) systematic datasets recorded as a function of pH and other conditions and/or ii) thermodynamic sorption models:
  - In the first case, extrapolation from experimental conditions to the conditions relevant for compacted MX-80 was done with the help of conversion factors taking into account differences in surface and radionuclide solution speciation as well as in sorption site density if a substrate other than MX-80 had been used. While the latter is straightforward, the conversion factors related to surface and solution speciation had to be evaluated carefully based on speciation calculations for both experimental and compacted systems.
  - In contrast, thermodynamic sorption models could be applied directly to the conditions relevant for the compacted system to yield K_d.
  - For most radionuclides, data derivation was based on experimental results and conversion procedures, due to the lack of reliable thermodynamic sorption models. It has to be further realised that many of the published sorption models had been calibrated in the absence of relevant chemical factors, such as carbonate or sulphate, and are therefore not well constrained when applied to a complex system. In some cases, the sorption data presently available in the literature would possibly allow to develop appropriate sorption models. However, such model development was not within the scope of the present project.

Sources and treatment of uncertainties

Uncertainties in input parameters can be related to two fundamentally different sources (see Figure 4-1 in section 4.1.2):

1. Uncertainties of the input parameters themselves: These include experimental uncertainties and uncertainties introduced by extrapolating conditional parameters (in particular K_d) from experimental to PA conditions. This type of uncertainty was addressed by explicitly deriving uncertainty limits for each parameter and radionuclide.
2. Uncertainties caused by expected variability in the PA conditions. Because of the conditional nature of the present input parameters, it is obvious that any significant deviation from the expected conditions will make the parameters les reliable. Thus, any potential uncertainty in conditions needs to be addressed as well in an overall evaluation of parameter uncertainty. This was addressed by specifically deriving input parameters for the reference boundary conditions as well as several other sets of boundary conditions to trace out the resulting variations in the input parameters.

Uncertainties in input parameters

Diffusion parameters (effective diffusivity D_e, and diffusion-available porosity ε) were evaluated directly as a function of bentonite density and composition, by analysing three different bentonites (including MX-80) with smectite contents ranging from 50% to > 95%:

- Physical porosity was calculated as a function of density. Based on the excellent agreement with measured data, no uncertainty was attributed to this value. In case of diffusion-available porosity for anions, the uncertainty for the reduction factor for ε followed directly from the experimental uncertainties reported in the original literature (section 5.3.4).
- A D_e value for HTO was recommended based on a regression of experimental data vs bentonite density. The standard deviation of the regression prediction at the reference density was taken as the uncertainty in D_e.
- In case of Cs, the uncertainty of D_e was defined by the interval between the highest value selected as reasonable for representing enhanced cation mobility and D_e for HTO.
- In case of D_e for anions, upper and lower limit were evaluated separately based on the range of experimental observations and electrical double layer calculations.

In the case of K_d values, uncertainties were defined in analogy to the approach used for data derivation:

- Where extrapolation from experimental conditions to the conditions relevant for compacted MX-80 was done with the help of conversion factors, uncertainties were quantified as follows:
    - An average experimental uncertainty was assumed, based on several representative data sets.
    - For each of the conversion factors used to extrapolate to PA conditions, a corresponding uncertainty factor was defined (see section 5.1.4). These factors were evaluated for each extrapolation procedure.
- The use of thermodynamic sorption models was considered to be associated with the same uncertainty in all cases.

Uncertainties caused by expected variability in the PA conditions

The influence of groundwater and porewater composition on diffusion parameters was not generally included (in contrast to K_d, see below), for the following reasons:

- Diffusion-available porosity can be viewed as a physical parameter for a given bentonite and density, except for anions.
- D_e refers to steady-state conditions where effects of porewater composition on sorption are not relevant. Effects of porewater composition on the actual diffusion process were implicitly included by pooling data sources referring to a fairly wide range of conditions.

Therefore, density and composition of bentonite are the main factors where variations in the PA conditions could cause significant uncertainties. Since all diffusion parameters were evaluated as a function of density, using data from different bentonites, possible variations are already taken into account.

On the other hand, K_d values were derived independently for several bentonite/porewater systems which reflected possible variations in groundwater and bentonite composition.

While such sets of K_d values for different conditions can be used to approximately trace out the effect of the considered variations on K_d, it has to be kept in mind that the K_d values are strictly valid only for the specific conditions they had been derived for. The systems considered for data derivation are described in section 5.2.

It is further pointed out that it is not possible to relate variations in groundwater composition directly to uncertainties in K_d; rather, this needs to be assessed through specifically calculated porewater compositions resulting from bentonite-groundwater interaction.

Uncertainties in redox conditions with respect to the sorption and diffusion of redox-sensitive elements were addressed by providing parameters separately for each relevant oxidation state. Where redox conditions for PA cannot be constrained sufficiently, overall parameter uncertainty will encompass the entire range of values derived for the relevant oxidation states.

Contents

1 Introduction

This document concerns data and uncertainty assessment of buffer migration data in support of the SKB Safety Assessment SR-Can. The report follows a given outline, provided by SKB, where the authors are instructed to answer various questions as set out by this outline.

1.1 Background

SKB, the Swedish Nuclear Fuel and Waste Management Co, is currently preparing license applications to locate, build and operate i) the deep repository for spent nuclear fuel and ii) an encapsulation plant in which the spent fuel will be emplaced in canisters to be deposited in the deep repository. Several investigations are conducted in support of these license applications.

1.1.1 Planned safety assessments

SKB is currently pursuing site investigations for a deep repository in the municipalities of Östhammar and Oskarshamn. The investigations are conducted in two stages, an initial phase followed, if the expected site suitability is confirmed, by a complete site investigation phase. The aim is to build a deep repository at one of these candidate sites, provided that the bedrock and other relevant conditions are found suitable.

Two safety reports will be produced within the next five years; one for the application to build an encapsulation plant, SR-Can, and one for the application to build the repository, SR-Site. SR-Can will be based on site data from the initial site investigation phase and SR-Site on data from the complete site investigation. After an initial phase of the SR-Can project, an SR-Can Interim report will be produced, with the main purpose of demonstrating the adopted methodology, so that this can be reviewed before it is used for the applications. Also, preliminary safety evaluations /SKB, 2002/, of each site will be made as sub-tasks within the SR-Can project.

1.1.2 Assessing input data – need for traceable expert decision

All input data to quantitative aspects of the safety assessment will exhibit uncertainties. The quality of the results of any calculation in the assessment will, among other factors, depend on the quality of the input data and on the rigor with which input data uncertainties have been managed. A common and methodological philosophy for the determination of input data and the subsequent management of data uncertainty is therefore required.

In SR 97, a standardised procedure was employed for all input data to radionuclide transport calculations. The outcome was presented in the SR 97 Data Report /Andersson, 1999/. The uncertainty treatment in SR 97 is discussed by the SKI/SSI review /SKI and SSI, 2001/. The authorities have since conducted some investigations on Expert Judgement /e.g. Wilmot and Galson, 2000; Wilmot et al, 2000; Hora and Jensen, 2002; Hora, 2002/. Also SKB has continued development work /Hedin, 2002, 2003/.

Among other things the reviewers required quantification of uncertainties into a form suitable for probabilistic assessment and traceable records on the expert input to data selection and uncertainty assessment. A new procedure, based on the one used in SR 97 and taking into account review comments is therefore established for SR-Can.

1.2 Scope and Objectives

The set of input data parameters to a full safety assessment is very large. Some input data uncertainties will have a decisive influence on safety related output uncertainty whereas others will essentially not influence output uncertainty at all. An obvious example of the latter is transport properties of those radionuclides that never give a significant contribution to the total dose. It is thus appropriate to identify input data to which output is sensitive and use these insights in allocating resources to the determination of input data uncertainties.

Based on such reasoning the SR-Can project team has identified various data where there is a need for a subject specific data report. The information and judgement supplied in these reports are those of the report authors. It should be noted that there will be several different such subject specific data reports. Furthermore, all parameter and uncertainty estimates will also be compiled and further assessed in a SR-Can Data Report. Judgements made in the SR-Can Data Report are usually made by the SR-Can project team (if not explicitly noted else by proper referencing etc).

1.2.1 Specific objectives

This report supplies data with uncertainty to the buffer migration properties, i.e. diffusivity (De), porosity (ε) and distribution coefficients Kd, for all relevant elements. Also apparent diffusivities Da, should be supplied, although dependent on the first set, as this would simplify comparison with some laboratory data and with other data sets.

1.3 Procedures

1.3.1 Predefined instructions

The procedure for the data and uncertainty assessment presented in this report is based on:

- a standardized outline with detailed instructions – supplied by the SR-Can project team and
- required input (marked by <text within brackets> in this outline) from the experts listed as author(s) to this report addressing the pre-defined instructions.

The instructions are generally marked "Instructions – issues to be addressed" and are usually the first subsection in a given report section. Subsequent subsections contain the input and judgement made by the expert authors.

The standardised outline with instructions aim at establishing:

- Context; the use of the input data in SR-Can, results of sensitivity analyses, correlation to other input data.

- Sources of information (experimental data, site investigation data, model calculations etc).
- Qualitative uncertainty assessment (a description of what types of uncertainty affect the data).
- Quantitative uncertainty assessment (the actual assigning of e.g. data values, data intervals or probability distributions).

1.3.2 Experts involved etc

Instructions – issues to be addressed

Depending on practicalities and judgements on the importance of the data different procedures for addressing these issues have been used for different sets of data. This section should record the procedures for judgements etc made as regards the data discussed in this report. The following should be addressed:

- Which experts (both SKB internal and SKB external) have been involved in the report and it content? (CV etc may be supplied in appendix).
- What has been there role in this context?
- Have there been special measures for expert elicitation of data and uncertainties (this may e.g. range from single expert judgement, evaluation with the SR-Can data review committee, workshop like procedures etc)? Please provide details (if lengthy in an appendix).

Experts and their role for assessing buffer migration data

The scientific content and judgements made in this report are made by the report authors, i.e. Michael Ochs and Caterina Talerico, BMG Engineering Ltd. Their work is based on various scientific and technical input as referenced in the normal scientific way.

The report has been assessed by a subset of the SR-Can Project Team consisting of Patrik Sellin (SKB), Allan Hedin (SKB), Fredrik Vahlund (SKB) and Johan Andersson (JA Streamflow AB). Their role has been to technically review the report and to make sure it serves the need as input to SR-Can and the SR Can Data report. The scientific content has also been reviewed by members of the SKB SIERG committee.

2 Use in SR-Can

This chapter briefly discusses how the parameter will be used in SR-Can and if there is any information as regards its importance. As the section concern the interface between safety assessment and the specific model, the content is produced jointly by SKB and the experts producing this document.

2.1 Applicable SR-Can conditions

This section should list the various “conditions” for which parameter and uncertainty estimates are needed. “Conditions” refer to boundary conditions, states and other circumstances, which potentially may affect the values of the parameters to be estimated. Changes of a “condition” may be due to various initial states, evolution within a scenario or conditions under different scenarios.

Specific for buffer migration parameters

As regards buffer migration parameters data with uncertainties are solicited for the following situations:

- A “full” range of near field groundwater flow.
- A “full” range of near-field groundwater compositions.
- Various deposition hole geometries.
- A range of temperatures.
- Various buffer densities.
- Various potential initial defects.
- Impact of gas transport.

Table 2-1 lists the conditions for which buffer migration data are actually supplied in the report, together with an assessment on the sensitivity to these various conditions. The specific ranges of condition, as well as the assessed sensitivity to these conditions are defined in subsequent chapters of the report.

Table 2-1. SR-Can conditions for buffer migration parameters.

Condition	Importance
groundwater flow, geometry, defects	/
groundwater composition (pe, pCO_2)	very high
temperature	probably medium
buffer density	high
gas transport	?
bentonite composition (salt inventory, exchangeable cations)	very high
porewater composition (choice of approach)	very high
buffer/porewater evolution (choice of approach)	very high

2.2 Models

2.2.1 Instructions – issues to be addressed

This section should address the following:

- In what model or other circumstances are the parameter(s) used in SR-Can?
- Will there be differences between ranges of conditions (see 0)?

The actual model used (or other use) should be referred to – not all possibilities. For the latter refer to the Process Report.

2.2.2 Models used for buffer migration

The buffer migration parameters are primarily used in the COMP23 (#ref) near-field migration code. It assumes constant values of (De), porosity (ε) and distribution coefficients Kd in each compartment.

Migration parameters are also used in assessments of buffer evolution. These analyses primarily concern other elements, but consistency with RN-migration parameters is still needed.

Buffer porosity is a key parameter when assessing earth-quake impacts. Consistency in data choice is needed.

2.2.3 Differences in models for different conditions

COMP23 is probably applicable to most foreseen calculation cases. However, there may be problems – or at least need for special considerations – in cases of channels through the buffer – or other cases with inhomogeneous buffer. In cases without buffer (should they be formulated), the buffer migration are not needed anyway!

2.3 Results of sensitivity analysis – if any?

2.3.1 Instructions – issues to be addressed

This section should discuss whether the parameter has been included in a sensitivity analysis in a Safety Assessment context (provide reference). This concern any sensitivity analysis conducted prior to the final SR-Can analyses (i.e. also analyses set up during the course of producing this report). However, the reason to discuss this here is to help limiting the scope of the data and uncertainty evaluation – not to make final judgements on the importance of different parameters. Overall conclusions on importance are to be made in the SR-Can report.

In addressing importance and sensitivity it is also necessary to consider various calculation endpoints. Endpoints are not restricted to yearly risk (although this is the ultimate endpoint), but also include isolation potential, barrier performance etc (the relevant endpoints will be further determined in coming planning documents to be provided by SKB).

In case sensitivity analyses have been performed, discuss:

- At what ranges of the parameter is the impact on Safety Assessment significant and are there ranges where the impact is negligible? (For example, an elemental solubility larger than say 0.1 mole/dm^3 is unlikely to imply any solubility limitation. Consequently, we need not be very precise in estimating such solubilities as long as it is established that the solubility is "high enough").
- Is the impact monotonous, i.e. higher/lower values will always provide "worse" performance – is there an "optimal" value – or is the impact complicatedly dependent upon the values of other input parameters?
- What precision is needed to have an impact on Safety Assessment results (this answer may be different for different parameter ranges)?
- Do the answers apply to all scenarios listed in section 0 – or only to some?

In answering the above, do consider if the cited sensitivity analyses are sufficiently general to provide definitive answers.

2.3.2 Sensitivity of buffer migration parameters

As regards the buffer migration parameters the following may be stated:

- For some nuclides the impact is linear, e.g. for I-129 De is linearly proportional to dose. The impact from K_d depends on half-life and canister containment time, but may be at least linear for some nuclides, i.e. is isotope specific. Impact on porosity less severe (but porosity affects other buffer conditions as well).
- In general impact from Kd and De is monotonous, i.e. low Kd and high De tend to increase risk. However, if biosphere modelling does not take appropriate account of accumulation etc modelling artefact may result (e.g. U-234 released into the biosphere may not produce high doses, but left to decay in the NF/FF the daughter Ra-226 will produce high doses). Anyway, we should provide arguments in SR-Can why containment, even if restricted in time, always is a good safety feature!
- The impact of porosity is monotonous on RN-migration in the same way as for Kd.
- As regards precision, this should be related to the fact that impact on risk may be essentially linear to parameter value input (see previous).

3 Sources of information

This chapter should describe the sources for the estimating the parameter and the uncertainty estimates provided. In complex cases references to underlying reports would usually be needed. Still the text in this chapter should provide enough information to the reader making it possible to understand the factual basis for the values provided in the report. If the source of information is part of a Site Description /e.g. SKB, 2003/ usually only short text, with reference, is needed. All factual information in this chapter is provided by the experts listed as authors to the report

3.1 Sources of data

3.1.1 Instructions – issues to be addressed

This section should address the following:

- Which sources of data have been used?
- Are data based on measurements made in the field, in the laboratory or more generic?
- Under which conditions (e.g. water composition, type of rock, temperature etc) are the data measured?
- Who has produced the data?

If the database essentially is obtained from modelling, still try to provide the above information for the data used as input to this modelling. (Make it short though).

3.1.2 Sources of data for buffer migration parameters

Data sources to be considered as basis for selecting diffusion parameters and distribution coefficients for compacted MX-80 bentonite in contact with specific groundwaters need to fulfil two requirements:

- They have to correspond to, or allow the derivation of parameters applicable to the compacted state (1,590 kg/m^3 in this case).
- They have to correspond to, or allow the derivation of parameters applicable to the relevant geochemical conditions. In particular, this includes the porewater composition corresponding to the compacted state.

Both issues are discussed below. Based on the evidence presented, it is concluded that batch sorption data can be applied to compacted systems. In contrast to diffusion studies, batch sorption data are often measured as a function of several conditions, which is very important for the derivation of K_d values corresponding specifically to the present reference conditions. Further, batch sorption data are comparatively easy to interpret, since they are the direct result of relatively simple experiments that can be well controlled. In contrast, diffusion coefficients need to be extracted from the raw experimental data through models, and care must be taken in interpreting the experimental results (see /Yu and Neretnieks, 1997/, for a discussion of potential experimental problems).

Therefore, the derivation of distribution coefficients and diffusion parameters for the specified conditions was generally based on element-specific batch sorption data and diffusion parameters for HTO (see section 5.3 regarding exceptions for anions and Cs). This is considered as significantly more reliable than a possible attempt of deriving K_d values based on data for compacted bentonite. A final consistency check was done wherever possible, by calculating D_a for all reference conditions from the derived K_d values and diffusion parameters and comparing it with independent experimental D_a measurements. The good agreement observed further supports the validity of the chosen approach (see section 5.3).

Table 3-1 gives an overview of the advantages and disadvantages of batch sorption vs diffusion experiments. Table 3-2 shows the overall data hierarchy used for the derivation of the present buffer migration parameters. Details of source data selection are given in section 5.3.

Table 3-1. Overview of data sources for buffer migration parameters.

type of experiment	advantage	disadvantage
batch experiments	K_d directly measured parameter variation process understanding / model	(very) low solid/water ratio
diffusion experiments	relatively close to reality (compacted clay)	somewhat of a black-box results are model-dependent

Table 3-2. Data hierarchy for the derivation of buffer migration parameters.

Sorption	Diffusion (general)
1. large systematic data set / model for MX-80 or similar	1. data as f(density) in pre-equilibrated bentonite
2. representative model	2. data as f(density) for MX-80
3. few systematic data for MX-80	3. data as f(density) for other bentonite
4. few systematic data for other bentonite (1. edge, 2. isotherms)	4. data for single condition MX-80
5. single condition datasets for MX-80	5. “ other bentonite
6. “ for other bentonite	
7. analogy with similar element	
8. chemical reasoning	
	specific for D_e:
	1. data for mobile elements / HTO are preferred over data for sorbing RN
	2. data as f(density) are preferred over single-density data
	3. type of bentonite is of 2nd priority

Relevance of data for the compacted state

Diffusion data

In case of diffusion parameters, the situation is relatively straightforward as most diffusion studies available to date for MX-80 bentonite have been carried out at relatively high degrees of compaction (see section 5.3.4). While few data correspond directly to the present reference density, it is included in the span of densities covered by the various studies. In addition, diffusion coefficients measured as a function of density for other compacted bentonites and clays (Kunigel-V1, Kunipia-F) generally agree with data for MX-80 (see sections 5.3.4 and 5.3.5 for examples) and show the same linear dependence on density. Thus, parameters applicable the reference density can be derived by simple interpolation.

K_d values

The situation is more difficult for the derivation of K_d values for compacted bentonite. Practically all sorption measurements are carried out in dilute suspensions. Due to experimental difficulties, no reliable sorption measurements in compacted material are available. Moreover, it is extremely difficult to obtain pore solution from compacted bentonite, and the representativeness of extracted solutions is questionable. This situation requires the application of sorption data from batch experiments to compacted material; i.e. the transfer of data from low to very high solid/water ratios. In principle, K_d is independent of the solid/water ratio, and no transfer is necessary given that the available specific surface area or sorption site density and solution composition remain constant. With regard to the available surface area, /Bradbury and Baeyens, 1998/ measured similar BET values for loose and compacted (2,000 kg/m^3) MX-80 and Montigel bentonites. The diffusion data by /Kato et al, 1995/ also suggest that no reduction of sorption-available surface area takes place upon compaction. Based on these studies, it is concluded that batch data can be directly applied to compacted systems, provided that any differences in solution composition are accounted for. This point is critical, as further discussed in the following section.

Consistency with the porewater composition in compacted bentonite

Diffusion data

Because of the timeframes typically needed for diffusion experiments, and the difficulties in externally controlling conditions in compacted bentonite, diffusion data are typically only available for a few conditions that are often not well constrained. In particular, D_e values for reactive elements are very sparse, and/or do not correspond to the appropriate reference conditions. Therefore, D_e values for most elements were selected based on data for HTO, which are not sensitive to the specific chemical conditions and thus more representative than element-specific data obtained under single conditions. The electrostatic potential in bentonite pores was taken into account in selecting D_e values for anions and Cs.

K_d values

As pointed out in section 5.1.3, the derivation of K_d values in this report is based on calculated porewater compositions that are representative for the pore solution in compacted bentonite. There are good indications that most apparent discrepancies between batch and intact systems can be accounted for by calculating the appropriate porewater composition as a function of all relevant factors, including compaction (i.e. solid/water ratio); see /Ochs et al, 2003; Bradbury and Baeyens, 2003a/, as well as the sections on diffusion and sorption in the process report /SKB, 2004/. Because of the variability of geochemical conditions that need to be considered (see sections 2.1 and 4.2), and the conditional nature of sorption data for reactive elements, it is critical that the data sources used provide enough information to allow the derivation of K_d values that are consistent with the various specified reference conditions.

In general, highest priority was given to systematic sets of high quality data where parameters are given as a function of conditions. If possible, data were used that had been obtained directly for the bentonite of interest to the present data derivation (MX-80). As indicated in Table 3-2, other bentonites as well as single clay minerals (montmorillonite) were also considered:

- A large portion of the systematic sorption data available has been obtained for simplified systems containing montmorillonite rather than whole bentonite. As montmorillonite is the main sorbing component of bentonite (see Appendix B), the respective sorption data are considered as being representative for bentonite. The transfer of sorption data to the conditions specific for the targeted system with MX-80 bentonite can be done using the procedures discussed in section 5.1.
- Most diffusion data available in the literature have been obtained with actual bentonite samples. Because of the importance of bentonite density for many parameters relevant for diffusion, high priority was assigned to datasets that had been obtained as a function of bentonite density. A significant portion of such data had been measured for Japanese bentonites, Kunigel-V1 and Kunipia-F. Their properties are also given in Appendix B). Kunigel-V1 is considered as fairly representative for MX-80, although it contains less smectite. Kunipia-F is a purified material consisting almost exclusively of smectite and may therefore be less representative, particularly at high degrees of compaction. However, the data presented in Figures 5-3, 5-4 and 5-6 show that diffusion data for these bentonites do not differ substantially from data for MX-80.

The main databases used for the derivation of the buffer migration parameters given in the present report are listed below; see also the specific discussion and data presentation for each radionuclide

- A recent Nagra report on selected K_d values for MX-80 /NTB 02-18; Bradbury and Baeyens, 2003a/, and original data sources cited therein.
- SKB reports on K_d, D_e/D_a and groundwater /SKB TR-97-12, Yu and Neretnieks, 1997; SKB TR-98-03, Laaksoharju et al, 1998/, and original data sources cited therein.
- JNC reports on diffusion in Kunigel-V1 and Kunipia-F bentonites as a function of dry density (mainly by Sato and co-workers).

3.2 Use of models for data derivation

3.2.1 Instructions – issues to be addressed

This section should address the following:

- Is the database the result of some kind of modelling?
- Specify, and also list critical assumptions made in this modelling.

For example, information obtained from Site Descriptions is usually the result of various modelling activities, with the actually measured data as input (see e.g. /Andersson, 2003/ for an overview). Another example could be the inventory, which results from various burn-up calculations.

3.2.2 Modelling used to support the data

Some modelling considerations are made in order to address various surrounding groundwater compositions, various temperatures, various bentonite densities, etc. Here, the use of models in different stages of data derivation needs to be distinguished:

i) Models were used in defining the various conditions and some of the databases underlying the derivation of buffer migration parameters:
   - Groundwater composition, including pe and pCO_2.
   - Bentonite composition (salt inventory, exchangeable cations, edge site density).
   - Measured diffusion coefficients (and porosity, in some cases).

ii) Models were used in this report for calculating underlying system properties:
   - The porewater composition in the buffer cannot be directly measured and was calculated using a surface complexation/ion exchange model.
   - Radionuclide speciation in experimental solutions and bentonite porewater was calculated (using the TDB specified for each element, see Appendix F, and the Davies equation to carry out activity coefficient corrections).

iii) Models were used directly for parameter derivation in this report:
   - For Cs, Sr/Ra, Ni, and Eu (as an analogue for Ce, Ho and Sm) thermodynamic sorption models where directly used to calculate K_d values.
   - For the selection of D_e values, results of electric double layer model calculations were considered.

4 Uncertainty assessment

This chapter assesses in general terms the different sources of uncertainty affecting the parameter estimates. The actual estimates of the parameter(s) and associated uncertainties, are presented in the next chapter. All factual information in this chapter is provided by the experts listed as authors to the report.

4.1 Overview

4.1.1 Instructions – issues to be addressed

The expert may provide an overview of the different sources of uncertainty affecting the data estimates. (i.e. this overview section is optional).

4.1.2 Overall uncertainties (experts view)

Figure 4-1 provides an overview of the various contributions to overall uncertainty of the recommended data. In order to define overall uncertainties in a traceable fashion, is important to distinguish between uncertainties at the following different levels:

1. **Uncertainty at the source condition:**

   In the case of K_d values, this corresponds to the experimental error. In the case of diffusion coefficients, this corresponds to the experimental error as well as any uncertainty introduced in the required modelling for raw data reduction. Additional conceptual uncertainties are introduced in the interpretation of the diffusivity and diffusion-available porosity of anions (as well as of certain mobile cations, in particular Cs).

2. **Uncertainty at defined, PA-relevant application conditions :**

   Almost invariably, the conditions relevant for PA will not be covered exactly by matching experimental data. This necessitates the conversion of the source data to the application conditions (condition A in Figure 4-1) through models or estimation procedures. The overall uncertainty at the application condition will then include any uncertainties introduced by the applied conversion procedures in addition to the uncertainties already listed under point 1 above.

3. **Uncertainties in the application conditions themselves:**

   If there are significant uncertainties associated with the application conditions themselves, it is critical to take the conditional nature of the relevant migration parameters into account. K_d values in particular are highly conditional and need to be derived for each specified set of (expected) conditions. In the present report, variability of geochemical conditions was therefore addressed by deriving K_d values separately for several sets of possible geochemical conditions.

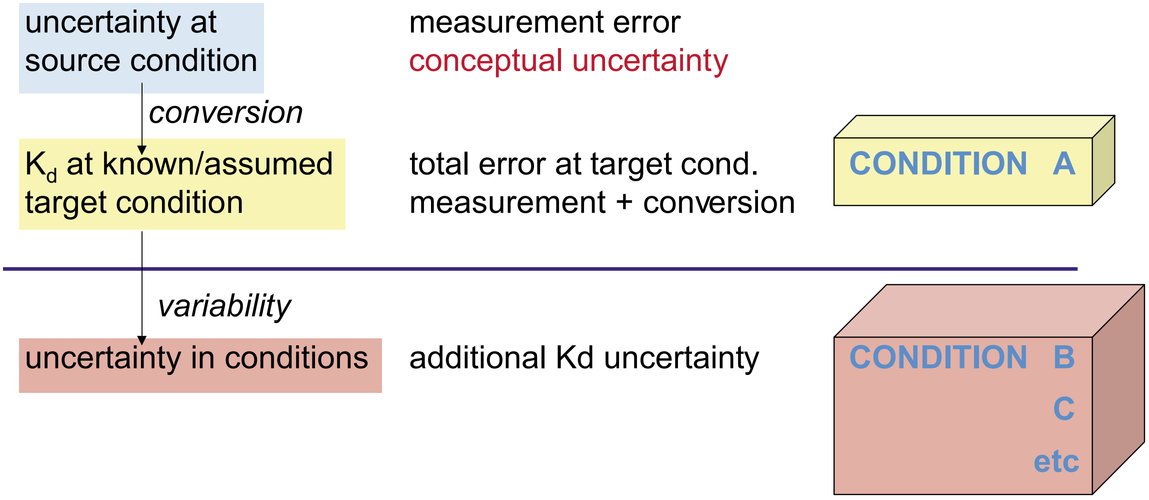

Figure 4-1. *Overview of the various sources of overall uncertainty at different levels, illustrated for the derivation of K_d values.*

At the same time, it is not possible to cover the expected variability in geochemical conditions by considering only an individual chemical parameter (e.g. pH). Because of the interplay of the various geochemical factors (pH, carbonate concentration…) in affecting RN behaviour, the expected variability has to be addressed by providing complete and self-consistent sets of porewater composition and bentonite characteristics corresponding to given boundary conditions.

The following sections describe in some detail the general aspects of uncertainties related to the three points above. Conceptual uncertainties regarding sorption and diffusion processes are discussed in the process report, these discussions are not repeated here. An overview of how overall uncertainties are treated in the data derivation process can be found in section 5.1.2.

4.2 Uncertainty related to different conditions

4.2.1 Instructions – issues to be addressed

This section should discuss if and how the parameter is influenced by the various conditions as specified in section 0 and how uncertainty is influenced. (For example, solubility depends on groundwater composition, which in term may depend on the scenario due to differences in future groundwater flow evolution for e.g. climatic change scenarios and stable climate scenarios.)

Also consider whether there are other conditions, but those specified in section 0 that influence the data?

In answering, the expert(s) should separate between their own opinion and what they would suggest being the range of answers provided by other acknowledged scientist/experts in the field. (If their opinion is the same as all others – state this as well).

4.2.2 Conditions affecting buffer migration parameters

Figure 4-2 illustrates that variations in geochemical conditions influence RN migration not directly, but through their influence on the composition of the porewater in compacted bentonite. The latter has to be derived based on model calculations, which introduces an additional (conceptual) uncertainty (see section 4.3). The overall resulting uncertainties in buffer migration parameters were assessed based on different defined sets of conditions and the corresponding porewater compositions (see section 5.2.5).

One of the main conditions influencing the calculated porewater composition is the way pCO_2 in the bentonite buffer is handled: If the buffer is assumed to be closed with respect to an exchange of CO_2 with the surrounding host rock (or if the kinetics of this exchange are sufficiently slow), pCO_2 in the buffer is the result of bentonite-groundwater interaction and, thus, is determinated by groundwater composition and bentonite properties. The edge sites are the most important pH buffer system in this case. If the bentonite buffer is assumed to be open with respect to an exchange of CO_2 with the surrounding host rock, the various carbonate equilibria make up the main pH buffer system and porewater pH in the bentonite is controlled by the external pCO_2 imposed by the host formation.

In view of the developments made in the derivation of RN migration parameters in the last decade or so, it is fair to state that the present approach, fully taking into account the dependency of K_d on the porewater composition of the compacted buffer, represents the state of the art /cf Bradbury and Baeyens, 2003a,b/. To date, there is substantial consensus /cf OECD/NEA, 2004/ that the appropriate description of overall solution and geochemistry is the key to minimising the uncertainties in K_d, irrespectively of whether this is done through thermodynamic sorption models or estimation procedures (see section 5.1.4). How, in detail, geochemical conditions and bentonite properties should be taken into account for the calculation of the buffer porewater composition still is a matter of debate to some degree (see section 5.2.5). However, it seems that the different approaches lead to approximately comparable results.

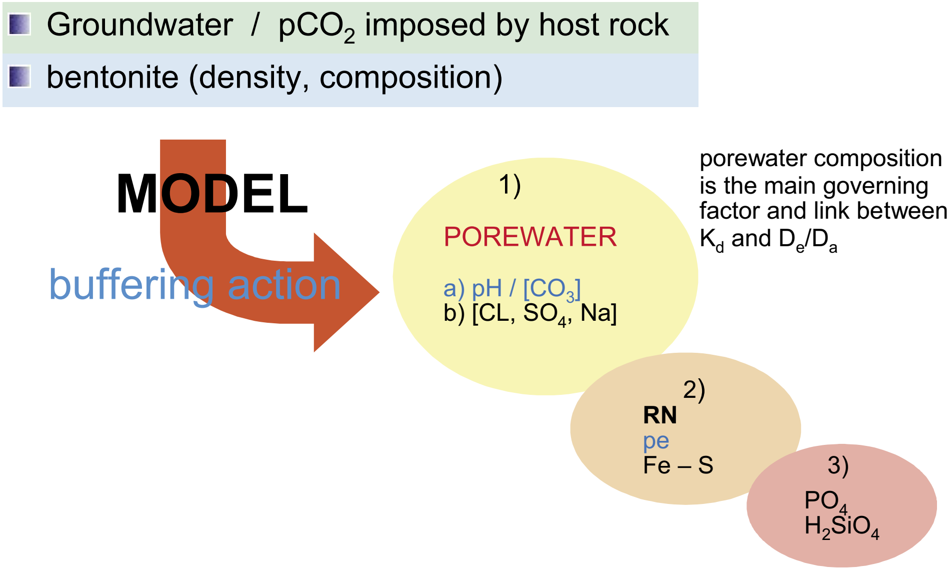

Figure 4-2. *Illustration of the influence of conditions on buffer migration parameters: The calculated composition of bentonite porewater is the central factor governing RN migration; variations in geochemical conditions are only effective through porewater composition (Figure 4-3). This model calculation also introduces some conceptual uncertainties (see section 4.3). The degree to which these can be covered based on present knowledge is indicated by the sequence 1) better than 2) better than 3).*

4.3 Conceptual uncertainties

4.3.1 Instructions – issues to be addressed

With reference to the Process Report and the actual modelling in SR-CAN (see section 2.2), this section should discuss:

- Are there conceptual uncertainties related to the model where the parameter is used?
- Are there conceptual uncertainties related to models used for deriving the parameter value?
- In light of the previous point, can the conceptual (model) uncertainty be expressed/illustrated as a parameter uncertainty in the given model (see chapter 2). (For example, the modelling uncertainty related to various sorption processes may possibly be handled by an increased range in K_d).

In answering, the expert(s) should separate between their own opinion and what they would suggest being the range of answers provided by other acknowledged scientist/experts in the field. (If their opinion is the same as all others – state this as well).

4.3.2 Conceptual uncertainties in buffer migration parameters

For the derivation of buffer migration parameters, the conceptual uncertainties discussed below were identified. Note that only point 1 refers to conceptual uncertainties directly related to the data derivation process; points 2–4 are related to underlying databases and models.

1. Several related conceptual uncertainties exist regarding the interpretation of, and self-consistency among, batch K_d values and diffusivities of sorbing RN on one hand, and of diffusivities and diffusion-available porosities of anions on the other. Both issues are discussed to some detail in the SR-Can Process Report /SKB, 2004/ and in section 5.3.4. These issues are also related to the following point:
2. There are some open questions regarding the fundamental, underlying chemistry of radionuclides in aqueous solutions. This is also acknowledged in recent TDB compilations /e.g. Hummel et al, 2002/. For example, the importance of actinide(III)-silicate, mixed actinide(IV)–OH-CO_3 and Ni-CO_3 complexes is not established to date. There are also uncertainties regarding the solution speciation of many of the less well researched elements, such as Nb, Zr, etc. The TDB used for the present data derivation is indicated for each element in Appendix F. Use of different TDBs, or future updates in SKB's reference TDB could lead to different migration parameters (see example Am).
3. There are significant scientific shortcomings regarding the derivation of porewater composition in compacted bentonite and its evolution over time under repository conditions. For the present purpose, it is important to note that the porewater composition of compacted bentonite cannot be determined experimentally with any certainty, and is therefore calculated through thermodynamic surface chemical models. Several published models are available for this purpose. While they are based on the same principles, they differ in a number of details regarding e.g. the treatment of specific surface chemical equilibria. These differences are small in comparison to other uncertainties, however. Further questions regarding the effects of electrical double layers in the porespace on e.g. the amount of "free" water, water activity etc are clearly beyond the present scientific understanding.
4. There are uncertainties related to the interpretation of raw diffusion data (concentration profiles, fluxes) by different researchers.

4.4 Data uncertainty, spatial and temporal variation

4.4.1 Instructions – issues to be addressed

This section should address the following:

- What is known about the spatial variation (e.g. scales, variography, discrete feature statistics,..) of the parameter? Is there any information about the uncertainty in the spatial variability? (Usually all this information can be supplied by referring to the Site Descriptive Model report for the different sites). How is this considered in the parameter and uncertainty estimates?
- What is known about the temporal variability of the parameter? How is this considered in the parameter and uncertainty estimates?
- If the parameter value and its uncertainty is drawn from a database, is this site specific or "generic"? In the latter case, how would the lack of site specific data influence the uncertainty?
- Are parameter and uncertainty estimates based on analyses of field/laboratory data? Are there any measurement errors etc and how are they considered in the uncertainty estimates?
- If data for estimating the parameter have been produced using a model, what uncertainties does this introduce? Conceptual uncertainties in the model (e g EQ3/6, ORIGEN)? Uncertainties in model input (e g cross sections in ORIGEN)? In particular, the uncertainty discussion in the Site Descriptive Model reports /see e.g. SKB, 2003/ should be drawn upon.

In answering, the expert(s) should separate between their own opinion and what they would suggest being the range of answers provided by other acknowledged scientist/experts in the field. (If their opinion is the same as all others – state this as well).

4.4.2 Spatial, temporal and site-specific variation

On the scale of a typical buffer, bentonite can be considered homogeneous. Therefore, spatial variation is not considered relevant for a bentonite buffer.

Temporal variation becomes important when buffer/porewater evolution is being considered. As was already discussed for the definition of porewater composition in general (section 4.2.2), the evolution of porewater and buffer composition over time has to be assessed through models. The corresponding uncertainties can be viewed as an extension of the uncertainty introduced by variable groundwater chemistry. As no independent model results for the scenarios of SKB were available at the time of the present data selection, some extreme situations were included in the porewater derivation. These included interactions of groundwater with bentonite converted to the Ca-form or depleted of impurities (see Figure 4-3).

The sorption and diffusion data as well as the various models underlying the present data selection are generic and therefore not site-specific. However, the extracted buffer migration parameters will be site-sensitive to the extent that they were derived based on site-specific conditions (including the respective variability). Of particular importance are groundwater composition (including redox conditions) and pCO_2 imposed by the host rock formation.

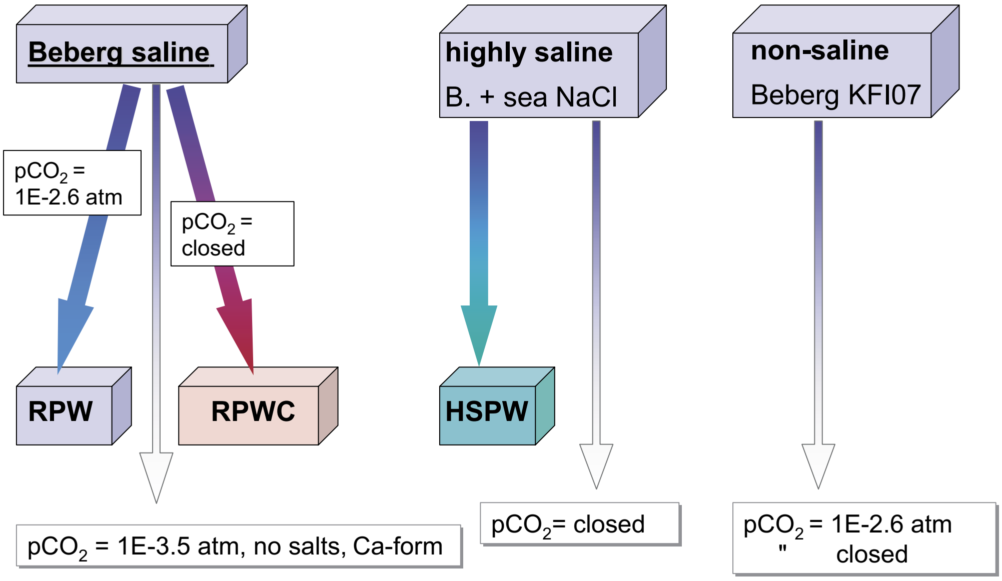

Figure 4-3. *Influence of conditions on porewaters in compacted bentonite. The reference condition (Beberg saline groundwater, BFI01 $pCO_2 = 1x10^{-2.6}$ atm) leads to the porewater RPW, all other compositions address the respective variability. The compositions RPW, RPWC and HSPW were applied in the derivation of parameters for each RN, the other compositions in selected cases only. See Appendix C for details on the porewater composition.*

4.5 Correlations among migration parameters

4.5.1 Instructions – issues to be addressed

The extensive work with the FEPs databases and the Process report should imply that most functional dependencies between parameters should be identified – and the important one also implemented in the Safety Assessment models. Also the assessment of impacts from various conditions should cover most potential correlations. Still other statistical correlation may exist. This section should address the following questions:

- If the data varies in space or time – is anything known about its autocorrelation structure?
- Is there any other reason (apart from already cited functional relations etc) to suspect correlation between parameters considered as input to SR-CAN?

In answering, the expert(s) should separate between their own opinion and what they would suggest being the range of answers provided by other acknowledged scientist/experts in the field. (If their opinion is the same as all others – state this as well).

4.5.2 Correlations among buffer migration data

The following important correlations can be identified

- Following their chemical characteristics, the RN considered can be organised into groups of elements and oxidation states whose migration behaviour will generally show a similar response to variations in porewater composition caused by e.g. variations in groundwater composition, bentonite evolution, etc. Moreover, elements handled via chemical analogies obviously correlate with the respective analogues. Overall, the following grouping is suggested, where analogies are also indicated (X/Y: both elements were treated identically in the data derivation; X(Y): X was derived based on analogy with Y)

1. Alkaline and alkaline earth elements: Cs, (Ra/Sr).
2. Other di-valent elements: Pb, Ni.
3. Tri-valent elements: Am, (Cm/Am), PuIII(Am), Sm/Ho/Ce(Eu).
4. Tetra-valent elements: Th, UIV(Th), PuIV(Th), NpIV(Th). Due to lack of reliable element-specific data, Tc(IV), Zr and Sn(IV) were also evaluated on the basis of data for Th, and the derived K_d values show therefore some correlation (because Th is not an ideal analogue for these elements, additional uncertainties are associated with the resulting K_d values).
5. Penta-valent elements: NpV, PuV(NpV).
6. Hexa-valent elements: UVI, PuVI(UVI).
7. Non-sorbing anions: (Cl^-/I^-/TcO_4^-/SeO_4^{2-}/HSe^-/simple organic anions).
8. The weakly sorbing anions SeO_3^{2-} and carbonate will not correlate as it is proposed to handle the latter via isotope exchange.
9. Some elements are not known well enough to assess correlations: Pa, Nb, Pd, Ag.
10. Gases: (Rn, CH_4).

- The redox-sensitive radionuclides will take on higher oxidation states if oxidising conditions are considered, generally leading to lower K_d values. An exception is: Se(–II→ IV).

- A lower porewater pH (within the range presently considered) will decrease the K_d of most radionuclides (actinides, lanthanides, transition elements, heavy metals) in a similar way. An exception are penta-and hexavalent actinides that form oxo-cations: U(VI), Np(V), Pu(VI/V).

- Similarly, an increase in major cation concentration will lower K_d values for alkaline and alkaline earth elements.

- A lower density of the buffer will lead to higher D_e and D_a values.

5 Quantification of data and uncertainties

In this chapter the various sources of uncertainty are combined in order to provide quantitative uncertainty estimates of the parameter(s) being analysed.

In this chapter, the actual estimates of the parameters (K_d, D_e and porosity in this case, with D_a as an additional parameter for comparisons) and of the associated uncertainties are made. Uncertainties from different sources are combined to give overall values.

5.1 Methods and approaches

5.1.1 Instructions – issues to be addressed

The uncertainty estimates should be made subjectively, i.e. "what is the believed probability that a parameter has a value (less than) a certain number" – not actually measured ranges – although the latter could have a large impact on the subjective probabilities). (But we should also be aware of 'risk dilution').

If the parameter shows spatial (or temporal) variability:

- Consider how this variability is at the scale of description – not at the measurement scale, some of the measured/simulated variability may in fact be averaged out at the scale of description – other would not,
- Describe how the variability is accounted for. Is it included in the uncertainty estimate or given as stochastic process etc with different realisations? Are there alternative models for describing the variability – if so are they equally likely?

Describe correlations.

5.1.2 General approach

The general approach used for the derivation of buffer migration data and uncertainties is described in chapters 2.3.1 and 4. Details regarding the various conditions considered are given in the following section 5.2. As outlined in Figure 4-1, data and uncertainties are defined for three levels:

Level 1: data source

Level 2: reference condition

Level 3: further (alternative) conditions, reflecting the variability in conditions at level 2

The likelihood for any data to fall within the recommended ranges is expressed using "soft terminology". This is supported by consistency checks using independent data and a traceable and extensive documentation of data derivation in appendices. The likelihood for a given range to encompass all possible data for the given conditions is expressed as (decreasing confidence):

- extremely likely,

- very likely,
- likely,
- probable.

To cope with the necessity to convert data from experimental to PA-conditions, the data selection procedure relied strongly on sorption data obtained in batch experiments. For the reasons given in section 5.3.4, no element-specific D_e values were derived for reactive elements; instead, the selected D_e value for HTO was relied upon. D_e values for anions and Cs were selected to take into account the electrostatic potential in bentonite pores. Data derivation and assessment of uncertainties was carried out in four steps as described in the following sections:

1. Definition of all conditions to be considered, and calculation of the bentonite porewater composition corresponding to the reference density (see section 5.2). Uncertainties in boundary conditions (groundwater and bentonite characteristics) are addressed by carrying out the derivation of migration parameters for several self-consistent bentonite/porewater systems. No further uncertainties are assumed for each of these systems.
2. Derivation of D_e values and diffusion-available porosity (ε) for the specified reference density (sections 5.3.3 and 5.3.4). Uncertainties related to the influence of conditions on diffusion-relevant bentonite characteristics (poresize, etc) are assumed to be included in the uncertainties given for D_e in each case, as these data are derived based on experimental measurements that already cover different conditions.
   a) Selection of D_e values and associated uncertainties for HTO, to be used together with the entire physical porosity for all elements except non-sorbing anions and Cs (see below), and for all conditions. Because D_e refers to steady-state conditions, the influence of uncertainties in conditions through radionuclide speciation and average ionic charge is assumed to be contained in the uncertainty given for D_e of HTO.
   b) Selection of D_e values and associated uncertainties for all non-sorbing anions (Cl^-, I^-, TcO_4^-, SeO_4^{2-}, HSe^-, simple organic anions) to be used for all conditions together with the selected anion diffusion-available porosity. Uncertainties in radionuclide speciation are not relevant in this case.
   c) Selection of D_e value for Cs, to be used together with the physical porosity. Uncertainties in radionuclide speciation are not relevant in this case.
3. Derivation of K_d values for each element (section 5.3.5, see also Figure 4-1):
   a) Selection of source data and quantification of their experimental uncertainty.
   b) Conversion of source data to the selected reference conditions and quantification of the additional uncertainties introduced in this process.
4. Calculation of D_a values for the specified reference density based on the results for points 2 and 3 above, and comparison with independent experimental data. Final assessment of overall consistency and uncertainty.

5.1.3 Definition of conditions

The conditions to be considered in the data derivation were defined through calculated porewater compositions (Appendix C), which were based on defined combinations of

- the chosen buffer material, MX-80, at the reference density of 1,590 kg/m^3, including some alternative compositions;

- the relevant groundwater composition given in /Laaksoharju et al, 1998/, as well as some modified compositions (see Appendix A).

Further details are given in section 5.2.

5.1.4 Derivation of K_d values

The general hierarchy followed in selecting source data is laid out in Table 3-2. It shows that high priority is given to systematic data obtained on MX-80 bentonites. It is believed that the uncertainty introduced in extrapolating sorption data from source to the present target or application ("PA") conditions can be significantly higher than experimental uncertainties (see Figure 4-1) and will increase with the extend of extrapolation. It is further proposed that this holds for any extrapolation method, i.e. both thermodynamic model applications as well as semi-quantitative estimations. Therefore, systematic data obtained on MX-80 bentonite in solutions that closely match the present application conditions may be preferred over thermodynamic sorption models that had been calibrated in the absence of key chemical parameters, such as carbonate. While thermodynamic models in principle have the better scientific foundation, they are often not sufficiently constrained in terms of parameterisation. Thus, application of a model calibrated exclusively with data from simple systems to the complex MX-80/porewater system often involves an extensive extrapolation, which limits the value of the model. Recent results from the NEA Sorption Project /NEA, 2004/ also indicate that apparent shortcomings in the application of sorption models may often be traced back to limitations in parameterisation rather than to any fundamental problem with the model itself. In some cases, it would be worthwhile to consider re-calibration or development of sorption models based on available experimental data; however, model development was outside of the present scope.

In their recent report on near-field sorption data, /Bradbury and Baeyens, 2003a/ report a significant amount of supplementary and systematic sorption data for many radionuclides that had been obtained with MX-80 in equilibrium with a synthetic porewater. Because of the chemical similarity of their experimental conditions with the present application conditions, their work could be used in many cases as starting point. In case of several radionuclides, the experimental data made available in their report represent the most relevant and reliable dataset for MX-80 that could be found. A specific discussion for each element is given in section 5.3.

In general, the selection of source data was aimed at obtaining the best available starting values for the further data derivation. Thus, subjective choices (e.g. consideration of "conservatism") were completely avoided, as they would lead to a decrease in transparency and traceability. These best available starting values are listed under the column "Data Source" in the data derivation tables (Appendix E).

Conversion procedures

The derivation of K_d values corresponding to the desired conditions in compacted bentonite from experimental data almost invariably involves an extrapolation step. Where possible, this extrapolation was done with the help of an appropriate thermodynamic sorption model. Where such a model is not available, the semi-quantitative conversion procedures documented below were applied. As explained above, these procedures were also preferred in case where it would allow to use data that correspond significantly better to the desired application conditions than the data underlying a model.

The employed extrapolation procedures are related to the sorption capacity of bentonite and the behaviour of the various RN under the different conditions. The basic approach is taken from /Bradbury and Baeyens, 2003a/, and the conversion procedure related to sorption capacity was accepted as is. On the other hand, the conversion procedures related to surface and radionuclide speciation were interpreted differently, as detailed below. The actual conversion factors were in all cases calculated specifically for the present source data sets and application conditions.

Sorption capacity

The sorption capacity of a typical bentonite, such as MX-80, is determined by its content of smectite clay minerals (typically dominated by montmorillonite). While most bentonites contain a number of important impurities, these are often not very relevant for sorption reactions and present evidence suggest that smectite minerals are dominating the actual sorption processes through surface complexation and ion exchange, at least in typical bentonites. This is supported by the work of /Wanner et al, 1996; Ochs et al, 1998; Pabalan and Turner, 1997; Bradbury and Baeyens, 2002b/, as well as by the results of the recent NEA modelling exercise /NEA, 2004/. Of course, through their large effect on porewater chemistry, impurities are indirectly important for sorption.

To scale selected K_d values obtained for bentonites or clays other than MX-80 to the MX-80 application conditions, a conversion factor based on the respective CEC values was applied following /Bradbury and Baeyens, 2003a/:

$$\text{CF-CEC} = \text{CEC (application)} / \text{CEC (data source)} \qquad (5.1)$$

In this relation, CEC is used as a measure for total site density, based on the reasonable assumption that the density of surface complexation (edge) sites is proportional to the CEC.

pH

The pH is the most critical geochemical parameter for the sorption of most elements, as it determines both the speciation of the surface complexation sites as well as of the sorbing element itself. Note that pH does not only determine the hydrolysis of a RN, but also its interaction with other ligands, in particular those that undergo (de)protonation in the relevant pH range (e.g. carbonate). This is illustrated in Figure 5-1.

Where possible, data sources were selected that allowed the selection of K_d values at the pH values corresponding to the application conditions (in the data derivation tables in Appendix E, this is indicated by a pH-conversion factor of 1). Where this was not possible, scaling to the appropriate application pH could in many cases be made on the basis of additional data for the same RN, such as sorption edges on a montmorillonite. In such cases, scaling to the application pH was done following /Bradbury and Baeyens, 2003a/, using the conversion factor defined below:

$$\text{CF-pH} = K_d\text{(pH data source)} / K_d\text{(pH application)} \qquad (5.2)$$

In contrast to /Bradbury and Baeyens, 2003a/, CF-pH is interpreted as a factor addressing the overall surface/solution speciation. Thus, the conversion factor for additional radionuclide speciation effects defined below (CF-spec) addresses only effects not included in CF-pH, i.e. does not take into account hydrolysis.

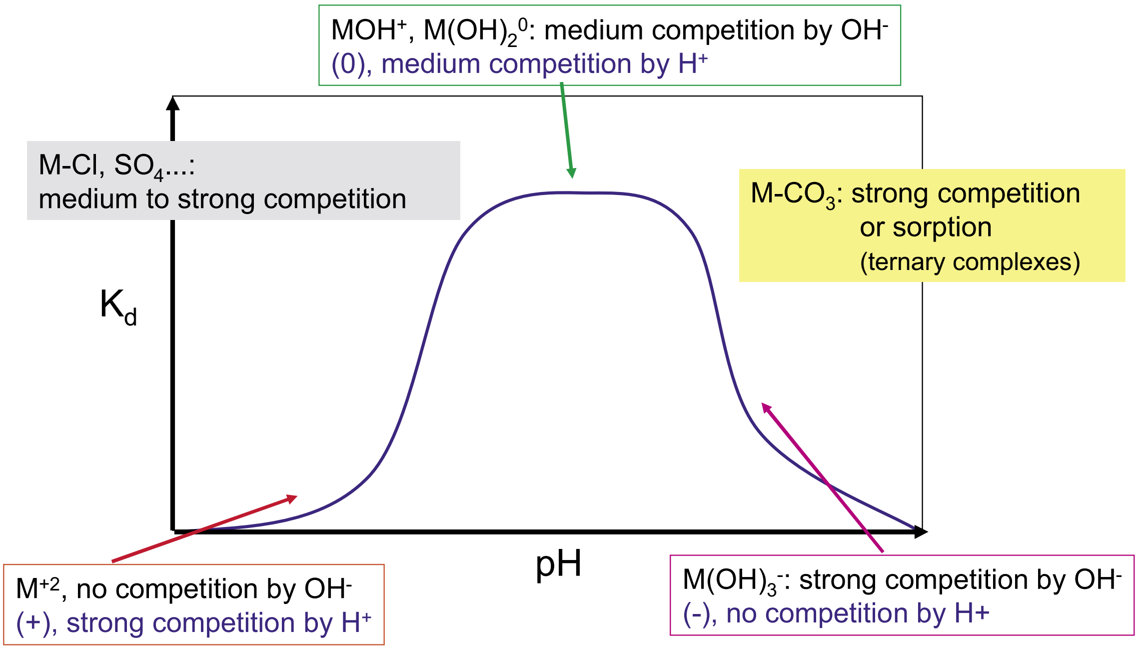

Figure 5-1. *Schematic illustration of the dependency of* K_d *on pH. M stands for a hydrolysable RN (metal), surface speciation is indicated in blue. In the absence of other ligands, sorption is low at low and high pH because of the strong competition by* H^+ *for the available surface sites and by dissolved* OH^- *for the RN, respectively. Ligands that are not protonated at relevant pH (indicated in grey) can compete for the dissolved RN at any pH. On the other hand, the concentration of* CO_3^{2-} *is pH-dependent itself (at a given total carbonate level), and strong competition by the carbonate ion takes place only at high pH.*

Additional effects of other ligands on radionuclide surface/solution speciation

As illustrated in Figure 5-1, the presence of dissolved ligands can have a significant influence on radionuclide sorption. Therefore, scaling of K_d to application conditions should be carried out in all cases where the source data correspond to a solution composition different from that of MX-80 porewater (which is nearly always the case). Unfortunately, only thermodynamic sorption models are capable of consistently taking into account all speciation effects, but such models are available for a few elements only. Therefore, it was attempted to account for variable solution compositions in a semi-quantitative, but fully traceable fashion.

The conversion factor CF-spec takes into account differences in the competition for the RN by those dissolved ligands present in the different solutions that are not already covered by CF-pH. Again, the formal definition of this factor is similar as in /Bradbury and Baeyens, 2003a/.

$$\text{CF-spec} = F_{sorb}\,(\text{application}) \,/\, F_{sorb}\,(\text{data source}) \qquad (5.3a)$$

where

$$F_{sorb} = (RN_{tot} - RN_{cmp}) \,/\, RN_{tot} \qquad (5.3b)$$

with RN_{tot} as the total dissolved concentration of a given radionuclide, and RN_{cmp} as the total concentration of all dissolved RN complexes evaluated as being competitive with regard to sorption.

However, the application of this factor is not straightforward, and the evaluation procedure used here differs considerably from that of /Bradbury and Baeyens, 2003a/. First, Figure 5-1 shows that the conversion factor CF-pH will already include one or more of the effects of speciation. The following differences in speciation are therefore not included in the factor CF-spec, as the effects would be counted twice:

- Effects of RN hydrolysis will be included in CF-pH, except at very dissimilar RN concentrations or in cases where a K_d has to be based on an analogy with a somewhat dissimilar element (see the example of Zr).
- Complexation of a given RN with the carbonate ion (CO_3^{2-}) can differ between two solutions because of i) different total carbonate concentrations, or ii) different pH values leading to different concentrations of CO_3^{2-} even when total carbonate levels are the same. In case ii), the effect will also be included in the conversion factor CF-pH.

Second, several elements, especially IV- and higher-valent actinides are known or suspected to form mixed hydroxo-carbonato complexes. By analogy, the formation of ternary RN-carbonato surface complexes at the clay edge sites can be assumed. For some cases, the existence of such complexes has been confirmed by spectroscopy (e.g. for UVI sorption on iron oxide by /Bargar et al, 2001/). Therefore, it is highly questionable in these cases whether the presence of carbonate should be counted as a competitive factor. Therefore, scaling of K_d to account for speciation was carefully evaluated for each element. As a basis for further evaluation, CF-spec was calculated twice in many cases, taking into account or neglecting competition by complexation involving carbonate ions.

- CF-spec 2: Complexation of a radionuclide with carbonate is viewed as being fully competitive with respect to sorption.
- CF-spec 3: Complexation of a radionuclide with carbonate is viewed as being not competitive with respect to sorption. One reason to use CF-spec 3 may be the formation of ternary surface carbonato complexes, which would contribute to overall sorption. Further, CF-spec 3 should also be used where effects of carbonate complexation are already included in CF-pH; i.e. CF-spec 3 would then only include competition by e.g. chloride or sulphate.

The above points are particularly critical, as hydrolysis and formation of carbonato complexes are in many cases the most important speciation effects (i.e. CF-spec is often of minor importance).

Overall modification (scaling) of selected K_d values

Selected Kd values were scaled to the appropriate application conditions using an overall conversion factor:

$$\text{CF-total} = \text{CF-CEC} \times \text{CF-pH} \times \text{CF-spec} \quad (5.4)$$

Following the above discussion, for a number of elements CF-total had to be defined for different ways of scaling with respect to speciation:

$$\text{CF-total 1} = \text{CF-CEC} \times \text{CF-pH} \quad (5.5a)$$

where speciation was considered to be completely included in CF-pH; and

$$\text{CF-total 2} = \text{CF-CEC} \times \text{CF-pH} \times \text{CF-spec 2} \quad (5.5b)$$

$$\text{CF-total 3} = \text{CF-CEC} \times \text{CF-pH} \times \text{CF-spec 3} \quad (5.5c)$$

depending on how carbonate complexation was evaluated. The final choice made is discussed for every element in section 5.3.5.

Uncertainties

Uncertainty estimates for K_d are based on the general procedure outlined in Figure 4-1, distinguishing between

- uncertainty at a given application condition,
- uncertainty as a function of variable conditions.

Uncertainty estimates of K_d for a given application condition

There is no obvious reason for choosing between quantifying uncertainties as an error on a linear scale (i.e, K_d ± error) vs a logarithmic scale (i.e, log K_d ± log error). Because several careful sorption studies /e.g. Bradbury and Baeyens, 1997/ report errors that are symmetric on a log scale, the latter type of representation was adopted for the present purpose. On a linear scale, this translates to K_d multiplied/divided by an uncertainty factor UF:

$$\log K_d \text{ (upper, lower limit)} = \log K_d \pm \log \text{uncertainty, or} \qquad (5.6a)$$

$$K_d \text{ upper limit} = K_d \times \text{UF and } K_d \text{ lower limit} = K_d / \text{UF} \qquad (5.6b)$$

As statistical distribution functions can only be assumed, it is not realistic to assign percentiles (likelihood for a datum to be within the indicated range at a statistical confidence level) in a standard way to the upper/lower limits. Instead, uncertainties are evaluated in a way that makes it generally very likely that the indicated limits encompass all possible values. Where data are more uncertain, this is discussed specifically. For each element, this is supported with illustrations and consistency checks using diffusion data to facilitate an independent interpretation by the user of this report, where required.

The following uncertainty factors (log errors) are considered:

1. Uncertainty of source data (UF-starting K_d)
   - Experimental data
     For good quality experimental data an uncertainty of log K_d ± 0.2 log units is proposed based on the findings of /Bradbury and Baeyens, 1997/. This gives an uncertainty factor
     → UF-starting K_d = 1.6
   - Model data:
     /Bradbury and Baeyens, 2003a/ suggest an uncertainty factor of 3. However, a recent extensive modelling exercise /NEA, 2004/ showed that good sorption models are able to reproduce experimental data very closely, and we propose to use the same uncertainty as for experimental data.
2. Uncertainty introduced by scaling to application conditions
   - CEC conversion (UF-CEC):
     It is estimated that CEC can be measured within an uncertainty of ca 10%, and that SOH density can be scaled via CEC again within an uncertainty of ca 20%. This gives an overall uncertainty of ± 30% or about a factor of 2 between highest and lowest value. Thus, we propose
     → UF-CEC = 1.4

- pH conversion:
  This is only needed where CF-pH ≠ 1, i.e. where scaling to application pH had to be done via additional data and equation (5.2). Because CF-pH contains uncertainties of two K_d values (read off at pH-data source and pH-application, respectively), an uncertainty log starting $K_d \pm 2\times0.2$ log units is used:
  → UF-pH conversion = 2.5
- Speciation (UF-speciation):
  Following the evaluation by /Hummel and Berner, 2002/, who propose a factor of 2 between highest and lowest value, a UF-speciation = 1.4 is used. Note, however, that this is the uncertainty associated with the use of a given complete TDB. If certain species are missing or erroneous (see e.g. the discussion on mixed actinide OH-CO_3 complexes above), uncertainties could be much higher. Also, this UF does not take into account any inappropriate evaluation of CF-spec, as discussed above (this had to be evaluated with consistency examinations and "what-if" calculations as described above, rather than via formal uncertainties).
- Analogy considerations:
  Where a K_d was based entirely on data and chemistry of an analogue element, an additional uncertainty factor UF-analogue was introduced; this is discussed for each element. Where a K_d was derived using sorption data for an analogue element but speciation was evaluated directly for the element under investigation (e.g. in the case of using sorption data for Th to evaluate K_d for PuIV), the additional uncertainty was taken into account by using for log starting $K_d \pm 2\times0.2$ log units in case of good analogues (e.g. tetravalent actinides),
  → UF-starting K_d = 2.5

  or log starting $K_d \pm 2\times0.3$ log units in case of more questionable analogues (e.g. use of Th for Zr),
  → UF-starting K_d = 4.0
- Conversion of batch data to conditions in compacted bentonite:
  Arguments for the applicability of the K_d values derived in this report to compacted conditions are presented in section 3.1.2. Accordingly, CF-batch→ compacted is unity and no UF is proposed for this conversion per se. However, an additional uncertainty factor is introduced to acknowledge possible uncertainties in the application conditions (i.e. in the porewater composition, resulting from model uncertainties and effects from variations in the amount of impurities present in bentonite samples; /see Ochs et al, 2004/). Based on the differences in the K_d values derived for three difference reference porewaters (section 5.3.5), this uncertainty factor is set to two:
  → UF-batch→ compacted = 2.

5.2 Conditions for which parameter values are to be supplied

5.2.1 Instructions – issues to be addressed

Based on the assessment of impact from the various conditions made in chapter 4, it may be needed to split up the data and uncertainty quantification into different set of conditions. This section should specify this set of conditions, with justification.

5.2.2 Buffer migration parameters

The impact from density may possibly be handled by providing a functional relation, i.e. a wide range of densities can be handled by a single set of data – provided this relation is used.

The impact from groundwater composition may probably require different tables of data and uncertainty for different type waters. Such a case would correspond to different conditions – one for each type water. However, it is not totally clear if there will be type waters in SR-Can. Furthermore, we are interested in the transition between different type waters, i.e. there should be a strive to describe impact from groundwater composition with functional relations, i.e. there may be a threshold value for the impact from Eh, but a more continuous impact from pH and TDS?. Possibly, the best way to handle the situation would be to supply a full set of data and uncertainties for a selection of type conditions and then add how to handle cases in-between these type situations.

5.2.3 Groundwater

The selected groundwater conditions are based on /Laaksoharju et al, 1998/. It is realised that all PA calculations (radionuclide transport, buffer evolution, etc) should be based on consistent groundwater compositions. For the purpose of the present SR-CAN report it is considered by SKB that the saline Beberg water (BFI01) fulfils this requirement and was therefore accepted as reference groundwater. Alternative groundwater compositions, covering what was estimated to be a reasonable range in terms of salinity and pH, included a non-saline Beberg groundwater as well as a hypothetical water where the salinity of the saline Beberg water was raised to that of typical seawater. In an exploratory evaluation, the range of hypothetical groundwaters was extended to include alkaline and hyperalkaline groundwater. Possible effects of salt-saturated groundwater are discussed briefly in Appendix C.2.

These groundwaters are the basis for determining the final bentonite porewater composition. The groundwater compositions are given in Appendix A.

5.2.4 Bentonite density and composition

The effect of density was evaluated for De and ε, and quantitative relations are given in sections 5.3.3 and 5.3.4. The evaluation of sorption data was carried out only for the reference density of MX-80 bentonite (1,590 kg/m^3). However, there is clear evidence that the porewater composition and, therefore, radionuclide sorption, is not significantly influenced by limited variations in buffer density. In comparisons to uncertainties regarding e.g. externally imposed pCO$_2$, such effects are negligible.

The bentonite composition considered is given in Appendix B. The following variations were considered for some cases:

- Bentonite converted completely to the Ca-form.
- Bentonite completely depleted of soluble impurities (NaCl, KCl, gypsum).

5.2.5 Porewater compositions

As illustrated in Figure 4-2, the bentonite porewater corresponding to the reference density forms the central element for the evaluation of migration parameters, in particular K_d.

The pore solution in compacted bentonite is practically inaccessible for chemical analysis. Even at very high squeezing pressures it is difficult to obtain sufficient quantities of pore solution, and it is questionable whether the sampled solution is actually representative. Therefore, porewater compositions were evaluated by using thermodynamic models. The results of these model calculations are dependent on i) the composition of the bentonite and the geochemical boundary conditions, but ii) also on the chosen modelling approach.

Model calculations were done with the help of a surface chemical thermodynamic model that simultaneously treats solution/mineral equilibria as well as protolysis and ion exchange reactions at the edge and siloxane surfaces of clay minerals. Model parameters are given in Appendix D. Acid-base reactions at the clay edge surfaces were treated using the diffuse layer model, ion exchange equilibria were calculated using the equivalent-fraction (Gaines-Thomas) formalism /Stumm and Morgan, 1996; Fletcher and Sposito, 1989/ with the help of a modification of the code MINSURF /Berner, 1993; see also Appendix D/. Thermochemical data for dissolved species and solids were all taken from /Pearson and Berner, 1991/ and /Pearson et al, 1991/. Activity coefficient corrections were done using the Davies equation.

To evaluate the influence of the chosen modelling approach on porewater composition, some calculations were carried out using an alternative thermodynamic model. The model developed for montmorillonite by /Bradbury and Baeyens, 1997/ was chosen for this purpose, as it differs significantly from that of /Wanner et al, 1994/ in how protolysis reactions at clay edge sites are treated, which is the main surface chemical factor for controlling pH. The model parameters are also given in Appendix D. In contrast to /Wanner et al, 1994/, /Bradbury and Baeyens, 1997/ did not include any electrostatic correction terms, and their model has a much larger difference between pK_1 and pK_2.

The resulting porewater compositions are given in Appendix C. Variations in the calculated porewater compositions result from variability in (see also Figure 4-3):

- the incoming groundwater,
- whether CO_2 gas is allowed to leave/enter the compacted buffer; i.e. whether pCO_2 in the bentonite buffer is the result of groundwater-bentonite reactions (closed system) or whether pCO_2 in the bentonite buffer is imposed by the CO_2 level in the host rock (open system),
- the bentonite composition,
- In addition, it is shown that the calculated porewater composition is also a function of the modelling approach chosen.

The reference conditions for K_d derivation illustrated in Figure 4-3 were extended in an exploratory evaluation to include alkaline and hyper-alkaline groundwater. The results of these calculations are also given in Appendix C. The calculated porewater compositions show that a significant increase of porewater pH is only to be expected when no exchange of CO_2 between bentonite buffer and host rock formation is considered (closed system). If carbonate equilibria in the bentonite buffer are externally controlled by the CO_2 level in the host formation, the calculated porewater pH does not increase significantly. Expected effects of these changes in pH are discussed qualitatively for different elements in section 5.3.5. Further possible effects by the presence of extremely saline groundwater are briefly discussed in Appendix C.

5.2.6 Treatment of variable conditions in the quantification of data and uncertainties

The underlying premise of the present report is the direct use of K_d values in performance assessment consequence calculations. Because K_d is a conditional lump-sum parameter, it is critical that values are derived specifically for the conditions that are to be considered in the consequence calculations. I.e. direct use of experimental data is only possible if experimental and PA-relevant conditions are matched.

Because of the conditional nature of K_d, all variations in conditions are expressed through defined and discrete bentonite porewater compositions (see Figure 4-2 and Appendix C) in the present assessment. Because of the importance of bentonite-water interaction, this is considered as the only possible method of translating changes in conditions to effects on migration parameters, in particular K_d.

The only exception to this was the treatment of variations in redox conditions. Because of the uncertainties regarding redox conditions in bentonite porewaters, and the large effect that this parameter can have on radionuclide behaviour, the influence of pe on redox-sensitive RN was quantified by deriving migration parameter sets for each oxidation state. It has to be admitted that this approach neglects possible additional effects by pe through alterations of the porewater composition, such as changes in the sulphate/sulphide ratio, etc.

The question then needs to be asked how intermediate conditions, which are not explicitly covered by the calculated groundwater-porewater combinations should be assessed. Because of the relations shown in Figure 4-2, it is not possible to directly (without prior calculation of the resulting porewater composition) assess e.g. the effect of an "intermediate" groundwater composition on migration parameters :

- the buffering action of bentonite has to be taken into account; this is only possible through the kind of calculations used for this work,
- pH, pCO_2, etc are closely related and have to be treated together.

For an approximate estimation of the possible effects of variations in the porewater composition not explicitly covered in the present report, the diagrams in section 5.3.5 can be used in an interpolative fashion. Extrapolation should be avoided; instead, the respective K_d values should be derived following the procedures used in this report.

On the other hand, the influence of buffer density on porosity and D_e can be quantified through simple relations or regression equations (see section 5.3.3 and 5.3.4), based on the present knowledge. Note that the corresponding K_d values still would have to be derived following the procedures applied in this work. An example of the influence of buffer density on K_d is shown in Figure 5-2. Note that this type of direct calculation is only possible in case of a few elements, where thermodynamic sorption models are available. However, these data suggest that moderate deviations from the present reference density should not have significant effects within the overall uncertainty.

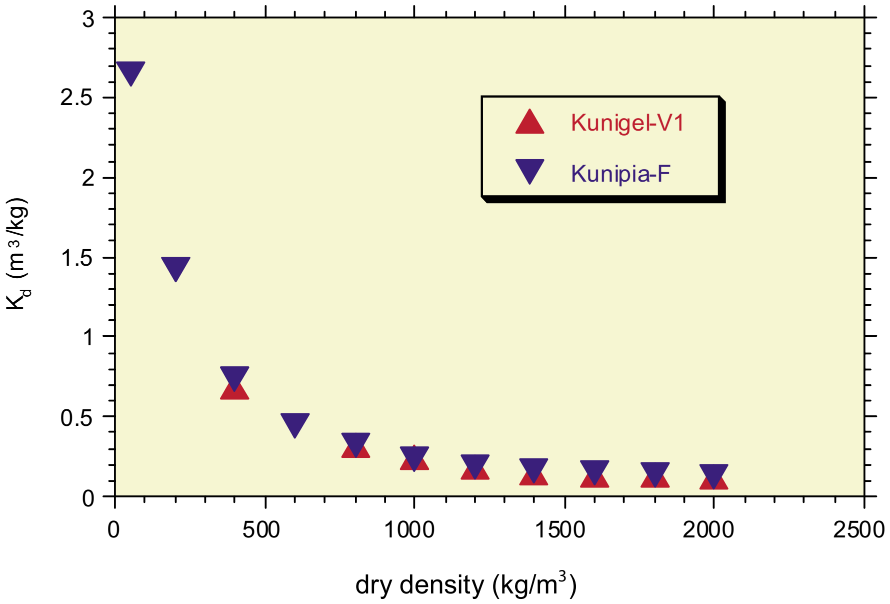

Figure 5-2. *K_d calculated for Sr on crude (Kunigel-V1) and purified (Kunipia-F) bentonite with the thermodynamic model given in Appendix D as a function of density (all other conditions were kept constant, input solution was pure water). Data from /Ochs et al, 2001/.*

5.3 Data and uncertainty estimates

5.3.1 Instructions – issues to be addressed

Based on the assessment in chapter 4, i.e. also considering conceptual uncertainty etc and the general instructions above provide motivated uncertainty estimates of the parameter(s) for each condition defined and motivated in section 5.2 above. Depending on possibilities and assessed importance (see section 2.2.1) for the Safety Assessment, the uncertainty estimates may be given as:

- A distribution function if it can be motivated. (For example, for a spatially varying function well described by a given stochastic process, like variagraphy or DFN, a potential distribution function may be to state that all realisations of this spatially varying function are equally probable).
- Subjective percentiles a_i in the distribution function: $P(x<a_i)=p_i$, i.e. a_i is the parameter value where subjective probability that the parameter will take a value less than a_i is p_i. In general the percentiles corresponding to the following p_i:s: 0.01, 0.1, 0.3, 0.5, 0.7, 0.9, 0.99, should be supplied. However, sensitivity analyses (see section 2.2.1) may show that only part of the range really has an impact on the Safety Assessment. In such a case, less effort may be given to parameter values outside this range.
- A range.

The uncertainty estimates should also provide information on correlations.

- For spatially/temporal varying function information provide information about auto-correlation etc.
- List other parameter to which the parameter in question may be correlated, and where this correlation is not already taken care of by functional relations in the Safety Assessment Models. For these parameters also discuss whether a correlation function set to one (1) may be a pessimistic choice.

In answering, the expert(s) should separate between their own opinion and what they would suggest being the range of answers provided by other acknowledged scientist/experts in the field. (If their opinion is the same as all others – state this as well).

5.3.2 Buffer migration parameters

For a given groundwater composition the uncertainty in parameters mainly originates from laboratory measurement errors. For this it may be reasonable to assume a normal distribution. We then need to sort out the meaning of ranges supplied. Do they refer to one standard deviation or to the "final" range?

5.3.3 Physical porosity

Porosity ε is calculated using the following simple relationship /Sato et al, 1995; Ochs et al, 2001; Schwyn, 2003/:

$$\varepsilon = 1 - (\rho/\rho_s) \qquad (5.6)$$

where ρ is the dry density and ρs the specific density of bentonite. For ρs, a value of 2,760 kg/m^3 /Schwyn, 2003/ was used. The results (Figure 5-3) show good agreement with experimental data and indicate that little variation has to be expected as a function of possible uncertainties in the bentonite composition.

For a dry density of 1,590 kg/m^3, a total physical porosity of 0.43 is recommended for all elements. For all elements except Cs and non-sorbing anions, the diffusion-available porosity corresponds to this value.

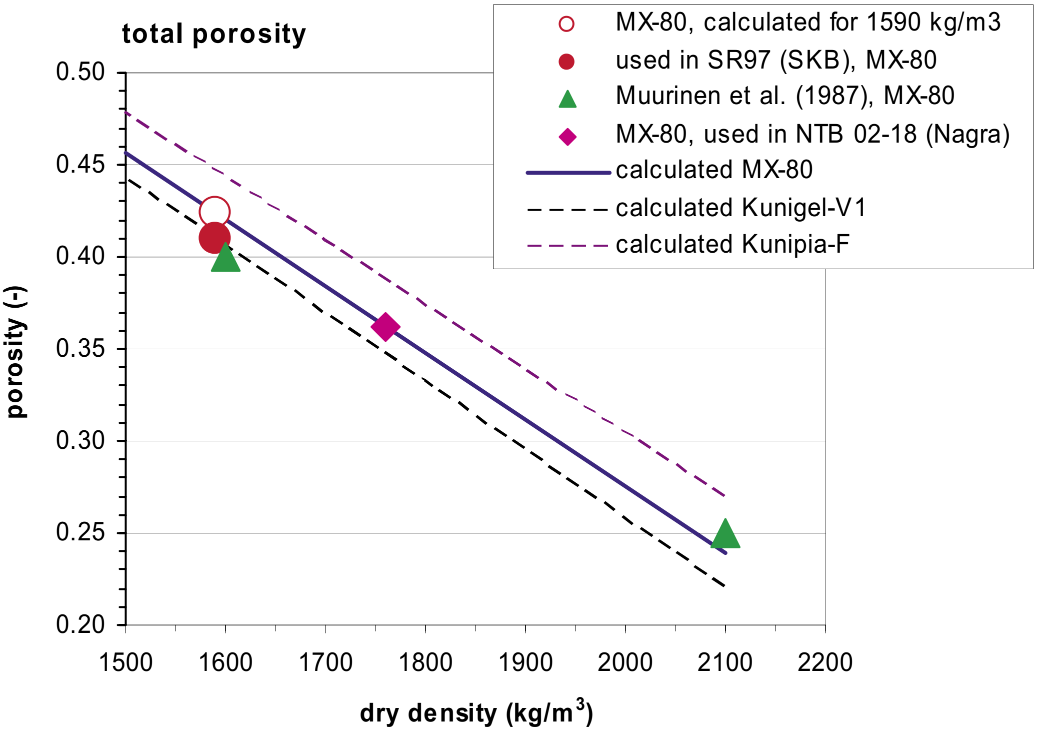

Figure 5-3. *Comparison of calculated (eq. 5.6) and experimentally determined total available porosity for MX-80. Calculations for bentonites with 45–50% smectite (Kunigel-V1) and with >95% smectite (Kunipia-F) are shown for comparison.*

It is considered that the calculation of porosity with equation (5.6) gives the correct value. Therefore, no uncertainty range is given for this parameter.

The derivation of the diffusion-available porosity for anions and Cs is discussed in the following sections.

5.3.4 Effective diffusivity and diffusion-available porosity for anions

As pointed out previously (section 5.1.2), no RN-specific effective diffusivities are derived, due primarily to the incomplete and uncertain database. Instead, D_e for HTO is considered and recommended as being representative for all elements except anions and Cs. As discussed in the following sections on anions and Cs, D_e values of diffusing species are influenced by their charge. Thus, use of the uncharged HTO as surrogate for most radionuclides does not take into account their speciation and related ionic charge. On the other hand, most radionuclides exist as a number of species, which may include cationic, neutral and negatively charged species (see Appendix F). Therefore, in the absence of reliable species-specific D_e measurements, use of HTO is considered to be more appropriate than the use of a cation (such as an alkali element) for representing the average ionic charge and effective diffusivity of all radionuclides except Cs (and anions).

In contrast to the derivation of K_d values, which is done specifically for each condition considered, the diffusion parameters are not derived for particular sets of conditions. Instead, they are considered to be generally valid within the boundary conditions used for the present data derivation. This is done for several reasons:

- On one hand, the limited number of systematic diffusion data sets simply does not allow to derive diffusion parameters as a function of variable input conditions (except bentonite density).
- On the other hand, diffusion experiments are invariably carried out in compacted bentonite, which implies that the porewater conditions are largely determined by the bentonite itself in most cases. Therefore, porewater conditions in a given compacted bentonite show comparatively little variation as a function of input solution. This clearly contrasts batch experiments, where typically a (very) low bentonite/water ratio is used and where, as a consequence, the solution composition is controlled by the input solution.
- Further, the parameters selected for the present report (D_e, ε for anions and HTO) are typically derived from through-diffusion experiments under steady-state conditions, where the influence of porewater conditions on sorption is not relevant.

HTO

D_e values obtained for HTO in different bentonites are plotted in Figure 5-4 as a function of dry density. Data for Kunigel-V1 and MX-80 are in quite close agreement and can be quantified as follows by a regression equation ($r^2 = 0.94$):

$$D_e = 6.7785\text{E}{-9} \times e^{-2.5671\text{E}{-3} \times \rho} \qquad (5.7)$$

For a dry density of 1,590 kg/m^3, a D_e for HTO of $1.2 \times 10^{-10} \pm 7.06 \times 10^{-11}$ m^2/s is recommended (25°C).

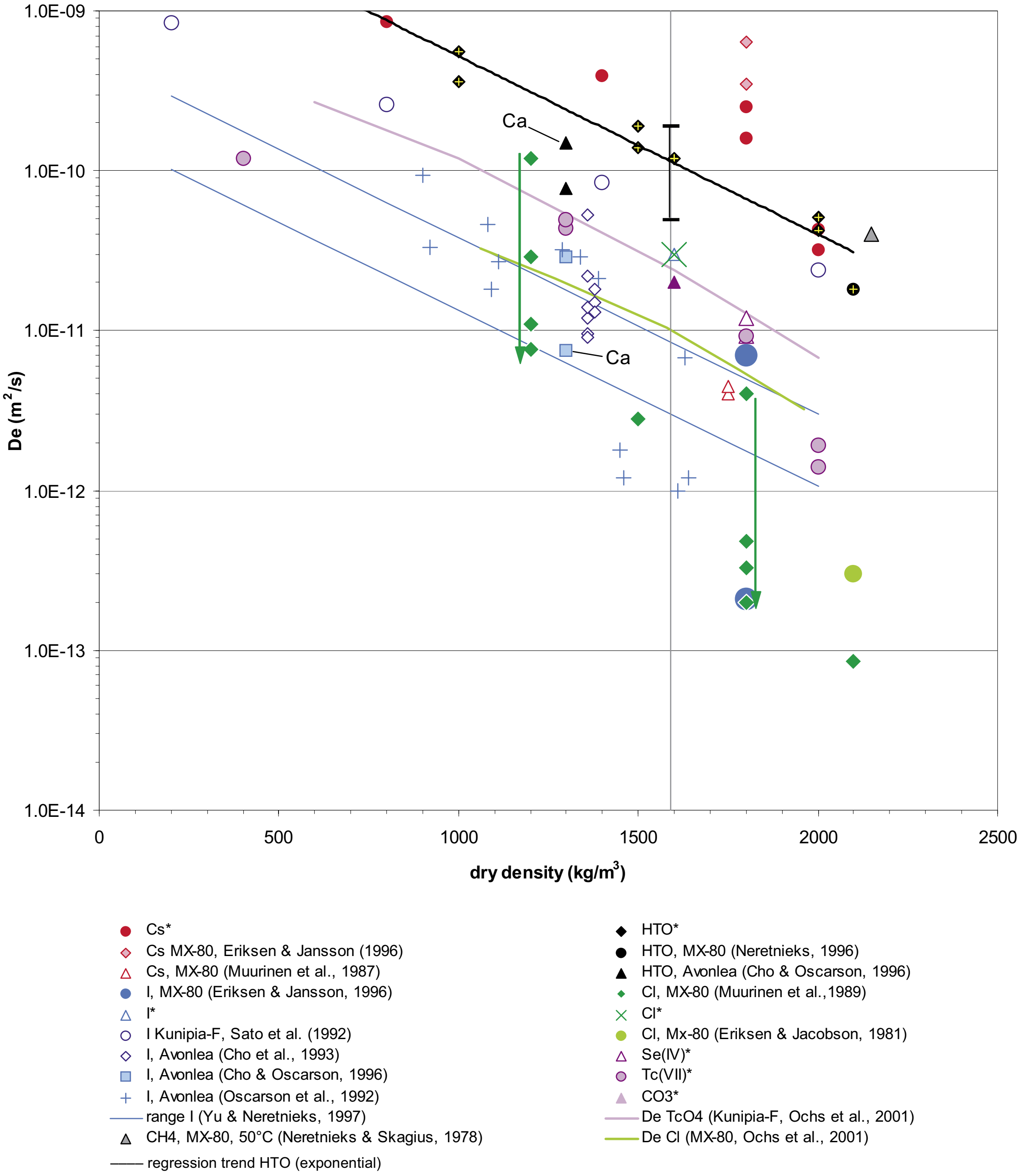

*Figure 5-4. Plot of effective diffusivities for Cs, HTO and various anions as a function of dry density. All data labelled * are for Kunigel-V1 bentonite /from Sato, 1998a/. The reference density of 1,590 kg/m^3 and uncertainty of D_e for HTO is indicated. For the Cl diffusion data in MX-80 /Muurinen et al, 1989/, the decrease of D_e with decreasing ionic strength of the input solution (1→0.01 M) is indicated. The model calculations by /Ochs et al, 2001/ correspond to pure water as input solution; note that this leads to a calculated ionic strength of ca 0.2–0.4 M at 1,590 kg/m^3. The range calculated for I following /Yu and Neretnieks, 1997/ is based on their estimation of $D_e = 3 \times 10^{-12}$ m^2/s for 1,600–2,000 kg/m^3. This D_e value at the low/high end of the indicated density was taken as minimum/maximum, and the same slope of D_e vs density as for HTO and the model calculations was assumed.*

The above value is in close agreement with the value of 1.0×10^{-10} m^2/s recommended by /Yu and Neretnieks, 1997/. The corresponding uncertainty represents the statistical standard error for the estimation of D_e by equation (5.7) based on the experimental data in Figure 5-4. To take into account a temperature increase from ambient conditions to max. 50°C, /Schwyn, 2003/ doubles the selected value; i.e. in this case a value of 2.4×10^{-10} m^2/s would result.

Anions

D_e and D_a values for anions show a significant scatter, especially in the case of MX-80 (Figure 5-4 and Figure 5-6), reflecting the fact that relatively many investigators measured data, sometimes for a range of conditions, but only for a limited range of dry densities. In particular, few systematic data are available for solutions of intermediate-high salinity (ionic strength > 0.3 M). On the other hand, diffusivities reported for low ionic strengths refer in all likelihood actually to ionic strength values of 0.2–0.3 M, as it is not considered possible to have a lower ionic strength in the pore solution of compacted bentonite (see section 5.1.3). While using slightly different approaches to porewater modelling, /Bradbury and Baeyens, 2003c/ and /Wersin, 2003/ also conclude that the large buffering capacity of bentonite and the dissolution of soluble impurities and accessory minerals invariably leads to pore solutions of intermediate ionic strength. /Ochs et al, 2004/ show that even in the case that the amount of soluble impurities would be significantly decreased, the pore solution in compacted bentonite still would have an ionic strength of > 0.1 M. Part of the experimental scatter is probably attributable to experimental difficulties /cf Yu and Neretnieks, 1997/, and in case of D_e possibly also to difficulties in assigning D_e and ε values for interpreting the measured raw data /see e.g. van Loon et al, 2003a,b/. Overall, it is estimated that the uncertainty in experimental diffusion coefficients is at least half an order of magnitude.

Despite the scattering of experimental data, it can clearly be seen that anions have significantly lower effective diffusivities than HTO. This is corroborated by model predictions for the diffusion of monovalent anions for MX-80 and Kunipia-F shown in Figure 5-4 (integrated sorption-diffusion model ISD, /Ochs et al, 2001/). These predictions are made by electric double layer models and do not take into account any reduction in available anion porosity. Note that these models had been calibrated based on data for Cs on Kunipia-F bentonite; they were then applied to anion diffusion and other bentonites in a purely predictive way.

The abovementioned problem of distinguishing between D_e and ε (more specifically, between D_e and the capacity factor $\alpha = \varepsilon + K_d\rho$) makes the selection of a self-consistent set of D_e and ε values somewhat ambiguous. A consistency check using corresponding D_a values is of limited use, because of the relation:

$$D_a = D_e / (\varepsilon + K_d\rho) \text{ or } D_a = D_e / \alpha \qquad (5.8)$$

Therefore, a given measured value for D_a can be explained by any combination of D_e and α (or D_e and ε if $K_d = 0$ is assumed). This is illustrated in Figure 5-5.

Based on this situation, the following approach was followed: First, D_e and the corresponding uncertainty was evaluated independently of any considerations regarding ε or α. In a second step, these values were related to corresponding values for ε and α, and a final selection was made.

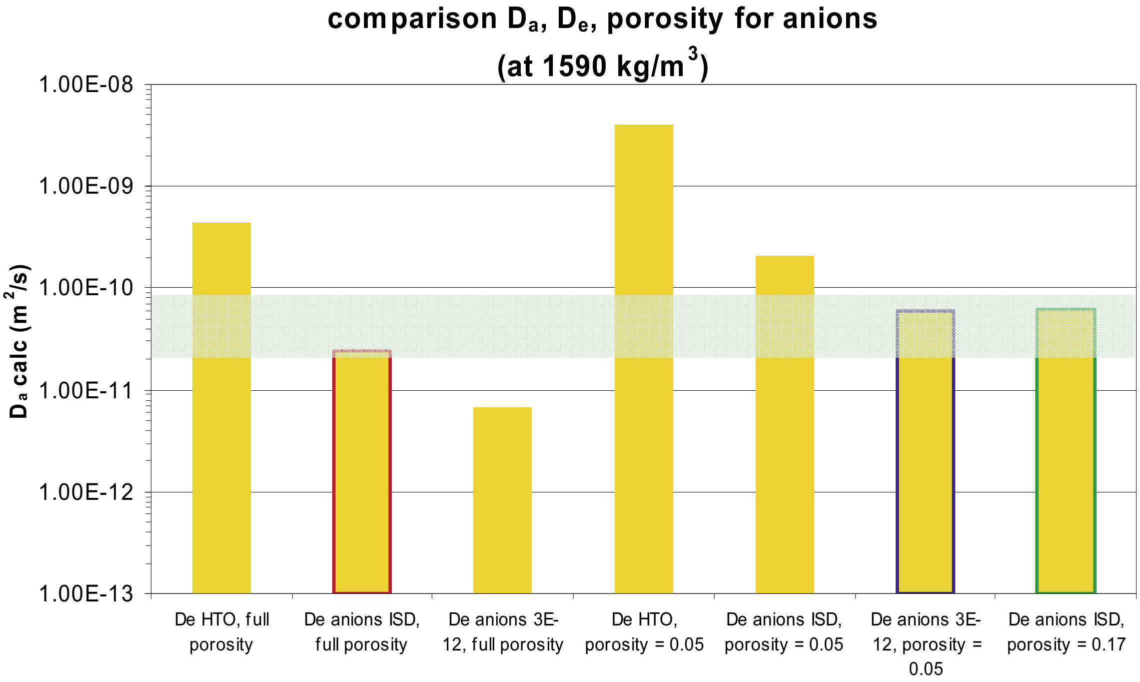

Figure 5-5. *Illustration of calculated D_a values resulting from different combinations of D_e and ε (or D_e and α, if a $K_d \neq 0$ is assumed). The green band indicates the range of expected D_a values (Figure 5-6). D_e HTO = 1.2E–10 m^2/s (see above), D_e anions ISD = 1.0E–11 m^2/s, full porosity = 0.43.*

Effective diffusivity

D_e was selected from Figure 5-4, in a first step. The two calculations by /Ochs et al, 2001/, representing completely independent estimates, agree with the bulk of the experimental data i) in terms of trend of D_e vs bentonite density as well as ii) in terms of magnitude. At the same time, the model calculation for MX-80 is in reasonably good agreement with the experimental data for Cl and I at intermediate to high salinity (0.22–1.0 M input solutions), which corresponds fairly closely to the upper limit of the range calculated based on the recommendation of /Yu and Neretnieks, 1997/.

Note that the model prediction for MX-80 by /Ochs et al, 2001/ corresponds to an ionic strength of ca 0.25 M in the pore solution at dry densities > ca 1,600 kg/m^3, which we consider to be minimum values at this buffer density. Some data in Figure 5-4 suggest that very dilute groundwaters lead to lower diffusivities, but the database is not sufficient to allow that conclusion. In particular, it is not clear that equilibration of the input solution with the bentonite was sufficient: This process should lead to an ionic strength of ca 0.2–0.3 M, and all D_e values for dilute input solutions should start to approach each other; this is actually indicated by the data obtained at 1,800 kg/m^3 by /Muurinen et al, 1989/. Ionic strength effects diffusion of anions via its influence on electric double layer properties. According to the findings of /Kozaki et al, 1998/ and /Ochs et al, 2004/, this is only relevant in sufficiently narrow pores; i.e. above a dry density of ca 1,200–1,400 kg/m^3.

Based on the above discussion, a D_e for anions of 1.0×10^{-11} m^2/s is recommended for a dry density of 1,590 kg/m^3 (25°C). This value is considered to be a realistic estimate for groundwaters of intermediate to high salinity (ca 0.2 to 1 M). Based on D_e values for dry densities > 1,800 kg/m^3, it appears that dilute input groundwaters lead to D_e values that are significantly lower, but the available database does not allow to draw this conclusion with certainty.

Upper and lower limits for D_e were evaluated based on the following observations (Figure 5-4):

- As lower limit for D_e, the minimum value of 3.0×10^{-12} m^2/s at 1,600 kg/m^3 estimated by /Yu and Neretnieks, 1997/ is accepted for a density of 1,590 kg/m^3. This value is in close agreement with the data obtained by /Muurinen et al, 1989/ for Cl at intermediate densities, using dilute as well as pre-equilibrated input solutions.
- As upper limit, a value of 3.0×10^{-11} m^2/s at 1,600 kg/m^3 is taken. This is based on measured D_e values for several anions in compacted Kunigel-V1, as well as on the model prediction by /Ochs et al, 2001/ for Kunipia-F.

Figure 5-4 shows that the band corresponding to these limits encompasses the majority of the D_e values plotted.

Diffusion-available porosity, and comparison with D_a

Diffusion-available anion porosity is selected based on the findings of /van Loon et al, 2003a,b/, who made an explicit effort to distinguish D_e from ε in their data interpretation. Their data for chloride suggest a reduction of the diffusion-available porosity from HTO to anions by a factor of 1.8–3.5 (if a K_d of 0 is assumed). Based on this finding, a reduction factor of 2.5 is proposed, resulting in an anion diffusion-available porosity of 0.17 for the present case. Use of the reduction factors 1.8 and 3.5 results in porosities of 0.24 and 0.12 as limiting values. Figure 5-5 and Figure 5-6 show that this reduction in porosity is consistent with independent D_a measurements when used together with the selected D_e for anions given above. It is also illustrated that use of the limiting values for diffusion-available anion porosity is reasonable in view of the measured D_a values. On the other hand, use of the full physical porosity leads to calculated D_a values that underpredict most of the measured data.

Figure 5-6 also shows the effect of the uncertainties in D_e proposed above with respect to D_a. It can be seen that the resulting minimum and maximum D_a values actually encompass the entire range of measured data at the dry density of 1,590 kg/m^3.

Selected values and uncertainties for anion diffusion parameters

Based on the introductory discussion to this section, it has to be made clear that the selected anion diffusion parameters have to be evaluated together. Figure 5-6 shows that the proposed values represent a self-consistent data set that is also consistent with independently measured D_a values. It is therefore evaluated as extremely likely that any combined dataset of D_e and ε (and K_d) under the specified scenario (as expressed by the resulting D_a) would be within the indicated ranges.

For non-sorbing anions ($K_d = 0$), it is recommended to use at a dry density of 1,590 kg/m^3

- a diffusion-available anion porosity of 0.17, with upper and lower limits of 0.24 and 0.12, respectively,
- a D_e of 1.0×10^{-11} m^2/s, with upper and lower limits of 3.0×10^{-11} m^2/s and 3.0×10^{-12} m^2/s, respectively.

The diffusion-available anion porosity can be related to dry density using equation (5.6) and a constant reduction factor of 2.5 (equation 5.9).

$$\varepsilon_{anion} = (1 - (\rho/\rho_s))/2.5 \qquad (5.9)$$

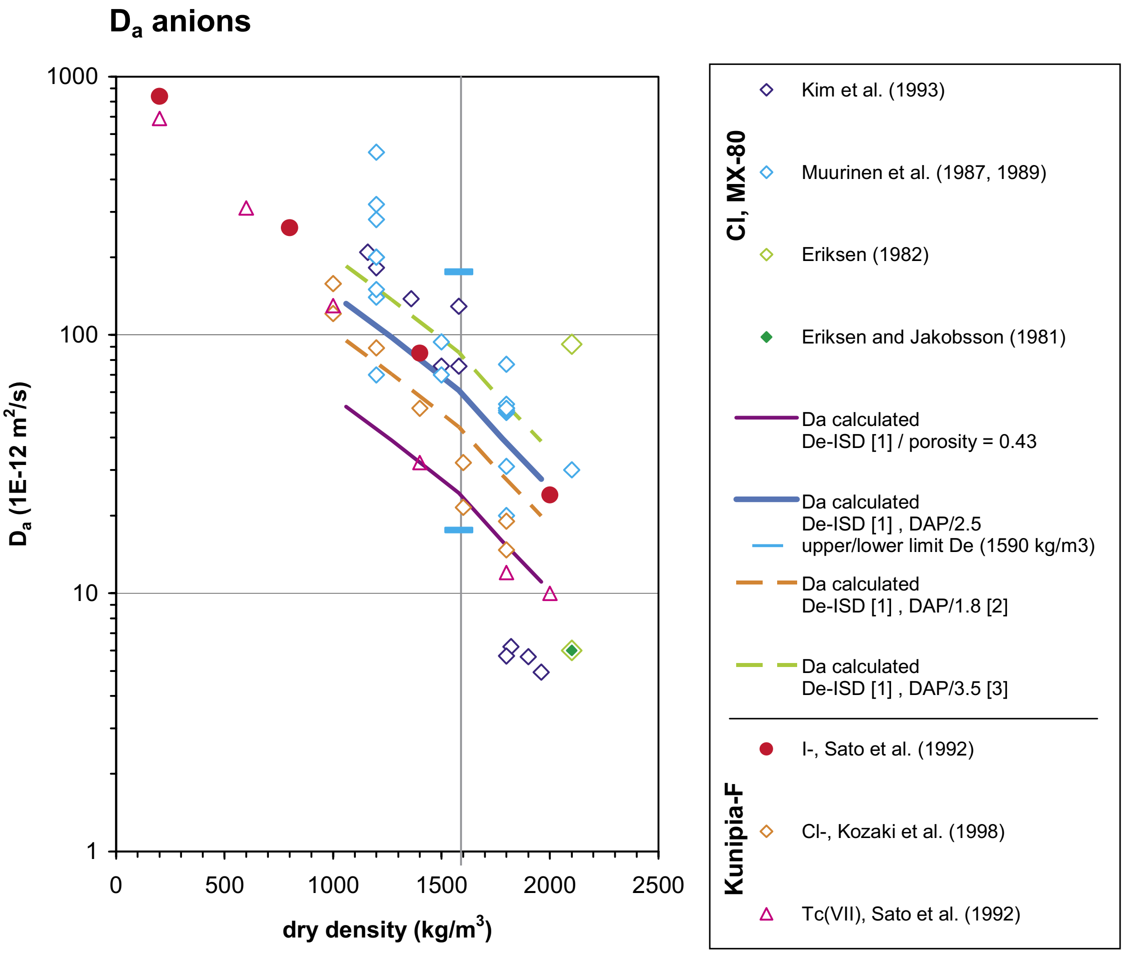

Figure 5-6. *Apparent diffusivities for different anions in MX-80 and Kunipia-F bentonite in comparison to model predictions:* D_a *was calculated using ISD-model [1] derived* D_e *values and the corresponding uncertainty limits in combination with different choices for anion porosity:*

1) *the entire physical porosity; this corresponds directly to the prediction for* Cl^- *in MX-80 shown in Figure 5-4.*
2) *maximum diffusion-available anion porosity (DAP) based on the data of [2] for chloride; and HTO*
3) *minimum diffusion-available anion porosity (DAP) based on the data of [3] for chloride; and HTO*

[1] /Ochs et al, 2001/; [2] /van Loon et al, 2003a/; [3] /van Loon et al, 2003b/

The De for anions as a function of density is given by the line in Figure 5-4 representing the model prediction by /Ochs et al, 2001/. To avoid the use of the respective underlying electrical double layer model, a 3rd degree polynomial function can be used which reproduces the model predictions as a function of density for a density range of ca 1,000–2,000 kg/m^3 exactly (i.e. follows the slight curve of the model predictions resulting from changes in the porewater chemistry as a function of density; $r^2 = 0.998$):

$$D_e = -1.1844\times10^{-20} \times \rho^3 + 8.130\times10^{-17} \times \rho^2 - 1.9473\times10^{-13} \times \rho + 1.6167\times10^{-10} \qquad (5.10)$$

An approximate representation of the model predictions can also be given by a logarithmic relation similar to eq. (5,7): $D_e = 5.30087\text{E}-10 \times e^{-2.561\text{E}-3 \times \rho}$ ($r^2 = 0.918$).

Cs

Following the same arguments used to explain anion exclusion (i.e. interaction of negatively charged diffusant with electrical double layer extending from negatively charged pore walls), /Kato et al, 1995; Sato et al, 1995; Ochs et al, 2001/ used an electric double layer model to explain the apparently enhanced diffusion of certain cations (see section on diffusion in the SR-Can Process Report /SKB, 2004/). This model is able to explain D_a values for Cs obtained for different bentonites and densities, without having to rely on a surface diffusion coefficient. Some model results are reproduced in Figure 5-11.

Based on these studies, and on consistency of D_e and D_a values determined under comparable conditions, a D_e value of 3×10^{-10} m^2/s is recommended for Cs.

This value also serves as upper limit; the lower limit is given by the lower limit for HTO. D_e for Cs is considered to show the same dependency on density as D_e for HTO, differing by a constant factor of 3 (at most, see above).

Note that the above considerations are in all likelihood not relevant for any other of the "cationic" elements, as they exist largely as a mix of positively, negatively and uncharged species (see also /Ochs et al, 2003/).

5.3.5 Derivation of K_d values, comparison with diffusion data

In the following sections, the derivation of K_d is discussed for each element, and the consistency of the selected data is evaluated through the calculation of D_a values and comparisons with independent experimental data. The selected source data as well as the results obtained after conversion to application conditions are tabulated in detail in Appendix E, including all conditions, conversion factors, uncertainties, resulting recommended values and upper/lower limits. The D_a values used for comparisons were preferably taken from studies where diffusion had been studied as a function of density (see section 2.3.1).

Based on a large number of calculated porewater compositions (Appendix C), three representative porewaters were selected that spanned a wide range of the possible conditions, including pH, ligand concentrations (in particular carbonate) and salinity. This allowed to assess uncertainty as a result of the variability in conditions using these three porewaters in most cases. The selected porewaters are (Appendix C).

- the reference porewater (RPW), based on the saline reference Beberg groundwater and a pCO_2 imposed by the host formation according to /Laaksoharju et al, 1998/,
- a water defined as RPW above, but treating bentonite as a closed system with respect toCO_2 (RPWC),
- a porewater based on highly saline groundwater (HSPW).
- Qualitatively, an increase of pH outside the reference range is also addressed where relevant; this is restricted to the effect of pH per se and does not include further potential concomitant changes in dissolved carbonate levels.

Americium

K_d values were derived based on the study of /Gorgeon, 1994/, as it is the only available study, to our knowledge, where Am sorption on smectite was studied systematically as a function of pH: /Gorgeon, 1994/ determined two adsorption edges from pH 3–11 in 0.1 and 1 M $NaClO_4$ solutions on smectite extracted from Wyoming bentonite. Based on speciation calculations (Appendix F), Am was below the solubility limit in all experiments. A shortcoming of this study is that pCO_2 had not been controlled rigorously, but at least an estimate of total dissolved carbonate is given in /Gorgeon, 1994; Ochs et al, 1998/ also had used the data of /Gorgeon, 1994/ as the most systematic dataset available for the development of a thermodynamic sorption model. While their proposed model is probably too simple[1], it clearly shows that Am sorption on smectite in the pH range 3–10 can be described by surface complexation and ion exchange (the latter becoming important only at near-neutral to low pH values in solutions of low ionic strength). This is also consistent with the model developed by /Bradbury and Baeyens, 2002a/ for the sorption of Eu on montmorillonite. /Shibutani et al, 1994/ also measured Am sorption as a function of pH on Kunigel-V1 bentonite. However, all their data points correspond to nearly 100% sorption, which can cause large errors and renders them less reliable.

Based on the above discussion, K_d values for Am were derived from the data of /Gorgeon, 1994/ using the CF-approach. It is believed that the model by /Ochs et al, 1998/ would not be superior to the CF-approach, because it is probably too simple (see above) and because it is based on the same dataset and does therefore not contain any additional chemical informationThe resulting K_d values and uncertainties are plotted as a function of conditions in Figure 5-7. The predicted increase of K_d with pH is consistent with a surface complexation mechanism (i.e. corresponds to the rising slope in Figure 5-1). Except for RPWC, the results obtained with CF-total 1–3 agree very well. The dominant dissolved Am species is $AmCO_3^+$ (Appendix F), and the effect of full corrections for solution speciation (CF-total 3) is therefore directly related to the differences in carbonate concentration between data source and application conditions. As no systematic sorption data under variable carbonate concentration are available, the effect of carbonate on Am sorption cannot be predicted with certainty. For example, it cannot be excluded that $AmCO_3^+$ is involved in ion exchange, as postulated by /Shibutani et al, 1994/, which would contribute to sorption especially in the RPWC system. Therefore, the selected data are based on CF-total 3.

Overall, the uncertainties of the selected data (using CF-total 3) also encompass the values that would result from treating the scaling of speciation in different ways (i.e. using CF-total 1 or 2) even in case of RPWC. It is, therefore, extremely likely that that any K_d for Am under the specified scenario would be within the indicated ranges.

Calculated D_a values based on D_e for HTO and the selected K_d values are compared with experimental data in Figure 5-7. It is shown that the calculated D_a values are very consistent with measured data, and that the uncertainties for K_d cover well the scatter observed for D_a, corroborating the robustness of the indicated data and ranges. Am speciation was calculated using the TDB of /Silva et al, 1995/. The influence of updated TDB was evaluated using the data given in /Guillaumont et al, 2003/. Values calculated with these two TDBs are identical and agree within a factor 2 for RPW, RPWC, and HSPW.

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[1] At the time of publication, the aim was to use a model consistent with the basic bentonite model by /Wanner et al, 1994/, which treats surface complexation by a one-site diffuse layer model. Subsequent preliminary work (unpublished) showed that a two-site model would allow significantly better fits at near-neutral pH.

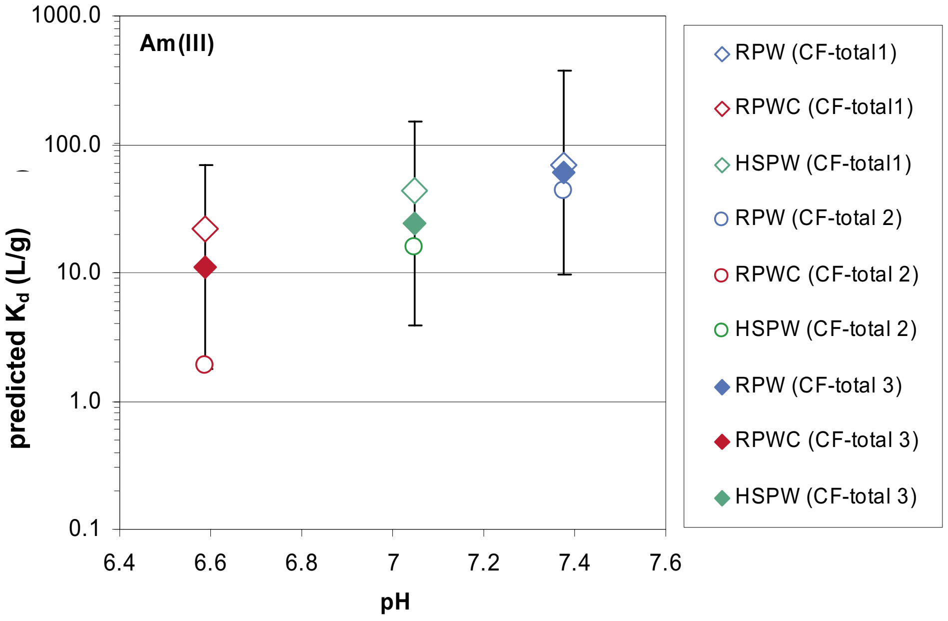


Figure 5-7. *K_d values for Am derived as a function of conditions. The selected values are indicated by solid symbols (CF-total 3); the error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4. Am speciation is calculated using the data by /Silva et al, 1995/.*

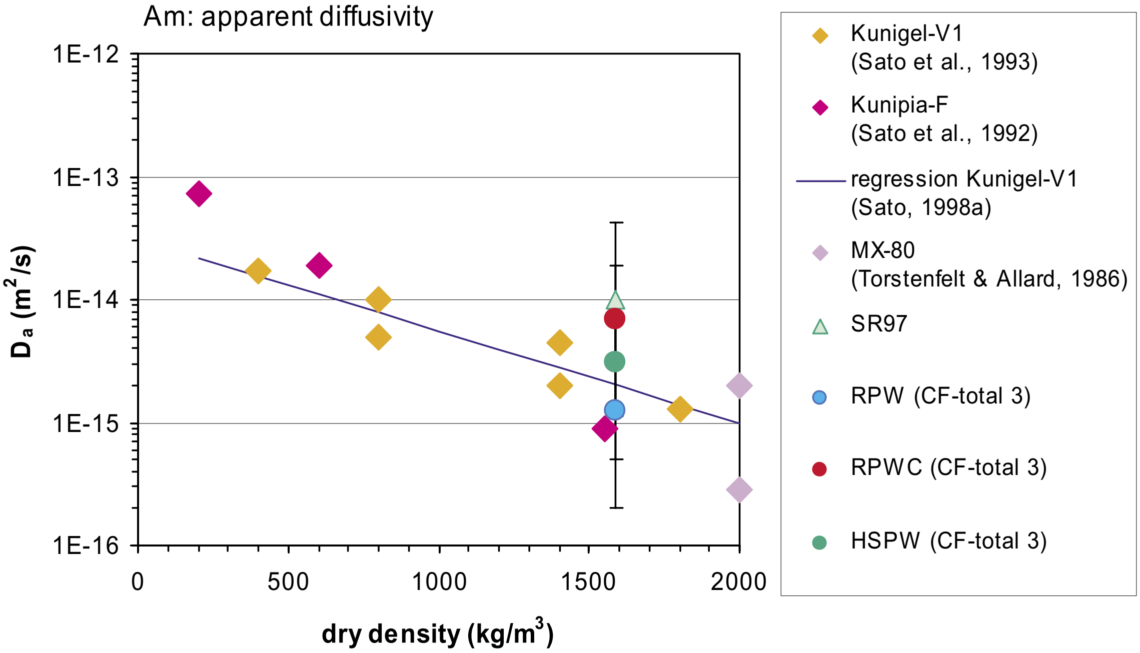


Figure 5-8. *Calculated D_a values for Am based on D_e for HTO and selected K_d derived as a function of conditions. The data by Sato and co-workers were obtained with pure water as input solution, SR97 refers to the D_a value selected by /Yu and Neretnieks, 1997/.*

The data by /Gorgeon, 1994/ suggest that K_d may increase up to a porewater pH of ca 11. However, at more elevated carbonate concentrations, K_d may start to decrease above a pH of about 8–9, due to increased competition through complexation with dissolved carbonate (formation of negatively charged Am-carbonato complexes). For even higher pH values, no reliable data are available.

Caesium

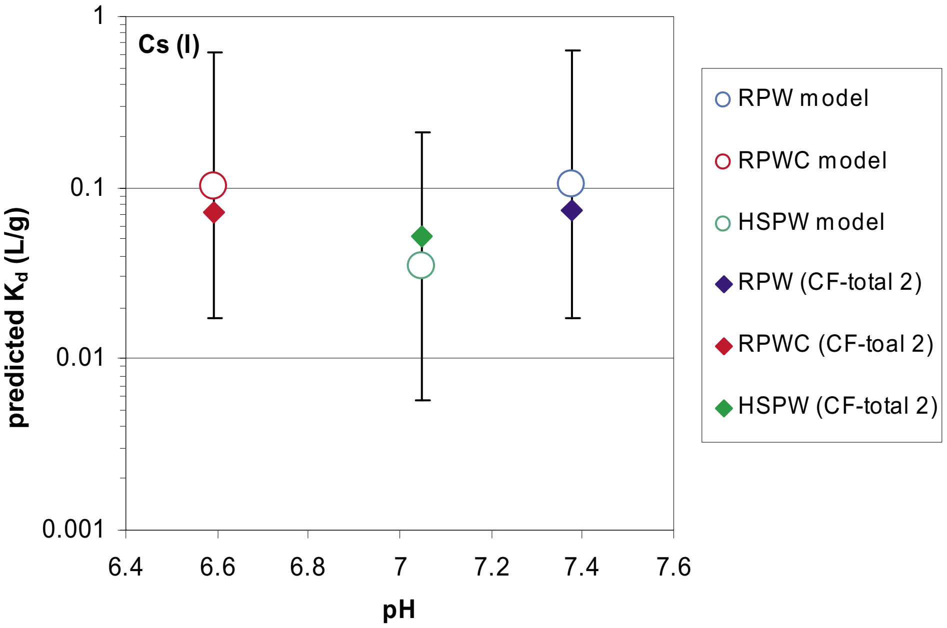
A large number of sorption studies on bentonite is available for Cs (not discussed in detail here; see e.g. the compilation of /Yu and Neretnieks, 1997/, as well as several ion exchange studies on pure clay minerals. While the data obtained on bentonite are more directly applicable to the present purpose, most studies involving bentonite are not systematic enough to allow data transfer to different conditions. It is well established that Cs sorbs via cation exchange /e.g. Wanner et al, 1996/, whereas the contribution of surface complexation is negligible. This renders sorption of Cs very sensitive with respect to changes in the major cation composition of the aqueous phase.

The study of /Wanner et al, 1996/ and the measurements reported by /Bradbury and Baeyens, 2003a/ were considered the most systematic data sources directly applicable to MX-80 and were selected for the present data derivation. Both studies used untreated MX-80 bentonite. /Wanner et al, 1996/ report a number of K_d values measured in various 1:1 and 2:1 electrolyte solutions, as well as an isotherm obtained in 0.1 M NaCl. Most of their data correspond to solid/water ratios ≤ 0.1 g/L. /Bradbury and Baeyens, 2003a/ report a detailed sorption isotherm on MX-80 in synthetic bentonite porewater with an ionic strength of 0.7 M, using a solid/water ratio of 60 g/L. /Hurel et al, 2002/ also give more limited isotherms for MX-80 (4 g/L) corresponding to pH 7.4 and 8.2 in a dilute synthetic groundwater (I = 0,05 M). The isotherms from these three studies are nearly parallel over 5–6 orders of magnitude in terms of Cs concentration, but cover about one order of magnitude in terms of K_d. This is consistent with sorption edges by /Hurel et al, 2002/ using purified and un-purified MX-80 and can be explained with the difference in ionic strength (i.e. the concentration of competing cations) between the two studies.

Using the data discussed above, /Wanner et al, 1996/ developed a thermodynamic sorption model based on a reversible one-site ion exchange of Cs. They also applied this model successfully to some literature data. For the present purpose, their ion exchange constant for Cs was incorporated in the model used to calculate bentonite-groundwater interaction; see Appendix D for details. K_d values calculated for the present reference systems are shown in Figure 5-9 as a function of pH and ionic strength. The model calculations are compared with values derived using the CF approach based on the experimental data by /Bradbury and Baeyens, 2003a/. Because of the predominance of ion exchange for Cs sorption, the pH-conversion factor was replaced in this case by a CF-cation conversion (see Appendix E), with a UF-cation conversion of 2.5. Because of the sensitivity of Cs sorption to major cation concentrations, the model calculations were extended to cover additional application conditions (Figure 5-10, see also Appendix C). It can be seen that uncertainties introduced by considering further variability in the conditions (loss of impurities, conversion to Ca-bentonite, different groundwater composition) leads to calculated K_d values that fall well within the uncertainty limits indicated in Figure 5-9.

Both Figures show that the model calculations and the values derived from the data of /Bradbury and Baeyens, 2003a/ agree very well, although the values derived with the CF-approach show a less pronounced dependency on ionic strength. The reason for this may be that the CF-approach does not include effects of cation selectivity. However, it also should be noted that the data underlying the model of /Wanner et al, 1996/ correspond to experiments in low-ionic strength solutions, whereas the data of /Bradbury and Baeyens, 2003a/ were determined at high ionic strength. Thus, the slightly different trend of K_d vs ionic strength observed with the tow approaches may also reflect the different starting conditions for model development and data derivation.

In summary, it is considered to be extremely likely that any K_d for Cs under the specified scenarios would be within the indicated ranges, based on the relatively good consistency among the calculated and derived K_d values .



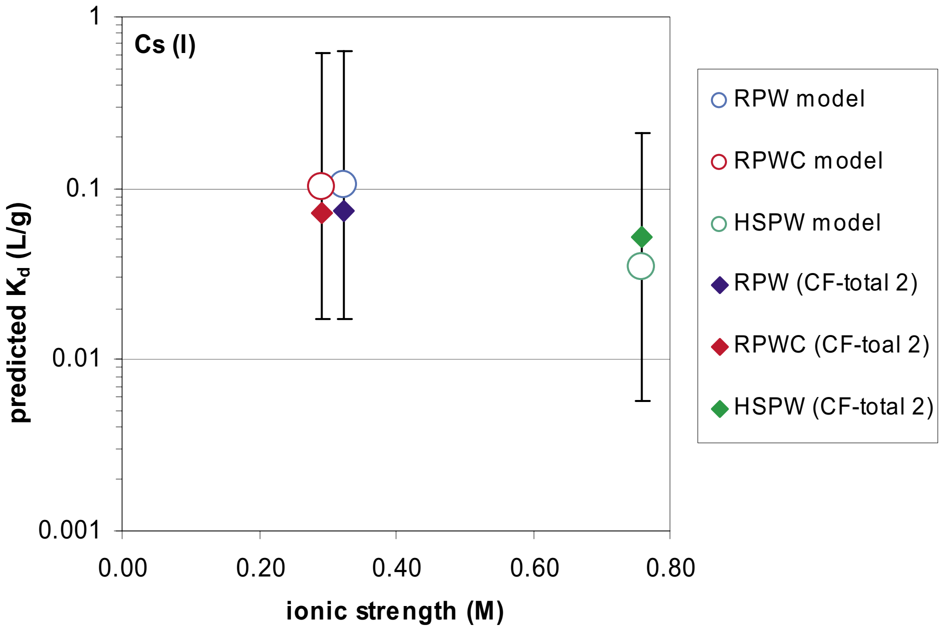


Figure 5-9. *K_d values for Cs calculated as a function of conditions with the Cs sorption model of /Wanner et al, 1996/. Values derived based on the experimental data by /Bradbury and Baeyens, 2003a/ are shown for comparison. The selected values are indicated by open circles (model); the error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*

In Figure 5-11, this assessment is corroborated by comparing D_a values calculated using the K_d values derived based on the data by /Bradbury and Baeyens, 2003a/ as well as the values calculated with the sorption model of /Wanner et al, 1996/ together with the diffusion parameters selected for Cs. The agreement of the calculated D_a values with experimental data and diffusion model predictions is excellent, and the uncertainties derived for K_d accommodate well the variation of the experimental diffusion data.

For Cs, a D_e value of 3E–10 m^2/s is recommended (see section 5.3.4). Figure 5-11 shows that this choice leads to an overall consistent set of migration parameters for Cs.

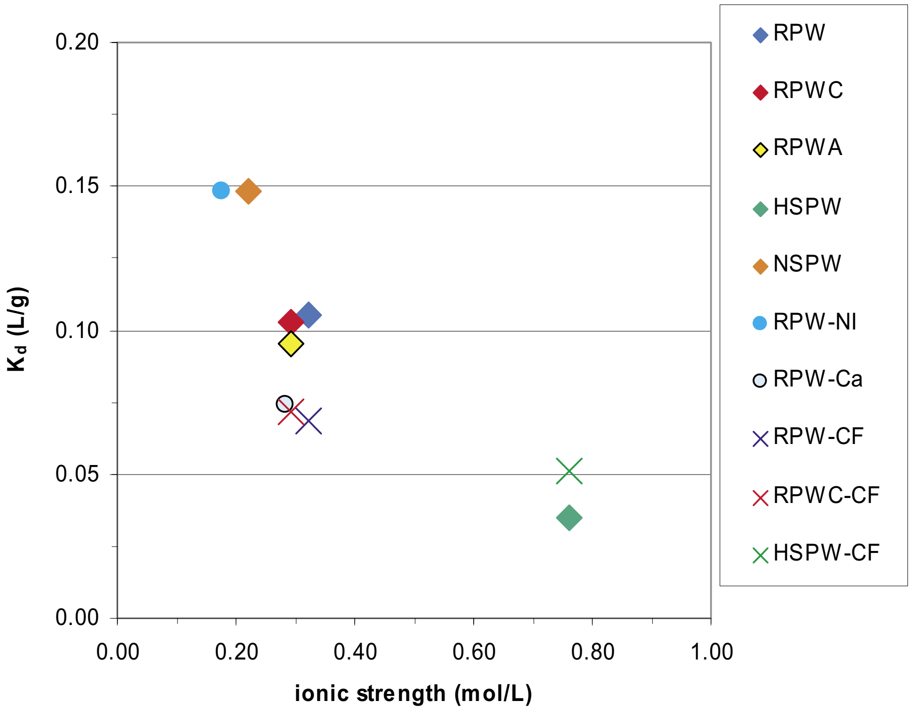


Figure 5-10. *K_d values for Cs calculated using the Cs sorption model of /Wanner et al, 1996/. The values derived using the CF approach (CF-total 2) based on the experimental data by /Bradbury and Baeyens, 2003a/ are shown for comparison.*

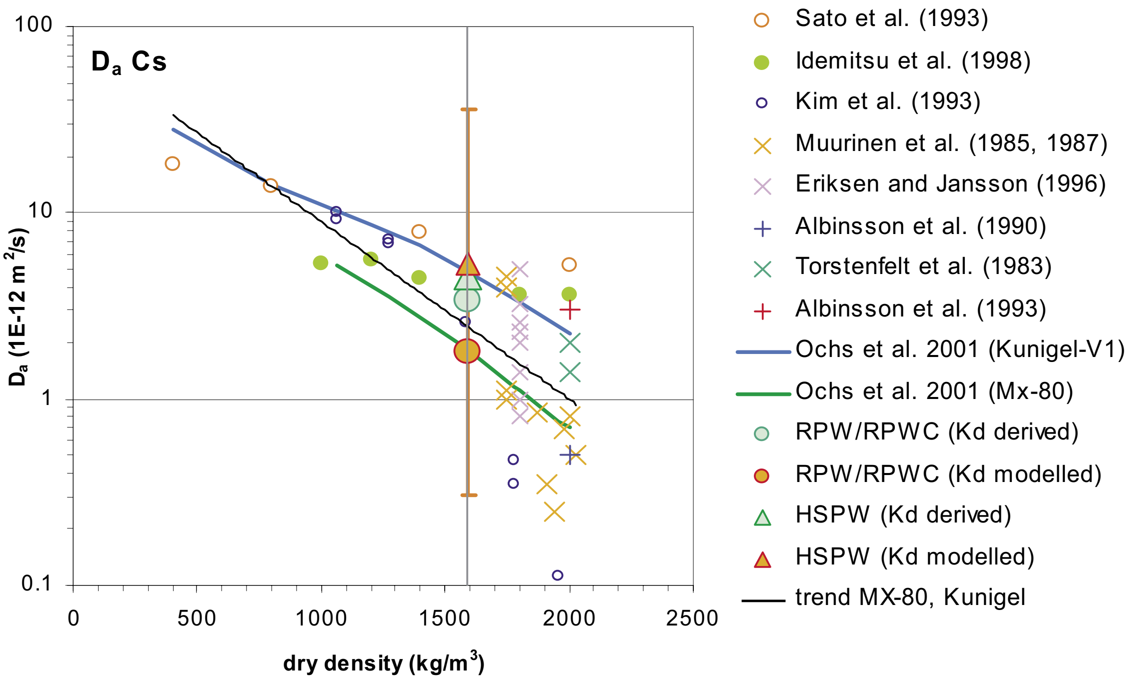


Figure 5-11. *Calculated D_a values for Cs based on D_e for Cs and selected K_d calculated using the model of /Wanner et al, 1996/ or derived as a function of conditions with the CF approach. Experimental data obtained on Kunigel-V1 are shown as circles, data obtained on MX-80 as crosses. Sorption-diffusion model calculations /Ochs et al, 2001/ and the result of a regression analysis are also shown. The error bar spans the entire uncertainty in K_d for RPW, RPWC and HSPW.*

Based on the major cation concentration in the calculated porewater compositions (Appendix C), the influence of (highly) alkaline groundwater on K_d for Cs is expected to be within the limits given by the three reference porewaters.

Carbon

Carbon can exist in various forms, depending on the origin of the carbon and the relevant redox conditions: Considered here are carbonate species, simple organic acids, or methane.

D_e and ε for carbonate species are treated analogously to the values selected for chloride, even though the carbonate ion has a charge of –II and may also sorb weakly. The data in Figure 5-4 do not point to a significant difference between carbonate species and other anions, however. Further, considering the inventory of stable carbonate in the bentonite (as calcite), it is most likely that removal of ^{14}C from the solution takes place through isotopic exchange with calcite. K_d values can then be readily calculated based on the respective solution chemistry and the amount of accessible calcite in MX-80.

In case of methane, a K_d of zero and the D_e as well as porosity used for HTO (see Figure 5-4) are proposed.

In case of simple organic acids, no reliable K_d values were found in the literature. Model calculations for acetic acid, using the approach by /Ochs and Talerico, 2003/, indicated that K_d on MX-80 is < 1E–7 m^3/kg. The reason for this is mainly that silicate competes effectively for the same type of sites (edge sites). Therefore, a K_d of zero and the D_e as well as porosity derived for anions are proposed. It is realised that slightly more complex organic molecules, featuring e.g. 2 carboxyl groups instead of just one (as in case of acetic acid), may exhibit significantly stronger sorption on clay edges, based on analogy with Al-oxide surfaces /e.g. Kummert and Stumm, 1980/. As the nature of the organic molecules is not known, however, this possibility is not considered. As the use of a simple organic acid is considered to be a conservative approach, no additional UF is introduced.

Cerium, holmium, and samarium

No reliable and relevant sorption data could be found for any of these elements. Therefore, K_d values were derived using Eu as analogue element. Eu sorption on smectite has been investigated in detail by Bradbury and Baeyens. /Bradbury and Baeyens, 2002a/ report sorption edge as well as isotherm data obtained on Na- as well as Ca-montmorillonite (SWy-1) in $NaClO_4$ and $Ca(NO_3)_2$ background electrolytes. These data form the basis for a thermodynamic sorption model (two-site surface complexation without EDL term, plus ion exchange) developed by the same authors. In addition, /Bradbury and Baeyens, 2003a/ report an isotherm for pH 7,6 on MX-80 in artificial porewater (I = 07 M).

K_d values derived by the CF-approach using MX-80 source data are given in Figure 5-12, together with values calculated using the thermodynamic sorption model of /Bradbury and Baeyens, 2002a/. Data derived on the basis of SWy-1 by the CF-total 2 and CF-total 3 methods are also shown and bracket the model data within about an order of magnitude, as should be expected (Appendix E). While the sorption model has the better scientific foundation, it has to be realised that robustness in terms of extrapolation to different conditions depends to a large degree on model parameterisation. Unfortunately, the effects of practically all major anions (including carbonate) are not included in the dataset for SWy-1 (and therefore in the corresponding model). In that sense, it is encouraging that the difference between the model based on the simplified SWy-1/electrolyte system and the CF-approach based on the more complex MX-80/porewater system is less than an order of magnitude.

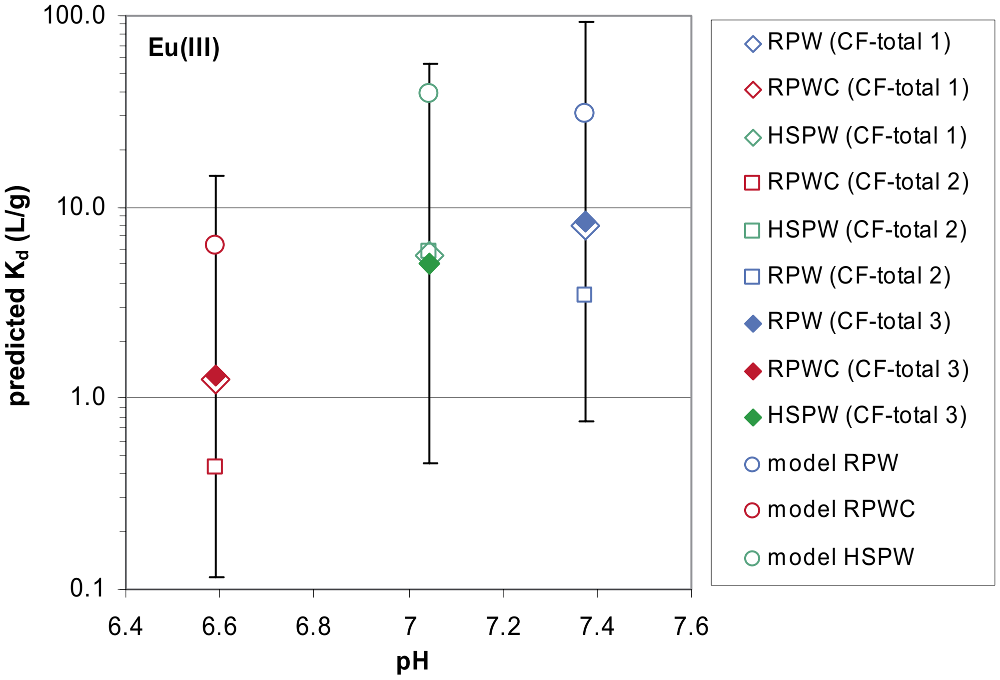


Figure 5-12. *K_d values for Eu derived as a function of conditions based on the experimental data by /Bradbury and Baeyens, 2003a/ for MX-80. Values calculated using the Eu sorption model of /Bradbury and Baeyens, 2002a/ are also shown. The selected values are indicated by solid symbols (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*

Based on a comparison with the available D_a measurements (Figure 5-13), it is recommended to use the values derived from the MX-80 source data; i.e. to rely on source data that are comparatively close to the application conditions, rather than on the sorption model. However, it is recommended to use the values obtained in the model calculations as the upper limit of the recommended data, while the lower limit should be based on the MX-80 source data. These limits are very likely to encompass any K_d for trivalent lanthanides under the specified scenarios. No additional uncertainty factors are proposed to account for the use of Eu as analogue element.

No reliable data for (highly) alkaline conditions are available, but the experimental data by /Bradbury and Baeyens, 2002a/ clearly show an increasing trend of K_d for Eu up to pH 9, which is consistent with the data for Am.

Chloride

Both D_e and ε selected for anions are proposed, together with a K_d of zero. No additional uncertainties are considered.

Curium

No reliable, systematic sorption data for Cm on relevant minerals could be found. The chemistry of Cm appears to be nearly identical to that of Am, but no TDB of comparable quality is available. Therefore, Am is used directly as analogue element; no additional UF-analogue is considered for this case.

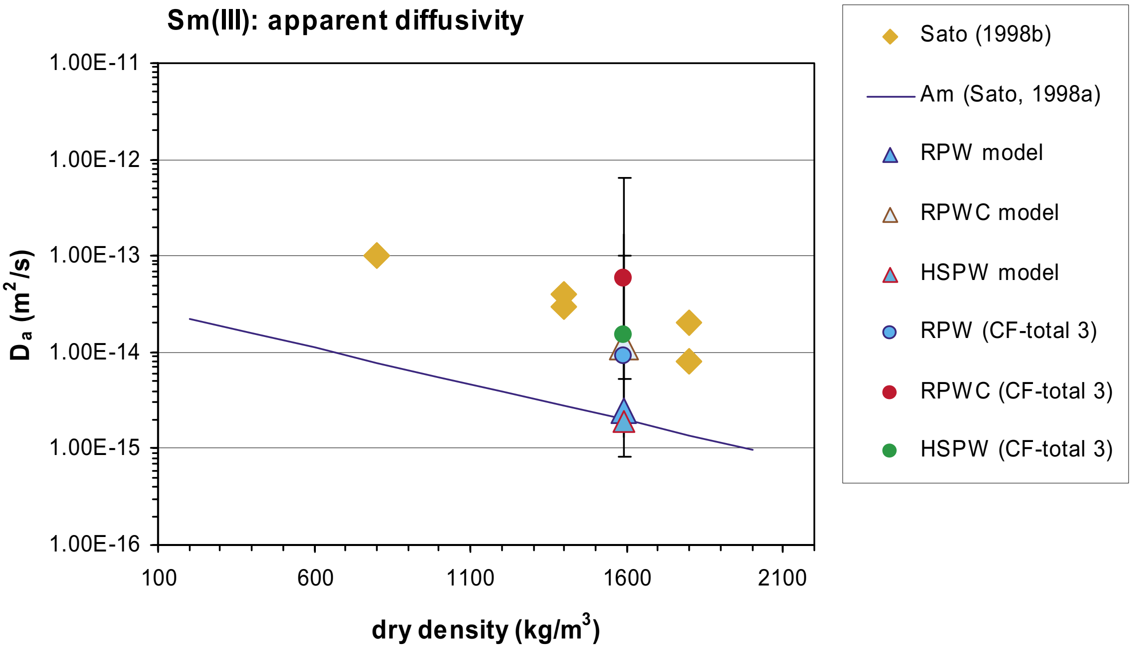


Figure 5-13. *Calculated D_a values for Eu(III) based on D_e for HTO and K_d values from Figure 5-12 in comparison to experimental data for Sm obtained on Kunigel-V1. For comparison, the regression line representing Am (from Figure 5-8) is also shown.*

Holmium

See section on cerium, holmium and samarium.

Iodine

It is considered that iodine will exist exclusively as iodide anion under relevant conditions. There is circumstantial evidence that iodide may exhibit very low, but notable sorption; see e.g. the compilation of /Liu and von Gunten, 1988; Yu and Neretnieks, 1997/. However, no unambiguous data could be found. Further, it may be that iodide sorption is more related to illite than smectite minerals /Kaplan et al, 2000/. Therefore, iodide is treated analogously to chloride: A K_d of zero is proposed together with D_e and ε selected for anions.

Lead

Several studies on Pb sorption on different montmorillonites are available, but no reliable diffusion data were found. An overview of Pb sorption data is e.g. given in /Ochs et al, 1998/, who also showed that the different studies are approximately consistent with each other, using a simple sorption model (not considered for the present purpose because of its preliminary nature). /Ulrich and Degueldre, 1993/ worked with trace concentrations of Pb throughout, and their study is selected as most representative. K_d was derived using the CF-approach, and the resulting values under application conditions are shown in Figure 5-14. This figure shows that scaling to application conditions is not very sensitive with respect to CF-speciation. It is considered to be very likely that any K_d for Pb under the specified scenarios would be within the indicated ranges, despite the lack of diffusion data for comparison.

No reliable data for (highly) alkaline conditions are available. Based on the expected solution speciation of Pb, it cannot be excluded that sorption may decrease at pH > 9 or so.

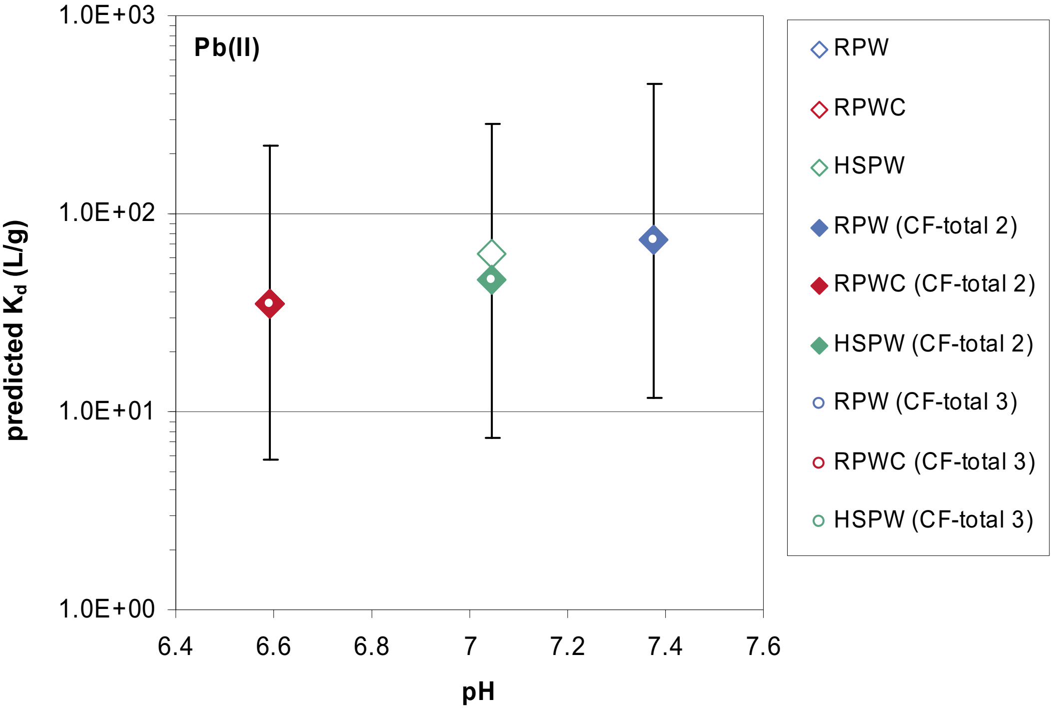


Figure 5-14. *K_d values for Pb derived as a function of conditions based on the experimental data by /Ulrich and Degueldre, 1993/. The selected values are indicated by solid symbols (CF-total 2); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*

Neptunium

In relevant aqueous solutions, stable oxidation states of Np can be IV or V, depending on redox conditions. Because of the uncertainty regarding redox conditions, both oxidation states are treated separately below, following the approach for uranium. The overall uncertainty for the K_d of Np encompasses the entire combined data range if variable redox conditions need to be taken into account.

For Np(IV), no relevant sorption data were found in the open literature, and K_d was derived based on analogy considerations and the source data set used for Th. The results are shown in Figure 5-15, the comparison with Da values is shown in Figure 5-16. As in the case of U, the data show that inclusion of carbonate species in the speciation-conversion leads to results that are completely inconsistent with diffusion data for Th as well as Np. Therefore, the K_d values based on CF-total 3 are recommended. It can be seen from Figure 5-16 that the selected sorption data are not inconsistent with the available D_a values for Th and those for Np obtained under the most reducing conditions.

As for U(IV), it is considered likely that most of the diffusion experiments may not have been controlled well enough to avoid the presence of Np(V), and the overall diffusion may represent a mix of reduced and oxidised Np fractions. It is considered to be likely that any K_d for Np(IV) under the specified scenarios would be within the indicated ranges.

Since the hydrolysis behaviour of Np(IV) appears to be identical to that of Th at high pH /Lemire et al, 2001/, no significant influence of a pH increase on K_d is expected.

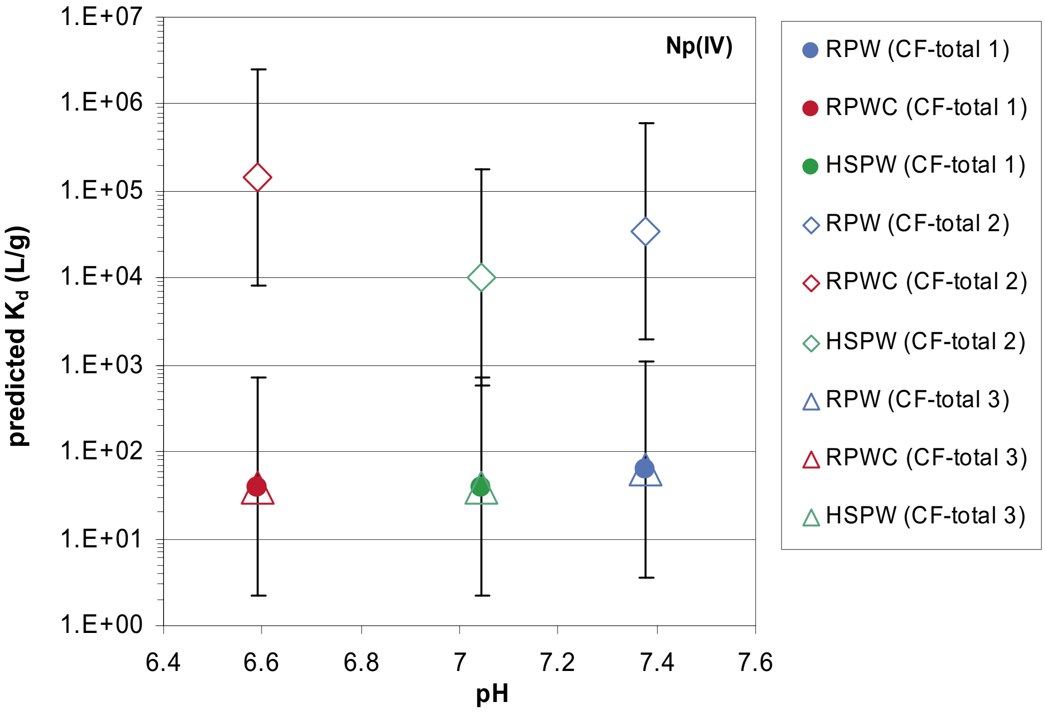
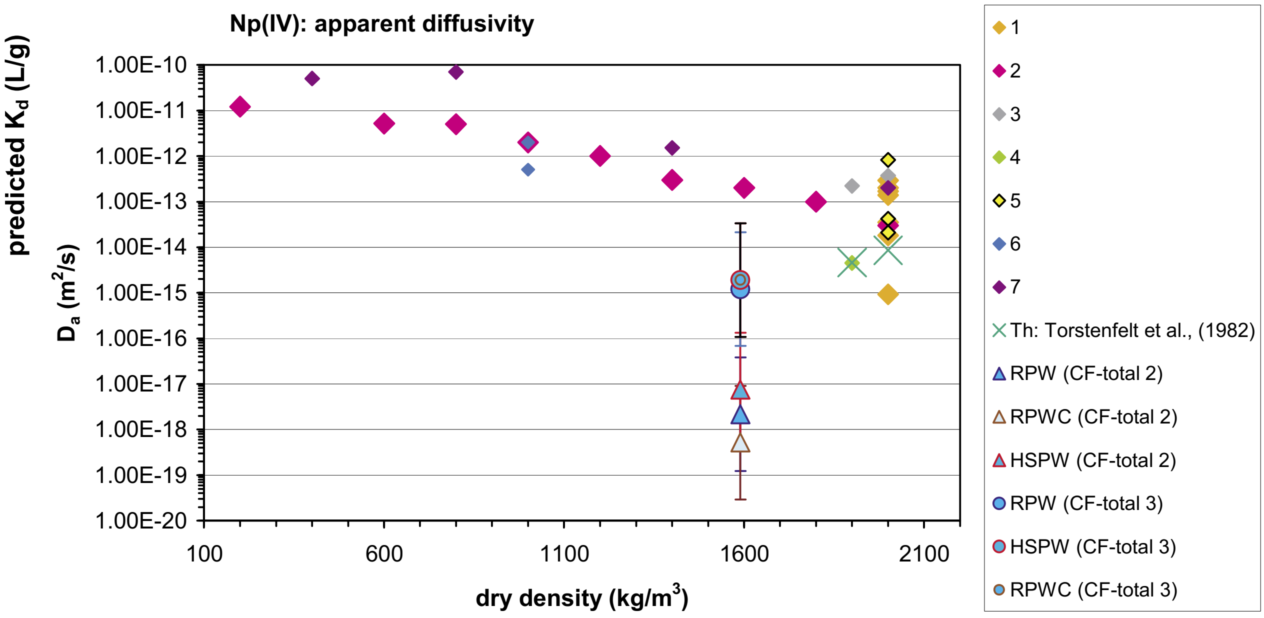


Figure 5-15. *K_d values for Np(IV) derived as a function of conditions based on the experimental data for Th by /Bradbury and Baeyens, 2003a/. The selected values were derived based on CF-total 3; error bars are given for these values and for the values based on CF-total 2. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1	Na-montmorillonite (impurities) Albinsons et al., (1990b)	Albinsons et al., (1990b)
2	Na-bentonite DW Sato et al., 1992	Sato et al., 1992
3	MX-80 Na-montomorillonite	Torstenfelt et al., 1982
4	MX-80 Na-montomorillonite (impurities)	Torstenfelt et al., 1983
5	MX-80 Na-bentonite	Torstenfelt & Allard, 1986
6	Kunigel V1 Na-bentonite	Tsukamoto et al., 1994
7	Kunigel V1 Na-bentonite	Sato et al., 1993

Figure 5-16. *Calculated D_a values for Np(IV) based on D_e for HTO and K_d values from Figure 5-15 in comparison to experimental data (experiments where a reducing agent had been used are depicted by open symbols). For comparison, experimental D_a values for Th are also shown.*

The most systematic and complete data set for the sorption of Np(V) on smectite available in the open literature has been published by /Turner et al, 1998; Bertetti et al, 1998/. They determined Np(V) sorption on SAz-1 Na-montmorillonite as a function of pH and pCO_2 in 0.1 M $NaNO_3$, using both adsorption and desorption experiments. These data are also consistent with the work of /Gorgeon, 1994/, who determined two adsorption edges from pH 3-11 in 0.1 and 1 M $NaClO_4$ solutions on smectite extracted from Wyoming bentonite. These datasets had also been chosen for the recent NEA Sorption Project modelling exercise /NEA, 2004/, but no reliable and well-tested sorption models are available as yet. However, this exercise showed that the inclusion of ternary Np-carbonato surface complexes improves a model's ability to describe the experimental data at elevated pH and in the presence of carbonate. This supports the choice of CF-total 3 (which does not treat dissolved carbonate complexes as competitive with respect to surface complexation) as conversion procedure.

The K_d values derived based on the data by /Turner et al, 1998; Bertetti et al, 1998/ using the CF-approach are shown in Figure 5-17. Because of the similarity of conditions, the speciation-conversion factor has only little influence; i.e. CF-total 1–3 give nearly identical results. The comparison with independent D_a values is given in Figure 5-18. The calculated data using CF-total 3 are not inconsistent with the experimental diffusion data, and it is considered to be very likely that any K_d for Np(V) under the specified conditions would be within the indicated ranges.

The data by /Turner et al, 1998/ indicate that the sorption of Np(V) on montmorillonite increases up to pH ≈ 10.5 in the absence of significant amounts of dissolved carbonate. At atmospheric pCO_2, sorption starts to decrease at pH ≈ 8.5.

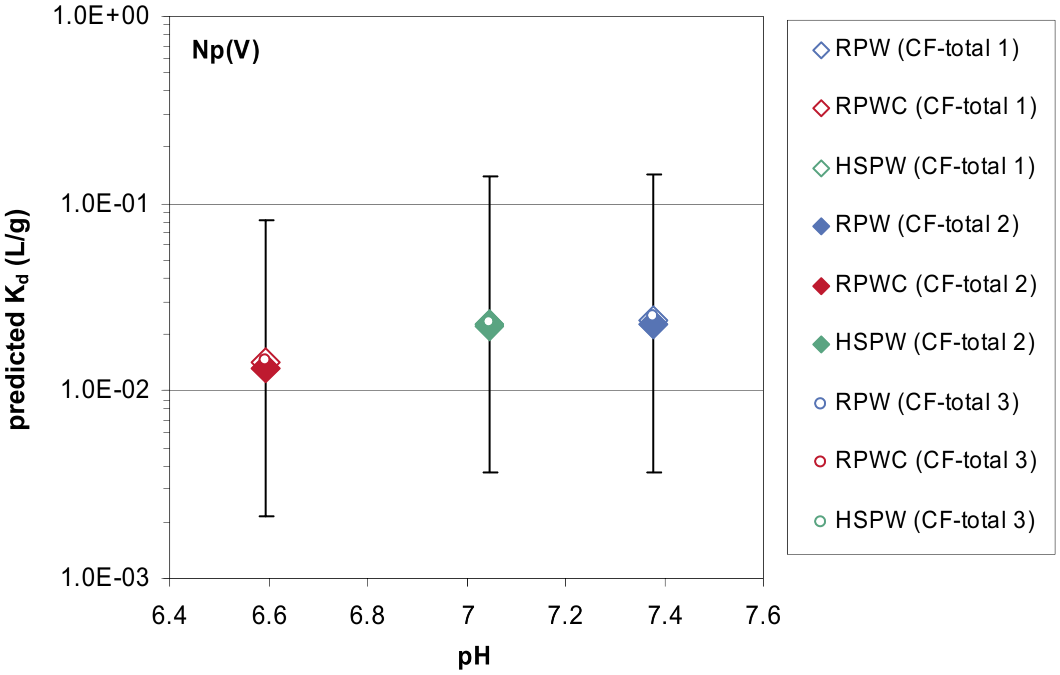
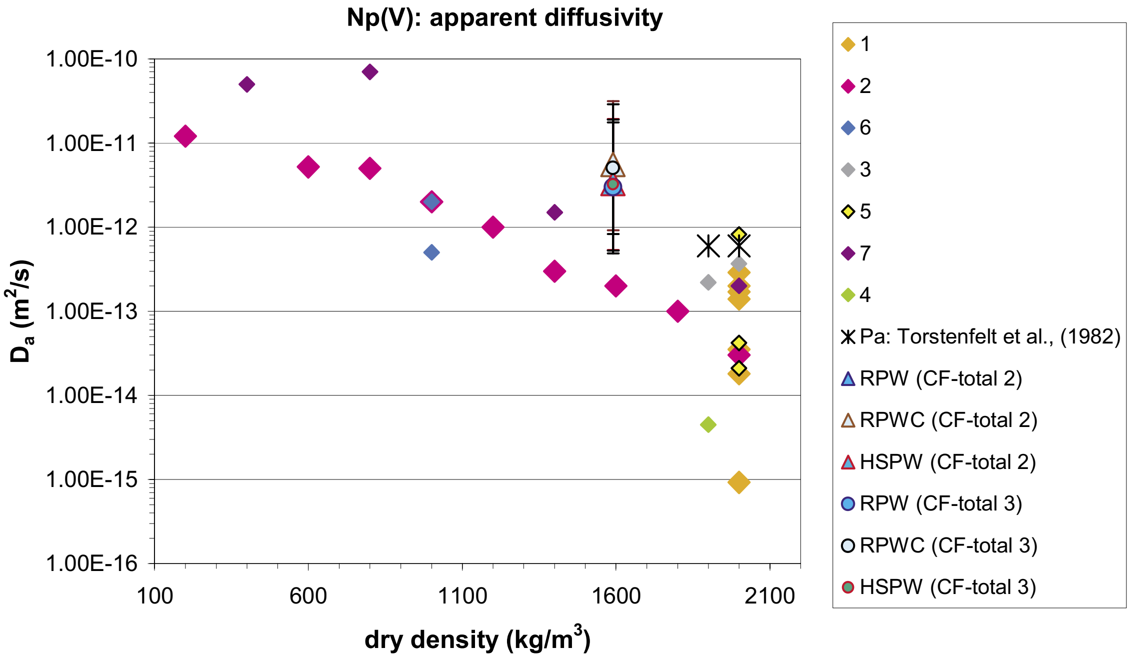


Figure 5-17. *K_d values for Np(V) derived as a function of conditions based on the experimental data by /Turner et al, 1998/. The selected values are based on CF-total 3; error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1	Na-montmorillonite (impurities)	Albinsons et al., (1990b)
2	Na-bentonite DW	Sato et al., 1992
3	MX-80 Na-montomorillonite	Torstenfelt et al., 1982
4	MX-80 Na-montomorillonite (impurities)	Torstenfelt et al., 1983
5	MX-80 Na-bentonite	Torstenfelt & Allard, 1986
6	Kunigel V1 Na-bentonite	Tsukamoto et al., 1994
7	Kunigel V1 Na-bentonite	Sato et al., 1993

Figure 5-18. *Calculated D_a values for Np(V) based on D_e for HTO and K_d values from Figure 5-17 in comparison to experimental data (experiments where a reducing agent had been used are depicted by open symbols).*

Nickel

The most extensive and systematic sorption data set available for Ni is given by /Baeyens and Bradbury, 1997/, who determined Ni sorption on Na-montmorillonite (SWy-1) in $NaClO_4$ solutions as a function of pH, ionic strength and Ni concentration. /Bradbury and Baeyens, 1997/ modelled these data using a surface complexation/ion exchange model In a follow-up study /Bradbury and Baeyens, 1999/, the sorption of Ni on Ca-montmorillonite (SWy-1) was also investigated and modelled. It was concluded that the model parameters for the Na- and Ca-form are identical within uncertainties. In addition, /Bradbury and Baeyens, 2003a/ determined a sorption isotherm for Ni on MX-80 in artificial bentonite porewater at pH 7.6.

For the present purpose, K_d values were calculated using the thermodynamic sorption model by /Bradbury and Baeyens, 1997/. The results were compared with values derived with the CF-approach using the sorption data on Na-SWy-1 and MX-80. The resulting K_d values are summarised in Figure 5-19. It can be seen that the choice of data source appears to be important. Both the model application and the CF-approach using the SWy-1 source data result in higher predictions of K_d in comparison to the CF-approach using the MX-80 source data. The exact reason is not clear at the moment, but the results shown in Figure 5-19 suggest very strongly that the observed discrepancy is indeed related to the data source used for upscaling to application conditions rather than the actual method employed (sorption model or CF-approach). The sorption model had been calibrated based on the SWy-1 data, and application of this model vs application of the CF-approach to the SWy-1 data

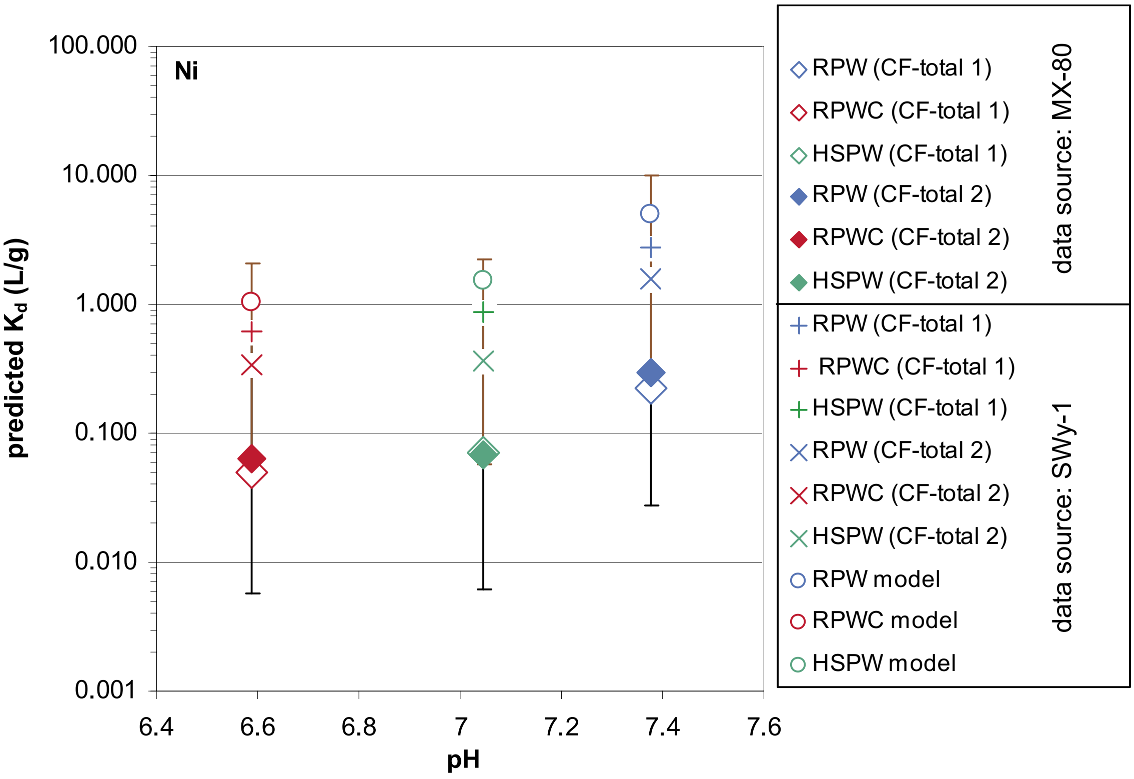


Figure 5-19. *K_d values for Ni derived as a function of conditions based on the experimental data for SWy-1 montmorillonite and MX-80 bentonite by /Bradbury and Baeyens, 1997, 2003a/ and calculated using the Ni sorption model of /Bradbury and Baeyens, 1997/. The selected values are indicated by solid symbols. Error bars are given for the values derived from data on SWy-1(brown) and MX-80 (black) using CF-total 2. For an explanation of CF-total 1/2/3, see section 5.1.4.*

give nearly identical results. In comparison, upscaling based on MX-80 source data gives K_d values that are about an order of magnitude lower. It should be further noted that the speciation-conversion has very little influence on upscaling from any given data source (CF-total 2 and CF-total 3 give practically identical results, because under the specified conditions Ni-carbonato complexes are not important in comparison to complexation of Ni with sulphate and chloride according to the thermodynamic data given in /Hummel et al, 2002/).

Based on this evidence, the K_d values derived from the MX-80 source data using the CF-approach are preferred over values derived from SWy-1 source data either directly (CF-approach) or implicitly (sorption model). The main reason behind this decision is the closer proximity of the present application conditions and the chemical conditions corresponding to the MX-80 source data. This means that upscaling from the MX-80 source conditions to the application conditions requires a smaller degree of extrapolation than upscaling from the SWy-1 source data.

A comparison with the few available D_a measurements (Figure 5-20) is not conclusive due to the lack of more systematic diffusion data. However, if it is assumed that D_a of Ni shows the same trend vs dry density as D_a of Co, Cs and Am, the derived K_d values based on MX-80 source data are more consistent with apparent diffusivities than values based on SWy-1 source data. However, all calculated D_a values fall within the range given by experimental data for Ni and Co.

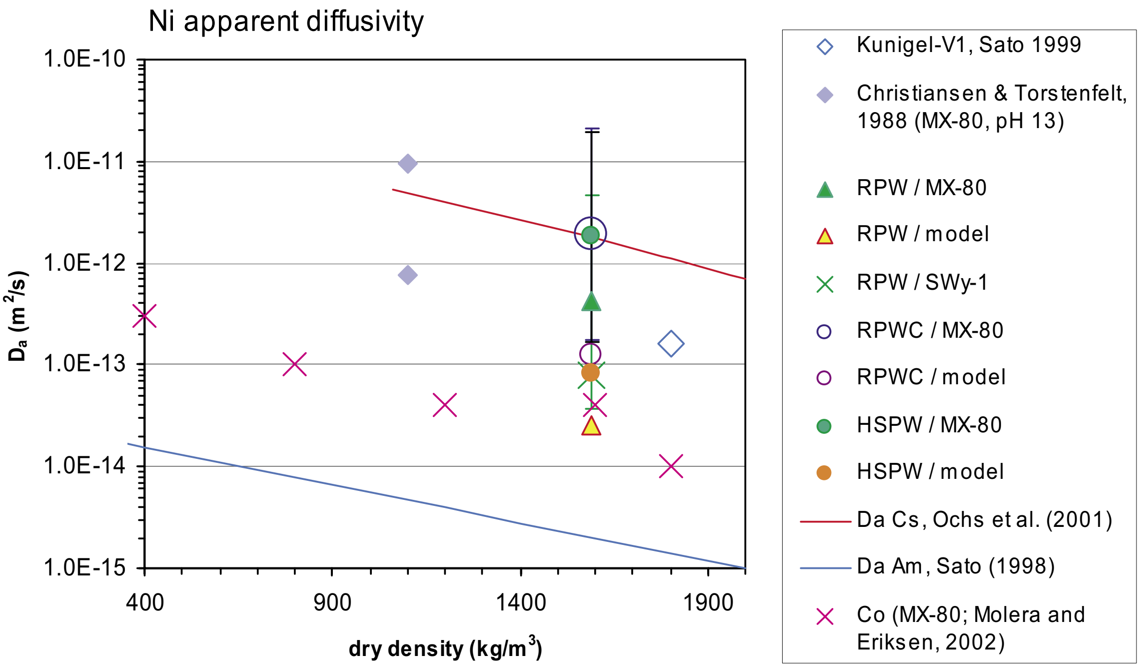


Figure 5-20. *Calculated D_a values for Ni based on D_e for HTO and selected K_d values derived as a function of conditions using the CF-approach or calculated using the model of /Bradbury and Baeyens, 1997/. Experimental data obtained on Kunigel-V1 and MX-80 are given for comparison. The high pH indicated by /Christiansen and Torstenfelt, 1988/ may hold only for the input solution, but probably not for the actual porewater. To put the D_a values for Ni into perspective, experimental data for the similar element cobalt are also shown, and trends of D_a vs density are indicated for Cs (model calculation for MX-80 by /Ochs et al, 2001/; from Figure 5-11) and for Am (regression line for Kunigel-V1 by /Sato, 1998a/; from Figure 5-8).*

In summary, it is recommended to use the values derived from the MX-80 source data as best estimate and the respective lower limit, but to base the upper limit of the recommended data on the uncertainties for the SWy-1 source data. Thus, the upper limit coincides approximately with the thermodynamic model calculations. These limits are very likely to encompass any K_d for Ni under the specified scenarios.

The data by /Bradbury and Baeyens, 1997/ indicate that K_d for Ni is likely to decrease above pH 10.

Niobium

Only few sorption data for bentonite were found, they are reproduced in Figure 5-21. It is likely that the data by /Erdal et al, 1977; Taki and Hata, 1991/ have been obtained in oversatured systems, reflecting solubility limits rather than sorption. Based on the poor database, a K_d value of 3 m^3/kg is proposed together with an UF-overall of 15. As Nb is expected to exist nearly exclusively as uncharged penta-hydroxo complex in the pH range considered, this value is proposed for all conditions. No assessments for higher pH can be made.

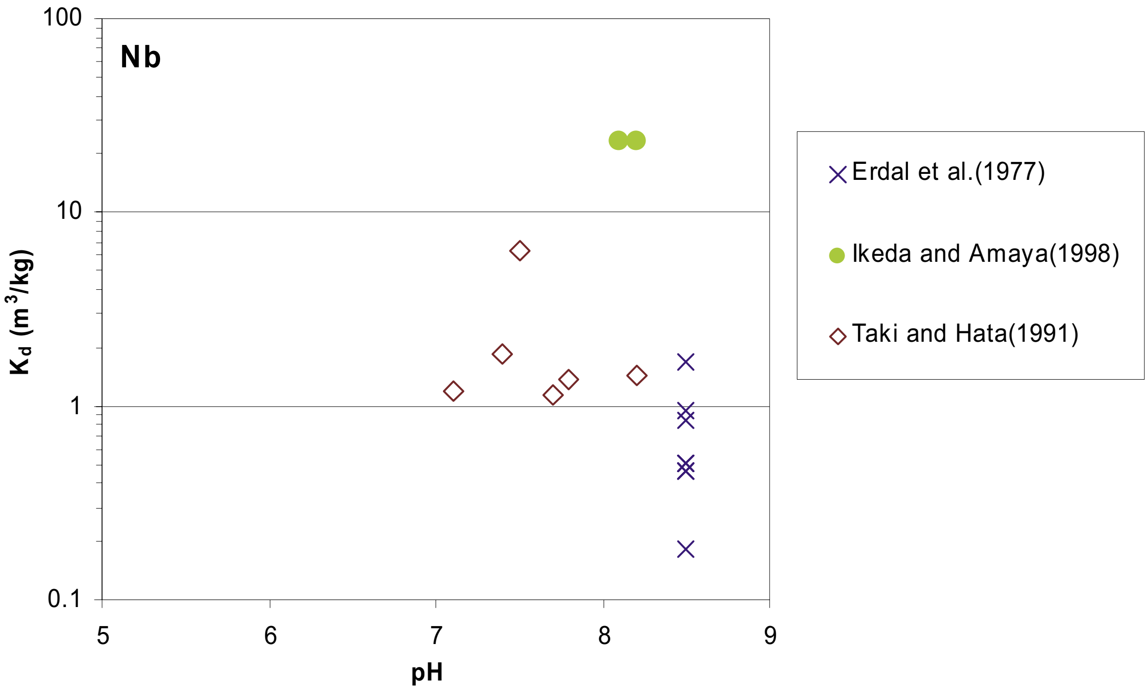


Figure 5-21. *Sorption data for Nb on different bentonites.*

Palladium

Under reducing conditions, Pd is virtually insoluble /Hummel et al, 2002/, and for the present purpose only Pd(II) is considered as potentially relevant. No relevant and reliable sorption data, and no diffusion data for Pd(II) were found. /Tachi et al, 1999/ studied Pd sorption on Kunigel-V1 bentonite as a function of pH and ionic strength, but it cannot be excluded that their data reflect solubility limitation rather than sorption. Assuming sorption to be the relevant process would lead to a mean K_d of ca 8 m^3/kg at pH 8 and I=0.1 M. This is relatively close to the value of 5 m^3/kg deduced by /Bradbury and Baeyens, 2003a/ on the basis of analogies with Ni and Pb. For the present purpose, their estimate is accepted, including the UF-overall of 15. It is considered probable that any K_d for Pd(II) under the specified scenarios would be within the indicated ranges.

Plutonium

Depending on redox conditions, Pu can take on the oxidation states III-VI. Because of the uncertainty regarding redox conditions, all oxidation states are treated separately below. If variable redox conditions need to be taken into account, the overall uncertainty for the K_d of Pu will encompass the entire data range for all oxidation states that will be present.

For Pu(III)), no relevant sorption data were found, and K_d was derived based on analogy considerations and the source data set used for Am. The results are shown in Figure 5-22, the comparison with D_a values is shown in Figure 5-23. Inclusion of carbonate species in the speciation-conversion leads to results that are inconsistent with the trend of K_d vs pH observed for Am. Therefore, the K_d values based on CF-total 3 are recommended. It can be seen from Figure 5-23 that the selected sorption data are consistent with available D_a values for III-valent elements and Pu. Therefore, it is considered to be very likely that any K_d for Pu(III) under the specified scenarios would be within the indicated ranges.

Based on Figure 5-22, a decrease of K_d for Pu(III) at pH > 10 cannot be excluded.

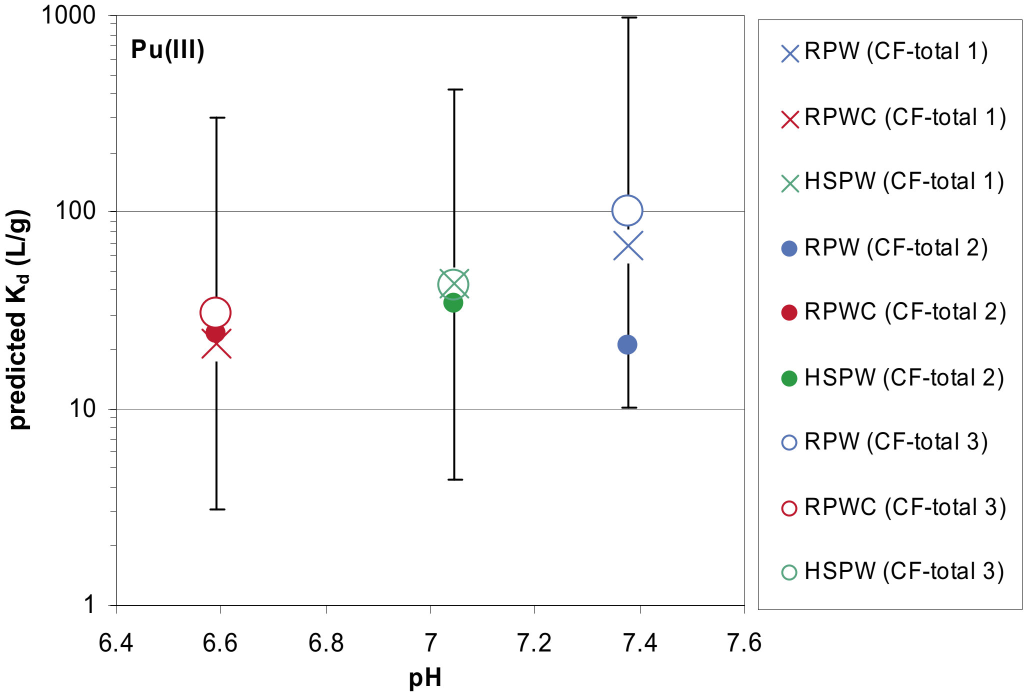
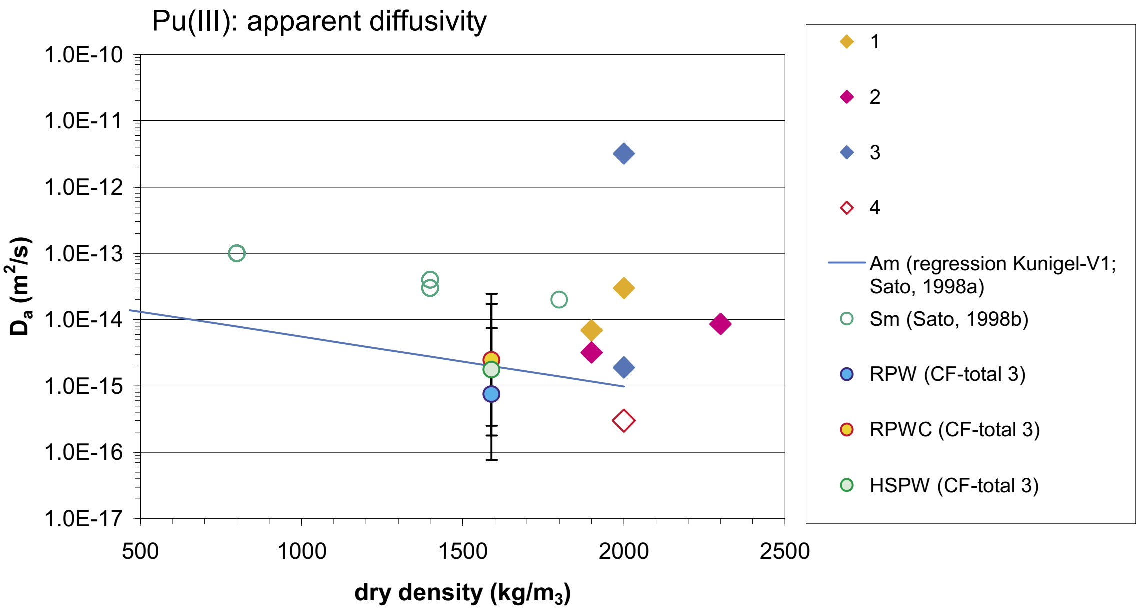


Figure 5-22. *K_d values for Pu(III) derived as a function of conditions based on the experimental data for Am by /Gorgeon, 1994/. The selected values are indicated by open circles (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1	MX-80 Na-bentonite	Torstenfelt et al. (1982)
2	MX-80 Na-bentonite	Torstenfelt et al. (1983)
3	MX-80 Na-bentonite	Torstenfelt and Allard (1986)
4	MX-80 Na-bentonite, 1% FeO	Albinsson et al. (1991)

Figure 5-23. *Calculated D_a values for Pu(III) based on D_e for HTO and K_d values from Figure 5-22 in comparison to experimental data (the value by /Albinsson et al, 1991/, is a maximum value). For comparison, experimental D_a values for Sm and the regression line representing Am (from Figure 5-8) are also shown.*

For Pu(IV), no relevant and reliable sorption data could be found. K_d was derived based on analogy considerations and the source data set used for Th. The results are shown in Figure 5-24, the comparison with D_a values is shown in Figure 5-25. The data show that inclusion of carbonate species in the speciation-conversion leads to results for RPWC that are inconsistent with diffusion data for Th as well as Pu. Therefore, the K_d values based on CF-total 3 are recommended. It can be seen from Figure 5-25 that the selected sorption data are consistent with available D_a values for Th and Pu. Therefore, it is considered to be likely that any K_d for Pu(IV) under the specified scenarios would be within the indicated ranges.

Since the hydrolysis behaviour of Pu(IV) appears to be identical to that of Th at high pH /Lemire et al, 2001; Hummel et al, 2002/, no significant influence of a pH increase is expected.

For Pu(V), no relevant and reliable sorption data could be found. K_d was derived based on analogy considerations and the source data set used for Np(V). The results are shown in Figure 5-26, the comparison with D_a values is shown in Figure 5-25. The data show that the speciation-conversion appears to have little influence in this case. To be consistent with the approach chosen for other actinides, the K_d values based on CF-total 3 are recommended. It can be seen from Figure 5-25 that the selected sorption data are fairly consistent with available D_a values for Np(V). Good agreement can also be observed with the higher diffusivity reported by /Torstenfelt and Allard, 1986/, which reportedly corresponds to a small, mobile fraction of Pu (presumably the oxidised fraction). Therefore, it is considered to be likely that any K_d for Pu(V) under the specified scenarios would be within the indicated ranges.

Based on the analogy with Np(V) it is expected that the sorption of Pu(V) on montmorillonite increases up to pH ≈ 10.5 in the absence of significant amounts of dissolved carbonate. At atmospheric pCO_2, sorption may start to decrease at pH ≈ 8.5.

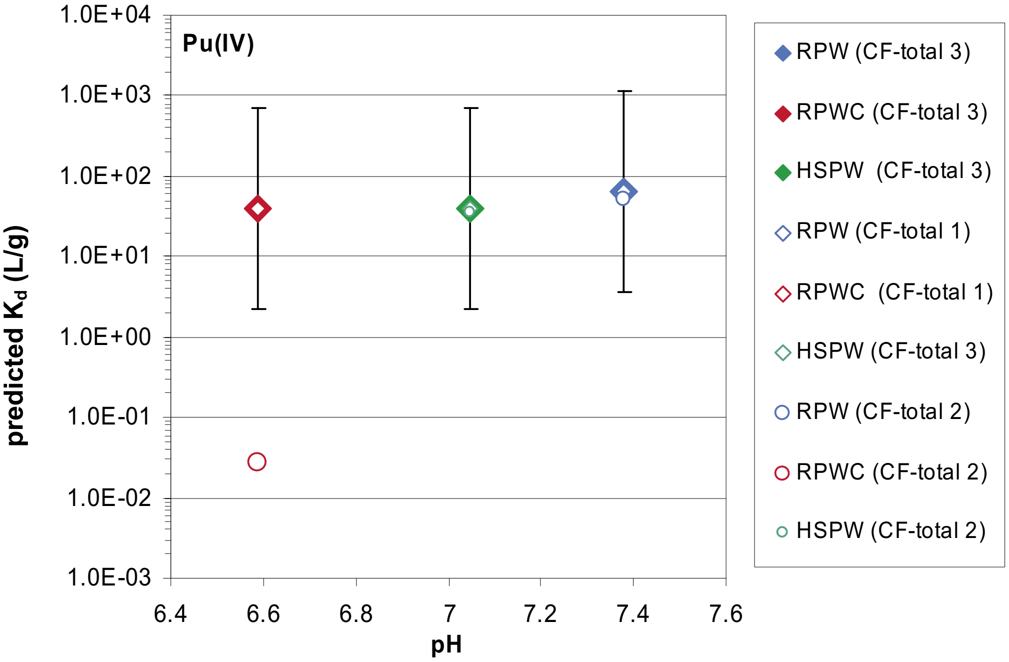


Figure 5-24. *K_d values for Pu(IV) derived as a function of conditions based on the experimental data for Th by /Bradbury and Baeyens, 2003a/. The selected values are indicated by solid symbols (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*

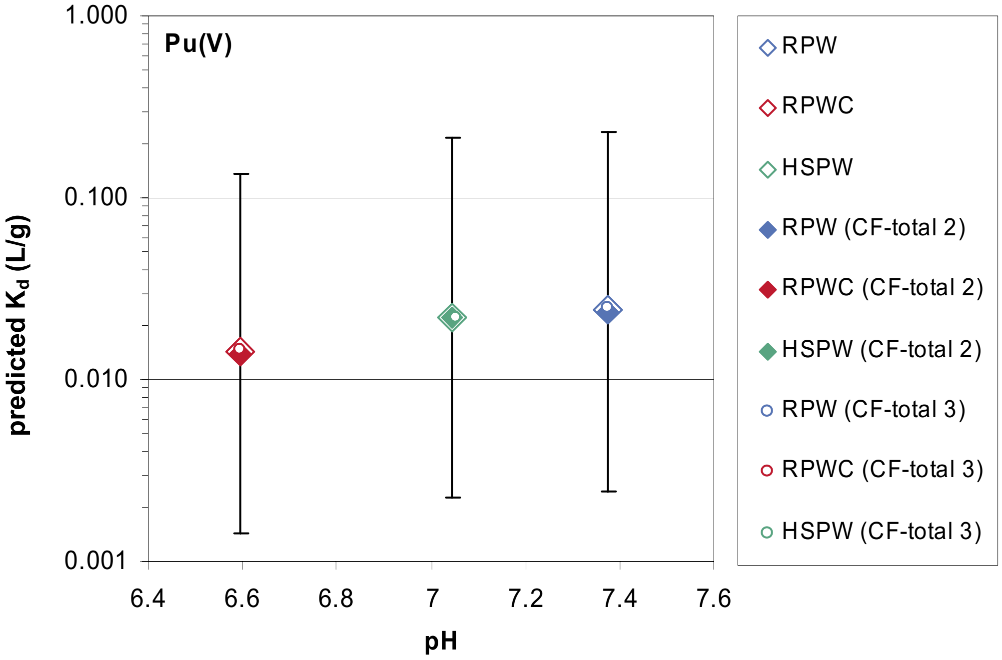


Figure 5-25. *Calculated D_a values for Pu(IV) based on D_e for HTO and K_d values from Figure 5-24 in comparison to experimental data (the datum by /Albinsson et al, 1991/, is a maximum value). For comparison, experimental D_a values for Th are also shown.*

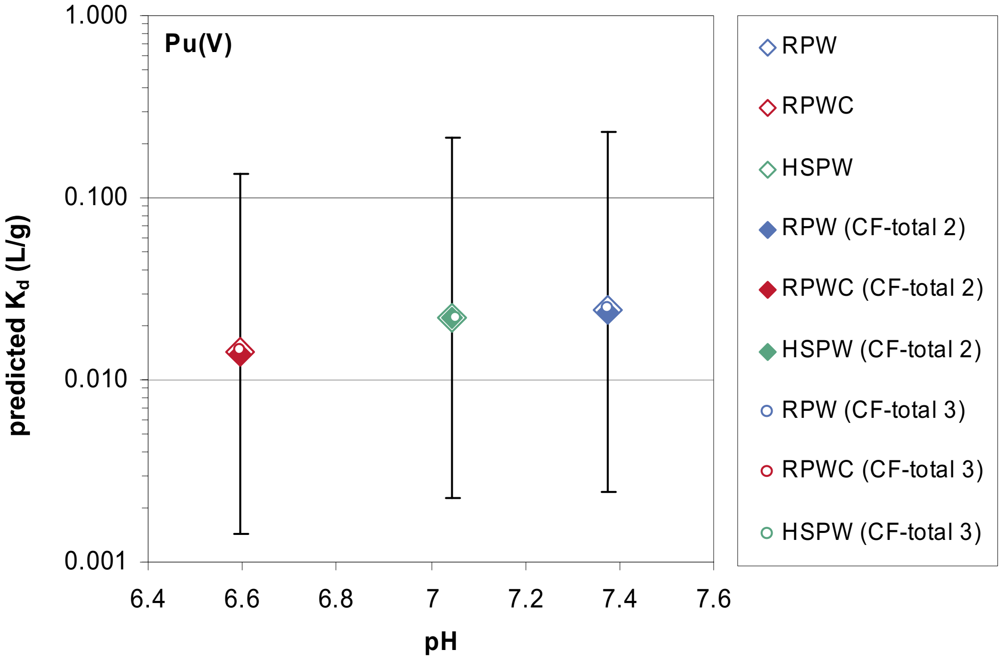
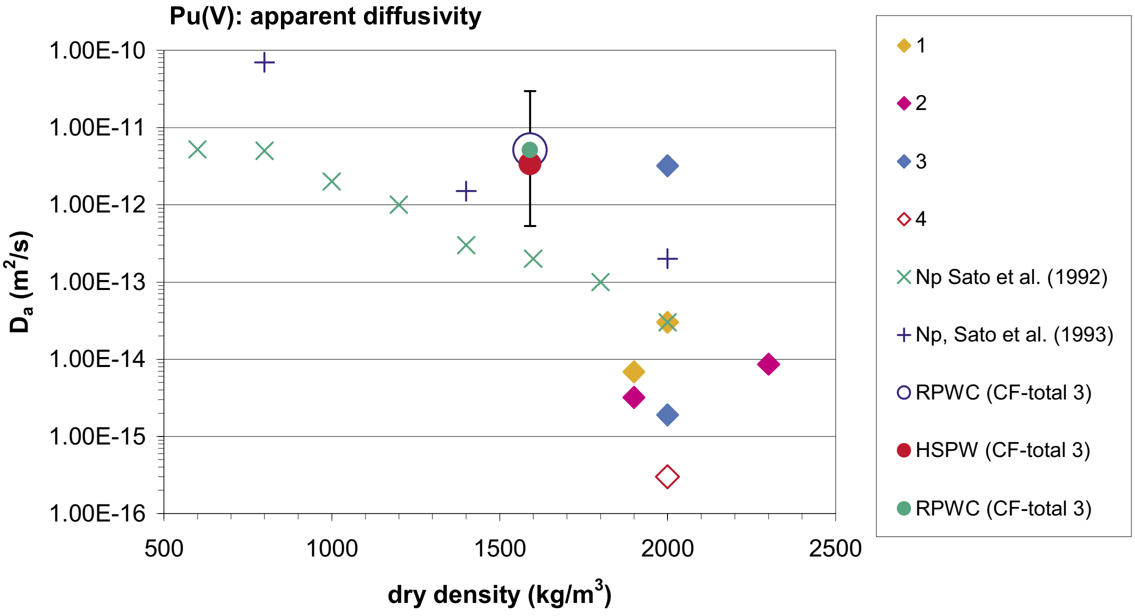


Figure 5-26. *K_d values for Pu(V) derived as a function of conditions based on the experimental data for Np(V) by /Turner et al, 1998; Bertetti et al, 1998/. The selected values are indicated by open circles (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1	MX-80 Na-montorillonite	Torstenfelt et al. (1982)
2	MX-80 Na-montorillonite	Torstenfelt et al. (1983)
3	MX-80 Na-montomorillonite	Torstenfelt et Allard 1986
4	MX-80 Na-bentonite, 1% FeO	Albinsson et al. (1991)

Figure 5-27. Calculated D_a values for Pu(V) based on D_e for HTO and K_d values from Figure 5-26 in comparison to experimental data (the datum by /Albinsson et al, 1991/, is a maximum value). For comparison, some experimental D_a values for Np(V) from Figure 5-18 are also shown.

Also for Pu(VI), no relevant and reliable sorption data could be found. K_d was derived based on analogy considerations and the source data set used for U(VI). The results are shown in Figure 5-28, the comparison with D_a values is shown in Figure 5-29. The data show that inclusion of carbonate species in the speciation-conversion leads to deviating results for RPWC. To be consistent with the approach chosen for other actinides, the K_d values based on CF-total 3 are recommended. It can be seen from Figure 5-25 that the selected sorption data are fairly consistent with available D_a values for U(VI). It is considered to be likely that any K_d for Pu(VI) under the specified scenarios would be within the indicated ranges.

Based on analogy with U(VI), a significant decrease of Pu(VI) is expected for $pH > 8$.

Protactinium

The aqueous chemistry of Pa is not sufficiently known, but it seems to be fairly accepted that it is different enough from that of other actinides to make the use of analogue data highly questionable /Hummel et al, 2002; Baes and Mesmer, 1976/. To our knowledge, no significant new information has become available since /Yu and Neretnieks, 1997/. The K_d values selected by these authors are fairly consistent with the two D_a values given in their report. For the present purpose, a K_d value of 3 m^3/kg is selected for all conditions, together with a UF-overall of 15. This gives a range that is also approximately compatible with data for IV- and V-valent actinides. It is considered probable that any K_d for Pa under the specified scenarios would be within this range. No assessment for elevated pH values is made.

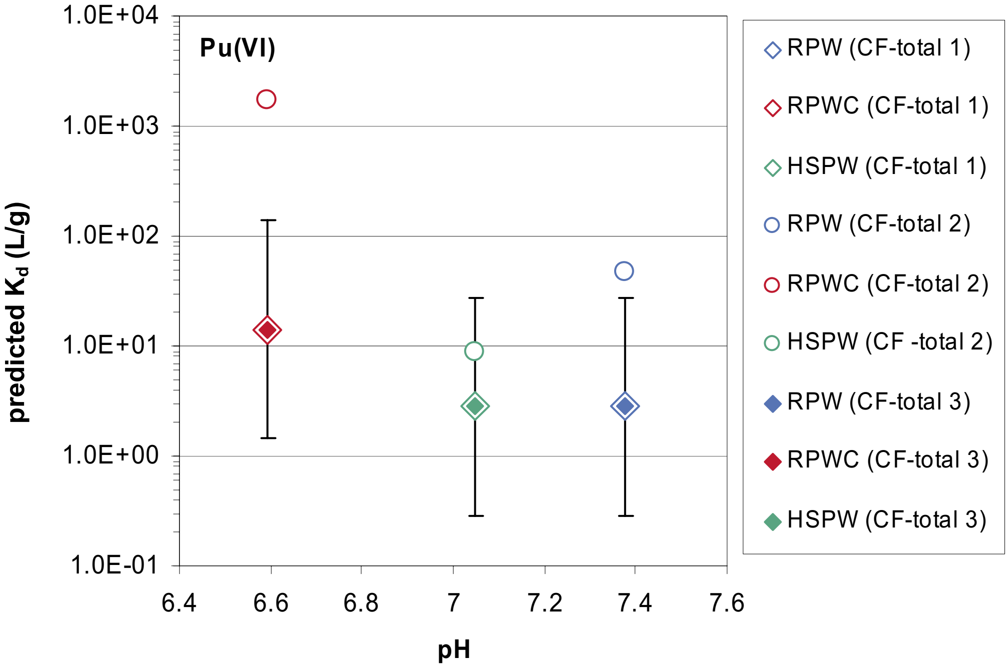
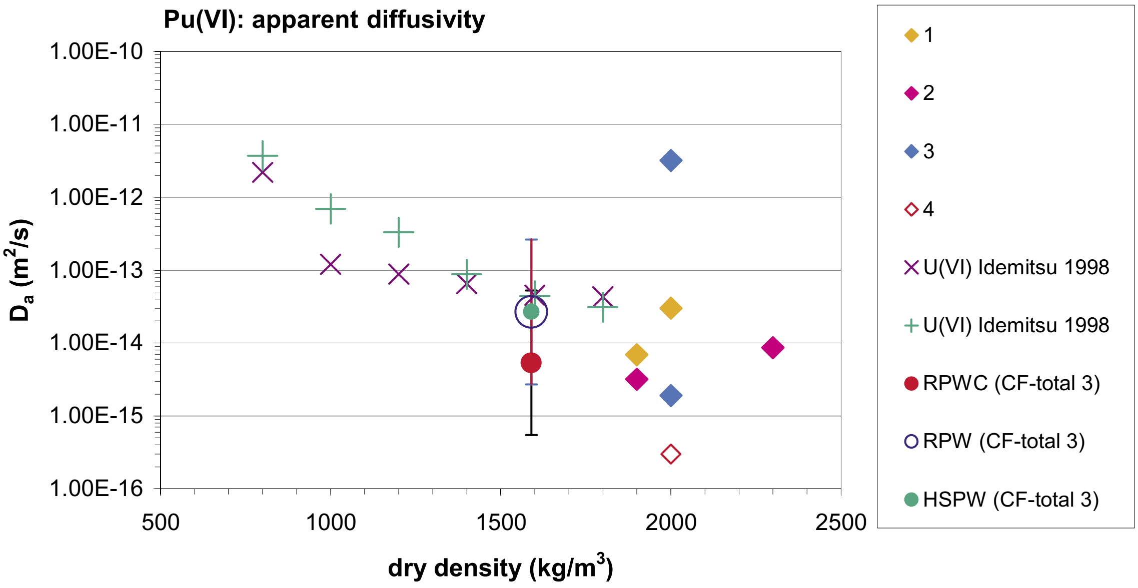


Figure 5-28. *K_d values for Pu(VI) derived as a function of conditions based on the experimental data for U(VI) by /Pabalan and Turner, 1997/. The selected values are indicated by closed symbols (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1	MX-80 Na-montorillonite	Torstenfelt et al. (1982)
2	MX-80 Na-montorillonite	Torstenfelt et al. (1983)
3	MX-80 Na-montomorillonite	Torstenfelt et Allard (1986)
4	MX-80 Na-bentonite, 1% FeO	Albinsson et al. (1991)

Figure 5-29. *Calculated D_a values for Pu(VI) based on D_e for HTO and K_d values from Figure 5-28 in comparison to experimental data (the datum by /Albinsson et al, 1991/, is a maximum value). For comparison, some experimental D_a values for U(VI) from Figure 5-41 are also shown.*

Radium and strontium

These two elements were treated identically, based on their chemical similarity. No systematic and reliable sorption data for these elements were found in the literature. Therefore, a thermodynamic sorption model was used to calculate K_d, where for Sr and Ra the same selectivity coefficient as for Ca is used /see Fletcher and Sposito, 1989/. This approach had already been used by /Ochs et al, 1998/ to re-calculate K_d values for Sr and Ra for a variety of bentonite-water systems. /Ochs et al, 2001, 2003/ also successfully used this approach to model K_d and D_a values for compacted Kunigel-V1 bentonite. The results are shown in Figure 5-30, the comparison with D_a values is given in Figure 5-31. The uncertainty ranges of the calculated D_a values based on the selected data shown in Figure 5-30 accommodate the scatter of the experimental data, with very few exceptions. Therefore, it is considered to be likely that any K_d for Sr and Ra under the specified scenarios would be within the indicated ranges.

Based on the corresponding calculated porewater compositions (Appendix C), the influence of (highly) alkaline groundwater on K_d for Sr/Ra is expected to be within the limits given by the three reference porewaters.

Radon

Radon is a noble gas. In analogy to methane, a K_d of zero, together with the diffusion parameters for HTO are proposed.

Samarium

See section on cerium, holmium and samarium.

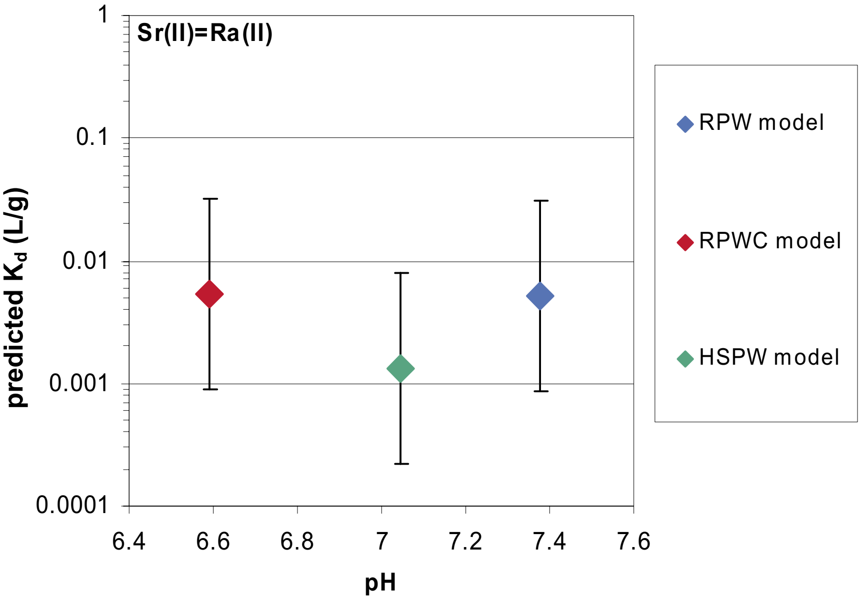
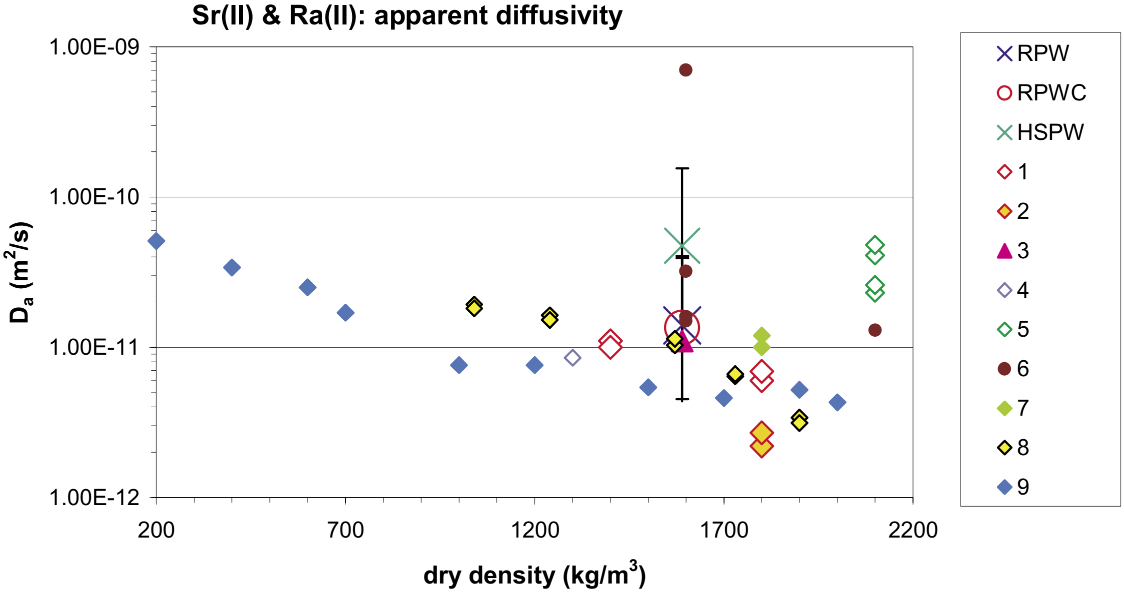


Figure 5-30. *K_d values for Sr and Ra calculated with the thermodynamic sorption model used by /Ochs et al, 1998/.*



1	Ra: Kunigel-V1	Tachi et al., 2001
2	Ra: Kunigel-V1 (3% NaCl)	Tachi et al., 2001
3	Sr: Ca bentonite (Avonlea)	Choi etal., 1992
4	Sr: Na bentonite (Avonlea)	Choi & Oscarson, 1996
5	Sr: Na/Ca MX-80, 25°C / 70°C	Eriksen et al., 1981
6	Sr: Na/Ca MX-80	Eriksen and Jacobsson 1981
7	Sr: Na MX-80	Eriksen and Jansson 1996
8	Sr: Na MX-80	Kim et al., 1993
9	Sr: Kunigel-V1	Sato et al., 1992

Figure 5-31. *Calculated D_a values for Sr/Ra based on D_e for HTO and K_d calculated with the model used by /Ochs et al, 1998/.*

Selenium

Relevant oxidation states in aqueous solutions include –II, IV and VI, with HSe^-, SeO_3^{2-} and SeO_4^{2-} as the most important species in typical waters. As in the case of other redox-sensitive elements, if variable redox conditions need to be taken into account the overall uncertainty for the K_d of Se would encompass the combined data range for all oxidation states predicted to be present.

Sorption of selenate and selenite on metal oxides has been studied, confirming inner-sphere surface complexation/ligand exchange as predominant sorption mechanism for selenite /Hayes, 1987; Davis and Kent, 1990; Séby et al, 1998/. However, only two reliable studies have been found for the sorption of selenite on bentonite or smectite under relevant conditions /Bar-Yosef and Meek, 1987; Bradbury and Baeyens, 2003a/. /Bar-Yosef and Meek, 1987/ determined isotherm as well as pH-edge sorption data for selenite on Ca-Wyoming montmorillonite in 5 mM $CaCl_2$ electrolyte. /Bradbury and Baeyens, 2003a/ report a sorption isotherm on MX-80 bentonite in a porewater solution at pH 7.8 and a sorption edge on Na-SWy-1 at trace concentrations of selenite. At approximately comparable Se concentrations and pH, these two studies give nearly identical results (the data by /Bar-Yosef and Meek, 1987/, fall within the uncertainty limits indicated by /Bradbury and Baeyens, 2003a/). /Saha et al, 2004/ very recently also investigated selenite adsorption on montmorillonite, but unfortunately limited their experiments to pH 4.5. /Boult et al, 1998/ also investigated Se(IV) sorption on bentonite, but used only high intial Se concentrations. As they do not report details of the solution composition, oversaturation with respect to $CaSeO_3$(s) cannot be excluded with certainty.

Following the above discussion, the data given for MX-80 in /Bradbury and Baeyens, 2003a/ were selected as the most reliable and directly applicable sorption data. The resulting derived K_d values as a function of conditions are shown in Figure 5-32. K_d values were additionally derived from SWy-1, they are largely contained in the range of uncertainty given for the data derived based on MX-80, and use of the latter is recommended. Note that these values are valid for Se concentrations < 1e–6 M only.

The comparison with D_a measurements is given in Figure 5-33. Because it is not clear which Se concentration was used in the diffusion experiment, it must be assumed that the concentrations were high enough to lower the K_d of Se(IV) to near zero (i.e. around 0.001 M, according to the isotherm data of /Bradbury and Baeyens, 2003a/). The experiments by /Sato et al, 1995/ were conducted under absence of oxygen, and

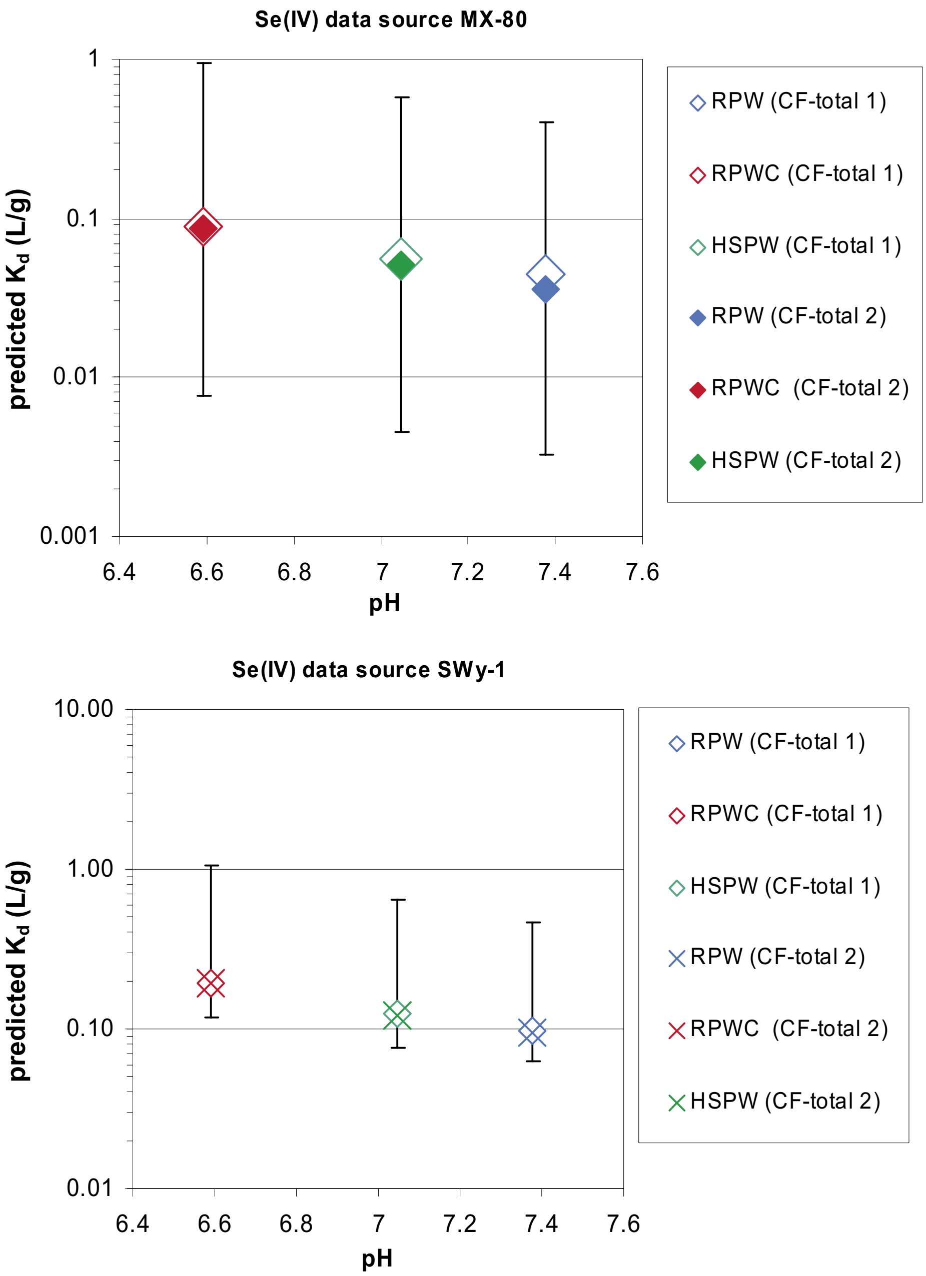


Figure 5-32. *K_d values for Se(IV) derived as a function of conditions based on the experimental data by /Bradbury and Baeyens, 2003a/. The selected values (solid symbols) are based on CF-total 2); error bars refer to these values. For an explanation of CF-total 1/2, see section 5.1.4.*

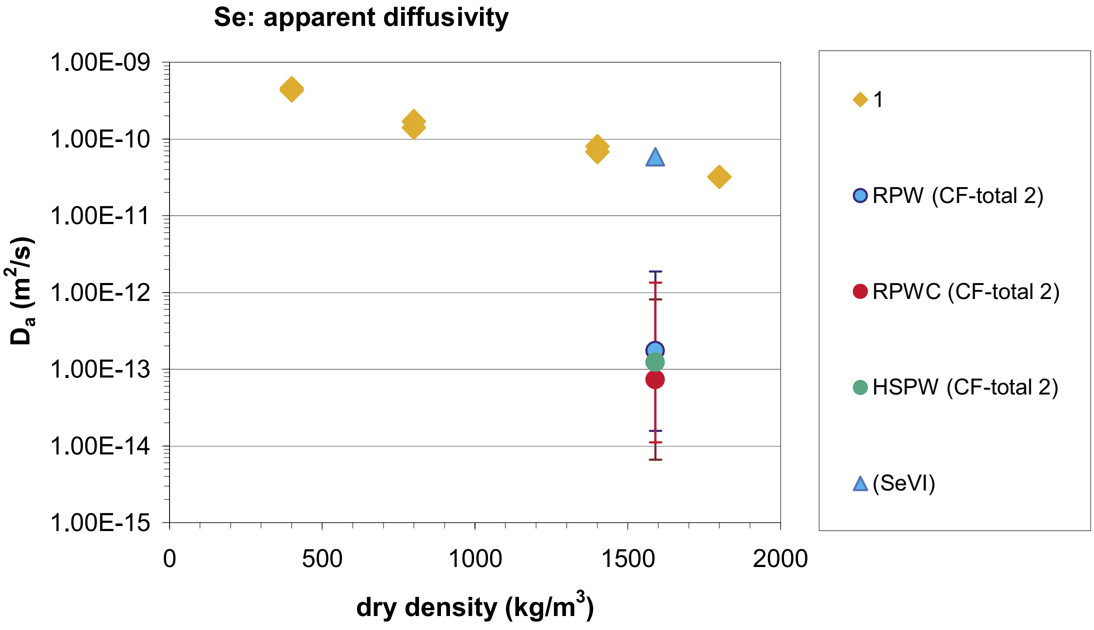
oxidation of Se(IV) to Se(VI) can probably be excluded. On the other hand, Figure 5-33 corroborates the choice of diffusion parameters for non-sorbing anions.

Based on the batch sorption data, it is considered to be likely that any K_d for Se(IV) under the specified scenarios would be within the indicated ranges.

The data by /Bradbury and Baeyens, 2003a/ and by /Bar-Yosef and Meek, 1987/ suggest that sorption of Se(IV) decreases sharply above pH 8–9, which would be consistent with a ligand exchange mechanism.

No reliable and relevant sorption data have been found in case of selenate and selenide. Therefore, a K_d of zero is assigned to HSe^- and SeO_4^{2-}, together with the diffusion parameters selected for anions (section 5.3.4). No different diffusion parameters are proposed for SeO_4^{2-}, even though anion exclusion effects could be more prominent due to its double negative charge.

Note that assuming zero sorption is probably conservative in the case of selenate. /Bar-Yosef and Meek, 1987/ determined isotherm as well as pH-edge sorption data for selenate on Ca-kaolinite in 5 mM $CaCl_2$ electrolyte. At pH 6.7, a K_d of ca 0.02 L/g can be deduced from their data. However, in their experiments the dissolved selenate concentration is close to the initial concentration at this pH, and indistinguishable from it at pH 8, which makes reliable measurements difficult. Further, /Bar-Yosef and Meek, 1987/ used a very dilute background electrolyte, and the data by /Hayes, 1987/ show that selenate sorption on goethite is highly dependent on the concentration of the background electrolyte ($NaNO_3$ in their case) and suggest that dissolved anions, in particular sulphate, may strongly compete with selenate sorption on bentonite. This is in line with spectroscopic data that show that selenate sorbs via inner- and outer-sphere complexation /Peak and Sparks, 2002/ and modelling work by /Hiemstra and van Riemsdijk, 2004/, which indicates that the relative importance of inner-sphere binding decreases with increasing pH.



1 Kunigel-V1 Sato et al. 1995

Figure 5-33. *Calculated D_a values for Se(IV) and Se(VI) based on diffusion parameters for anions and K_d values from Figure 5-32 for Se(IV) in comparison to experimental data reported for Se(IV). D_a for Se(VI) was calculated with K_d zero.*

Silver

No reliable sorption data and no diffusion data were found. /Legoux et al, 1992/ determined four K_d values for Ag on four sediment samples containing ca 10% illite and smectite. These values range from 1.2–17 m^3/kg. On the other hand, /Bradbury and Baeyens, 2003a/ carried out calculations with a thermodynamic sorption model, considering only ion exchange (based on a selectivity coefficient taken from /Pleysier and Cremers, 1975/). These calculations gave K_d values < 1E–7 m^3/kg. This low value may possibly be attributable to the neglect of surface complexation in their model.

Based on the above, an overall K_d range of 0–15 m^3/kg is proposed for Ag, with no mean or median value, for all conditions considered. It is considered probable that any K_d for Ag under the specified scenarios would fall in this range. No assessment for the effects of elevated pH is made.

Technetium

Relevant oxidation states of Tc in aqueous solutions are VII and IV. If variable redox conditions need to be taken into account the overall uncertainty for the K_d of Tc would encompass the combined data range for all oxidation states predicted to be present.

Tc(VII) exist as the pertechnetate anion, TcO_4^-. For this oxidation state, a K_d of zero is proposed together with the diffusion parameters for anions.

For Tc(IV), no relevant sorption data were found. Because Tc(IV) and Th are both tetravalent and exists at circumneutral pH primarily as the uncharged species ($TcO(OH)_2^0$, $Th(OH_4^0)$) K_d values for Tc(IV) were derived based on analogy considerations and the source data set used for Th. However, Th and Tc(IV) do not form identical species in solution and may, therefore, also show different sorption behaviour. To account for this additional uncertainty, UF-starting K_d was increased to 4.0 (see section 5.1.4).

The results are shown in Figure 5-34, and the corresponding calculated D_a values are compared in Figure 5-35 with experimental data for Th. Diffusivities of Th were used for comparison because no diffusion data were found for Tc where it was clearly demonstrated that no oxidation to Tc(VII) took place. The data show that inclusion of carbonate species in the speciation-conversion leads to very high K_d values that are inconsistent with sorption data for Th; and would further lead to equally unrealistic D_a values of ca 10^{-18} m^2/s. Therefore, the K_d values based on CF-total 3 are recommended. It can be seen from Figure 5-39 that the sorption data selected on this basis are not inconsistent with available D_a values for Th. It is considered to be likely that any K_d for Tc(IV) under the specified scenarios would be within the indicated ranges.

Based on the solubility/hydrolysis behaviour of Tc(IV) /Hummel et al, 2002/, it is expected that pH has no significant influence on sorption up to pH $\approx$ 10.

Thorium

The data obtained by /Bradbury and Baeyens, 2003a/, a sorption isotherm on MX-80 in synthetic porewater as well as a sorption edge on SWy-1 montmorillonite in 0.1 M $NaClO_4$, were considered to be the most reliable and directly applicable data source available to date. Because of the significant uncertainty in evaluating i) the formation of mixed hydroxo-carbonato complexes and ii) the formation of ternary surface carbonato complexes, the MX-80 source data are preferable because of the relative similarity of this system to the application conditions (see appendices C and F). The derived K_d values are shown in Figure 5-36, a comparison with the few available D_a values is given in Figure 5-37.

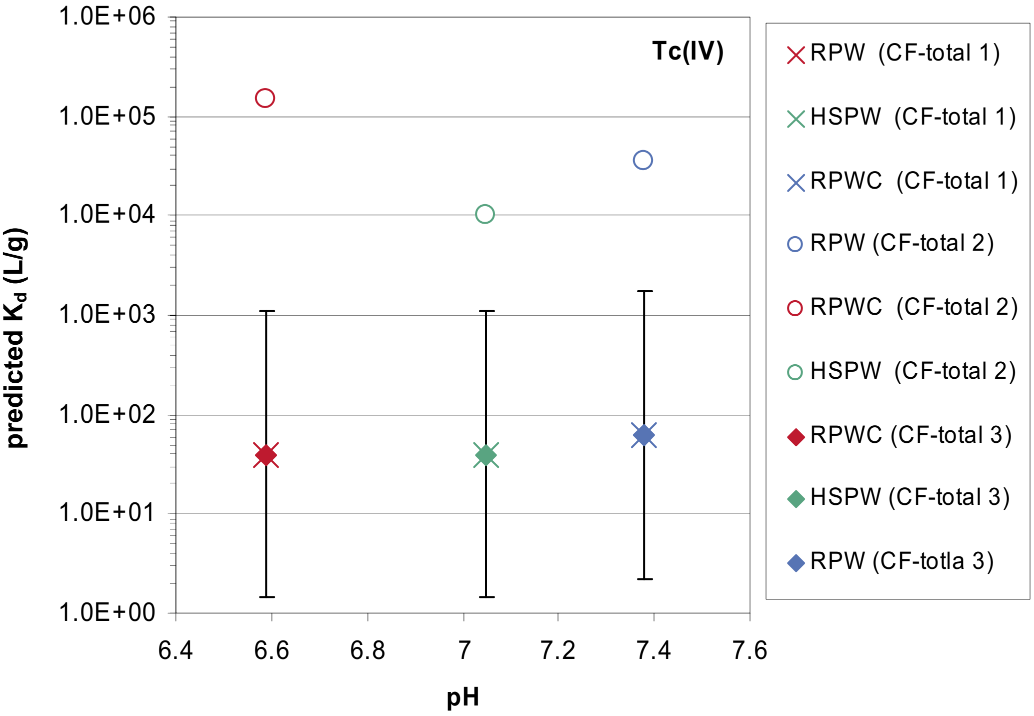


Figure 5-34. *K_d values for Tc(IV) derived as a function of conditions based on the experimental data for Th by /Bradbury and Baeyens, 2003a/. The selected values are indicated by solid symbols (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*

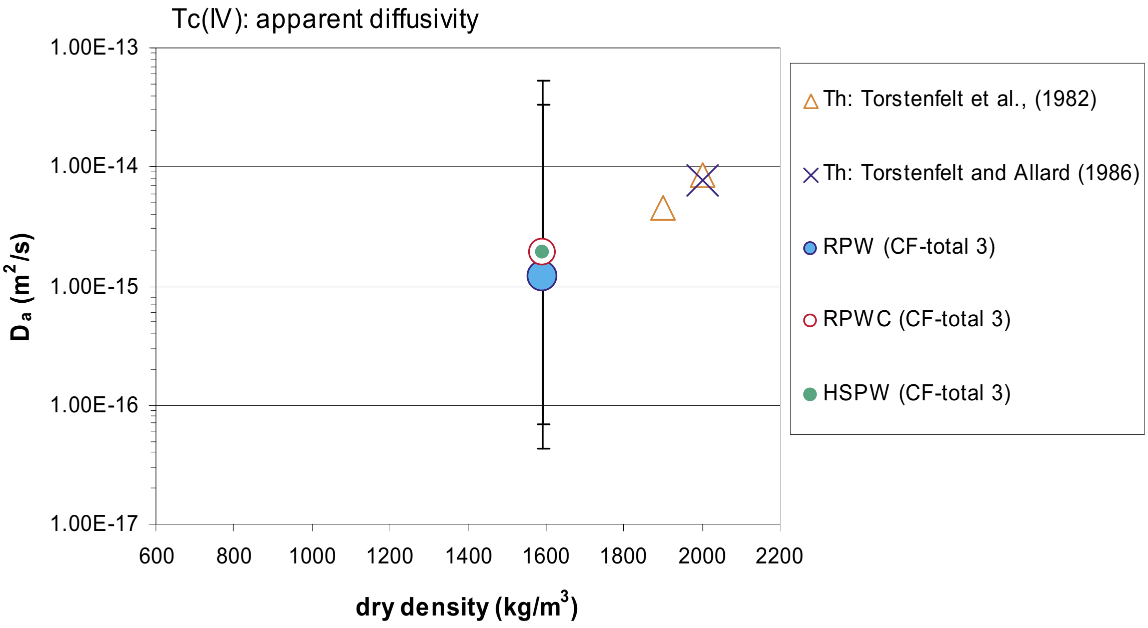


Figure 5-35. *Calculated D_a values for Tc(IV) based on D_e for HTO and K_d values from Figure 5-36 in comparison to experimental data for Th (from Figure 5-37).*

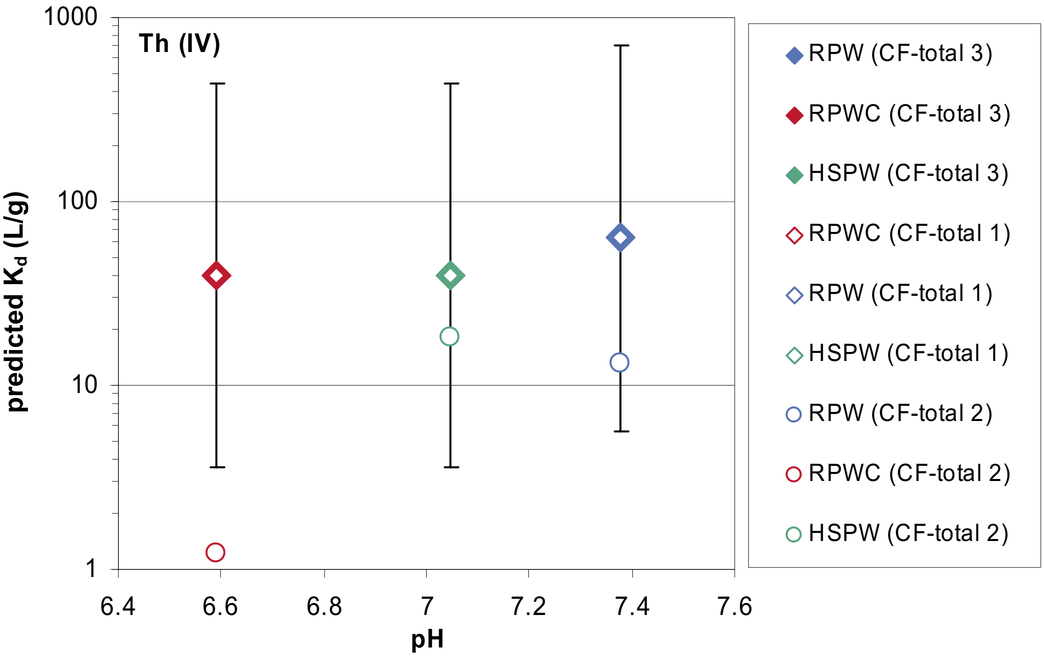
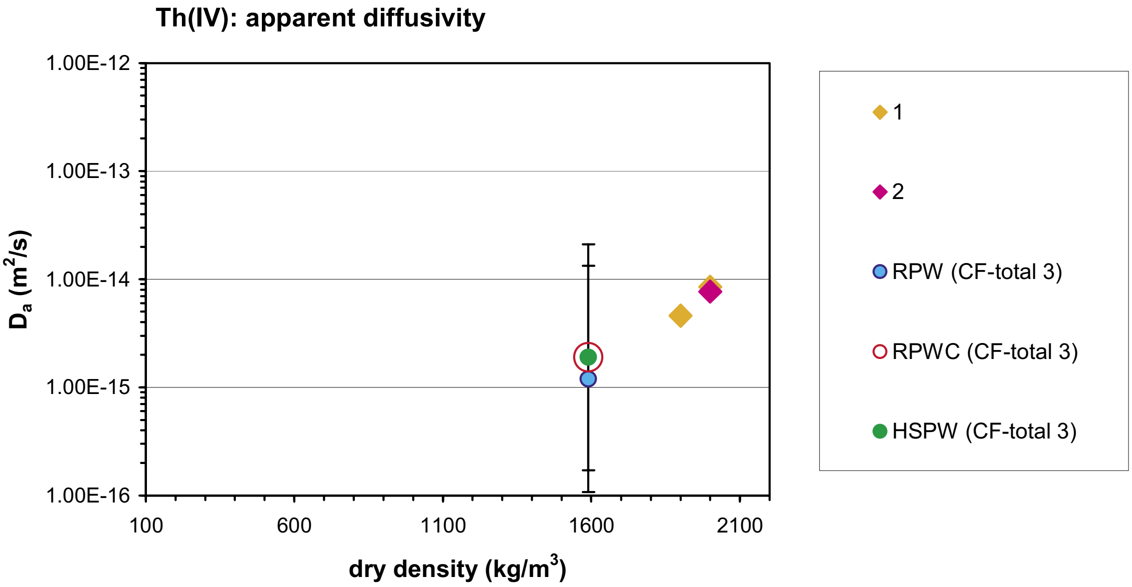


Figure 5-36. *K_d values for Th derived as a function of conditions based on the isotherm data determined by /Bradbury and Baeyens, 2003a/ on MX-80 at pH 7.2–7.7. The selected values are indicated by solid symbols (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1 MX-80 Na-montmorillonite Torstenfelt et al., (1982)
2 MX-80 Na-montmorillonite Torstenfelt and Allard (1986)

Figure 5-37. *Calculated D_a values for Th based on D_e for HTO and K_d values from Figure 5-36 in comparison to experimental data.*

Considering all evidence, the inclusion of Th-carbonate species in CF-speciation is considered inappropriate, and the data based on CF-total 3 are recommended. The resulting D_a values are not inconsistent with independent experimental data, and it is considered to be very likely that any K_d for Th under the specified scenarios would be within the indicated ranges.

The sorption data obtained by /Bradbury and Baeyens, 2003a/ as a function of pH on SWy-1 montmorillonite indicate no decrease of Th sorption up to pH 11–11.5.

Tin

No reliable and relevant sorption or diffusion data for Sn(IV) were found. Sn(II) is not considered for the present purpose, as it will form only under extremely reducing conditions. /Bradbury and Baeyens, 2003a/ present a sorption edge for Sn which suggests that K_d values may be as high as > 800 m^3/kg. Their data are compatible with the findings of /Tachi et al, 1999/. However, initial Sn concentrations in the latter study were near or above the solubility limit as determined by /Amaya et al, 1997/. /Bradbury and Baeyens, 2003a/ do not report the initial Sn concentration, and their data are also not considered, therefore.

Based on the fact that both Sn(IV) and Th exist as uncharged tetra-hydroxo species in the pH range of about 6.0–7.5 /Hummel et al, 2002/, it is proposed to use Th directly as analogue for Sn(IV). Following the discussion in section 5.1.4, a UF-starting K_d of 4.0 (instead of 1.6 for Th) is proposed to account for differences in the chemical behaviour of Sn(IV) and Th in the relevant pH range 6.6–7.4, but no further uncertainties are proposed. Note that this assessment holds only for the pH range under consideration, as the hydrolysis behaviour of Th and Sn(IV) starts to differ more significantly outside of this pH range.

Based on the hydrolysis behaviour of Sn(IV) /Amaya et al, 1997/, it seems very likely that the K_d will decrease at pH values > 8 (in contrast to the sorption behaviour of Th).

Uranium

In relevant aqueous solutions, stable oxidation states of U can be IV or VI, depending on redox conditions. Because of the uncertainty regarding redox conditions, both oxidation states are treated separately below. The overall uncertainty for the K_d of U encompasses the entire combined data range if variable redox conditions need to be taken into account.

For U(IV), no relevant sorption data were found, and K_d was derived based on analogy considerations and the source data set used for Th. The results are shown in Figure 5-38, the comparison with D_a values is shown in Figure 5-39. The data show that inclusion of carbonate species in the speciation-conversion leads to very high K_d values that are inconsistent with sorption data for Th; and would further lead to equally unrealistic D_a values of ca 10^{-18} m^2/s. Therefore, the K_d values based on CF-total 3 are recommended. It can be seen from Figure 5-39 that the selected sorption data are not consistent with available D_a values for U. Comparison with the D_a values for Th indicates that the redox state in the U diffusion experiments may not have been controlled well enough to completely exclude the presence of oxidised uranium species. The overall diffusion may thus represent a mix of reduced and oxidised U fractions /see also Torstenfelt and Allard, 1986/. Therefore, more weight is placed on the derived K_d values in the present assessment, and it is considered to be likely that any K_d for U(IV) under the specified scenarios would be within the indicated ranges.

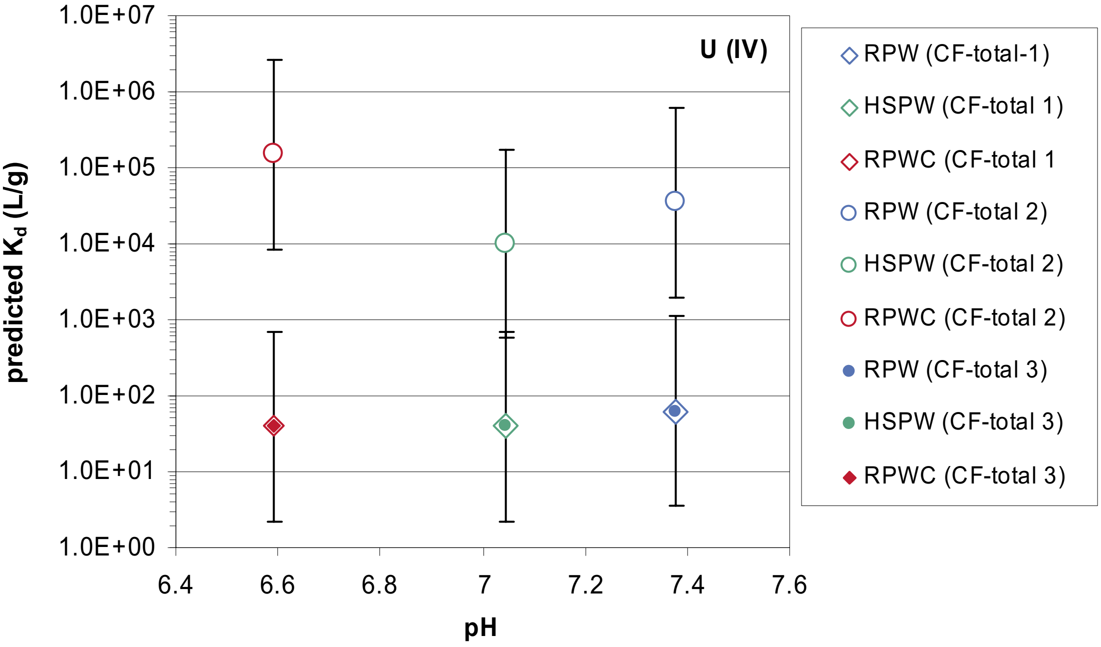
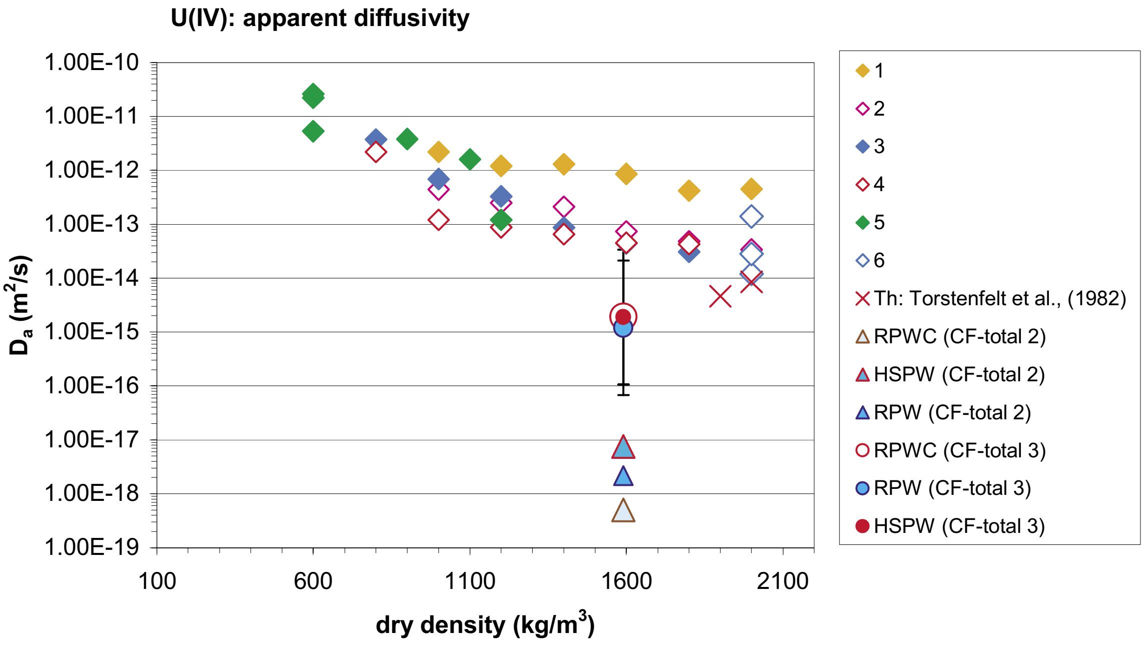


Figure 5-38. *K_d values for U(IV) derived as a function of conditions based on the isotherm data determined by /Bradbury and Baeyens, 2003a/ for Th on MX-80 at pH 7.2–7.7. The selected values are indicated by solid symbols (CF-total 3); error bars are given for CF-total 2, 3. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1	Kunigel-V1 Na-bentonite	Idemitsu et al., 1996
2	Kunigel-V1 Na-bentonite+carbon steel	Idemitsu et al., 1996
3	Kunipia-F Na-bentonite	Idemitsu et al., 1996
4	Kunipia-F Na-bentonite+carbon steel	Idemitsu et al., 1996
5	Na-bentonite salt and HCO3-	Muurinen et al., 1989
6	Na-bentonite (1%,Fe; 1% FeO; 1% Cu)	Albinsson et al., 1991

Figure 5-39. *Calculated D_a values for U(IV) based on D_e for HTO and K_d values from Figure 5-38 in comparison to experimental data (experiments where a reducing agent had been used are depicted by open symbols). For comparison, experimental D_a values for Th are also shown.*

Based on the solubility/hydrolysis behaviour of U(IV) /Hummel et al, 2002/, no decrease of K_d is expected up to pH 11 or higher, following the analogy with Th.

In case of U(VI), the literature on sorption is relatively extensive, but the majority of studies is concerned with Fe(III)- and other metal oxides as well as with kaolinite, because of their importance for the substrates found at the Koongarra uranium deposit analogue site /cf Waite et al, 2000; Davis, 2001, and references therein/. Less work has been done on bentonite or smectite minerals in comparison. There are several spectroscopic studies that confirm that uranyl ions sorb to montmorillonite by inner-sphere surface complexation at edge sites and outer-sphere complexation at exchange sites, with the latter being predominant only at low pH /Sylvester et al, 2000; Chisholm-Brause et al, 2001/.

Only a limited number of studies addresses the sorption behaviour of U(VI) on montmorillonite or bentonite as a function of conditions. In particular, few systematic data are available regarding the influence of carbonate, which appears to be a critical factor for uranyl sorption, both in terms of competition by forming dissolved uranium carbonato complexes and in terms of forming ternary surface complexes. /Davis, 2001/. There are several studies where U(VI) sorption on smectite or bentonite is investigated in the presence of low but ill-defined carbonate concentrations /see e.g. Boult et al, 1998/; these are generally not considered for the present work and not discussed further. Zachara and co-workers /Turner et al, 1996; McKinley et al, 1995/ studied uranyl adsorption on SWy-1 montmorillonite and a natural smectite as a function of pH and ionic strength, but in the absence of carbonate. Moreover, the sample of natural smectite was reportedly a ferrogenous beidellite, which may have different properties than montmorillonite, the principal smectite mineral in bentonites. /Pabalan et al, 1998/ and /Pabalan and Turner, 1997/ published uranyl sorption data on Na-montmorillonite (SAz-1) as a function of pH, solid/water ratio and uranyl concentration at ambient pCO_2. As the only systematic study carried out in the presence of carbonate, their experiments were considered to have the closest chemical proximity to the present reference conditions and were selected as representative source data set. In comparison to other studies /e.g. Turner et al, 1996/ the appropriate choice and variation of solid/water ratio renders their data also more trustworthy and easier to interpret. Both of the above datasets had been used for the development of thermodynamic sorption models /Pabalan and Turner, 1997; Turner et al, 1996/, but both models have significant shortcomings as they neglect the formation of ternary U-carbonato surface complexes and were therefore not used.

K_d values derived with the CF-approach are shown in Figure 5-40. It can be seen that the highest sorption is reached at the lowest pH value according to these data. However, this trend is consistent with data for U(VI) sorption on montmorillonite, clinoptilite, and quartz /Pabalan et al, 1998/. It is therefore considered that this trend is relevant. As the formation of ternary U-carbonato surface complexes enhances sorption, K_d is underpredicted when complexation of uranyl with carbonate is taken as competitive with respect to sorption (CF-total 2). On the other hand, CF-total 1 and 3 give identical results, indicating that carbonate species and the hydroxo ion are the only relevant ligands effecting surface complexation. Ion exchange is not important at the relevant ionic strengths /Pabalan and Turner, 1997/.

The comparison with D_a values can be seen in Figure 5-41. As in the case of U(IV), the comparison is not conclusive. The discrepancy between D_a values for RPW and HSPW calculated from K_d values derived with either CF-total 3 or CF-total 2 is within the scatter of experimental data, represented by the measurements of /Idemitsu et al, 1996/ in Kunigel-V1 on one hand vs /Idemitsu et al, 1996/ in Kunipia –F and /Muurinen et al, 1989/ in MX-80 on the other. The latter data might be the closest representation of the relevant system and agree better with D_a values calculated from K_d values derived with CF-total 3.

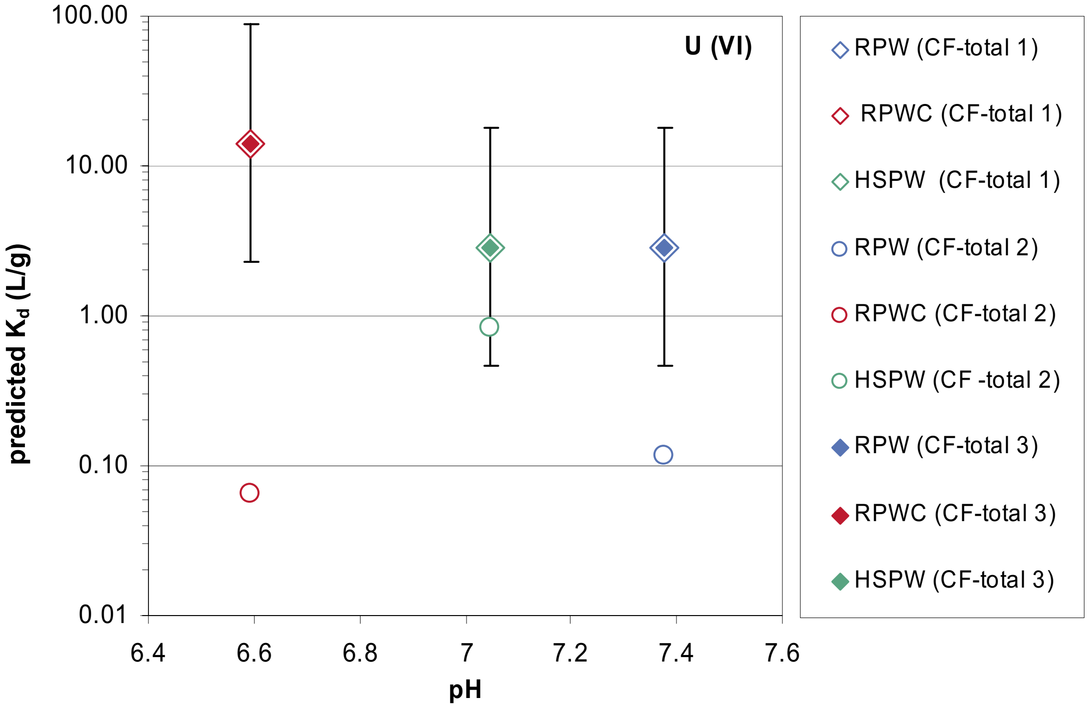
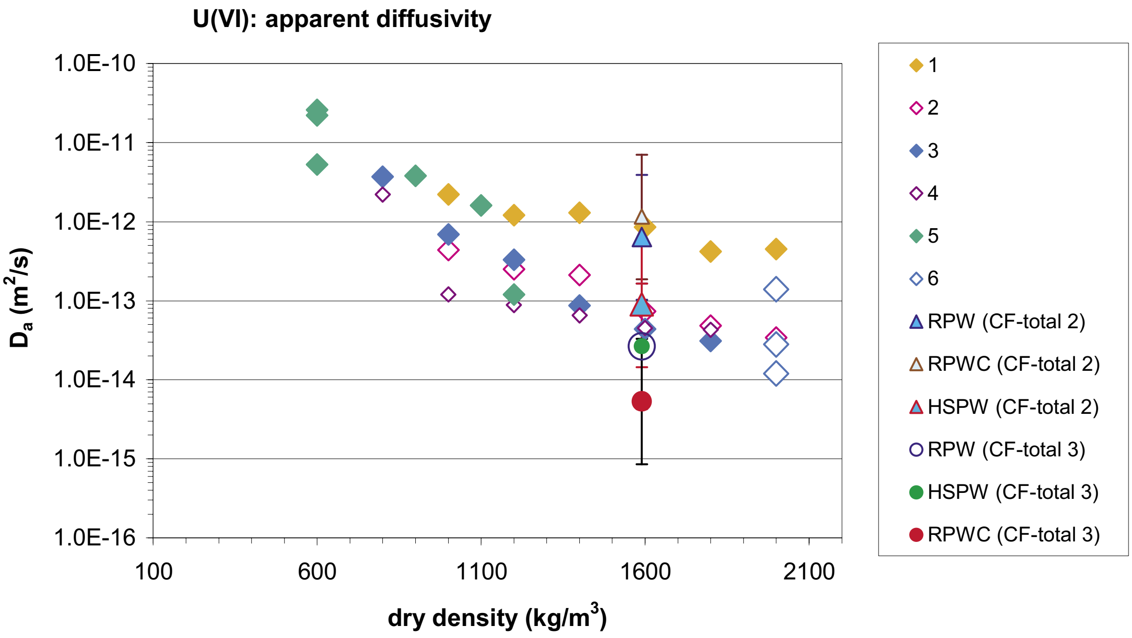


Figure 5-40. *K_d values for U(VI) derived as a function of conditions based on the experimental data by /Pabalan and Turner, 1997/. The selected values are indicated by solid symbols (CF-total 3); error bars are given for these values and the data derived using CF-total 2. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1	Kunigel-V1 Na-bentonite	Idemitsu et al., 1996
2	Kunigel-V1 Na-bentonite+carbon steel	Idemitsu et al., 1996
3	Kunipia-F Na-bentonite	Idemitsu et al., 1996
4	Kunipia-F Na-bentonite+carbon steel	Idemitsu et al., 1996
5	MX-80 Na-bentonite (added salt and HCO3-)	Muurinen et al., 1989
6	MX-80 Na-bentonite (1%,Fe; 1% FeO; 1% Cu)	Albinsson et al., 1991

Figure 5-41. *Calculated D_a values for U(VI) based on D_e for HTO and K_d values from Figure 5-40 in comparison to experimental data (experiments where a reducing agent had been used are depicted by open symbols).*

For the same reasons as for U(IV), more weight is placed on the batch source data in the present assessment, and it is considered to be likely that any K_d for U(VI) under the specified scenarios would be within the indicated ranges.

Based on the data by /Pabalan and Turner, 1997/, a significant decrease of K_d above pH 8–9 is expected.

Zirconium

No sorption data measured in systematic and well-controlled conditions could be found. K_d for Zr was derived based on analogy considerations and the source data set used for Th. The results are shown in Figure 5-42. Because the hydrolysis behaviour of Zr(IV) starts to differ from that of Th(IV) at circumneutral pH values (in contrast to Th, Zr forms $Zr(OH)_5^-$ species, see /Hummel et al, 2002/), dissolved hydroxo –complexes were explicitly included in the speciation conversion (see appendices E and F). As in the case of Tc(IV), the additional uncertainty due to different hydrolysis behaviour is taken into account by increasing UF-starting K_d to 4.0 (instead of to 2.6 as for well-matched analogues, see section 5.1.4). The recommended data are based on CF-total 3, as in the case of Th.

The resulting D_a values are compared with experimental data in Figure 5-43. Based on the good agreement, it is estimated as very likely that any K_d for Zr under the specified scenarios would be within the indicated ranges

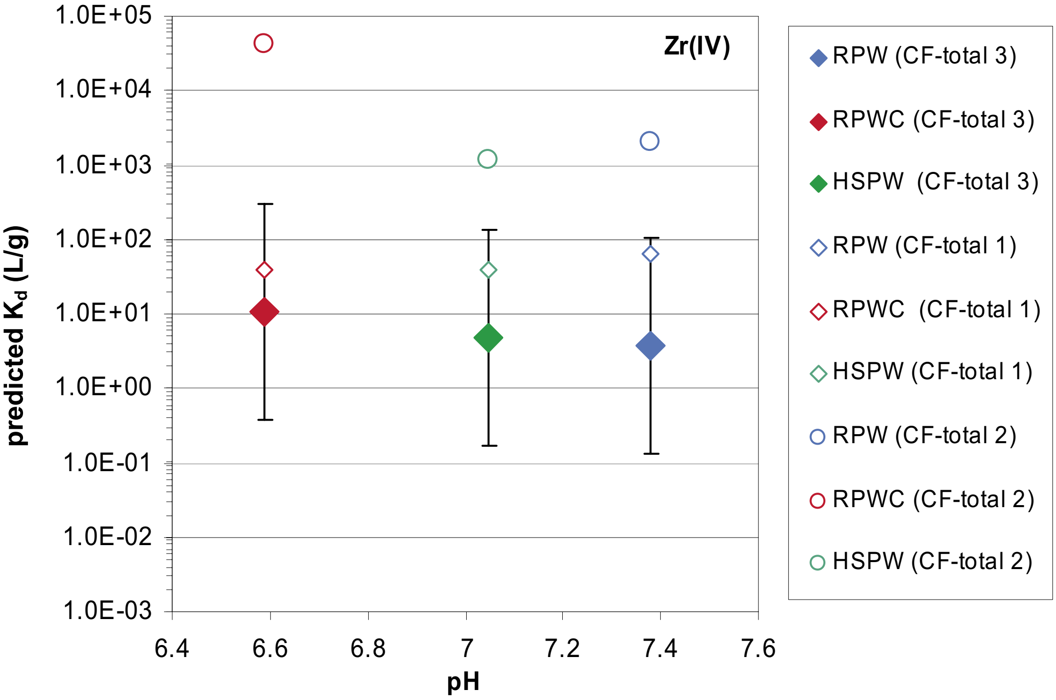
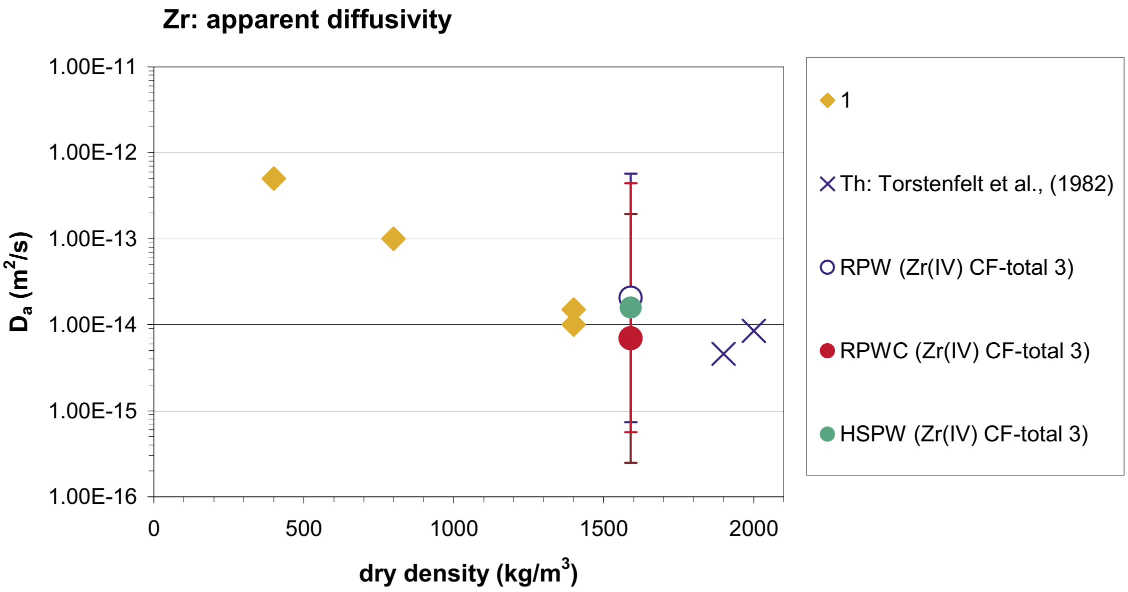


Figure 5-42. *K_d values for Zr(IV) derived as a function of conditions based on the isotherm data determined by /Bradbury and Baeyens, 2003a/ for Th on MX-80 at pH 7.2–7.7. The selected values are indicated by solid symbols (CF-total 3); error bars refer to these values. For an explanation of CF-total 1/2/3, see section 5.1.4.*



1 Kunigel-V1 Sato et al., 1995

Figure 5-43. *Calculated D_a values for Zr based on D_e for HTO and the K_d value and uncertainty proposed above in comparison to experimental data. D_a values for Th are given for comparison.*

5.4 Data Summary

This section summarises the migration parameters and associated uncertainties derived in section 5.3 for a bentonite buffer corresponding to the KBS-3 concept (see also section 5.2.6). The derived migration parameters are:

- effective diffusivity (D_e),
- diffusion-available porosity (ε),
- distribution coefficient (K_d).

In addition, apparent diffusivities (D_a) were selected from the literature to evaluate the self-consistency of the selected migration parameters. These parameters as well as the associated uncertainties were derived for 26 radionuclides. In case of redox-sensitive elements, each relevant oxidation state was evaluated separately. The validity range of the derived data in terms of bentonite properties and density, as well as in terms of geochemical conditions is summarised below; a detailed discussion is provided in chapters 4 and 5.

Bentonite composition and density

K_d

The derived migration parameters were derived for MX-80 bentonite of a given composition (Appendix B) at the specified reference density of 1,590 kg/m^3. Because of the strong dependency of K_d on bentonite porewater composition, these data are strictly valid for these conditions only. However, it is not likely that a limited variation of the buffer density (e.g. within a range of about 1,400–1,700 kg/m^3) will have a significant influence on porewater composition or K_d, in particular when pCO_2 is imposed by the host rock formation (see below). Similarly, the bentonite composition was varied for the present evaluation to include a pure Ca-form of MX-80 as well as a MX-80 depleted of soluble impurities. The resulting variability of porewater composition was found to be within the variability due to uncertainties in the groundwater composition and pCO_2. It follows from the above, that under comparable conditions, the derived values will also have a certain validity for other bentonites, as long as the CEC is similar to that of MX-80.

Porosity

For all elements except non-sorbing anions, the same value is proposed for diffusion-available and total porosity. As shown in Figure 5-3, total porosity depends on buffer density, but is not significantly influenced by composition. According to eq. (5.6), total porosity is readily calculated as $\varepsilon = 1-(\rho/\rho_s)$. In the same manner, diffusion-available porosity for non-sorbing anions is given by $\varepsilon_{anion} = (1-(\rho/\rho_s))/2.5$; see eq. (5.8).

D_e

For all elements except non-sorbing anions and Cs, D_e for HTO is used. The D_e values plotted in Figure 5-4 for four different bentonites as a function of density show a clear dependency of D_e on density. Using eq. (5.7), this dependency can be expressed as:

$$D_e = 6.7785E{-}9 \times e^{-2.5671E-3 \times \rho}$$

Similarly, using eq. (5.9), the dependency of D_e for non-sorbing anions can be expressed as a function of density; this relation is valid for a density range of ca 1,000–2,000 kg/m^3:

$$D_e = -1.1844\times10^{-20} \times \rho^3 + 8.130\times10^{-17} \times \rho^2 - 1.9473\times10^{-13} \times \rho + 1.6167\times10^{-10}$$

For Cs, no explicit relation of De vs density is given, but it is indicated in section 5.3.4 that the same dependency on density as for HTO may be used, with D_e for Cs being larger by a constant factor of 3.

Very little quantitative information is available regarding the dependency of D_e on bentonite composition. Based on Figure 5-4, it can be estimated, however, that the variation of D_e among significantly dissimilar bentonites (assuming all other experimental conditions being the same) is within a factor of ca 5; i.e. within experimental error.

Geochemical conditions (groundwater composition, pCO_2, redox conditions)

As pointed out in Figure 4-2 and Figure 4-3, migration parameters were selected for specific sets of bentonite porewater compositions. These porewater compositions are the result of bentonite-groundwater interaction and correspond to particular combinations of i) buffer composition and density (see above) and ii) geochemical conditions (groundwater composition, pCO_2). It is pointed out that changes in groundwater composition do not translate directly to corresponding changes in porewater composition, due to the buffering effect of bentonite. An approximate estimation of the possible effects of variations in the groundwater composition may be possible based on the results given in Appendix C. The effect of redox conditions was addressed by separately evaluating each relevant oxidation state in case of redox-sensitive elements.

As discussed for each element in scetion 5.3.5, K_d values can be very sensitive with regard to porewater composition. Therefore, the validity of the selected data is bounded by the ranges of conditions covered by the porewater compositions considered: (pH 6.6 / pCO_2 1×10^{-1} atm) to (pH 7.4 / pCO_2 $1\times10^{-2.6}$ atm), reflecting closed and open conditions with respect to CO_2. It is not advisable to extrapolate K_d values to conditions outside these ranges. Salinity is somewhat of an exception to this, because of the comparative “inertness” of Na and Cl; it is not expected that an increase of salinity to ca 1 M will have a significant effect on K_d (except for Cs, Sr, Ra).

For an approximate estimation of the possible effects of variations in the porewater composition, the diagrams in section 5.3.5 can be used. Interpolation between the three reference porewater conditions is possible for salinity, but should to be done with great care for parameters that are directly linked to others (pH, pCO_2).

In general, not enough diffusion data are available as a function of conditions to allow a sound assessment of the effects of variable conditions. The effect of high salinity (up to 1M) on D_e of non-sorbing anions can be estimated from Figure 5-4. No significant effects are expected for such salinities. Whether even higher salinities will lead to significantly increased D_e values for anions cannot be answered conclusively to date. For sorbing elements, it is expected that the uncertainty of D_e as a function of conditions will not be relevant in comparison to the corresponding uncertainty in K_d.

Temperature

The selected data are valid for 25°C. An increase to 50°C is expected to lead to a twofold increase of D_e (see 5.3.4). Based on the data available to date, it is not possible to assess the influence of temperature on K_d with any certainty. However, no significant effects are expected for an interval of ca 10–50°C. No effect on porosity is expected for this temperature range.

Summary of D_e and ε values

Radionuclide (Redox State)	D_e (m^2/s)	Upper D_e limit (m^2/s)	Lower D_e limit (m^2/s)	ε (–)	Upper ε limit (–)	Lower ε limit (–)
Ag(I)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Am(III)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
C, carbonate species	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
C, methane	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.17	0.12	0.24
C, organic acids	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
Ce(III)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Cl(-I)	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
Cm(III)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Cs(I)	3.0 x 10^{-10}	3.0 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Eu(III)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Ho(III)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
I(-I)	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
Nb(V)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Ni(II)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Np(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Np(V)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pa(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pa(V)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pb(II)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pd(II)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pu(III)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pu(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pu(V)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Pu(VI)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Ra(II)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Rn(-)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Se(-II)	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
Se(IV)	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
Se(VI)	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
Sm(III)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Sn(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Sr(II)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Tc(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Tc(VII)	1.0 x 10^{-11}	3.0 x 10^{-11}	3.0 x 10^{-12}	0.17	0.12	0.24
Th(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
U(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
U(VI)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-
Zr(IV)	1.2 x 10^{-10}	1.91 x 10^{-10}	4.94 x 10^{-11}	0.43	-	-

Reference porewater (RPW)			
Radionuclide (Redox State)	K_d (m^3/kg)	Upper K_d limit (m^3/kg)	Lower K_d limit (m^3/kg)
Ag(I)	-	15	0
Am(III)	61	378	10
C, carbonate species	isotope exchange	-	-
C, methane	0	-	-
C, organic acids	0	-	-
Ce(III)	8	93	0.8
Cl(-I)	0	-	-
Cm(III)	61	378	10
Cs(I)	0.11	0.6	0.018
Eu(III)	8	93	0.8
Ho(III)	8	93	0.8
I(-I)	0	-	-
Nb(V)	3	45	0.2
Ni(II)	0.30	3.3	0.03
Np(IV)	63	1113	4
Np(V)	0.02	0.2	0.004
Pa(IV)	3	45	0.2
Pa(V)	3	45	0.2
Pb(II)	74	457	12
Pd(II)	5	75	0.3
Pu(III)	100	984	10
Pu(IV)	63	1111	4
Pu(V)	0.02	0.2	0.002
Pu(VI)	3	28	0.3
Ra(II)	0.005	0.03	0.001
Rn(-)	0	-	-
Se(-II)	0	-	-
Se(IV)	0.04	0.4	0.003
Se(VI)	0	-	-
Sm(III)	8	93	0.8
Sn(IV)	63	1764	2.3
Sr(II)	0.005	0.031	0.0009
Tc(IV)	63	1764	2.3
Tc(VII)	0	-	-
Th(IV)	63	700	6
U(IV)	63	1113	3.6
U(VI)	3	18	0.5
Zr(IV)	4	103	0.1

Reference porewater for closed system with respect to CO_2 (RPWC)			
Radionuclide (Redox State)	K_d (m^3/kg)	Upper K_d limit (m^3/kg)	Lower K_d limit (m^3/kg)
Ag(I)	-	15	0
Am(III)	11	68	2
C, carbonate species	isotope exchange	-	-
C, methane	0	-	-
C, organic acids	0	-	-
Ce(III)	1	14	0.1
Cl(-I)	0	-	-
Cm(III)	11	68	2
Cs(I)	0.10	0.6	0.017
Eu(III)	1	14	0.1
Ho(III)	1	14	0.1
I(-I)	0	-	-
Nb(V)	3	45	0.2
Ni(II)	0.06	0.7	0.01
Np(IV)	40	703	2
Np(V)	0.01	0.1	0.002
Pa(IV)	3	45	0.2
Pa(V)	3	45	0.2
Pb(II)	35	219	6
Pd(II)	5	75	0.3
Pu(III)	30	300	3
Pu(IV)	40	703	2
Pu(V)	0.01	0.1	0.001
Pu(VI)	14	139	1.4
Ra(II)	0.005	0.03	0.001
Rn(-)	0	-	-
Se(-II)	0	-	-
Se(IV)	0.09	1.0	0.008
Se(VI)	0	-	-
Sm(III)	1	14	0.1
Sn(IV)	40	1113	1.4
Sr(II)	0.005	0.03	0.0009
Tc(IV)	40	1113	1.4
Tc(VII)	0	-	-
Th(IV)	40	442	4
U(IV)	40	703	2.3
U(VI)	14	88	2
Zr(IV)	11	305	0.4

Highly saline porewater (HSPW)			
Radionuclide (Redox State)	**K_d (m^3/kg)**	**Upper K_d limit (m^3/kg)**	**Lower K_d limit (m^3/kg)**
Ag(I)	-	15	0
Am(III)	24	152	4
C, carbonate species	isotope exchange	-	-
C, methane	0	-	-
C, organic acids	0	-	-
Ce(III)	5	57	0.5
Cl(-I)	0		
Cm(III)	24	152	4
Cs(I)	0.03	0.2	0.006
Eu(III)	5	57	0.5
Ho(III)	5	57	0.5
I(-I)	0	-	-
Nb(V)	3	45	0.2
Ni(II)	0.07	0.8	0.01
Np(IV)	40	702	2
Np(V)	0.02	0.1	0.004
Pa(IV)	3	45	0.2
Pa(V)	3	45	0.2
Pb(II)	46	287	7
Pd(II)	5	75	0.3
Pu(III)	43	421	4
Pu(IV)	40	700	2
Pu(V)	0.02	0.2	0.002
Pu(VI)	3	28	0.3
Ra(II)	0.001	0.01	0.0002
Rn(-)	0	-	-
Se(-II)	0	-	-
Se(IV)	0.05	0.6	0.005
Se(VI)	0	-	-
Sm(III)	5	57	0.5
Sn(IV)	40	1113	1.4
Sr(II)	0.001	0.008	0.0002
Tc(IV)	40	1113	1.4
Tc(VII)	0	-	-
Th(IV)	40	442	4
U(IV)	40	703	2.3
U(VI)	3	18	0.5
Zr(IV)	5	134	0.2

6 Concluding remarks

For the present selection of radionuclide migration parameters for the bentonite buffer, significant efforts were made to select the scientifically best and most defendable values, and to clearly define the associated uncertainties. To this end, different contributions to the overall uncertainties were quantified separately. Relevant uncertainties can stem from

- uncertainties in the source data (experimental error),
- uncertainties in applying the source data to the expected in-situ conditions for PA (errors in parameter transfer),
- uncertainties in defining the expected in-situ conditions for PA (variability of conditions).

It follows directly form this list that the critical points for minimising uncertainties in selected radionuclide migration parameters for the bentonite buffer are

- to obtain the best possible description of the solution chemistry under the in-situ conditions of interest; and
- to be able to rely on data sources that closely match these solution conditions.

The goal of the present data evaluation was the selection of parameters applicable to the conditions in compacted MX-80 bentonite. While diffusion parameters could be derived directly for compacted conditions, K_d values from batch experiments needed to be converted to compact conditions. This was done by fully taking into account the dependency of K_d on the calculated, expected porewater composition of the compacted bentonite buffer.

The distribution of uncertainties among the relevant sources also allowed to document all data derivation procedures with a high degree of transparency and traceability. This is obviously important to increase confidence, but will also facilitate any subsequent updates or changes (due e.g. to modifications in the expected groundwater composition, etc).

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Appendix A

Groundwater compositions

	Saline GW (I)	Non-saline GW (II)	Highly saline GW (III)
Na^+ (mol/l)	7.390E-02	1.455E-02	5.739E-01
K^+ (mol/l)	3.320E-04	5.120E-05	3.320E-04
Ca^{+2} (mol/l)	4.120E-02	9.650E-04	4.116E-02
Mg^{+2} (mol/l)	4.530E-03	6.990E-04	4.530E-03
CO_3^{-2} (mol/l)	7.700E-04	1.985E-03	7.248E-04
H+ (mol/l)	8.589E-04	2.010E-03	7.700E-04
Cl- (mol/l)	1.557E-01	1.495E-02	6.550E-01
SO_4^{-2} (mol/l)	3.850E-03	5.100E-04	3.850E-03
pH (-)	7.000	7.904	7.175
pCO_2 (-)	-2.558	-2.867	-2.792
Charge balance (%)	0.995	-0.005	0.336
Precipitated solids	-	calcite	calcite
Ionic strength (mol/l)	0.2075	0.1979	0.7062

I) pH and charge balance correction
II) pH correction with addition of NaOH
III) Saline GW with the addition of 0.5 M of NaCl

	Saline GW (IV)	Saline GW (IV)
Na^+ (mol/l)	8.3870E-02	3.7990E-01
K^+ (mol/l)	3.3200E-04	3.3200E-04
Ca^{+2} (mol/l)	4.0437E-02	2.1644E-03
Mg^{+2} (mol/l)	2.4003E-04	2.5217E-08
CO_3^{-2} (mol/l)	7.1213E-06	1.0971E-04
H+ (mol/l)	-5.3007E-04	-2.1919E-01
Cl- (mol/l)	1.5570E-01	1.5570E-01
SO_4^{-2} (mol/l)	3.8500E-03	3.8500E-03
pH (-)	10.499	13.154
pCO_2 (-)	-9.419	-13.141
Charge balance (%)	0.995	0.489
Precipitated solids	brucite	0.489
	calcite	brucite
		calcite
		portlandite
Ionic strength (mol/l)	0.20223	0.23024

IV) Saline GW at high pH (addition of NaOH for pH correction)

Appendix B

Bentonite characteristics

Composition of bentonites

The composition of MX-80 bentonite, Kunipia-F and Kunigel-V1 as used for the calculation of the Kd and Da values is given in Table A.1 and Table A.2.

Table B.1. Composition and other specific parameters of Wyoming bentonite MX-80.

Parameters	MX-80	Reference
Minerals:		
smectite	88.6% [1]	-
quartz	10%	/van Olphen and Fripiat, 1979/
calcite	0.7%	/Müller-Vonmoos and Kahr, 1983/
Soluble impurities:		
NaCl	0.007%	/Wanner et al, 1992/
CaSO4	0.34%	/Wanner et al, 1992/
Surface chemical parameters:		
CEC	85 meq/100g	/Wieland et al, 1994/
exchangeable Na^+	81.7%	/Müller-Vonmoos and Kahr, 1983/
exchangeable K^+	0.3%	/Müller-Vonmoos and Kahr, 1983/
exchangeable Mg^{2+}	3.9%	/Müller-Vonmoos and Kahr, 1983/
exchangeable Ca^{2+}	14.1% [1]	-
SOH site density	2.52×10^{-5} mol/g [2]	/Wieland et al, 1994/

[1] Calculated by difference

[2] Obtained for pretreated MX-80 which had a CEC of 108 meq/100g. Adapted for the smectite content of untreated MX-80.

Table B.2. Kunigel-V1 and Kunipia-F: Composition and other specific parameters relevant to ISD modeling. The references are given in the footnote.

	Kunigel-V1	**Kunipia-F**
Minerals:		
smectite	46–49% [1]	99% /2/; >95% [1]
quartz	29–38% [1]	traces [1]
feldspar	2.7–5.5% [1]	
calcite	2.1–2.6% [1]	traces [1]
dolomite	2.0–3.8% [1]	
zeolite	3.0–3.5% [1]	
pyrite	0.5–0.7% [1]	
Soluble impurities:		
NaCl	0.001% [3]	0.071% [3]
$CaSO_4$	0.38% [3]	0.694% [3]
KCl	0.004% [3]	0.005% [3]
Surface sites and cation exchange parameters:		
SOH sites (edge sites)	1.36×10^{-5} mol/g [4]	2.84×10^{-5} mol/g [4]
Cation exchange capacity, CEC	60.1 meq/100g [1]	108 meq/100g [5]
exchangeable Na^+	85.3% [6]	97.1% [5]
exchangeable K^+	1.5% [6]	0.9% [5]
exchangeable Mg^{2+}	2.3% [6]	1.3% [5]
exchangeable Ca^{2+}	10.9% [6]	0.7% [5]
Surface area:		
surface area of layer sites, S(layer)	810 m^2/g [7]	810 m^2/g [7]
surface area of edge sites, S(edge)	3 m^2/g [from 4]	3 m^2/g [from 4]

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[1] /Sasaki et al, 1995/

[2] /Ashida et al, 1994/

[3] /Ochs et al, 1999/

[4] /Wieland et al, 1994/ obtained for pretreated MX-80 which had a CEC of 108 meq/100g, adapted for the smectite content of Kunigel-V1

[5] /Yajima, 1993/

[6] /Ochs et al, 1999/. Estimated based on the amount of leachable cations reported by /Sasaki et al, 1995/

[7] /Sato et al, 1995/

Appendix C

Porewater compositions

This appendix includes a detailed description of calculated porewater compositions (C.1) as well as a brief discussion on potential effects of extremely saline groundwaters on porewater composition (C.2).

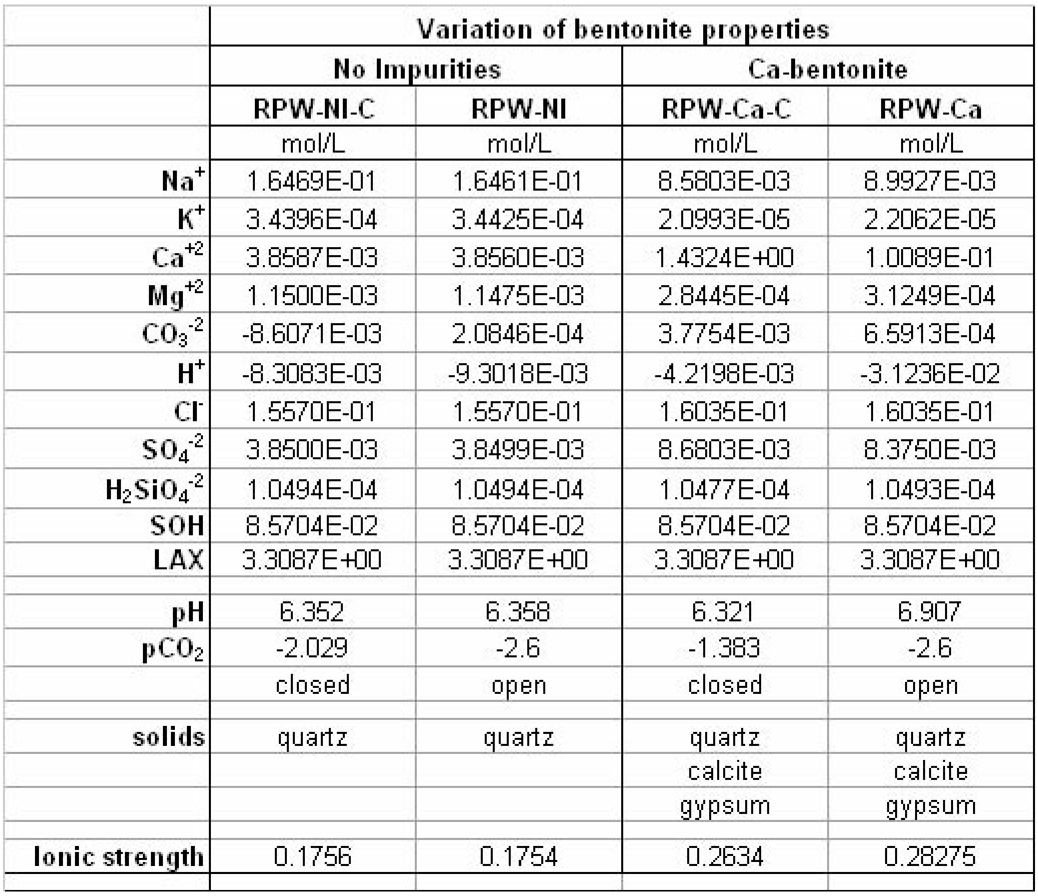
C.1 Calculation of Porewater composition

- Porewater compositions were calculated using the bentonite model of /Wieland et al, 1994/.
- SOH surface sites densities were scaled by a factor 0.79 (= ratio of CEC values) to account for geochemical characteristics of the substrate MX-80 in comparison to the montmorillonite used by /Wanner et al, 1994/.
- For comparison porewater compositions were also calculated with the bentonite model of /Bradbury and Baeyens, 1997/ (data not shown).
- For systems open toCO_2, the pH conditions obtained using alternatively the model by /Wieland et al, 1994/ or the model by /Bradbury and Baeyens, 1997/ are similar (ΔpH=0.02 units). In CO_2 open systems, the pH conditions are controlled by the carbonate buffer. In closed systems, a ΔpH≈0.4 units was observed.

Table C-1. Calculated porewater compositions reflecting variation of groundwater chemistry (salinity) and CO_2 conditions.

	Variation of groundwater salinity						
	Saline-GW (SGW)			High-saline GW		Non-saline GW	
	RPWC	RPW	RPWA	HSPWC	HSPW	NSPWC	NSPW
	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	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-04	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	quartz	quartz	quartz	quartz	quartz	quartz
	calcite	calcite	calcite	calcite	calcite	calcite	calcite
	gypsum	gypsum	gypsum	gypsum	gypsum	gypsum	gypsum
Ionic strength	0.29311	0.29046	0.29159	0.74481	0.75992	0.23259	0.2211

Table C-2, Calculated porewater compositions reflecting variation of MX-80 bentonite properties.



	Variation of bentonite properties			
	No Impurities		Ca-bentonite	
	RPW-NI-C	RPW-NI	RPW-Ca-C	RPW-Ca
	mol/L	mol/L	mol/L	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	3.8560E-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	1.0493E-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	quartz
			calcite	calcite
			gypsum	gypsum
Ionic strength	0.1756	0.1754	0.2634	0.28275

Table C-3. Calculated porewater composition reflecting pH variation of the reference groundwater chemistry (RPW).

	Variaton of GW-pH				
	GW-pH = 10.5			GW-pH = 13.2	
	RPW-pH10.5-C	**RPW-pH10.5-C**	**RPW-pH10.5**	**RPW-pH13.2-C**	**RPW-pH13.2**
	mol/L	mol/L	mol/L	mol/L	mol/L
Na+	2.4802E-01	2.81E-01	2.5476E-01	3.1050E-01	3.0571E-01
K+	5.2928E-04	6.01E-04	5.5014E-04	6.0233E-04	5.9643E-04
Ca^{+2}	1.5303E-02	1.75E-02	1.4387E-02	1.6222E-02	1.2998E-02
Mg^{+2}	3.6909E-03	7.40E-03	3.8234E-03	5.4939E-06	4.9052E-03
CO_3^{-2}	1.2452E-02	1.88E-05	1.4797E-03	1.4967E-05	1.7705E-03
H+	-4.1256E-03	-8.53E-02	-4.3243E-02	-9.0285E-02	-4.9235E-02
Cl-	1.6035E-01	1.60E-01	1.6035E-01	1.6035E-01	1.6035E-01
SO_4^{-2}	4.7791E-02	4.19E-02	4.3089E-02	4.5560E-02	6.3647E-02
$H_2SiO_4^{-2}$	1.0000E-25	1.00E-25	9.9999E-26	1.0000E-25	9.9999E-26
SOH	8.5704E-02	8.57E-02	8.5704E-02	8.5704E-02	8.5705E-02
LAX	3.3087E+00	3.31E+00	3.3087E+00	3.3087E+00	3.3087E+00
pH	6.607	9.84	7.378	11.465	7.457
pCO_2	-1.008	-7.57	-2.6	-10.764	-2.6
	closed	closed	open	closed	open
solids	calcite	calcite	calcite	brucite	calcite
	gypsum	brucite	brucite	gypsum	gypsum
		gypsum		calcite	
Ionic strength	0.2932	0.3039	0.2906	0.3151	0.3338

C.2 Potential influence of very high salinity on porewater composition

For the various reference groundwater conditions illustrated in Figure 4-3, as well as for further groundwater variations that include hyper-alkaline conditions, porewater compositions calculated with a thermodynamic bentonite-water interaction model are given in Appendix C.1. The highest salinity level addressed in Appendix C.1 is represented by the highly saline groundwater that leads to the HSPW porewater with an ionic strength of ca 0.8 M. In addition to these conditions, questions may arise with regard to the potential effect of extremely saline groundwater, such as salt-saturated solutions with an ionic strength of ca 6 M.

As in the case of any groundwater, the effects of extremely saline groundwaters on migration parameters for radionuclides will manifest themselves only through the resulting bentonite porewater composition. Due to a lack of experimental data and adquate calculational tools and concepts for calculating porewater composition in the presence of salt-saturated solutions, only some qualitative assessments can be made:

- When groundwaters of such high ionic strengths have to be considered, it becomes very important whether an electrostatic correction term is used for the water-bentonite edge site interaction. If yes (as in the model by /Wieland et al, 1994/), the high ionic strength will invariably lead to lower pH due to deprotonation of the edge sites, because of the surface-charge vs -potential relationships of electric double layer models (cf /Stumm and Morgan, 1996/. On the other hand, the use of a non-electrostatic model (e.g. the model by /Bradbury and Baeyens, 1997/) will in all likelihood lead to a lesser influence on porewater pH.
- On the other hand, MX-80, as well as other bentonite, contain calcite. Compacted bentonite in combination with a pCO_2 imposed by the host rock formation represents a system that is very well buffered with respect to pH. It is not unlikely that ionic strength effects on pH will only be significant in case of a bentonite buffer closed with respect to CO_2.
- At the same time, it is not clear that the porespace of compacted bentonite can be accessed by a concentrated NaCl solution, due to the permanent negative charge of smectite. It may be speculated that some of the chloride may not able to enter, due to anion exclusion effects.
- Considering the introduction of a concentrated salt solution into the bentonite pores, it cannot be excluded that K_d for most radionuclides could be affected:
  - Competition by high Na concentartions would lower the K_d for Cs, Sr, Ra.
  - Complexation by high chloride concentrations would also lower K_d. This could be sigificant for transition metals and Pb, but possibly also for actinides and lanthanides, in particular in combination with a lowered pH.
  - A significantly lowered pH would lead to a decrease of K_d for most radionuclides.

Appendix D

Thermodynamic sorption models and calculational tools

Calculational tools

The speciation code MIN_SURF and underlying TDB

MIN_SURF /Berner, 1993/ is a surface and solution chemical speciation code based on MINEQL/PSI and DSURF /cf Dzombak and Morel, 1990/. MIN_SURF offers the generalized two-layer/diffuse double layer model to calculate surface complexation reactions in the solid surface/water interface, cf /Dzombak and Morel, 1990; Stumm and Morgan, 1996/. The formalisms used to calculate double layer characteristics are based on /Hunter, 1981/ and /de Levie, 1990/. The BMG-version of MIN_SURF includes the possibility to model ion exchange reactions, using either the mole fraction or equivalent fraction approach /cf Sposito, 1981/ to calculate the activity of the exchanger species. The code MINEQL/PSI corresponds to the code MINEQL/EIR (EIR was the former Swiss Federal Institute for Reactor Research, now named Paul Scherrer Institute, PSI). Under the latter name, it was made available for the NEA data bank in 1986 /OECD/NEA, 1986, 1994/. This code is an extension of the well-known speciation code MINEQL /Westall et al, 1976/ and was developed at EIR as documented in two technical notes /Schweingruber, 1982, 1984/ which are reproduced in the NEA user's guide /OECD/NEA, 1986/. The extension essentially consists in the inclusion of activity coefficients and temperature dependency routines. Ionic strength corrections are done by using the well-known Davies equation.

The TDB used together with the MIN_SURF code includes the contents of the Nagra/PSI TDB, recently updated by /Hummel et al, 2002/. The geochemical core data are from the NEA-TDB project (including the CODATA key values), or from /Nordstrom et al, 1990/.

Bentonite-water model and sorption models used for Ni, Cs, Sr/Ra and Eu

The relevant surface complexation and ion exchange constants for these models are given in the following tables. Both the underlying bentonite-water interaction model as well as the additional ion exchange constant for Cs were taken from the work of Wanner and colleagues. Sorption modelling of Ra and Sr was implemented in the same framework by setting the respective ion exchange constants equal to that of Ca /cf Fletcher and Sposito, 1989/. In case of Ni and Eu, all constants related to the amphoteric edge sites (including surface protolysis constants) were directly taken from the work of Bradbury and Baeyens. Ion exchange was again addressed by the basic bentonite model, using consistent constants for Ni and Eu. Because the protolysis reactions used in the models of Bradbury and Baeyens would lead to a porewater pH that is slightly different from that calculated by the model of Wanner et al, (see section 5.2.5), the pH values for the reference porewaters were imposed in these calculations.

bentonite-water interaction model		
Species	log K^0	Reference
Surface site master species:		Z (ion exchange), log K^0
ZNa	20.00	by definition
ZH	23.00	Wieland et al., (1994)
ZK	20.26	Fletcher & Sposito (1989)
Z_2Mg	40.46^{I}	Wanner et al. (1992)
Z_2Ca	40.53^{I}	Wanner et al. (1992)
Surface site master species:		SOH (surface complexation), log K^0
SOH^{+2}	5.4^{II}	Wanner et al. (1994)
SO^-	-6.7^{II}	Wanner et al. (1994)

I) Corresponding to the equivalent fraction model

II) Corresponding to the diffuse double layer model

Ni		
Species	log K^0	Reference
Surface site master species:		Z (ion exchange), log K^0
ZNa	20.00	by definition
ZH	23.00	Wieland et al., (1994)
ZK	20.26	Fletcher & Sposito (1989)
Z_2Mg	40.46^{I}	Wanner et al. (1992)
Z_2Ca	40.53^{I}	Wanner et al. (1992)
Z_2Ni	40.53^{II}	Lothenbach & Ochs (1999)
Surface site master species: ^{III}		SOH (surface complexation), log K^0
S^sOH^{+2}	4.5	Bradbury & Baeyens (1997)
S^sO^-	-7.9	Bradbury & Baeyens (1997)
$S^{w1}OH_2^+$	4.5	Bradbury & Baeyens (1997)
$S^{w1}O^-$	-7.9	Bradbury & Baeyens (1997)
$S^{w2}OH_2^+$	6	Bradbury & Baeyens (1997)
$S^{w2}O^-$	-10.5	Bradbury & Baeyens (1997)
S^sONi^+	-0.1	Bradbury & Baeyens (1997)
$S^{w1}ONi^+$	-3.1	Bradbury & Baeyens (1997)

I) Corresponding to the equivalent fraction model

II) Set equal to the constant for Ca, based on Fletcher & Sposito (1989) and Bradbury & Baeyens (1997)

III) Corresponding to surface complexation without electrostatic correction term

Cs

Species	log K^0	Reference
Surface site master species:		Z (ion exchange), log K^0
ZNa	20.00	by definition
ZH	23.00	Wieland et al., (1994)
ZK	20.26	Fletcher & Sposito (1989)
Z_2Mg	40.46[I]	Wanner et al. (1992)
Z_2Ca	40.53[I]	Wanner et al. (1992)
ZCs	21.6[I]	Wanner et al., (1996)
Surface site master species:		SOH (surface complexation), log K^0
SOH^{+2}	5.4[II]	Wanner et al. (1994)
SO^-	-6.7[II]	Wanner et al. (1994)

I) Corresponding to the equivalent fraction model
II) Corresponding to the diffuse double layer model

Eu

Species	log K^0	Reference
Surface site master species:		Z (ion exchange), log K^0
ZNa	20.00	by definition
ZH	23.00	Wieland et al., (1994)
ZK	20.26	Fletcher & Sposito (1989)
Z_2Mg	40.46[I]	Wanner et al., (1992)
Z_2Ca	40.53[I]	Wanner et al., (1992)
Z_3Eu	64.6[I]	Wang et al., (1998)
Surface site master species: [II]		SOH (surface complexation), log K^0
S^sOH^{+2}	4.5	Bradbury & Baeyens (1997)
S^sO^-	-7.9	Bradbury & Baeyens (1997)
$S^{w1}OH_2^+$	4.5	Bradbury & Baeyens (1997)
$S^{w1}O^-$	-7.9	Bradbury & Baeyens (1997)
$S^{w2}OH_2^+$	6	Bradbury & Baeyens (1997)
$S^{w2}O^-$	-10.5	Bradbury & Baeyens (1997)
$S^sOEu^{+2} + H^+$	1.8	Bradbury & Baeyens (2002)
$S^sOEuOH^+ + 2H^+$	-5.4	Bradbury & Baeyens (2002)
$S^sOEu(OH)_3^- + 2H^+$	-22.1	Bradbury & Baeyens (2002)
$S^{w1}OEu^{+2} + H^+$	-0.5	Bradbury & Baeyens (2002)

I) Corresponding to the equivalent fraction model
II) Corresponding to surface complexation without electrostatic correction term

Appendix E

Data derivation tables for K_d values

Explanations are provided in the following two tables, see section 5.3.5 for details.

List of evluated radionuclides:

- Americium
- Ceasium
- Carbon: no data derivation table given
- Cerium, holmium, and samarium: K_d derived using Eu as analogue element
- Chloride: no data derivation table given
- Curium: no data derivation table given
- Iodine: no data derivation table given
- Lead
- Neptumium
- Nickel
- Niobium: no data derivation table given
- Palladium: no data derivation table given
- Plutonium
- Protactinium: no data derivation table given
- Radium and strontium
- Radon: no data derivation table given
- Selenium
- Silver: no data derivation table given
- Technetium
- Thorium
- Tin: no data derivation table given
- Uranium
- Zirconium

		A	B	C	D	E	F	G	H	I	J	K	L
	Th(IV)		Conditions								Conversion (C) / Uncertainty (U) Factor(F)		
			Data source (a)	Additional information (b)				Application			CF		
	Solution		SBPW	0.1 M NaClO$_4$				RPW	RPWC	HSPW	RPW	RPWC	HSPW
	Substrate		MX-80	SWy-1	SWy-1	SWy-1	SWy-1	MX-80	MX-80	MX-80	MX-80	MX-80	MX-80
1	CEC	(meq/100g)		87	87	87	87	85.32	85.32	85.32	G1/B1	H1/B1	I1/B1
2	pH		7.6	7.6	7.377	6.59	7.046	7.377	6.59	7.046			
3	K$_d$ for 0.1 M NaClO$_4$ (pH conversion) (b)			355	355	224	224				D3/C3	E3/C3	F3/C3
4	CF-total 1										J1·J3	K1·K3	L1·L3
	Speciation												
5	CF-spec 2		0.0087					0.0018	0.0003	0.0040	G5/B5	H5/B5	I5/B5
6	CF-spec 3		1.0000					1.0000	0.9996	1.0000	G6/B6	H6/B6	I6/B6
7	CF-total 2										J4·J5	K4·K5	L4·L5
8	CF-total 3										J4·J6	K4·K6	L4·L6
											UF		
9	Experimental K$_d$	/g)	63										
10	Predicted K$_d$ (CF-to							B9·J4	B9·K4	B9·L4			
11	UF-starting K$_d$										1.6	1.6	1.6
12	UF-batch -> compac										2.0	2.0	2.0
13	UF-total										J11·J12	K11·K12	L11·L12
14	K$_d$ upper limit							G10·J13	G10·K13	G10·L13			
15	K$_d$ lower limit							G10/J13	G10/K13	G10/L13			
16	Predicted K$_d$ (CF-total 2)	(L/g)						B9·J7	B9·K7	B9·L7			
17	UF-starting K$_d$										1.6	1.6	1.6
18	UF-speciation										1.4	1.4	1.4
19	UF-batch -> compacted										2.0	2.0	2.0
20	UF-total										J17·J18·J19	K17·K18·K19	L17·L18·L19
21	K$_d$ upper limit	(L/g)						G16·J20	G16·K20	G16·L20			
22	K$_d$ lower limit	(L/g)						G16/J20	G16/K20	G16/L20			
23	Predicted K$_d$ (CF-total 3)	(L/g)						B9·J8	B9·K8	B9·L8			
24	UF-starting K$_d$										1.6	1.6	1.6
25	UF-speciation										1.4	1.4	1.4
26	UF-batch -> compacted										2.0	2.0	2.0
27	UF-total										J24·J25·J26	K24·K25·K26	L24·L25·L26
28	K$_d$ upper limit	(L/g)						G23·J27	G23·K27	G23·L27			
29	K$_d$ lower limit	(L/g)						G23/J27	G23/K27	G23/L27			

K$_d$ value for the source data pH condition obtained from the experimental sorption edge

ratio between the calculated sorbing RN-fraction and the total dissolved RN concentration in the source system (CO$_3$ complexes as sorption competitive complexes)

ratio between the calculated sorbing RN-fraction and the total dissolved RN concentration in the source system (no CO$_3$ complexes)

K$_d$ values for the application pH conditions obtained from the experimental sorption-edge

ratio between the calculated sorbing RN-fraction and the total dissolved RN concentration in the application systems (CO$_3$ complexes as sorption competitive complexes)

ratio between the calculated sorbing RN-fraction and the total dissolved RN concentration in the application systems (no CO$_3$ complexes)

experimental K$_d$ value obtained from the corresponding sorption isotherm

specific uncertainty factors

specific uncertainty factors

specific uncertainty factors

ratio between CEC of the application and CEC of the source material. If for both systems the substrates are the same CF-CEC=1

if source data are sorption edge data → pH CF for each pH condition is CF = 1

(a): K$_d$ value from Th(IV) sorption isotherm (NAGRA NRB 02-18)
(b): K$_d$ values from Th(IV) sorption edge (NAGRA NRB 02-18)
SBPW: Synthetic bentonite porewater used in the sorption of Th on MX-80 (Bradbury&Baeyens, 2003)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
	Tc(IV) analogue to Th(IV)		**Conditions**											**Conversion (C) / Uncertainty (U) Factor(F)**		
			Data source (a)	**Additional information (b)**			**Additional information (c)**				**Application**			**CF**		
	Solution		**SBPW**	**RPW**	**RPWC**	**HSPW**	**0.1 M $NaClO_4$**				**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
	Substrate		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**SWy-1**	**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
1	**CEC**	(meq/100g)	79	85.32	85.32	85.32	87	87	87	87	85.32	85.32	85.32	**J1/B1**	**K1/B1**	**L1/B1**
2	**pH**		7.6	7.377	6.59	7.046	7.6	7.377	6.59	7.046	7.377	6.59	7.046			
3	K_d for 0.1 M $NaClO_4$ (pH conversion) (c)		63				355	355	224	224				**G3/F3**	**H3/F3**	**I3/H3**
4	**CF-total 1**													**M1·M3**	**N1·N3**	**O1·O3**
	Speciation															
5	CF-spec 2 (b)			0.0018	0.0003	0.0040					1.0000	0.9998	1.0000	**J5/C5**	**K5/D5**	**L5/E5**
6	CF-spec 3 (b)			1.0000	0.9996	1.0000					1.0000	1.0000	1.0000	**J6/C6**	**K6/D6**	**L6/E6**
7	**CF-total 2**													**M4·M5**	**N4·N5**	**O4·O5**
8	**CF-total 3**													**M4·M6**	**N4·N6**	**O4·O6**
9	**Experimental K_d (a)**	(L/g)	**63.00**											**UF**		
10	**Predicted K_d (CF-total 1)**	(L/g)									**B9·M4**	**B9·N4**	**B9·O4**			
11	UF-starting K_d													1.6	1.6	1.6
12	UF-batch -> compacted													2.0	2.0	2.0
13	UF-total													**M11·M12**	**N11·N12**	**O11·O12**
14	K_d upper limit	(L/g)									**J10·M13**	**K10·N13**	**L10·O13**			
15	K_d lower limit	(L/g)									**J10/M13**	**K10/N13**	**L10/O13**			
16	**Predicted K_d (CF-total 2)**	(L/g)									**B9·M7**	**B9·N7**	**B9·O7**			
17	UF-starting K_d													1.6	1.6	1.6
18	UF-speciation													1.4	1.4	1.4
19	UF-batch -> compacted													2.0	2.0	2.0
20	UF-total													**J17·J18·J19**	**K17·K18·K19**	**L17·L18·L19**
21	K_d upper limit	(L/g)									**J16·M20**	**K16·N20**	**L16·O20**			
22	K_d lower limit	(L/g)									**J16/M20**	**K16/N20**	**L16/O20**			
23	**Predicted K_d (CF-total 3)**	(L/g)									**B9·M8**	**B9·N8**	**B9·O8**			
24	UF-starting K_d													1.6	1.6	1.6
25	UF-speciation													1.4	1.4	1.4
26	UF-batch -> compacted													2.0	2.0	2.0
27	UF-total													**J24·J25·J26**	**K24·K25·K26**	**L24·L25·L26**
28	K_d upper limit	(L/g)									**J23·M27**	**K23·N27**	**L23·O27**			
29	K_d lower limit	(L/g)									**J23/M27**	**K23/N27**	**L23/O27**			

ratio between the calculated sorbing analogue RN-fraction and the total dissolved analogue RN concentration in the source system (CO_3 complexes as sorption competitive complexes)

ratio between the calculated sorbing analogue RN-fraction and the total dissolved analogue RN concentration in the source system (no CO_3 complexes)

ratio between the calculated sorbing RN-fraction and the total dissolved RN concentration in the application systems (CO_3 complexes as sorption competitive complexes)

ratio between the calculated sorbing RN-fraction and the total dissolved RN concentration in the application systems (CO_3 complexes as sorption competitive complexes)

(a): Data from Nagra NTB 02-18 for Th
(b): Th speciation for MX-80 application
(c): pH conversion from Th (Bradbury & Baeyens, unpublished data in Nagra NRB 02-18)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Am(III). Data source: Experimental K_d values for Am(III) sorption on smectite (speciation calculated with TDB of Silva et al., 1995)

Am(III)		**Conditions**						**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)			**Application**			**CF**		
Solution		**0.1 M NaClO$_4$**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**Smectite**	**Smectite**	**Smectite**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	79	79	85.32	85.32	85.32	1.08	1.08	1.08
pH		7.377	6.593	7.046	7.377	6.59	7.046	1	1	1
pCO2		-3.5	-3.5	-3.5	-2.6	-0.98	-2.6			
CF-total 1								1.080	1.080	1.080
Speciation										
CF-spec. 2 (b)		0.792	0.979	0.906	0.505	0.0863	0.334	0.637	0.088	0.368
CF-spec. 3 (b)		1.000	1.000	1.000	0.893	0.5060	0.567	0.893	0.506	0.567
CF-total 2 (b)								0.688	0.095	0.398
CF-total 3 (b)								0.964	0.546	0.613

								UF		
Experimental K_d	(L/g)	**63.10**	**19.95**	**39.81**						
Predicted K_d (CF-total 1)	(L/g)				**68.14**	**21.55**	**43.00**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.4	4.4	4.4
K_d upper limit	(L/g)				*302.4*	*95.6*	*190.8*			
K_d lower limit	(L/g)				*15.36*	*4.86*	*9.69*			
Predicted K_d (CF-total 2) (b)	(L/g)				***43.427***	***1.899***	***15.834***			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				*269.805*	*11.797*	*98.375*			
K_d lower limit	(L/g)				*6.990*	*0.306*	*2.549*			
Predicted K_d (CF-total 3) (b)	(L/g)				***60.827***	***10.904***	***24.387***			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				*377.902*	*67.743*	*151.514*			
K_d lower limit	(L/g)				*9.791*	*1.755*	*3.925*			

(a): Na-smectite at 0.1 M NaClO4 (Gorgeon, 1994). Speciation calculated with TDB of Silva et al., (1995)
(b): Speciation calculated with TDB of Silva et al., (1995)
(c): Speciation calculated with TDB of Guillaumont et al., (2003)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Am(III). Data source: Experimental K_d values for Am(III) sorption on smectite (speciation calculated with TDB of Guillaumont et al., 2003)

Am(III)		**Conditions**						**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)			**Application**			**CF**		
Solution		**0.1 M NaClO$_4$**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**Smectite**	**Smectite**	**Smectite**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	79	79	85.32	85.32	85.32	1.08	1.08	1.08
pH		7.377	6.593	7.046	7.377	6.59	7.046	1	1	1
pCO2		-3.5	-3.5	-3.5	-2.6	-0.98	-2.6			
CF-total 1								1.080	1.080	1.080
Speciation										
CF-spec. 2 (c)		0.441	0.949	0.742	0.107	0.0684	0.267	0.242	0.072	0.360
CF-spec. 3 (c)		1.000	1.000	1.000	0.883	0.8915	0.861	0.883	0.892	0.861
CF-total 2 (c)								0.262	0.078	0.389
CF-total 3 (c)								0.954	0.963	0.930

								UF		
Experimental K_d	(L/g)	**63.10**	**19.95**	**39.81**						
Predicted K_d (CF-total 1)	(L/g)				**68.14**	**21.55**	**43.00**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.4	4.4	4.4
K_d upper limit	(L/g)				*302.4*	*95.6*	*190.8*			
K_d lower limit	(L/g)				*15.36*	*4.86*	*9.69*			
Predicted K_d (CF-total 2) (c)	(L/g)				***16.511***	***1.553***	***15.491***			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				*102.576*	*9.647*	*96.245*			
K_d lower limit	(L/g)				*2.658*	*0.250*	*2.493*			
Predicted K_d (CF-total 3) (c)	(L/g)				***60.202***	***19.211***	***37.022***			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				*374.022*	*119.357*	*230.011*			
K_d lower limit	(L/g)				*9.690*	*3.092*	*5.959*			

(a): Na-smectite at 0.1 M NaClO4 (Gorgeon, 1994). Speciation calculated with TDB of Guillaumont et al., (2003)
(b): Speciation calculated with TDB of Silva et al., (1995)
(c): Speciation calculated with TDB of Guillaumont et al., (2003)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Cs(I). Values calculated based on the model by Wanner et al. (1996)

Cs(I)					**Conversion (C) / Uncertainities (U) Factor(F)**		
Solution		**Application**			**CF**		
Substrate		**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Material		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	85.32	85.32	85.32			
pH		7.377	6.593	7.046			
I	(M)	0.32	0.29	0.76			
pCO_2	(atm)	-2.6	-0.98	-2.6			
					UF		
Calculated Kd (b)	(L/g)	**0.1050**	**0.1030**	**0.0348**			
UF-model					3.0	3.0	3.0
UF-batch -> compacted					2.0	2.0	2.0
UF-total					6.0	6.0	6.0
Kd upper limit	(L/g)	0.6300	0.6180	0.2088			
Kd lower limit	(L/g)	0.0175	0.0172	0.0058			
positive error bar		*0.5250*	*0.5150*	*0.1740*			
negative error bar		*0.0875*	*0.0858*	*0.0290*			

(a): Data-Source for Sr from NAGRA NRTB 02-18 and reference therein

(b): For starting condition Kd value calculated for MX-80 and reference porewater (NAGRA NRTB 02-18)

RPW: Reference porewater (saline Beberg water)

RPWC: Reference porewater (saline Beberg water) for a closed system

HSPW: High saline porewater (Beberg/sea water)

Predicted K_d values for Cs(I). Data source: Experimental K_d values for Cs(I) sorption on MX-80

Cs(II)		Conditions				Conversion (C) / Uncertainty (U) Factor(F)		
		Data source (a)	Application			CF		
Solution		SBPW	RPW	RPWC	HSPW	RPW	RPWC	HSPW
Substrate		MX-80	MX-80	MX-80	MX-80	MX-80	MX-80	MX-80
CEC	(meq/100g)	79	85.32	85.32	85.32	1	1	1
pH		7.6	7.377	6.59	7.046			
pCO2		-3.5	-2.6	-0.98	-2.6			
Na dissolved			0.2518	0.2518	0.6118			
Sum of cations	(mol/L)	6.77E-01	0.2942	0.2863	0.7397	0.43	0.42	1.09
CF-total 1						0.43	0.42	1.09
Speciation								
CsCl/Cs tot		0.21869	0.06492	0.06488	0.23301			
CF-spec						3	3	1
CF-total 2						1.46	1.43	1.03

						UF		
Experimental Kd	(L/g)	**0.050**						
Predicted Kd (CF-total 1)	(L/g)		**0.022**	**0.021**	**0.055**			
UF-starting Kd						1.6	1.6	1.6
UF-cations conversion						2.5	2.5	2.5
UF-batch -> compacted						2.0	2.0	2.0
UF-total						8.0	8.0	8.0
Kd upper limit	(L/g)		0.173	0.169	0.436			
Kd lower limit	(L/g)		0.003	0.003	0.007			
positive error bar			*0.152*	*0.148*	*0.381*			
negative error bar			*0.019*	*0.019*	*0.048*			
Predicted Kd (CF-total 2)	(L/g)		**0.073**	**0.071**	**0.051**			
UF-starting Kd						1.6	1.6	1.6
UF-cations conversion						2.5	2.5	2.5
UF-speciation						1.4	1.4	1.4
UF-batch -> compacted						2.0	2.0	2.0
UF-total						11.1	11.1	11.1
Kd upper limit	(L/g)		0.818	0.796	0.573			
Kd lower limit	(L/g)		0.007	0.006	0.005			
positive error bar			*0.744*	*0.725*	*0.522*			
negative error bar			*0.067*	*0.065*	*0.047*			
Calculated Kd	(L/g)		**0.105**	**0.103**	**0.0348**			

(a): Kd values from NAGRA NRB 02-18
SBPW: Synthetic bentonite porewater used in the sorption of Cs on MX-80 (Bradbury&Baeyens, 2003)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Eu(III). Data source: Experimental K_d values for Eu(III) sorption on MX-80

Eu(III)		**Conditions**								**Conversion (C) / Uncertainty (U) Factor(F)**		
		Source data (a)	**Additional information (b)**				**Application**			**CF**		
Solution		**SBPW**	**0.1 M NaClO$_4$**				**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**MX-80**	**SWy-1 (c)**	**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.6	7.377	6.59	7.046	7.377	6.59	7.046			
K_d for 0.1 M NaClO$_4$	(L/g)		354.81	223.87	35.48	158.49						
CF-pH										0.631	0.100	0.447
CF-total 1										0.631	0.100	0.447
Speciation												
CF-spec 2		0.120					0.052	0.041	0.125	0.437	0.341	1.044
CF-spec 3		0.539					0.57	0.555	0.49	1.054	1.031	0.904
CF-total 2										0.276	0.034	0.466
CF-total 3										0.665	0.103	0.404

										UF		
Experimental K_d	(L/g)	**12.6**										
Predicted K_d (CF-total 1)	(L/g)						**7.94**	**1.26**	**5.62**			
UF-starting K_d										1.6	1.6	1.6
UF-pH-conversion										2.5	2.5	2.5
UF-batch -> compacted										2.0	2.0	2.0
UF-total										7.9	7.9	7.9
K_d upper limit	(L/g)						*62.9*	*10.0*	*44.6*			
K_d lower limit	(L/g)						*1.00*	*0.16*	*0.71*			
Predicted K_d (CF-total 2)	(L/g)						***3.473***	***0.430***	***5.872***			
UF-starting K_d										1.6	1.6	1.6
UF-pH-conversion										2.5	2.5	2.5
UF-speciation										1.4	1.4	1.4
UF-batch -> compacted										2.0	2.0	2.0
UF-total										11.1	11.1	11.1
K_d upper limit	(L/g)						*38.533*	*4.791*	*65.460*			
K_d lower limit	(L/g)						*0.313*	*0.039*	*0.527*			
Predicted K_d (CF-total 3)	(L/g)						***8.376***	***1***	***5.084***			
UF-starting K_d										1.6	1.6	1.6
UF-pH-conversion										2.5	2.5	2.5
UF-speciation										1.4	1.4	1.4
UF-batch -> compacted										2.0	2.0	2.0
UF-total										11.1	11.1	11.1
K_d upper limit	(L/g)						*93.369*	*14*	*56.670*			
K_d lower limit	(L/g)						*0.751*	*0*	*0.456*			

(a) SBPW: Synthetic bentonite porewater used in the sorption of Eu on MX-80 (Bradbury&Baeyens, 2003)
(b) Eu sorption on Swy-1 in 0.1 NaClO4 solution for pH conversion
(c) Starting condition for pH conversion factor calculation
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted and calculated K_d values for Eu(III). Data source: experimental K_d values for Eu(III) sorption on SWy-1 montmorillonite.

Eu(III)		**Conditions**						**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data Source (a)			**Application**			**CF**		
Solution		**0.1 M NaClO4**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**Swy-1**	**Swy-1**	**Swy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	87	87	87	85.32	85.32	85.32	0.98	0.98	0.98
pH		7.377	6.59	7.046	7.377	6.59	7.046	1	1	1
CF-total 1								0.981	0.981	0.981
Speciation										
CF-spec 2		1.000	1.000	1.000	0.052	0.041	0.125	0.052	0.041	0.125
CF-spec 3		1.000	1.000	1.000	0.568	0.555	0.487	0.568	0.555	0.487
CF-total 2								0.051	0.040	0.123
CF-total 3								0.557	0.545	0.477

								UF		
Experimental Kd	(L/g)	**223.87**	**35.48**	**158.49**						
Predicted Kd (CF-total 1)	(L/g)				**219.55**	**34.80**	**155.43**			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.4	4.4	4.4
Kd upper limit	(L/g)				974.29	154.42	689.75			
Kd lower limit	(L/g)				49.47	7.84	35.02			
Predicted Kd (CF-total 2)	(L/g)				***11.52***	***1.43***	***19.47***			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
Kd upper limit	(L/g)				71.557	8.856	120.987			
Kd lower limit	(L/g)				1.854	0.229	3.134			
Predicted Kd (CF-total 3)					***124.68***	***19.32***	***75.68***			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
Kd upper limit					774.618	120.037	470.158			
Kd lower limit					20.069	3.110	12.181			
Calculated Kd (b)					**30.969**	**6.344**	**39.458**			

(a) Eu sorption on Na-SWy-1 in 0.1 NaClO4 solution (Bradbury and Baeyens, 2003b)
(b) Calculated using the thermodynamic sorption model by Bradbury and Baeyens (2002a)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Pb(II). Data source: Experimental K_d values for Pb(II) sorption on montmorillonite

Pb(II)		Conditions						Conversion (C) / Uncertainty (U) Factor(F)		
		Data Source (a)			Application			CF		
Solution		0.1 M NaClO4			RPW	RPWC	HSPW	RPW	RPWC	HSPW
Substrate		montmorillonite			MX-80	MX-80	MX-80	MX-80	MX-80	MX-80
CEC	(meq/100g)	76	76	76	85.32	85.32	85.32	1.12	1.12	1.12
pH		7.377	6.593	7.046	7.377	6.593	7.046	1	1	1
		-3.5	-3.5	-3.5	-2.6	-0.98	-2.6			
CF-total 1								1.12	1.12	1.12
Speciation										
CF-spec. 2		0.9999	1.0000	1.0000	0.9908	0.9907	0.7305	0.9909	0.9907	0.7305
CF-spec. 3		1.0000	1.0000	1.0000	0.9921	0.9922	0.7305	0.9921	0.9922	0.7305
CF-total 2								1.112	1.112	0.820
CF-total 3								1.114	1.114	0.820

								UF		
Experimental K_d	(L/g)	**66.069**	**31.623**	**56.234**						
Predicted Kd (CF-total 1)	(L/g)				**74.17**	**35.50**	**63.13**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.4	4.4	4.4
K_d upper limit	(L/g)				329.15	157.54	280.15			
K_d lower limit	(L/g)				16.71	8.00	14.23			
Predicted K_d (CF-total 2)	(L/g)				**73.50**	**35.17**	**46.12**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				456.63	218.51	286.52			
K_d lower limit	(L/g)				11.83	5.66	7.42			
Predicted K_d (CF-total 3)	(L/g)				**73.58**	**35.22**	**46.12**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				457.16	218.84	286.53			
K_d lower limit	(L/g)				11.84	5.67	7.42			

(a): Pb(II) sorption on montmorillonite (Ulrich & Degueldre, 1993)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Np(IV). Data source: Experimental K_d values for Th(IV) sorption on MX-80.

Np(IV) analogue to Th(IV)			Conditions										Conversion (C) / Uncertainty (U) Factor(F)		
		Data source (a)	**Additional information (b)**			**Additional information (c)**				**Application**			**CF**		
Solution		**SBPW**	**RPW**	**RPWC**	**HSPW**	**0.1 M NaClO4**				**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**SWy-1**	**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	85.32	85.32	85.32	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.377	6.593	7.046	7.6	7.377	6.59	7.046	7.377	6.59	7.046			
Kd for 0.1 M NaClO4 (pH conversion) (a)						355	355	224	224	-2.6	-0.98	-2.6	1.0000	0.6310	0.6310
CF-total 1													1.0000	0.6310	0.6310
Speciation															
CF-spec 2 (b)			0.0018	0.0003	0.0040					0.99988	0.97249	1.00000	551.5263	3.66E+03	251.7173
CF-spec 3 (b)			1.0000	0.9996	1.0000					0.99989	1.00000	1.00000	0.9999	1.0004	1.0000
CF-total 2													551.53	2309.42	158.823
CF-total 3													0.9999	0.6312	0.6310

													UF		
Experimental Kd (a)	(L/g)	63.00													
Predicted Kd (CF-total 1)	(L/g)									**63.0**	**39.8**	**39.8**			
UF-starting Kd													2.5	2.5	2.5
UF-pH-conversion													2.5	2.5	2.5
UF-batch -> compacted													2.0	2.0	2.0
UF-total													12.6	12.6	12.6
Kd upper limit	(L/g)									795.0	501.6	501.6			
Kd lower limit	(L/g)									5.0	3.2	3.2			
Predicted Kd (CF-total 2)	(L/g)									**34746.2**	**145493.5**	**10005.8**			
UF-starting Kd													2.5	2.5	2.5
UF-pH-conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													17.7	17.7	17.7
Kd upper limit	(L/g)									613853.6	2570405.1	176771.2			
Kd lower limit	(L/g)									1966.7	8235.4	566.4			
Predicted Kd (CF-total 3)	(L/g)									**63.0**	**39.8**	**39.8**			
UF-starting Kd													2.5	2.5	2.5
UF-pH-conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													17.7	17.7	17.7
Kd upper limit	(L/g)									1112.9	702.5	702.3			
Kd lower limit	(L/g)									3.6	2.3	2.3			

(a): Data from Nagra NTB 02-18 for Th
(b): Th speciation for MX-80 application
(c): pH conversion from Th (Bradbury & Baeyens, unpublished data in Nagra NRB 02-18)
SBPW: Synthetic bentonite porewater used in the sorption of Th on MX-80 (Bradbury&Baeyens, 2003)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Np(V). Data source: Experimental K_d values for Np(V) sorption on SAz-1.

Np(V)		**Conditions**						**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)			**Application**			**CF**		
Solution		**0.1 M NaNO3**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**SAz-1**	**SAz-1**	**SAz-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	120	120	120	85.32	85.32	85.32	0.711	0.711	0.711
pH		7.377	6.593	7.046	7.377	6.593	7.046	1	1	1
CF-total 1								0.711	0.711	0.711
Speciation										
CF-spec 2		0.94795	0.94794	0.94794	0.897244	0.885968	0.975747	0.947	0.935	1.029
CF-spec 3		0.94795	0.94794	0.94794	0.980163	0.977987	0.995317	1.034	1.032	1.050
CF-total 2								0.673	0.665	0.732
CF-total 3								0.735	0.734	0.747

								UF		
Experimental Kd	(L/g)	**0.034**	**0.020**	**0.031**						
Predicted Kd (CF-total 1)	(L/g)				**0.024**	**0.014**	**0.022**			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.4	4.4	4.4
Kd upper limit	(L/g)				0.107	0.063	0.098			
Kd lower limit	(L/g)				0.005	0.003	0.005			
Predicted Kd (CF-total 2)	(L/g)				**0.023**	**0.013**	**0.023**			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
Kd upper limit	(L/g)				0.142	0.082374	0.141			
Kd lower limit	(L/g)				0.004	0.002134	0.004			
Predicted Kd (CF-total 3)	(L/g)				**0.025**	**0.015**	**0.023**			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
Kd upper limit	(L/g)				0.155	0.090930	0.143			
Kd lower limit	(L/g)				0.004	0.002356	0.004			

(a): Np(V) sorption on SAz-1 Na-montmorillonite in 0.1 M NaNO3 (Turner et al., 1998)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Ni. Data source: experimental K_d values for Ni(II) sorption on MX-80

Ni(II)		Conditions								Conversion (C) / Uncertainty (U) Factor(F)		
		Data source (a)	Additional information (b)				Application			CF		
Solution		SBPW	0.1 M NaClO4				RPW	RPWC	HSPW	RPW	RPWC	HSPW
Substrate		MX-80	Swy-1	Swy-1	Swy-1	Swy-1	MX-80	MX-80	MX-80	MX-80	MX-80	MX-80
CEC	(meq/100g)	79	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.6	7.377	6.59	7.046	7.377	6.59	7.046			
Kd for 0.1 M NaClO4 (pH conversion) (a)	(L/g)		3.162	2.818	0.631	0.891				0.891	0.200	0.282
CF-total 1										0.891	0.200	0.282
Speciation												
CF-spec 2		0.4268					0.572	0.544	0.409	1.340	1.275	0.958
CF-spec 3		0.4273					0.574	0.546	0.409	1.342	1.278	0.958
CF-total 2										1.194	0.254	0.270
CF-total 3										1.196	0.255	0.270

										UF		
Experimental Kd	(L/g)	**0.2512**										
Predicted Kd (CF-total 1)	(L/g)						**0.224**	**0.050**	**0.071**			
UF-starting Kd										1.6	1.6	1.6
UF-pH conversion										2.5	2.5	2.5
UF-batch -> compacted										2.0	2.0	2.0
UF-total										7.9	7.9	7.9
Kd upper limit	(L/g)						1.8	0.4	0.6			
Kd lower limit	(L/g)						0.03	0.01	0.01			
Predicted Kd (CF-total 2)	(L/g)						***0.300***	***0.064***	***0.068***			
UF-starting Kd										1.6	1.6	1.6
UF-pH conversion										2.5	2.5	2.5
UF-speciation										1.4	1.4	1.4
UF-batch -> compacted										2.0	2.0	2.0
UF-total										11.1	11.1	11.1
Kd upper limit	(L/g)						3.328	0.709	0.753			
Kd lower limit	(L/g)						0.027	0.006	0.006			
Predicted Kd (CF-total 3)	(L/g)						***0.300***	***0.064***	***0.068***			
UF-starting Kd										1.6	1.6	1.6
UF-pH conversion										2.5	2.5	2.5
UF-speciation										1.4	1.4	1.4
UF-batch -> compacted										2.0	2.0	2.0
UF-total										11.1	11.1	11.1
Kd upper limit	(L/g)						3.334	0.711	0.752			
Kd lower limit	(L/g)						0.027	0.006	0.006			

(a): Nagra NTB 02-18
(b): Ni sorption data for Na-SWy1 (Baeyens and Bradbury, 1997)
SBPW: Synthetic bentonite porewater used in the sorption of Ni+2 on MX-80 (Table 4 in Nagra NTB 02-18)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted and calculated K_d values for Ni. Data source: experimental K_d values for Ni(II) sorption on SWy-1.

Ni+2		**Conditions**						**Conversion (C) / Uncertainty (U) Factor(F)**		
		Starting (a)			**Application**			**CF**		
Solution		**0.1 M NaClO4**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**Swy-1**	**Swy-1**	**Swy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	87	87	87	85.32	85.32	85.32	0.98	0.98	0.98
pH		7.377	6.59	7.046	7.377	6.59	7.046	1.000	1.000	1.000
CF-total 1								0.981	0.981	0.981
Speciation										
CF-spec. 2		1.000	1.000	1.000	0.5719	0.5442	0.4091	0.572	0.544	0.409
CF-total 2								0.561	0.534	0.401
								UF		
Experimental Kd	(L/g)	**2.8184**	**0.6310**	**0.8913**						
Predicted Kd (CF-total 1)	(L/g)				**2.764**	**0.619**	**0.874**			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.5	4.5	4.5
Kd upper limit	(L/g)							12.4	2.8	3.9
Kd lower limit	(L/g)				0.62	0.14	0.20			
Predicted Kd (CF-total 2)	(L/g)				**1.581**	**0.337**	**0.358**			
UF-starting Kd								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.3	6.3	6.3
Kd upper limit	(L/g)				9.913	2.112	2.243			
Kd lower limit	(L/g)				0.252	0.054	0.057			
Calculated Kd (b)	(L/g)				**4.964**	**1.020**	**1.496**			

(a): Ni sorption data for Na-SWy1 (Baeyens and Bradbury, 1997)
(b): Calculated using the thermodynamic sorption model of Bradbury and Baeyens (1997)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Pu(III). Data source: Experimental K_d values for Am(III) sorption on montmorillonite.

Pu(III) analogue to Am(III)		**Conditions**									**Conversion (C) / Uncertainities (U) Factor(F)**		
		Data Source (a)			**Additional information (b)**			**Application**			**CF**		
Solution		**0.1 M NaClO$_4$**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**Smectite**	**Smectite**	**Smectite**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	79	79	85.32	85.32	85.32	85.32	85.32	85.32	1.08	1.08	1.08
pH		7.377	6.593	7.046	7.377	6.59	7.046	7.377	6.59	7.046	1	1	1
CF-total 1											1.080	1.080	1.080
Speciation													
CF-spec 2 (95Sil/Bid-TDB for Am) (b)	(mol/L)				0.505	0.086	0.334	0.1568	0.0967	0.2659	0.311	1.121	0.797
CF-spec 3 (03Gui/Fan-TDB for Am) (b)	(mol/L)				0.107	0.068	0.267	0.1568	0.0967	0.2659	1.466	1.413	0.994
CF-total 2											0.335	1.210	0.861
CF-total 3											1.583	1.526	1.074

											UF		
Experimental K_d (b)	(L/g)	**63.10**	**19.95**	**39.81**									
Predicted K_d (CF-total 1)	(L/g)							**68.14**	**21.55**	**43.00**			
UF-starting K_d											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											7.0	7.0	7.0
K_d upper limit	(L/g)							*479.3*	*151.6*	*302.4*			
K_d lower limit	(L/g)							*9.69*	*3.06*	*6.11*			
Predicted K_d (CF-total 2)	(L/g)							***21.162***	***24.146***	***34.263***			
UF-starting K_d											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-speciation											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											9.8	9.8	9.8
K_d upper limit	(L/g)							*208.369*	*237.757*	*337.370*			
K_d lower limit	(L/g)							*2.149*	*2.452*	*3.480*			
Predicted K_d (CF-total 3)	(L/g)							***99.901***	***30.448***	***42.749***			
UF-starting K_d											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-speciation											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											9.8	9.8	9.8
K_d upper limit	(L/g)							*983.681*	*299.810*	*420.929*			
K_d lower limit	(L/g)							*10.146*	*3.092*	*4.341*			

(a): Am(III) used as analogue for Pu(III) (Gergeon, 1994)
(b): Am speciation for MX-80 application calculated with different TDB
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Pu(IV). Data source: Experimental K_d values for Th(IV) sorption on MX-80.

Pu(IV), analogy with Th (IV)			**Conditions**										**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)	**Additional information (b)**			**Additional information (c)**				**Application**			**CF**		
Solution		**SBPW**	**RPW**	**RPWC**	**HSPW**	**0.1 M NaClO4**				**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**SWy-1**	**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	85.32	85.32	85.32	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.377	6.593	7.046	7.6	7.377	6.59	7.046	7.377	6.59	7.046			
Kd for 0.1 M NaClO4 (pH conversion) (b)						355	355	224	224				1.0000	0.6310	0.6310
CF-total 1													1.000	0.631	0.631
Speciation															
CF-spec 2			0.0018	0.0003	0.0040					0.0015020	0.0000002	0.0035631	8.28E-01	6.93E-04	8.97E-01
CF-spec 3			1.0000	0.9996	1.0000					0.9985	1.0000	0.9965	0.999	1.000	0.997
CF-total 2													0.82849	0.00044	0.56591
CF-total 3													0.99851	0.63119	0.62876

													UF		
Experimental Kd for Th (a)	(L/g)	**63.00**													
Predicted Kd (CF-total 1)	(L/g)									**63.00**	**39.75**	**39.75**			
UF-starting Kd													2.5	2.5	2.5
UF-pH conversion													2.5	2.5	2.5
UF-batch -> compacted													2.0	2.0	2.0
UF-total													12.6	12.6	12.6
Kd upper limit	(L/g)									*795.0*	*501.6*	*501.6*			
Kd lower limit	(L/g)									*4.99*	*3.15*	*3.15*			
Predicted Kd (CF-total 2)	(L/g)									**52.19**	**0.03**	**35.65**			
UF-starting Kd													2.5	2.5	2.5
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													17.67	17.67	17.67
Kd upper limit	(L/g)									*922.1*	*0.5*	*629.9*			
Kd lower limit	(L/g)									*2.95*	*0.00*	*2.02*			
Predicted Kd (CF-total 3)	(L/g)									**62.91**	**39.76**	**39.61**			
UF-starting Kd													2.5	2.5	2.5
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													17.67	17.67	17.67
Kd upper limit	(L/g)									*1111.3*	*702.5*	*699.8*			
Kd lower limit	(L/g)									*3.56*	*2.25*	*2.24*			

(a): Data from Nagra NTB 02-18 (Bradbury and Baeyens, 2003a) for Th
(b): Th speciation for MX-80 application
(c): pH conversion from Th (Bradbury & Baeyens 2003a)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Pu(V). Data source: Experimental K_d values for Np(V) sorption on Saz-1.

Pu(V) analogue to Np(V)		**Conditions**									**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data Source (a)			**Additional information (b)**			**Application**			**CF**		
Solution		**0.1 M NaNO3**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**SAz-1**	**SAz-1**	**SAz-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	120	120	120	85.32	85.32	85.32	85.32	85.32	85.32	0.711	0.711	0.711
pH		7.377	6.593	7.046	7.377	6.593	7.046	7.377	6.593	7.054	1	1	1
CF-total 1											0.711	0.711	0.711
Speciation													
CF-spec 2 (analogue)					0.8972	0.8860	0.9757	0.8825	0.8696	0.9719	0.984	0.982	0.996
CF-spec 3 (analogue)					0.9802	0.9780	0.9953	1.0000	1.0000	1.0000	1.020	1.023	1.005
CF-total 2											0.699	0.698	0.708
CF-total 3											0.725	0.727	0.714

											UF		
Experimental K_d	(L/g)	**0.034**	**0.020**	**0.031**									
Predicted K_d (CF-total 1)	(L/g)							**0.024**	**0.014**	**0.022**			
UF-starting K_d											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											7.0	7.0	7.0
K_d upper limit	(L/g)							0.169	0.100	0.155			
K_d lower limit	(L/g)							0.003	0.002	0.003			
Predicted K_d (CF-total 2)	(L/g)							**0.024**	**0.014**	**0.022**			
UF-starting K_d											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-speciation											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											9.8	9.8	9.8
K_d upper limit	(L/g)							0.233	0.137103	0.215			
K_d lower limit	(L/g)							0.002	0.001414	0.002			
Predicted K_d (CF-total 3)	(L/g)							**0.025**	**0.015**	**0.022**			
UF-starting K_d											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-speciation											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											9.8	9.8	9.8
K_d upper limit	(L/g)							0.242	0.142831	0.217			
K_d lower limit	(L/g)							0.002	0.001473	0.002			

(a): Np(V) sorption on SAz-1 Na-montmorillonite in 0.1 M $NaNO_3$ (Turner et al., 1998)
(b): Np(V) speciation for MX-80 application
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Pu(VI). Data source: Experimental K_d values for U(VI) sorption on Saz-1.

Pu(VI), analogy with U (VI)		**Conditions**									**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)			**Additional information (b)**			**Application**			**CF**		
Solution		**0.1 M NaNO3**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**Saz-1**	**Saz-1**	**Saz-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	120	120	120	85.32	85.32	85.32	85.32	85.32	85.32	0.711	0.711	0.711
pH		7.377	6.593	7.046	7.377	6.593	7.046	7.377	6.593	7.046	1	1	1
CF-total 1											0.711	0.711	0.711
Speciation													
CF-spec 2 (analogue)					0.03560	0.00455	0.28489	0.59629	0.55225	0.88289	16.750	121.361	3.099
CF-spec 3 (analogue)					1.00000	1.00000	1.00000	0.99297	0.99294	0.98615	0.993	0.993	0.986
CF-total 2											11.9095	86.2877	2.2034
CF-total 3											0.7060	0.7060	0.7012
											UF		
Experimental Kd	(L/g)	**4**	**20**	**4**									
Predicted Kd (CF-total 1)	(L/g)							**2.844**	**14.22**	**2.844**			
UF-starting Kd											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-batch -> compacted											2	2	2
UF-total											7.0	7.0	7.0
Kd upper limit	(L/g)							20.003	100.013	20.003			
Kd lower limit	(L/g)							0.404	2.022	0.404			
Predicted Kd (CF-total 2)	(L/g)							**47.638**	**1725.754**	**8.814**			
UF-starting Kd											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-speciation											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											9.8	9.8	9.8
Kd upper limit	(L/g)							469.074	16992.796	86.784			
Kd lower limit	(L/g)							4.838	175.264	0.895			
Predicted Kd (CF-total 3)	(L/g)							**2.824**	**14.120**	**2.805**			
UF-starting Kd											2.5	2.5	2.5
UF-CEC											1.4	1.4	1.4
UF-speciation											1.4	1.4	1.4
UF-batch -> compacted											2.0	2.0	2.0
UF-total											9.8	9.8	9.8
Kd upper limit	(L/g)							27.807	139.029	27.616			
Kd lower limit	(L/g)							0.287	1.434	0.285			

(a): U(VI) Saz-1 montmorillonite in 0.1 NaNO3 (Pabalan & Turner, 1997)
(b): U(VI) speciation for MX-80 application
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Calculated K_d values for Sr(II) and Ra(II): Thermodynamic sorption model based on the ion exchange constant given for Ca^{2+} in Fletcher and Sposito (1989).

Sr(II) or Ra(II)					**Conversion (C) / Uncertainities (U) Factor(F)**		
Solution		**Application**			**CF**		
Substrate		**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Material		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	85.32	85.32	85.32			
pH		7.377	6.593	7.046			
					UF		
Calculated K_d	(L/g)	**0.0051**	**0.0053**	**0.0013**			
UF-model					3.0	3.0	3.0
UF-batch -> compacted					2.0	2.0	2.0
UF-total					6.0	6.0	6.0
K_d upper limit	(L/g)	0.0308	0.0319	0.0080			
K_d lower limit	(L/g)	0.0009	0.0009	0.0002			

RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Se (IV) Data source: Experimental K_d values for Se(IV) sorption on MX-80. K_d values for Se(VI) are zero.

Se(IV)		**Conditions**								**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data Source (a)	**Additional information (b)**				**Application**			**CF**		
Solution		**SBPW**	**0.1 M $NaClO_4$**				**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**MX-80**	**SWy-1 (c)**	**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.8	7.8	7.377	6.59	7.046	7.377	6.59	7.046			
K_d for 0.1 M $NaClO_4$	(L/g)		0.079	0.1259	0.2512	0.1585				1.58	3.16	2.00
CF-pH conversion												
CF-total 1										1.585	3.162	1.995
Speciation												
CF-spec 2		1.000					0.809	0.963	0.909	0.809	0.963	0.909
CF-total 2										1.283	3.044	1.813

										UF		
Experimental K_d	(L/g)	**0.03**										
Predicted Kd (CF-total 1)	(L/g)						**0.04**	**0.09**	**0.06**			
UF-starting Kd										1.6	1.6	1.6
UF-pH-conversion										2.5	2.5	2.5
UF-batch -> compacted										2.0	2.0	2.0
UF-total										8.0	8.0	8.0
K_d upper limit	(L/g)						*0.4*	*0.7*	*0.4*			
K_d lower limit	(L/g)						*0.01*	*0.01*	*0.01*			
Predicted K_d (CF-total 2)	(L/g)						***0.036***	***0.086***	***0.051***			
UF-starting Kd										1.6	1.6	1.6
UF-pH-conversion										2.5	2.5	2.5
UF-speciation										1.4	1.4	1.4
UF-batch -> compacted										2.0	2.0	2.0
UF-total										11.1	11.1	11.1
K_d upper limit	(L/g)						*0.403*	*0.956*	*0.570*			
K_d lower limit	(L/g)						*0.003*	*0.008*	*0.005*			

(a) SBPW: Synthetic bentonite porewater used in the sorption of Se(IV) on MX-80 (Nagra NTB 02-18)
(b) SeIV sorption on Swy-1 in 0.1 NaClO4 solution for pH conversion
(c) Starting condition for pH conversion factor calculation
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Tc(IV). Data source: Experimental K_d values for Th(IV) sorption on MX-80.

Tc(IV), analogy with Th(IV)		**Conditions**											**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)	**Additional information (b)**			**Additional information (c)**				**Application**			**CF**		
Solution		**SBPW**	**RPW**	**RPWC**	**HSPW**	**0.1 M NaClO4**				**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**SWy-1**	**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	85.32	85.32	85.32	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.377	6.59	7.046	7.6	7.377	6.59	7.046	7.377	6.59	7.046	1	1	1
Kd for 0.1 M NaClO4 (pH conversion) (c)		63				355	355	224	224				1	0.6310	0.6310
CF-total 1													1	0.6310	0.6310
Speciation															
CF-spec 2 (b)			0.0018	0.0003	0.0040					1.0000	0.9998	1.0000	551.59	3763.03	251.72
CF-spec 3 (b)			1.0000	0.9996	1.0000					1.0000	1.0000	1.0000	1.00	1.00	1.00
CF-total 2													551.59	2374.31	158.82
CF-total 3													1.000	0.631	0.631

Experimental Kd (a)	(L/g)	**63.00**											**UF**		
Predicted Kd (CF-total 1)	(L/g)									**63.000**	**39.750**	**39.750**			
UF-starting Kd													4.0	4.0	4.0
UF-pH conversion													2.5	2.5	2.5
UF-batch -> compacted													2.0	2.0	2.0
UF-total													20.0	20.0	20.0
Kd upper limit	(L/g)									1260.000	795.006	795.006			
Kd lower limit	(L/g)									3.150	1.988	1.988			
Predicted Kd (CF-total 2)	(L/g)									**34750**	**149582**	**10006**			
UF-starting Kd													4.0	4.0	4.0
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													28.0	28.0	28.0
Kd upper limit	(L/g)									973011	4188285	280163			
Kd lower limit	(L/g)									1241	5342	357			
Predicted Kd (CF-total 3)	(L/g)									**63.00**	**39.76**	**39.75**			
UF-starting Kd													4.0	4.0	4.0
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													28.0	28.0	28.0
Kd upper limit	(L/g)									1764.01	1113.42	1112.99			
Kd lower limit	(L/g)									2.25	1.42	1.42			

(a) Data from Bradbury and Baeyens (2003a) for Th
(b) Th speciation for MX-80 application
(c) pH conversion based on data for Th reported by Bradbury and Baeyens (2003a)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Th(IV). Data source: Experimental K_d values for Th(IV) sorption on MX-80

Th(IV)		Conditions								Conversion (C) / Uncertainty (U) Factor(F)		
		Data source (a)	Additional information (b)				Application			CF		
Solution		SBPW	0.1 M NaClO4				RPW	RPWC	HSPW	RPW	RPWC	HSPW
Substrate		MX-80	SWy-1	SWy-1	SWy-1	SWy-1	MX-80	MX-80	MX-80	MX-80	MX-80	MX-80
CEC	(meq/100g)	79	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.6	7.377	6.59	7.046	7.377	6.59	7.046			
Kd for 0.1 M NaClO4 (pH conversion) (b)		63	355	355	224	224				1	0.6310	0.6310
CF-total 1										1	0.6310	0.6310
Speciation												
CF-spec 2		0.0087					0.0018	0.0003	0.0040	0.209	0.031	0.457
CF-spec 3		1.0000					1.0000	0.9996	1.0000	1.000	1.000	1.000
CF-total 2										0.209	0.019	0.289
CF-total 3										1.000	0.631	0.631

										UF		
Experimental Kd	(L/g)	**63**										
Predicted Kd (CF-total 1)	(L/g)						**63.096**	**39.811**	**39.811**			
UF-starting Kd										1.6	1.6	1.6
UF-pH conversion										2.5	2.5	2.5
UF-batch -> compacted										2.0	2.0	2.0
UF-total										7.9	7.9	7.9
Kd upper limit	(L/g)						500.000	315.479	315.479			
Kd lower limit	(L/g)						7.962	5.024	5.024			
Predicted Kd (CF-total 2)	(L/g)						**13.168**	**1.218**	**18.206**			
UF-starting Kd										1.6	1.6	1.6
UF-pH conversion										2.5	2.5	2.5
UF-speciation										1.4	1.4	1.4
UF-batch -> compacted										2.0	2.0	2.0
UF-total										11.1	11.1	11.1
Kd upper limit	(L/g)						146.084	13.509	201.981			
Kd lower limit	(L/g)						1.187	0.110	1.641			
Predicted Kd (CF-total 3)	(L/g)						**63.096**	**39.796**	**39.811**			
UF-starting Kd										1.6	1.6	1.6
UF-pH conversion										2.5	2.5	2.5
UF-speciation										1.4	1.4	1.4
UF-batch -> compacted										2.0	2.0	2.0
UF-total										11.1	11.1	11.1
Kd upper limit	(L/g)						699.999	441.507	441.670			
Kd lower limit	(L/g)						5.687	3.587	3.588			

(a) Kd value from Th(IV) sorption isotherm (Bradbury and Baeyens, 2003a)
(b) Kd values from Th(IV) sorption edge (Bradbury and Baeyens, 2003a)
SBPW: Synthetic bentonite porewater used in the sorption of Th on MX-80 (Bradbury and Baeyens, 2003a)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Th(IV). Data source: Experimental K_d values for Th(IV) sorption on SWy-1.

Th(IV)		**Conditions**						**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)			**Application**			**CF**		
Solution		**0.1 M $NaClO_4$**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	87	87	87	85.32	85.32	85.32	0.9807	0.9807	0.9807
pH		7.377	6.59	7.046	7.377	6.59	7.046	1	1	1
CF-total 1								0.9807	0.9807	0.9807
Speciation										
CF-spec 2		1.0000	1.0000	1.0000	0.0018	0.0003	0.0040	0.0018	0.0003	0.0040
CF-spec 3		1.0000	1.0000	1.0000	1.00000	0.99963	1.00000	1.0000	0.9996	1.0000
CF-total 2								0.0018	0.0003	0.0039
CF-total 3								0.9807	0.9803	0.9807

								UF		
Experimental K_d	(L/g)	**355**	**224**	**224**						
Predicted K_d (CF-total 1)	(L/g)				**347.962**	**219.549**	**219.549**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.4	4.4	4.4
K_d upper limit	(L/g)				1544.150	974.293	974.293			
K_d lower limit	(L/g)				78.410	49.474	49.474			
Predicted K_d (CF-total 2)	(L/g)				**0.631**	**0.058**	**0.872**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				3.919	0.362	5.419			
K_d lower limit	(L/g)				0.102	0.009	0.140			
Predicted K_d (CF-total 3) (b)	(L/g)				**347.961**	**219.468**	**219.549**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				2161.808	1363.508	1364.010			
K_d lower limit	(L/g)				56.007	35.325	35.338			

(a): K_d values from NAGRA NRB 02-18

(b): Predicted K_d values are similar to Kd values predicted with CF-total 1

SBPW: Synthetic bentonite porewater used in the sorption of Th on MX-80 (Bradbury&Baeyens, 2003)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for U(IV). Data source: Experimental K_d values for Th(IV) sorption on MX-80

U(IV), analogy with Th(IV)		Conditions												Conversion (C) / Uncertainty (U) Factor(F)		
		Data source (a)	Additional information (b)			Additional information (c)				Application			CF		
Solution		SBPW	RPW	RPWC	HSPW	0.1 M NaClO4				RPW	RPWC	HSPW	RPW	RPWC	HSPW
Substrate		MX-80	MX-80	MX-80	MX-80	SWy-1	SWy-1	SWy-1	SWy-1	MX-80	MX-80	MX-80	MX-80	MX-80	MX-80
CEC	(meq/100g)	79	85.32	85.32	85.32	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.377	6.593	7.046	7.6	7.377	6.59	7.046	7.377	6.593	7.046	1	1	1
Kd for 0.1 M NaClO4 (pH conversion) (c)						355	355	224	224				1	0.6310	0.6310
CF-total 1													1	0.6310	0.6310
Speciation															
CF-spec. 2 analogue (b)			0.001813	0.000266	0.003973					1.000000	1.000000	1.000000	551.5941	3763.7124	251.7174
CF-spec. 3 analogue (b)			0.999999	0.999631	0.999999					1.000000	1.000000	1.000000	1.0000	1.0004	1.0000
CF-total 2													551.5941	2374.7420	158.8229
CF-total 3													1.0000	0.6312	0.6310

													UF		
Experimental Kd (a)	(L/g)	**63.00**													
Predicted Kd (CF-total 1)	(L/g)									**63.00**	**39.75**	**39.75**			
UF-starting Kd													2.5	2.5	2.5
UF-pH conversion													2.5	2.5	2.5
UF-batch -> compacted													2.0	2.0	2.0
UF-total													12.6	12.6	12.6
Kd upper limit	(L/g)									795.006	501.615	501.615			
Kd lower limit	(L/g)									4.992	3.150	3.150			
Predicted Kd (CF-total 2)	(L/g)									**34750**	**149609**	**10006**			
UF-starting Kd													2.5	2.5	2.5
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													17.7	17.7	17.7
Kd upper limit	(L/g)									613929	2643109	176771			
Kd lower limit	(L/g)									1967	8468	566			
Predicted Kd (CF-total 2)	(L/g)									**63.00**	**39.76**	**39.75**			
UF-starting Kd													2.5	2.5	2.5
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													17.7	17.7	17.7
Kd upper limit	(L/g)									1113	703	702			
Kd lower limit	(L/g)									4	2	2			

(a) Kd values from for Th (Bradbury and Baeyens, 2003a)
(b) Th speciation for MX-80 application
(c) pH conversion based on data for Th reported by Bradbury and Baeyens (2003a)
SBPW: Synthetic bentonite porewater used in the sorption of Th on MX-80 (Bradbury and Baeyens, 2003)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for U(VI). Data source: Experimental K_d values for U(VI) sorption on Saz-1

U(VI)		**Conditions**						**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)			**Application**			**CF**		
Solution		**0.1 M NaNO3**			**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**Saz-1**	**Saz-1**	**Saz-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	120	120	120	85.32	85.32	85.32	0.711	0.711	0.711
pH		7.377	6.593	7.046	7.377	6.593	7.046	1	1	1
CF-total 1								0.711	0.711	0.711
Speciation										
CF-spec 2		0.8595	0.9954	0.9669	0.0356	0.0046	0.2849	0.041	0.005	0.295
CF-spec 3		1.0000	0.9998	1.0000	1.0000	1.0000	1.0000	1.000	1.000	1.000
CF-total 2								0.029	0.003	0.210
CF-total 3								0.711	0.711	0.711

								UF		
Experimental K_d	(L/g)	4	20	4						
Predicted K_d (CF-total 1)	(L/g)				**2.844**	**14.22**	**2.844**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								4.4	4.4	4.4
K_d upper limit	(L/g)				12.621	63.104	12.621			
K_d lower limit	(L/g)				0.641	3.204	0.641			
Predicted K_d (CF-total 2)	(L/g)				**0.118**	**0.065**	**0.838**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				0.732	0.404	5.206			
K_d lower limit	(L/g)				0.019	0.010	0.135			
Predicted K_d (CF-total 3)	(L/g)				**2.844**	**14.224**	**2.844**			
UF-starting K_d								1.6	1.6	1.6
UF-CEC								1.4	1.4	1.4
UF-speciation								1.4	1.4	1.4
UF-batch -> compacted								2.0	2.0	2.0
UF-total								6.2	6.2	6.2
K_d upper limit	(L/g)				17.669	88.368	17.670			
K_d lower limit	(L/g)				0.458	2.289	0.458			

(a): U(VI) Saz-1 montmorillonite in 0.1 NaNO3 (Pabalan&Turner, 1997)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Predicted K_d values for Zr(IV). Data source: Experimental K_d values for Th(IV) sorption on MX-80

Zr(IV), analogy with Th (IV)			**Conditions**										**Conversion (C) / Uncertainty (U) Factor(F)**		
		Data source (a)	**Additional information (b)**			**Additional information (c)**				**Application**			**CF**		
Solution		**SBPW**	**RPW**	**RPWC**	**HSPW**	**0.1 M NaClO4**				**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
Substrate		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**SWy-1**	**SWy-1**	**SWy-1**	**SWy-1**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
CEC	(meq/100g)	79	85.32	85.32	85.32	87	87	87	87	85.32	85.32	85.32	1	1	1
pH		7.6	7.377	6.593	7.046	7.6	7.377	6.59	7.046	7.377	6.59	7.046	1	1	1
Kd for 0.1 M NaClO4 (pH conversion) (b)						355	355	224	224				1.0000	0.6310	0.6310
CF-total 1													1.000	0.631	0.631
Speciation															
CF-spec 2			0.0018	0.0003	0.0040					0.0582	0.2735	0.1202	32.1	1029.4	30.3
CF-spec 3			1.0000	0.9996	1.0000					0.0582	0.2735	0.1202	0.058	0.274	0.120
CF-total 2													32.12004	649.52566	19.08855
CF-total 3													0.05823	0.17264	0.07583

													UF		
Experimental Kd for Th (a)	(L/g)	**63.00**													
Predicted Kd (CF-total 1)	(L/g)									**63.00**	**39.75**	**39.75**			
UF-starting Kd													4.0	4.0	4.0
UF-pH conversion													2.5	2.5	2.5
UF-batch -> compacted													2.0	2.0	2.0
UF-total													20.0	20.0	20.0
Kd upper limit	(L/g)									*1260.0*	*795.0*	*795.0*			
Kd lower limit	(L/g)									*3.15*	*1.99*	*1.99*			
Predicted Kd (CF-total 2)	(L/g)									**2023.56**	**40920.12**	**1202.58**			
UF-starting Kd													4.0	4.0	4.0
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													28.00	28.00	28.00
Kd upper limit	(L/g)									*56659.8*	*1145763.3*	*33672.2*			
Kd lower limit	(L/g)									*72.27*	*1461.43*	*42.95*			
Predicted Kd (CF-total 3)	(L/g)									**3.67**	**10.88**	**4.78**			
UF-starting Kd													4.0	4.0	4.0
UF-pH conversion													2.5	2.5	2.5
UF-speciation													1.4	1.4	1.4
UF-batch -> compacted													2.0	2.0	2.0
UF-total													28.00	28.00	28.00
Kd upper limit	(L/g)									*102.7*	*304.5*	*133.8*			
Kd lower limit	(L/g)									*0.13*	*0.39*	*0.17*			

(a) Data from Bradbury and Baeyens (2003a) for Th
(b) Th speciation for MX-80 application
(c) pH conversion based on data for Th reported by Bradbury and Baeyens (2003a)
RPW: Reference porewater (saline Beberg water)
RPWC: Reference porewater (saline Beberg water) for a closed system
HSPW: High saline porewater (Beberg water)

Appendix F

Radionuclide speciation tables

The speciation of each radionuclide was calculated for the main application systems (RPW, RPWC and HSPW) and for the experimental K_d data source system.

The speciation data for each RN are summarized in the following tables.

The conversion factor (CF) for speciation was calculated following equations 5.3a and 5.3b (see text).

The CFs for speciation were calculated in two different ways:

1) Including the RN CO_3 complexes in the sum of the competitive complexes (orange).
2) Excluding the RN CO_3 complexes from the sum of the competitive complexes (blue).

Abbreviation used in the tables:

Dissolved RN complexes which are considered competitive with respect to sorption = RN cmp

Dissolved RN complexes which are considered non competitive with respect to sorption = RN non cmp

Total dissolved RN concentration = RN tot

List of evaluated radionuclides:

- Americium
- Ceasium: no speciation table given
- Carbon: no speciation table given
- Cerium, holmium, and samarium: derived using Eu as analogue element
- Chloride: no speciation table given
- Curium: no speciation table given
- Iodine: no speciation table given
- Lead
- Neptumium
- Nickel
- Niobium: no speciation table given
- Palladium: no speciation table given

- Plutonium
- Protactinium: no speciation table given
- Radium and strontium
- Radon: no speciation table given
- Selenium
- Silver: no speciation table given
- Technetium
- Thorium
- Tin: no speciation table given
- Uranium
- Zirconium

Am(III) speciation (TDB Silva et al., 1995)

System		Application			Data source		
Substrate		MX-80			Na-smectite		
Solution		RPW	RPWC	HSPW	0.1 M NaClO4		
Am^{+3} added							
pH		7.377	6.593	7.046	7.377	6.628	7.136
pCO_2		-2.6	-0.98	-2.6	-3.5	-3.5	-3.5
Am^{+3} dissolved	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-10	1.00E-10	1.00E-10
Am^{+3}	(mol/L)	6.21E-10	6.38E-10	1.49E-09	1.77E-11	6.61E-11	3.68E-11
$AmCl^{+2}$	(mol/L)	1.82E-10	1.86E-10	2.14E-09			
$AmCO_3^+$	(mol/L)	3.52E-09	4.05E-09	2.32E-09	2.07E-11	2.09E-12	9.37E-12
$Am(CO_3)_2^-$	(mol/L)	1.13E-10	1.46E-10	1.61E-11	8.41E-14	2.29E-16	8.30E-15
$Am(CO_3)_3^{-3}$	(mol/L)	2.46E-10	1.49E-12	2.52E-14	5.96E-17	4.39E-21	1.28E-18
$Am(SO_4)^+$	(mol/L)	1.02E-12	3.60E-09	2.06E-09			
$Am(SO4)_2^-$	(mol/L)	8.91E-10	1.15E-09	1.27E-10			
∑ competitive Am complexes (Am-cmp)	(mol/L)	4.95E-09	9.14E-09	6.66E-09	2.08E-11	2.09E-12	9.38E-12
Am tot-Am-cmp	(mol/L)	5.049E-09	8.627E-10	3.34E-09	7.92E-11	9.79E-11	9.06E-11
(Am tot- (Am-cmp)) / Am tot	(mol/L)	**0.505**	**0.086**	**0.334**	**0.79**	**0.98**	**0.91**

Am^{+3} dissolved	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-10	1.00E-10	1.00E-10
Am^{+3}	(mol/L)	6.21E-10	6.38E-10	1.49E-09	1.77E-11	6.61E-11	3.68E-11
$AmCl^{+2}$	(mol/L)	1.82E-10	1.86E-10	2.14E-09			
$AmCO_3^+$	(mol/L)	3.52E-09	4.05E-09	2.32E-09	2.07E-11	2.09E-12	9.37E-12
$Am(CO_3)_2^-$	(mol/L)	1.13E-10	1.46E-10	1.61E-11	8.41E-14	2.29E-16	8.30E-15
$Am(CO_3)_3^{-3}$	(mol/L)	2.46E-10	1.49E-12	2.52E-14	5.96E-17	4.39E-21	1.28E-18
$Am(SO_4)^+$	(mol/L)	1.02E-12	3.60E-09	2.06E-09			
$Am(SO4)_2^-$	(mol/L)	8.91E-10	1.15E-09	1.27E-10			
∑ competitive Am complexes (Am-cmp)	(mol/L)	1.07E-09	4.94E-09	4.33E-09	0.00E+00	0.00E+00	0.00E+00
Am tot-Am-cmp	(mol/L)	8.926E-09	5.060E-09	5.67E-09	1.00E-10	1.00E-10	1.00E-10
(Am tot- (Am-cmp)) / Am tot	(mol/L)	**0.893**	**0.506**	**0.567**	**1.00**	**1.00**	**1.00**

Am(III) speciation (TDB Guillaumont et al., 2003)

System		Application			Data source		
Substrate		MX-80			Na-smectite		
Solution		RPW	RPWC	HSPW	0.1 M NaClO4		
Am^{+3} added		1.00E-08	1.00E-08	1.00E-08	1.00E-10	1.00E-10	1.00E-10
pH		7.377	6.593	7.046	7.377	6.628	7.136
pCO_2		-2.6	-0.98	-2.6	-3.5	-3.5	-3.5
Am^{+3} dissolved	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-10	1.00E-10	1.00E-10
Am^{+3}	(mol/L)	7.80E-10	6.48E-10	2.25E-09	2.92E-11	8.83E-11	6.07E-11
$AmCl^{+2}$	(mol/L)	3.53E-11	2.93E-11	4.99E-10			
$AmCl_2^{+1}$	(mol/L)	1.77E-13	1.46E-13	1.15E-11			
$AmCO_3^+$	(mol/L)	7.00E-09	6.53E-09	5.53E-09	5.40E-11	4.42E-12	2.45E-11
$Am(CO_3)_2^-$	(mol/L)	5.64E-10	5.90E-10	9.67E-11	5.52E-13	1.22E-15	5.44E-14
$Am(CO_3)_3^{-3}$	(mol/L)	8.11E-13	9.56E-13	2.39E-14	6.20E-17	3.71E-21	1.33E-18
$AmHCO_3^{+2}$	(mol/L)	1.96E-10	1.11E-09	3.05E-10	1.26E-12	6.28E-13	1.23E-12
$Am(SO_4)^+$	(mol/L)	1.11E-09	1.03E-09	8.75E-10			
$Am(SO4)_2^-$	(mol/L)	2.23E-11	2.34E-11	3.83E-12			
$AmOSi(OH)_3^{+2}$	(mol/L)	1.71E-15	1.42E-15	4.92E-15			
∑ competitive Am complexes (Am-cmp)	(mol/L)	8.93E-09	9.32E-09	7.33E-09	5.59E-11	5.05E-12	2.58E-11
Am tot-Am-cmp	(mol/L)	1.070E-09	6.842E-10	2.67E-09	4.41E-11	9.49E-11	7.42E-11
(Am tot- (Am-cmp)) / Am tot	(mol/L)	**0.11**	**0.07**	**0.27**	**0.44**	**0.95**	**0.74**
$AmCl^{+2}$	(mol/L)	3.53E-11	2.93E-11	4.99E-10			
$AmCl_2^{+1}$	(mol/L)	1.77E-13	1.46E-13	1.15E-11			
$AmCO_3^+$	(mol/L)	7.00E-09	6.53E-09	5.53E-09	5.40E-11	4.42E-12	2.45E-11
$Am(CO_3)_2^-$	(mol/L)	5.64E-10	5.90E-10	9.67E-11	5.52E-13	1.22E-15	5.44E-14
$Am(CO_3)_3^{-3}$	(mol/L)	8.11E-13	9.56E-13	2.39E-14	6.20E-17	3.71E-21	1.33E-18
$AmHCO_3^{+2}$	(mol/L)	1.96E-10	1.11E-09	3.05E-10	1.26E-12	6.28E-13	1.23E-12
$Am(SO_4)^+$	(mol/L)	1.11E-09	1.03E-09	8.75E-10			
$Am(SO4)_2^-$	(mol/L)	2.23E-11	2.34E-11	3.83E-12			
$AmOSi(OH)_3^{+2}$	(mol/L)	1.71E-15	1.42E-15	4.92E-15			
∑ competitive Am complexes (Am-cmp)	(mol/L)	1.17E-09	1.08E-09	1.39E-09	0.00E+00	0.00E+00	0.00E+00
Am tot-Am-cmp	(mol/L)	8.835E-09	8.915E-09	8.61E-09	1.00E-10	1.00E-10	1.00E-10
(Am tot- (Am-cmp)) / Am tot	(mol/L)	**0.88**	**0.89**	**0.86**	**1.00**	**1.00**	**1.00**

Eu(III) speciation (TDB from Hummel et al., 2002)

System		**Data source**	**Application**			**Data source**	**Application**		
Substrate		**MX-80**	**MX-80**			**MX-80**	**MX-80**		
Solution		**SBPW**	**RPW**	**RPWC**	**HSPW**	**SBPW**	**RPW**	**RPWC**	**HSPW**
Eu^{+3} added	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10
pH		7.6	7.377	6.593	7.046	7.6	7.377	6.593	7.046
pCO_2		-3.5	-2.6	-0.98	-2.6	-3.5	-2.6	-0.98	-2.6
Eu^{+3} dissolved	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10	1.00E-10
Eu^{+3}	(mol/L)	8.79E-12	4.51E-12	4.01E-12	1.16E-11	8.79E-12	4.51E-12	4.01E-12	1.16E-11
$Eu(OH)_4^-$	(mol/L)	1.46E-18	8.15E-20	5.25E-23	1.25E-20	1.46E-18	8.15E-20	5.25E-23	1.25E-20
$EuCO_3^+$	(mol/L)	4.17E-11	5.10E-11	5.09E-11	3.61E-11	4.17E-11	5.10E-11	5.09E-11	3.61E-11
$Eu(CO_3)_2^-$	(mol/L)	1.50E-13	5.17E-13	5.79E-13	7.93E-14	1.50E-13	5.17E-13	5.79E-13	7.93E-14
$EuSO_4^+$	(mol/L)	2.34E-11	2.86E-11	2.85E-11	2.02E-11	2.34E-11	2.86E-11	2.85E-11	2.02E-11
$Eu(SO_4)_2^-$	(mol/L)	3.74E-12	1.29E-11	1.45E-11	1.98E-12	3.74E-12	1.29E-11	1.45E-11	1.98E-12
$EuCl^{+2}$	(mol/L)	1.26E-11	1.48E-12	1.31E-12	1.87E-11	1.26E-11	1.48E-12	1.31E-12	1.87E-11
$EuCl_2^+$	(mol/L)	6.37E-12	1.78E-13	1.57E-13	1.04E-11	6.37E-12	1.78E-13	1.57E-13	1.04E-11
$EuH_3SiO_4^{+2}$	(mol/L)	4.09E-19	1.13E-19	1.65E-20	1.58E-19	4.09E-19	1.13E-19	1.65E-20	1.58E-19
∑ competitive Eu complexes (Eu- cmp)	(mol/L)	8.80E-11	9.48E-11	9.59E-11	8.75E-11	4.61E-11	4.32E-11	4.45E-11	5.13E-11
Eu tot- (Eu-cmp)		1.20E-11	5.25E-12	4.10E-12	1.25E-11	5.39E-11	5.68E-11	5.55E-11	4.87E-11
(Eu tot- (Eu-cmp)) / Eu tot		**0.120**	**0.052**	**0.041**	**0.125**	**0.539**	**0.568**	**0.555**	**0.487**

Pb(II) speciation (TDB Yui et al., 1999)

System		**Application**			**Data Source**		
Substrate		**MX-80**			**Montmorillonite (Ulrich & Degueldre, 1993)**		
Solution		**RPW**	**RPWC**	**HSPW**	**0.1 M $NaClO_4$**		
Pb^{+2} added	(mol/L)	1.00E-11	1.00E-11	1.00E-11	1.00E-11	1.00E-11	1.00E-11
pH		7.377	6.593	7.046	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-3.5	-3.5	-3.5
Pb^{+2} dissolved	(mol/L)	1.00E-11	1.00E-11	1.00E-11	1.00E-11	1.00E-11	1.00E-11
Pb^{+2}	(mol/L)	9.00E-12	8.48E-13	3.79E-13	4.29E-12	9.22E-12	7.25E-12
$PbOH^{+}$	(mol/L)	2.67E-13	4.13E-14	5.73E-14	1.53E-12	5.40E-13	1.21E-12
$Pb(OH)_2$	(mol/L)	1.71E-15	4.33E-17	1.76E-16	1.04E-14	6.03E-16	3.82E-15
$PbCO_3^{+}$	(mol/L)	5.42E-12	5.73E-12	5.57E-13	4.17E-12	2.43E-13	1.54E-12
$PbSO_4^{+}$	(mol/L)	1.42E-12	1.50E-12	1.46E-13			
$PbCl^{+}$	(mol/L)	1.52E-12	1.43E-12	2.97E-12			
$PbCl_2$	(mol/L)	3.76E-13	3.54E-13	3.19E-12			
$Pb(OH)_3^{-}$	(mol/L)	4.69E-19	1.95E-21	2.18E-20	2.68E-18	2.56E-20	4.60E-19
$Pb(CO_3)_2^{-2}$	(mol/L)	1.25E-14	1.48E-14	2.48E-16	9.55E-16	1.50E-18	7.67E-17
$Pb(SO_4)_2^{-2}$	(mol/L)	1.36E-14	1.62E-14	2.70E-16			
$PbCl_3^{-}$	(mol/L)	6.17E-14	5.80E-14	2.16E-12			
$PbCl_4^{-2}$	(mol/L)	3.97E-15	3.73E-15	5.38E-13			
∑ competitive Pb complexes (Pb-cmp)	(mol/L)	9.17E-14	9.27E-14	2.69E-12	9.55E-16	1.50E-18	7.67E-17
Pb tot-(Pb-cmp)	(mol/L)	9.908E-12	9.907E-12	7.305E-12	9.998E-12	1.000E-11	1.000E-11
(Pb tot- (Pb-cmp)) / Pb tot		**0.9908**	**0.9907**	**0.7305**	**0.9999**	**1.0000**	**1.0000**

Pb(II) speciation (TDB Yui et al., 1999)

System		Application			Data Source		
Substrate		MX-80			Montmorillonite (Ulrich & Degueldre, 1993)		
Solution		RPW	RPWC	HSPW	0.1 M $NaClO_4$		
Pb^{+2} added	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-11	1.00E-11	1.00E-11
pH		7.377	6.593	7.046	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-3.5	-3.5	-3.5
Pb^{+2} dissolved	(mol/L)	1.00E-11	1.00E-11	1.00E-11	1.00E-11	1.00E-11	1.00E-11
Pb^{+2}	(mol/L)	9.00E-12	8.48E-13	3.79E-13	4.29E-12	9.22E-12	7.25E-12
$PbOH^{+}$	(mol/L)	2.67E-13	4.13E-14	5.73E-14	1.53E-12	5.40E-13	1.21E-12
$Pb(OH)_2$	(mol/L)	1.71E-15	4.33E-17	1.76E-16	1.04E-14	6.03E-16	3.82E-15
$PbCO_3^{+}$	(mol/L)	5.42E-12	5.73E-12	5.57E-13	4.17E-12	2.43E-13	1.54E-12
$PbSO_4^{+}$	(mol/L)	1.42E-12	1.50E-12	1.46E-13			
$PbCl^{+}$	(mol/L)	1.52E-12	1.43E-12	2.97E-12			
$PbCl_2$	(mol/L)	3.76E-13	3.54E-13	3.19E-12			
$Pb(OH)_3^{-}$	(mol/L)	4.69E-19	1.95E-21	2.18E-20	2.68E-18	2.56E-20	4.60E-19
$Pb(CO_3)_2^{-2}$	(mol/L)	1.25E-14	1.48E-14	2.48E-16	9.55E-16	1.50E-18	7.67E-17
$Pb(SO_4)_2^{-2}$	(mol/L)	1.36E-14	1.62E-14	2.70E-16			
$PbCl_3^{-}$	(mol/L)	6.17E-14	5.80E-14	2.16E-12			
$PbCl_4^{-2}$	(mol/L)	3.97E-15	3.73E-15	5.38E-13			
∑ competitive Pb complexes (Pb-cmp)	(mol/L)	7.93E-14	7.79E-14	2.69E-12	0.00E+00	0.00E+00	0.00E+00
Pb tot-(Pb-cmp)	(mol/L)	9.921E-12	9.922E-12	7.305E-12	9.999E-12	1.000E-11	1.000E-11
(Pb tot- (Pb-cmp)) / Pb tot		**0.9921**	**0.9922**	**0.7305**	**1.0000**	**1.0000**	**1.0000**

NpIV speciation (TDB Hummel et al., 2002)

System		Application			Data Source
Substrate		MX-80			MX-80
Solution		RPW	RPWC	HSPW	SBPW
Np^{+4} added	(mol/L)	1.00E-09	1.00E-09	1.00E-09	1.00E-09
pH		7.377	6.593	7.046	7.6
pCO_2		-2.6	-0.98	-2.6	-3.5
Np^{+4} dissolved	(mol/L)	1.00E-09	1.00E-09	1.00E-09	1.00E-09
Np^{+4}	(mol/L)	2.49E-27	3.34E-24	3.31E-26	2.28E-28
$Np(OH)^{+3}$	(mol/L)	3.65E-21	8.04E-19	2.78E-20	6.47E-22
$Np(OH)_4$	(mol/L)	1.00E-09	9.72E-10	1.00E-09	1.00E-09
$Np(CO_3)_4^{-4}$	(mol/L)	1.28E-14	2.75E-11	3.79E-16	1.85E-17
$Np(CO_3)_5^{-6}$	(mol/L)	4.73E-19	1.15E-15	1.69E-21	1.58E-22
$Np(SO_4)_2$	(mol/L)	1.41E-22	2.39E-19	1.41E-22	2.28E-24
$NpSO_4^{+2}$	(mol/L)	3.73E-24	5.62E-21	1.53E-23	1.56E-25
NpCl	(mol/L)	1.12E-27	1.50E-24	7.73E-26	4.68E-28
∑ competitive Np(IV) complexes (Np(IV) cmp)	(mol/L)	1.28E-14	2.75E-11	3.79E-16	1.85E-17
Np(IV) -tot- Np(IV) cmp		1.00E-09	9.72E-10	1.00E-09	1.00E-09
(Np(IV) tot- Np(IV) cmp / Np(IV) tot		**0.9999**	**0.9725**	**1.0000**	**1.0000**

Np^{+4} dissolved	(mol/L)	1.00E-09	1.00E-09	1.00E-09	1.00E-09
Np^{+4}	(mol/L)	2.49E-27	3.34E-24	3.31E-26	2.28E-28
$Np(OH)^{+3}$	(mol/L)	3.65E-21	8.04E-19	2.78E-20	6.47E-22
$Np(OH)_4$	(mol/L)	1.00E-09	9.72E-10	1.00E-09	1.00E-09
$Np(CO_3)_4^{-4}$	(mol/L)	1.28E-14	2.75E-11	3.79E-16	1.85E-17
$Np(CO_3)_5^{-6}$	(mol/L)	4.73E-19	1.15E-15	1.69E-21	1.58E-22
$Np(SO_4)_2$	(mol/L)	1.41E-22	2.39E-19	1.41E-22	2.28E-24
$NpSO_4^{+2}$	(mol/L)	3.73E-24	5.62E-21	1.53E-23	1.56E-25
NpCl	(mol/L)	1.12E-27	1.50E-24	7.73E-26	4.68E-28
∑ competitive Np(IV) complexes (Np(IV) cmp)	(mol/L)	1.45E-22	2.44E-19	1.57E-22	2.44E-24
Np(IV) -tot- Np(IV) cmp		1.00E-09	1.00E-09	1.00E-09	1.00E-09
(Np(IV) tot- Np(IV) cmp / Np(IV) tot		**0.9999**	**1.0000**	**1.0000**	**1.0000**

Np(V) speciation (TDB Hummel et al., 2002)

System		Application			Data Source		
Substrate		MX-80			Na-montmorillonite (Saz-1)		
Solution		RPW	RPWC	HSPW	0.1 NaNO3		
NpO_2^+ added	(mol/L)	1.00E-07	1.00E-07	1.00E-07	1.00E-07	1.00E-07	1.00E-07
pH		7.377	6.593	7.136	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-3.5	-3.5	-3.5
NpO_2^+ dissoved	(mol/L)	1.00E-07	1.00E-07	1.00E-07	1.00E-07	1.00E-07	1.00E-07
NpO_2^+	(mol/L)	8.97E-08	8.86E-08	9.76E-08	9.48E-08	9.48E-08	9.48E-08
$NpO_2(OH)$	(mol/L)	7.92E-12	1.28E-12	4.13E-12	8.88E-12	1.46E-12	4.15E-12
$NpO_2(OH)_2^-$	(mol/L)	1.28E-16	3.41E-18	3.02E-17	1.35E-16	3.65E-18	2.94E-17
NpO_2SO_4	(mol/L)	1.98E-09	2.20E-09	4.68E-10			
NpO_2NO_3	(mol/L)				5.21E-09	5.21E-09	5.21E-09
$NpO_2(OH)(CO_2)_2^{-4}$	(mol/L)	1.03E-15	2.13E-16	1.60E-17	2.65E-60	6.61E-63	2.34E-61
$NpO_2(CO_2)$	(mol/L)	8.29E-09	9.20E-09	1.96E-09	6.81E-31	8.38E-32	2.95E-31
$NpO_2(CO_2)_2^{-3}$	(mol/L)	3.52E-12	4.40E-12	1.43E-13	1.38E-56	2.10E-58	2.61E-57
$NpO_2(CO2)_3^{-5}$	(mol/L)	4.24E-17	5.98E-17	2.34E-19	4.89E-84	9.14E-87	4.01E-85
∑ competitive NpO_2^+ complexes (NpO2+ cmp)	(mol/L)	1.03E-08	1.14E-08	2.43E-09	5.21E-09	5.21E-09	5.21E-09
(NpO_2^+ tot) - (NpO_2^+ cmp)	(mol/L)	8.97E-08	8.86E-08	9.76E-08	9.48E-08	9.48E-08	9.48E-08
(NpO_2^+ tot- (NpO_2^+ cmp)) / NpO_2^+ tot		**0.897244**	**0.885968**	**0.975747**	**0.947946**	**0.947942**	**0.947944**
NpO_2SO_4	(mol/L)	1.98E-09	2.20E-09	4.68E-10			
NpO_2NO_3	(mol/L)				5.21E-09	5.21E-09	5.21E-09
$NpO_2(OH)(CO_2)_2^{-4}$	(mol/L)	1.03E-15	2.13E-16	1.60E-17	2.65E-60	6.61E-63	2.34E-61
$NpO_2(CO_2)$	(mol/L)	8.29E-09	9.20E-09	1.96E-09	6.81E-31	8.38E-32	2.95E-31
$NpO_2(CO_2)_2^{-3}$	(mol/L)	3.52E-12	4.40E-12	1.43E-13	1.38E-56	2.10E-58	2.61E-57
$NpO_2(CO2)_3^{-5}$	(mol/L)	4.24E-17	5.98E-17	2.34E-19	4.89E-84	9.14E-87	4.01E-85
∑ competitive NpO_2^+ complexes (NpO2+ cmp)	(mol/L)	1.98E-09	2.20E-09	4.68E-10	5.21E-09	5.21E-09	5.21E-09
(NpO_2^+ tot) - (NpO_2^+ cmp)	(mol/L)	9.80E-08	9.78E-08	9.95E-08	9.48E-08	9.48E-08	9.48E-08
(NpO_2^+ tot- (NpO_2^+ cmp)) / NpO_2^+ tot		**0.980163**	**0.977987**	**0.995317**	**0.947946**	**0.947942**	**0.947944**

Ni(II) speciation (TDB Hummel et al., 2002)

Substrate		Application			Data source
Substrate		MX-80			MX-80
Solution		RPW	RPWC	HSPW	SBPW
Ni^{+2} added	(mol/L)	1.00E-07	1.00E-07	1.00E-07	1.00E-07
pH		7.451	6.628	7.136	7.6
pCO_2		-2.6	-0.98	-2.6	-3.5
Ni^{+2} dissolved	(mol/L)	1.000E-07	1.00E-07	1.000E-07	1.00E-07
Ni^{+2}	(mol/L)	5.70E-08	5.44E-08	4.08E-08	4.24E-08
$Ni(OH)_3^-$	(mol/L)	6.21E-16	2.62E-18	4.91E-17	2.29E-15
$Ni(OH)_4^{-2}$	(mol/L)	2.32E-23	1.61E-26	7.83E-25	1.34E-22
$NiCO_3$	(mol/L)	1.72E-10	1.84E-10	3.00E-11	4.94E-11
$Ni(CO_3)_2^{-2}$	(mol/L)	5.85E-14	7.05E-14	1.98E-15	5.47E-15
$NiSO_4$	(mol/L)	2.78E-08	2.98E-08	4.86E-09	7.99E-09
$Ni(SO_4)_2^{-2}$	(mol/L)	5.82E-09	7.02E-09	1.97E-10	5.44E-10
NiCl+	(mol/L)	6.83E-09	6.52E-09	2.26E-08	2.14E-08
$NiCl_2$	(mol/L)	2.17E-09	2.07E-09	3.14E-08	2.74E-08
∑ competitive Ni complexes (Ni-cmp)	(mol/L)	4.28E-08	4.56E-08	5.9089E-08	5.73E-08
Ni tot-Ni cmp with $Ni-CO_3$	(mol/L)	5.72E-08	5.44E-08	4.09E-08	4.27E-08
(Ni tot- (Ni-cmp)) / Ni tot		**0.572**	**0.5442**	**0.4091**	**0.427**
Ni^{+2} dissolved	(mol/L)	1.000E-07	1.00E-07	1.000E-07	1.00E-07
Ni^{+2}	(mol/L)	5.70E-08	5.44E-08	4.08E-08	4.24E-08
$Ni(OH)_3^-$	(mol/L)	6.21E-16	2.62E-18	4.91E-17	2.29E-15
$Ni(OH)_4^{-2}$	(mol/L)	2.32E-23	1.61E-26	7.83E-25	1.34E-22
$NiCO_3$	(mol/L)	1.72E-10	1.84E-10	3.00E-11	4.94E-11
$Ni(CO_3)_2^{-2}$	(mol/L)	5.85E-14	7.05E-14	1.98E-15	5.47E-15
$NiSO_4$	(mol/L)	2.78E-08	2.98E-08	4.86E-09	7.99E-09
$Ni(SO_4)_2^{-2}$	(mol/L)	5.82E-09	7.02E-09	1.97E-10	5.44E-10
NiCl+	(mol/L)	6.83E-09	6.52E-09	2.26E-08	2.14E-08
$NiCl_2$	(mol/L)	2.17E-09	2.07E-09	3.14E-08	2.74E-08
(Ni-cmp)	(mol/L)	4.26E-08	4.54E-08	5.91E-08	5.73E-08
Ni tot-Ni cmp without $Ni-CO_3$	(mol/L)	5.736E-08	5.461E-08	4.094E-08	4.273E-08
(Ni tot- (Ni-cmp)) / Ni tot		**0.574**	**0.546**	**0.409**	**0.427**

Pu(III) speciation (TDB Hummel et al., 2002)

System		Application			Data Source		
Substrate		**MX-80**			**Na-smectite**		
Solution		**RPW**	**RPWC**	**HSPW**	**0.1 M NaClO4**		
Pu^{+3} added	(mol/L)	1.00E-09	1.00E-09	1.00E-09	1.00E-07	1.00E-07	1.00E-07
pH		7.377	6.628	7.046	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-3.5	-3.5	-3.5
precipitated solid							
Pu^{+3} total	(mol/L)	1.00E-09	1.00E-09	1.00E-09	1.00E-07	1.00E-07	1.00E-07
Pu^{+3}		9.45E-11	8.72E-11	1.96E-10	5.28E-08	8.72E-08	7.06E-08
$Pu(OH)^{+2}$	(mol/L)	6.23E-11	9.44E-12	6.98E-11	4.72E-08	1.28E-08	2.94E-08
$PuSO_4^+$	(mol/L)	2.70E-10	3.15E-10	3.34E-11			
$Pu(SO_4)_2^-$		5.34E-10	5.53E-10	3.04E-10			
$PuCl^{+2}$	(mol/L)	3.90E-11	3.59E-11	3.97E-10			
∑ competitive Pu(III) complexes (Pu(III) cmp)	(mol/L)	8.43E-10	9.03E-10	7.34E-10	0.00E+00	0.00E+00	0.00E+00
Pu(III) tot - Pu(III) cmp	(mol/L)	1.57E-10	9.67E-11	2.66E-10	1.00E-07	1.00E-07	1.00E-07
(Pu(III) tot - Pu(III) cmp) / Pu(III) tot		**0.1568**	**0.0967**	**0.2659**	**1.0000**	**1.0000**	**1.0000**

Pu(IV) Speciation (TDB Hummel et al., 2002)

System		Application			Application		
Substrate		MX-80			MX-80		
Solution		RPW	RPWC	HSPW	RPW	RPWC	HSPW
Pu^{+4} added	(mol/L)	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09
pH		7.377	6.593	7.046	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-2.6	-0.98	-2.6
precipitated solid		PuO_2		PuO_2	PuO_2		PuO_2
Pu^{+4} dissolved	(mol/L)	2.16E-12	1.00E-09	4.19E-13	2.16E-12	1.00E-09	4.19E-13
Pu^{+4}	(mol/L)	3.94E-35	1.29E-32	5.24E-34	3.94E-35	1.29E-32	5.24E-34
$Pu(OH)^{+3}$	(mol/L)	2.29E-29	1.21E-27	1.71E-28	2.29E-29	1.21E-27	1.71E-28
$Pu(OH)_2^{+2}$		2.96E-24	2.61E-23	1.21E-23	2.96E-24	2.61E-23	1.21E-23
$Pu(OH)_3^{+}$		2.85E-20	4.11E-20	5.93E-20	2.85E-20	4.11E-20	5.93E-20
$Pu(OH)_4$	(mol/L)	3.16E-17	7.49E-18	3.16E-17	3.16E-17	7.49E-18	3.16E-17
$Pu(OH)_5^{-}$	(mol/L)	3.23E-15	1.26E-16	1.46E-15	3.23E-15	1.26E-16	1.46E-15
$Pu(OH)_3CO_3^{-}$	(mol/L)	5.75E-22	9.33E-22		5.75E-22	9.33E-22	
$PuSO_4^{+2}$	(mol/L)	5.26E-33	1.93E-30	2.16E-32	5.26E-33	1.93E-30	2.16E-32
$Pu(SO_4)^{2}$	(mol/L)	3.16E-31	1.30E-28	3.16E-31	3.16E-31	1.30E-28	3.16E-31
$Pu(SO_4)_3^{-2}$	(mol/L)	1.70E-31	7.89E-29	3.29E-32	1.70E-31	7.89E-29	3.29E-32
$PuCl^{+3}$	(mol/L)	4.45E-36	1.46E-33	3.07E-34	4.45E-36	1.46E-33	3.07E-34
$PuCl_2^{+2}$	(mol/L)	1.16E-36	3.78E-34	3.93E-34	1.16E-36	3.78E-34	3.93E-34
$Pu(CO_3)^{+2}$	(mol/L)	1.32E-23	4.87E-21	5.44E-23	1.32E-23	4.87E-21	5.44E-23
$Pu(CO_3)_2$	(mol/L)	4.00E-16	1.65E-13	4.00E-16	4.00E-16	1.65E-13	4.00E-16
$Pu(CO_3)_3^{-2}$	(mol/L)	2.16E-12	1.00E-09	4.17E-13	2.16E-12	1.00E-09	4.17E-13
$Pu(CO_3)_4^{-4}$	(mol/L)						
$Pu(CO_3)_5^{-6}$	(mol/L)						
∑ competitive Pu(IV) complexes (Pu(IV) cmp)	(mol/L)	2.16E-12	1.00E-09	4.17E-13	4.92E-31	2.11E-28	3.71E-31
Pu(IV) tot - Pu(IV) cmp	(mol/L)	3.25E-15	1.84E-16	1.49E-15	2.16E-12	1.00E-09	4.19E-13
(Pu(IV) tot- Pu(IV) cmp) / Pu(IV) tot		**0.001502**	**0.00000018**	**0.00356**	**1.00**	**1.00**	**1.00**

Pu(V) speciation (Hummel et al., 2002)

System		**Application**		
Substrate		**MX-80**		
Solution		**RPW**	**RPWC**	**HSPW**
PuO_2^+ added	(mol/L)	1.00E-08	1.00E-08	1.00E-08
pH		7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6
PuO_2^+ dissolved	(mol/L)	1.00E-08	1.00E-08	1.00E-08
PuO_2^+		8.80E-09	8.69E-09	9.70E-09
$PuO_2(OH)$	(mol/L)	2.88E-11	4.68E-12	1.53E-11
$PuO_2(CO_3)_3^{-5}$	(mol/L)	1.31E-18	1.85E-18	7.36E-21
$PuO_2(CO_3)^-$	(mol/L)	1.17E-09	1.30E-09	2.81E-10
∑ competitive PuO_2^+ complexes (PuO_2^+ cmp)	(mol/L)	1.17E-09	1.30E-09	2.81E-10
(PuO_2^+ tot)-(PuO_2^+ cmp)	(mol/L)	8.83E-09	8.70E-09	9.72E-09
(PuO_2^+ tot- (PuO_2^+ cmp)) / PuO_2^+ tot		**0.8825**	**0.8696**	**0.9719**
$PuO_2(CO_3)_3^{-5}$	(mol/L)	1.31E-18	1.85E-18	7.36E-21
$PuO_2(CO_3)^-$	(mol/L)	1.17E-09	1.30E-09	2.81E-10
∑ competitive PuO_2^+ complexes (PuO_2^+ cmp)	(mol/L)	0.00E+00	0.00E+00	0.00E+00
(PuO_2^+ tot)-(PuO_2^+ cmp)	(mol/L)	1.00E-08	1.00E-08	1.00E-08
(PuO_2^+ tot- (PuO_2^+ cmp)) / PuO_2^+ tot		**1.0000**	**1.0000**	**1.0000**

Pu(VI) speciation (Hummel et al., 2002)

System		**Application**		
Substrate		**MX-80**		
Solution		**RPW**	**RPWC**	**HSPW**
PuO_2^{+2} added	(mol/L)	7.50E-09	7.50E-09	7.50E-09
pH		7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6
PuO_2^{+2} dissolved	(mol/L)	7.50E-09	7.50E-09	7.50E-09
PuO_2^{+2}	(mol/L)	6.95E-12	6.08E-12	3.99E-11
PuO_2OH^+	(mol/L)	2.11E-10	3.03E-11	6.17E-10
$PuO_2(OH)_2$	(mol/L)	7.42E-11	1.75E-12	1.04E-10
PuO_2CO_3	(mol/L)	4.18E-09	4.10E-09	5.86E-09
PuO_2SO_4	(mol/L)	3.98E-11	3.91E-11	5.58E-11
$PuO_2(SO_4)_2^{-2}$	(mol/L)	1.12E-11	1.24E-11	3.05E-12
$PuO_2(CO_3)_2^{-2}$	(mol/L)	2.84E-09	3.13E-09	7.69E-10
$PuO_2(CO_3)_3^{-4}$	(mol/L)	1.37E-10	1.71E-10	5.69E-12
PuO_2Cl^+	(mol/L)	1.66E-12	1.45E-12	4.42E-11
PuO_2Cl_2	(mol/L)	7.28E-15	6.36E-15	8.44E-13
∑ competitive PuO_2^{+2} complexes (PuO_2^{+2} cmp)	(mol/L)	3.03E-09	3.36E-09	8.78E-10
(PuO_2^{+2} tot)-(PuO_2^{+2} cmp)	(mol/L)	4.47E-09	4.14E-09	6.62E-09
(PuO_2^{+2} tot)-(PuO_2^{+2} cmp) / PuO_2^{+2} tot		0.596290	0.55224956	0.88289
PuO_2SO_4	(mol/L)	3.98E-11	3.91E-11	5.58E-11
$PuO_2(SO_4)_2^{-2}$	(mol/L)	1.12E-11	1.24E-11	3.05E-12
$PuO_2(CO_3)_2^{-2}$	(mol/L)	2.84E-09	3.13E-09	7.69E-10
$PuO_2(CO_3)_3^{-4}$	(mol/L)	1.37E-10	1.71E-10	5.69E-12
PuO_2Cl^+	(mol/L)	1.66E-12	1.45E-12	4.42E-11
PuO_2Cl_2	(mol/L)	7.28E-15	6.36E-15	8.44E-13
∑ competitive PuO_2^{+2} complexes (PuO_2^{+2} cmp)	(mol/L)	5.27E-11	5.30E-11	1.04E-10
(PuO_2^{+2} tot)-(PuO_2^{+2} cmp)	(mol/L)	7.45E-09	7.45E-09	7.40E-09
(PuO_2^{+2} tot)-(PuO_2^{+2} cmp) / PuO_2^{+2} tot		0.992968	0.992936	0.986148

Se(IV) speciation (TDB Grenthe et al., 1990 and Pearson et al., 1991)

System		**Data source**			**Application**		
Substrate		**NaSWy-1**			**MX-80**	**MX-80**	**MX-80**
Solution		**0.1 M $NaClO_4$**			**RPW**	**RPWC**	**HSPW**
Se^{+4} added	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-07	1.00E-07	1.00E-07
pH		7.377	6.593	7.046	7.377	6.593	7.046
pCO_2		-3.5	-3.5	-3.5	-2.6	-0.98	-2.6
SeO_3^{-2} dissolved	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-07	1.00E-07	1.00E-07
H_2SeO_3	(mol/L)	1.74E-13	1.22E-12	4.08E-13	1.58E-12	1.15E-11	3.93E-12
SeO_3^{-2}		1.64E-09	3.12E-10	8.38E-10	1.91E-08	3.72E-09	9.14E-09
$HSeO_3^-$	(mol/L)	8.36E-09	9.69E-09	9.16E-09	8.09E-08	9.63E-08	9.09E-08
∑ competitive Se complexes (Se-cmp)	(mol/L)	8.36E-09	9.69E-09	9.16E-09	8.09E-08	9.63E-08	9.09E-08
(Se(IV) tot - Se(IV)-cmp / Se(IV) tot		**0.8360**	**0.9686**	**0.9161**	**0.8094**	**0.9626**	**0.9086**

Tc(IV) speciation (TDB Guillaumont et al., 2003)

System		Application			Data Source
Substrate		MX-80			MX-80
Solution		RPW	RPWC	HSPW	SBPW
TcO^{+2} added	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10
pH		7.377	6.593	7.046	7.6
pCO_2		-2.6	-0.98	-2.6	-3.5
TcO^{+2} dissolved	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10
TcO^{+2}	(mol/L)	1.45E-25	3.29E-23	1.32E-24	2.93E-26
$TcO(OH)^+$	(mol/L)	4.42E-20	1.64E-18	2.04E-19	1.58E-20
$TcO(OH)_2$	(mol/L)	2.46E-15	1.50E-14	5.44E-15	1.51E-15
$TcO(OH)_3^-$	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10
$TcOCO_3$	(mol/L)	6.95E-17	1.76E-14	1.54E-16	5.40E-18
$TcOCO_3(OH)_3^-$	(mol/L)	1.18E-17	4.91E-16	1.18E-17	1.50E-18
∑ competitive Tc(IV) complexes (Tc(IV)-cmp)	(mol/L)	8.13E-17	1.81E-14	1.65E-16	6.90E-18
Tc(IV) tot-(Tc(IV)-cmp)	(mol/L)	1.000E-10	9.998E-11	1.000E-10	1.000E-10
(Tc(IV) tot- (Tc(IV)-cmp)) / Tc(IV) tot		**0.9999992**	**0.9998186**	**0.9999983**	**0.9999999**
TcO^{+2} dissolved	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10
TcO^{+2}		1.45E-25	3.29E-23	1.32E-24	2.93E-26
$TcO(OH)^+$	(mol/L)	4.42E-20	1.64E-18	2.04E-19	1.58E-20
$TcO(OH)_2$	(mol/L)	2.46E-15	1.50E-14	5.44E-15	1.51E-15
$TcO(OH)_3^-$	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10
$TcOCO_3$	(mol/L)	6.95E-17	1.76E-14	1.54E-16	5.40E-18
$TcOCO_3(OH)_3^-$	(mol/L)	1.18E-17	4.91E-16	1.18E-17	1.50E-18
∑ non competitive TcO^{+2} complexes	(mol/L)	1.00E-10	1.00E-10	1.00E-10	1.00E-10
∑ Tc(IV)-cmp	(mol/L)	-3.51E-16	3.83E-18	2.06E-15	5.40E-15
Tc(IV) tot-(Tc(IV)-cmp)	(mol/L)	1.000E-10	1.000E-10	1.000E-10	9.999E-11
(Tc(IV) tot- (Tc(IV)-cmp)) / Tc(IV) tot without Tc(IV)-CO_3		**1.000**	**1.000**	**1.000**	**1.000**

Th(IV) speciation (TDB Yui et al., 1999)

System		**Application**			**Data Source**
Substrate		**MX-80**			**MX-80**
Solution		**RPW**	**RPWC**	**HSPW**	**SBPW**
Th^{+4} added	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-10
pH		7.377	6.593	7.046	7.6
pCO_2		-2.6	-0.98	-2.6	-3.5
Th^{+4} dissolved	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-10
Th^{+4}	(mol/L)	3.59E-19	7.26E-17	1.05E-17	1.57E-21
$Th(OH)_4$	(mol/L)	1.82E-11	2.66E-12	4.01E-11	8.69E-13
$ThCl^{+3}$	(mol/L)	6.42E-20	1.30E-17	9.79E-18	1.29E-21
$ThCl_2^{+2}$	(mol/L)	8.38E-22	1.69E-19	6.26E-19	7.36E-23
$ThCl_3^{+}$	(mol/L)	2.83E-22	5.70E-20	9.78E-19	1.05E-22
$ThCl_4$	(mol/L)	1.01E-23	2.03E-21	1.52E-19	1.50E-23
$Th(OH)_3CO_3^{-}$	(mol/L)	9.98E-09	9.99E-09	9.96E-09	9.91E-11
$Th(CO_3)_5^{-6}$	(mol/L)	2.06E-19	7.51E-17	1.63E-21	3.30E-24
$ThCO_3$	(mol/L)	9.59E-16	2.17E-13	8.67E-15	1.92E-18
$Th(SO_4)_3^{-2}$	(mol/L)	1.29E-14	3.69E-12	5.49E-15	3.24E-18
∑ competitive Th complexes (Th-cmp) with Th-CO_3	(mol/L)	9.98E-09	1.00E-08	9.96E-09	9.91E-11
Th tot-(Th-cmp)	(mol/L)	1.813E-11	2.657E-12	3.973E-11	8.687E-13
(Th tot- (Th-cmp)) / Th tot		**0.0018129**	**0.0002657**	**0.0039727**	**0.0086871**
$ThCl^{+3}$	(mol/L)	6.42E-20	1.30E-17	9.79E-18	1.29E-21
$ThCl_2^{+2}$	(mol/L)	8.38E-22	1.69E-19	6.26E-19	7.36E-23
$ThCl_3^{+}$	(mol/L)	2.83E-22	5.70E-20	9.78E-19	1.05E-22
$ThCl_4$	(mol/L)	1.01E-23	2.03E-21	1.52E-19	1.50E-23
$Th(OH)_3CO_3^{-}$	(mol/L)	9.98E-09	9.99E-09	9.96E-09	9.91E-11
$Th(CO_3)_5^{-6}$	(mol/L)	2.06E-19	7.51E-17	1.63E-21	3.30E-24
$ThCO_3$	(mol/L)	9.59E-16	2.17E-13	8.67E-15	1.92E-18
$Th(SO_4)_3^{-2}$	(mol/L)	1.29E-14	3.69E-12	5.49E-15	3.24E-18
∑ competitive Th complexes (Th-cmp) without Th-CO_3	(mol/L)	1.29E-14	3.69E-12	5.50E-15	3.24E-18
Th tot-(Th-cmp) without Th-CO4	(mol/L)	9.9999E-09	9.9962E-09	1.0000E-08	1.0000E-10
(Th tot- (Th-cmp)) / Th tot		**0.9999987**	**0.9996314**	**0.9999994**	**0.99999997**

Th(IV) speciation (TDB Yui et al., 1999)

System		**Application**			**Data Source**		
Substrate		**MX-80**			**Na-SWy1 montmorillonite**		
Solution		**RPW**	**RPWC**	**HSPW**	**0.1 $NaClO_4$**		
Th^{+4} added	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-10	1.00E-10	1.00E-10
pH		7.377	6.593	7.046	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-	-	-
Th^{+4} dissolved	(mol/L)	1.00E-08	1.00E-08	1.00E-08	1.00E-10	1.00E-10	1.00E-10
Th^{+4}	(mol/L)	3.59E-19	7.26E-17	1.05E-17	7.49E-19	1.02E-15	1.58E-17
$Th(OH)_4$	(mol/L)	1.82E-11	2.66E-12	4.01E-11			
$ThCl^{+3}$	(mol/L)	6.42E-20	1.30E-17	9.79E-18			
$ThCl_2^{+2}$	(mol/L)	8.38E-22	1.69E-19	6.26E-19			
$ThCl_3^{+}$	(mol/L)	2.83E-22	5.70E-20	9.78E-19			
$ThCl_4$	(mol/L)	1.01E-23	2.03E-21	1.52E-19			
$Th(OH)_3CO_3^{-}$	(mol/L)	9.98E-09	9.99E-09	9.96E-09	4.02E-30	3.01E-30	3.75E-30
$Th(CO_3)_5^{-6}$	(mol/L)	2.06E-19	7.51E-17	1.63E-21			
$ThCO_3$	(mol/L)	9.59E-16	2.17E-13	8.67E-15	3.23E-37	5.44E-35	2.96E-36
$Th(SO_4)_3^{-2}$	(mol/L)	1.29E-14	3.69E-12	5.49E-15			
∑ competitive Th complexes (Th-cmp)	(mol/L)	1.29E-14	3.69E-12	5.50E-15	0.00E+00	0.00E+00	0.00E+00
Th tot-(Th-cmp)	(mol/L)	1.000E-08	9.996E-09	1.000E-08	1.000E-10	1.000E-10	1.000E-10
(Th tot- (Th-cmp)) / Th tot		**0.9999987**	**0.9996314**	**0.9999994**	**1.0000**	**1.0000**	**1.0000**

U(IV) speciation (TDB Grenthe et al., 1992)

System		**Application**			**Application**		
Substrate		**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**	**MX-80**
Solution		**RPW**	**RPWC**	**HSPW**	**RPW**	**RPWC**	**HSPW**
U(IV) added	(mol/L)	1.00E-07	1.00E-07	1.00E-07	1.00E-07	1.00E-07	1.00E-07
pH		7.377	6.593	7.046	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-2.6	-0.98	-2.6
precipitated solids		UO_2	UO_2	UO_2	UO_2	UO_2	UO_2
U(IV) total dissolved	(mol/L)	3.39E-10	3.39E-10	3.39E-10	3.39E-10	3.39E-10	3.39E-10
U(IV)	(mol/L)	4.53E-33	4.58E-30	6.02E-32	4.53E-33	4.58E-30	6.02E-32
$U(OH)^{+3}$	(mol/L)	3.82E-27	6.83E-25	2.91E-26	3.82E-27	6.83E-25	2.91E-26
$U(OH)_4$	(mol/L)	3.39E-10	3.39E-10	3.39E-10	3.39E-10	3.39E-10	3.39E-10
$U(OH)_5^-$	(mol/L)	1.07E-14	1.91E-15	4.84E-15	1.07E-14	1.91E-15	4.84E-15
$U(CO3)_4^{-4}$	(mol/L)	1.86E-23	1.39E-18	1.86E-23	1.86E-23	1.39E-18	1.86E-23
$U(CO3)_5^{-6}$	(mol/L)	7.39E-29	5.14E-23	7.40E-29	7.39E-29	5.14E-23	7.40E-29
USO_4^{+2}	(mol/L)	1.49E-29	5.65E-27	1.49E-29	1.49E-29	5.65E-27	1.49E-29
$U(SO_4)_2$	(mol/L)	7.41E-29	1.29E-25	7.41E-29	7.41E-29	1.29E-25	7.41E-29
UCl^{+3}	(mol/L)	2.33E-31	4.66E-30	2.33E-31	2.33E-31	4.66E-30	2.33E-31
∑ competitive U(IV) complexes (U(IV) cmp)	(mol/L)	1.86E-23	1.39E-18	1.86E-23	8.93E-29	1.35E-25	8.93E-29
U(IV) tot - U(IV) cmp		3.39E-10	3.39E-10	3.39E-10	3.39E-10	3.39E-10	3.39E-10
U(IV) tot - U(IV) cmp / U(IV) tot		**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**

U(VI) speciation (TDB Grenthe et al., 1992)

System		Application			Data source		
Substrate		MX-80			Na-montmorillonite SAz-1		
Solution		RPW	RPWC	HSPW	0.1 M NaNO3		
UO_2^{+2} added	(mol/L)	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09
pH		7.377	6.593	7.046	7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6	-3.5	-3.5	-3.5
UO_2^{+2} dissolved	(mol/L)	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09
UO_2^{+2}	(mol/L)	2.73E-14	2.07E-14	9.07E-13	5.85E-13	2.50E-11	3.06E-12
UO_2CO_3	(mol/L)	3.44E-11	2.92E-11	2.78E-10	1.19E-10	1.37E-10	1.36E-10
$UO_2(OH)_3^{-2}$	(mol/L)	9.21E-12	3.08E-14	3.37E-11	2.36E-10	4.48E-11	1.25E-10
$UO_2(OH)_4^{-6}$	(mol/L)	8.63E-18	7.74E-21	1.35E-17	1.84E-16	5.75E-18	4.57E-17
$(UO_2)_3(OH)_7^-$	(mol/L)	2.98E-22	4.15E-28	7.14E-20	5.68E-18	1.43E-18	3.92E-18
$UO_2(CO_3)_2^{-2}$	(mol/L)	2.74E-09	2.62E-09	4.28E-09	9.45E-10	2.95E-11	2.34E-10
$(UO_2)(CO_3)_3^{-4}$	(mol/L)	4.49E-09	4.84E-09	1.07E-09	9.47E-11	7.98E-14	5.12E-12
$(UO_2)_2(CO_3)(OH)_3^{-3}$	(mol/L)	1.62E-13	4.62E-16	4.80E-12	1.44E-11	3.15E-12	8.73E-12
$UO_2NO_3^+$	(mol/L)				4.33E-14	1.85E-12	2.27E-13
$(UO_2)_{11}(CO_3)_6(OH)_{12}^{-2}$	(mol/L)	1.00E-56	1.00E-77	4.97E-57	5.30E-56	7.00E-57	4.90E-56
∑ competitive U(VI) complexes (U(VI) cmp)	(mol/L)	7.23E-09	7.47E-09	5.36E-09	1.05E-09	3.46E-11	2.48E-10
U(VI) tot - U(VI) cmp	(mol/L)	2.67E-10	3.41E-11	2.14E-09	6.45E-09	7.47E-09	7.25E-09
U(VI) tot - U(VI) cmp / U(VI) tot		**0.035599**	**0.004550**	**0.284893**	**0.859482**	**0.995393**	**0.966866**
UO_2^{+2} dissolved	(mol/L)	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09
UO_2^{+2}	(mol/L)	2.73E-14	2.07E-14	9.07E-13	5.85E-13	2.50E-11	3.06E-12
UO_2CO_3	(mol/L)	3.44E-11	2.92E-11	2.78E-10	1.19E-10	1.37E-10	1.36E-10
$UO_2(OH)_3^{-2}$	(mol/L)	9.21E-12	3.08E-14	3.37E-11	2.36E-10	4.48E-11	1.25E-10
$UO_2(OH)_4^{-6}$	(mol/L)	8.63E-18	7.74E-21	1.35E-17	1.84E-16	5.75E-18	4.57E-17
$(UO_2)_3(OH)_7^-$	(mol/L)	2.98E-22	4.15E-28	7.14E-20	5.68E-18	1.43E-18	3.92E-18
$UO_2(CO_3)_2^{-2}$	(mol/L)	2.74E-09	2.62E-09	4.28E-09	9.45E-10	2.95E-11	2.34E-10
$(UO_2)(CO_3)_3^{-4}$	(mol/L)	4.49E-09	4.84E-09	1.07E-09	9.47E-11	7.98E-14	5.12E-12
$(UO_2)_2(CO_3)(OH)_3^{-3}$	(mol/L)	1.62E-13	4.62E-16	4.80E-12	1.44E-11	3.15E-12	8.73E-12
$UO_2NO_3^+$	(mol/L)				4.33E-14	1.85E-12	2.27E-13
$(UO_2)_{11}(CO_3)_6(OH)_{12}^{-2}$	(mol/L)	1.00E-56	1.00E-77	4.97E-57	5.30E-56	7.00E-57	4.90E-56
∑ competitive U(VI) complexes (U(VI) cmp)	(mol/L)	0.00E+00	0.00E+00	0.00E+00	4.33E-14	1.85E-12	2.27E-13
U(VI) tot - U(VI) cmp	(mol/L)	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09	7.50E-09
U(VI) tot - U(VI) cmp / U(VI) tot		**1.000000**	**1.000000**	**1.000000**	**0.999994**	**0.999754**	**0.999970**

Zr(IV) speciation (TDB Hummel et al., 2002)

System		**Application**		
Substrate		**MX-80**		
Solution		**RPW**	**RPWC**	**HSPW**
Zr^{+4} added	(mol/L)	1.00E-09	1.00E-09	1.00E-09
pH		7.377	6.593	7.046
pCO_2		-2.6	-0.98	-2.6
solids		ZrO_2	ZrO_2	ZrO_2
Zr^{+4} dissolved	(mol/L)	4.31E-11	9.18E-12	2.09E-11
Zr^{+4}	(mol/L)	4.96E-30	6.86E-27	6.61E-29
$Zr(OH)^{+3}$	(mol/L)	2.83E-23	6.42E-21	2.15E-22
$Zr(OH)_4$	(mol/L)	2.51E-12	2.51E-12	2.51E-12
$Zr(OH)_5^-$	(mol/L)	4.06E-11	6.67E-12	1.84E-11
$ZrCl^{+3}$	(mol/L)	2.23E-30	3.08E-27	1.54E-28
$Zr(SO_4)^{+2}$	(mol/L)	1.05E-26	1.63E-23	4.31E-26
∑ competitive Zr complexes (Zr-cmp)	(mol/L)	4.06E-11	6.67E-12	1.84E-11
Zr tot-(Zr-cmp)	(mol/L)	2.512E-12	2.512E-12	2.512E-12
(Zr tot- (Zr-cmp)) / Zr tot		**0.0582313**	**0.2735142**	**0.1201876**

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