

**R-06-75**

# **Data and uncertainty assessment for radionuclide Kd partitioning coefficients in granitic rock for use in SR-Can calculations**

James Crawford, Ivars Neretnieks, Maria Malmström  
Department of Chemical Engineering and Technology  
Royal Institute of Technology (KTH)

October 2006

**Svensk Kärnbränslehantering AB**

Swedish Nuclear Fuel  
and Waste Management Co  
Box 5864  
SE-102 40 Stockholm Sweden  
Tel 08-459 84 00  
+46 8 459 84 00  
Fax 08-661 57 19  
+46 8 661 57 19



ISSN 1402-3091

SKB Rapport R-06-75

# **Data and uncertainty assessment for radionuclide $K_d$ partitioning coefficients in granitic rock for use in SR-Can calculations**

James Crawford, Ivars Neretnieks, Maria Malmström  
Department of Chemical Engineering and Technology  
Royal Institute of Technology (KTH)

October 2006

This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

A pdf version of this document can be downloaded from [www.skb.se](http://www.skb.se)

## Abstract

SKB is currently preparing licence applications related to the proposed deep repository for spent nuclear fuel as well as the encapsulation plant required for canister fabrication. The present report is one of several specific data reports that form the data input to an interim safety report (SR-Can) for the encapsulation plant licence application.

This report concerns the derivation and recommendation of generic  $K_d$  data (i.e. linear partitioning coefficients) for safety assessment modelling of far-field radionuclide transport in fractured granitic rock. The data are derived for typical Swedish groundwater conditions and rock types distinctive of those found on the Simpevarp peninsula and Forsmark.

Data have been derived for 8 main elements (Cs, Sr, Ra, Ni, Th, U, Np, Am) and various oxidation states. The data have also been supplied with tentative correction factors to account for artefacts that have not been previously considered in detail in previous compilations. For the main reviewed solutes the data are given in terms of a best estimate  $K_d$  value assumed to be the median of the aggregate set of selected data. A range corresponding to the 25–75% inter-quartile range is also specified and probable ranges of uncertainty are estimated in the form of an upper and lower limit to the expected variability. Data for an additional 19 elements that have not been reviewed are taken from a previous compilation by /Carbol and Engkvist 1997/.

# Sammanfattning

SKB förbereder en ansökan för en inkapslingsanläggning för använt kärnbränsle. Denna rapport är en i en serie som levererar specifika data till säkerhetsredovisningen (SR-Can) som ingår i ansökan.

Rapporten gäller framtagandet av data (fördelningskoefficienter) som används för beräkningar av radionuklidtransport i berg. De framtagna data är representativa för svenska förhållanden och är specifikt ämnade för grundvatten och bergarter typiska för Simpevarphalvön och Forsmarksområdet.

Data har framtagits för 8 prioriterade ämnen (Cs, Sr, Ra, Ni, Th, U, Np, Am) med diverse oxidationstillstånd. Dessa data är levererade tillsammans med korrektionsfaktorer för att preliminärt korrigera för felaktigheter som inte har tagits upp i detalj i andra tidigare studier. Osäkerhetsintervall har även angivits för varje ämne i form av ett "best estimate" värde som antas vara medianvärdet på den utvalda datauppsättningen. Ett intervall som motsvarar 25–75% procentilintervallet samt en övre och lägre gräns för den förväntade parametervariationen också anges. Data för ytterligare 19 ämnen som har inte detaljstuderats är tagna från en tidigare sammanställning av /Carbol och Engkvist 1997/.

# Extended summary and road map

This work has brought out several questions that have not been discussed in depth or quantified in previous compilations of sorption data. They give rise to considerable uncertainties when attempting to recommend  $K_d$  values and their uncertainties for use in safety assessment modelling.

They arise mainly from the following considerations:

1. Sorption measurements are made on crushed samples in the laboratory (crushing induces the formation of new surfaces).
2. In situ rock has not been disturbed in the same way that bore cores and other excavated material may be.
3. In situ rock is under lithostatic stress that compresses pores and may shut off some pores.
4. Water formulations used in laboratory experiments are mostly synthetic and may not contain all relevant trace substances present in formation waters.
5. Contact times for sorption measurements in the laboratory vary and data generally are not evaluated with consideration of experimental artefacts that may cause bias.
6. Often crucial information on experimental conditions is lacking or poorly documented in literature sources.
7.  $K_d$  values are reported per mass of solid, but there is reason to believe that they should be normalised with regard to sorption surface area and reported as  $K_a$  values instead.

In this work we have attempted to bound the effects of items 1–3 to together lower correctly measured and reported laboratory data to values appropriate for in situ conditions in Swedish granitic rock.

Items 4–7 and other items not mentioned above are sometimes element specific, from what we have seen in the analysis made so far. Some appreciation of the difficulties can be gained by consideration of the large span of reported laboratory derived  $K_d$  values. They typically span over 2–4 orders of magnitude for seemingly similar conditions.

Owing to the time constraints of SR-Can, we have examined sorption data for a sub-group of nuclides in detail (Cs, Sr, Ra, Ni, Th, U, Np, Am) in order to provide updated estimates of  $K_d$ . Data for nuclides that we have not had opportunity to examine in detail have been taken from the previous compilation of radionuclide sorption coefficients by /Carbol and Engkvist 1997/. Some of the nuclides that we have not reviewed in detail may be important for uncertainty estimates of far-field activity release in SR-Can. These will be reviewed and updated data provided as they become available.

Our aim in this work has been to examine the geochemistry of each nuclide in detail as an aid to understanding element specific characteristics, as well as to provide a thorough analysis of literature data sources in a rigorous and transparent manner. The lack of detailed and transparent analysis of data sources has been a major criticism of previously compiled sorption databases /McKinley and Scholtis 1993/. All reviewed data are detailed in a separate master table for each radionuclide set up in a spreadsheet program (MS Excel). For transparency and traceability, these tables contain both an initial compilation of data obtained from the open literature and other sorption databases as well as a smaller subset of data selected to be relevant for application within SR-Can (data sheets are available from the main author upon request). The inclusion of both data sets in the master table allows the user to be fully aware of criteria used for data selection.

The selected  $K_d$  data is presented in the form of a “best estimate” for granitic rock under laboratory reference conditions. In addition, a subjectively estimated range of uncertainty is given in the form of the 25–75% interquartile range and a lower and upper bound for the aggregate set of selected data. Correction factors are also tentatively supplied to account for items 1–3 in the list of confounding variables described above.

The main findings are described in somewhat more detail below:

## Overview of main findings

The authors of this report have reviewed sorption data from the open literature and from proprietary databases for the purpose of recommending a set of generic partitioning coefficients ( $K_d$  data) for use in the SR-Can Safety Assessment. In addition to the acquisition of  $K_d$  data, efforts were made towards defining conditions of applicability for the  $K_d$  approach itself within safety assessment (SA) as well as defining and quantifying sources of uncertainty.

There are many factors that influence radionuclide sorption. Some of these factors are well defined, or at least reasonably easy to identify in a safety analysis as important variables influencing sorption variability. Principal variables of this kind might include rock-type, mineral surface area, temperature, ionic strength, pH, redox state, the presence or absence of complexing ligands, and radionuclide concentration.

Although there are many caveats that restrict the usage of  $K_d$  data, it is thought that the general approach is sound and scientifically defensible in a broad sense, provided that appropriate values are chosen for the modelled repository conditions. When the scientific basis for data selection is ambiguous, as is frequently the case with sorption data acquired from the open literature, expert judgment takes on a particularly important role.

Most of the databases that have been used in previous safety assessments involving crystalline rock give intervals for  $K_d$  data that appear to be mutually consistent. A problem, however, is that there appears to have been very little critical evaluation of data sources (i.e. documented analysis) in these previous efforts and the criteria for selection are frequently less than transparent. It is not always obvious why certain data sets have been selected while others have been rejected, nor why a subset of sorption data from a particular source is considered more relevant than other data that is neglected.

For compilations of recommended  $K_d$  data to be credible, detailed documentation must be supplied to support expert decisions that are made in their selection or derivation /McKinley and Scholtis 1993/. The authors of this report believe that this has not been done previously in a sufficiently rigorous manner for the selection and recommendation process to be transparent. The fact that different data compilations recommend similar central values and ranges of uncertainty does not establish that the data is correct, as confirmation bias tends to influence the selection process. Experimental data that is used as a basis for  $K_d$  recommendations must be thoroughly documented in the database or compilation to avoid the “validation snowball” effect whereby badly executed experiments or poorly reported data are given equal weight and implicit validity amongst “good” data owing to the absence of corroborating information for critical analysis.

In this report, we have attempted to thoroughly review all available data and give a detailed analysis explaining the range of behaviour observed by different researchers. This is done partly to enable the modeller to decide if the recommended data is truly applicable for the situation being modelled, as well as to convey a subjective perception of the data uncertainty that cannot be adequately captured by a probability distribution. All relevant data for individual radionuclides has also been documented in a spreadsheet format in order to facilitate intercomparison.

Uncertainty appears at a number of different levels in the acquisition and use of  $K_d$  data. In order to define aggregate uncertainties in a traceable fashion we have considered three different levels:

**1. Uncertainty in the recommended  $K_d$  data itself**

This includes sources of random error, mineralogical variability of rock samples, subtle differences in water chemistry, methodological flaws in measurement and interpretation, documentation flaws, as well as sources of systematic bias (“frame shift” and “frame dilation”).

**2. Uncertainty related to the use of generic data in site-specific SA**

Application conditions may not exactly match the conditions under which the experimental data have been obtained. This could potentially include both differences in water chemistry as well as the use of generic data for rock types where site-specific data is unavailable.

**3. Uncertainty in the application conditions**

It is not possible to know the actual flow paths and rock types that a water package encounters while flowing through fractured rock and consequently, the material properties averaged over a representative volume (block) is uncertain. In addition, the future state of relevant geochemical parameters may not be accurately known owing to transient flow effects that have not been well characterised.

Some sources of uncertainty are expected to impact upon SA predictions in a random fashion. These are called irreducible or “aleatory” uncertainties and are relatively straightforward to deal with in a stochastic analysis, as the exact value is known to be always somewhere within the range of the stated distribution of possible values. Other, so-called “epistemic” uncertainties relate to a lack of understanding or knowledge about a system and cannot usually be dealt with in the framework of a probability distribution. Often, however, the distinction between the two is imprecise.

The experimentally derived  $K_d$  data incorporates many forms of uncertainty that are difficult to tease apart. Some components of this uncertainty may be “averaged out” along a flowpath and some components will remain. The stochastic variability of the material properties when averaged over a representative volume may then have a narrower or broader probability distribution than the original data.

Previously, uncertainty ranges given for the compiled generic  $K_d$  data have been used directly for assigning uncertainties in SA models without reflection upon the wider implications of the underlying assumptions. In light of the different levels of uncertainty outlined above, the authors of this report believe that this is an incorrect use of  $K_d$  data, as the assigned values clearly do not represent appropriate uncertainties for risk analysis. This has not been handled well in previous safety assessments.

An epistemic uncertainty that has not been handled well in previous investigations is the role of systematic bias, in the experimental acquisition of  $K_d$  data. This uncertainty may not be visible in safety assessment predictions, as it may not have even been considered in the analysis. A particularly egregious aspect of this bias in the context of  $K_d$  data is that all literature sources may be similarly affected, possibly leading to a significant overestimation of recommended  $K_d$  values. To describe this, we use the term “frame shift” bias as it highlights the fact that we are dealing with a unidirectional shift in the true value of a parameter that may lie well outside the recommended probability range. Other forms of bias that have no preferred direction relative to the true range of variability are referred to here as “frame dilation” biases or uncertainties. These are subtly different to what in the risk literature is sometimes referred to as “expert overconfidence” /e.g. Hammit and Shlyakhter 1999, Bier 2004/. Expert overconfidence relates to the use of overly optimistic bounds of uncertainty, but does not specifically consider a systematic shift of the data baseline in a given direction, nor frame dilation effects, both of which relate to the representativity of laboratory data relative to in situ conditions.

During the course of this work it has become increasingly apparent that there may be substantial biases that must be accounted for in order to recommend credible  $K_d$  data.

We have attempted to focus upon two principal sources of bias that have serious implications for  $K_d$  data recommendations. The first relates to the use of crushed rock materials in the acquisition of  $K_d$  data. It is customary for sorption measurements to be made using samples that are crushed and sieved. Moreover, many groups choose to use small size fractions as they can be expected to reach equilibrium quickly. The process of crushing rock samples produces additional surfaces for sorption that results in a substantial tendency to overestimate  $K_d$  values. This is a well-known deficiency of sorption databases /e.g. Vandergraaf et al. 1993/, although it is rarely mentioned in  $K_d$  data compilations.

Although sorption site density is not the same for all minerals, the  $N_2$ -BET surface area is a reasonably good proxy for estimating sorption surface areas. It is clear from the literature data that crushed material typically has a sorption surface area 10–100 times larger than that of intact rock pieces. Furthermore, in situ electrical measurements of effective diffusivity give values that are consistently an order of magnitude lower than those measured in the laboratory. It is thought that some of this discrepancy may be due to the closing of pores in the in situ rock matrix as a result of formation stresses as well as damage acquired during drilling and bore core retrieval. It is therefore conceivable that the effects of formation stresses and sampling artefacts could upwardly bias the estimated available surface area for sorption in situ.

As well as the creation of new sorption surfaces in crushed rock material, there is evidence to suggest that  $K_d$  values may be biased by neglect of additional processes relating to contact time and the apparent time dependency of sorption processes. It is currently unclear whether this leads to a positive or negative bias in the aggregate data set as the physical interpretation of time dependent sorption characteristics is currently unclear. The dynamic behaviour typically observed in sorption experiments could represent physicochemical phenomena that are relevant for the parameterisation of in situ rock sorption properties or could represent experimental artefacts that lead to substantial overestimation of  $K_d$  values.

Sorption measurements are regularly carried out with contact times of a week or less, and occasionally with contact times less than a day. Most experiments are carried out with a contact time of 2–3 weeks, and only few data relate to contact times longer than perhaps a month. From the ranges of contact times reported in the literature it is clear that the bulk of experiments will be influenced to a greater or lesser degree by this.

## **Content and organisation of the present report**

The present report deals with the estimation and recommendation of generic  $K_d$  data for in situ conditions in fractured granitic rock typical for the Simpevarp peninsula and Forsmark. The recommended data takes the form of a “best estimate” for each radionuclide as well as ranges of uncertainty given for the expected variation. There is neither sufficient resolution in the aggregate data set, nor evidence that the observed variation is a result of true geochemical variability for the rigorous estimation of probability density functions for in situ  $K_d$  uncertainty. The recommended data are derived based upon thorough examination and critical evaluation of the literature data, although the choices of individual data sets and ranges are ultimately subjective in nature.

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

- The recommended data and uncertainty ranges are detailed for individual solutes in Chapter 5 and summarised in Chapter 7. The rationale for the derivation procedure is outlined in Chapter 6.



- General discussions on data sources and treatment of uncertainties are given in Chapters 3 and 4.
- Detailed analysis of parameters influencing  $K_d$  values is given in Chapter 5 together with detailed analysis of literature data and geochemistry of individual nuclides.
- Chapters 1 and 2 provide a general introduction and explain the purpose of the present report in SR-Can.

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 that the reader consult the pertinent sections of the process report for background information.

# Contents

<b>1</b>	<b>Introduction</b>	13
1.1	Background	13
1.1.1	Planned safety assessments	13
1.1.2	Assessing input data – need for traceable expert decision	13
1.2	Scope and objectives	14
1.2.1	Specific objectives	14
1.2.2	Limitations in scope	14
1.3	Procedure for data and uncertainty assessment	15
1.3.1	Predefined instructions	15
1.3.2	Experts involved	15
<b>2</b>	<b>Use in SR-Can</b>	17
2.1	Application to SR-Can conditions	17
2.1.1	Instructions – issues to be addressed	17
2.1.2	Conditions for which data are supplied	17
2.2	Models	25
2.2.1	Instructions – issues to be addressed	25
2.2.2	Codes used for far-field radionuclide transport calculations	25
2.2.3	Differences in models for different conditions	25
2.3	Results of sensitivity analysis – if any?	25
2.3.1	Instructions – issues to be addressed	25
2.3.2	Sensitivity of partitioning coefficient data	26
<b>3</b>	<b>Sources of information</b>	27
3.1	Databases	27
3.1.1	Instructions – issues to be addressed	27
3.1.2	Databases for partitioning coefficient data	27
3.2	Modelling etc	28
3.2.1	Instructions – issues to be addressed	28
3.2.2	Modelling used to support the data	28
<b>4</b>	<b>Evaluation of sources affecting uncertainty</b>	31
4.1	Overview	31
4.1.1	Instructions – issues to be addressed	31
4.1.2	Experts view (overall uncertainties)	31
4.2	Uncertainty related to different conditions	32
4.2.1	Instructions – issues to be addressed	32
4.2.2	Conditions affecting partitioning coefficients	33
4.3	Conceptual uncertainties	35
4.3.1	Instructions – issues to be addressed	35
4.3.2	Conceptual uncertainties affecting partitioning coefficients	35
4.4	Data uncertainty, spatial and temporal variation	37
4.4.1	Instructions – issues to be addressed	37
4.4.2	Spatial, temporal and site specific variation	38
4.4.3	Lack of knowledge, errors etc	41
4.5	Correlations	51
4.5.1	Instructions – issues to be addressed	51
4.5.2	Correlations among partitioning coefficients for specific radionuclides and parameters influencing partitioning coefficient data	51

<b>5</b>	<b>Quantification of data and uncertainties</b>	55
5.1	Methods and approaches for uncertainty estimation	55
5.1.1	Instructions – issues to be addressed	55
5.1.2	General approach	55
5.2	Conditions for which parameter values are to be supplied	58
5.2.1	Instructions – issues to be addressed	58
5.2.2	Water type	58
5.2.3	Rock type	62
5.2.4	Mineral surface area and sorption site density	62
5.2.5	Redox state	63
5.2.6	Radionuclide concentration	63
5.3	Data and uncertainty estimates	64
5.3.1	Instructions – issues to be addressed	64
5.3.2	Alkali and alkaline earth metals	65
5.3.3	Lanthanides	76
5.3.4	Actinides	76
5.3.5	Transition elements	89
5.3.6	Other elements	92
<b>6</b>	<b>Rationale for derivation of recommended values including upper and lower bounds</b>	93
<b>7</b>	<b>Concluding remarks and summary of recommended, generic <math>K_d</math> data for sorption in granitic rocks</b>	97
<b>8</b>	<b>References</b>	101
<b>Appendix A</b>	Water classification of the Simpevarp area used as reference groundwaters in this investigation	117
<b>Appendix B</b>	Water compositions used for sorption experiments as reported in source literature references	119

# 1 Introduction

This document concerns data and uncertainty assessment of radionuclide  $K_d$  partitioning coefficients in granitic rock 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 be associated with 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 used 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).

The authors of the present report emphasise strongly that the prioritisation of specific radionuclides based upon their impact upon contribution to total dose in safety assessment is only partially established insofar as all relevant interactions involving the specific radionuclide and its environment have been elucidated. It is therefore necessary to continuously re-evaluate radionuclides that may have previously been downgraded in importance in the light of updated information relating to variables which may potentially alter their status. This is particularly relevant for (although not exclusively restricted to) radionuclides currently perceived to be strongly sorbing although known to be influenced considerably by projected geochemical conditions which may be amended in future safety case scenarios.

### 1.2.1 Specific objectives

This report supplies data with uncertainty to the following SR-Can parameter(s):

- Recommended distribution coefficients ( $K_d$  values) for relevant radionuclides in generic rock types of granitic nature.

### 1.2.2 Limitations in scope

Only a small sub-group of nuclides (Cs, Sr, Ra, Ni, Th, U, Np, Am) have been examined in detail to provide updated estimates of  $K_d$  for use in safety assessment. The focus upon this sub-group has been necessitated by time constraints within the SR-Can programme and will need to be expanded as appropriate in future versions of this document to encompass all other radionuclides of relevance for safety assessment. The choice is in part motivated by the selection of radionuclides outlined in /Widestrand et al. 2003/ for use within the site investigation programme. The chosen radionuclides are intended to represent a broad range of oxidation states and chemical behaviour that can be partly extrapolated to other radionuclides by way of geochemical analogy.

Data for other, non-reviewed nuclides have been taken from the previous compilation by /Carbol and Engkvist 1997/.

In addition to the compiled  $K_d$  data, a procedure of applying correction factors is described to account for experimental biases which render the sorption data non-representative for in situ conditions. This has not been considered in detail in previous compilations. Currently, only surface area effects (relating to the use of crushed material in laboratory sorption measurements) are considered in a rudimentary and somewhat subjective fashion, although the authors note that a more detailed analysis of measurement biases would be considered prudent in future compilations.

## 1.3 Procedure for data and uncertainty assessment

### 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

#### ***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 its content? (CV etc may be supplied as appendices).
- What has been their 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 radionuclide partitioning coefficients

The scientific content and judgements made in this report are made by the report authors; Dr. James Crawford (Kemakta Konsult AB), Professor Ivars Neretnieks and Dr. Maria Malmström (Department of Chemical Engineering and Technology, Division of Chemical Engineering, Royal Institute of Technology (KTH), Stockholm).

## 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 concerns the interface between safety assessment and the specific model, the content is produced jointly by SKB and the experts producing this document.

### 2.1 Application to SR-Can conditions

#### 2.1.1 Instructions – issues to be addressed

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.

#### 2.1.2 Conditions for which data are supplied

Only sorption processes as described by the linear  $K_d$  concept are treated in this report. When assessing the retention properties of rock, the key parameters are effective diffusivity  $D_e$  (m<sup>2</sup>/s) and the storage capacity of the rock  $K_d^* \rho_b$  (–) incorporating both sorbed concentration on mineral surfaces as well as that dissolved in the water-filled porosity of the rock matrix. Issues concerning matrix effective diffusivity and porosity are dealt with in a companion report to this current document /Liu et al. 2006 (in preparation)/.

The partitioning coefficient data delivered in this report is primarily intended for the following applications:

- Modelling within safety assessments.
- Interpretation of laboratory and in situ experiments.

For safety assessment, partitioning coefficient data representative for the rock and geochemical conditions at repository depth are required. The data that is of interest for far-field transport modelling encompasses the rock volume on the order of about 1 km<sup>3</sup>, surrounding the repository. Data specific for repository depth and the nearest geological blocks adjoining the repository are expected to be of particular importance for safety assessment. The “block” referred to here means the representative elementary volume (REV) or otherwise relevant scale used for modelling purposes. Additionally, the data should also reflect the possibility of slowly changing geochemical conditions over time as a result of glaciation-deglaciation cycles.

Data pertaining to altered, or otherwise weathered rock immediately adjacent to flow channels, possible fracture filling materials, as well as unaltered matrix rock at some distance from the fractures is of interest. For safety assessment, however, the properties of the unaltered matrix rock may be of greater importance than the properties of either fracture filling materials or altered rock. This depends, of course, upon the effective matrix penetration depth experienced by the migrating solute and the relative retention properties of the altered and unaltered rock. The influence of alteration layers, however, has not been established conclusively and further work will need to be done to resolve this issue.

The partitioning coefficient or  $K_d$  value is simply the ratio of immobilised and dissolved solute that is specific for a particular solid phase composition, water chemistry, and solute concentration. It is an empirical “snap-shot” of a system that is only strictly applicable under those exact

conditions under which it is measured and is not explicitly dependent upon any specific sorption mechanism or speciation considerations. In this report we consider the notion of  $K_d$  as relating purely to adsorptive interaction of radionuclides with the surfaces of geologic materials which occurs principally by way of the association of ionic solutes with charged mineral surfaces. In this definition we specifically exclude non-sorption processes such as precipitation and surface precipitation, although we note that under certain conditions and high surface loadings the transitional distinction may not be absolutely clear. Although defined to only consider sorption processes, we note that laboratory measurements of  $K_d$  typically do not discriminate between different partitioning mechanisms and expert judgement must therefore be exercised in data selection.

Sorption of ionic solutes is usually described as being an ion-exchange or surface complexation process. In the former, solutes sorb at permanently charged sites at mineral surfaces that arise by way of isomorphic substitutions within mineral crystals (typically layered silicates). A sorbing solute with a higher affinity will generally displace a cation of lower affinity already occupying these permanently charged sites, hence the expression ion-exchange. The sorption is purely electrostatic in nature and tends to be relatively weak and sensitive to ionic strength owing to mass action effects (i.e. when a high concentration of a poorly sorbing cation out-competes the more strongly sorbing solute). Surface complexation occurs at variably charged sites which arise through aqueous protonation/deprotonation reactions of surface oxide groups of mineral crystals. Surface complexation can be both electrostatic (outer-sphere complexation) or be the result of covalent bond formation with surface groups (inner-sphere complexation). Similarly to ion-exchange, outer-sphere complexes are sensitive to ionic strength effects. Inner sphere complexes, on the other hand, are largely insensitive to ionic strength effects (neglecting secondary speciation considerations). Owing to pH-dependent charge of the surface functional groups, both outer sphere and inner sphere complexes are strongly influenced by pH.

Thereby, the use of a constant  $K_d$  value in transport modelling is usually contingent upon the following conditions being fulfilled:

- The modelled process is a true (equilibrium) sorption process.
- The water chemistry, mineralogy, and physical state of the rock are identical to those used in partitioning coefficient data acquisition and do not vary in time or space.
- The solute concentration range encountered along the transport path (for the radionuclide of interest) must not invalidate the fundamental assumption of sorption linearity.

There are many factors that influence sorption partitioning coefficients. Some of these factors are well defined, or at least reasonably straightforward to identify in a safety analysis as important variables influencing  $K_d$  variability. Principal variables of this kind might include rock-type and alteration, mineral surface area, temperature, ionic strength, pH, redox state, and radionuclide concentration. There may be uncertainty concerning the state of these variables owing, for example, to the often transient nature of water chemistry when samples are taken from boreholes, or perhaps variation in the distribution of different rock types surrounding the repository. These are often referred to as “aleatory uncertainties”, or uncertainties relating to random variation of known variables within well-defined limits.

Other factors are less easily defined and do not necessarily relate to potentially observable variables, but rather to questions of data applicability. These questions may include, for example:

Are the experimentally derived measurement data for  $K_d$  values sufficiently unambiguous and actually appropriate for the postulated conditions in the repository environment? (Perhaps even more importantly, can sorption processes be reasonably assumed to be responsible for SA-scale radionuclide retardation, or do we need to consider other geochemical processes such as precipitation and co-precipitation?)

What physical phenomena do the experimentally determined  $K_d$  values actually represent?



Do there possibly exist latent variables in the experimentally derived  $K_d$  values that undermine confidence in their validity for the given scenario?

Are the rock types encountered by flowing water approximately representative of the bulk rock volume?

These questions relate to “epistemic uncertainty”, or uncertainty due to inaccurate or incomplete knowledge about the system.

Although the distinction between these two principal forms of uncertainty is often vague and imprecise, they both have important consequences for the level of confidence that is appropriate when interpreting safety assessment calculations. It should also be emphasised that some of the aleatory uncertainties given above could arguably be classified as epistemic uncertainties depending upon our level of system understanding. Aleatory uncertainty is relatively transparent and straightforward to deal with when stochastic modelling is used in safety assessment. Epistemic uncertainty, on the other hand, is frequently hidden in assumptions and boundary conditions of the system and is much more difficult to distinguish.

In safety assessment, the requirement of constant conditions along a transport path is rarely met in a rigorous sense. For spatial variation, averaging of properties along a flowpath may be required /Neretnieks 2002, SKB 2004c/. Provided that the  $K_d$  variation can be adequately characterised by knowledge of lithological and geochemical heterogeneity, flowpath averaging of the so-called materials property group (MPG) can be shown to be rigorous. In an alternative approach,  $K_d$  values can be assigned at “run-time” (i.e. during calculations) from a parametric equation (a response surface) or look-up table that incorporates major variables of influence through multivariate regression.

Some variation (temporal variation, for example, due to saltwater or freshwater intrusion) is difficult to handle in a rigorous fashion owing to coupling between the solute mass balance equations and the variables that influence the partitioning coefficients. To deal with this rigorously requires more sophisticated modelling techniques; this is the realm of process-based, mechanistic modelling.

The added complexity of solving coupled transport equations introduces further uncertainty that is not easy to quantify in a transparent manner. Owing to the computational difficulty most safety assessment models do not use mechanistic approaches directly within transport calculations. Parametric data from statistically based or thermodynamic sorption models (TSM's), however, have been used to abstract site-specific data and associated probability distribution functions, or PDF's for use in stochastic simulation models /Vandergraaf et al. 1993, Turner et al. 1999, Turner and Pabalan 1999/. This is the principal means by which aleatory uncertainty is currently integrated into safety assessment codes.

The authors of this report note that there have been considerable advances in the use of thermodynamic sorption models (TSMs) for the modelling of sorption processes on complex, heterogeneous substrates since the mid 1990's. TSMs are uniquely suited for this purpose owing to the possibility of elucidating the effects of variable geochemistry on sorption equilibria in a coherent and internally consistent manner that serves to reduce uncertainty in the transfer of data from reference conditions to uncertain or variable in situ conditions. Such mechanistic approaches thus far have been used to support understanding of sorption processes in model systems and in a limited extent for the prediction of  $K_d$  values, although the use of such models directly in safety assessment as a replacement for  $K_d$  values is generally not done. The reader is directed to the Phase II report from the NEA sorption forum for a more detailed discussion on the state of the art with regard to sorption modelling using TSMs /NEA 2005/.

The use of TSMs for the prediction of  $K_d$  data is beyond the scope of this report and in the current investigation we have restricted ourselves to a survey of published measurement data. The authors strongly recommend, however, that TSM supported data analysis be considered in future investigations for the reduction of uncertainties associated with  $K_d$  selection for safety assessment applications and as a complement to the data compiled in this survey.

The actual conditions for which data is used will vary according to what scenario is being contemplated. In addition, the way in which the data is used (e.g. if flowpath averaging is employed) will also vary amongst different simulation codes. The choice of data and the way in which it is used is ultimately a partially subjective choice made by the modeller and it is very much up to the skill of the modeller to determine whether the  $K_d$  chosen for the system in question is indeed appropriate. Provided that an appropriate  $K_d$  is chosen for the modelled system and that the solution chemistry isn't subject to large variations in composition (pH, Eh, ionic strength, etc), the methodology is scientifically defensible and robust in a broad sense.

Historically, the goal of safety assessment has generally not been to model solute transport and retardation processes exactly as they would be observed in nature. Indeed, /McKinley and Scholtis 1993/ state that instead, “the primary objective is to establish a theoretically based picture of potential radiological risk associated with different scenarios of waste repository evolution. When applying linear  $K_d$  sorption data to such analyses, even when such an approach may not be strictly valid, approximate  $K_d$  values should be chosen to ensure that they conservatively overpredict radiological consequences”. This, of course, should also be balanced against the requirement to provide realistic and not over-conservative estimates which can be detrimental for overall system understanding and confidence building with regard to safety analyses. The  $K_d$  values used in safety assessment should therefore be chosen judiciously to be appropriate for the task at hand and the timescales considered. In this sense, a clear distinction must be drawn between the objectives of site characterisation and safety assessment. Notwithstanding this, however, as our knowledge of site specific conditions and understanding of sorption processes becomes more sophisticated, the data used in safety assessment should be continuously reviewed with the aim of simulating the repository system in as much detail as is reasonably possible given the prevailing level of characterisation and system understanding.

It is the opinion of the authors that the quality of presently available sorption data in the open literature is not sufficiently good to permit the use of statistically regressed parametric equations in safety assessment applications. Their use may, in fact, be counterproductive in safety assessment as they lend an appearance of accuracy that belies their inherent uncertainty. Instead, the aim of this report is to streamline the  $K_d$  data selection process by reducing the currently available partitioning coefficient data into a set of approximately representative groups that give reasonable estimates and associated uncertainties for specific in situ conditions and a reduced set of primary variables. We therefore identify the following items to be of major significance for  $K_d$  data selection:

### ***Rock type***

In this parameter we consider both the basic rock-type (i.e. granite, granodiorite, etc) as well as any relevant descriptors that refer to alteration and weathering. Here, we consider classifications such as mylonite and cataclasite to be structural/textural sub-categories of a parent rock-type. Recognising the fact that rock types in the site investigation subareas encompass a number of different major and subordinate rock types that are not necessarily granites, we use the term “granitic rock” in a more general sense where we loosely include the entire family of crystalline, intrusive igneous rocks comprising granite, granodiorite, diorite, gabbro and their various intermediate forms that are characteristic of the site investigation areas at Forsmark and Simpevarp/Laxemar.

In this report alteration is taken to mean the extent to which both tectonic and hydrothermal processes have changed the material properties of the rock matrix adjacent to fractures. Tectonic processes generally change the physical structure of the rock by way of shear forces. On the other hand, hydrothermal alteration or weathering is taken to be any process that by way of chemical interaction (e.g. dissolution-precipitation resulting from hydrothermal interactions) changes the identity of mineral phases comprising the rock. It may also be relevant to introduce additional descriptors, discriminating granitic rocks from different locations (distinguishing between, for example, Olkiluoto, Stripa, or Finnsjön granite). This may help in understanding data variations that may not be immediately apparent in the basic rock-type descriptors.

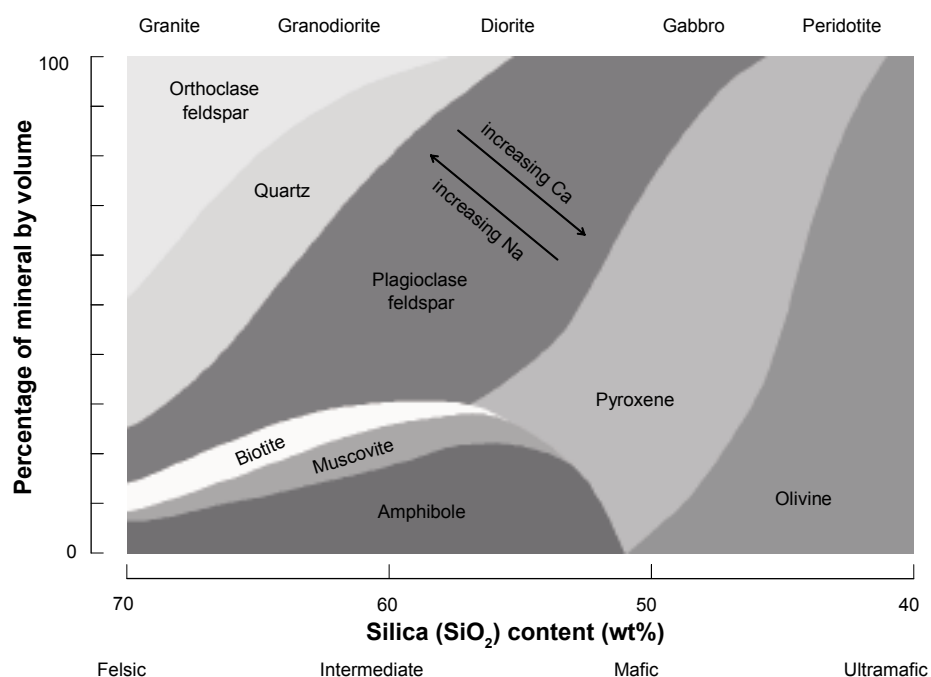
Although rock-type is in principle a “hard” variable, the taxonomic distinction between closely related rock samples and transitional varieties is not always clear. This is true both for the identification of rock-types and sub-classes within data application (i.e. safety assessment) as well as for data acquisition. This is a possible source of data selection bias. It is evident, for example, in the literature data that there are many more data points relating to the rock-type granodiorite than either granite or diorite. The explanation may be that it is easier to label a sample as a transitional form when it is not entirely clear whether the rock belongs in one category or the other. The reason for this becomes more apparent when considering the fact that there is a continuum of different compositions between different rock types as can be seen in Figure 2-1 below.

The rock-types and additional descriptors are difficult to separate, as there is often semantic overlap in their definitions. For this reason, the authors of this report feel that definitions of these variables in the context of data in the open literature should not be treated too rigidly, but rather as more imprecise property classes to avoid unnecessary bias and truncation of datasets.

During the compilation of the data set which makes up the latter parts of this report, it was observed that the differences between different rock types were frequently much smaller than variation within rock types. This could be due to taxonomical artefacts as discussed above, or due to that there are no large, discernable differences between the different rock types (or possibly both effects). Whatever the underlying cause may be, it seems that on the basis of the compiled data, there is no strong argument for separating data for different rock types into strictly defined groupings and the consolidation of data into a loosely defined category of crystalline, “granitic-type” rock thereby appears reasonable.

### **Mineralogical heterogeneity**

The geology of a site may be lithologically homogeneous or heterogeneous. Here, we consider heterogeneity arising from variation in the distribution of individual mineral phases on different scales. Even for apparently homogeneous plutons, there will be large differences in the distribution of mineral phases on a centimetre to decimetre scale. As most sorption data is typically derived from experiments using crushed rock samples consisting of perhaps 0.1–10 g,



**Figure 2-1.** Classification model of intrusive igneous rocks. Adapted from /Press and Siever 1998/.

the variation between samples is high. In safety assessment where block sizes on the order of some tens of metres or more are considered, the potential stochastic variation on the block-scale is expected to be much reduced. This should hold for both homogeneous blocks as well as for heterogeneous rock masses that may contain a number of distinct rock types at the block-scale. The influence of heterogeneity will be most apparent in how the flowpath averaging of material properties is handled. Averaging of properties over larger scales will automatically give lower estimates of property variability.

### ***Mineral surface area (Structural heterogeneity)***

The sorption  $K_d$  of many radionuclides has been observed to be correlated with mineral surface area /e.g. Bertetti et al. 1996, 1998, Pabalan et al. 1998, Prikryl et al. 2001/. The correlation is expected to be quite strong for radionuclides that mostly sorb by way of a surface complexation mechanism and to some extent independent of the type of mineral phases present /Turner et al. 1999/. This is thought to be because the variably charged, surface functional groups of most silicate minerals are similar and consist of a mixture of amphoteric silanol and aluminol sites /Bradbury and Baeyens 1997/.

For permanent charge sites that are important in ion exchange, there is also a correlation between  $K_d$  and surface area although the correlation is not as clear owing to the fact that not all minerals sorb equally well. It is well known, for example, that mica minerals such as biotite overwhelmingly dominate the sorption of Cs(I) in granitic rocks /e.g. Torstenfelt et al. 1982b, 1983a/. The relative sorption of Cs(I), however, can still be correlated with the overall mineral surface area of the rock if the ratio of biotite sorption surface area to total surface area is roughly the same between different rock samples or rock types, although this may not always be the case.

The sorption of many radionuclides can frequently be shown to correlate with the cation exchange capacity (CEC) of minerals. The CEC is closely related to BET surface area although it also implicitly takes account of the relative sorption properties of different surfaces in complex mineral assemblages /Allard et al. 1983a/. There are, however, many different methods used to estimate CEC that are not entirely comparable and the precision of such correlations is subject to much uncertainty, particularly when comparing data from different sources.

### ***Groundwater chemistry***

Groundwater chemistry encompasses a number of parameters that have a strong influence upon sorption. These are:

#### **pH**

This parameter influences sorption by way of altering both the type and distribution of charged surface groups as well as the speciation of radionuclides and other solutes in solution. In addition, there can also be competition for sorption sites at low pH where there is a high concentration of competing hydrogen ions ( $H^+$ ), or at high pH where there is a high concentration of hydroxyl ions ( $OH^-$ ). The pH influences the  $K_d$  of solutes that sorb by way of a surface complexation mechanism more so than those that sorb by ion exchange. This is largely due to the changing charge distribution of amphoteric surface groups as a function of pH. The pH does not influence the distribution of permanent surface charge in any way.  $K_d$  values are generally reduced at both high pH and low pH.

For the Swedish final repository concept, it is thought that the pH will be relatively fixed in a narrow range between roughly pH 7.0 and pH 9.0. Recommended  $K_d$  values in this report are intended for in situ pH conditions in this range.

## Redox conditions

Certain radionuclides such as, for example, U(IV,VI) and Np(IV,VI) are sensitive to redox conditions and can exist in different valence states that have dissimilar sorption characteristics. Under mildly oxidising (e.g. ambient) conditions these radionuclides are sorbed poorly and their precipitated forms have a high solubility. Under sufficiently reducing conditions, however, they are strongly sorbed and their mineral forms typically have very low solubilities.

Literature sorption data for redox sensitive radionuclides in their reduced state is notoriously poorly documented and frequently much sparser than the data available for the same radionuclide under oxidising conditions. This is partly due to the difficulty involved in carrying out experiments for redox sensitive substances under reducing conditions, but more due to the fact that the focus of such work is frequently related to transport processes in near surface and therefore, oxic environments. Moreover, different radionuclides have different redox characteristics that are considerably influenced by solution speciation effects, and it is not always possible to establish a clear Eh cut-off point for the relative predominance of oxidised and reduced forms. This is particularly true for redox-sensitive actinides that are complexed strongly by dissolved carbonate. In laboratory experiments kinetic phenomena and disproportionation of valence states may also complicate data interpretation.

Reducing conditions are commonly simulated in laboratory experiments by addition of, for example, sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) /e.g. Baston et al. 1997/. Generally this gives very low Eh values on the order of  $-400$  to  $-450$  mV which may be considerably more reducing than that obtained at repository depth in granitic bedrock. Some experimenters use sparging with  $\text{N}_2$  gas in a glove box, although this cannot by itself guarantee sufficiently reducing conditions to be indisputable. In the absence of a detailed rationale for selecting a generalised cut-off point for oxidising and reducing conditions, we have chosen to use the reference level of  $-250 \pm 100$  mV as discussed in /Langmuir 1997/ and /McKinley and Savage 1996/ to correspond to reducing conditions (this has also been used as a reference level for establishing solubility controls on radionuclide release). It should be noted that this is approximately the median value of predicted Eh values obtained by consideration of different redox couples (chiefly the redox couples  $\text{SO}_4^{2-}/\text{S}^{2-}$ ,  $\text{CH}_4/\text{CO}_2$ , and  $\text{Fe}^{2+}/(\text{OH})_3$ ) likely to be controlling redox chemistry and is also broadly consistent with potentiometric measurements of Eh in Swedish groundwater at repository depth.

For Swedish conditions, we therefore consider two possibilities; strongly reducing or mildly oxidising where the reference level given above constitutes the cut-off point. The  $K_d$  values given in this report consider both situations (when relevant) for each radionuclide. We emphasise, however, that the experimental conditions under which the data are obtained for the reducing state may not necessarily correspond to site specific reducing conditions and care must be exercised in selecting data for use on the basis of assumed oxidising or reducing species predominance in the given system.

## Ionic strength (Water type)

Ionic strength influences sorption properties by way of competitive effects between the various ionic species that are present in the porewater. Indirectly, ionic strength can also influence sorption through changes to the apparent equilibrium constants of both aqueous phase and surface complexation reactions. For surface complexation reactions, additional ionic strength dependencies can arise due to surface charge and electrostatic effects. The available empirical data in the literature are not sufficiently detailed to discriminate between the effects of different ionic components in the porewater, with the exception of a few special cases where unusual water compositions have been studied. For this reason it is necessary to correlate sorption properties using the broader concept of ionic-strength that includes all aqueous charged species.

For SR-Can, a number of reference water types have been defined for transport properties evaluation /Byegård et al. 2005/ (see Appendix A). These correspond to a non-saline water (Type-I), brackish-saline water (Type-II) and (Type-III), and a brine (Type-IV). The sorption data in the literature can only be roughly delineated owing to that the experimental data generally represent

a continuum of water types ranging between the Type-I and Type-IV definitions. We note, however, that the water compositions represented in the literature exhibit considerable clustering bias and particular reference water types appear frequently amongst the compiled experimental data sets (e.g. different variations of “Allard-type” water; see Appendix B). Furthermore, there are large gaps in the data which makes it difficult to predict sorption properties for intermediate salinity levels. The  $K_d$  values given in this report therefore only consider the two main groups (i.e. non-saline and saline). These approximately represent the range of groundwater chemistries relevant for safety assessment calculations in the Swedish programme, although it should be recognised that the data give only very approximate indications of ionic strength dependency that are not statistically well founded when considering the aggregate data set.

### **Complexing Agents**

Complexing agents reduce sorption by acting as competitors with sorption sites for the binding of radionuclides. The most ubiquitous and well-characterised complexing agent in typical groundwaters is carbonate ( $\text{HCO}_3^-$ ). The sorption of certain radionuclides (e.g. Am(III), U(VI), Pu(III)) is thought to be strongly diminished in the presence of carbonate as it forms strong complexes with these solutes (e.g. /Langmuir 1997/). It is noted that in many cases this effect is hypothesised on the basis of theoretical interpretation of macroscopic data using literature stability constants for carbonate complexation and is not always directly supported by spectroscopic evidence.

In addition, there are other complexing agents in groundwater including humic and fulvic substances as well as bacterial siderophores. Bacterial siderophore substances are particularly strong complexing agents, although are typically produced only under oxidising conditions (i.e. when  $\text{Fe}^{3+}$  availability is low) by those microbes that use the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple as an energy source. The extent to which these substances could influence sorption processes therefore depends upon the likelihood of oxygenated water intrusion (i.e. water of near surface origin) at repository depth. This has not been considered in the present report, although is noted as a possible factor influencing data applicability in scenario analyses involving such events.

Owing to scarcity of literature data, no attempt has been made to correlate  $K_d$  values with the presence of complexing agents. It is thought, however, that humic and probably also fulvic substances are present at such low concentrations in Swedish groundwater at repository depth that they are inconsequential in safety analyses for the central safety case that assumes contemporary groundwater conditions as the norm. Generally speaking, the ranges of conditions chosen in the experimental determination of  $K_d$  values implicitly include the effects of carbonate concentrations typically encountered in groundwater and thereby this does not necessarily need to be treated as a separate parameter (i.e. by way of the variable carbonate content of synthetic groundwaters used in  $K_d$  measurement).

We note, however, that the extent to which the selected water chemistries are consistent with diluted carbonate concentrations which may be present in the wake of deglaciation events is currently unclear and this should be considered as a possible complicating factor that is poorly constrained in the current data set.

### **Colloids**

Colloidal substances are usually defined as suspended solids in the size range 1 nm to 1  $\mu\text{m}$ . They are abundant in surface waters and in marine environments, although are thought to be present at only low concentration at repository depth. They are destabilised in water of high ionic strength and tend to coagulate and be removed from flowing water. For this reason they are considered to be most important under non-saline conditions where they can persist in the flowing water. Colloids, being essentially transportable solids, reduce the apparent partitioning coefficient for strongly sorbing solutes. Owing to the low colloid concentrations naturally encountered in Swedish groundwater at repository depth it is thought that they are inconsequential for safety analyses /Allard et al. 1991/ and have therefore not been included as

a data selection parameter in this report. The status of colloids in diluted groundwater intruding to repository depth in the wake of deglaciation events is poorly constrained in the current data set and should be considered in more detail in such scenarios.

### **Temperature**

Temperature has a weak influence upon partitioning coefficients by way of changing the apparent equilibrium constants of both aqueous phase and surface complexation reactions. Temperature changes can give rise to either an increased or decreased partitioning coefficient, depending upon the particular solute. Temperature dependency is rarely reported in the literature and most investigations have historically been carried out at room temperature. In situ temperatures at repository depth are expected to be in the range of 4–12°C. Owing to the weak impact of temperature changes in relation to the aggregate uncertainty in the  $K_d$  data, no attempt has been made to introduce temperature as a correlating parameter in this report.

## **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 2.1)?

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 Codes used for far-field radionuclide transport calculations**

There are a number of different codes used for the calculation of far field radionuclide transport. A full discussion of the different codes used in safety assessment is beyond the scope of this investigation. The reader is instead directed to consult the relevant SKB reports describing these codes.

### **2.2.3 Differences in models for different conditions**

See Section 2.2.2.

## **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 (reference should be provided). This concerns 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.

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, a solute equilibrium concentration larger than say 0.1 mole/dm<sup>3</sup> 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 conditions listed in Section 2.1 – 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 partitioning coefficient data**

No detailed sensitivity analysis has been made of the impact of  $K_d$  uncertainty upon safety assessment predictions at this time. We can, however, point out that weakly and moderately sorbing nuclides that have a transport residence time (i.e. the time taken for a radionuclide to be transported from the repository to the biosphere) less than a couple of half-lives may be strongly influenced by uncertainty in the  $K_d$  value used in simulations. For strongly sorbing substances that have transport times corresponding to some tens of half-lives, uncertainty in the actual  $K_d$  value may not have a significant impact on far-field activity release. The same can be said of weakly or moderately sorbing substances that have sufficiently long transport times compared to their half-life that their activity decays to negligible levels during transport to the biosphere.

The nuclides selected for detailed study in this report have been selected on the basis of their potential to give elevated levels of far-field activity release when pessimistic transport scenarios are considered. The selection of these nuclides was based upon the predictions made in the SR-97, Radionuclide Transport Calculations report /Lindgren and Lindström 1999/.



## 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 2004b/) usually only short text, with reference, is needed. The experts listed as authors to the report provide all factual information in this chapter.

### 3.1 Databases

#### 3.1.1 Instructions – issues to be addressed

This section should address:

- Which databases 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 Databases for partitioning coefficient data

Most of the data presented in this compilation are derived from primary literature references in the form of journal articles and peer-reviewed conference proceedings. A smaller subset of data were only available in the form of secondary references (i.e. cited “second-hand” in other sorption compilations). Secondary references were largely obtained from the JNC sorption database /Shibutani et al. 1999/, although some data were also taken from the Nagra sorption database /Stenhouse 1995/.

For this compilation, we have considered the range of “granitic-type” rocks as described in Figure 2-1 although with a strong bias towards Felsic and Intermediate rock-types. We also have included rocks that have been altered or weathered by tectonic or hydrothermal processes as well as metamorphic types (e.g. granite-gneiss, etc). The authors acknowledge the fact that the term “granite” as such is somewhat more restrictive than the range of rock types described above, although the term is used in a more general sense as previously described in Section 2.1.2.

The measurements are generally based upon crushed material and a wide range of aqueous geochemical conditions. Owing to the range of aqueous geochemical conditions represented in the aggregate data set, it is not possible to provide accurate, quantitative data detailing the influence of individual geochemical parameters. For this reason, recommended  $K_d$  values are given for two representative water types. These are; non-saline ( $< 400 \text{ mg/l Cl}^-$ ) and saline ( $\geq 400 \text{ mg/l Cl}^-$ ). In only one case (Sr(II)) was there sufficiently detailed data available to give data for additional salinity classifications. In this case, the saline water class was expanded to include the sub-categories weakly-saline ( $400 \text{ mg/l} \leq \text{Cl}^- < 4,000 \text{ mg/l}$ ) and strongly-saline ( $\geq 4,000 \text{ mg/l Cl}^-$ ).

Chloride ion (Cl<sup>-</sup>) is chosen as the main parameter describing water composition here owing to that it is the dominant anion in most Swedish groundwaters of interest for safety assessment. Being the dominant anion, the Cl<sup>-</sup> concentration is closely related to both ionic strength and electrical conductivity, making it a good proxy for the classification of different water types. It is noted that the definitions of non-saline and saline are slightly different to those adopted by /Carbol and Engkvist 1997/ although the impact upon data selection is minimal.

The sorption data are typically measured at room temperature (i.e. 20–25°C), which is somewhat higher than that characteristic of deep groundwaters (≈ 12°C).

There is very little data in the literature that have studied the influence of low temperatures (i.e. below room temperature) on sorption properties. It is generally thought, however, that the influence is very weak and mostly due to alteration of equilibrium constants. The influence of temperature on the competitive effect of surface relative to aqueous complexation could potentially be estimated theoretically using geochemical modelling, provided the temperature dependence of dominating surface and aqueous complexation reactions can be elucidated. This, however, is somewhat beyond the scope of the current investigation and it is noted as a future possibility in updated sorption compilations.

Many of the abovementioned issues are discussed in more detail in Chapter 5.

## **3.2 Modelling etc**

### **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**

No modelling has been used in the derivation of K<sub>d</sub> data used in this compilation. Although reinterpretation of results using a diffusion model may have given more accurate data in some cases, there is sufficient uncertainty concerning key parameters and the physical interpretation of observed time dependent behaviour that this was not possible to carry out in a rigorous fashion.

In an earlier compilation by Nagra /Stenhouse 1995/, K<sub>d</sub> data for different rock types were estimated using a weighted average of K<sub>d</sub> values (i.e. on a mass fraction basis) for individual mineral phases comprising the rock. Although a reasonable first approximation, it has been previously shown by /Andersson et al. 1983/ that this approach tends to give overly conservative results, particularly for solutes such as Cs and Sr that sorb by way of an ion exchange mechanism and to a lesser extent for actinides that form surface complexes.

It has also been observed by a number of researchers that sorption appears to be insensitive to mineral identity and more closely related to sorption site density (see discussion in Section 5.2.4). This is thought to be because the binding sites on the surface of most silicate minerals are very similar and only differ in density between different mineral surfaces. In principle, therefore, it is possible to extrapolate the sorption properties of any rock type

to another just by knowing the relative sorption site densities of different mineral phases comprising the rock. Although relatively simple for framework silicates that possibly have no perceptible heterogeneity in their distribution of binding sites, it is not entirely straightforward for micas and clay minerals owing to the fact that different crystal planes can have dissimilar site densities. The overall site density is then highly sensitive to the particle size and shape and therefore difficult to estimate. Additionally, when a complex assemblage is considered such as granite, it is necessary to consider the effects of armouring (i.e. where one mineral phase partially or totally covers the sorption surface area of another mineral).

In practice, the site density cannot be determined rigorously for complex mineral assemblages and the BET surface area is usually used instead as a proxy. This information can be used to extrapolate data measured on the complex assemblages themselves (i.e. extrapolating  $K_d$  values measured for granite to specific surface areas applicable for in situ rock) or to predict sorption by assuming the rock to be a simple composite of mineral phases and using sorption  $K_a$  data measured for those individual mineral phases. When BET surface area is used to normalise sorption data in this way, the effect of site density is implicitly included in the measurement of the mineral specific  $K_a$  values. As indicated by /Stenhouse 1995/, this approach is not fundamentally different to that using a weighted average of  $K_d$  data owing to the simple relation between  $K_d$  and  $K_a$  (i.e.  $K_a = K_d / A_{BET}$ ) and the concepts are thus mutually interchangeable.

It is the opinion of the authors of this compilation that the weighted average approach outlined above contains many implicit assumptions that are difficult to quantify in a satisfactory fashion. We have therefore chosen to present only data measured for representative granitic rock samples and not extrapolate from data for pure mineral phases. Instead of predicting sorption  $K_d$  data from the sorption properties of individual mineral phases, it is more robust to use BET surface areas to extrapolate between samples of similar rock-types as artefacts such as armouring effects and the creation of new surfaces during sample preparation are, to some extent, already incorporated in the data.

As mentioned previously, there has been an explosion in the use of Thermodynamic Sorption Models (TSMs) in the past decade that has significantly increased our understanding of the mechanistic basis of sorption processes (see e.g. /Langmuir 1997/ for a general overview). These developments have gone hand in hand with the development of new spectroscopic methods of analysis that allow the independent identification of reaction mechanisms hypothesised in TSM modelling approaches (e.g. /Bargar et al. 1997, 1999, 2000, Farquar et al. 1997, Koretsky et al. 1997, Eggleston et al. 1998, Peak et al. 1999, Strawn and Sparks 1999, Sylwester et al. 2000, Villalobos and Leckie 2001, Stumpf et al. 2001, 2002, Stumpf and Fanghänel 2002, Bostick et al. 2002, Hennig et al. 2002, Waychunas et al. 2002, 2003, Dähn et al. 2003/). Generally speaking TSM modelling approaches can be classified as being “bottom up” or “top down” methods. Bottom-up methods (so-called component additive or, CA approaches) are similar to the  $K_d$ - weighting approach described above, where it is assumed that the heterogeneous solid can be approximated as a mixture of well-defined minerals, although in this case provision is made for the inclusion of competitive effects amongst different sorption sites. In this approach sorption sites for individual minerals have reactive properties as determined from independent experimental measurements involving the pure mineral phases. Top-down methods, on the other hand, (so-called generalised composite, or GC approaches) are based upon the fitting of a semi-empirical TSM to experimental data for the heterogeneous solid itself. The authors acknowledge the extensive work that has been done within the OECD/NEA Sorption Project /NEA 2001, 2005/ where there has been extensive discussion of “bottom up” vs. “top down” approaches to sorption modelling using TSMs and emphasise that such mechanistic modelling approaches should be developed in future investigations as a complement to the somewhat simplistic compilation of literature  $K_d$  data presented in this report.

## 4 Evaluation of sources affecting uncertainty

This chapter assesses different sources of uncertainty affecting the parameter estimates. The actual estimates of the parameter(s) and associated uncertainties, are made in the next chapter. All factual information and judgements made in this chapter are 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 Experts view (overall uncertainties)

Uncertainty appears at a number of different levels in the acquisition and use of partitioning coefficient data. In order to define overall uncertainties in a traceable fashion, it is necessary to distinguish between uncertainties at the following levels /Ochs and Talerico 2004/:

**1. Uncertainty in the compiled  $K_d$  data itself**

This uncertainty relates to experimental error including random error, sample variability, systematic errors and methodological flaws in  $K_d$ -determination as well as uncertainty concerning the way in which experimental data have been obtained owing to flawed documentation. Uncertainty relating to the interpretation of experimental data is also included at this level. We consider data selection bias (see Chapter 5), “frame shift” and “frame dilation” bias (see explanation following) to be also relevant at this level.

**2. Uncertainty related to the use of generic data in site-specific SA**

This uncertainty relates to the need to use experimentally derived data in safety assessment applications where the conditions may not exactly match the conditions under which the experimental data have been obtained. This level also covers potential uncertainty relating to the use of generic data for granitic rock where site-specific data are unavailable.

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

If there are significant uncertainties associated with the application conditions themselves, it is critical to take into account the conditional nature of the  $K_d$  data into account. In this report  $K_d$  data are supplied for a range of possible conditions that may be relevant for safety assessment. Additionally,  $K_d$  data may not necessarily address issues related to variation of material properties along a flowpath owing to the small sample size typically used in sorption measurement. It has been shown in Section 2.2 that flowpath averaging of the material properties group will reduce some of the uncertainty relating to random  $K_d$  variability.

The different sources of uncertainty can impact differently upon the outcome of safety assessment.  $K_d$  values chosen to be conservative under a given set of repository conditions can quickly become non-conservative if the porewater chemistry changes in such a way that the sorption of radionuclides is adversely affected. As discussed later in Section 4.3.2 this may occur, for example, in the case where there is a sudden concentration pulse of a competing component that can displace a sorbed species from the rock matrix. In this case, choosing a “conservatively” low  $K_d$  value may not actually be conservative. Some sources of uncertainty are expected to impact upon safety assessment predictions in a random fashion although always within a well-defined range. This can be handled using probability density functions (PDF's) for uncertain variables that can be described in this way.

Other forms of uncertainty (so-called epistemic uncertainties) may impact upon the validity of results, although this may not be always directly visible in predictions as, by definition, they relate to a lack of understanding or knowledge about the system and may not even have been considered in the analysis. Some of these uncertainties are such that the central value of a variable is shifted well outside the range of uncertainty as described by the PDF. The authors of this report refer to this particular effect as a “frame shift” bias or uncertainty. An additional form of uncertainty which we term “frame dilation” uncertainty results from processes that influence laboratory measurements in such a way that the apparent data variability is significantly greater than that which is relevant for in situ conditions. As mentioned previously, these are subtly different to the concept of “expert overconfidence” which refers to the underestimation of uncertainty owing to the use of an excessively small data set.

There is good reason to believe that frame shifting and frame dilation are real phenomena and they have broad implications for the use of experimentally derived  $K_d$  data in safety assessment applications. These issues are discussed more fully in Section 4.4.3.

Particularly important epistemic uncertainties relate to the validity of the  $K_d$  concept itself and the representativity of measurement data obtained from materials that are fundamentally altered relative to the in situ rock. This includes uncertainties related to the assumption that experimentally derived data represent true (linear) equilibrium sorption processes as well as the underlying assumptions that sorption kinetics, freshly exposed mineral surfaces, weathering reactions, and other specious phenomena or experimental “artefacts” do not invalidate or otherwise influence the interpretation of measurement data significantly nor its application to predicted field conditions.

It is important to note that the PDF for random property variation on the scale of the transport path length (here loosely referred to as the “block scale”) may be narrower or broader than that for the original  $K_d$  data. Averaging of properties naturally gives rise to a smaller variation between blocks where localised mineralogical variations within a rock-type are concerned. The averaging procedure, however, is also subject to additional uncertainties such as variable aqueous geochemistry under application conditions, or variation in the proportion of various rock types believed to comprise a block. Furthermore, we do not know the actual water flowpaths and thus which mineral assemblages a water “package” encounters along a flowpath. These uncertainties would tend to broaden the calculated PDF. The PDF description of variability doesn’t include types of epistemic uncertainty that may give frame shift effects and other forms of systematic bias.

Although somewhat outside the scope of this report, the issue of “scale-up” and its impact upon parameter uncertainty is very important and hasn’t been handled well in previous safety assessments. The consequences of this for safety assessment predictions must be investigated in more detail. The reader is directed to /Lake and Srinivasan 2004/ for a general discussion on issues of scale-up and volume averaging in heterogeneous environmental systems.

The following sections describe some general aspects of uncertainties related to the issues outlined above.

## **4.2 Uncertainty related to different conditions**

### **4.2.1 Instructions – issues to be addressed**

Discuss if and how the parameter is influenced by the various conditions as specified in Section 2.1 and how uncertainty is influenced. (For example, solubility depends on groundwater composition, which in turn 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 2.1 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 partitioning coefficients**

Partitioning coefficient data are sensitive to the variables described in Section 2.1.2. Of key importance is the groundwater composition, which influences not only the radionuclide speciation in the aqueous phase, but also the ionic strength. The solubility, which is dependent on the aqueous speciation, puts a natural roof on the radionuclide concentration above which consideration of sorption reactions are unimportant. There is, however, a continuum between sorption and precipitation of solid phases, via mechanisms of surface precipitation and co-precipitation. It is also noted that there are studies available in the scientific literature that discuss the continuous transition between surface sorption and surface precipitation for specific solutes, although these typically relate to pure phases and solute concentrations some orders of magnitude higher than those considered here to be relevant for sorption in the far-field (e.g. /Scheidegger and Sparks 1996, Scheidegger et al. 1996, 1998/). These aspects, however, are beyond the scope of the current investigation and have therefore not been dealt with in detail with the exception of where data sets have been excluded on the basis of suspicious partitioning behaviour. The authors indicate that this may need to be investigated more fully on a case by case basis for those radionuclides which may be influenced such processes both during data measurement and under application (i.e. repository) conditions.

It is important to note that both sorption and solubility equilibria may govern the free concentration of a radionuclide in a groundwater system. This free concentration, however, makes up a variable part of the total dissolved concentration of the radionuclide, depending on its speciation. Formation of aqueous complexes may therefore greatly affect the overall distribution of the radionuclide between the solid and aqueous phases. Indirect effects of speciation, where the formation of soluble complexes (e.g. carbonate complexation of actinides) decreases the sorption and precipitation tendency, are thus commonly important under typical repository conditions. Direct effects on sorption, where a soluble aqueous complex shows stronger sorption than the aqueous ion itself, have also been reported in the literature /e.g. Bargar et al. 1999, and references therein/.

Ligands that have been reported to be particularly important for radionuclide speciation include hydroxyl ions (involved in hydrolysis), carbonate and bicarbonate, phosphate, small organic acids, siderophores, as well as fulvic and humic substances. Organic complexing agents can be formed during the degradation of organic material in repositories or associated with the presence of microorganisms. Saccharic acid, gluconate, and EDTA have often been used as proxies for natural low molecular weight degradation products in studies of radionuclide complexation, and have been shown to promote the migration of radionuclides /e.g. Read et al. 1998/. As it is the anionic form of these ligands that form complexes with metal ions most strongly, the importance of organic acids for the radionuclide speciation will be pH dependent. Siderophores, which are excreted from microorganisms under iron-limiting conditions in order to enhance their access to iron, bind metal ions very strongly. Although siderophores are highly selective for iron, they also have a strong affinity for other metallic ions such as, for example, Pu(IV), Pu(VI), and Th(IV) /White et al. 1995/ and may thus affect the radionuclide speciation even at relatively low concentrations. It is worth noting here that synthetic groundwaters used in sorption experiments, typically do not contain any of these additional substances and thus their utility for predicting in situ sorption is associated with further uncertainty in those situations where such substances may be present.

High molecular weight organic acids, such as fulvic acid (FA) and humic acid (HA) substances, also bind radionuclides; this has been subject of intensive research in recent years owing to their ubiquitous presence in terrestrial environments and importance for mobilisation of toxic elements. The high molecular weight organic acid can either be dissolved in the aqueous phase, and thereby contribute to increased mobility and higher aqueous concentration of the radionuclide, or be in the solid phase, and then act as a sorbent. Solid phase FA and HA substances may be immobile or mobile (particulate or colloidal) in nature. The active complexing sites on FA and HA include carboxylic-, phenolic-, and amino functional groups with variable characteristics /e.g. Stumm and Morgan 1996, Morel and Hering 1993/, and can form monodentate and polydentate complexes /e.g. Tipping 1996/.

Aqueous complexation of radionuclides has been the subject of intensive research over some decades and extensive databases exist in the literature /see, for example, Spahiu and Bruno 1995, and references therein/. While probably the best reviewed aqueous speciation thermodynamic databases available in the scientific literature concern radionuclides, uncertainty in speciation still remains /e.g. Bruno et al. 1997/. Such uncertainties in formation constants and the actual composition of the complexes, which are often deduced by fitting macroscopic experimental data to models, imply uncertainty in radionuclide speciation. These uncertainties are propagated through to  $K_d$ -determinations.

This is an important aspect that strongly influences partitioning coefficients although, as indicated previously in Section 2.1.2, provided that the groundwater type that is considered in safety assessment is sufficiently similar to the water used for  $K_d$  data acquisition, these effects should be implicitly included in the recommended data.

For some radionuclides (e.g. U, Np, Am, Tc, Pu), redox speciation places an important control on chemical behaviour. This is particularly true for elements that switch between anionic and cationic forms when they change redox state. Other important instances occur when one of the redox states is much more readily soluble, or less prone to sorb than the other as, for example, uranium, in its oxidised +VI form (commonly  $UO_2^{2+}$ ) that is much more soluble than the reduced +IV form. In this report, we consider only two redox (Eh or pe) conditions; “reducing”, where all radionuclides are assumed to be in their naturally occurring reduced form (i.e. at Eh levels typical for deep groundwater), and “oxidising”, where they are assumed to be in their naturally occurring oxidised form (i.e. ambient conditions). Based upon previous reference levels used in safety assessment studies, we have chosen the reference level for reducing conditions in situ to be on the order of  $-250 \pm 100$  mV, although we note that in laboratory  $K_d$  measurements, the relevant Eh for simulated reducing conditions may differ significantly from this (as discussed previously in Section 2.1.2).

Besides speciation effects related to presence of various ligands, such as those described in Section 2.1.2, and a continuum of processes controlling the partitioning of trace elements between the aqueous and solid phase, there are also effects of physicochemical conditions, such as ionic strength and temperature. Ionic strength effects include direct influences, such as ions in solution competing for surface complexation and ion exchange sites on the solid surface, and indirect effects owing to variations in the chemical equilibrium constants. Over small temperature ranges, indirect temperature effects on equilibrium constants are deemed to be dominant, but over larger temperature intervals changes in surface complex co-ordination also possibly become important.

The most obvious ionic strength effect on the partitioning of trace elements between the solid and aqueous phase involves competition of main components for ion exchange and surface complexation sites. This effect is especially important for ion exchange at permanently charged surface sites. The influence of ionic strength on homogeneous chemical equilibria is well known and readily modelled through the use of activity coefficients. The relation between ionic strength and species activity is established through various empirical and theoretical treatments (e.g. the Debye-Hückel and Davis approaches, as well as ion association, and specific ion

interaction approaches). For a general description see, for example, /Stumm and Morgan 1996/. In the case of surface reactions, additional ionic strength dependencies are related to surface charge and electrostatic effects.

While sorption data at different ionic strengths are readily available in the scientific literature, data on the temperature dependence of sorption reactions are more scarcely reported. Recently, theoretical approaches for estimating the temperature dependence of surface reactions have been presented in the literature /e.g. Sahai 2000, Machesky et al. 2001/. The results of /Sahai 2000/ suggest that cation surface complexation increases with temperature for most oxides, whereas anion complexation decreases, with relatively small temperature effects.

## **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?
- What alternative conceptual models exist (and what influence might they have on the safety assessment?)
- In light of the previous points, 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 affecting partitioning coefficients**

There is strong evidence in the open literature that the transport of radionuclides is retarded in varying degrees by matrix diffusion and partitioning processes (although not necessarily by way of sorption on mineral surfaces) within rocks both in laboratory /e.g. Torstenfelt et al. 1982b, 1983a, Ittner et al. 1988, Skagius 1986, Eriksen and Locklund 1989, Johansson et al. 1998, Yamaguchi and Nakayama 1998/ and field studies /e.g. Elert and Svensson 2001, Gustafsson and Nordqvist 2005, Gustafsson et al. 2005/ as well as in natural analogues represented in the geological record /e.g. Alexander et al. 1990, Smellie et al. 1986, 1999, Payne et al. 2001/. We note, however, that it is generally not possible to “directly” observe or corroborate the existence of field-scale sorption processes and there are certainly alternative explanatory mechanisms for macroscopically observed retardation. Similarly, most natural analogues (frequently based on U-disequilibrium studies) are also open to alternative lines of interpretation according to different physical process hypotheses. The hypothesis of sorption being the main mechanism by which field scale retardation occurs is substantially unresolved, although there are strong indications that retardation by this mechanism should occur even if the conjecture is based solely upon interpretation of laboratory data. There are, for example, a large number of recent laboratory studies of sorption that directly demonstrate the existence of sorbed species on mineral surfaces by way of spectroscopic data interpretation thereby lending support to certain postulated sorption mechanisms (see Section 3.2.2). Given the very strong spectroscopic evidence that sorption occurs in laboratory studies, it seems unlikely that similar processes do not also occur in the field. The question remains, however, as to which is the best means of modelling these processes for safety assessment purposes.



It is well known that the  $K_d$  concept is subject to severe limitations. In spite of this, there are two strong arguments in favour of the use of  $K_d$  data in safety assessment modelling.

The first argument relates to transparency of the modelling process. The hydrological setting of safety assessment studies is frequently so complex that it is very difficult to simultaneously integrate a highly sophisticated treatment of sorption chemistry and hydrogeology. The inherent non-linearity of sophisticated chemistry, sub-modules also makes it exceedingly difficult to distinguish between real non-linear phenomena and spurious numerical artefacts. Coupled models using a simplified linear approach to sorption chemistry give easily interpretable results that are more readily understood than approaches involving highly non-linear models of sorption.

In addition to this, safety assessment frequently involves specialist input from a variety of different fields. By using a linear  $K_d$ , a large amount of uncertainty relating to sorption is concentrated into a single variable, the applicability of which can be evaluated by experts independently of its implementation in transport simulation codes. The perception of retardation implied by the magnitude of the  $K_d$  value for the particular radionuclide of concern has a powerful significance, as it is possible to attach a precise physical interpretation to its meaning. This is not always possible to achieve with non-linear, mechanistic approaches, as their physical interpretation (i.e. in terms of intrinsic binding constants, etc) is often unclear with respect to solute retardation. This does not mean that they are not useful for understanding field-scale retardation processes, but that coupled flow and geochemical transport modelling is required to elucidate how variation of specific TSM parameters influences sorption dynamics in the context of advective transport.

The second argument relates to numerical expediency relating to both the ability to incorporate field-scale variability and scenario variations in a relatively straightforward fashion. The linear nature of transport models incorporating the  $K_d$ -concept are convenient to work with as variations in material properties and hydrological features along a transport flowpath can be handled by convolution of analytical transfer functions for individual hydrologic and material units, or flowpath averaging of transport properties as discussed in Section 2.2. This is also of great consequence when combining sub-modules describing near field, far field, and biosphere transport processes. The radiological consequences, for example, of different scenarios of near-field release may be easily determined by convolution of the near field release boundary condition with the far field transfer function obtained by simulating the breakthrough characteristics of an instantaneous Dirac pulse solute release. For approximately linear sorption processes that are described by a constant  $K_d$ , this can be shown to be mathematically rigorous.

It is often presumed that “mechanistic” models that simulate ion exchange and surface complexation phenomena using fundamental principles of mass action, electrostatics, and aqueous speciation are reliable and accurate. For well-defined systems studied in a controlled laboratory environment this may be true, although it is somewhat more doubtful for complex field systems considering the present state of the art. Moreover, it is difficult to extract meaningful parameters for these models in the absence of detailed multidimensional datasets, which as yet do not exist for heterogeneous mineral systems such as granite. It is not currently possible to apply such models directly in transport simulation codes in a rigorous manner given the complexity of field conditions and the fact that the  $K_d$  approach “may be completely adequate for the goals of safety assessment” /Westall 1995/.

For the Swedish KBS-3 repository and projected environmental conditions it is thought that a  $K_d$ -based approach is sound and scientifically defensible in a broad sense, provided appropriate values are chosen for modelled repository conditions. Large changes in pH, for example, are not likely to occur in the far-field environment surrounding a KBS-3 type repository for spent nuclear fuel. The main scenario that might give rise to substantial pH changes would be a hyper-alkaline plume resulting from the leaching of concrete. This will not occur in the Swedish concept, as there will be no large volumes of concrete used in the repository construction. At repository depth, there is the possibility of freshwater-saltwater intrusion and mixing

events in the wake of glaciation periods. This can be handled in a parametric  $K_d$  framework, provided care is taken to preserve the mass balance of sorbed solute in the system. In a similar fashion, redox conditions at repository depth are expected to be either strongly reducing, or oxidising at atmospheric intensity. Owing to the rapid kinetics and on-off nature of aqueous redox states in deep groundwater, it is thought that these can also be handled efficiently using parametric  $K_d$  values. The sorption database provided in this report contains these parametric qualifications of  $K_d$  values and there is no reason at this time to suspect that the methodology is unrealistic or non-conservative from a safety assessment perspective.

To elaborate on the previous discussion in Section 2.1.2 and drawing upon some of the details discussed in later sections, we provide the following general caveats on the use of conditional  $K_d$  data:

- A  $K_d$ -based modelling approach is inappropriate when mechanisms other than ion exchange and surface complexation govern the radionuclide partitioning between the aqueous and solid phases. This may occur at concentrations much lower than that predicted by the solubility of pure mineral phases, owing to surface precipitation or co-precipitation phenomena.
- Given constant redox conditions, pH, and ionic strength over the considered temporal and spatial scales, a  $K_d$ -based modelling approach, using appropriately selected conditional  $K_d$  values, is applicable for describing sorption reactions. If the conditions vary, the response of sorption behaviour to changes in chemical and physicochemical conditions may need to be considered.
- In order to have as wide a range of applicability as possible, conditional  $K_d$  values should be determined at conditions that mimic those in the field as closely as possible. This is particularly important with respect to redox condition, ionic strength, pH, colloids and the presence of ligands (including, for example, carbonate and bicarbonate, humic and fulvic acids, as well as biologically generated organic ligands such as siderophores and low molecular weight organic acids). If there are ligands or colloids present under in situ conditions that have not been considered in the formulation of synthetic groundwaters used for  $K_d$  data acquisition, the “carrying capacity” of these substances may need to be estimated and calculations adjusted to reflect this.
- For scenarios where radionuclide partitioning into the solid phase is considered to be reversible, a “conservative estimate” of the retention strength and capacity will possibly underestimate the load of radionuclides available upon remobilisation (e.g. as a result of changes in chemical or physicochemical conditions). If an excessively low  $K_d$  value (although conservatively estimated for retention) is used, for example, the actual amount of radionuclide that is remobilised may be subsequently underestimated owing to that it may have diffused to a greater depth in the rock matrix. Furthermore, the travel time for a remobilised radionuclide to a nearby water conducting fracture upon remobilisation may also be overestimated. This implies that the peak load and the timing of the release of radionuclides may be erroneously predicted. Scenarios of this type are not well handled in safety assessment models at present.

## **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 2004b/ 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**

Here, we primarily discuss the subcategory of uncertainty relating to the application conditions themselves (i.e. Level 3 uncertainties as described in Section 4.1.2).

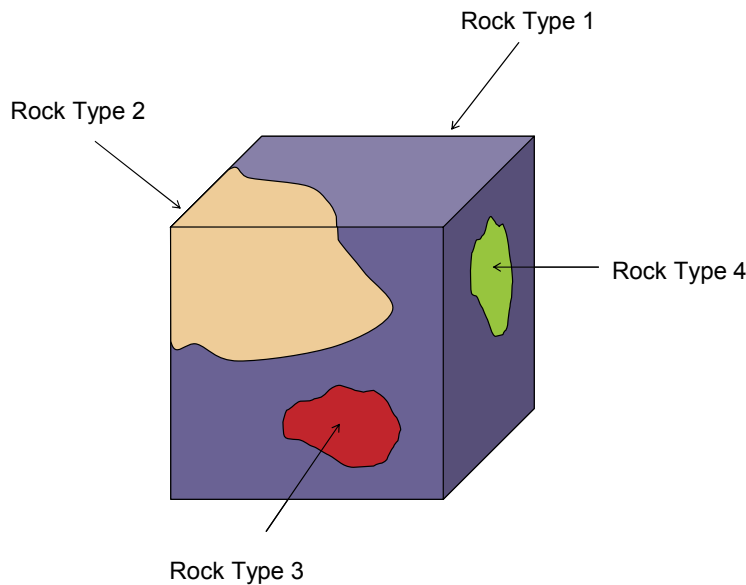
This discussion largely concerns random variation over limited spatial and time scales and uncertainties relating to the actual application conditions. These uncertainties implicitly include those relating to correctly estimating relevant in situ conditions and also how these are expected to vary over larger spatial and temporal scales. We note that it is not always possible to separate questions of variability and uncertainty in a rigorous fashion and therefore there is some crossover in the descriptions of variability given below and discussions of uncertainty relating to a lack of knowledge as described in the subsequent Section 4.4.3.

##### ***Variability in rock matrix mineralogy and sorption properties***

As discussed previously, most sorption data are derived from crushed rock samples where the total amount of solid may amount to a few grams, or less of material. A large rock block, on the other hand, will contain a significantly larger quantity of rock. If we presuppose that the flowpath weighted average is correctly calculated, the dissimilarity due to random mineralogical variation for lithologically comparable blocks should be far less than that in the original data which relates to small samples (here, mineralogical variability is assumed to include variations in sorption site density and mineral specific affinities for various solutes). Although this analysis is somewhat simplistic, we note that for retention properties which are potentially describable as Gaussian random variables along a transport path (either log-normally or normally distributed data), the variance of the effective mean or the variance of the path length integrated value for a specific rock type is expected to decrease on increasing length scales.

It should be emphasised that this only considers localised variation of material properties in an otherwise homogeneous rock block. Most blocks will, in fact, be lithologically heterogeneous and possibly contain a number of distinct rock types in the form of dykes, alteration bands, etc on a scale of a few centimetres to several metres (see Figure 4-1 below). The distribution of rock types amongst different blocks may not be known, although it is possible to estimate this uncertainty from bore core statistics.

As mentioned above, variation of material properties along a transport flowpath must be dealt with by some form of flowpath averaging procedure as outlined in Section 2.2 or by dynamically allocating appropriate  $K_d$  values at run-time. How this is done will vary between different safety assessment codes and will not be discussed in detail here. Notwithstanding this, however, the “effective”  $K_d$  for a large rock block such as that exemplified in Figure 4-1 will contain the following components of variability and uncertainty.



**Figure 4-1.** Illustration of different rock types that may comprise a block. Small-scale mineralogical variation within each rock type will be smoothed out on larger scales. Property variation between rock types that comprise significant fractions of the block may then dominate the overall uncertainty for the block.

- a) Local variability of mineralogy and sorption site density within homogeneous rock-types.
- b) Uncertainty relating to proportions of different rock types characterising a transport path through the rock block.
- c) Uncertainty relating to the “expected” average properties of individual rock types within a block.

Based upon the previous discussion, it would seem that the uncertainties relating to item (b) and (c) above will overwhelm any intrinsic material property variability within a given rock type (a). It should also be noted that (c) does not relate to the representativity of the generic  $K_d$  values for projected application conditions (which is discussed in Section 4.4.3), but rather the uncertainty concerning whether the application conditions are indeed what we expect them to be on the basis of information obtained from the site investigation.

Strictly speaking, both items (b) and (c) amount to a lack of knowledge (as discussed in Section 4.4.3) although they can be reasonably delimited using statistical information from boreholes and outcrops. As such, these uncertainties can be relegated to the class of aleatory uncertainties and are therefore amenable to treatment in a PDF framework, provided the data are unbiased and representative of the target rock volume. If we neglect changes in rock mineralogy resulting from future hydrothermal processes and tectonic alteration, items (a)–(c) are predominantly spatial in character and are not expected to vary in time.

The important point to note here is that for sufficiently dissimilar rock types comprising a block, the aggregate uncertainty is possibly dominated by item (b) and to a lesser extent by (c) and will not be particularly influenced by the probability density function (PDF) describing the variability and uncertainty of the generic  $K_d$  data (or its applicability for in situ conditions).

### **Variability in aqueous geochemical conditions**

The application aqueous geochemical conditions (i.e. water compositions) may also have variability and uncertainty associated with them. These may be both spatial and temporal in nature. The impact that spatial variability will have upon the overall uncertainty at the block scale depends upon whether the geochemical conditions are conceptualised to vary locally over

small scales (e.g. a few decimetres) or over larger scales on the order of the block size itself. The impact of localised random variations may vanish when averaged over the block, whereas large-scale trends may not. The block-scale variance may also be influenced if the local scale variations are correlated strongly in space and time. An additional complicating factor is that we may not know exactly what the average state of the groundwater is, nor how it will evolve over time. The aqueous geochemistry can therefore be considered to contain the following components of variability and uncertainty:

- a) Localised, spatial and temporal variability of actual aqueous geochemical conditions;
- b) Uncertainty in “expected” contemporary aqueous geochemical conditions owing to limitations in measurement methodology and bias during site characterisation;
- c) Uncertainty in large scale spatial trends in aqueous geochemical conditions (i.e. different water types at different locations in the rock volume) owing to incomplete or biased site characterisation data;
- d) Uncertainty in future state of aqueous geochemical conditions owing to uncertain scenarios of repository evolution;

As previously, we note that the uncertainties listed above are additional to that concerning representativity of the generic  $K_d$  values for projected application conditions which are discussed more fully in Section 4.4.3.

Items (a)–(c) are potentially aleatory in nature and could be handled in a PDF framework if enough site characterisation data are available, although we note that in practice there is no way of being able to distinguish between (a) and (b) in a rigorous fashion (i.e. it is not always clear how much of the perceived groundwater geochemical variability is artefactual and how much is real). Item (d), on the other hand, is epistemic and can only be dealt with by consideration of different scenarios for repository evolution. As already indicated for material properties (i.e. mineralogical and sorption property variability), the relation between the application uncertainties discussed above and the combined variability and uncertainty represented in the PDF describing the generic  $K_d$  data is not absolutely clear.

### ***Handling of site specific variability and uncertainty***

The experimentally derived, generic data incorporate many forms of variability and uncertainty that are difficult to tease apart. Some components of this variability and uncertainty will be “averaged out” and some will remain on the spatial and temporal scales relevant for safety assessment modelling. Other elements of variability and uncertainty will appear under application conditions and are additional to those inherent in the generic data.

If the rock types and water compositions at the application site differ significantly from those upon which the generic data are based, this could give a significant frame shift bias (i.e. Level 2 uncertainties as discussed in Section 4.1.2). We propose, however, that because the generic data is based upon rocks from many different locations and a broad range of water compositions, most of the possible variation is likely to fall somewhere within that range. This presupposes that there has been no selection bias in the acquisition of the generic  $K_d$  data (i.e. that the generic  $K_d$  data are not biased towards rocks from a particular location or a particular water composition).

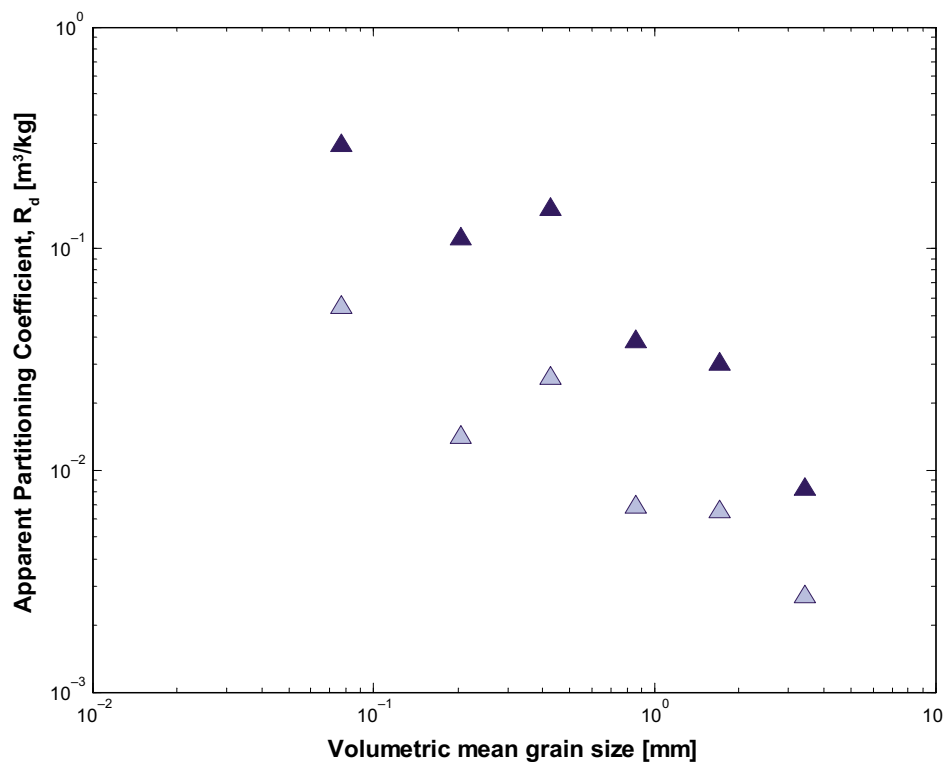
As a first approximation, the  $K_d$  variability tabulated for individual radionuclides could be used directly for estimating aggregate variability and uncertainty for safety assessment. In the light of the above discussions we note that this is most likely to be incorrect. This, however, is the standard approach that has been used in most safety assessment studies without reflection upon the wider implications of the underlying assumptions. Further studies will need to be initiated to develop appropriate means of handling application uncertainties that differ from those inherent in the generic  $K_d$  data. Given the complex interrelationship between rock mineralogy, mineral-specific sorption properties, and aqueous geochemistry this will most likely require the use of thermodynamic sorption modelling (TSM) approaches.

### 4.4.3 Lack of knowledge, errors etc

In this section we focus specifically upon epistemic uncertainties and, in particular, those that may give rise to particular frame shift effects, as these cannot usually be handled by means of a PDF approach. Many of these aspects have already been examined in Section 4.4.2 in the context of level 2 and 3 uncertainties (i.e. in the hierarchy of uncertainties described in Section 4.1.2). The discussion in this section deals largely with Level 1 uncertainties and focuses upon the acquisition of  $K_d$  estimates from laboratory data. Epistemic uncertainties that give rise to the apparently random variation in  $K_d$  measurement results obtained by different groups (as reported in the literature) are discussed and, as far as reasonably possible, are also dealt with in Chapter 5 on an individual basis for different radionuclides. It is noted that much of the discussion in this section is equally applicable to data used as a basis for mechanistic TSM modelling and is not restricted to the  $K_d$  concept.

The foremost frame shift uncertainty of concern for sorption  $K_d$  data relates to the fact that most sorption measurements are carried out on crushed rock. In a typical experiment, crushed rock samples are contacted with a spiked groundwater sample or synthetic groundwater analogue for a period of time. The experiment may be carried out with a single size fraction or perhaps the crushed material may be sieved into different size fractions in order to obtain some information relating to how the apparent partitioning coefficient varies with particle size.

The apparent partitioning coefficient, or  $R_d$ , that is measured is known to vary as a function of particle size and contact time (we prefer the term  $R_d$  to distinguish the apparent partitioning coefficient from the “true”  $K_d$  value for in situ fractured rock /McKinley and Alexander 1993/). A good example of this variation can be found in /Byegård et al. 1998/ where Cs(I) sorption was measured on various crushed fractions of Äspö diorite. These data, which exhibit a spread in  $R_d$  values of up to two orders of magnitude, are shown in Figure 4-2 below.



**Figure 4-2.** Apparent partitioning coefficient,  $R_d$  ( $m^3/kg$ ) for Cs(I) sorption on different size fractions of crushed Äspö Diorite using data taken from /Byegård et al. 1998/. Plotted data correspond to  $R_d$  values obtained after a contact time of 1 day (light symbols) and 14 days (dark symbols).

The use of crushed material and synthetic groundwaters introduces a range of additional uncertainties into the use of laboratory derived  $K_d$  values for safety assessment. There are many facets to this discussion and a full deliberation is beyond the scope of this study, although some general aspects of relevance for the interpretation of batch  $R_d$  data are discussed in the following sections.

### **Surface area effects**

The rock matrix is conceptualised to consist of mineral grains with both intergranular and intragranular porosity. The intergranular porosity (along mineral grain boundaries) results from the differential thermal expansion of mineral grains in the slowly crystallising magma during rock formation. Intragranular porosity takes the form of microfractures within individual mineral grains caused by tectonic processes and the differential expansion and contraction stresses encountered during magmatic cooling. Owing to their sheet crystalline structure, phyllosilicate (clay) minerals also have internal porosity arising that may be accessible to certain radionuclides (Cs(I) sorption in the interlayers of clay minerals is a particularly well-known example).

Given that the sorption of solutes takes place on the surfaces of geological materials, the sorption properties of rock are very strongly correlated with the available surface area of mineral grains within the porosity of the rock matrix. Sorption measurements are typically carried out using crushed material. In the process of crushing rock samples, additional surface area is created that is not representative of the intact, in situ rock. This may include both freshly cleaved mineral surfaces as well as surfaces belonging to previously disconnected pores within the rock. These new surface areas can provide additional sorption capacity – a phenomenon which is clearly evident in Figure 4-2.

Certain minerals such as micas and clays that are present in small amounts in most granitic rocks are also thought to strongly dominate sorption of, for example, Cs(I). Some researchers /e.g. Stenhouse 1995, and references therein/ have suggested that quartz and feldspar minerals are concentrated towards the top of the size distribution owing to their hardness and initially coarse grain sizes. Clay and mica minerals, which dominate ion exchange processes, on the other hand, tend to occupy the lower end of the size distribution owing to their initially fine-grained nature.

Most groups choose small particle size fractions for experiments as they reach equilibrium more quickly and are less influenced by diffusive uptake mechanisms. Occasionally, rock samples are crushed to a particle size described as “less than” a certain value (say,  $\leq 0.063$  mm) thereby giving a particle size distribution that ranges from a few  $\mu\text{m}$  up to the specified size /Stenhouse 1995/. As mentioned above, sorption properties may not scale linearly with particle size, owing to fractionation of different minerals in different size fractions. In the study by /Byegård et al. 1998/, it was found that the biotite content of granite varied between 17% to 25% between the largest and smallest particle size fraction of Åspö diorite. The difference in biotite content, however, could not satisfactorily explain the large variations in  $R_d$  measured for Cs(I) which differed by as much as a factor of 40.

Crushed rock samples may also have enhanced surface reactivity relative to intact rocks and may weather at an accelerated rate giving rise to secondary minerals that may contribute significant sorptive capacity to the crushed sample. This particular effect is discussed in more detail in the following section (time dependent uptake).

The additional surface area for sorption available in crushed materials is a significant and serious source of bias that results in a substantial overestimation of  $K_d$  values. The main problem is that almost all the data in the literature are biased in this way. This is the source of the frame shift effect. For some radionuclides, the “true”  $K_d$  appropriate for safety assessment modelling may lie outside the PDF describing the perceived variability of the parameter based upon the literature data. Cs(I) Sorption measurements by /André et al. 2006/, for example, have suggested  $R_d$  values for different size fractions of crushed rock that are as much as an order of magnitude greater than the  $R_d$  values measured for intact rock pieces using an electromigration method.

This problem is a well-known deficiency of sorption databases. Some researchers /e.g. Vandergraaf et al. 1993, Turner et al. 1999/ suggest the use of surface area normalised  $K_d$  values instead to circumvent this problem. These are customarily referred to as  $K_a$  values.

The surface area of rock samples is typically measured by way of the BET method using the sorption of gas molecules ( $N_2$  or Ar) to a surface /Brunauer et al. 1938/. Some researchers have pointed out /e.g. Jenne 1998/ that the surface area of desiccated samples may not correspond well to the surface area available for sorption when the samples are hydrated. Measurements made with other probe molecules, such as EG (ethylene glycol) or EGME (ethylene glycol monoethyl ether), also give different estimates of surface area /e.g. Allard et al. 1983a, Brotas de Carvalho et al. 1996/. For this reason, the BET surface area should only be seen as a relative measure of the number of sorption sites at the mineral surface.

It has been recently suggested that pulsed field gradient, nuclear magnetic resonance (PFG-NMR) techniques can be used to obtain specific surface areas of wetted granular materials /e.g. Mitra et al. 1992, 1993, Mitra, 1997/. Such measurements may be a better proxy for sorption surface area than BET measurements on crushed material owing not only to that they directly probe the hydrated surface area that is relevant for sorption, but also because they can potentially give information concerning how the surface area to pore volume ratio scales with particle size.

For extrapolation of  $K_d$  data from crushed material to intact in situ rock, it is typically assumed that the pore volume is proportional to  $d_g^3$  and the surface area is proportional to  $d_g^2$  ( $d_g$  being the volumetric mean particle size) /e.g. Widestrand et al. 2003/. For particles that have a constant, scale-independent sphericity, the surface to pore volume ratio therefore scales with  $d_g^{-1}$ . This may be an incorrect assumption if the size fractions of crushed rock exhibit fractal scaling relations or are contaminated with fines. Using PFG-NMR it has been observed by /Stallmach et al. 2002, Stallmach and Kärger 2003/, for example, that the surface to pore volume ratio of glacial sand has a scaling proportionality of  $\approx d_g^{-0.7}$  possibly indicating a fractal scaling phenomenon. This is mentioned as a possible avenue for future investigation for more robust extrapolation of laboratory determined  $K_d$  values using crushed materials to in situ conditions.

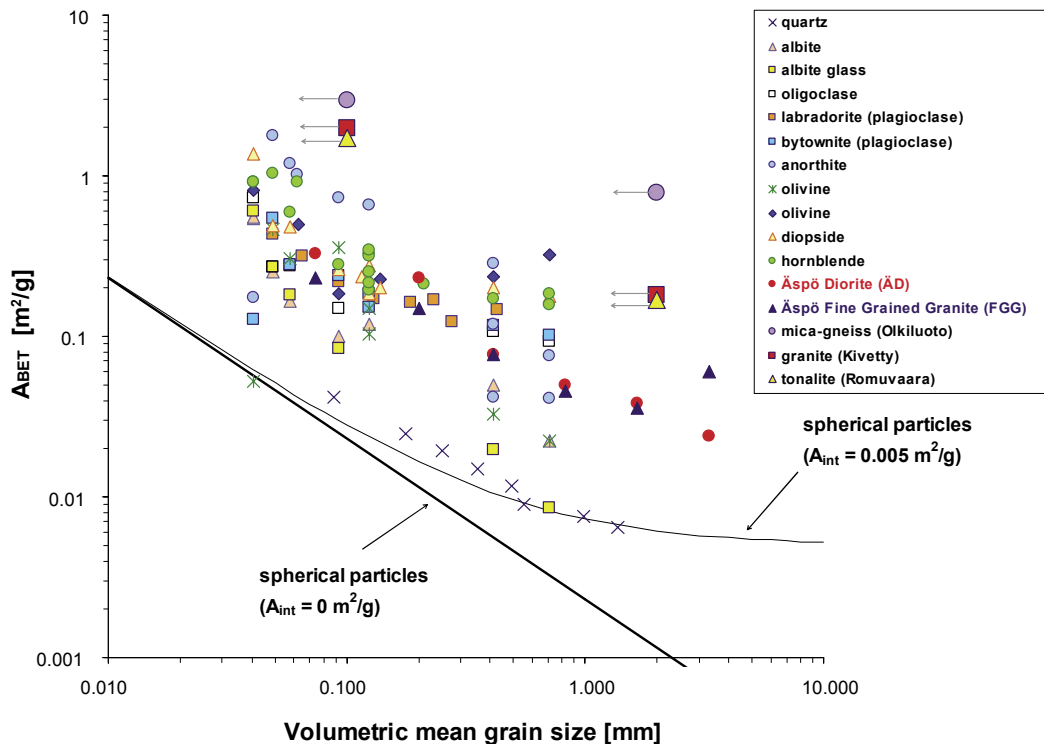
Some care should be taken when using literature based  $K_a$  values, however, as they are not always defined in terms of BET surface area (i.e. some  $K_a$  data are based upon geometric particle or fracture surface area rather than BET or other probe-molecule-derived surface area). Unfortunately, it appears that only in a small number of references in the literature has there been any effort actually made to determine surface areas of rock samples. Similarly to mass-based sorption, we use the term  $R_a$ , to distinguish between apparent sorption coefficients reported in laboratory experiments and “true”  $K_a$  values representative of in situ, fractured rock.

It should also be emphasised that the correlation between sorption  $K_d$  and surface area is only approximate as different mineral surfaces have different intrinsic sorption site densities (both fixed and variable charge). In /Allard et al. 1983a/, for example, a far from perfect correlation was obtained between cation exchange capacity (CEC) and BET surface area, indicating a more complex and mineral dependent relationship between the sorption capacity and surface area for ion-exchanging solutes. More recent studies (e.g. /Bertetti et al. 1996, Jenne 1998, Prikryl et al. 2001, Davis et al. 2004/) lend strong support to the concept of BET surface area normalisation, although there do appear to be intrinsic differences between the sorption properties of specific minerals, in terms of both the overall density of sorption sites and also different reactivities on different crystal edges (specifically, clay minerals).

Figure 4-3 below shows typical variation in the  $N_2$ -BET surface area for various pristine samples of granitic minerals as well as for some Swedish and Finnish granitic rocks:

It is clear from the experiments carried out with granitic mineral phases (Figure 4-3) that BET surface areas of crushed rock samples may be as much as 1–2 orders of magnitude higher than that of intact rock, if we take the largest size fractions to be an approximate match for intact rock. This does not seem to be an unreasonable assumption, as the BET surface area tends to level off with increasing particle sizes larger than about 1 mm in diameter.





**Figure 4-3.** Variation of  $N_2$ -BET specific surface area [ $m^2/g$ ] with volumetric mean grain size [mm] for a number of primary granitic mineral phases (crushed, pristine samples). Data for single minerals are taken from /Brantley and Mellot 2000/, with the exception of quartz data, which are taken from /Höltta et al. 1997/. Data for Äspö rock types are taken from /Byegård et al. 1998/. Data for Finnish igneous rocks (mica-gneiss, granite, tonalite) are taken from /Kulmala and Hakanen 1995/. Curves indicate theoretical surface area of uniform spherical particles both with (broken curve) and without internal sorption surfaces (unbroken curve). Horizontal, leftward pointing arrows indicate measurements made on samples with size specified as  $\leq$  given grain sizes.

The measured BET surface area of crushed particles is equal to the sum of the external surface area and a contribution from internal surfaces. Only the internal surface area of the rock is of relevance for sorption within the rock matrix. As already mentioned above, the situation is complicated by the possible formation of additional internal microfractures in mineral grains during crushing and the potential for alteration of newly exposed mineral surfaces to form secondary minerals with high surface areas. It is also possible that some of the intergranular porosity is not contiguous and crushing of rock thereby has the potential to allow access to porosity that may not be accessible to diffusing substances in intact rock. Clay minerals also typically have higher sorption reactivity on crystal sheet edges relative to their basal planes. Finely ground clay minerals therefore have a sorption reactivity that is neither correlated with total surface area nor particle size in a simple manner.

/Vandergraaf et al. 1993/ propose higher discrepancies of up to three orders of magnitude for unspecified rocks, while /Bradbury and Baeyens 1998/ suggest roughly one order of magnitude difference for both orthoclase and Grimsel granodiorite with particle size  $\leq 0.063$  mm. In principle, statistical regression of BET surface areas as a function of particle size can be used to estimate the internal surface area of intact rock, although there is frequently a large (apparently random) variation in measured values for different size fractions. From the site investigation data for major rock types from the Laxemar subarea /Byegård et al. 2006/, the 0.063–0.125 mm size fraction shows 5–50 times higher BET surface area than the 2–4 mm size fraction. Very similar values were also found for rock from Simpevarp /Byegård et al. 2005/.

It is not clear whether the sorption surface area of in situ rock at formation pressure is different to that in large pieces of de-stressed rock in the laboratory. Drill bit damage and subsequent sawing may also influence the sorption surface area in bore cores brought to the surface. This may be particularly noticeable in bore cores taken from highly stressed rock formations.

It is not known whether de-stressing influences the sorption capacity of the rock significantly, although it is thought that these effects may substantially influence effective diffusivities. In the companion report on diffusive properties of crystalline rock, /Liu et al. 2006/ show that the formation factor measured in situ roughly is 10 times lower than that found in the laboratory for highly stressed granodiorite from Forsmark. There is no systematic trend with depth suggesting that the effect may come from drill bit damage, although it could be equally well explained by de-stressing processes if the horizontal rock stress is considerably greater than the vertical rock stress.

There are two conceivable modes by which the effective diffusivity could be reduced by in situ rock stress. One is that the effective diameter of all pores is reduced proportionately. This should not have an appreciable impact upon the sorption capacity, as there is still the same surface area available for sorption. On the other hand, the reduced effective diffusivity could also result from some percentage of the pore space being closed off at formation pressures. This would have an impact upon the sorption capacity owing to physical inaccessibility of the surface area in such pores. The actual influence is likely to be somewhere between these two extremes.

### ***Time dependent uptake***

Many investigations reported in the open literature involving sorption of ionic solutes on pure phase minerals and more complex substrates such as granitic rock have given indications of time dependent behaviour. The reasons for this are not entirely clear and there are many plausible mechanisms that can be used to describe the data equally well. Some of the possibilities are listed below:

### **Diffusion limited uptake**

Here, we consider ordinary diffusion in macropores ( $> 50$  nm) and mesopores (2–50 nm) as well as “surface” or “configurational” diffusion in micropores ( $\leq 2$  nm). It should be noted that the theory of ordinary diffusion in pores considers the effective diffusivity of the rock matrix to be related to the molecular diffusivity in infinitely dilute aqueous solution by way of a geometric “formation factor” that accounts for the tortuosity and constrictivity of the pores which restricts diffusion /e.g. Ohlsson 2000, Löfgren 2004/. Surface diffusion, on the other hand, is conceptualised to be restricted to the electrical double layer (EDL) immediately adjacent to mineral surfaces /e.g. Ohlsson and Neretnieks 1998, Axe et al. 2002/. Surface diffusion is thought to be an activated process whereby outer-sphere surface complexes and ions occupying ion-exchange positions (i.e. non-specifically sorbed ions) jump from site to site along a charged surface. The concept of surface diffusion has previously been invoked to explain anomalous diffusion in low ionic strength systems where solute transport occurred significantly faster than could be explained by normal pore diffusion /e.g. Skagius and Neretnieks 1988/. Surface diffusion of solutes such as cesium and strontium can be important at low ionic strength where the sorption of these species is enhanced thereby giving a larger concentration gradient for diffusion along the EDL. Surface diffusion is thought to occur in all pores, although in very small micropores it may be rate limiting owing to the absence of ordinary diffusion.

The relative impact of surface sorption is dependent upon the sorbing characteristics of individual solutes and the thickness of the electrical double layer relative to the pore diameter. Surface sorption coefficients for a variety of divalent cations have been estimated by /Trivedi and Axe 2001a/ for microporous Al, Fe, and Mn (hydr)oxides from theoretical consideration of cation hydrated radius and sorption hydration energy and show excellent agreement with experimental data. These diffusivities range over many orders of magnitude and may have

some significance for the interpretation of solute apparent migration in porous rock particles, particularly in micropore constrictivities where surface diffusion may be the limiting diffusive transport resistance. This would occur in situations where the thickness of the electrical double layer is of the same order of magnitude or larger than the pore diameter. Experimental data obtained at low ionic strength /e.g. Skagius and Neretnieks 1982/ show indications of anion exclusion effects in crystalline rocks which should only occur in such cases. The transport of solutes that have low surface diffusivities may be limited by such diffusion bottlenecks and give rise to anomalously slow diffusive uptake relative to what would be expected for normal pore diffusion /e.g. Papelis et al. 1995, Trivedi and Axe 2000/. It is also noted that for minerals with a strong surface charge variation with pH, the surface diffusivity can be expected to vary owing to variable charged site density.

In some studies /e.g. Skagius et al. 1982/ it has been suggested that diffusion is responsible for the observed time dependent behaviour in granitic rock. Indeed, the notion of diffusion is the focal point of the retardation paradigm used to make estimates of radionuclide transport times in safety analysis. One of the major findings of the work carried out by /Skagius et al. 1982/ was that a very long time was required to obtain equilibrium for even mildly sorbing solutes in contact with crushed rock. In that particular study, it was found for particles on the order of a couple of mm in size, that as much as a year or more was required to reach an “apparent” equilibrium with the test solutions for Cs and Sr. Matching the macroscopic data to a model of particle diffusion gave a very good match for the observed time dependency. An interesting characteristic that was observed was a trend of decreasing effective diffusivity with decreasing particle size. In /Skagius et al. 1982/ particles in the size range 100–120  $\mu\text{m}$  were found to have effective diffusivities some 20 times lower than for 4–5 mm particles based upon macroscopic interpretation of Cs(I) uptake profiles. For Sr(II) uptake, the discrepancy was roughly a factor of 50. This observation has since been confirmed independently by /Byegård et al. 1998/ where very large differences (two, or more orders of magnitude) were obtained for the fitted effective diffusivity for Cs(I) uptake on different particle size fractions.

Although diffusive uptake has been directly demonstrated for larger pieces of rock (e.g. by depth profiling of concentration gradients in monolithic samples /Itner et al. 1988, Torstenfelt et al. 1982b, 1983a/) and also for the rock matrix under in situ conditions (e.g. /Birgersson et al. 1992/), the authors note that it is not absolutely clear whether this mechanism is responsible for time dependent behaviour observed in measurement data using finely crushed material.

It should also be emphasised that evidence of diffusion is frequently based solely upon interpretation of macroscopic data. There are only a few instances in the open literature where migration of solutes to inner surfaces of crushed particles has been directly demonstrated by spectroscopic or microprobe techniques. Specifically this has been done by /Zachara et al. 2002/ and /Liu et al. 2003/ for Cs(I) uptake on biotite and muscovite minerals and it has also been demonstrated for U(IV/VI) uptake on plagioclase particles by /Liu et al. 2004/ although in the latter case, sequestered internally in the particles in the form of U(IV) microprecipitates.

### **Sorption specific chemical kinetics**

Some studies have suggested chemical kinetic mechanisms to explain slow solute uptake in sorption experiments /e.g. Hayes and Leckie 1986, Wehrli et al. 1990, Jeon et al. 2003, 2004/. Although we restrict our discussion here to the sorption of solutes in fixed oxidation states, the authors note that the redox sensitive solutes frequently exhibit sorption dynamics that can, at least in part, be related to chemical kinetic phenomena /Wehrli et al. 1989, Liger et al. 1999, Fredrickson et al. 2002, Wersin et al. 1994, Nakata et al. 2000, 2002/.

For surface complexing species of fixed oxidation state, kinetically limited solute uptake has been postulated to occur by way of a fast sorption reaction forming outer-sphere surface complexes followed by a slow redistribution of solute to inner sphere complexes /e.g. Stumm and Morgan 1996/. It is noted that in /Jeon et al. 2004/ the experiments were also carefully controlled to rule out effects related to diffusion.

For a number of sorbing divalent cations, the rate limiting step has been measured directly by pressure jump kinetic studies and it has been shown that the intrinsic rate for conversion of outer to inner-sphere complexes is directly related to the rate of water exchange for the hydrolysed ion in the outer sphere complex /e.g. Hachiya et al. 1984, Wu et al. 1998, 1999 and references therein/. This “dissociative” mechanism appears to only limit the rate of inner-sphere sorption of divalent cations and is not relevant for cations that sorb by way of a non-specific ion-exchange mechanism which is generally considered to be a fast process /e.g. Sparks 2000/. It is also noted that trivalent cations and oxyanions form inner sphere complexes by way of an “associative” mechanism which is fundamentally different to that for divalent cations and cannot be related to water exchange rates as described above /Wehrli et al. 1990, Chang et al. 1993, 1994, Lin et al. 1997, Wu et al. 1999/.

From the experiments reviewed by /Wu et al. 1999/ it appears that the rate of inner-sphere complex formation for trivalent solutes and oxyanions is at least as fast as, or faster than that for divalent metal cations. It remains unclear, however, whether these chemical kinetic aspects of sorption can adequately explain the time dependency observed in sorption measurements as time constants for sorption vary strongly as a function of pH and are likely to be influenced by competitive effects from faster sorbing solutes. The authors note, however, that in certain model systems /e.g. Stumm and Morgan 1996/ the time constant for solute uptake can be shown to be roughly in agreement with observed uptake rates in sorption experiments on crushed granitic rock. Based upon these results, chemical kinetic effects as outlined above could be a plausible mechanism for the time dependent sorption of some solutes.

### **Weathering and alteration processes**

It has been suggested that the crushing of rock results in the formation of fresh fracture surfaces that may have higher reactivity and are therefore not representative of the mineral surfaces in intact rock /e.g. Stenhouse 1995/. Weathering reactions involving these fresh surfaces could give rise to an increase in reactive surface area over time /see e.g. Brantley 2004 and references therein/ or leached solutes could precipitate secondary phases giving additional sorption surface area. Under oxidising conditions, alteration of Fe(II)-containing minerals such as biotite and chlorite may lead to the formation of amorphous ferric oxyhydroxides that could give strongly upward-biased estimates of  $K_d$  relative to intact rock under in situ (and typically reducing) conditions. Leaching rates of Fe(II) from biotite and chlorite at far from equilibrium conditions in a flow through reactor are sufficiently fast /e.g. Malmström et al. 1996, 1997/ to give substantially biased estimates of  $K_d$  if the same processes were to occur during the course of batch sorption measurements using trace solute concentrations.

In a study by /Torstenfelt et al. 1983b/ it was found that Swedish granites typically contain between 1–10% by weight of iron, of which a substantial proportion (70–90%) is generally in the reduced state. In that study it was also found that crushed granite particles (90–125  $\mu\text{m}$ ) would react slowly with oxygenated water, giving an oxygen reduction half-life of 12–30 days for solid/liquid ratios in the range 0.1–10 g/l. The slow reduction of oxygen is strongly suggestive of a weathering process involving reduced Fe(II) and it is of some relevance that the timescale of the oxygen reduction is similar to the typical ranges of contact times reported in the literature for sorption measurements (see Figure 4-4 below).

The precipitation of secondary phases may be kinetically limited depending upon pH and redox conditions. It is also noted that such processes typically result in the formation of microporous aggregates of nanometre sized particles where solute uptake may be limited by surface diffusion or chemical kinetic effects as described previously. Such microporous precipitates could form on vessel walls, as colloids in solution, as coatings on the external surfaces of particles, or even within the macro- and mesoporous spaces of the crushed rock particles themselves. Amorphous precipitates may even slowly recrystallise over time to form more stable phases (e.g. transformation of ferric oxyhydroxide to goethite /e.g. Trivedi and Axe 2001b/). These processes would typically lead to a decrease in sorption capacity although may occur over longer timescales than typical of most sorption experiments and therefore can possibly be neglected.

### **Time dependent surface precipitation and co-precipitation phenomena involving the target solute**

Some studies have indicated the formation of surface precipitates and co-precipitates at concentrations well below solubility limits for pure mineral phases /e.g. Scheidegger and Sparks 1996, Scheidegger et al. 1998, Elzinga and Sparks 2001, Scheckel and Sparks 2001, Dähn et al. 2002/. These processes are generally associated with time dependent solute uptake behaviour when reported in the literature.

The authors note that these studies frequently involve solute concentrations and surface loadings far in excess of what would be relevant for transport of radionuclides in the rock surrounding a repository (typically three orders of magnitude higher concentration). The use of high solute concentrations and high surface loadings in many cases is motivated in order to perform spectroscopic studies of speciation owing to that the properties of solutes sorbed at low concentrations are difficult to quantify against background noise. While it seems that these effects may have limited importance at the concentration levels considered relevant for safety assessment, it is unclear at what point in the sorption spectrum these effects might need to be considered owing to their emergence at concentrations significantly lower than pure phase solubility limits predicted for precipitated forms of the solute concerned. For certain radionuclides, this could be a potential artefact influencing the applicability of reported  $K_d$  values although, in the absence of detailed supporting data, it cannot be quantified in any meaningful way.

### **Other measurement artefacts relating to time dependent behaviour**

It has been suggested that much of the observed time dependent behaviour in experimental sorption studies is an artefact related to non-constant physicochemical conditions /Lützenkirchen 2001/. Weathering effects, pH and redox buffering reactions and precipitation of secondary minerals can, for example, lead to non-constant pH and redox conditions during the experimental timespan. For granitic rocks with substantial amounts of Fe(II) containing minerals, redox buffering reactions resulting from the slow release of Fe(II) can have consequences both for the speciation of solutes and the pH of contact solutions.

Slowly changing pH can influence sorption measurements in a number of different ways. Small changes in pH, even as little as 0.1–0.3 pH units could potentially affect both the solubility and the surface charge of minerals (particularly secondary minerals such as ferric oxyhydroxides) sufficiently to give large changes in apparent  $R_d$  values when using very low solute concentrations. For solute concentrations on the order of 0.1  $\mu\text{mol/l}$  or lower, the precipitation of a few tens of nanograms of ferric oxyhydroxide is potentially sufficient for  $R_d$  to be overestimated by as much as an order of magnitude under typical experimental conditions. These artefacts are not possible to control for unless variables such as pH are monitored during the course of the sorption experiment. Measurement of BET surface area both before and after sorption experiments could potentially reveal spurious behaviour although this is seldom reported in the literature.

Another experimental artefact that, although not necessarily related to time dependent behaviour, can have a strong influence upon interpreted  $R_d$  values in experimental studies of sorption is partitioning of solute onto the surfaces of reaction vessels. This is customarily controlled for by measuring the loss of solute from a blank measurement (i.e. an identical contact solution in a vessel not containing any sorbing solids) and using a mass balance approach to estimate the “actual”  $R_d$  for the vessel containing geological material. This assumes, of course, that the contact solution in the blank is identical to that in the test vessel which is unlikely to be the case particularly if we consider possible pH and redox buffering reactions that may result from weathering and alteration processes. This is largely a problem if  $R_d$  values are estimated based upon monitoring the depletion of solute in the aqueous phase. Occasionally when using radioactive solutes it is possible to measure solute activities directly on the solid phase (and vessel walls for that matter) thus avoiding spurious artefacts relating to sorption on vessel walls. It is generally not feasible to measure solute activity directly on the solid phase for solute uptake that is measured periodically during a sorption experiment and in such cases any inaccuracies in

the estimation of vessel wall partitioning will also be propagated to later measurements through mass balancing required to account for withdrawn sample quantities.

### ***The use of synthetic groundwater***

The use of synthetic groundwater compositions is a possible source of bias owing to that very few experimental data have been derived using authentic groundwater samples. In some cases, the  $K_d$  obtained using synthetic groundwater may be higher than that for authentic groundwater owing to the absence of ligands such as humic and fulvic acids, as well as colloids and possibly bacterial siderophores (under oxidizing conditions). Minor constituents of groundwater that are not included in synthetic formulations (e.g.  $Ba^{2+}$ ,  $PO_4^{2-}$ ,  $NH_4^+$ , etc) may also have an impact by way of absent competitive interactions and altered solute speciation. The authors note that the importance of these are somewhat case specific and will not be relevant for all groundwater types. Although potentially a form of frame shift uncertainty, the impact of some of these substances can be approximately accounted for if some simplifying assumptions are made. This is discussed more fully in Section 5.2.2.

A more important aspect related to the use of synthetic groundwaters is that if there is any difference between the water as it is formulated and the original porewater with which the rock has been in contact with, weathering and alteration reactions are much more likely to occur owing to disequilibrium effects. Artefacts relating to these processes have already been discussed in the context of time dependent uptake above and will not be discussed further here.

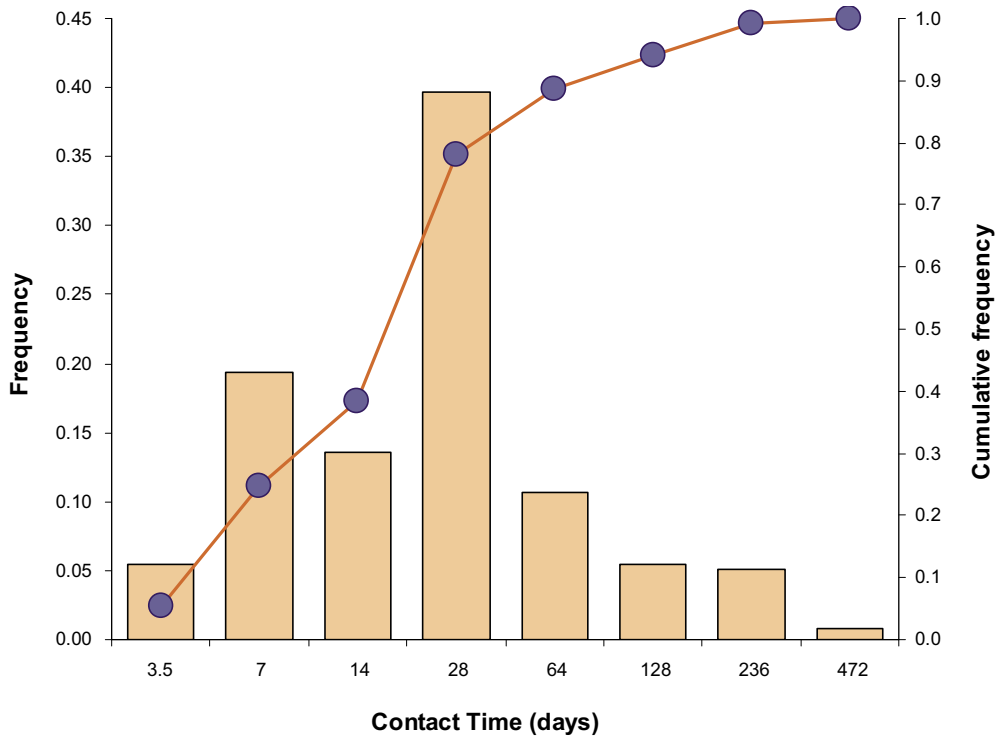
It should also be emphasised that synthetic groundwaters are frequently based upon formulations previously described in the literature and there is potential for significant selection bias in this respect. This is also discussed more fully in Section 5.2.2 in the context of individual groundwater formulations reported in various studies.

### ***Overall impact of uncertainties and consequences for data interpretation***

The use of crushed material is clearly associated with a risk for overestimation of  $K_d$  values for use in safety assessment studies. On the one hand, crushing of rock produces particles with specific surface areas much greater than that of large intact pieces or the in situ rock. Additionally, the time dependent behaviour frequently exhibited in sorption experiments means that data obtained using different contact times will result in a sorption variability that is not representative of true mineralogical- or aqueous geochemical variability. Given that it is currently unclear which physical processes underlie sorption time dependency, it is not self evident that longer contact times will give data that are more representative of “equilibrium” sorption than data obtained from short contact times. Indeed, if weathering processes and precipitation of highly sorptive secondary phases occur during the course of sorption experiments, longer contact times may actually result in a significant overestimation of  $K_d$  that is not appropriate for the in situ rock.

Occasionally desorption experiments are performed to ascertain the reversibility of sorption. The authors note that what is frequently regarded as evidence of irreversible sorption in short-term batch desorption tests is possibly a subtle effect of diffusion kinetics for particles that have only been partially equilibrated during solute uptake. Owing to the ambiguous interpretation of such experiments, only results for sorption uptake have been considered in the recommended data presented in this report.

Particle sizes used in batch sorption measurements are usually in the range of about 50  $\mu m$  up to 2–3 mm, although larger “coupons” or thin sections are also sometimes used in static tests. Sorption measurements are also regularly carried out with contact times of a week or less, and occasionally with contact times less than one day. Very few experiments are carried out for periods longer than perhaps a month. Based upon typical particle sizes and the ranges of equilibration times reported, it is clear that the bulk of experiments exhibit substantial variability that relates to time dependent uptake effects (see Figure 4-4 below).



**Figure 4-4.** Statistics for contact times used by various researchers performing sorption experiments on crushed crystalline rock. The data are based upon roughly 7,000 values reported in the JNC sorption database /Shibutani et al. 1999/.

As mentioned previously, the use of detailed mass-balancing based upon aqueous phase depletion of solute can be an inaccurate means of estimating  $K_d$  if there is substantial sorption on vessel surfaces. In general,  $K_d$  estimates based upon direct measurement of activity in the solid phase are preferable, although this is not the most common method used. It is also unclear in many cases, to what extent consideration of such artefacts has been internalised in data analysis, thereby introducing additional uncertainty for the applicability of generic data reported in the literature for use in safety assessment.

In the absence of a detailed set of comparative data relating typical  $K_d$  values, CEC, and BET surface areas of crushed and intact rock pieces, the authors of this report recommend that the laboratory-based  $K_d$  estimates should be rounded down by a factor of at least 10 and possibly as much as 100 in safety assessment modelling to ensure that retention properties are not overestimated. If the reduced effective diffusivity measured in situ is a result of pores being closed off due to lithostatic stress, then an additional rounding down factor may be necessary, although at present we have no rationale upon which to base a quantitative estimate for this. Any effect due to lithostatic stress, however, is likely to be small in comparison to the other uncertainties inherent in the data set.

Some experiments have been carried out with sorbing tracers in through-diffusion tests. From these types of experiments the effective diffusivity,  $D_e$ , and the rock capacity factor ( $\alpha = \varepsilon_p + K_d \rho_s$ ) can be simultaneously determined. Under saline and brine conditions, it is possible that these tests give more accurate estimates of  $K_d$  as they are typically carried out on pieces on the order of 0.5–2.0 cm thickness, and are thereby less influenced by particle size effects relating to creation of new surface areas. Under low ionic strength conditions, however, surface diffusion phenomena may complicate the data interpretation unless this is specifically accounted for.

Monoliths used for through diffusion experiments can have microfractures or larger, healed fractures that penetrate the entire thickness of the piece. The presence of such features has the potential to bias the results by way of providing fast short-cuts through the rock coupon. It is also noted that the simplified models typically used for data interpretation may not always give accurate results in the presence of heterogeneous diffusion pathways, multiple porosities, and weathering effects. As there are so few data in the literature for through-diffusion with sorbing species and also owing to the uncertain interpretation of experiments, we have chosen not to include such data in this report.

## **4.5 Correlations**

### **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 (see Section 4.2) should cover most potential correlations. Still other statistical correlations may exist. Address the following questions:

- If the data varies in space or time – is anything known about its autocorrelation structure?
- If the parameter concerns element specific values (e.g.  $K_d$ , solubilities) or nuclide specific values (e.g. inventory, IRF, EDF:s), what is known about the correlation of the parameter values between different element or between different nuclides?
- 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 partitioning coefficients for specific radionuclides and parameters influencing partitioning coefficient data**

We have identified two core groups of correlated parameters:

- correlations between major groundwater species,
- correlations in the sorption of chemically related radionuclides.

These aspects are discussed in the following sections.

#### ***Correlations between major groundwater species***

The prevailing hydrogeochemical conditions at Äspö HRL have been previously described as being constrained by mixing processes involving a number of end member water types /e.g. Laaksoharju et al. 1999ab/. Similar mixing processes between end member water types has also recently been invoked to explain the geochemistry of groundwater at both Forsmark /Laaksoharju et al. 2004a/ and the Simpevarp area /Laaksoharju et al. 2004b/ as well as the reference waters used in the SR97 safety assessment /Laaksoharju 1999/. Knowledge of the composition of these end-member water types, allows the calculation of all possible water compositions provided they result from ideal mixing processes. On a practical level, this means that proportions of the major ions in deep Swedish groundwater should be strongly correlated.



In a broader sense, it is possible to identify certain controlling processes that govern the composition of groundwater, resulting in correlated major ion compositions. The buffering effects of the  $\text{CaCO}_3(\text{s}) - \text{H}_2\text{O} - \text{CO}_2(\text{g})$  system, for example, largely determines the pH of groundwaters, although at repository depth this is thought to be tempered by aluminosilicate weathering products and ion exchange processes /e.g. Andersson et al. 1983, Frøpe et al. 1984, Nordstrom et al. 1989, Gascoyne 2004/. The concentrations of the major cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  are mostly thought to be interrelated by ion-exchange processes with clays and mineral dissolution-precipitation equilibria /e.g. Trotignon et al. 1999/.  $\text{Ca}^{2+}$  concentrations, in particular, are governed predominantly by calcite equilibrium. Concentrations of the minor anions fluoride ( $\text{F}^-$ ) and phosphate ( $\text{PO}_4^{2-}$ ) are generally thought to be governed by equilibrium with fluorite and apatite, respectively. Redox state (Eh) is related to pH, although most Swedish groundwaters are expected to be either strongly reducing or oxidising at roughly atmospheric intensity. This has already been discussed in some detail in Section 2.1.2. Iron and sulphur redox pairs, often involving mineral sinks such as  $\text{Fe}(\text{OH})_3$  and  $\text{FeS}_2$ , are usually assumed to be controlling  $E_h$  levels. Sulphate and carbonate concentrations can also be inversely related by way of sulphate reduction reactions in the presence of methane or other organic sources of carbon /Laaksoharju 1999/.

Chloride ion ( $\text{Cl}^-$ ) is the dominant anion for most groundwaters in Sweden that are relevant for safety assessment studies. It is generally conserved in groundwater and is therefore a good tracer for mixing and dilution processes. For Swedish conditions, it appears that there is a strongly linear correlation between chloride concentration and electrical conductance and consequently also ionic strength. This feature makes chloride a very good proxy for quickly determining the geochemical nature of sampled groundwaters.

### ***Correlations in the sorption of chemically related radionuclides***

There are a number of specific correlations between chemically related radionuclides. Some of these relate to direct similarities in sorption behaviour while others relate to the way in which the sorption of certain radionuclides responds to speciation effects etc. This was considered previously in /Ochs and Talerico 2004/ and we repeat some of the main aspects of that discussion here:

Certain radionuclides share chemical similarities that enable them, in varying degrees, to be used interchangeably as sorption “analogues” for each other. This is useful for estimating sorption properties where there are gaps in the literature data, or for combining data sets from closely related radionuclides to obtain a more detailed picture of variability. Analogous radionuclides can be grouped into a number of categories where group members have similar sorption characteristics. Some of these are (excluding non-sorbing species):

1. Alkali elements: Cs, K, Na, Rb
2. Alkaline earth elements: Ba, Ra, Sr
3. Divalent transition elements: Cd, Co, Ni, Pb, Pd
4. Trivalent elements: Ac, Am, Ce, Cm, Eu, Ho, Pu(III), Pm, Sm
5. Tetravalent elements: Np(IV), Pa(IV), Pu(IV), Sn, Th, U(IV), Zr
6. Pentavalent elements: Nb, Np(V), Pa(V), Pu(V)
7. Hexavalent elements: Pu(VI), U(VI)

Not all of the analogies listed above are very good and there can be some deviation between individual members in the groups listed above. Although, having roughly the same chemistry, many of them have sufficiently dissimilar hydrolysis and stability constants for complexation that there can be significant uncertainty concerning their “analogous” behaviour. The list is intended mainly for illustrative purposes and individual analogies should be considered on a case-by-case basis.

Some redox sensitive radionuclides such as U(IV,VI) and Np(IV,V) sorb more strongly under reducing conditions. This is not always true, however, and the redox behaviour of radionuclides needs often to be considered on a case by case basis. Pu(III,IV,V,VI) and Se(II,IV,VI), for example, exhibit more complex sorption chemistry redox dependencies that don't fall into this simple pattern.

Although the pH is not expected to vary outside quite a narrow interval (pH 7–9) under repository conditions, a short discussion on pH effects is warranted here. Changes in pH do not influence the sorption of radionuclides equally. Radionuclides that sorb by way of ion-exchange mechanisms (i.e. alkali and alkaline earth metals), for example, are not strongly influenced by pH changes in granitic rock systems. Radionuclides that have a surface complexation sorption mechanism are influenced to varying degrees depending upon their propensity to form different cationic and anionic aqueous complexes /e.g. Langmuir 1997/. In addition, the surface charge characteristics of minerals are strongly dependent upon pH, which complicates the inter-comparison of different radionuclides. Similarly, the presence of carbonate can have both a positive or negative effect on solute sorptive strength depending upon the nature of carbonate complexes that are formed.

For alkaline and alkaline earth radionuclides an increase in major cation concentration will lead to a decrease in  $K_d$  owing to competition for sorption sites. For radionuclides that sorb by surface complexation there may be other more indirect effects of ionic strength. These were discussed previously in Section 4.2.2.

## 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. All factual information and judgements made in this chapter are provided by the experts listed as authors to the report.

### 5.1 Methods and approaches for uncertainty estimation

#### 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

Many literature sources have been examined and data compiled for some of the more important sorbing radionuclides. For reasons of data transparency and traceability a master table for each radionuclide was set up in a spreadsheet program (MS Excel) where the following data fields were recorded:

**Table 5-1. Tabulated data fields for sorption measurement data obtained from literature sources.**

Data field	Description of parameter
Species	Radionuclide including presumed valence/redox state (e.g. Pu(IV), Cs <sup>+</sup> , Am <sup>+3</sup> )
Ref. #	Reference number from list of references
Ref. Type	Primary or secondary reference type (see discussion below)
Solid Phase	Name of rock type and additional descriptors
Experiment type	Batch (crushed material), batch (monolith), through diffusion, etc
L/S	Liquid to solid ratio if relevant (i.e. ml aqueous phase/g solid)
Temp (C)	Temperature at which experiment was performed
Water Type	Name of water used (e.g. Allard_pH7, Aq293, etc) as well as pre-equilibration details if available (major ion composition listed in separate data sheet).
Water Class	Category of water (i.e. saline/non-saline/brine/other)
Ionic Strength (mol/l)	(Initial) Ionic strength of aqueous phase
pH init	Initial pH of aqueous phase

Data field	Description of parameter
pH end	Final pH of aqueous phase
Eh init	Initial Eh of aqueous phase
Eh end	Final Eh of aqueous phase
C spike (mol/l)	Concentration of radionuclide added as a "spike"
C total (mol/l)	Total concentration of sorbing species including background concentration of non-radioactive forms if relevant
Contact Time	Contact time upon which sorption measurement is based
Particle size (mm)	Sieve sizes of particles, or coupon dimensions where appropriate
Separation procedure	Detail of phase separation – e.g. Centrifugation (rpm and time), filtration (filter size)
Measurement Mode	Method used to estimate data (e.g. aqueous activity difference, solid and liquid phase activity, etc)
$A_{\text{BET}}$ (m <sup>2</sup> /g)	Surface area as measured by BET (N <sub>2</sub> or Ar)
CEC (μeq/g)	Measured cation exchange capacity (CEC) of solid phase
CEC method	Method used for CEC estimation (e.g. isotope dilution, Ag-thiourea, estimation from major cation mass balance, etc)
$K_d$ app (m <sup>3</sup> /kg)	Measured apparent $K_d$ or distribution coefficient $R_d$
$K_d$ error (m <sup>3</sup> /kg)	Error of $K_d/R_d$ measurement based upon replicate measurements (1-sigma unless contra-indicated)
$k_f$ (L <sup>n</sup> /g.mol <sup>(n-1)</sup> )	Freundlich constant if available (Note: $K_d = k_f \cdot C_w^{(n-1)}$ )
n	Freundlich exponent if available
$D_a$ (m <sup>2</sup> /s)	Apparent diffusivity derived from through diffusion or batch monolith experiment
$D_a$ error (m <sup>2</sup> /s)	Error in apparent diffusivity based upon replicate measurements (1-sigma unless contra-indicated)
Diffusion model	Model used to interpret measurement data (e.g. Crank 2ed. Eq 4.22, etc)
$F_i$ (HTO)	Formation factor as measured by through-diffusion using tritiated water or uranine (state which if not tritium)
$D_e$ (m <sup>2</sup> /s)	Estimated effective diffusivity of diffusing species at 25°C
$D_e$ error (m <sup>2</sup> /s)	Error in effective diffusivity based upon replicate measurements (1-sigma unless contra-indicated)
Replicates	Number of replicate measurements (if any)
Reported data	Type of data reported in primary reference (e.g. log $K_d$ , $D_e$ , $D_a$ , etc)
Reinterpreted data	Reinterpreted data in this database (e.g. $K_d$ , $D_e$ , $D_a$ , etc)
Atm./Redox condition	Redox conditions under which experiment was carried out (e.g. ambient, reducing, N <sub>2</sub> -glovebox, etc)
Density (kg/m <sup>3</sup> )	Measured density of rock
Porosity (%)	Measured porosity of rock
Mineralogy (wt%)	Mineralogical composition in condensed notation (e.g. Bi(25),Pl(35),Or(6),Q(22),Ep(7),Ap(2),Tt(2),Op(2))
Elemental composition (wt%)	Elemental composition in condensed notation (e.g. Si(60.1),Al(14.6),Ca(4.5),Fe(7.9),K(3.3),Mg(3.1),.... etc)
Trace elements (mg/kg)	Trace elemental composition in condensed notation (e.g. Rb(108),Cs(3.1),Sr(932),Ba(1290),Zr(1130),Hf(25.6),.... etc)
Reference	Full reference to original source in Harvard format (i.e. Smith and Jones 1998 "Radionuclides & rocks", Journal of Rock, pp 10–30)
Comments	Additional comments concerning the data

These data sheets (one for each radionuclide investigated) are included as an addendum to this report and are available from the main author upon request. The “minimum” requirement for inclusion in the survey was generally that the approximate composition of the water used in the experiment should be recorded in addition to the rock being of a relevant granitic rock type for safety assessment studies under Swedish conditions. It is noted, however, in the case of Am(III) and Np(IV) the requirement for documented water composition was relaxed somewhat owing to their relative insensitivity to ionic strength effects.

There is, however, a large variation in the quality of documentation and sophistication of data sets that makes a definitive set of selection criteria difficult to define. In many cases, crucially important information (including, but not restricted to, particle size, contact time, liquid-solid ratio, phase separation procedure, measurement procedure, “spike” concentration, and background concentration) have not been adequately reported, or there is some ambiguity concerning which parameter values correspond to which measurements. Additionally, it is often not clear whether reported error values relate to replicate measurements or radiometric counting statistics.

From the initial selection of literature data described above, a subset was then chosen as a basis for establishing representative ranges of  $R_d$  values for use in SR-Can. This was done largely on the basis of expert judgement where well documented datasets demonstrating good experimental practice were given precedence over data sets with less transparent documentation of relevant procedural aspects and experimental conditions. Any data sets containing unclear definitions of water chemistry, rock-type, and steps taken to replicate oxidising or reducing conditions in the case of redox sensitive substances were immediately excluded. Likewise, any datasets containing dubious data and inappropriate water compositions were excluded from the selection (as judged by the author on the basis of water chemistry and element geochemistry arguments). Given the subjective nature of the selection process, both the first and second data selections are given in the accompanying data sheets in their entirety with the aim of increasing transparency and to facilitate independent review of the selection procedures.

A number of sources of selection bias have been identified in this investigation as potential sources of uncertainty. Among these are the “Elsevier effect” where references obtained show a bias that reflects the search engine or search method used (This term is coined after the observation that the widely used, internet-based, scientific search engine SCIRUS, returns references that are overwhelmingly biased towards Elsevier publications). Similarly, references that are available in a readily downloadable electronic format (e.g. pdf-documents) gain significance in sorption compilations that may not necessarily reflect their quality.

Radionuclides that are less popular research objects owing to strict regulation (e.g. Plutonium) or that are difficult to study owing to the necessity of complex experimental procedures (generally the case for redox sensitive substances) have apparent ranges of uncertainty that may be biased by the relatively smaller number of measurements existing in the open literature.

It is also often not clear whether literature data have been duplicated in different publications by the same author, thereby giving a false sense of data variation when data is pooled from a number of references.

In some cases, data relates to internal reports or proprietary data that is not obtainable as an original reference owing to age, or lack of publication status. Such references are referred to here as “secondary” references. These data sets were assembled from other databases or reports and it is frequently not possible to authenticate the veracity of the data by way of a primary literature reference. Moreover, some datasets are incorrectly referenced when obtained from other databases and their provenance is thereby indeterminate. This raises the possibility of the “validation snowball effect”, whereby badly executed experiments or poorly documented data are given equal weight and implicit validity within sorption databases where primary references are not available for scrutiny.

In addition to the above uncertainties, there are still a number of outstanding issues concerning interpretation of laboratory data that have not been adequately resolved. Firstly, the use of crushed material in laboratory sorption experiments results in the creation of new surfaces for sorption that cannot be always be quantified in a satisfactory and unambiguous fashion. This raises the possibility that the recommended  $K_d$  values derived from laboratory experiments on crushed material may be significantly overestimated and therefore non-conservative in Safety Assessment.

Secondly, there is some evidence to suggest that recommended  $K_d$  values based upon literature data might be associated with significant uncertainty owing to the neglect of sorption time dependency effects. Depending upon the processes which these time dependencies represent, this could result in an upward or downward biasing effect on  $K_d$  values, although based on the range of contact times reported in the literature it is likely to give a frame dilation effect on the aggregate  $K_d$  uncertainty range.

Similarly, artefacts and uncertainties introduced by differing water compositions, rock types and experimental methods can potentially give substantial deviations from what would be considered a reasonable range of uncertainty for intact rock under in situ field conditions.

The combined effect of the different biases and uncertainties is expected to substantially dilate and possibly shift the range of uncertainty estimated for sorbing radionuclides (see Section 4.4.3 for more detailed discussions of frame shift and frame dilation effects).

For each radionuclide and water class, ranges of reported values are first given in the form of horizontal bar plots that itemise the data in accordance to reference and rock type. These represent the overall range (i.e. minimum-maximum span) of values reported for the partitioning coefficient ( $R_d$ ) in each reference. Owing to the varying quality of these data sets and the large number of mineralogical, geochemical, and other variables represented in the data, this is intended mostly for illustrative purposes to give an indication of the aggregate data variability in the literature.

Based upon the data available for each radionuclide, recommendations are then given for appropriate safety assessment  $K_d$  values and their associated uncertainty. It should be remembered that the generic data contains many epistemic uncertainties unrelated to and superimposed upon effects arising from geochemical and mineralogical variability (e.g. choice of experimental conditions, separation procedures, contact time, etc). The variability expressed in the  $K_d$  data should therefore be considered as being approximate and possibly an overprediction of the true uncertainty if these confounding factors were to be removed from the data.

## **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 Water type**

The sorption data in the literature can be roughly categorised into three groups relating to the contact water composition; these are non-saline, brackish, and strongly saline water. Some data included in the master table were based upon water types that are not specifically applicable to Swedish groundwater conditions. These are classified as “other” and typically relate to experiments performed using pure electrolytes such as NaCl, NaClO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub>. Although not directly relevant for safety assessment data selection, they are nonetheless informative for identifying systematic geochemical trends in sorption data (e.g. for discerning ionic strength

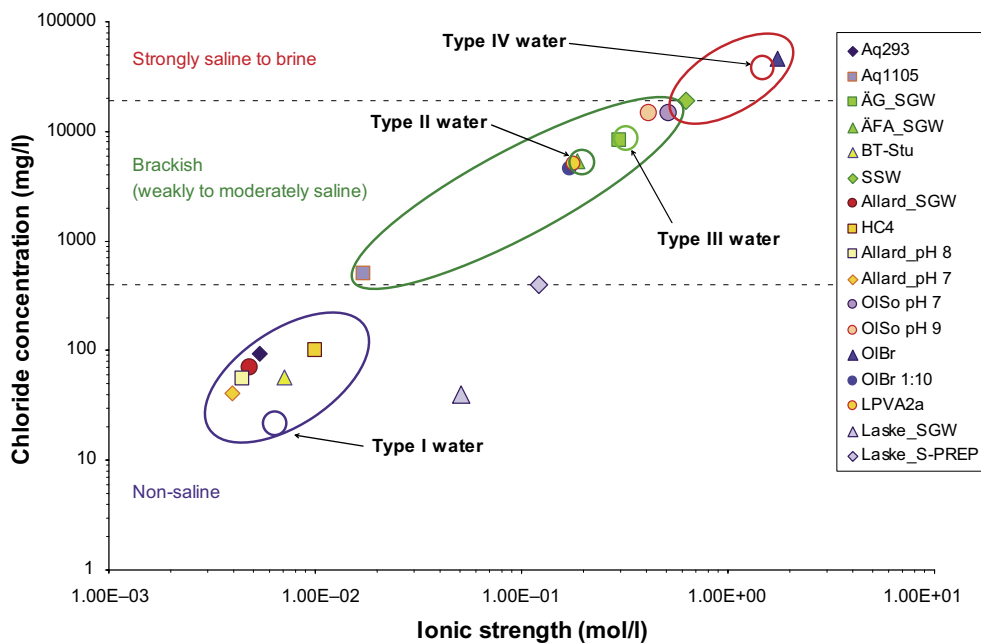
effects etc). Owing to the lack of data for some radionuclides, some measurements made using distilled or deionised water have been categorised as non-saline even though they tend to represent ionic strengths and compositions that are unlikely to exist under field conditions. Otherwise, we have avoided the use of data for water types classified as “other”. The rationale for this was to prevent systematic bias resulting from the absence of species that would be expected to compete for sorption sites or otherwise hinder sorption in some way. The authors of this report deem that the non-representative water compositions included in the definition of “other” water types generally tend to give overestimates of  $K_d$  values.

In the previous sorption data compilation by /Carbol and Engkvist 1997/, the lower (500 mg/l  $\text{Cl}^-$ ) and upper (6,500 mg/l  $\text{Cl}^-$ ) boundary for the definition of saline water was different to that adopted in this report. Here, we consider water with a chloride concentration in the range 400–19,000 mg/l to be brackish (weakly to moderately saline), noting that the upper limit of this range roughly corresponds to the chloride concentration of normal oceanic seawater. Water with 19,000–36,000 mg/l  $\text{Cl}^-$  is termed strongly saline, while water with  $\geq 36,000$  mg/l  $\text{Cl}^-$  is considered to be brine.

The lower limit for brackish water used in this report is set at 400 mg/l  $\text{Cl}^-$  in order that  $R_d$  data based upon the “Laske\_S-PREP” water /Laske 1980/ is categorised at the low end of a saline category rather than as a non-saline water (see Figure 5-1 below). This is due to the large gaps in the data for water compositions spanning chloride concentrations of 100–400 mg/l and 500–4,000 mg/l. Given that there are large data gaps in these intervals, the choice of 400 mg/l or 500 mg/l as the cutoff point for non-saline and saline conditions makes very little practical difference in most cases. We also note that the definitions of brackish, strongly saline, and brine used here are arbitrarily chosen to fit the needs of  $K_d$  data selection and do not necessarily correspond to salinity definitions based upon practical salinity units (psu) or other standards.

For SR-Can, a number of reference water types have been defined /Byegård et al. 2005/. These reference water types (see Appendix A) correspond to non-saline water (Type-I), brackish-saline water (Type-II) and (Type-III), and brine (Type-IV).

Examples of some of the water types represented in the literature are given below in Figure 5-1 where chloride concentration is plotted against ionic strength:



**Figure 5-1.** Examples of water types used in reviewed sorption experiments (see Appendix B for explanations of individual waters). The four reference water types considered relevant for SR-Can conditions are indicated in the figure as Type I–IV and are marked with small, empty circles (Appendix A).

Most water types that have  $\text{Cl}^-$  as the dominant anion component tend to follow a roughly linear trend as can be seen clearly in the figure for the relation between ionic strength and  $\text{Cl}^-$  concentration. In addition, there is well-characterised correlation between  $\text{Cl}^-$  concentration and measured electrical conductivity of in situ waters in Sweden, which makes  $\text{Cl}^-$  concentration a reasonably good proxy for quickly estimating the geochemical nature of sampled groundwater. The two main exceptions in the synthetic groundwaters depicted above are those investigated by /Laske 1980/ (see non-saline outliers to the right in Figure 5-1), which were dominated by  $\text{SO}_4^{2-}$  anion.

Most of the water types shown in Figure 5-1 above are synthetic groundwater mixtures. The only exception is the LPVA2 water type /Huitti et al. 1996/, which was a true groundwater sample. Owing to the relatively large amount of iron in this sample (6 mg/l), the water was allowed to equilibrate at atmospheric conditions for a week followed by filtration (0.22  $\mu\text{m}$ ) to remove colloidal material. It is noted that although care is taken in most cases to formulate representative synthetic groundwaters, there is always the possibility that the absence of trace substances may influence the laboratory measurement data. Substances that may be absent from synthetic groundwaters could include  $\text{PO}_4^{2-}$ , background traces of non-radioactive isotopes or analogues of the target solute, as well as humic- and fulvic acids, colloids and possibly bacterial siderophores (where appropriate). On the other hand, if there are substantial changes in the geochemistry of authentic groundwater samples taken from the field owing to precipitation of colloids, for example, these may not either be representative of actual in situ groundwaters (as in the case of the LPVA2 water type described above). Such artefacts are a possible source of bias in the data.

It is possible, in principle, to approximately account for the influence of colloids and bacterial siderophores if the total “carrying capacity” of these substances can be estimated. If the total concentration of siderophores or surface area of colloids suspended in the flowing water is known, it is relatively straightforward to estimate an upper limit for the detrimental influence that they may have upon sorption properties by assuming an irreversible binding process. It has been shown by /Degueldre et al. 1996, 2000/ that colloid concentration can be predicted from the groundwater composition.

To make scoping calculations, we could assume as a first approximation that the colloids have roughly the same sorption properties as intact host rock (based upon surface area normalised data). For colloidal substances that cannot penetrate the rock matrix, the concentration of solute available for diffusive-sorptive uptake to the rock should then be reduced by an appropriate amount. In the case of ligands that can penetrate the rock matrix (i.e. non-colloidal humic and fulvic substances or siderophores) the  $K_d$  value can be reduced to account for the decreased sorption.

There is a great deal of small-scale variation in the geochemical conditions chosen by individual experimenters in the formulation of synthetic groundwaters. This introduces some degree of uncertainty when considering the influence of various geochemical parameters on  $K_d$  values. The synthetic groundwaters tend to have a pH in the range 7.0–9.0 unless spiked with acid or base to investigate the influence of pH. Carbonate ( $\text{HCO}_3^-$ ) concentrations are typically in the range 10–300 mg/l with a median of about 80 mg/l. The dominant anion in the synthetic groundwaters is usually  $\text{Cl}^-$ , although the  $\text{HCO}_3^-$  concentration is frequently higher amongst the non-saline synthetic groundwaters. Amongst the selected data used in the  $K_d$  compilation, sulphate ( $\text{SO}_4^{2-}$ ) is mostly present as a minor anion at a substantially lower concentration than  $\text{Cl}^-$  (although with some exceptions).

It is difficult to provide generic data for specific geochemical conditions as the variability of synthetic groundwater compositions, mineral phases, and small differences in experimental technique between different groups tends to obscure any systematic trends beyond a very rough classification according to water- and rock-type.

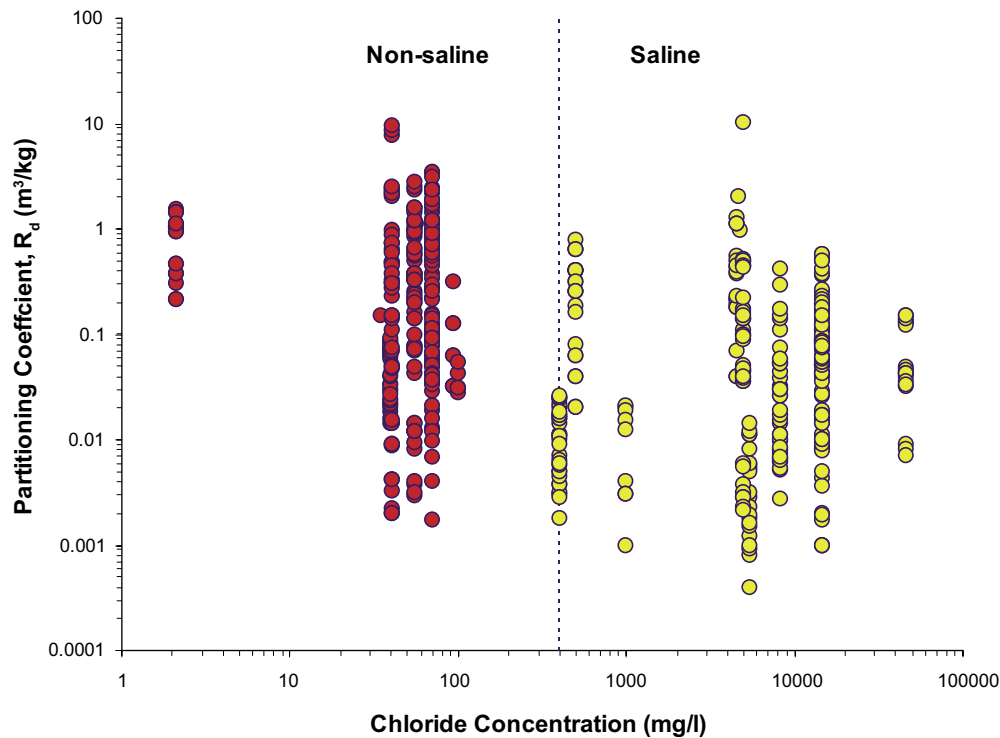
In addition, the variability represented in the experimental data probably reflects the statistics of chosen experimental conditions rather than true geochemical variability. Amongst the non-saline synthetic groundwaters, for example, many experimenters have chosen to use water compositions that are roughly the same as that described by /Allard and Beall 1979/



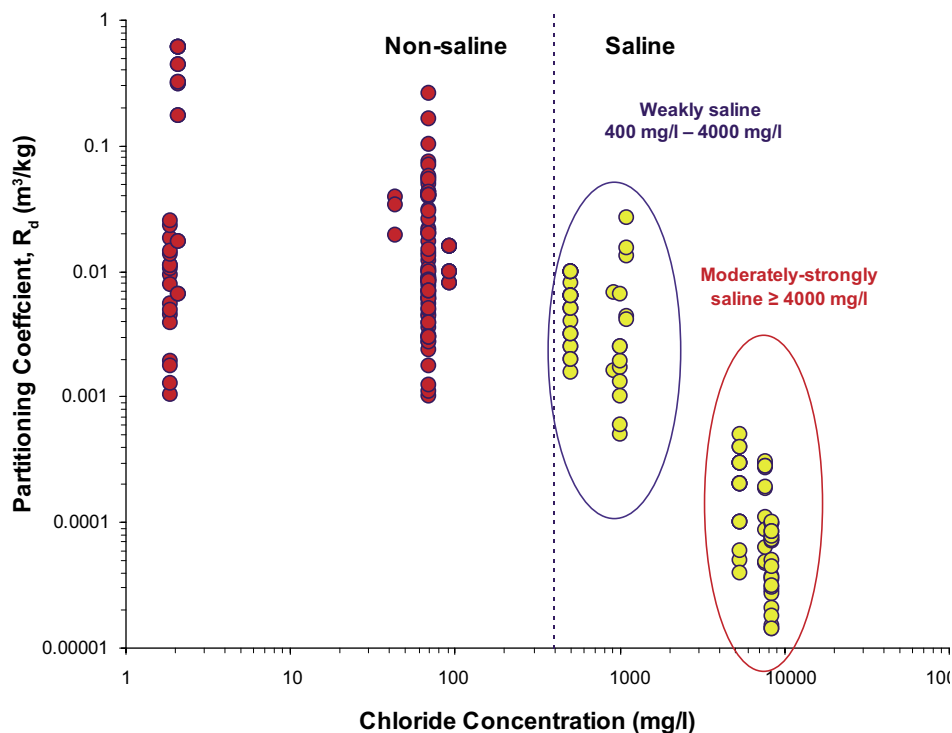
(“Allard\_SGW” in Figure 5-1). There are, however, a smaller number of datasets having compositions deviating outside that particular composition. The variability in the aggregate data set therefore possibly reflects dissimilarities in the individual water compositions although with a systematic bias towards Allard-type synthetic groundwater that determines the location of the mean geochemical condition. The effect of this will be most profound for nuclides that sorb by way of an ion-exchange mechanism, although it is noted that other nuclides such as the actinides may also be affected by, for example, dissimilarities in carbonate concentration.

The sorption data reported in the literature are difficult to delineate robustly into salinity groups owing to a general sparsity of good quality data. Moreover, the range of water compositions used by various investigators is sufficiently broad that chloride concentration is not a very good correlating parameter for  $K_d$  when considering the aggregate data set. This appears to be the case even for ion-exchanging solutes that are known to exhibit significant ionic strength dependencies for sorption. The authors believe that this is at least partly due to the differing ion exchange selectivities of competing cations in the different water formulations used for data acquisition. The broad distribution of major ion composition represented in the aggregate data set thereby tends to mask the direct impact of ionic strength upon sorption. The ionic strength effect is further complicated in the case of Cs(I) by non-linear sorption effects related to the solute concentration. This is illustrated in Figure 5-2 below where partitioning coefficients reported in the literature for Cs(I) sorption are plotted against chloride concentration.

For the purposes of this report, and considering the availability and quality of data, recommended  $K_d$  values for most solutes are therefore only given for non-saline water ( $< 400 \text{ mg/l Cl}^-$ ) and a broadly defined saline water type ( $\geq 400 \text{ mg/l Cl}^-$ ). In the special case of Sr(II), however, owing to its generally poor sorption and exceptional sensitivity to ionic strength a special case is made and  $K_d$  recommendations can be made for three salinity categories. These are non-saline ( $< 400 \text{ mg/l Cl}^-$ ), weakly-saline ( $400 \text{ mg/l} \leq \text{Cl}^- < 4,000 \text{ mg/l}$ ), and moderately-to-strongly saline ( $\geq 4,000 \text{ mg/l Cl}^-$ ). The sensitivity of Sr(II) to ionic strength effects is illustrated in Figure 5-2 below where partitioning coefficients reported in the literature for Sr(II) sorption are plotted against chloride concentration.



**Figure 5-2.** Partitioning coefficient,  $R_d$  ( $\text{m}^3/\text{kg}$ ) for sorption of Cs(I) on granitic rock types plotted as a function of chloride concentration. The data shown in the figure are the same as those used for deriving recommended  $K_d$  values for Cs(I) in this report.



**Figure 5-3.** Partitioning coefficient,  $R_d$  ( $m^3/kg$ ) for sorption of Sr(II) on granitic rock types plotted as a function of chloride concentration. The data shown in the figure are the same as those used for deriving recommended  $K_d$  values for Sr(II) in this report.

### 5.2.3 Rock type

As discussed in Section 2.1.2, we consider here both the basic rock-type (i.e. granite, granodiorite, etc) as well as any relevant descriptors that describe alteration and weathering. As there is a continuum of mineralogical compositions spanning different rock-types this introduces a taxonomic uncertainty in rock-type identification. This is an issue both for interpretation of literature data as well as for site characterisation data. For this reason, we do not attempt to strongly delineate different rock types, but treat them as indistinct property classes unless there are very clear differences apparent in the literature data. There is evidence, however, to suggest that sorption site density is far more important than mineral identity for determining sorption properties of granitic rocks (see discussion in Section 4.4.3 and below).

### 5.2.4 Mineral surface area and sorption site density

Given that the adsorption of radionuclides takes place by way of the association of ionic solutes with charged mineral surfaces, the quantification of available surface areas is an important predictor of the sorption capacity of the rock. Although at this stage no method is available for establishing a quantitative relationship between specific surface areas and sorption site density, results of BET surface area measurements are a reasonably good proxy that appear to be more important than rock-type for determining sorption properties. This correlation appears to be particularly strong for radionuclides that sorb by way of a surface complexation mechanism, although there is evidence to suggest that the non-specific sorption of ion-exchanging substances is also at least partly correlated with mineral surface area (these issues have been discussed in detail in Section 2.1.2 and 4.4.3).

Owing to the paucity of data where surface area measurements have been made, we have adopted the approach of reporting raw, mass-based partitioning coefficients in Section 5.3 and subsequently introducing an approximate correction factor to extrapolate reported data to  $K_d$  values that are reasonable for in situ conditions.

We believe that this makes the data more transparent, as well as allowing a larger pool of data to be used for making generic recommendations as there are very few measurements reported in the literature where the BET surface area has been determined for the materials used in experiments.

### 5.2.5 Redox state

Redox conditions at repository depth are expected to be either strongly reducing, or oxidising at atmospheric intensity. Owing to the relatively rapid kinetics (i.e. relative to advective travel times) and on-off nature of aqueous redox states in deep groundwater, it is thought that these can also be handled efficiently in a conditional  $K_d$  framework (see discussion in Section 2.1.2).

In this compilation, data are supplied for both oxidising and reducing conditions when appropriate. This will only be important for certain radionuclide species. It should be noted that only in a very few cases has the identity of the dominant redox-sensitive species been directly identified in experiments. Instead, it is usual for the identity of the sorbing species to be presumed on the basis of theoretical speciation calculations. This introduces some uncertainty into measurement data, particularly in cases where steps have not been taken to adequately ensure reducing conditions. It is therefore possible that there are systematic variations arising due to differences in experimental technique between different researchers. Some experimenters, for example, use only a nitrogen gas atmosphere in a glove box while others spike the test solutions with sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) to ensure reducing conditions. In practice, however, there are typically such large differences in sorption properties between oxidising and reducing conditions that any obvious errors due to redox state uncertainty are relatively easy to identify from the magnitude of the reported partitioning coefficient.

This, however, has the potential to introduce a substantial selection bias that is somewhat subjective in nature. On the basis of known geochemical properties of U(IV,VI) and Np(IV,V), for example, we would expect sorption under reducing conditions to be much stronger than under oxidising conditions. The relevant question here is should we exclude  $K_d$  values from the data selection for reducing conditions if they seem too low? This is a particular problem when redox conditions are not monitored or the methods used for maintaining reducing conditions are not documented adequately. The inclusion of both the initial literature data selection and the refined data selection (which is used for recommending  $K_d$  values) in the accompanying MS Excel data sheets goes some way towards making this selection process more transparent and allowing such biases to be scrutinised.

### 5.2.6 Radionuclide concentration

Certain radionuclides exhibit non-linear  $K_d$  behaviour down to very low concentrations. Such non-linear concentration dependency is typically described by way of a Freundlich or Langmuir isotherm in the literature data.

Although it is generally not possible to obtain simple closed form solutions for the sorption phenomena described by non-linear isotherms in transport modelling, it is always possible to choose  $K_d$  values that will “bracket” the actual residence time distribution (RTD) of the solute, or at least to conservatively estimate the earliest possible arrival time of the concentration front with all other things being equal. Owing to the tailing effect of non-linear isotherms, the peak breakthrough flux is generally higher for an equivalent linear  $K_d$  model and therefore biosphere dosage rates will also be conservatively overestimated. This is also true for rate-limited sorption processes where the kinetics of solute uptake and desorption are non-negligible over the timescale of the associated transport processes /Weber et al. 1991/.

Although care has been taken to include only data for solute concentrations that are reasonably appropriate for expected in situ conditions, the solute “spike” concentrations reported in the literature data typically span some orders of magnitude. It is also noted that the spike concentration doesn't necessarily say a great deal about the final “equilibrium” concentration

of the system after a given contact time. This is particularly true in those cases where a substantial background concentration of the solute is expected (such as for Cs(I) which is expected to have a background concentration equal to or greater than that of the radiocesium released from a repository). For this reason, we consider any sorption non-linearity related to solute concentration to be internalised in the reported range of  $R_d$  values and as such, we do not consider these effects explicitly. This additional source of uncertainty should be considered in safety assessment calculations for these radionuclides.

## 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 2.3) for the Safety Assessment, the uncertainty estimates may be given *either* as a *distribution function*, *subjective percentiles* or as a *range*

The preferable option is to describe the uncertainty as a *distribution function*, but the distribution has to be motivated if it can be motivated. For example, for a spatially varying function well described by a given stochastic process, like variography or DFN, a potential distribution function may be to state that all realisations of this spatially varying function are equally probable.

- Another option is to only provide *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 2.3) 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.

If the expert is uneasy in supplying distribution functions or subjective percentiles, the uncertainty may instead be described as a *range*. However, the meaning of the range must then be provided, e.g. does it represent all possible values, all “realistically possible” values or just the more likely values? Preferably, the expert should provide two ranges i) the range where it is extremely unlikely that the parameter would lie outside this range and ii) a range where it is likely that the parameter would lie within. (A typical example of the latter range if the parameter was to follow a normal distribution this range would be  $\pm$  one standard deviation).

The uncertainty estimates should also provide information on correlations.

- For spatially/temporal varying function information provide information about auto-correlation etc.
- List other parameters 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. An important example to consider is correlation between different elements (e.g.  $K_d$  values, solubilities) or between different nuclides (e.g. inventory, IRF, EDF:s). 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 Alkali and alkaline earth metals

#### Cesium (Cs)

Cesium (including the radioisotopes  $^{134}\text{Cs}$ ,  $^{135}\text{Cs}$ , and  $^{137}\text{Cs}$ ) is one of the most well characterised radionuclides originating in spent nuclear fuel.

Radioisotopes of cesium are fission products, meaning that they are formed as a direct product of nuclear fission reactions. The three principal isotopes of Cs in spent nuclear fuel have respective half-lives of 2.065 y ( $^{134}\text{Cs}$ ),  $2.3 \times 10^6$  y ( $^{135}\text{Cs}$ ), and 30.17 y ( $^{137}\text{Cs}$ ) /Audi et al. 2003/. A typical inventory of Cs radioisotopes at different times in BWR waste is:

The radioisotopes  $^{134}\text{Cs}$ ,  $^{135}\text{Cs}$ , and  $^{137}\text{Cs}$  undergo  $\beta$ -decay to form the stable isotopes  $^{134}\text{Ba}$ ,  $^{135}\text{Ba}$ , and  $^{137}\text{Ba}$ , respectively. Some of the  $^{137}\text{Cs}$  decay may proceed via the metastable  $^{137\text{m}}\text{Ba}$  metastable isomer (which subsequently undergoes  $\gamma$ -decay) although it has a relatively short half-life (2.6 min) and its effects are usually attributed to Cs.

$^{135}\text{Cs}$  was one of the dominating radionuclides in the far-field release calculations for the SR-97 safety assessment /Lindgren and Lindström 1999/.

#### Geochemistry of Cs

Cs exists as free ions in the +1 oxidation state (i.e.  $\text{Cs}^+$ ) in groundwater and does not form stable complexes with common constituents likely to be encountered in granitic groundwaters /Andersson and Allard 1983, Albinsson 1991, US EPA 1999/. Cs is highly soluble and there are no solubility limiting minerals formed at the concentration levels likely to be of interest in safety assessment ( $\leq 10^{-4}$  mol/l) /Stenhouse 1995/.

The abundance of Cs in granitic rocks varies, although usually in the range of a few to some tens of ppm /IAEA 2005/. Granite from Stripa contains from 4–13 ppm Cs /Cui and Eriksen 1996/, Äspö diorite and Äspö fine-grained granite contain on the order of 1.5–3 ppm /Byegård et al. 1998/. Some of the Cs content of granitic rock may be sorbed, although it is probable that a large fraction is internally sequestered in, for example, feldspar minerals and thereby not accessible by the porewater.

Typical background Cs concentrations /Byegård et al. 1998/ in granitic groundwaters (Äspö) are in the range 1–5  $\mu\text{g/l}$  ( $8 \times 10^{-9}$ – $4 \times 10^{-8}$  mol/l). Background Cs concentrations in granitic waters at Stripa /Cui and Eriksen 1996 (and references therein)/ were found to be on the order of 70  $\mu\text{g/l}$  ( $5 \times 10^{-7}$  mol/l). /Carbol and Engkvist 1997/ report “in situ” distribution coefficients for Cs of 10–290  $\text{m}^3/\text{kg}$ , while /Cui and Eriksen 1996/ give values of 0.06–0.02  $\text{m}^3/\text{kg}$ . Such “in situ” distribution coefficients merely represent the ratio of solid and aqueous phase concentrations and should not be used in safety assessment modelling. This is because they implicitly do not consider the matrix-bound component and therefore do not represent true sorption equilibria /McKinley and Alexander 1993/.

**Table 5-2. Inventory (Bq/ton U) of Cs radioisotopes at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.**

	40 y	100 y	1,000 y	10,000 y
$^{134}\text{Cs}$	$1.67 \times 10^{10}$	n/a	n/a	n/a
$^{135}\text{Cs}$	$2.89 \times 10^{10}$	$2.89 \times 10^{10}$	$2.89 \times 10^{10}$	$2.88 \times 10^{10}$
$^{137}\text{Cs}$	$2.53 \times 10^{15}$	$6.32 \times 10^{14}$	$5.87 \times 10^5$	–

## Cs sorption mechanisms

Cs is expected to sorb primarily by way of a non-specific, ion exchange mechanism at fixed charge sites on silicate minerals /Andersson and Allard 1983 (and references therein), Stenhouse 1995/.

Cs sorption appears strongest on phyllosilicates, which also tend to have considerably higher CEC than other primary granitic minerals /Allard et al. 1983a/. Many studies also point to the importance of high affinity “frayed-edge sites” (FES) for the sorption capacity of phyllosilicates /e.g. Comans and Hockley 1992 (and references therein), Zachara et al. 2002, Steefel et al. 2003/. FES consist of partially delaminated silica-alumina sheets at the edge of phyllosilicate laminae formed by the removal of interlayer  $K^+$  ions during alteration or weathering. These sites have been observed to sorb more strongly than either basal plane or inter-layer sites.

There is some evidence that Cs sorption is a multi-step process involving initial, rapid uptake onto low-affinity sites followed by a slow redistribution of  $Cs^+$  to the more sparsely distributed FES and interlayer sites of phyllosilicate minerals. It has also been hypothesised that  $Cs^+$  sequestered in interlayer sites may be trapped irreversibly owing to interlayer collapse. This may be true, although experimental evidence of sorption hysteresis is complicated by the fact that diffusion effects in grain boundary pores will also give rise to apparent sorption irreversibility if the desorption step is carried out before the rock is fully equilibrated (see discussion in Section 4.4.3).

In near-surface environments such as soils and sediments, illite (a weathering product of biotite) has been frequently identified as one of the dominant minerals for Cs sorption /e.g. Comans and Hockley 1992/. In granitic rock it is generally thought that biotite and other related micaceous minerals are dominant. In autoradiograph studies of granite /Torstenfelt et al. 1982b/ found sorbed radiocesium to be almost exclusively associated with biotite, chlorite, and hornblende (an inosilicate) mineral grains. In a similar study, /Huitti et al. 1998/ identify sericite (paragonite) and muscovite as dominant sorbing minerals, along with biotite and chlorite. In that particular study, cordierite and to a lesser extent biotite were found to dominate the sorption capacity of mica-gneiss. In granodiorite, sericitised plagioclase, chlorite, and biotite were dominating. In granite the greatest sorption capacity was associated with muscovite. The relative sorbing strength of different minerals does not seem to be completely resolved, however, as other researchers (although working with sediments) identify biotite as a stronger sorbent than muscovite for Cs sorption /McKinley et al. 2004/.

$Cs^+$  is relatively large ion (ionic radius of 1.81 Å), which means that it has weak ion-dipole interactions with water and consequently is weakly hydrated. It can approach charged sites more closely and thus associate more strongly than other competing ions that have a larger sphere of hydration. This also implies that it competes strongly against other cations in groundwater for electrostatic ion-exchange sites. It is worth noting that the ammonium ion ( $NH_4^+$ ) also is only weakly hydrated and, as a consequence, strongly competes against  $Cs^+$  for sorption sites.

This sequence of affinities, however, is also strongly dependent upon mass-action effects and although  $Cs^+$  may bind more strongly than the major solution cations  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  or  $K^+$ , high concentrations of these ions can significantly hinder the sorption of  $Cs^+$ . The apparent distribution coefficient of  $Cs^+$  in marine water, for example, is typically 1–2 orders of magnitude less than that obtained for the same geological material under non-saline conditions /Hsu et al. 2002/. This is largely due to competitive effects from both  $K^+$  and  $Na^+$  that are present in very high concentrations in seawater. Although not all cationic species compete equally effectively for ion-exchange sites, the distribution coefficient for  $Cs^+$  is strongly correlated with ionic strength.

Most studies indicate either an indeterminate or very weak pH-dependency for Cs sorption /Andersson and Allard 1983, Andersson et al. 1983, Torstenfelt et al. 1982a/, which is probably a result of surface complexation reactions involving variable charge sites that only have a low affinity for  $Cs^+$ .

Sorption of Cs on mineral phases is strongly correlated with their CEC /Allard et al. 1983/, although not all CEC-bearing minerals are equal in terms of their affinity for Cs<sup>+</sup>. It is possible for the total CEC of non-micaceous minerals in granite, for example, to be greater than the total CEC of micas even though it is these that preferentially sorb Cs. The relation between the Cs distribution coefficient and BET-surface area is also correlated although more weakly than for CEC owing to disparities between the CEC and specific surface areas of individual mineral phases.

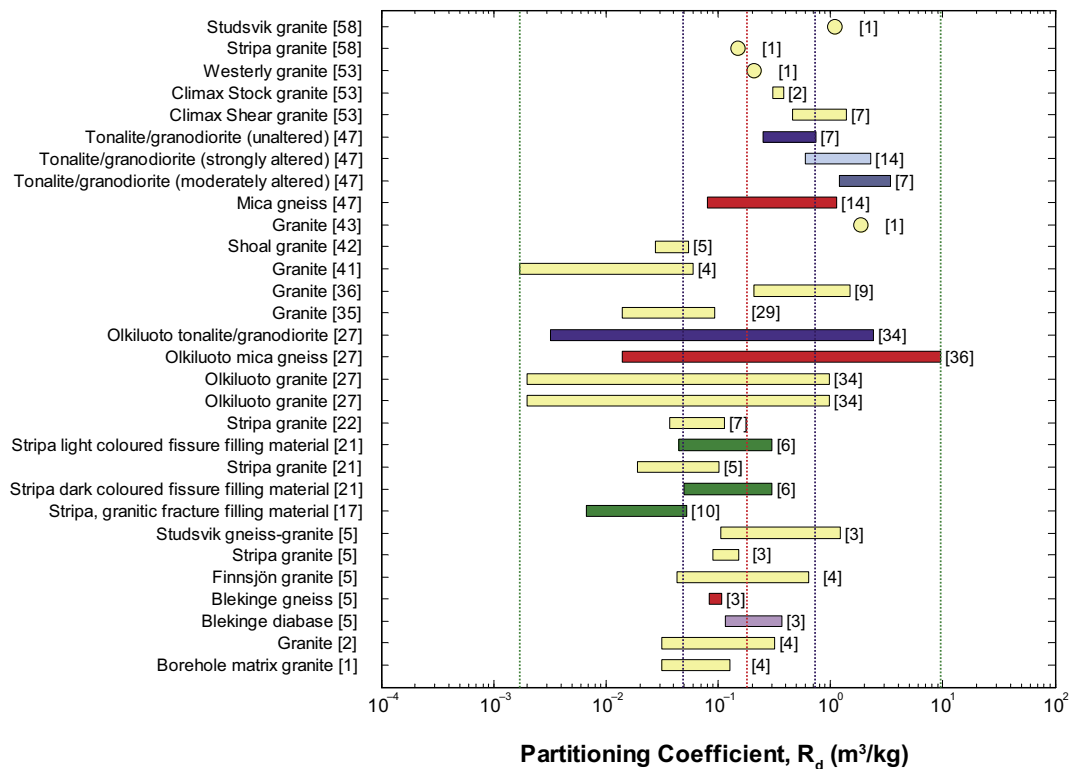
Cs is unusual amongst the SA-relevant radionuclides in that it exhibits strongly non-linear sorption behaviour right down to very low concentrations. This is a well-characterised property of Cs, and it can be described quite acceptably by the Freundlich isotherm (provided all other variables are maintained constant).

### R<sub>d</sub> data ranges for Cs sorption reported in the literature

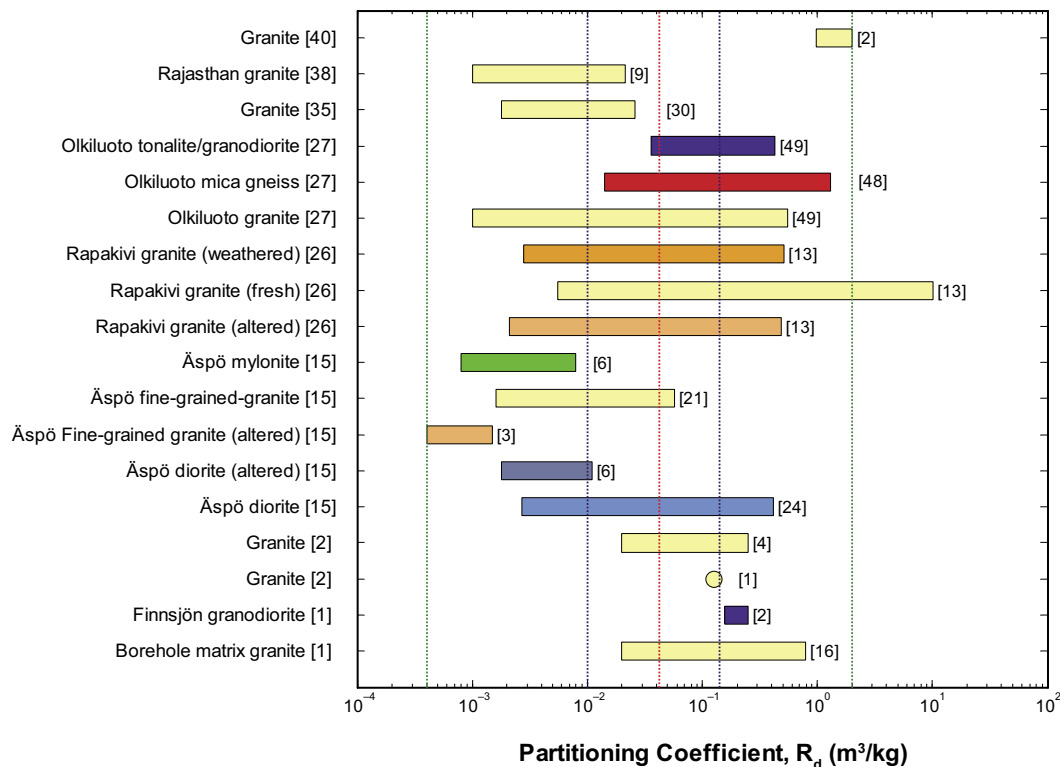
1,276 individual R<sub>d</sub> measurements for Cs(I) sorption have been examined of which, 701 values were rejected for various reasons. Of the remaining data, 266 values were found to be applicable for non-saline conditions and 309 for saline conditions.

Data are available for a number of rock types including granite, diorite, granodiorite, tonalite, mica-gneiss as well as some alteration forms. There do not appear to be very significant differences amongst the different rock types and it is thought that any variation between rock types is obscured by the influence of different water compositions used in measurements.

The ranges of reported distribution coefficients in the data selection are given in Figure 5-4 below for non-saline water (Cl<sup>-</sup> < 400 mg/l) and in Figure 5-5 for saline water (Cl<sup>-</sup> ≥ 400 mg/l).



**Figure 5-4.** Ranges of reported distribution coefficients, R<sub>d</sub> (m<sup>3</sup>/kg) for Cs(I) sorption as given in literature sources for non-saline water (Cl<sup>-</sup> < 400 mg/l). Bars correspond to R<sub>d</sub> ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-5.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for  $Cs(I)$  sorption as given in literature sources for saline water ( $Cl^- \geq 400$  mg/l). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).

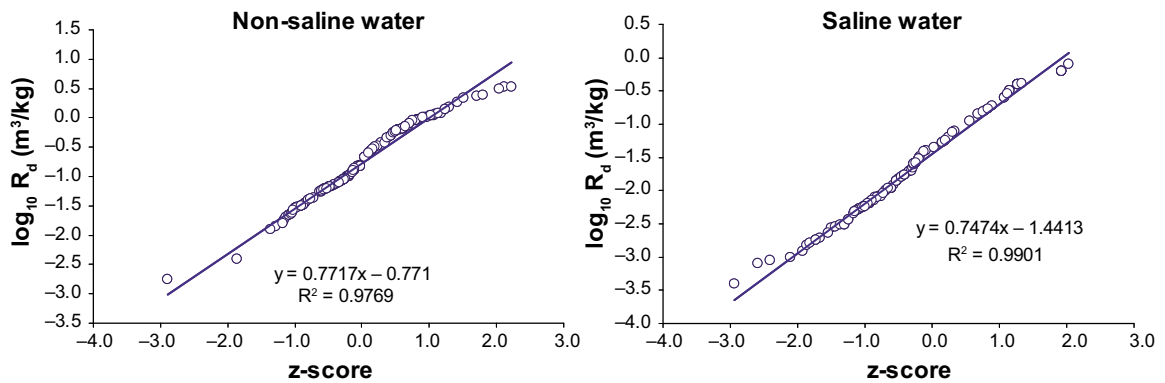
The influence of alteration and weathering upon sorption properties appears to vary among the different rock-types. In some cases, alteration processes appear to increase the sorptive strength of the rock materials. This was observed for the comparison between fresh and weathered granodiorite [47] /Siitari-Kauppi et al. 1999/ and also for Stripa granite when compared with associated fissure filling material, assumed to be a weathering product of the granite [21] /Erikssen and Locklund 1987/. For Stripa granite, however, the result isn't unequivocal when compared against data obtained in other studies. The data obtained by [10] /Cui and Erikssen 1996/, for example, suggests that granitic fracture filling material has a lower sorption capacity than Stripa granite.

In other studies, there appears to be a decrease of the sorption capacity as a result of alteration. This was true for the data obtained by [26] /Huitti et al. 1998/ comparing fresh, altered, and weathered granite. The same trend was also observed by [15] /Byegård et al. 1998/ in the case of Äspö fine-grained granite and Äspö diorite. The authors in [15] suggest that the difference arises due to alteration of biotite to the less strongly sorbing chlorite mineral. It is not clear, however, whether the reduced sorption capacity is due to alteration processes, or the fact that a larger representative particle size fraction was used for the experiments involving altered materials.

Normal probability plots for the aggregate data sets are given in Figure 5-6 below for the  $\log_{10}$ -transformed data.

The data for both non-saline and saline conditions appear to be approximately log-normally distributed. The median values for non-saline and saline conditions only differ by about an order of magnitude with the non-saline value being slightly higher.





**Figure 5-6.** Normal probability plots ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Cs(I) sorption as given in literature sources.

### Strontium (Sr)

Strontium ( $^{90}\text{Sr}$ ) is a very well characterised radionuclide that is initially present in spent nuclear fuel at relatively high concentrations. Along with Cs, it is one of the most well characterised radionuclides. This is partly due to the fact that it is relatively easy to work with, but also because it is only weakly sorbing and thus interesting for studying tracer transport in natural systems. The radioisotopes  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  dominate the radioactivity of high-level waste for the first hundred years /Albinsson 1991/ and are the most important isotopes of radiological concern emanating from the accidental release of spent nuclear fuel and reprocessing wastes into the environment.

$^{90}\text{Sr}$  is a fission product and it has a half-life of 28.79 y and undergoes  $\beta$ -decay to form  $^{90}\text{Y}$  (half-life 64 h) subsequently followed by a further  $\beta$ -emission giving stable  $^{90}\text{Zr}$  as a final product. A typical inventory of  $^{90}\text{Sr}$  at different times in BWR waste is: (see Table 5-3).

Owing to its short half-life,  $^{90}\text{Sr}$  was not found to be an important radionuclide in the far-field release calculations for the SR-97 safety assessment /Lindgren and Lindström 1999/.

### Geochemistry of Sr

Sr is only present in the +2 oxidation state and is chemically very similar to Ca. In groundwater it exists predominantly as  $\text{Sr}^{2+}$  and is not strongly complexed by inorganic ligands, although /Bruno et al. 1997, 2002/ have suggested that  $\text{SrSO}_4$  is the predominant complexed species in water with high sulphate concentrations. It has also been hypothesised by /Andersson et al. 1983/ that the formation of hydrolysed species and carbonate complexes can occur at elevated pH ( $\text{pH} > 9$ ) and carbonate levels.

**Table 5-3.** Inventory (Bq/ton U) of  $^{90}\text{Sr}$  at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.

	40 y	100 y	1,000 y	10,000 y
$^{90}\text{Sr}$	$1.49 \times 10^{15}$	$3.40 \times 10^{14}$	$8.04 \times 10^4$	n/a

Sr is highly soluble and can precipitate in the form of strontianite ( $\text{SrCO}_{3(s)}$ ) and celestite ( $\text{SrSO}_{4(s)}$ ). Groundwater concentrations of Sr, however, are frequently 2–3 orders of magnitude lower than what would be expected on the basis of these pure mineral phase solubilities, although can be rationalised in terms of a solid solution of Sr-substituted calcite /Bruno et al. 2002/. In terms of ionic radius,  $\text{Sr}^{2+}$  (1.27 Å) is intermediate in size between  $\text{Ca}^{2+}$  (1.06 Å) and  $\text{K}^+$  (1.33 Å), with the consequence that it can substitutively associate with both Ca and K containing minerals /Stenhouse 1995/. In general, there is a very strong correlation between Sr and Ca concentrations in groundwater /Bruno et al. 2002/, although /Nordstrom et al. 1992/ have also described a correlation with groundwater phosphate concentration in groundwater at Poços de Caldas possibly indicating some kind of association with phosphate containing minerals at this location.

Äspö diorite contains on the order of 900–1,300 ppm Sr, while Äspö fine-grained granite typically contains 180–240 ppm Sr /Byegård et al. 1998/. Granite from Stripa in Sweden as found to contain roughly 300 ppm Sr /Andrews et al. 1982/. Typical groundwater concentrations of Sr at Äspö are in the range 20–35 mg/l /Byegård et al. 1998/.

### **Sr sorption mechanisms**

Sr(II) is expected to sorb primarily by way of a non-specific ion exchange mechanism and is therefore sensitive to ionic strength effects. It is not redox sensitive, although moderately sensitive to pH changes. It is noted that the positive correlation between Sr and Ca groundwater concentrations could indicate a competitive effect related to ion-exchange equilibria, although it is also compatible with the notion of solid solution solubility control.

### **$R_d$ data ranges for Sr sorption reported in the literature**

491 individual  $R_d$  measurements for Sr(II) sorption have been examined of which, 260 values were rejected for various reasons. Of the remaining data, 124 values were found to be applicable for non-saline conditions, 45 for weakly saline conditions and 58 for strongly-saline conditions. Of the solutes studied, only Sr(II) exhibited sufficient sorption variation as a function of ionic strength to motivate the additional salinity subdivision of weakly- and strongly-saline.

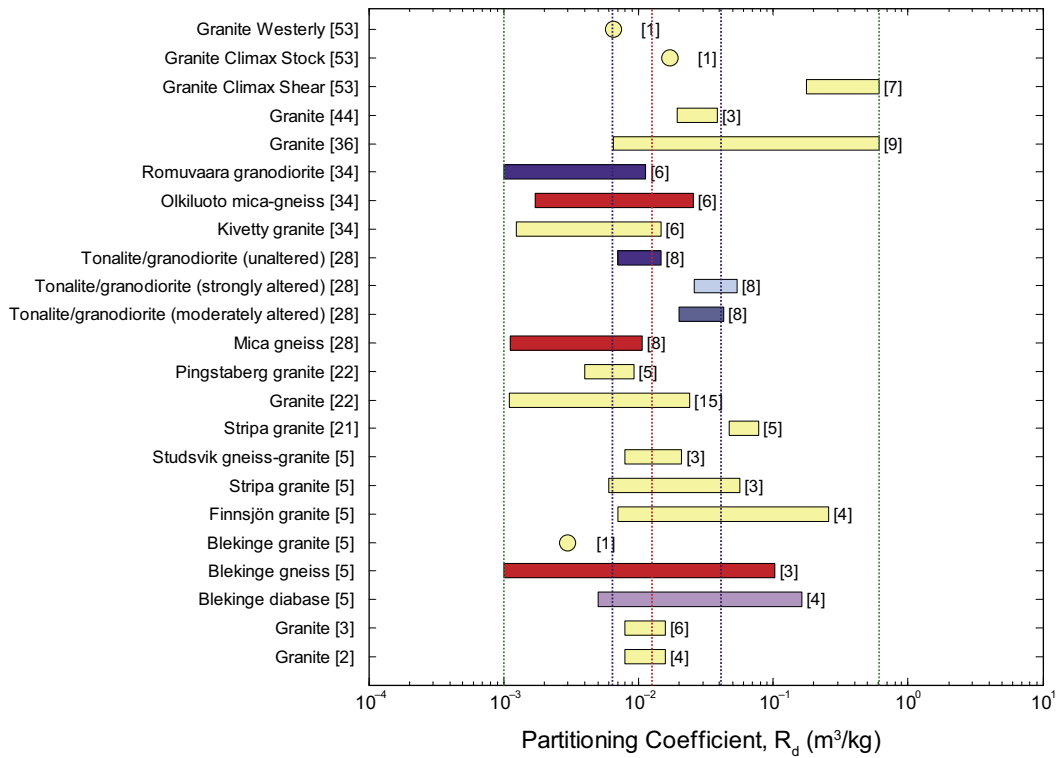
Data are available for a number of rock types including granite, diorite, granodiorite, tonalite, mica-gneiss as well as some alteration forms. There do not appear to be very significant differences amongst the different rock types and it is thought that any variation between rock types is obscured by the influence of different water compositions used in measurements.

The ranges of reported distribution coefficients in the data selection are given in Figure 5-7 below for non-saline water ( $\text{Cl}^- < 400 \text{ mg/l}$ ). Data for weakly-saline water (400–4,000 mg/l  $\text{Cl}^-$ ) and moderately to strongly-saline water ( $\geq 4,000 \text{ mg/l Cl}^-$ ) are given in Figure 5-7 and Figure 5-8 below.

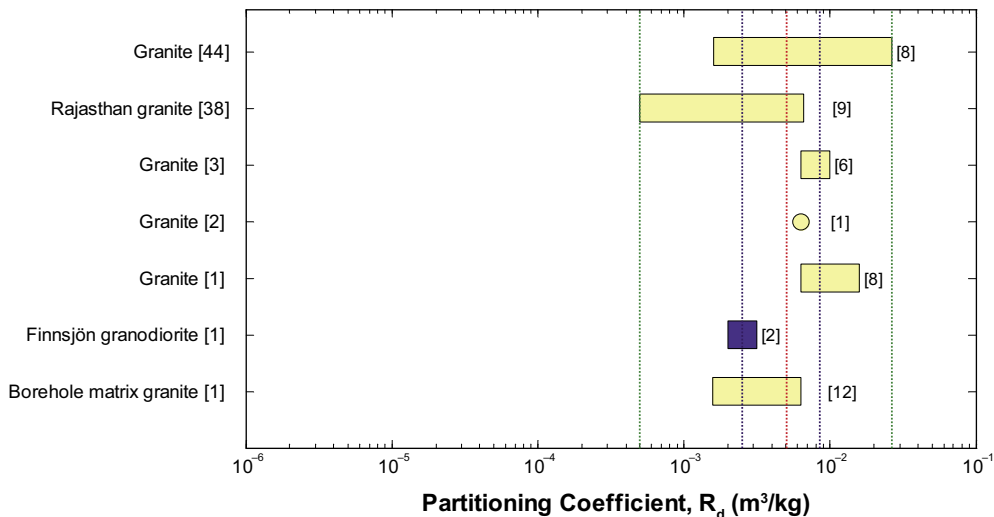
Similarly to Cs(I), rock alteration appears to give increased sorptivity for Sr(II). This is true for the data obtained by [28] /Höltta et al. 1997/ and it is noted that the trend was similar for the same rock types discussed in the context of Cs(I) sorption (i.e. [47] /Siitari-Kauppi et al. 1999/). For the data obtained by [15] /Byegård et al. 1998/, on the other hand, there is an increased sorptivity for Sr(II) associated with altered forms, although this is the opposite of what was observed for Cs(I) sorption on the same rock types.

Normal probability plots for the aggregate data sets are given in Figure 5-10 below for the  $\log_{10}$ -transformed data.

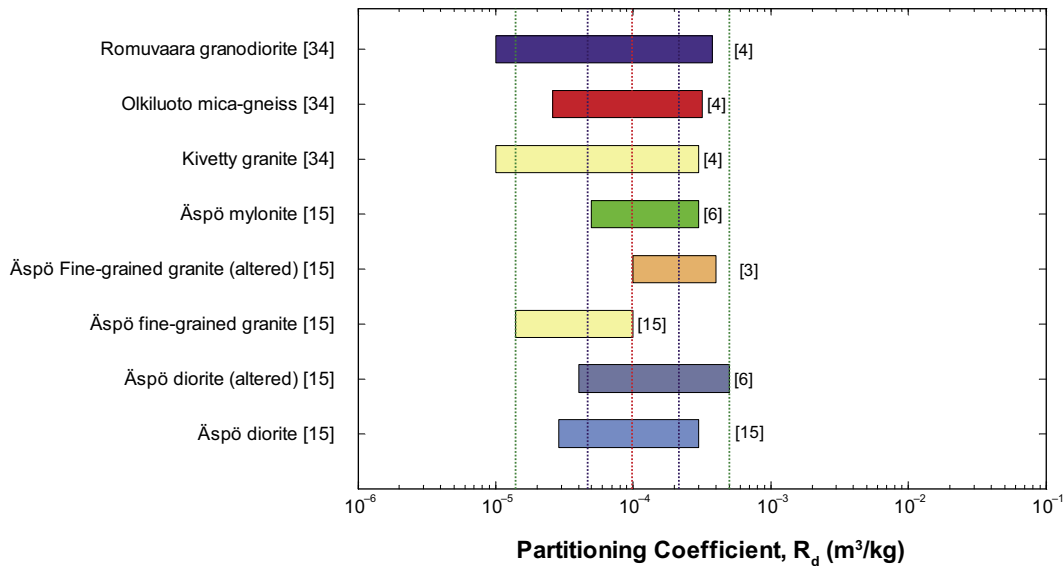
The data for all water types appear to be approximately log-normally distributed. The median  $K_d$  value for non-saline conditions is about two orders of magnitude higher than the corresponding value for moderately to strongly-saline water, although only about twice that for weakly-saline water.



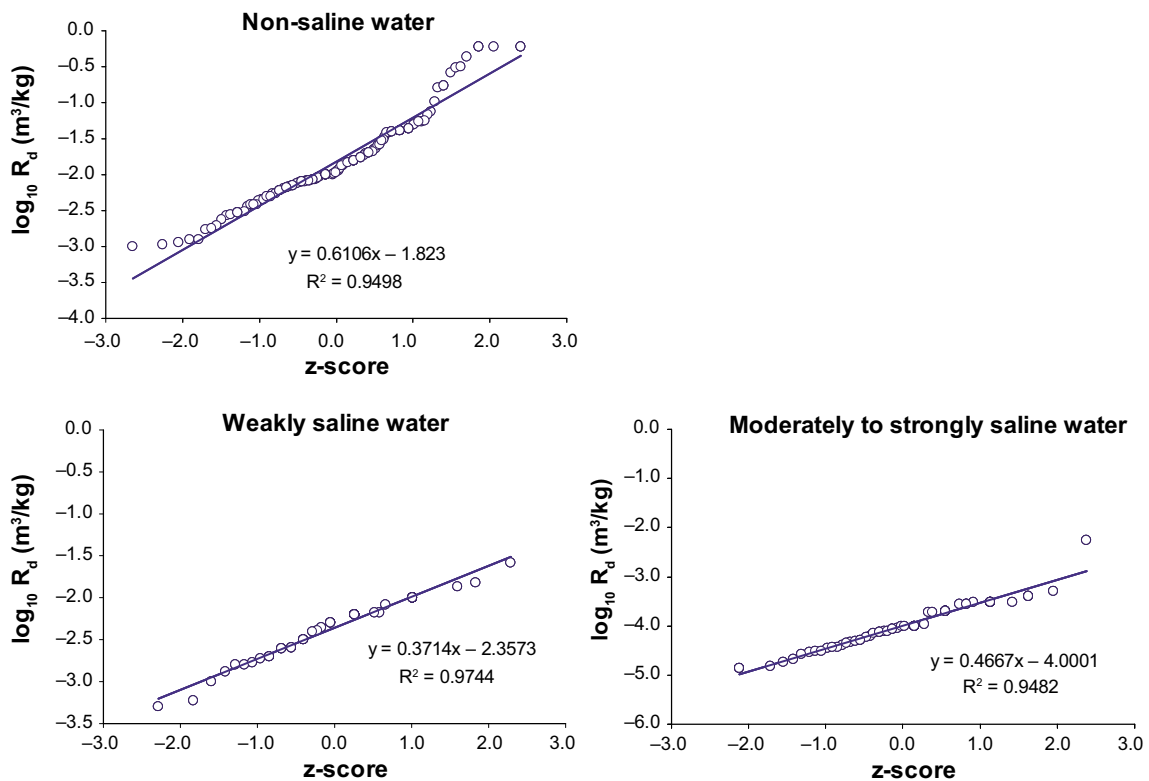
**Figure 5-7.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Sr(II) sorption as given in literature sources for non-saline water ( $Cl^- < 400$  mg/l). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-8.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Sr(II) sorption as given in literature sources for weakly saline water ( $400$  mg/l  $\leq Cl^- < 4,000$  mg/l). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-9.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Sr(II) sorption as given in literature sources for saline water ( $Cl^- \geq 4,000$  mg/l). Bars correspond to  $R_d$  ranges given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-10.** Normal probability plots ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Sr(II) sorption as given in literature sources.

## Radium (Ra)

Although radium occurs naturally in the granitic bedrock, its sorption behaviour is not as well characterised as either Cs or Sr. It is a decay chain member for a number of actinides. The four principal isotopes of radium and their half-lives are  $^{223}\text{Ra}$  (11.43 d),  $^{224}\text{Ra}$  (3.66 d),  $^{225}\text{Ra}$  (14.9 d), and  $^{226}\text{Ra}$  (1,600 y). Although the first three isotopes have very short half-lives, they persist largely owing to secular equilibrium with the long-lived  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  isotopes. The Ra isotopes undergo  $\alpha$ -decay to form further daughter products in the Uranium decay chain series, eventually culminating in the formation of stable lead isotopes. Only the long-lived  $^{226}\text{Ra}$  is of consequence for safety assessment transport calculations. A typical inventory of Ra isotopes at different times in BWR waste is: (see Table 5-4).

The  $^{226}\text{Ra}$  radionuclide was a significant contributor to far field, activity release after very long times in the SR97 safety assessment /Lindgren and Lindström 1999/.

## Geochemistry of Ra

In granitic groundwaters, the free divalent form ( $\text{Ra}^{2+}$ ) is thought to be the dominant species of radium with  $\text{RaSO}_4$  being the main complexed form /Bruno et al. 1997/. It has been suggested by /Porcelli and Swarzenski 2003/ that complexation as  $\text{RaSO}_4$ ,  $\text{RaCO}_3$ , and  $\text{RaCl}^+$  will only occur in brines where the associated ligands are present at high concentrations. Ra is not sensitive to redox conditions.

Possible solubility limiting phases that have been suggested are  $\text{RaSO}_4$  (s) and  $\text{RaCO}_3$  (s) or co-precipitates with sulphate or carbonate minerals of Ba, Sr, Ca /Bruno et al. 1997/. /Langmuir and Melchior 1985/ observe that Ra concentrations in groundwater are always too low to be explained by way of equilibrium with a pure mineral phase of Ra. Instead, it is suggested that Ra concentrations in groundwater are more likely to be controlled by sorption processes and possibly by solid solution formation (i.e. co-precipitation) with barite ( $\text{BaSO}_4$ ) and celestite ( $\text{SrSO}_4$ ).

A number of researchers have observed a strong correlation between groundwater Ra concentrations and the concentration of other major cations /e.g. Bruno et al. 2002/ or the total concentration of dissolved solids /e.g. Gascoyne 1989/. This suggests a strong sorption control on groundwater concentrations as high concentrations of competing cations are envisaged to inhibit sorption of Ra. As for Sr, it is noted that this observation is also consistent with the hypothesis of a solid solution solubility control. /Zukin et al. 1987/, however, indicates that at least part of the effect may be due to increased chloride complexation under highly saline conditions. Although the speciation of Ra is not directly influenced by redox conditions, it has been suggested that the absence of  $\text{MnO}_2$  under reducing conditions may influence the sorption of Ra negatively as Ra is known to sorb strongly on this mineral and its various hydroxide forms /Zukin et al. 1987, Sturchio et al. 2001/.

**Table 5-4. Inventory (Bq/ton U) of Ra radioisotopes at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.**

	100 y	1,000 y	10,000 y	100,000 y
$^{223}\text{Ra}$	n/a	n/a	$3.78 \times 10^7$	$3.81 \times 10^8$
$^{224}\text{Ra}$	$2.20 \times 10^9$	$5.45 \times 10^5$	n/a	n/a
$^{225}\text{Ra}$	n/a	n/a	$8.21 \times 10^8$	$1.93 \times 10^{10}$
$^{226}\text{Ra}$	n/a	n/a	$8.50 \times 10^9$	$6.66 \times 10^{10}$

The geochemistry of Ra is similar to both Sr and Ba, although it is thought that Sr may not be a good analogue for Ra owing to its much weaker sorption /Carbol and Engkvist 1997/. In spite of this, if either Ba<sup>2+</sup> or Sr<sup>2+</sup> are present at sufficiently high concentrations in groundwater, this may influence the sorption of Ra<sup>2+</sup> owing to competitive effects as well as the potential for formation of solid solutions with celestite (SrCO<sub>3</sub>) or barite. Ca<sup>2+</sup>, which although much less strongly sorbing than Ra<sup>2+</sup>, can also competitively inhibit sorption because of its typically much higher relative concentration.

Natural groundwater concentrations are very low both in absolute terms and in comparison with its analogue elements. Dissolved concentrations of Ba, for example, are typically 10<sup>7</sup> times greater than that of Ra /Porcelli and Swarzenski 2003/. The natural background level of Ba<sup>2+</sup> in Swedish granitic groundwaters is usually in the range 10<sup>-7</sup>–10<sup>-5</sup> mol/l (0.01–1.0 mg/l).

The background concentration of <sup>226</sup>Ra varies significantly in deep granitic groundwaters, although it appears to be generally in the range 0.1–100 Bq/l /e.g. Edlund et al. 1999, King et al. 1982, Griffault et al. 1993, Krishnaswami et al. 1991/. For <sup>226</sup>Ra, this corresponds to a concentration of 10<sup>-11</sup>–10<sup>-14</sup> mol/l (i.e. 8.27×10<sup>12</sup> Bq/mol). Higher radium concentrations are found in saline waters, while non-saline waters tend to have lower concentrations. Radioisotopes other than <sup>226</sup>Ra may actually be present in groundwater at higher activities, although this is because of their short half-life and thus molar concentrations of these are exceedingly low.

### **Ra sorption mechanisms**

Ra(II) is expected to sorb primarily by way of a non-specific ion exchange mechanism and is therefore sensitive to ionic strength effects. It is not redox sensitive and only mildly sensitive to pH.

Owing to the relatively high natural concentrations of geochemically similar elements (Ba, Sr, and possibly Ca) in groundwater it is probable that partitioning coefficients for Ra sorption are not very sensitive to the concentration of Ra, but are likely to be strongly influenced by competition with other cations.

### **R<sub>d</sub> data ranges for Ra sorption reported in the literature**

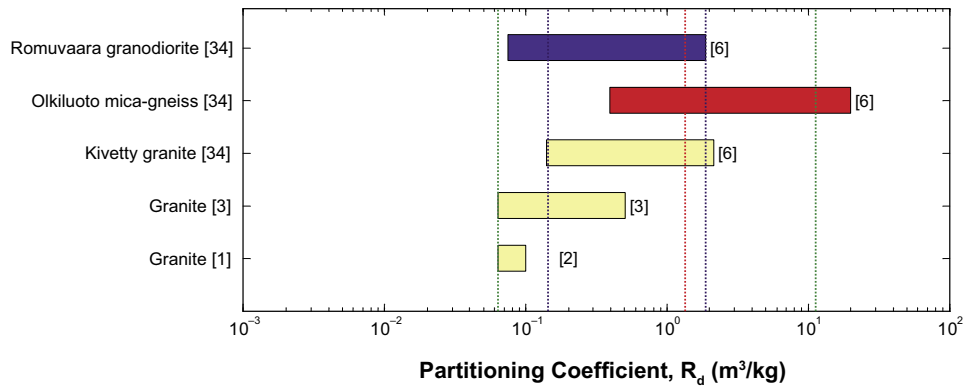
The data for Ra sorption are scarce in the open literature, although a couple of comprehensive studies have been undertaken since 1995. In total, 278 individual R<sub>d</sub> measurements for Ra(II) sorption have been examined of which 214 values were rejected for various reasons (mostly owing to inappropriate water compositions). Of the remaining data, 23 values were found to be applicable for non-saline conditions and 41 for saline conditions.

Although there are only a limited amount of data available for Ra(II) sorption, they encompass a number of rock types including granite, granodiorite, tonalite, mica-gneiss as well as some alteration forms. There do not appear to be very significant differences amongst the different rock types and it is thought that any variation between rock types is obscured by that arising due to the different water compositions used in measurements.

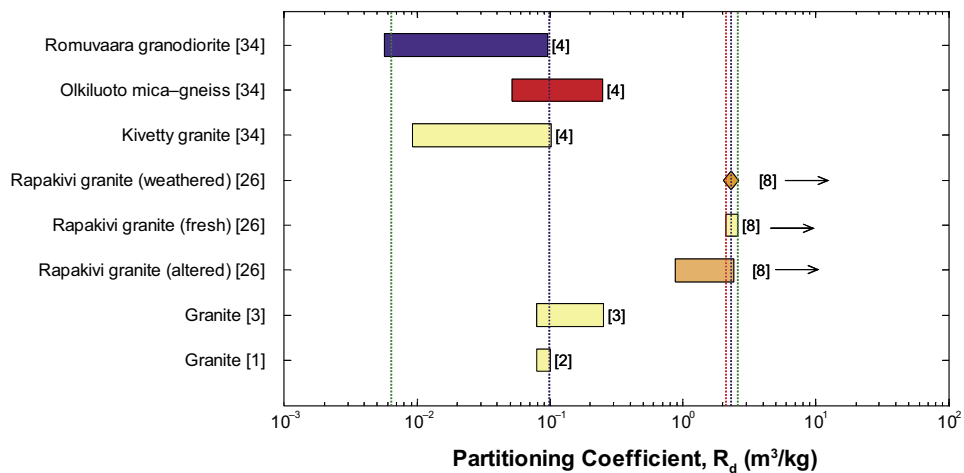
The ranges of reported distribution coefficients in the data selection are given in Figure 5-11 below for non-saline water (Cl<sup>-</sup> < 400 mg/l) and in Figure 5-12 for saline water (Cl<sup>-</sup> ≥ 400 mg/l).

It should be noted in Figure 5-12 that the upper end of the data sets in reference [26] /Huitti et al. 1996/ (indicated with arrows) were censored owing to measurement limit considerations and it is therefore unclear if alteration or weathering has a substantial impact upon sorption. Similarly the censoring of data causes the median of the aggregate data set to be very close to the 75% quartile and the upper data limit. The range of data for Ra sorption under saline conditions should therefore be treated with some caution.

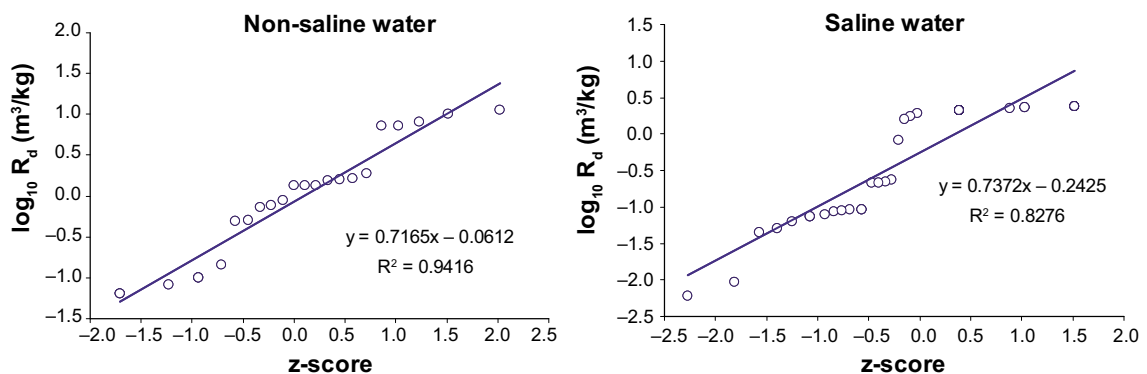
Normal probability plots for the aggregate data sets are given in Figure 5-13 below for the log<sub>10</sub>-transformed data.



**Figure 5-11.** Ranges of reported distribution coefficients,  $R_d$  ( $\text{m}^3/\text{kg}$ ) for Ra(II) sorption as given in literature sources for non-saline water ( $\text{Cl}^- < 400 \text{ mg/l}$ ). Bars correspond to  $R_d$  ranges given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-12.** Ranges of reported distribution coefficients,  $R_d$  ( $\text{m}^3/\text{kg}$ ) for Ra(II) sorption as given in literature sources for saline water ( $\text{Cl}^- \geq 400 \text{ mg/l}$ ). The diamond marker indicates that the values in the reference were numerically identical. Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-13.** Normal probability plots ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $\text{m}^3/\text{kg}$ ) for Ra(II) sorption as given in literature sources.

Owing to the sparsity of data and censoring effects, the range of  $K_d$  values for both non-saline and saline waters do not appear to follow any well-defined distribution. The overall range for  $K_d$  values non-saline water lies somewhat higher than that for saline water, although the median values are very similar.

### 5.3.3 Lanthanides

#### *Trivalent lanthanides (Sm, Eu, Ho)*

Sorption data for the trivalent lanthanides have not been reviewed at this time. This was partly owing to their known sorption properties as well as because they are not present in appreciable quantities in spent nuclear fuel. They are, however, useful as analogues of the trivalent actinides, particularly in those cases where the actinide is redox sensitive and difficult to work with in the trivalent form /e.g. Krauskopf 1986, Leroy and Turpin 1988, Wood 1990, Johannesson et al. 1996, Moulin et al. 1999/.

The strong sorption of these substances is expected to delay their transport sufficiently that they will not influence far-field activity release significantly. Recommended data for these nuclides have therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### 5.3.4 Actinides

#### *Protactinium (Pa)*

Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Pa at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

#### *Actinium (Ac)*

Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Ac at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

#### *Thorium (Th)*

The radioisotopes of thorium are produced by the decay of long-lived actinides. The isotopes of thorium and their half-lives are;  $^{227}\text{Th}$  (18.68 d),  $^{228}\text{Th}$  (1.9116 y),  $^{229}\text{Th}$  ( $7.34 \times 10^3$  y),  $^{230}\text{Th}$  ( $7.538 \times 10^4$  y),  $^{231}\text{Th}$  (25.52 h), and  $^{234}\text{Th}$  (24.10 d). The first four of the above radionuclides decay by  $\alpha$ -particle emission, while  $^{231}\text{Th}$  and  $^{234}\text{Th}$  undergo  $\beta$ -decay. Although  $^{227}\text{Th}$ ,  $^{231}\text{Th}$ , and  $^{234}\text{Th}$  have short half-lives, they persist at later times owing to secular equilibrium with parent radionuclides. It is noted that  $^{231}\text{Th}$  exists in fast secular equilibrium with  $^{235}\text{U}$  and is actually present in appreciable quantities already from 100 y although this is not indicated in the table. A typical inventory of Th isotopes at different times in BWR waste is:

**Table 5-5. Inventory (Bq/ton U) of Th radioisotopes at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.**

	100 y	1,000 y	10,000 y	100,000 y
$^{227}\text{Th}$	n/a	n/a	$3.73 \times 10^7$	$3.75 \times 10^8$
$^{228}\text{Th}$	$2.20 \times 10^9$	$5.45 \times 10^5$	n/a	n/a
$^{229}\text{Th}$	n/a	n/a	$8.21 \times 10^8$	$1.93 \times 10^{10}$
$^{230}\text{Th}$	n/a	n/a	$1.09 \times 10^{10}$	$6.63 \times 10^{10}$
$^{231}\text{Th}$	n/a	n/a	$2.30 \times 10^8$	$4.88 \times 10^8$
$^{234}\text{Th}$	$1.15 \times 10^{10}$	$1.15 \times 10^{10}$	$1.15 \times 10^{10}$	$1.15 \times 10^{10}$



Thorium was not found to be a major contributor to far field activity release in the SR97 safety assessment /Lindgren and Lindström 1999/ (with the possible exception of  $^{229}\text{Th}$  in some of the pessimistic scenarios), although the  $^{226}\text{Ra}$  daughter of  $^{230}\text{Th}$  could potentially have a non-trivial impact on far-field activity release.

### Geochemistry of Th

Under normal conditions, it is thought that the thorium is only present in the tetravalent (+4) state and it is not sensitive to redox conditions. At the circumneutral to weakly alkaline pH levels typical of granitic groundwaters, Th(IV) is strongly hydrolysed and is principally present in the form of  $\text{Th}(\text{OH})_4^0$ . At these pH levels  $\text{Th}(\text{HPO}_4)_3^{2-}$  or  $\text{Th}(\text{OH})_4\text{PO}_4^{3-}$  could also be important species, although this is strongly limited by the concentration of  $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$  which is in turn regulated by apatite equilibrium ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) /Langmuir and Herman 1980, Bruno et al. 1997/. In Swedish deep groundwaters it is thought that the total phosphate concentration is probably on the order of about  $10^{-7}$  mol/l ( $\leq 0.01$  mg/l) /Bruno et al. 1997/ and phosphate complexation should therefore only play a very minor role in Th speciation.

/Bruno et al. 1997/ have suggested that  $\text{Th}(\text{CO}_3)_5^{6-}$  could have a strong influence on Th solubility in bentonite porewaters, although they believe it is probably not significant for far field transport processes. /Östhols et al. 1994/ and /Murphy et al. 1999/ propose that both  $\text{Th}(\text{CO}_3)_5^{6-}$  and  $\text{Th}(\text{OH})_3\text{CO}_3$  are principal solution species at circumneutral to alkaline pH levels for very low Th concentrations ( $10^{-13} \leq \text{Th} \leq 10^{-10}$  mol/l), although their relative predominance depends upon the total concentration of dissolved carbonate.

The minerals thorianite ( $\text{ThO}_2$ ) /Langmuir and Herman 1980/, thorite ( $\text{ThSiO}_4$ ) /Kaminen and Lemire 1991/, and amorphous  $\text{Th}(\text{OH})_4$  /Bruno et al. 1997/ have all been suggested as solubility controlling phases for Th, although in nature it is frequently found associated with monazite,  $(\text{Ce},\text{La},\text{Th},\text{U})\text{PO}_4$ . Amorphous forms of  $\text{Th}(\text{OH})_4$  are believed to be somewhat more soluble than the crystalline minerals /Krauskopf 1986/.

Th is less strongly hydrolysed than other tetravalent actinides such as U(IV), Np(IV) and Pu(IV) which is thought to be due to the larger ionic radius of Th(IV) /Albinsson 1991/. In general, Th has very low solubility and its concentration is not expected to exceed  $10^{-9}$  mol/l ( $2 \times 10^{-4}$  mg/l) /Bruno et al. 1997/. /Hummel et al. 2002/ point out that thermodynamic data for Th(IV) solubility in the open literature are not thermodynamically consistent and therefore it is difficult to assign unambiguous solubility limits on Th(IV). In spite of this, they note that for  $\text{pH} \geq 6$ , all measured solubility data for Th(IV) tend to fall in the range  $10^{-9}$ – $10^{-7}$  mol/l.

### Th sorption mechanisms

Th mobility is retarded very strongly in granitic rock and is thought to sorb primarily by way of a surface complexation mechanism at variable charge sites on aluminosilicates and other minerals (e.g. Fe-oxyhydroxides, etc) and is not sensitive to ionic strength effects or redox conditions. Because of this, Th(IV) is relatively easy to work with and is often used as an analogue for other radionuclides that have tetravalent redox states such as Zr, Hf, U, Np and Pu /e.g. Krauskopf 1986, Reiller et al. 2002/.

High concentrations of carbonate are known to reduce the sorption of Th, although it is not entirely clear how this occurs. There is some evidence, however, to suggest that the reduction of sorptivity is, at least in part, related to competition for surface binding sites with  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ , rather than being related to the formation of Th-carbonate complexes /e.g. La Flamme and Murray 1987/.

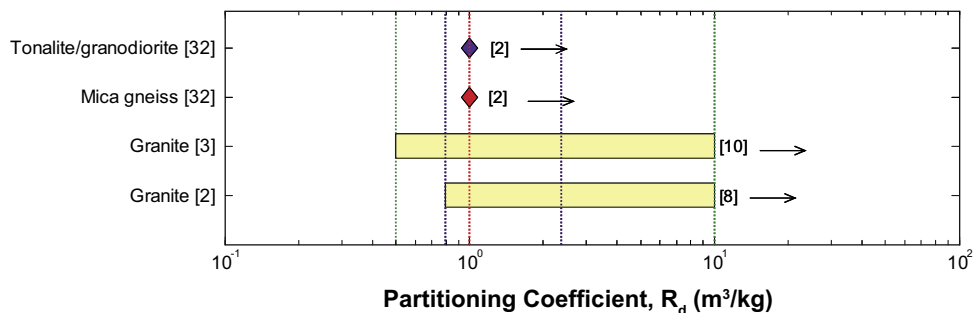
### R<sub>d</sub> data ranges for Th sorption reported in the literature

There is very little data for Th(IV) sorption in granitic rocks and most of the data comes from older references. The sorption of Th(IV) appears to be relatively insensitive to ionic strength, which is generally interpreted as an indication of inner sphere surface complexation /e.g. Hayes and Leckie 1987/. In total, 32 measurements of Th(IV) sorption have been examined, of which 8 were rejected for various reasons. The remaining 24 data values were deemed to be applicable for all water types and are given in Figure 5-14 below.

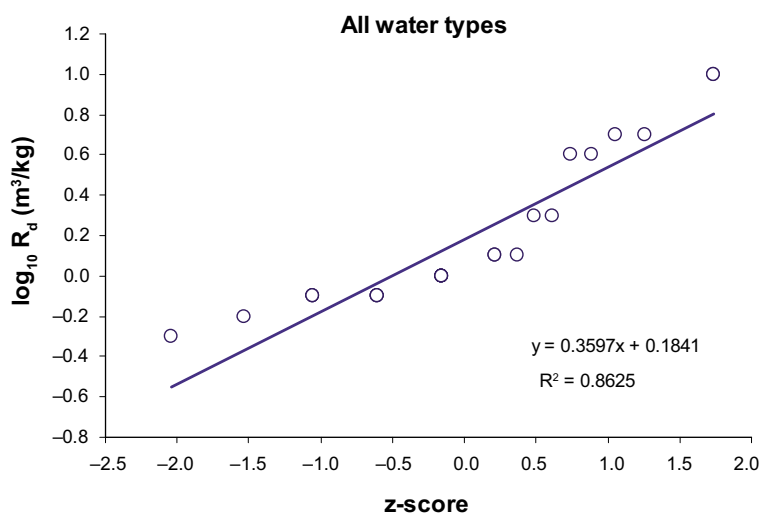
The upper limit for sorption in all references was censored owing to the limit of analytical measurement resolution. For this reason, arrows are used to denote data sets where there was no established upper limit. It should also be noted that the lower end of the data limit also is subject to some uncertainty owing to the resolution of the analytical methods used (much of the data is reported in the form of “≥” a given value).

The normal probability plot for the aggregate data set are given in Figure 5-15 below for the log<sub>10</sub>-transformed data:

It is clear from the data that the sorption of Th(IV) is very strong although owing to the sparsity of data and censoring effects, the range of K<sub>d</sub> values does not seem to follow any particular distribution.



**Figure 5-14.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Th(IV) sorption as given in literature sources for all water types. Bars correspond to  $R_d$  ranges given in the reference (y-axis). The diamond marker indicates that the values in the reference were numerically identical. Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-15.** Normal probability plots ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Th(IV) sorption as given in literature sources.

## Uranium (U)

The long-lived radioisotopes of uranium are the most abundant radionuclides in spent nuclear fuel as well as being ubiquitous in granitic rock. The isotopes of uranium and their half-lives are;  $^{232}\text{U}$  (68.9 y),  $^{233}\text{U}$  ( $1.592 \times 10^5$  y),  $^{234}\text{U}$  ( $2.455 \times 10^5$  y),  $^{235}\text{U}$  ( $7.04 \times 10^8$  y),  $^{236}\text{U}$  ( $2.342 \times 10^7$  y),  $^{237}\text{U}$  (6.75 d), and  $^{238}\text{U}$  ( $4.468 \times 10^9$  y).

$^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{236}\text{U}$  are daughter products of  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$  decay, respectively. The major proportion of  $^{236}\text{U}$ , however, is produced by neutron capture by  $^{235}\text{U}$  during reactor operation. It also is noted that  $^{234}\text{U}$  and  $^{235}\text{U}$  are present in both natural and enriched uranium as well as initially present in spent fuel.  $^{238}\text{U}$  occurs naturally in uranium ore and is also present in spent nuclear fuel although a miniscule amount of additional  $^{238}\text{U}$  is produced from  $^{242}\text{Pu}$  decay.  $^{233}\text{U}$  is formed from the decay of  $^{237}\text{Np}$ .  $^{232}\text{U}$  does not occur naturally, but is produced by complex neutron capture reactions by other uranium isotopes. Both  $^{233}\text{U}$  and  $^{235}\text{U}$  are fissile materials. All isotopes of uranium have complex decay chains and these will not be reviewed here. They initially decay by way of  $\alpha$ -particle emission, although daughter nuclides have different decay modes. A typical inventory of U isotopes at different times in BWR waste is: (see Table 5-6).

No isotopes of U were found to contribute directly to far field activity in the SR97 safety assessment /Lindgren and Lindström 1999/. The radium ( $^{226}\text{Ra}$ ) daughter of  $^{234}\text{U}$  could potentially have a non-trivial impact on far-field activity release.

## Geochemistry of U

Uranium is arguably one of the most well studied actinides partly because of its importance for nuclear waste safety and partly owing to its ubiquitous presence in environmental systems and special redox chemistry that allows it to be used as a marker of geochemical alteration processes. Uranium is redox sensitive and can exist in a number of different oxidation states from +III to +VI, although only the +IV (*uranous*) and +VI (*uranyl*) states are sufficiently stable to occur in groundwater.

Under reducing conditions, the solubility-limiting phase for U(IV) is expected to be uranium dioxide,  $\text{UO}_2$  (i.e. the spent fuel matrix) /Bruno et al. 1997/. The solubility of U within storage canisters and in the immediate near field is complicated by coupling between oxidative dissolution of the spent fuel and hydrogen generation from corrosion of the cast iron canister inserts, as well as radiolytic processes near the fuel-water interface /e.g. Shoosmith 2000, Liu and Neretnieks 2001/. In natural systems uraninite,  $\text{UO}_2$  (sometimes called pitchblende) and coffinite,  $\text{USiO}_4$  are frequently found to be solubility limiting mineral phases for U(IV) under reducing conditions /Langmuir 1997, Bruno et al. 2002/. Naturally occurring uraninite is often used as an analogue for spent nuclear fuel and is found in many of the uranium deposits that have been studied as natural analogues of deep geological repositories for nuclear waste /e.g. Janeczek et al. 1996/. Under reducing conditions, the solubility of U(IV) is very low and its aqueous speciation is dominated by  $\text{UOH}_4^0$  in the pH range likely to be encountered in groundwater of granitic character (i.e. pH 7–10). Under normal in situ conditions, U(IV) is not appreciably complexed by carbonate /Bruno et al. 1997/.

**Table 5-6. Inventory (Bq/ton U) of U radioisotopes at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.**

	100 y	1,000 y	10,000 y	100,000 y
$^{232}\text{U}$	$2.14 \times 10^9$	$5.36 \times 10^5$	n/a	n/a
$^{233}\text{U}$	n/a	n/a	$2.51 \times 10^9$	$2.14 \times 10^{10}$
$^{234}\text{U}$	$8.04 \times 10^{10}$	$1.27 \times 10^{11}$	$1.24 \times 10^{11}$	$9.90 \times 10^{10}$
$^{235}\text{U}$	$> 1.53 \times 10^8$	$> 1.53 \times 10^8$	$2.30 \times 10^8$	$4.88 \times 10^8$
$^{236}\text{U}$	$1.07 \times 10^{10}$	$1.10 \times 10^{10}$	$1.32 \times 10^{10}$	$1.45 \times 10^{10}$
$^{237}\text{U}$	$1.14 \times 10^9$	$1.51 \times 10^6$	n/a	n/a
$^{238}\text{U}$	$1.15 \times 10^{10}$	$1.15 \times 10^{10}$	$1.15 \times 10^{10}$	$1.15 \times 10^{10}$

For oxidising conditions schoepite,  $\beta$ - $\text{UO}_2(\text{OH})_2$  and a number of uranyl silicates including uranophane,  $\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$  have been identified as secondary mineral phases resulting from oxidative alteration of uraninite ores /Percy et al. 1994/. Uranium is also known to associate with vanadium in the form of carnotite,  $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2$  and tyuyamunite,  $\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2$ . These minerals have lower solubilities than other oxidised forms of uranium and are also the main oxidised ore minerals of uranium found in nature /Langmuir 1997/. Other minerals that can form under oxidising conditions are autunite,  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ , and rutherfordine,  $\text{UO}_2\text{CO}_3$ .

Under oxidising conditions, U(VI) is strongly complexed by dissolved carbonate which considerably increases its solubility. In the absence of dissolved carbonate, the dominant aqueous species of U(VI) are  $\text{UO}_2\text{OH}^+$ ,  $\text{UO}_2(\text{OH})_2^0$ , and  $\text{UO}_2(\text{OH})_3^-$  at pH 7–10 /Waite et al. 1994/. In the presence of dissolved carbonate, on the other hand, U(VI) forms a number of carbonate species including  $\text{UO}_2\text{CO}_3^0$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , and  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ . The relative predominance of the various hydroxo and carbonate species varies with both pH and  $\text{CO}_2$  partial pressure.

Typical uranium concentrations in granitic rocks are on the order of 2.2–15 mg/kg /Langmuir 1997/. Granite from Stripa in Sweden contains between 17–45 mg/kg of uranium /Andrews et al. 1982/, while Äspö fine-grained granite and Äspö diorite contain 3–7 mg/kg and 1–5 mg/kg, respectively /Byegård et al. 1998/. The high concentrations of uranium found in granite mean that sorption experiments must be carried out with isotopes such as  $^{232}\text{U}$  or  $^{233}\text{U}$  that are not naturally abundant in the rock.

Groundwater concentrations of uranium are highly variable, and are dependent upon the availability of uranium minerals in the rock, pH, redox,  $\text{CO}_2$  partial pressure as well as sorption and dissolution-precipitation processes. At Stripa, the concentration of dissolved uranium in deep (330–840 m) groundwater was found to vary from 0.5–12  $\mu\text{g}/\text{l}$  ( $2 \times 10^{-9}$ – $5 \times 10^{-8}$  mol/l), while at shallow depths the uranium concentration was 1–90  $\mu\text{g}/\text{l}$  ( $4 \times 10^{-9}$ – $4 \times 10^{-7}$  mol/l) /Andrews et al. 1982/. The redox state of the groundwater is expected to have the largest impact upon the solubility of uranium and at pH 8, the solubility can range from 0.024  $\mu\text{g}/\text{l}$  – 240 mg/l ( $10^{-10}$ – $10^{-3}$  mol/l) depending upon the redox state (Eh) of the groundwater. It is possible that uranium concentrations are close to equilibrium with secondary mineral phases in the low Eh environments found in deep granitic groundwater /Langmuir 1997/.

## U sorption mechanisms

The sorption of both U(IV) and U(VI) is thought to occur by way of a surface complexation mechanism on variably charged sites on aluminosilicates and other minerals (e.g. Fe-oxyhydroxides, etc). The sorption of both U(IV) and U(VI) is only weakly influenced by ionic strength, which is usually taken to be indicative of inner-sphere surface complexation. U(IV) sorbs very strongly in a similar fashion to Th(IV), which is often used as an analogue. Very little reliable data exists in the open literature concerning the sorption of U(IV), however, owing to its vanishingly low solubility as well as the difficulty of maintaining appropriate redox and pH conditions in the laboratory. In most cases it is not entirely clear whether measured  $R_d$  data for U(IV) represent true sorption or are contaminated by surface precipitation effects. There is also evidence to suggest that mixed oxidation states can occur in laboratory experiments owing to redox disequilibrium and stabilisation of U(VI) species by carbonate complexation /e.g. Wersin et al. 1994, Sani et al. 2004 and references therein/.

For pH dependent sorption of U(VI), there is a close correspondence between the field of maximum sorption and the region of maximum concentration of hydroxo complexes /Pabalan et al. 1998/. It is difficult, however, to explain the macroscopic sorption data using only hydroxo surface complexes and the presence of carbonate surface complexes provides a much better fit to data when simulated using surface complexation models /e.g. Waite et al. 1994/. There is also strong direct evidence in the way of spectroscopic measurements that ternary U(VI)-carbonate surface complexes can form /e.g. Bargar et al. 2000/. The sorption characteristics of U(VI) at different pH levels and  $\text{CO}_2$  partial pressures is thus a complex mix of effects resulting from competition between different U(VI) species and free carbonate for sorption sites as well as

solution speciation effects. Ionic strength has weak, although non-negligible influence upon the sorption of U(VI). Although this is frequently assumed to be evidence of the formation of outer sphere complexes, the effect can also result from speciation phenomena relating to the relative activities of various solution species at different ionic strengths /see e.g. Waite et al. 1994, Lützenkirchen 1997/.

### **R<sub>d</sub> data ranges for U sorption reported in the literature**

343 individual R<sub>d</sub> measurements for U sorption have been examined (312 for U(VI) and 31 for U(IV)). 103 values for U(VI) sorption were rejected, mostly owing to inappropriate water compositions given the sensitivity of U(VI) to carbonate speciation. No data were rejected for U(IV), although it is not possible to say with any certainty whether the reported K<sub>d</sub> data represent a true sorption process or possibly surface precipitation or co-precipitation phenomena. The remaining data values were deemed to be applicable for both non-saline and saline conditions owing to the relative insensitivity of U(IV)/U(VI) sorption to ionic strength. The median K<sub>d</sub> for U(VI) is about three orders of magnitude lower than the corresponding value for U(IV) obtained under strongly reducing conditions.

The available data for U(VI) sorption encompass a number of rock types including granite, granodiorite, and mica-gneiss as well as altered granite. There do not appear to be very significant differences amongst the different rock types and it is thought that any variation between rock types is obscured by that arising due to the different water compositions used in measurements. For U(IV), however, sorption data is only available for granodiorite.

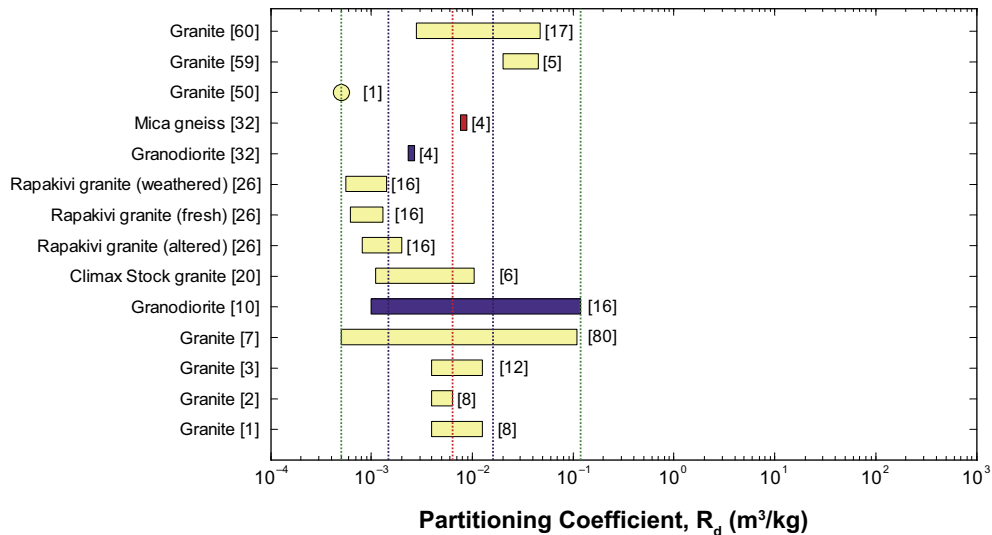
At this time this time there appears to be insufficient data to set a strict Eh limit for the boundary between oxidising and reducing conditions in granitic rocks as the situation is complicated by speciation considerations involving pH and carbonate as well as chemical kinetics. It is noted, however, that in the cases where reducing conditions were simulated in experiments using addition of sodium hydrosulphite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>), the equilibrium E<sub>h</sub> was typically found to be in the range -420 to -450 mV. Based upon predominance diagrams in /Langmuir 1997/, however, we can speculate that an E<sub>h</sub> as high as -300 to -400 mV could suffice in high carbonate waters at pH 7-8 and perhaps as high as -100 to -200 mV in very low carbonate containing waters.

The ranges of reported distribution coefficients in the data selection are given in Figure 5-16 (oxidising conditions) and Figure 5-17 (reducing conditions) below.

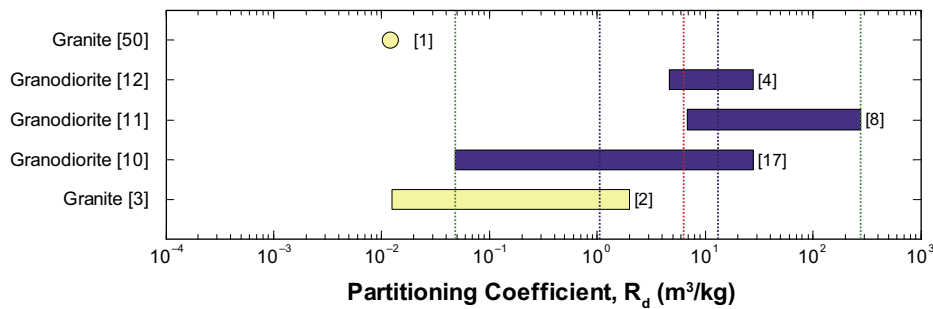
Most of the reported data for U sorption relate to measurements made under ambient conditions where it is assumed that the oxidised U(VI) redox valency is prevalent. In a couple of cases, sorption experiments have been carried out in an N<sub>2</sub> atmosphere or using “de-aerated” solutions. The data obtained for such experiments, however, is not unequivocally representative of reducing conditions and it has been assumed in these cases that U(VI) is still the dominant redox state. Very few data exist for U(IV) sorption on granitic rocks and most of the available measurements in the open literature appear to have been made by [10, 11, 12] /Baston et al. 1995, 1997, 1999/. In these measurements, reducing conditions were maintained by spiking the test solutions with Na-dithionite (2×10<sup>-3</sup> mol/l). In reference [3] /Allard et al. 1979/, 10-20 mg/l of Fe(II) was used instead. Conversely, we could also argue that Fe(II)-mediated redox buffering reactions may decrease the Eh of oxygenated water intended to simulate oxidising conditions, particularly if the experiments are carried out in a closed vessel or glove box. This could give unrealistically high R<sub>d</sub> values for conditions that otherwise are assumed to be oxidising.

It is not clear whether the sorption data for reducing conditions correspond to true sorption of U(IV) or a surface precipitation effect. It is noted that the initial spike concentrations could be higher than the solubility of U(IV) depending upon which mineral phase is assumed to be controlling. The equilibrium Eh was found for all data sets to be in the interval -420 mV to -460 mV.

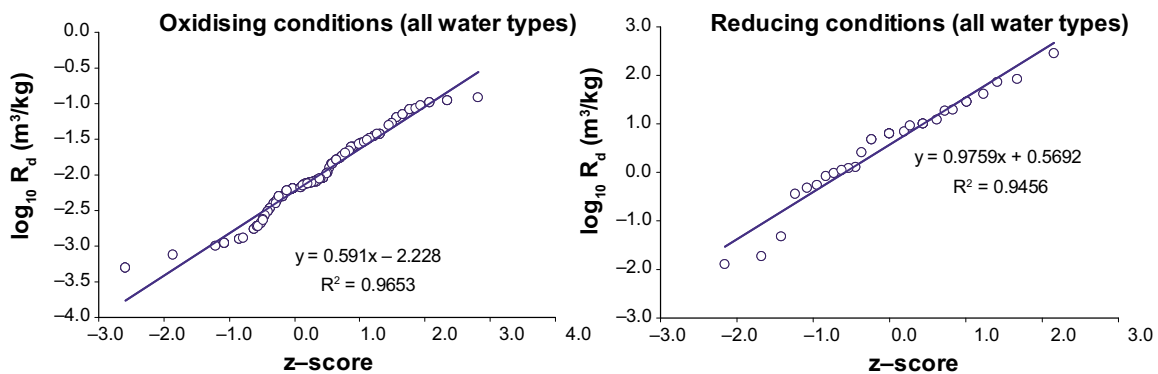
Normal probability plots for the aggregate data sets are given in Figure 5-18 below for the log<sub>10</sub>-transformed data.



**Figure 5-16.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for U(VI) sorption as given in literature sources for oxidising conditions (all salinities). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-17.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for U(IV) sorption as given in literature sources for reducing conditions (all salinities). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-18.** Normal probability plots ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for U(IV/VI) sorption as given in literature sources.

The data for both oxidising and reducing conditions appear to be log-normally distributed with the median  $K_d$  for reducing conditions being about three orders of magnitude higher than the median  $K_d$  measured under oxidising conditions.

### Neptunium (Np)

The radioisotopes of neptunium have half-lives of  $2.144 \times 10^6$  y ( $^{237}\text{Np}$ ), 2.117 d ( $^{238}\text{Np}$ ), and 2.356 d ( $^{239}\text{Np}$ ). In spent nuclear fuel  $^{237}\text{Np}$  is produced as a result of the decay of  $^{241}\text{Am}$ , although it is also present initially in spent nuclear fuel as a result of neutron capture by  $^{236}\text{U}$  and subsequent decay to  $^{237}\text{Np}$  during reactor operation.  $^{239}\text{Np}$  is present in spent nuclear fuel as a decay product of  $^{243}\text{Am}$ . Similarly,  $^{238}\text{Np}$  is formed by decay of  $^{242}\text{Am}$ . Both  $^{238}\text{Np}$  and  $^{239}\text{Np}$  decay by  $\beta$ -particle emission, while  $^{237}\text{Np}$  undergoes  $\alpha$ -decay. A typical inventory of Np isotopes at different times in BWR waste is: (see Table 5-7).

Neptunium was not found to be a significant contributor to far field activity release in the SR97 safety assessment /Lindgren and Lindström 1999/. The radium ( $^{226}\text{Ra}$ ) daughter of  $^{238}\text{Np}$  could potentially have a non-trivial impact on far-field activity release, although it is present in much smaller quantities than other  $^{226}\text{Ra}$  parents.

### Geochemistry of Np

Neptunium is redox sensitive and can exist in a number of oxidation states from Np(III) to Np(VII) /e.g. Degueldre 1995, 1997/. Only the Np(IV) and Np(V) redox states, however, are usually encountered under normal environmental conditions /e.g. Langmuir 1997/. The Np(V) species is sometimes referred to as *neptunyl*. It has been noted by /Maya 1984/ that it is possible for Np(VI) to form stable carbonate complexes at pH 7–10 and Eh values greater than +400 mV (i.e. oxidising conditions), although the extent to which this occurs under ambient conditions is unclear. /Kaszuba and Runde 1999/ suggest that this redox state is probably only important under brine conditions in the near field where radiolysis may be substantial. Np(III) is not normally present in groundwater as it reduces water /Nash et al. 1988/.

Under reducing conditions the Np(IV) species is highly insoluble and precipitates mainly in the form of amorphous  $\text{Np}(\text{OH})_4$  /Bruno et al. 1997/. Np(V), on the other hand, is very soluble although probably limited by the formation of  $\text{NpO}_2\text{OH}$  or  $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  solid phases /Efurd et al. 1998, Kaszuba and Runde 1999/. Under saline conditions with sufficient carbonate concentrations, it is also thought to be possible for  $(\text{Na,K})\text{NpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$  or  $(\text{Na,K})_3\text{NpO}_2(\text{CO}_3)_2$  to precipitate /Kaszuba and Runde 1999/.

Np(IV) exists mainly as the hydrolysed species,  $\text{Np}(\text{OH})_4^0$  at pH 7–10 in aqueous solution, while the oxidised Np(V) redox state is found mainly in the form of  $\text{NpO}_2^+$  and  $\text{NpO}_2(\text{OH})^0$ . Np(V) is thought to be strongly complexed by carbonate and these species may predominate at circumneutral to alkaline pH. Many researchers have studied the complexation of Np(V) with carbonate /e.g. Degueldre, 1995, 1997, Bertetti et al. 1996, Viswanathan et al. 1998, Efurd et al. 1998, Bertetti et al. 1998, Kaszuba and Runde 1999/. In the interval pH 7–10 and for carbonate concentrations typical of granitic groundwaters, the major carbonate species of Np(V) have been identified as  $\text{NpO}_2(\text{CO}_3)^-$  and  $\text{NpO}_2(\text{CO}_3)_2^{2-}$ . Only at pH  $\geq 12$  do the hydroxo-carbonate species,  $\text{Np}(\text{OH})(\text{CO}_3)_2^{3-}$  and  $\text{Np}(\text{OH})_2(\text{CO}_3)^{3-}$  become important for Np(V) speciation.

**Table 5-7. Inventory (Bq/ton U) of Np radioisotopes at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.**

	100 y	1,000 y	10,000 y	100,000 y
$^{237}\text{Np}$	$2.56 \times 10^{10}$	$5.31 \times 10^{10}$	$6.16 \times 10^{10}$	$6.00 \times 10^{10}$
$^{238}\text{Np}$	$1.75 \times 10^9$	$2.10 \times 10^7$	n/a	n/a
$^{239}\text{Np}$	$3.63 \times 10^{12}$	$3.34 \times 10^{12}$	$1.43 \times 10^{12}$	$3.08 \times 10^8$

For Np(IV), however, there is some disagreement in the open literature as to which carbonate and hydroxo-carbonate species form and neither is there reliable thermodynamic data for their stability. Unlike Np(V), data for hydroxo-carbonate complexation of Np(IV) is scarce and based mostly upon model fitting considerations rather than direct spectroscopic evidence. Species that have been proposed are  $\text{Np}(\text{CO}_3)_5^{6-}/\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$  /Rai et al. 1999/,  $\text{Np}(\text{OH})_3(\text{CO}_3)^{-}/\text{Np}(\text{OH})_4(\text{CO}_3)^{2-}$  /Eriksen et al. 1993/ and  $\text{Np}(\text{CO}_3)_4^+/\text{Np}(\text{CO}_3)_5^{6-}$  /Kaszuba and Runde 1999/.

Typical solubilities of Np(IV) in reducing granitic groundwaters (pH 7–10) are expected to be in the range  $5 \times 10^{-9}$ – $5 \times 10^{-8}$  mol/l depending upon the concentration of dissolved carbonate /Bruno et al. 1997/. The upper limit of this solubility considers a carbonate concentration of  $5 \times 10^{-3}$  mol/l (300 mg/l). For Np(V) under oxidising conditions and roughly the same pH levels and carbonate concentrations, the solubility could be as high as  $10^{-6}$ – $10^{-4}$  mol/l /Kaszuba and Runde 1999/. Concentrations of other potential ligands such as  $\text{PO}_4^{3-}$  are generally thought to be too low to have a significant influence upon either Np(IV) or Np(V) solubility under normal conditions.

Np is not a naturally occurring element and there is therefore no background concentration in rock or groundwater.

### **Np sorption mechanisms**

The sorption of both Np(IV) and Np(V) is thought to occur mostly by way of a surface complexation mechanism on variably charged sites on aluminosilicates and other minerals (e.g. Fe-oxyhydroxides, etc). The sorption of both Np(IV) and Np(V) is only weakly influenced by ionic strength, which is usually taken to be indicative of inner-sphere surface complexation. Np(IV) sorbs very strongly in a similar fashion to Th(IV), which is often used as an analogue. Very little reliable data exists in the open literature concerning the sorption of Np(IV), however, owing to its vanishingly low solubility as well as the difficulty of maintaining appropriate redox and pH conditions in the laboratory. In most cases it is not entirely clear whether measured  $R_d$  data for Np(IV) represent true sorption or are contaminated by surface precipitation effects.

The sorption of Np(V) is not as strong as for Np(IV) and, owing to its higher solubility under ambient conditions, the available data for Np(V) sorption is considered to be more reliable than that for Np(IV). Similarly to most solutes that form surface complexes, the sorption of Np(V) is sensitive to changes in pH. The situation is complicated, however, by the presence of carbonate. In low-carbonate or carbonate-free solutions, the sorption of Np(V) increases monotonically with pH /e.g. Allard 1982, Allard et al. 1983b, 1984/. In solutions with higher carbonate concentrations or where atmospheric exchange is allowed, Np(V) sorption achieves a maximum at pH 8.0–8.5 and decreases significantly at higher pH values /Bertetti et al. 1996, 1998, Kohler et al. 1999/ where the carbonate complexes of Np(V) begin to dominate. It should be noted that the negative impact of aqueous carbonate upon Np(V) sorption only is important at alkaline pH levels and the data for sorption in the range pH 8.0–8.5 is roughly the same as that obtained in the absence of carbonate. There is also strong evidence that the sorption of Np(V) is approximately the same for different minerals if normalised with respect to the number of sorption sites (i.e. the product of mineral surface area  $\times$  sorption site density) /Bertetti et al. 1998/.

The mechanism by which increasing aqueous carbonate concentration reduces Np(V) sorption is unclear. It has been suggested by /Del Nero et al. 2004, and references therein/ that the decrease in sorption could be a result of competition between Np(V) species and carbonate species for binding sites or competition between surface hydroxyl groups and carbonate ions for the complexation of  $\text{NpO}_2^+$ . /Kohler et al. 1999/ also propose the formation of ternary Np(V)-carbonate surface complexes to explain macroscopic sorption data.



### $R_d$ data ranges for Np sorption reported in the literature

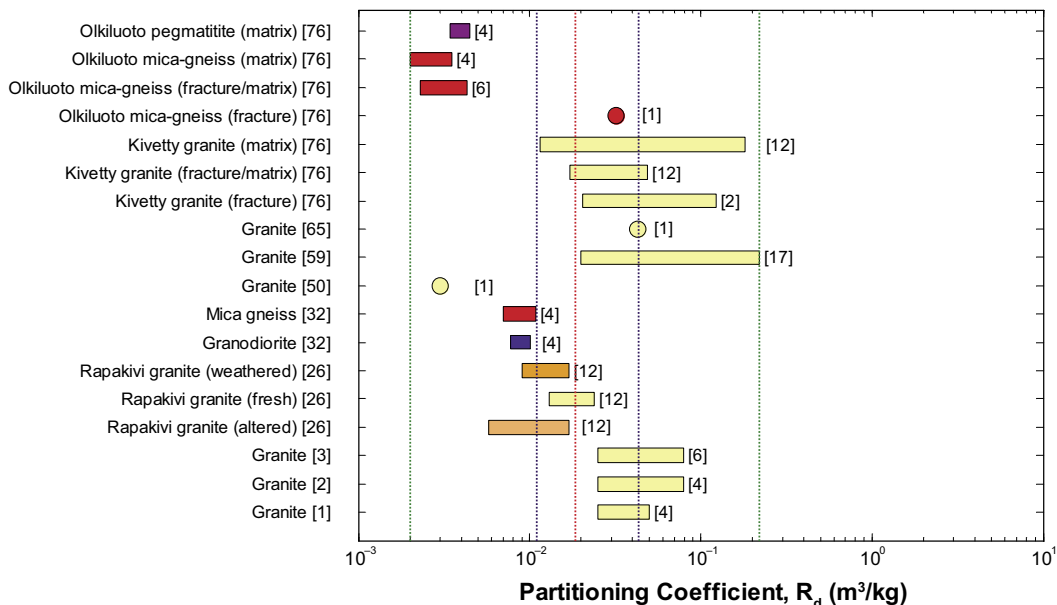
216 individual  $R_d$  measurements for Np sorption have been examined (176 for Np(V) and 40 for Np(IV)). 58 values for Np(V) sorption were rejected, mostly owing to inappropriate water compositions. No data were rejected for Np(IV). Similarly as for U(IV) it is not entirely clear in most cases whether the reported  $K_d$  data for Np(IV) represent true sorption or are biased by surface precipitation and co-precipitation phenomena. The remaining data values were deemed to be applicable for both non-saline and saline conditions owing to the relative insensitivity of Np(IV)/Np(V) sorption to ionic strength variations.

The available data for Np(V) sorption encompass a number of rock types including granite, granodiorite, and mica-gneiss as well as altered granite. There do not appear to be very significant differences amongst the different rock types and it is thought that any variation between rock types is obscured by that arising due to the different water compositions used in measurements. For Np(IV), however, sorption data is mostly for granodiorite with a single data point for granite.

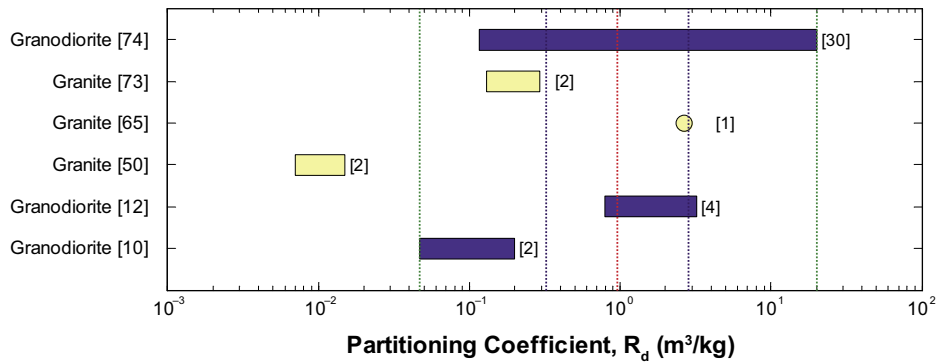
The ranges of reported distribution coefficients in the data selection are given in Figure 5-19 (oxidising conditions) and Figure 5-20 (reducing conditions) below.

Most of the reported data for Np sorption relate to measurements made under ambient conditions where it is assumed that the oxidised Np(V) redox valency is prevalent. There doesn't appear to be any discernable effect of ionic strength on Np(V) sorption in the selected data. In one case, indicated in Figure 5-19, measurements were made under apparently anaerobic conditions in an  $N_2$ -atmosphere [50] /Suksi et al. 1989/. Owing to the weak sorption observed in this experiment, we consider it doubtful that sufficiently reducing conditions were achieved (Eh was not documented) for the formation of Np(IV) and for this reason we have assumed that the results are characteristic for Np(V) sorption.

Many of the comments applied to the sorption of U(IV) apply equally well to Np(V). It is, for example, unclear whether the sorption data for reducing conditions correspond to true sorption of Np(IV) or a surface precipitation effect. In reference [12] /Baston et al. 1999/ reducing



**Figure 5-19.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Np(V) sorption as given in literature sources for oxidising conditions (all salinities). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-20.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for  $Np(IV)$  sorption as given in literature sources for reducing conditions (all salinities). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).

conditions were maintained using Na-dithionite ( $2 \times 10^{-3}$  mol/l). None of the other data sets for reducing conditions specify how this was achieved. Reference [10] /Baston et al. 1999/, [73] /Bondietti and Francis 1979/, and [74] /Tachi et al. 1999/, however, measured Eh of the contact water at the conclusion of the sorption experiment. In all cases the Eh values were measured to be in the range  $-200$  mV to  $-500$  mV.

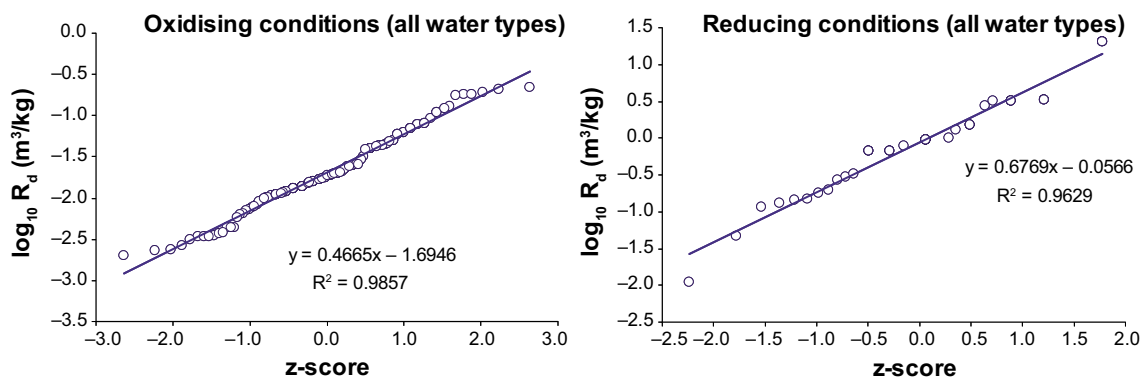
Normal probability plots for the aggregate data sets are given in Figure 5-21 below for the  $\log_{10}$ -transformed data:

The data for both oxidising and reducing conditions appear to be log-normally distributed with the median  $R_d$  for reducing conditions being about two orders of magnitude higher than the median  $R_d$  measured under oxidising conditions.

### Plutonium (Pu)

Plutonium was not found to be a significant contributor to far field activity release in the SR97 safety assessment /Lindgren and Lindström 1999/. The radium ( $^{226}Ra$ ) daughter of  $^{238}Pu$  could potentially have a non-trivial impact on far-field activity release.

Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Pu at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.



**Figure 5-21.** Normal probability plots ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for  $Np(IV/V)$  sorption as given in literature sources.

## Americium (Am)

The radioisotopes of americium can be produced by successive neutron capture and decay processes, in a similar fashion to plutonium. The  $^{241}\text{Am}$  isotope is formed primarily by decay of  $^{241}\text{Pu}$ . The isotopes of americium and their half-lives are;  $^{241}\text{Am}$  (432.2 y),  $^{242}\text{Am}$  (16.02 h),  $^{242\text{m}}\text{Am}$  (141 y), and  $^{243}\text{Am}$  ( $7.37 \times 10^3$  y).  $^{241}\text{Am}$  and  $^{243}\text{Am}$  both undergo alpha decay to form  $^{237}\text{Np}$  and  $^{239}\text{Np}$ .  $^{242}\text{Am}$  decays by  $\beta$ -particle emission forming  $^{242}\text{Cm}$ . The metastable  $^{242\text{m}}\text{Am}$  metastable isomer, on the other hand, undergoes an internal transition to form  $^{241}\text{Am}$ . A typical inventory of Am isotopes at different times in BWR waste is: (see Table 5-8).

No radioisotopes of Am were found to contribute directly to far field activity in the SR97 safety assessment /Lindgren and Lindström 1999/. The radium ( $^{226}\text{Ra}$ ) daughter of  $^{242}\text{Am}$  and  $^{242\text{m}}\text{Am}$  could potentially have a non-trivial impact on far-field activity release.

## Geochemistry of Am

Under normal conditions, Am is only present in the trivalent (+3) state and its valence is is therefore not sensitive to redox conditions. Am(III) exists mainly in a hydrolysed form as  $\text{Am}(\text{OH})_2^+$  and to a lesser extent  $\text{AmOH}^{2+}$  and  $\text{Am}(\text{OH})_3$ , while free trivalent  $\text{Am}^{3+}$  is only a minor species at the pH levels commonly encountered in granitic groundwaters. Am(III) is strongly complexed by carbonate and  $\text{AmCO}_3^+$ ,  $\text{Am}(\text{CO}_3)_2^-$ , and  $\text{Am}(\text{CO}_3)_3^{3-}$  can predominate in carbonate containing groundwaters at circumneutral to alkaline pH levels /e.g. Langmuir 1997, Choppin 2003/.

Am is not a naturally occurring element and there is therefore no background concentration in rock or groundwater.

## Am sorption mechanisms

Am(III) is expected to sorb primarily by way of a surface complexation mechanism at variable charge sites and is neither sensitive to ionic strength effects nor redox sensitive. Very little reliable data exists in the open literature concerning the sorption of Am(III) owing to its high radiotoxicity and much of its behaviour in natural environments is inferred based upon analogy with other trivalent lanthanides (e.g. Eu(III), Yb(III), etc).

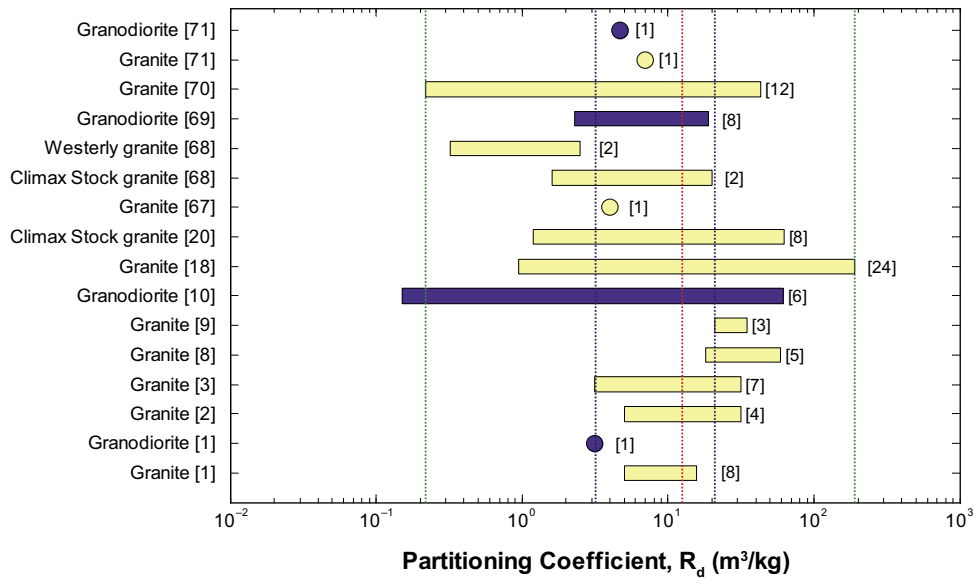
## $R_d$ data ranges for Am sorption reported in the literature

107 individual  $R_d$  measurements for Am(III) sorption have been examined of which 14 were rejected, mostly owing to inappropriate water compositions. The remaining 93 data values were deemed to be applicable for both non-saline and saline conditions owing to the insensitivity of Am(III) sorption to ionic strength variations.

The available data for Am(III) sorption are for granite and granodiorite. There do not appear to be very significant differences amongst the different rock types although insufficient data are available to draw specific conclusions. The ranges of reported distribution coefficients in the data selection are given in Figure 5-22 next page.

**Table 5-8. Inventory (Bq/ton U) of Am radioisotopes at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.**

	100 y	1,000 y	10,000 y	100,000 y
$^{241}\text{Am}$	$1.77 \times 10^{14}$	$4.22 \times 10^{13}$	$3.04 \times 10^{10}$	$2.00 \times 10^7$
$^{242}\text{Am}$	$3.90 \times 10^{11}$	$4.67 \times 10^9$	–	–
$^{242\text{m}}\text{Am}$	$3.88 \times 10^{11}$	$4.65 \times 10^9$	–	–
$^{243}\text{Am}$	$3.63 \times 10^{12}$	$3.34 \times 10^{12}$	$1.43 \times 10^{12}$	$3.08 \times 10^8$



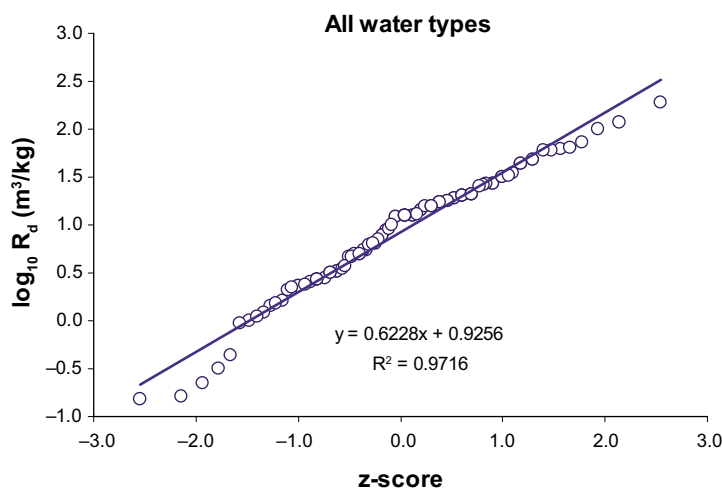
**Figure 5-22.** Ranges of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Am(III) sorption as given in literature sources for all water types. Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).

The normal probability plot for the aggregate data set is given in Figure 5-23 below for the  $\log_{10}$ -transformed data:

The data appear to be log-normally distributed although with a wide range of variability spanning some three orders of magnitude.

### Curium (Cm)

No radioisotopes of Cm were found to contribute to far field activity release in the SR97 safety assessment /Lindgren and Lindström 1999/. The radium ( $^{226}\text{Ra}$ ) daughter of  $^{242}\text{Cm}$ , however, could potentially have a non-trivial impact on far-field activity release.



**Figure 5-23.** Normal probability plot ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $m^3/kg$ ) for Am(III) sorption as given in literature sources.

Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Cm at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### 5.3.5 Transition elements

#### **Cobalt (Co)**

The  $^{60}\text{Co}$  radionuclide is an activation product resulting from irradiation of the metallic cladding of fuel elements with neutrons. It has only one radionuclide form ( $^{60}\text{Co}$ ) that has a half-life of 5.27 y and thus decays to insignificant levels within 50 years.  $^{60}\text{Co}$  undergoes  $\beta$ -decay to form stable  $^{60}\text{Ni}$ .

Owing to its short half-life,  $^{60}\text{Co}$  was not found to be an important radionuclide in the far field release calculations for the SR-97 safety assessment /Lindgren and Lindström 1999/. We have not reviewed sorption data for Co at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

#### **Nickel (Ni)**

Both  $^{59}\text{Ni}$  and  $^{63}\text{Ni}$  are activation products resulting from irradiation of the metallic cladding of fuel elements with neutrons. Its two main isotopes in spent nuclear fuel have half-lives of  $1.01 \times 10^5$  y ( $^{59}\text{Ni}$ ) and 100.1 y ( $^{63}\text{Ni}$ ).  $^{59}\text{Ni}$  decays by auger electron capture to form the stable  $^{59}\text{Co}$  isotope accompanied by the release of an X-ray.  $^{63}\text{Ni}$ , on the other hand, undergoes  $\beta$ -decay to form  $^{63}\text{Cu}$ , also a stable isotope. A typical inventory of Ni isotopes at different times in BWR waste is: (see Table 5-9).

The  $^{59}\text{Ni}$  radionuclide was one of the dominant contributors to far field activity release in the SR97 safety assessment /Lindgren and Lindström 1999/.

#### **Geochemistry of Ni**

In granitic groundwaters, nickel is mostly present in the free divalent form ( $\text{Ni}^{+2}$ ) and is not appreciably hydrolysed below about pH 10. It is not sensitive to redox conditions. Its geochemistry in groundwater is not particularly well understood and groundwater concentrations typically deviate strongly from predictions based upon postulated solubility controlling minerals /e.g. Bruno et al. 2002/. Carbonate complexation is thought to be very important for Ni speciation at the pH levels and carbonate concentrations typical for Äspö groundwater /Bruno et al. 1997/ although thermodynamic data for these reactions has been broadly criticised as being inaccurate /Hummel and Curti 2003/. The principal, aqueous carbonate complexes of Ni are thought to be  $\text{NiCO}_3^0$ ,  $\text{Ni}(\text{CO}_3)_2^{2-}$ , and  $\text{NiHCO}_3^+$ .

Some of the solubility limiting minerals that have been suggested for Ni are theophrastrite ( $\text{Ni}(\text{OH})_2$ ) and nickel-goethite co-precipitates. A number of nickel-containing clay minerals have also been proposed as controlling phases for groundwater Ni concentrations as well as the sulphide mineral, millerite ( $\text{NiS}$ ) that has been observed in nickel sulphide ores (Ni is also known to form co-precipitates with pyrite,  $\text{FeS}_2$ ).

**Table 5-9. Inventory (Bq/ton U) of Ni radioisotopes at various times in BWR spent nuclear fuel with a burn up ratio of 55 Mwd/kg U /Håkansson 2000/.**

	100 y	1,000 y	10,000 y	100,000 y
$^{59}\text{Ni}$	$8.78 \times 10^{10}$	$8.71 \times 10^{10}$	$8.02 \times 10^{10}$	$3.49 \times 10^{10}$
$^{63}\text{Ni}$	$6.13 \times 10^{12}$	$1.21 \times 10^{10}$	n/a	n/a

/McKinley and Savage 1996, and references therein/ compare different solubility databases that have been used for safety assessment of high-level nuclear waste. In most cases, the radionuclide solubilities are assigned by thermodynamic modelling using one or more assumed solubility limiting phases. The limiting solubilities of Ni used in these safety assessments were typically in the range  $10^{-3}$ – $10^{-4}$  mol/l, although in light of the discussion by /Hummel and Curti 2003/ it is questionable whether appropriate solubility limiting phases were chosen in these studies.

Concentrations of Ni in deep groundwater from the Simpevarp area are in the range of 1–2  $\mu\text{g/l}$  ( $2 \times 10^{-8}$ – $3 \times 10^{-8}$  mol/l) /Laaksoharju et al. 2004b/. It has been suggested that the availability of Ni in groundwater is most likely governed by sorption processes owing to the large discrepancy between calculated solubilities and observed concentrations /Bruno et al. 2002/.

### Ni sorption mechanisms

Ni is expected to sorb primarily by way of a surface complexation mechanism at variable charge sites on aluminosilicates and other minerals (e.g. Fe-oxyhydroxides, etc). /Albinsson 1991/ suggests that cobalt (Co) is a good analogue for Ni sorption as they have very similar chemistry. The sorption of Ni is not sensitive to redox conditions although it exhibits some sensitivity to ionic strength effects and pH.

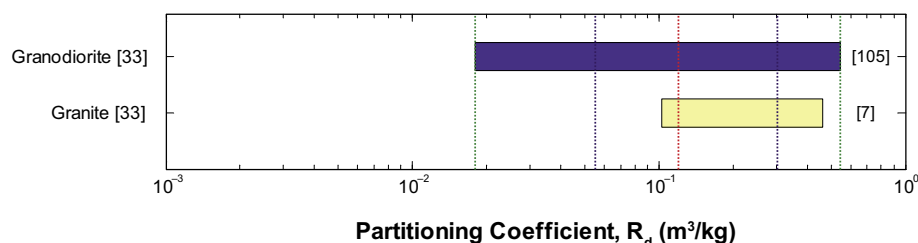
### $R_d$ data ranges for Ni sorption reported in the literature

The data for Ni sorption are scarce in the open literature. In all, 298 individual  $R_d$  measurements for Ni sorption have been examined of which, 66 were rejected for various reasons. Of the remaining data, 112 values were applicable for non-saline conditions and 120 for saline conditions. Much of the data were rejected as it was deemed that the measured partitioning coefficients were strongly biased by co-precipitation effects involving carbonate minerals. Measurements have only been reported for granite and granodiorite, although it appears that there are no large differences between the sorption properties of these rock types.

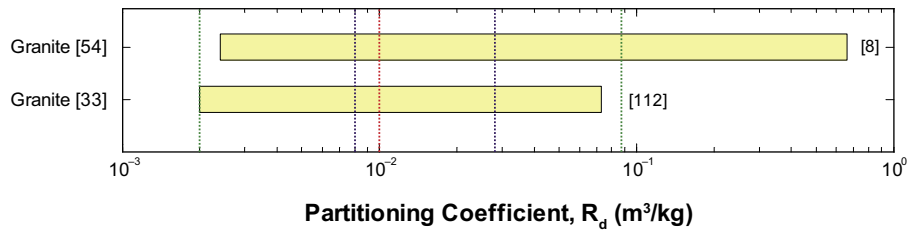
The ranges of reported distribution coefficients in the data selection are given in Figure 5-24 below for non-saline water and in Figure 5-25 for saline water.

Normal probability plots for the aggregate data sets are given in Figure 5-26 below for the  $\log_{10}$ -transformed data.

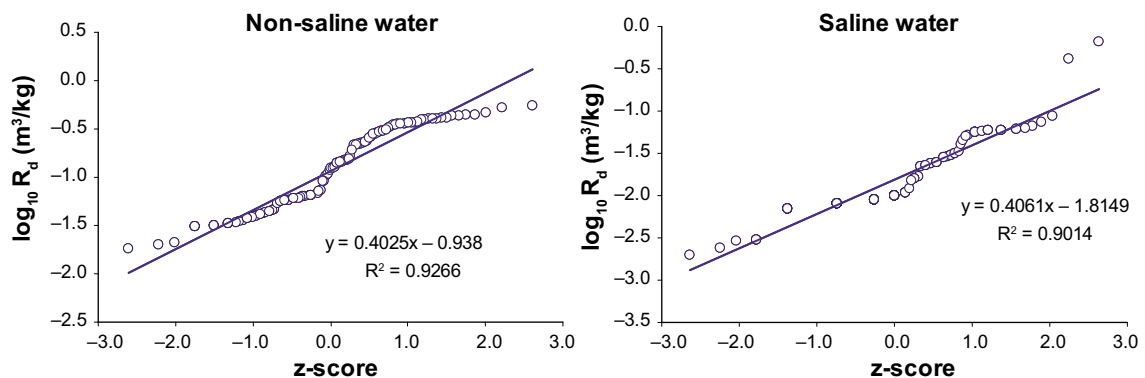
The data for non-saline conditions cover a range of about two orders of magnitude and do not appear to follow any simple, well-defined distribution. Actually, it could be argued that the data exhibit a bimodal distribution, although this is likely to be an artefact relating to the small number of data sources available in the literature. The data for saline water appear to be log-normally distributed with a median  $R_d$  about one order of magnitude higher than that for non-saline conditions.



**Figure 5-24.** Ranges of reported distribution coefficients,  $R_d$  ( $\text{m}^3/\text{kg}$ ) for Ni(II) sorption as given in literature sources for non-saline water ( $\text{Cl}^- < 400 \text{ mg/l}$ ). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-25.** Ranges of reported distribution coefficients,  $R_d$  ( $\text{m}^3/\text{kg}$ ) for Ni(II) sorption as given in literature sources for saline water ( $\text{Cl}^- \geq 400 \text{ mg/l}$ ). Bars correspond to  $R_d$  ranges; circular markers correspond to single values given in the reference (y-axis). Similar rock types are identifiable by colours as specified in the figure. Numbers of reported measurements are given in square brackets to the right of plotted data. Vertical broken lines correspond to aggregate median (red), interquartile 25–75% range (blue), and overall data limits excluding outliers (green).



**Figure 5-26.** Normal probability plots ( $\log_{10}$ -transformed data) of reported distribution coefficients,  $R_d$  ( $\text{m}^3/\text{kg}$ ) for Ni(II) sorption as given in literature sources.

### Zirconium (Zr)

The radionuclide  $^{93}\text{Zr}$  is a fission product in spent nuclear fuel. It has a half-life of  $1.53 \times 10^6$  y and undergoes  $\beta$ -decay to form  $^{93}\text{Nb}$ .

The  $^{93}\text{Zr}$  radionuclide was not found to be an important radionuclide in the far-field release calculations for the SR-97 performance assessment /Lindgren and Lindström 1999/. Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Zr at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### Niobium (Nb)

The radioisotopes  $^{93\text{m}}\text{Nb}$  and  $^{94}\text{Nb}$  are formed by neutron activation as well as being fission products. The  $^{93\text{m}}\text{Nb}$  metastable isomer has a half-life of 16.13 y and decays by internal transition to stable  $^{93}\text{Nb}$ , while  $^{94}\text{Nb}$  has a half-life of  $2.03 \times 10^4$  y and decays by  $\beta$ -particle emission to form stable  $^{94}\text{Mo}$ .

Niobium was not found to be an important radionuclide in the far-field release calculations for the SR-97 safety assessment. Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Nb at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Technetium (Tc)***

The radionuclide <sup>99</sup>Tc is a fission product in spent nuclear fuel. It has a half-life of  $2.111 \times 10^5$  y and undergoes  $\beta$ -decay to form stable <sup>99</sup>Ru.

The <sup>99</sup>Tc radionuclide was one of the dominant contributors to far field activity release in the SR97 safety assessment for cases where pessimistic rock material properties were simulated /Lindgren and Lindström 1999/.

We have not reviewed sorption data for Tc at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Palladium (Pd)***

Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Pd at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Silver (Ag)***

Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Ag at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Cadmium (Cd)***

Owing to its minor importance in the SR-97 calculations, we have not reviewed sorption data for Cd at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

## **5.3.6 Other elements**

### ***Carbon (C)***

We have not reviewed sorption data for C at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Chlorine (Cl)***

We have not reviewed sorption data for Cl at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Selenium (Se)***

We have not reviewed sorption data for Se at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Tin (Sn)***

We have not reviewed sorption data for Sn at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.

### ***Iodine (I)***

We have not reviewed sorption data for I at this time. Recommended data for this nuclide has therefore been taken from the previous compilation by /Carbol and Engkvist 1997/.



## 6 Rationale for derivation of recommended values including upper and lower bounds

Recommended generic  $K_d$  values for granitic rocks have been selected on the basis of experimental studies detailed in Section 5.3 as well as compilations that have been used in previous safety assessment studies /e.g. Carbol and Engkvist 1997, Albinsson 1991, Stenhouse 1995/. The data reported for most radionuclides reflect a broad range of experimental conditions, which tends to give large scatter in the aggregate data set.

Major factors influencing this variability are choices of water composition, spike concentration, liquid/solid ratio, rock type, particle size, and contact time. There is also some evidence to suggest that partitioning coefficients measured for certain redox sensitive radionuclides may be influenced by poorly controlled redox conditions in laboratory experiments. In addition to general scatter in the experimental data, there is strong evidence to suggest that the use of crushed material may give results that systematically overestimate in situ  $K_d$  values by at least an order of magnitude and possibly more. It is also unclear at this time what physicochemical processes time-dependent behaviour represents. In many studies it has been observed that partitioning coefficients tend to increase with increasing contact time. This could be a disequilibrium effect resulting from diffusion or chemical kinetics, a result of weathering processes, or possibly other experimental artefacts. These issues are discussed in detail in Section 4.4.3. In the absence of detailed and unambiguous evidence for the physical interpretation of such time dependency, we can only conclude that it results in a dilation of data uncertainty ranges.

The recommended data in this compilation takes the form of a “best estimate”  $K_d$  value for generic granitic rock at pH 7–9 and two different salinity levels as described in Section 5.2.2. For one solute, Sr(II) the data are sufficiently detailed that recommended  $K_d$  values can be given for three different salinity levels. For redox sensitive radionuclides, data are provided for strongly reducing conditions ( $E_h \leq -250 \pm 100$  mV) typical of deep groundwaters in granitic rocks, as well as for oxidising conditions at approximately atmospheric intensity. The rationale for this choice of redox conditions is described in detail in Section 2.1.2. The authors have chosen to regard the median of the relevant aggregate data set (i.e.  $\log_{10}$ -transformed data) as the best estimate  $K_d$  for laboratory reference conditions. In addition to the best estimate, the interquartile 25–75% range of the data is given as well as an upper and lower bound for the overall data variability. For data sets where there are no outliers, the bounds are simply the minimum and maximum reported values. Outliers are defined as values lying outside the range  $K_{d,low} - K_{d,high}$  defined by (see e.g. /Hoaglin et al. 1986, Carling 1998/):

$$\left. \begin{aligned} \log_{10} K_{d,low} &\geq Q_{25\%} - k \times (Q_{75\%} - Q_{25\%}) \\ \log_{10} K_{d,high} &\leq Q_{25\%} + k \times (Q_{75\%} - Q_{25\%}) \end{aligned} \right\} k = 1.5 \quad (6-1)$$

In such cases, the data bounds are equal to the values of  $K_{d,low}$  and  $K_{d,high}$  as appropriate given in the equation above where  $Q_{25\%}$  and  $Q_{75\%}$  correspond to the 25% and 75% quartiles of the  $\log_{10}$ -transformed data.

Although much of the literature data presented in Section 5.3 appears to be approximately log-normally distributed, it is the opinion of the authors that this is illusory and reflects the possibly biased statistics of water compositions, contact times, particle sizes, etc represented in the data as well as other methodological biases relating to the means by which  $R_d$  values are estimated and reported in the literature. As such, the apparent distributions are largely an artefactual product of the data selection process and may not result from true geochemical variability or uncertainty that is relevant for safety assessment purposes. It appears from the data, for

example, that these artefactual uncertainties tend to drown out any innate differences (if they exist) between different rock types in the aggregate data sets. For measurements carried out by specific researchers, however, there are indications of a small amount of variability that can possibly be related to rock type (specifically, observations of sorption on altered vs. non-altered rock by /Huitti et al. 1996, Byegård et al. 1998/).

The data is generally not sufficiently detailed or well-documented to permit the estimation of response surfaces or detailed parametric tables for  $K_d$ . For these reasons the use of best estimate  $K_d$  values and a uniform distribution of log-transformed,  $K_d$ -range data is preferable to the use of more sophisticated distributions.

The data is presented in the summary tables “as is” and are not corrected for surface area effects or other artefacts. Although not corrected to give data applicable for in situ conditions, a method based upon the use of correction factors is described in the following paragraphs which can be used to derive  $K_d$  values for in situ conditions. Although recommendations are given for reasonable correction factors to be used in safety assessment, these are sufficiently subjective that they cannot be considered unequivocal and should be considered in the light of supporting data from investigations at the sites concerned.

For the estimation of  $K_d$  values applicable to in situ conditions, the authors propose the use of correction factors to extrapolate the data in the summary tables. The applicable in situ  $K_d$  value is then given by:

$$K_d = K_d^0 \cdot f_{cr} \cdot f_{eq} \cdot f_{is} \cdot f_{chem} \quad (\text{m}^3/\text{kg}) \quad (6-2)$$

Where,

$K_d^0$  is the best estimate partitioning coefficient,  $K_d$  value obtained from the summary data tables below (referred to as the laboratory reference conditions);

$f_{cr}$  is a correction factor to account for surface area effects relating to the use of crushed material;

$f_{eq}$  is a correction factor to account for time dependent effects in the aggregate data set;

$f_{is}$  correction factor to account for in situ lithostatic stress;

$f_{chem}$  correction factor to account for the presence of additional complexing agents, competing species, colloids etc that may be present under in situ conditions although not necessarily internalised in summary table data;

Based upon the data presented in Figure 4-3 and typical particle sizes used in sorption experiments, the authors propose that the in situ mineral surface area may be as little as 0.01–0.1 that typical for crushed rock. For use in SR-Can, however, the authors believe a value of  $f_{cr} = 0.1$  is reasonable.

Owing to a current lack of understanding concerning the physical interpretation of time dependency effects in laboratory derived sorption data, the authors recommend a value of  $f_{eq} = 1.0$  to be used in SR-Can. Time dependency effects can therefore not be deemed to give an unambiguously positive or negative biasing effect on the aggregate data set.

The status of lithostatic stress as applicable to sorption processes is currently unclear. In situ resistivity measurements tend to give estimates for formation factors that are as much as an order of magnitude lower than those obtained in the laboratory. Assuming that much of the observed effect is due to a compression of pore volume rather than a physical closing off of the pore system, we propose a value for  $f_{is}$  in the range  $0.1 \leq f_{is} \leq 1.0$ . This could account for the possible irreversible formation of new micro cracks due to de-stressing when bore core samples are retrieved, as well as effects of in situ lithostatic stress upon pore accessibility. It is noted, however, that there are very large uncertainties present in the aggregate data sets and any additional uncertainty due to lithostatic stress effects are likely to have an insignificant impact upon overall uncertainty.

The use of the correction factor,  $f_{chem}$  is case specific and must be considered in the context of scenarios for repository evolution. It is therefore not possible to give any recommended values for this parameter in this compilation. As such, the authors propose the use of  $f_{chem} = 1.0$  as a base case scenario unless there are specific reasons for choosing a different value within SR-Can.

The different multiplying factors have been introduced with the following underlying idea: We deem that BET normalised  $K_d$  values can be measured reasonably accurately on given mineral surfaces for specific geochemical conditions. The BET surface areas of large monolithic pieces of rock that are more relevant for in situ rock properties will also be more accurately determined in the future. Furthermore, some site-specific conditions, namely Eh, pH, ionic strength, the presence of specific complexing agents, or unusually high concentrations of competing species, etc can be accounted for using different  $f_{chem}$ -factors. The advantage of using correction factors is that site-specific data can then be generated without changing the original recommended  $K_d$  data for the defined laboratory reference conditions.

## 7 Concluding remarks and summary of recommended, generic $K_d$ data for sorption in granitic rocks

Experimental sorption data reported in the open literature have been reviewed with the aim of providing recommended generic  $K_d$  estimates for radionuclide sorption in granitic rock. Given the limited amount of time available, we have concentrated upon a small sub-group of sorbing nuclides that we believe are of central importance for uncertainty in SR-Can safety assessment studies. Most of these nuclides were selected on the basis of their relative importance as identified from far field, radionuclide transport calculations detailed in the SR-97 safety report /Lindgren and Lindström 1999/. Other nuclides that we have not reviewed in detail may be important for uncertainty estimates of far-field activity release in SR-Can. These will be reviewed and updated data provided as they become available.

The main nuclides studied were Cs, Sr, Ra, Ni, Th, U, Np, and Am. Data for other nuclides were taken from /Carbol and Engkvist 1997/.

Best estimate  $K_d$  values (taken to be the median of the selected data set) and approximate ranges of uncertainty are given in Table 7-1 below for the main nuclides and for granitic rock typical of site investigation areas with the exception of Sr(II). Recommended data for Sr(II) are detailed separately in Table 7-2.

**Table 7-1.  $K_d$  ( $m^3/kg$ ) values for sorption of main selected radionuclides on granitic rock types under laboratory reference conditions. The data are recommended for use in radionuclide transport calculations for Forsmark, Simpevarp, and Laxemar after multiplication by the appropriate correction factors. Far right-hand column gives relevant correlation group for geochemical analogues.**

Nuclide/redox state		Non-Saline	Saline	Correction factors	Corr. group
Ni(II) <sup>1</sup>	Median	$1.2 \times 10^{-1}$	$1.0 \times 10^{-2}$	$f_{eq} = 0.1$	3
	$K_{d,25\%} - K_{d,75\%}$	$5.5 \times 10^{-2} - 3.0 \times 10^{-1}$	$8.0 \times 10^{-3} - 2.8 \times 10^{-2}$	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	$1.8 \times 10^{-2} - 5.4 \times 10^{-1}$	$2.0 \times 10^{-3} - 8.7 \times 10^{-2}$		
Cs(I) <sup>1</sup>	median	$1.8 \times 10^{-1}$	$4.2 \times 10^{-2}$	$f_{eq} = 0.1$	1
	$K_{d,25\%} - K_{d,75\%}$	$4.9 \times 10^{-2} - 7.2 \times 10^{-1}$	$1.0 \times 10^{-2} - 1.4 \times 10^{-1}$	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	$1.7 \times 10^{-3} - 9.6$	$4.0 \times 10^{-4} - 2.0$		
Ra(II) <sup>1</sup>	median	1.3	2.1	$f_{eq} = 0.1$	2
	$K_{d,25\%} - K_{d,75\%}$	$1.4 \times 10^{-1} - 1.9$	$9.9 \times 10^{-2} - 2.3$	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	$6.3 \times 10^{-2} - 11$	$6.4 \times 10^{-3} - 2.6$		
Th(IV)	median	1.0	1.0	$f_{eq} = 0.1$	5
	$K_{d,25\%} - K_{d,75\%}$	$7.9 \times 10^{-1} - 2.4$	$7.9 \times 10^{-1} - 2.4$	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	$5 \times 10^{-1} - 10$	$5 \times 10^{-1} - 10$		
U(IV) <sup>2</sup>	median	6.3	6.3	$f_{eq} = 0.1$	5
	$K_{d,25\%} - K_{d,75\%}$	1.1 - 13	1.1 - 13	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	$4.8 \times 10^{-2} - 280$	$4.8 \times 10^{-2} - 280$		
U(VI) <sup>2</sup>	median	$6.3 \times 10^{-3}$	$6.3 \times 10^{-3}$	$f_{eq} = 0.1$	7
	$K_{d,25\%} - K_{d,75\%}$	$1.5 \times 10^{-3} - 1.6 \times 10^{-2}$	$1.5 \times 10^{-3} - 1.6 \times 10^{-2}$	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	$5.0 \times 10^{-4} - 1.2 \times 10^{-1}$	$5.0 \times 10^{-4} - 1.2 \times 10^{-1}$		

Nuclide/redox state		Non-Saline	Saline	Correction factors	Corr. group
Np(IV) <sup>2</sup>	median	9.6×10 <sup>-1</sup>	9.6×10 <sup>-1</sup>	$f_{eq} = 0.1$	5
	$K_{d,25\%} - K_{d,75\%}$	3.2×10 <sup>-1</sup> – 2.8	3.2×10 <sup>-1</sup> – 2.8	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	4.7×10 <sup>-2</sup> – 20	4.7×10 <sup>-2</sup> – 20		
Np(V) <sup>2</sup>	median	1.8×10 <sup>-2</sup>	1.8×10 <sup>-2</sup>	$f_{eq} = 0.1$	6
	$K_{d,25\%} - K_{d,75\%}$	1.1×10 <sup>-2</sup> – 4.4×10 <sup>-2</sup>	1.1×10 <sup>-2</sup> – 4.4×10 <sup>-2</sup>	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	2.0×10 <sup>-3</sup> – 2.2×10 <sup>-1</sup>	2.0×10 <sup>-3</sup> – 2.2×10 <sup>-1</sup>		
Am(III)	median	13	13	$f_{eq} = 0.1$	4
	$K_{d,25\%} - K_{d,75\%}$	3.2 – 21	3.2 – 21	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	2.2×10 <sup>-1</sup> – 190	2.2×10 <sup>-1</sup> – 190		

Notes: Porewater categories are defined as non-saline ( $Cl^- < 400$  mg/l) and saline ( $Cl^- \geq 400$  mg/l) with a pH range 7–9, for both oxidising and reducing ( $Eh < -250 \pm 100$  mV) conditions.

<sup>1</sup> Solutes that exhibit sensitivity to ionic strength.

<sup>2</sup> Solutes that exhibit sensitivity to redox conditions.

For the special case of Sr(II) it was found that the saline category could be further subdivided into weakly saline and moderately-to-strongly saline owing to its considerable sensitivity to ionic strength. These data are given in Table 7-2 below.

Best-estimate  $K_d$  values and approximate ranges of uncertainty are given in Table 7-3 below for nuclides that have not been reviewed in this report. The data are taken directly from /Carbol and Engkvist 1997/ without modification. It should be noted, that although the definitions of salinity and redox are different to those adopted in the updated compilation presented in this report, the differences are likely to be negligible for most of the radionuclides concerned.

**Table 7-2.  $K_d$  (m<sup>3</sup>/kg) values for sorption of Sr(II) on granitic rock types under laboratory reference conditions. The data are recommended for use in radionuclide transport calculations for Forsmark, Simpevarp, and Laxemar after multiplication by the appropriate correction factors. Far right-hand column gives relevant correlation group for geochemical analogues.**

Nuclide/redox state		Non-saline	Saline	Correction factors	Corr. group
Sr(II)			(aggregate saline, $Cl^- \geq 400$ mg/l)		
	median	1.3×10 <sup>-2</sup>	3.1×10 <sup>-4</sup>	$f_{eq} = 0.1$	2
	$K_{d,25\%} - K_{d,75\%}$	6.5×10 <sup>-3</sup> – 4.1×10 <sup>-2</sup>	8.4×10 <sup>-5</sup> – 5.4×10 <sup>-3</sup>	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$	1.0×10 <sup>-3</sup> – 6.1×10 <sup>-1</sup>	1.4×10 <sup>-5</sup> – 2.6×10 <sup>-2</sup>		
			(weakly saline, $400 \leq Cl^- < 4,000$ mg/l)		
	median		5.0×10 <sup>-3</sup>	$f_{eq} = 0.1$	2
	$K_{d,25\%} - K_{d,75\%}$		2.5×10 <sup>-3</sup> – 8.6×10 <sup>-3</sup>	$0.1 \leq f_{is} \leq 1.0$	
	$K_{d,low} - K_{d,high}$		5.0×10 <sup>-4</sup> – 2.6×10 <sup>-2</sup>		
			(moderately-to-strongly saline, $Cl^- \geq 4,000$ mg/l)		
median		9.8×10 <sup>-5</sup>	$f_{eq} = 0.1$	2	
$K_{d,25\%} - K_{d,75\%}$		4.7×10 <sup>-5</sup> – 2.2×10 <sup>-4</sup>	$0.1 \leq f_{is} \leq 1.0$		
$K_{d,low} - K_{d,high}$		1.4×10 <sup>-5</sup> – 5.0×10 <sup>-4</sup>			

Notes: Porewater categories are defined as non-saline ( $Cl^- < 400$  mg/l), aggregate saline ( $Cl^- \geq 400$  mg/l), weakly saline ( $400 \leq Cl^- < 4,000$  mg/l), and moderately to strongly saline ( $Cl^- \geq 4,000$  mg/l) with a pH range 7–9, for both oxidising and reducing ( $Eh < -250 \pm 100$  mV) conditions. Aggregate saline corresponds to the pooled set of weakly saline and moderately-to-strongly saline data sets.

**Table 7-3.  $K_d$  ( $m^3/kg$ ) values for sorption of non-reviewed radionuclides on granitic rock types under laboratory reference conditions. The data are recommended for use in radionuclide transport calculations for Forsmark, Simpevarp, and Laxemar after multiplication by the appropriate correction factors. Far right-hand column gives relevant correlation group for geochemical analogues.**

Nuclide/redox state		Non-saline	Saline	Correction factors	Corr. group
C/HCO <sub>3</sub> <sup>-</sup>	Best estimate	1×10 <sup>-3</sup>	1×10 <sup>-3</sup>	$f_{eq} = 0.1$	n/a
	$K_{d,low} - K_{d,high}$	5×10 <sup>-4</sup> – 2×10 <sup>-3</sup>	5×10 <sup>-4</sup> – 2×10 <sup>-3</sup>	$0.1 \leq f_{is} \leq 1.0$	
Cl <sup>-</sup> ,I <sup>-</sup>	Best estimate	0	0		n/a
	$K_{d,low} - K_{d,high}$	n/a	n/a		
Co(II) <sup>1</sup>	Best estimate	1×10 <sup>-1</sup>	2×10 <sup>-2</sup>	$f_{eq} = 0.1$	3
	$K_{d,low} - K_{d,high}$	5×10 <sup>-2</sup> – 5×10 <sup>-1</sup>	1×10 <sup>-2</sup> – 1×10 <sup>-1</sup>	$0.1 \leq f_{is} \leq 1.0$	
Se(-II,IV,VI) <sup>2</sup>	Best estimate	1×10 <sup>-3</sup>	1×10 <sup>-3</sup>	$f_{eq} = 0.1$	n/a
	$K_{d,low} - K_{d,high}$	5×10 <sup>-4</sup> – 5×10 <sup>-3</sup>	5×10 <sup>-4</sup> – 5×10 <sup>-3</sup>	$0.1 \leq f_{is} \leq 1.0$	
Zr(IV)	Best estimate	1	1	$f_{eq} = 0.1$	5
	$K_{d,low} - K_{d,high}$	5×10 <sup>-1</sup> – 3	5×10 <sup>-1</sup> – 3	$0.1 \leq f_{is} \leq 1.0$	
Tc(IV) <sup>2</sup>	Best estimate	1	1	$f_{eq} = 0.1$	n/a
	$K_{d,low} - K_{d,high}$	5×10 <sup>-1</sup> – 3	5×10 <sup>-1</sup> – 3	$0.1 \leq f_{is} \leq 1.0$	
Tc(VII) <sup>2</sup>	Best estimate	0	0		n/a
	$K_{d,low} - K_{d,high}$	n/a	n/a		
Nb(V)	Best estimate	1	1	$f_{eq} = 0.1$	6
	$K_{d,low} - K_{d,high}$	5×10 <sup>-1</sup> – 3	5×10 <sup>-1</sup> – 3	$0.1 \leq f_{is} \leq 1.0$	
Pd(II) <sup>1</sup>	Best estimate	1×10 <sup>-1</sup>	1×10 <sup>-2</sup>	$f_{eq} = 0.1$	3
	$K_{d,low} - K_{d,high}$	1×10 <sup>-2</sup> – 5×10 <sup>-1</sup>	1×10 <sup>-3</sup> – 5×10 <sup>-2</sup>	$0.1 \leq f_{is} \leq 1.0$	
Ag(I) <sup>1</sup>	Best estimate	5×10 <sup>-1</sup>	5×10 <sup>-2</sup>	$f_{eq} = 0.1$	≈1
	$K_{d,low} - K_{d,high}$	1×10 <sup>-1</sup> – 1	1×10 <sup>-2</sup> – 1×10 <sup>-1</sup>	$0.1 \leq f_{is} \leq 1.0$	
Cd(II) <sup>1</sup>	Best estimate	1×10 <sup>-1</sup>	2×10 <sup>-2</sup>	$f_{eq} = 0.1$	3
	$K_{d,low} - K_{d,high}$	5×10 <sup>-2</sup> – 5×10 <sup>-1</sup>	1×10 <sup>-2</sup> – 1×10 <sup>-1</sup>	$0.1 \leq f_{is} \leq 1.0$	
Sn(IV)	Best estimate	1×10 <sup>-3</sup>	1×10 <sup>-3</sup>	$f_{eq} = 0.1$	5
	$K_{d,low} - K_{d,high}$	0 – 1×10 <sup>-2</sup>	0 – 1×10 <sup>-2</sup>	$0.1 \leq f_{is} \leq 1.0$	
Sm,Eu,Ho(III)	Best estimate	2	2	$f_{eq} = 0.1$	4
	$K_{d,low} - K_{d,high}$	1 – 5	1 – 5	$0.1 \leq f_{is} \leq 1.0$	
Pa(IV/V)	Best estimate	1	1	$f_{eq} = 0.1$	5/6
	$K_{d,low} - K_{d,high}$	5×10 <sup>-1</sup> – 5	5×10 <sup>-1</sup> – 5	$0.1 \leq f_{is} \leq 1.0$	
Pu(III/IV)	Best estimate	5	5	$f_{eq} = 0.1$	5/6
	$K_{d,low} - K_{d,high}$	1 – 10	1 – 10	$0.1 \leq f_{is} \leq 1.0$	
Ac,Cm(III)	Best estimate	3	3	$f_{eq} = 0.1$	4
	$K_{d,low} - K_{d,high}$	1 – 5	1 – 5	$0.1 \leq f_{is} \leq 1.0$	

Notes: Porewater categories are defined as non-saline (Cl<sup>-</sup> < 500 mg/l) and saline (500 < Cl<sup>-</sup> < 6,500 mg/l) with a pH ≥ 7, for both oxidising and reducing (Eh < -200 mV) conditions.

<sup>1</sup> Solutes that exhibit sensitivity to ionic strength.

<sup>2</sup> Solutes that exhibit sensitivity to redox conditions.

## 8 References

Note: References preceded by a number in square brackets (i.e. [#]) indicate sources used to compile recommended data tables.

**Albinsson Y, 1991.** Sorption of radionuclides in granitic rock. SKB Arbetsrapport AR-91-07, Svensk Kärnbränslehantering AB.

**Alexander W, McKinley I, MacKenzie A, Scott R, 1990.** Verification of matrix diffusion by means of natural decay series disequilibria in a profile across a water-conducting fracture in granitic rock. *Mat. Res. Soc. Symp. Proc.*, 176, pp 567–576.

**[1] Allard B, Kipatsi H, Rydberg J, 1977.** Sorption av långlivade radionuklider i lera och berg. KBS TR-55, Svensk Kärnbränslehantering AB.

**[2] Allard B, Kipatsi H, Torstenfelt B, 1978.** Sorption av långlivade radionuklider i lera och berg Del 2. KBS TR-98, Svensk Kärnbränslehantering AB.

**[3] Allard B, Rydberg J, Kipatsi H, Torstenfelt B, 1979.** Disposal of Radioactive Waste in Granitic Bedrock. In: ACS Symposium Series 100(4), Radioactive Waste Geological Storage, pp 47–73.

**[67] Allard B, Beall G, 1979.** Sorption of americium on geologic media. *Journal of Environmental Science and Health, Part A: Environmental Science and Engineering*, 6, pp 507–518.

**(Note: Secondary reference – data obtained from JNC Sorption Database)**

**[68] Allard B, Beall G, 1980.** The Sorption of Actinides in Igneous Rocks. *Nuclear Technology*, 49, pp 474–480.

**(Note: Secondary reference – data obtained from JNC Sorption Database)**

**Allard B, 1982.** Sorption of actinides in granitic rock. SKB TR-82-21, Svensk Kärnbränslehantering AB.

**Allard B, Karlsson F, Tullborg E-L, Larson S, 1983.** Ion exchange capacities and surface areas of some major components and common fracture filling materials of igneous rocks. SKB TR-83-64, Svensk Kärnbränslehantering AB.

**Allard B, Olofsson U, Torstenfelt B, Kipatsi H, 1983.** Sorption behaviour of well-defined oxidation states. SKB TR-83-61, Svensk Kärnbränslehantering AB.

**Allard B, Olofsson U, Torstenfelt B, 1984.** Environmental actinide chemistry. *Inorganica Chemica Acta*, 94, pp 205–221.

**Allard B, Karlsson F, Neretnieks I, 1991.** Concentrations of particulate matter and humic substances in deep groundwaters and estimated effects on the adsorption and transport of radionuclides. SKB TR-91-50, Svensk Kärnbränslehantering AB.

**Andersson K, Allard B, 1983.** Sorption of radionuclides on geologic media – A literature survey. I. Fission products. SKB TR-83-07, Svensk Kärnbränslehantering AB.

**[5] Andersson K, Torstenfelt B, Allard B, 1983.** Sorption of radionuclides in geologic systems. SKB TR-83-63, Svensk Kärnbränslehantering AB.

**Andersson J, 1999.** Data and data uncertainties. Compilation of data and data uncertainties for radionuclide transport calculations. SKB TR-99-09, Svensk Kärnbränslehantering AB.

**Andersson J, 2003.** Site descriptive modelling – strategy for integrated evaluation. SKB R-03-05, Svensk Kärnbränslehantering AB.

**André M, Malmström M, Neretnieks I, 2006 (manuscript in prep.).** Determination of sorption properties of intact rock samples: a new method based on electromigration, Department of Chemical Engineering and Technology, Royal Institute of Technology, Stockholm.

**Andrews J, Giles I, Kay R, Lee D, 1982.** Radioelements, radiogenic helium and age relationships for groundwaters from the granites at Stripa, Sweden. *Geochim. Cosmochim. Acta.*, 46(9), pp 1533–1543.

**Audi G, Bersillon O, Blachot J, Wapstra A, 2003.** The NUBASE evaluation of nuclear and decay properties. *Journal of Nuclear Physics A*, 729, pps 3–128.

**Axe L, Trivedi P, Anderson P, 2002.** Diffusion at oxide and related surfaces. *Encyclopedia of Surface and Colloid Science*, Marcel Dekker, New York.

[7] **Bajo C, Montovani M,** (Undocumented data for U sorption on granite)  
(Note: Secondary reference – data obtained from JNC Sorption Database)

**Bargar J, Brown G, Parks G, 1997.** Surface complexation of Pb(II) at oxide-water interfaces: I. XAFS and bond valence determination of mononuclear and polynuclear Pb(II) sorption products on aluminium oxides. *Geochim. Cosmochim. Acta*, 61(13), pp 2617–2673.

**Bargar J, Reiteyer R, Davis J, 1999.** Spectroscopic confirmation of uranium(VI)-carbonate adsorption complexes on hematite. *Environmental Science & Technology*, 36(5), pp 2481–2484.

**Bargar J, Reitmeyer R, Lenhart J, Davis J, 2000.** Characterization of U(VI)-carbonate ternary complexes on hematite: EXAFS and electrophoretic mobility measurements. *Geochim. Cosmochim. Acta.*, 64(16), pp 2737–2749.

[8] **Barney G, Anderson P, 1979.** The Kinetics and Reversibility of Radionuclide Sorption Reactions with Rocks – Progress Report for Fiscal Year 1978. PNL Report PNL-SA-7352, pp 163–218

(Note: Secondary reference – data obtained from JNC Sorption Database)

[9] **Barney G, Brown G, 1979.** The Kinetics and Reversibility of Radionuclide Sorption Reactions with Rocks. RHO-ST-29, pp 261–315.

(Note: Secondary reference – data obtained from JNC Sorption Database)

[11] **Baston G, Berry J, Brownsword M, Cowper M, 1995.** The sorption of uranium and technetium on bentonite, tuff and granodiorite. *Mat. Res. Soc. Symp. Proc.*, 353, pp 989–996.

[12] **Baston G, Berry J, Brownsword M, Heath T, Ilett D, Tweed C, Yui M, 1997.** The effect of temperature on the sorption of technetium, uranium, neptunium and curium on bentonite, tuff and granodiorite. *Mat. Res. Soc. Symp. Proc.*, 465, pp 805–812.

[10] **Baston G et al. 1999.** (Undocumented data for U, Pu, Am, Np on granodiorite)  
(Note: Secondary reference – data obtained from JNC Sorption Database)

[14] **Berry J A, Bond K A, Brownsword M, Ferguson D R, Green A, Littleboy A K, 1990.** “Radionuclide Sorption on Generic Rock Types”, Nirex Safety Series Report NSS/R182, Nirex.

**Bertetti F, Pabalan R, Turner D, Almedarez M, 1996.** Neptunium(V) sorption behaviour on clinoptilolite, quartz and montmorillonite. *Mat. Res. Soc. Symp. Proc.*, 412(1996), pp 631–638.

**Bertetti F, Pabalan R, Almedarez M, 1998.** Neptunium(V) sorption behaviour on quartz, clinoptilolite, montmorillonite, and  $\alpha$ -alumina. In: Jenne, ed., *Adsorption of Metals by Geomedia – Variables, Mechanisms, and Model Applications*, Academic Press, New York, pp 131–148.



**Bier V, 2004.** Implications of the research on expert overconfidence and dependence. *Reliability Engineering and System Safety*, 85, pp 321–329.

**Birgersson L, Widén H, Ågren T, Neretnieks I, 1992.** Tracer migration experiments in the Stripa Mine 1980–1991. SKB Stripa Project 92-25, Svensk Kärnbränslehantering AB.

[73] **Bondietti E, Francis C, 1979.** Geologic migration potentials of technetium-99 and neptunium-237. *Science* 203, pp 1337–1340.

(Note: Secondary reference – data obtained from JNC Sorption Database)

**Bostick B, Vairavamurphy M, Karthikeyan K, Chorover J, 2002.** Cesium adsorption on clay minerals: An EXAFS spectroscopic investigation. *Environ. Sci. Technol.*, 36, pp 2670–2676.

**Brantley S, Mellott N, 2000.** Surface area and porosity of primary silicate minerals. *American Mineralogist*, 85(11–12), pp 1767–1783.

**Brantley S, 2004.** Reaction kinetics of primary rock-forming minerals under ambient Conditions. *Fresh Water Geochemistry, Weathering, and Soils*, J.I. Drever (ed.), Vol 5 of *Treatise on Geochemistry*, K.K. Turekian and H.D. Holland (ed.), Pergamon Press, Oxford, 73–118.

**Bradbury M, Baeyens B, 1997.** A mechanistic description of Ni and Zn sorption on Namontmorillonite. Part II: modelling. *J. Cont. Hydrol.*, 27, pp 223–248.

**Bradbury M, Baeyens B, 1998.** N<sub>2</sub>-BET surface area measurements on crushed and intact minerals and rocks: A proposal for estimating sorption transfer factors. *Radioactive Waste Management and Disposal*, 122(2), pp 250–253.

**Brotas de Carvalho M, Pires J, Carvalho A, 1996.** Characterisation of clays and aluminium pillared clays by adsorption of probe molecules. *Microporous Materials*, 6(2), pp 65–77.

**Brunauer S, Emmet P H, Teller E, 1938.** Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, 60, pp 309–319.

**Bruno J, Cera E, de Pablo J, Duro L, Jordana S, Savage D, 1997.** Determination of Radionuclide Solubility Limits to be used in SR97: Uncertainties Associated to Calculated Solubilities. SKB TR-97-33, Svensk Kärnbränslehantering AB.

**Bruno J, Duro L, Grivé M, 2002.** The applicability and limitations of the geochemical models to simulate trace element behaviour in natural waters. Lessons learned from natural analogue studies. *Chemical Geology*, 190, pp 371–393.

[15] **Byegård J, Johansson H, Skålberg M, 1998.** The interaction of sorbing and non-sorbing tracers with different Äspö rock types – Sorption and diffusion experiments in the laboratory scale. SKB TR-98-18, Svensk Kärnbränslehantering AB.

**Byegård J, Gustavsson E, Tullborg E-L, 2005.** Bedrock transport properties: Preliminary site description Simpevarp subarea – version 1.2. SKB R-05-05, Svensk Kärnbränslehantering AB.

**Byegård J, Gustavsson E, Tullborg E-L, 2006.** Bedrock transport properties: Preliminary site description Laxemar subarea – version 1.2. SKB R-06-27, Svensk Kärnbränslehantering AB.

**Carbol P, Engkvist I, 1997.** Compilation of radionuclide sorption coefficients for safety assessment. SKB R-97-13, Svensk Kärnbränslehantering AB.

**Carling K, 1998.** Resistant outlier rules and the non-Gaussian case. *Computational Statistics and Data Analysis*, 33, pp 249–258.

**Chang K-S, Lin C-F, Lee D-Y, Lo S-L, 1993.** Mechanistic investigation of copper sorption onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using the relaxation technique. *Chemosphere*, 27(8), pp 1397–1407.

**Chang K-S, Lin C-F, Lee D-Y, Lo S-L, Yasunaga T, 1994.** Kinetics of Cr(III) adsorption/desorption at the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/water interface by the pressure-jump technique. *J. Colloid. Interface Sci.*, 165, pp 169–176.

**Choppin G, 2003.** Actinide speciation in the environment. *Radiochimica Acta*, 91, pp 645–649.

**Comans R, Hockley D, 1992.** Kinetics of cesium sorption on illite. *Geochim. Cosmochim. Acta*, 56, pp 1157–1164.

**[17] Cui D, Eriksen T, 1996.** Trace element distribution patterns in magnetically separated fractions of fracture filling material. *Mat. Rec. Soc. Symp. Proc.*, 412, pp 847–853.

**[18] Daniels W, 1981.** Laboratory Studies of Radionuclide Distributions between Selected Groundwaters and Geologic Media: October 1979 – September 1980. Los Alamos National Laboratory Report LA-8586-PR.

**(Note: Secondary reference – data obtained from JNC Sorption Database)**

**Davis J, Meece D, Kohler M, Curtis G, 2004.** Approaches to surface complexation modelling of Uranium(VI) adsorption on aquifer sediments. *Geochim. et Cosmochim. Acta*, 68(18), pp 3621–3641.

**Degueldre C, 1995.** Retention of redox sensitive elements in aquifers – the case of Neptunium. *J. Environ. Radioact.*, 29(1), pp 75–87.

**Degueldre C, Grauer R, Laube A, Oess A, Silby H, 1996.** Colloid properties in granitic groundwater systems. II: Stability and transport study. *Applied Geochemistry*, 11(5), pp 697–701.

**Degueldre C, 1997.** Letter to the Editor: Retention of redox sensitive elements in aquifers – the case of neptunium. *J. Environ. Radioact.*, 34(2), pp 211–214.

**Degueldre C, Triay I, Kim J-II, Vilks P, Laaksoharju M, Miekeley N, 2000.** Groundwater colloid properties: a global approach. *Applied Geochemistry*, 15(7), pp 1043–1051.

**Del Nero M, Assada A, Made B, Barillon R, Duplatre G, 2004.** Surface charges and Np(V) sorption on amorphous Al and Fe silicates. *Chemical Geology*, 211(1–2), pp 15–45.

**Dähn R, Scheidegger A, Manceau A, Schlegel M, Baeyens B, Bradbury M, Morales M, 2002.** Neoformation of Ni phyllosilicate upon Ni uptake on montmorillonite: A kinetics study by powder and polarized extended X-ray absorption fine structure spectroscopy. *Geochim. Cosmochim. Acta*, 66(13), pp 2335–2347.

**Dähn R, Scheidegger A, Manceau A, Schlegel M, Baeyens B, Bradbury M, Chateigner D, 2003.** Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite clay minerals: A polarized X-ray absorption fine structure study. *Geochim. et Cosmochim. Acta*, 67(1), pp 1–15.

**Edlund O, Bergström U, Hallberg B, Karlsson S, 1999.** A summary of biospheric research 1975–1997. SKB TR-99-40, Svensk Kärnbränslehantering AB.

**Efurd D, Runde W, Banar J, Janecky D, Kaszuba J, Palmer P, Roensch F, Tait C, 1998.** Neptunium and Plutonium Solubilities in a Yucca Mountain Groundwater. *Environ. Sci. Technol.*, 32(24), pp 3893–3900.

**Eggleston C, Hug S, Stumm W, Sulzberger B, Afonso M, 1998.** Surface complexation of sulfate by hematite surfaces: FTIR and STM observations. *Geochim. et Cosmochim. Acta*, 62(4), pp 585–593.

**Elert M, Svensson H, 2001.** Evaluation of the TRUE-1 radially converging tests with sorbing tracers. SKB TR-01-12, Svensk Kärnbränslehantering AB.

**Elzinga E, Sparks D, 2001.** Reaction Condition Effects on Nickel Sorption Mechanisms in Illite–Water Suspensions. *Soil Sci. Soc. Am. J.*, 65, pp 94–101.

**[20] Erdal B, Aguilar R, Bayhurst B, Daniels W, Duffy C, Lawrence F, Maestas S, Oliver P, Wolfsberg K, 1979.** Sorption-desorption studies on granite: 1. Initial studies of strontium, technetium, cesium, barium, cerium, europium, uranium, plutonium, and americium. Los Alamos Scientific Laboratory, Technical Report LA-7456-MS.

**(Note: Secondary reference – data obtained from JNC Sorption Database)**

**[21] Eriksen T, Locklund B, 1987.** Radionuclide sorption on granitic drill core material. SKB TR-87-22, Svensk Kärnbränslehantering AB.

**[22] Eriksen T, Locklund B, 1989.** Radionuclide sorption on crushed and intact granitic rock. Volume and surface effects. SKB TR-89-25, Svensk Kärnbränslehantering AB.

**Eriksen T, Ndalamba P, Cui D, Bruno J, Caceci M, Spahiu K, 1993.** Solubility of the redox-sensitive radionuclides <sup>99</sup>Tc and <sup>237</sup>Np under reducing conditions in neutral to alkaline solutions. Effect of carbonate. SKB TR-93-18, Svensk Kärnbränslehantering AB.

**Farquar M, Vaughan D, Hughes C, Charnock J, England K, 1997.** Experimental studies of the interaction of aqueous metal cations with mineral substrates: Lead, cadmium, and copper with perthitic feldspar, muscovite, and biotite. *Geochim. et Cosmochim. Acta*, 61(15), pp 3051–3064.

**Frape S, Fritz P, McNutt R, 1984.** Water-rock interaction and chemistry of groundwaters from the Canadian Shield. *Geochim. Cosmochim. Acta.*, 48, pp 1617–1627.

**Fredrickson J, Zachara J, Kennedy D, Liu C, Duff M, Hunter D, Dohnalkova A, 2002.** Influence of Mn oxides on the reduction of uranium(VI) by the metal-reducing bacterium *Shewanella putrefaciens*. *Geochim. Cosmochim. Acta*, 66(18), pp 3247–3262.

**Gascoyne M, 1989.** High levels of uranium and radium in groundwaters at Canada's underground research laboratory, Lac du Bonnet, Manitoba, Canada. *Applied Geochemistry*, 4, pp 577–591.

**Gascoyne M, 2004.** Hydrogeochemistry, groundwater ages and sources of salts in a granitic batholith on the Canadian Shield, southeastern Manitoba. *Applied Geochemistry*, 19, pp 519–560.

**Griffault L, Gascoyne M, Kamineni C, Kerrich R, Vandergraaf T, 1993.** Actinide and rare earth element characteristics of deep fracture zones in the Lac du Bonnet granitic batholith, Manitoba, Canada. *Geochim. Cosmochim. Acta.*, 57, pp 1181–1202.

**Gustafsson E, Nordqvist R, 2005.** Oskarshamn site investigation: Groundwater flow measurements and SWIW tests in boreholes KLX02 and KSH02. SKB P-05-28, Svensk Kärnbränslehantering AB.

**Gustafsson E, Nordqvist R, Thur P, 2005.** Forsmark site investigation: Groundwater flow measurements in boreholes KFM01A, KFM02A, KFM03A, KFM03B and SWIW tests in KFM02A, KFM03A. SKB P-05-77, Svensk Kärnbränslehantering AB.

**Hachiya K, Sasaki M, Ikeda T, Mikami N, Yasunaga T, 1984.** Static and Kinetic studies of adsorption-desorption of metal ions on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. 2. Kinetic study by means of pressure jump technique. *J. Phys. Chem.*, 88, pp 27–31.

**Hammit J, Shlyakhter A, 1999.** The expected value of information and the probability of surprise. *Risk Analysis*, 19(1), pp 135–152.

**Hayes K, Leckie J, 1986.** Mechanism of lead ion adsorption at the goethite-water interface. *ACS Symp. Ser.*, 323, pp 114–141.

- Hayes K, Leckie J, 1987.** Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. *J. Colloid Interface Sci.*, 115(2), pp 564–572.
- Hedin A, 2002.** Safety Assessment of a Spent Nuclear Fuel Repository: Sensitivity Analyses for Prioritisation of Research. Proceedings of the 6th International Conference on Probabilistic Safety Assessment and Management, PSAM6. Elsevier Science Ltd. (2002).
- Hedin A, 2003.** Probabilistic dose calculations and sensitivity analyses using analytic models. *Reliability Engineering and System Safety*, 79 (2003), pp 195–204.
- Hennig C, Reich T, Dähn R, Scheidegger A, 2002.** Structure of uranium sorption complexes at montmorillonite edge sites. *Radiochimica Acta*, 90(9–11), pp 653–657.
- Hoaglin D, Iglewicz B, Tukey J, 1986.** Performance of some resistant rules for outlier labeling. *Journal of the American Statistical Association*, 81, pp 991–999.
- Hora S, 2002.** Expert Opinion in SR 97 and the SKI/SSI Joint Review of SR 97. SSI report 2002:20, Swedish Radiation Protection Authority.
- Hora S, Jensen M, 2002.** Expert Judgement Elicitation. SSI report 2002:19, Swedish Radiation Protection Authority. SR-CAN process report.
- [25] Hsu C-N, Wei Y-Y, Chuang J-T, Tseng C-L, Yang J-Y, Ke C-H, Cheng H-P, Teng S-P, 2002.** Sorption of several safety relevant radionuclides on granite and diorite – a potential repository host rock in the Taiwan area. *Radiochimica Acta*, 90, pp 659–664.
- [26] Huittinen T, Hakanen M, Lindberg A, 1996.** Sorption of cesium, radium, protactinium, uranium, neptunium and plutonium on rapakivi granite. POSIVA 96-23, Posiva OY.
- [27] Huittinen T, Hakanen M, Lindberg A, 1998.** Sorption of cesium on Olkiluoto mica gneiss, granodiorite and granite. POSIVA 98-11, Posiva OY.
- Hummel W, Berner U, Curti E, Pearson F, Thoenen F, 2002.** Nagra/PSI chemical thermodynamic data base 01/01. *Radiochimica Acta*, 90, pp 805–813.
- Hummel W, Curti E, 2003.** Nickel aqueous speciation and solubility at ambient conditions: A thermodynamic elegy. *Monatshefte für Chemie (Chemical Monthly)*, 134, pp 941–973.
- Håkansson R, 2000.** Beräkning av nuklidinnehåll, resteffekt, aktivitet samt doshastighet för utbränt kärnbränsle. SKB R-99-74, Svensk Kärnbränslehantering AB.
- [28] Hölta P, Siitari-Kauppi M, Huikuri P, Lindberg A, Hautajärvi A, 1997.** The effect of specific surface area on radionuclide sorption on crushed crystalline rock. *Mat. Res. Soc. Symp. Proc.*, 465, pp 789–796.
- IAEA, 2005.** IAEA Database of Natural Matrix Reference Materials. International Atomic Energy Agency, URL: <http://www-naweb.iaea.org/nahu/nmrm/default.shtm>
- [69] Ikeda T, Amaya T, 1986.** Distribution Coefficients of Americium, Neptunium and Protoactinium for Selected Rocks. *The Memoirs of the Faculty of Engineering, Kyoto University*, 48(3), pp 275–283.
- (Note: Secondary reference – data obtained from JNC Sorption Database)**
- [29] Ittner T, Torstenfelt B, Allard B, 1988.** Migration of the fission products strontium, technetium, iodine, cesium and the actinides neptunium, plutonium, americium in granitic rock. SKB TR-88-02, Svensk Kärnbränslehantering AB.
- Janeczek J, Ewing R, Oversby V, Werme L, 1996.** Uraninite and UO<sub>2</sub> in spent nuclear fuel: a comparison. *J. Nucl. Mater.*, 238, pp 121–130.
- Jeon B-H, Dempsey B, Burgos W, Royer R, 2003.** Sorption kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II), and Fe(II)/Me(II) onto hematite. *Water Research*, 37, pp 4135–4142.

- Jeon B-H, Dempsey B, Burgos W, Royer R, 2004.** Modeling the sorption kinetics of divalent metal ions to hematite. *Water Research*, 38, pp 2499–2504.
- Jenne E A (ed), 1998.** Adsorption of Metals by Geomedia. Variables, Mechanisms, and Model Applications, Academic Press, New York.
- Johansson H, Siitari-Kauppi M, Skålberg M, Tullborg E-L, 1998.** Diffusion pathways in crystalline rock – examples from Äspö-diorite and fine-grained granite. *J. Contam. Hydrol.*, 35(1–3), pp 41–53.
- Johannesson K, Stetzenbach K, Hodge V, Lyons W, 1996.** Rare earth element complexation behavior in circumneutral pH groundwaters: Assessing the role of carbonate and phosphate ions. *Earth. Planet. Sci. Lett.*, 139(1–2), pp 305–319.
- Kaminni D, Lemire R, 1991.** Thorite in fault zones of a granitic pluton, Atikokan, Canada: Implications for nuclear fuel waste disposal. *Chemical Geology*, 90, pp 133–143.
- Kaszuba J, Runde W, 1999.** The aqueous geochemistry of neptunium: Dynamic control of soluble concentrations with applications to nuclear waste disposal. *Environ. Sci. Technol.*, 33(24), pp 4427–4433.
- [65] Kaukonen V, Hakanen M, Lindberg A, 1993.** Sorption of Cs, U, Np and Pu and diffusion of water, Cs and Np in basic plutonic rocks and vulcanite. Report YJT-93-13, Nuclear Waste Commission of Finnish Power Companies.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- [76] Kaukonen V, Hakanen M, Lindberg A, 1997.** Diffusion and sorption of Hto, Np, Na, and Cl in rocks and minerals of Kivetty and Olkiluoto, Posiva-97-07, Posiva OY.
- King P, Michel J, Moore W, 1982.** Ground water geochemistry of <sup>228</sup>Ra, <sup>226</sup>Ra and <sup>222</sup>Rn. *Geochim. Cosmochim. Acta.*, 46, pp 1173–1182.
- Kohler M, Honeyman B, Leckie J, 1999.** Neptunium(V) sorption on hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) in aqueous suspension: the effect of CO<sub>2</sub>. *Radiochimica Acta*, 85(1–2), pp 33–48.
- Koretsky C, Sverjensky D, Salisbury J, d’Aria D, 1997.** Detection of surface hydroxyl species on quartz,  $\gamma$ -alumina, and feldspars using diffuse reflectance infrared spectroscopy. *Geochim. et Cosmochim. Acta*, 61(11), pp 2193–2210.
- [32] Koskinen A, Alaluusa M, Pinnioja S, Jaakola T, Lindberg A, 1985.** Sorption of iodine, neptunium, technetium, thorium and uranium on rocks and minerals. Report YJT-85-36, Nuclear Waste Commission of Finnish Power Companies.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Krauskopf K, 1986.** Thorium and rare-earth metals as analogs for actinide elements. *Chemical Geology*, 55, pp 323–335.
- Krishnaswami S, Bhushan R, Baskaran M, 1991.** Radium isotopes and <sup>222</sup>Rn in shallow brines, Kharaghoda (India). *Chemical Geology (Isotope Geoscience Section)*, 87, pp 125–136.
- [33] Kulmala S, Hakanen M, 1993.** The Solubility of Zr, Nb and Ni in Groundwater and Concrete Water, and Sorption on Crushed Rock and Cement. Report YJT-93-21, Nuclear Waste Commission of Finnish Power Companies.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- [34] Kulmala S, Hakanen M, 1995.** Sorption of alkaline-earth elements Sr, Ba, and Ra from groundwater on rocks from TVO investigation areas. Report YJT-95-03, Nuclear Waste Commission of Finnish Power Companies.
- Laaksoharju M, 1999.** Groundwater characterisation and modelling: problems, facts and possibilities. SKB TR-99-42, Svensk Kärnbränslehantering AB.

- Laaksoharju M, Tullborg E-L, Wikberg P, Wallin B, Smellie J, 1999a.** Hydrogeochemical conditions and evolution at the Äspö HRL, Sweden. *Applied Geochemistry*, 14, pp 835–859.
- Laaksoharju M, Skårman C, Skårman E, 1999b.** Multivariate mixing and mass balance (M3) calculations, a new tool for decoding hydrogeochemical information. *Applied Geochemistry*, 14, pp 861–871.
- Laaksoharju M, Gimeno M, Auqué L, Gómez J, Smellie J, Tullborg E-L, Gurban I, 2004a.** Hydrogeochemical evaluation of the Forsmark site, model version 1.1. SKB R-04-05, Svensk Kärnbränslehantering AB.
- Laaksoharju M, Smellie J, Gimeno M, Auqué L, Gómez J, Tullborg E-L, Gurban I, 2004b.** Hydrogeochemical evaluation of the Simpevarp area, model version 1.1. SKB R-04-16, Svensk Kärnbränslehantering AB.
- La Flamme B, Murray J, 1987.** Solid/solution interaction: The effect of carbonate alkalinity on adsorbed thorium. *Geochim. Cosmochim. Acta.*, 51, pp 243–250.
- Lake L, Srinivasan S, 2004.** Statistical scale-up of reservoir properties: concepts and applications. *Journal of Petroleum Science & Engineering*, 44, pp 27–39.
- Langmuir D, 1997.** *Aqueous Environmental Geochemistry*, Prentice Hall, New Jersey.
- Langmuir D, Herman J, 1980.** The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta.*, 44, pp 1753–1766.
- Langmuir D, Melchior D, 1985.** The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Palo Duro Basin, Texas. *Geochim. Cosmochim. Acta.*, 49, pp 2423–2432.
- [35] Laske D, 1980.** (Undocumented data for Cs sorption on granite)  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Leroy J, Turpin L, 1988.** REE, Th and U behaviour during hydrothermal and supergene processes in a granitic environment. *Chemical Geology*, 68(3–4), pp 239–251.
- Liger E, Charlet L, Van Cappellen P, 1999.** Surface catalysis of uranium(VI) reduction by iron(II). *Geochim. Cosmochim. Acta*, 63(19/20), pp 2939–2955.
- Lin C-F, Chang K-S, Tsay C-W, Lee D-Y, Lo S-L, Yasunaga T, 1997.** Adsorption mechanism of Gallium(III) and Indium(III) onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. *J. Colloid Interface Sci.*, 188, pp 201–208.
- Lindgren M, Lindström F, 1999.** SR-97 Radionuclide transport calculations. SKB TR-99-23, Svensk Kärnbränslehantering AB.
- Liu L, Neretnieks I, 2001.** A coupled model for oxidative dissolution of spent fuel and transport of radionuclides from an initially defective canister, *Radioactive Waste Management and Disposal*, 135, pp 273–284.
- Liu C, Zachara J, Smith S, Mckinley J, Ainsworth C, 2003.** Desorption kinetics of radiocesium from subsurface sediments at Hanford site, USA. *Geochim. Cosmochim. Acta*, 67(16), pp 2893–2912.
- Liu C, Zachara J, Qafoku O, Mckinley J, Heald S, Wang Z, 2004.** Dissolution of uranyl microprecipitates in subsurface sediments at Hanford Site, USA. *Geochim. Cosmochim. Acta*, 68(22), pp 4519–4537.
- Liu J, Löfgren M, Neretnieks I, 2006 (report in prep.).** SR-Can data and uncertainty assessment: Matrix diffusivity and porosity in-situ. SKB TR-xx-yy, Svensk Kärnbränslehantering AB.
- Löfgren M, 2004.** Diffusive properties of granitic rock as measured by in-situ electrical methods, Ph.D. Thesis, Department of Chemical Engineering and Technology, Royal Inst. of Technology, Stockholm.

- Lützenkirchen J, 1997.** Ionic strength effects on cation sorption to oxides: Macroscopic observations and their significance in microscopic interpretation. *J. Colloid Interface Sci.*, 195, pp 149–155.
- Lützenkirchen J, 2001.** Evaluation of experimental procedures and discussion of two different modelling approaches with respect to long-term kinetics of metal cation sorption onto (hydr)oxide surfaces. *Aquatic Geochemistry*, 7, pp. 217–235.
- Machesky M, Wesolowski D, Palmer D, Ridley M, 2001.** On the temperature dependence of intrinsic surface protonation and equilibrium constants: an extension of the revised MUSIC model. *J. Colloid Interface Sci.*, 239(2), pp 314–327.
- [36] Maclean S, Coles D, Weed H, 1978.** The Measurement of Sorption Ratios for Selected Radionuclides on Various Geologic Media. UCID-17928, Lawrence Livermore Lab., Univ. California, Livermore, CA, USA.
- (Note: Secondary reference – data obtained from JNC Sorption Database)**
- Malmström M, Banwart S, Lewenhagen J, Duro L, Bruno J, 1996.** The dissolution of biotite and chlorite at 25°C in the near-neutral pH region. *J. Contam. Hydrol.*, 21, pp 201–213.
- Malmström M, Banwart S, 1997.** Biotite dissolution at 25°C: The pH dependence of dissolution rate and stoichiometry. *J. Contam. Hydrol.*, 61(14), pp 2779–2799.
- Maya L, 1984.** Carbonate complexation of dioxoneptunium(VI) at 25°C: Its effect on the Np(V)/Np(VI) potential. *Inorganic Chemistry*, 23(24), pp 3296–3930.
- McKinley I, Alexander W, 1993.** Assessment of radionuclide retardation: uses and abuses of natural analogue studies. *J. Contam. Hydrol.*, 13, pp 249–259.
- McKinley I, Scholtis A, 1993.** A comparison of radionuclide sorption databases used in recent safety assessments. *J. Contam. Hydrol.*, 13(1–4), pp 347–363.
- McKinley I, Savage D, 1996.** Comparison of solubility databases used for HLW safety assessment. *J. Contam. Hydrol.*, 21, pp 335–350.
- McKinley J, Zachara J, Heald S, Dohnalkova A, Newville M, Sutton S, 2004.** Microscale distribution of cesium sorbed to biotite and muscovite. *Environ. Sci. Technol.*, 38, pp 1017–1023.
- Mitra P, Pabitra N, Schwartz L, Le Doussal P, 1992.** Diffusion propagator as a probe of the structure of porous media. *Phys. Rev. Letters*, 68(24), pp 3555–3558.
- Mitra P, Pabitra N, Schwartz L, 1993.** Short-time behaviour of the diffusion coefficient as a numerical probe of porous media. *Phys. Rev. B*, 47(14), pp 8565–8574.
- Mitra P, 1997.** Diffusion in porous materials as probed by pulsed field gradient NMR measurements. *Physica A*, 241, pp 122–127.
- Morel F M M, Hering J G, 1993.** Principles and Applications of Aquatic Chemistry, Wiley, New York.
- Moulin C, Wei J, Iseghem P, Van Laszak I, Plancque G, Moulin V, 1999.** Europium complexes investigations in natural waters by time-resolved laser-induced fluorescence. *Anal. Chim. Acta*, 396(2–3), pp 253–261.
- [38] Murali M, Mathur J, 2002.** Sorption characteristics of Am(III), Sr(II) and Cs(I) on bentonite and granite. *J. Radioanal. Nucl. Chem.*, 254(1), pp 129–136.
- Murphy R, Lenhart J, Honeyman B, 1999.** The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. *Colloids Surf., A.*, 157, pp 47–62.

- Nakata K, Nagasaki S, Tanaka S, Sakamoto Y, Tanaka T, Ogawa H, 2000.** Sorption and desorption kinetics of Np(V) on magnetite and hematite. *Radiochim. Acta*, 88, pps 453–457.
- Nakata K, Nagasaki S, Tanaka S, Sakamoto Y, Tanaka T, Ogawa H, 2002.** Sorption and reduction of neptunium(V) on the surface of iron oxides. *Radiochim. Acta*. 90, pp 665–669.
- [70] Nakayama S, Moriyama H, Arimoto H, Higashi K, 1986.** Distribution Coefficients of Americium, Neptunium and Protoactinium for Selected Rocks. *The Memoirs of the Faculty of Engineering, Kyoto University*, 48(3), pp 275–283.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Nash K, Cleveland J, Rees T, 1988.** Speciation patterns of actinides in natural waters: a laboratory investigation. *J. Environ. Radioact.*, 7, pp 131–157.
- NEA, 2001.** Using thermodynamic sorption models for guiding radioelement distribution coefficient ( $K_d$ ) investigations. OECD-NEA.
- NEA, 2005.** NEA Sorption Project Phase II. Interpretation and prediction of radionuclide sorption onto substrates relevant for radioactive disposal using thermodynamic sorption models, OECD-NEA.
- Neretnieks I, 2002.** A Stochastic multi-channel model for solute transport – analysis of tracer tests in fractured rock. *J. Contam. Hydrol.*, 55(2002), pp 175–211.
- [40] Nikura** (Undocumented data for Cs sorption on granite)  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Nordstrom D, Ball J, Donahoe R, Whittemore D, 1989.** Groundwater chemistry and water-rock interactions at Stripa. *Geochim. Cosmochim. Acta.*, 53(1), pp 1727–1740.
- Nordstrom D, McNutt R, Puigdomènech I, Smellie J, Wolf M, 1992.** Ground water chemistry and geochemical modeling of water-rock interactions at the Osamu Utsumi mine and the Morro do Ferro analogue study sites, Poços de Caldas, Minas Gerais, Brazil. *J. Geochem. Explor.*, 45, pp 249–287
- Ochs M, Talerico C, 2004.** SR-Can data and uncertainty assessment. Migration parameters for the bentonite buffer in the KBS-3 Concept. SKB TR-04-18, Svensk Kärnbränslehantering AB.
- [41] Ohe** (Undocumented data for Cs sorption on granite)  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Ohlsson Y, Neretnieks I, 1998.** Some evidence for surface ion mobility in rock. *J. Contam. Hydrol.*, 35, pp 91–100.
- Ohlsson Y, 2000.** Studies of ionic diffusion in crystalline rock, Ph.D. Thesis, Department of Chemical Engineering and Technology, Royal Institute of Technology, Stockholm.
- Pabalan R, Turner D, Bertetti F, Prikryl J, 1998.** Uranium(VI) Sorption onto Selected Mineral Surfaces – Key Geochemical Parameters. In: Jenne, ed., *Adsorption of Metals by Geomedia – Variables, Mechanisms, and Model Applications*, Academic Press, New York, pp 100–128.
- Papelis C, Roberts P, Leckie J, 1995.** Modeling the rate of cadmium and selenite adsorption on micro- and mesoporous transition aluminas. *Environ. Sci. Technol.*, 29, pp 1099–1108.
- [42] Papelis C, 2001.** Cation and anion sorption on granite from the project Shoal test area, near Fallon, Nevada. *Advances in Environmental Research*, 5, pp 151–166.
- Payne T, Edis R, Fenton B, Waite T, 2001.** Comparison of laboratory uranium sorption data with “in situ distribution coefficients” at the Koongarra uranium deposit, Northern Australia. *J. Environ. Radioact.*, 57, pp 35–55.



**Peak D, Ford R, Sparks D, 1999.** An in situ ATR-FTIR investigation of sulfate bonding mechanisms on goethite. *J. Colloid Interface Sci.*, 218(1), pp 289–299.

**Pearcy E, Prikryl J, Murphy W, Leslie B, 1994.** Alteration of uraninite from the Nopal I deposit, Peña Blanca District, Chihuahua, Mexico, compared to degradation of spent nuclear fuel in the proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada. *Applied Geochemistry*, 9, pp 713–732.

[43] **Pinioja S, 1983.** (Undocumented data for Cs sorption on granite)  
(Note: Secondary reference – data obtained from JNC Sorption Database)

[71] **Pinnioja T, Jaakkola T, Miettinen J, 1984.** Comparison of batch and autoradiographic methods in sorption studies of radionuclides in rock and mineral samples. Report YJT-87-17, Nuclear Waste Commission of Finnish Power Companies.

(Note: Secondary reference – data obtained from JNC Sorption Database)

**Press F, Siever R, 1998.** *Understanding Earth*, 2 ed., W.H. Freeman and Company, New York.

**Prikryl J, Jain A, Turner D, Pabalan R, 2001.** Uranium(VI) sorption behaviour on silicate mineral mixtures, *J. Contam. Hydrol.*, 47(2001), pp 241–253.

**Porcelli D, Swarzenski P, 2003.** The behavior of U- and Th-series nuclides in groundwater. *Reviews in Mineralogy and Geochemistry*, 52(1), pp 317–361.

**Rai D, Hess N, Felmy A, Moore D, Yui M, 1999.** A thermodynamic model for the solubility of  $\text{NpO}_2(\text{am})$  in the aqueous  $\text{K}^+ - \text{HCO}_3^- - \text{CO}_3^{2-} - \text{OH}^- - \text{H}_2\text{O}$  system. *Radiochimica Acta*, 84(3), pp 159–169.

**Read D, Ross D, Sims R, 1998.** The migration of uranium through Clashach sandstone: the role of low molecular weight organics in enhancing radionuclide transport. *J. Contam. Hydrol.*, 35(1–3), pp 235–248.

**Reiller P, Moulin V, Casanova F, Dautel C, 2002.** Retention behaviour of humic substances onto mineral surfaces and consequences upon thorium (IV) mobility: case of iron oxides. *Applied Geochemistry*, 17, pp 1551–1562.

[44] **Relyea J, Ames L, Serne R, Fulton R, Washburne C, 1978.** Batch  $K_d$  Determinations with Common Minerals and Representative Groundwaters. In: WISAP Task 4, Second Contractor Meeting Proceedings, PNL Report PNL-SA-7352.

(Note: Secondary reference – data obtained from JNC Sorption Database)

**Sahai N, 2000.** Estimating adsorption enthalpies and affinity sequences of monovalent electrolyte ions on oxide surfaces in aqueous solution. *Geochim. Cosmochim. Acta.*, 64(1), pp 3629–3641.

**Sani R, Peyton B, Amonette J, Geesey G, 2004.** Reduction of uranium(VI) under sulfate-reducing conditions in the presence of Fe(III)-(hydr)oxides. *Geochim. Cosmochim. Acta.*, 68(12), pp 2639–2648.

**Scheckel K, Sparks D, 2001.** Temperature Effects on Nickel Sorption Kinetics at the Mineral–Water Interface. *Soil Sci. Soc. Am. J.*, 65, pp 719–728.

**Scheideger A, Lamble G, Sparks D, 1996.** Investigation of Ni sorption on pyrophyllite: An XAFS study. *Environ. Sci. Technol.*, 30, pp 548–554.

**Scheideger A, Sparks D, 1996.** Kinetics of the formation and the dissolution of nickel surface precipitates on pyrophyllite. *Chemical Geology*, 132, pp 157–164.

**Scheideger A, Strawn D, Lamble G, Sparks D, 1998.** The kinetics of mixed Ni-Al hydroxide formation on clay and aluminium oxide minerals: A time-resolved XAFS study. *Geochim. et Cosmochim. Acta*, 62(13), pp 2233–2245.

- Shibutani T, Suyama T, Shibata M, 1999.** Sorption database for radionuclides on bentonite and rocks. JNC Technical Report (in Japanese with English abstract) TN8410 99-050, Japan Nuclear Cycle Development Institute.
- Shoesmith D, 2000.** Fuel corrosion processes under waste disposal conditions. *J. Nucl. Mater.*, 282, pp 1–31.
- [47] Siitari-Kauppi M, Hölttä P, Pinnioja S, Lindberg A, 1999.** Cesium sorption on tonalite and mica gneiss. *Mat. Res. Soc. Symp. Proc.*, 556, pp 1099–1106.
- Skagius K, Neretnieks I, 1982.** Diffusion in crystalline rocks of some sorbing and non-sorbing species. SKBF/KBS Technical Report 82-12, Svensk Kärnbränslehantering AB.
- [49] Skagius K, Svedberg G, Neretnieks I, 1982.** A study of strontium and cesium sorption on granite, *Nuclear Technology*, 59, pp 302–313.
- Skagius K, 1986.** Diffusion of dissolved species in the matrix of some Swedish crystalline rocks. PhD Thesis, Department of Chemical Engineering and Technology, Royal Institute of Technology, Stockholm.
- Skagius K, Neretnieks I, 1988.** Measurements of cesium and strontium diffusion in biotite gneiss. *Water Resour. Res.*, 24, pp 75–84.
- SKB, 2002.** Preliminary Safety Evaluation, Based on Initial Site Investigation Data, Planning Document. SKB TR-02-28, Svensk Kärnbränslehantering AB.
- SKB, 2004a,** Interim process report for the safety assessment SR-Can. SKB R-04-33, Svensk Kärnbränslehantering AB.
- SKB, 2004b,** Preliminary Site Description of the Forsmark area (version 1.1). SKB R-04-15, Svensk Kärnbränslehantering AB.
- SKB, 2004c.** RETROCK Project: Treatment of geosphere retention phenomena in Safety Assessments – Scientific basis of retention processes and their implementation in Safety Assessment models (WP2). SKB R-04-48, Svensk Kärnbränslehantering AB.
- SKI and SSI, 2001.** SKI's and SSI's Joint Review of SKB's Safety Assessment Report, SR 97. Summary, SKI Report 01:3, Swedish Nuclear Power Inspectorate; SSI Report 2001:02, Swedish Radiation Protection Authority.
- Smellie J, Mackenzie A, Scott R, 1986.** An analogue study of natural radionuclide migration in crystalline rocks using uranium series disequilibrium studies. *Chemical Geology*, 55(3–4), pp 233–254.
- Smellie J, Karlsson F, 1999.** The use of natural analogues to assess radionuclide transport. *Engineering Geology*, 52(3–4), pp 193–220.
- Spahiu K, Bruno J, 1995.** A Selected Thermodynamic Database for REE to be used in HLNW Safety assessment Exercises. SKB TR-95-35, Svensk Kärnbränslehantering AB.
- Sparks D, 2000.** New frontiers in elucidating the kinetics and mechanisms of metal and oxyanion sorption at the soil mineral/water interface. *J. Plant Nutr. Soil Sci.*, 163, pp 563–570.
- Stallmach F, Vogt C, Kärger J, Helbig K, Jacobs F, 2002.** Fractal Geometry of Surface Areas of Sand Grains Probed by Pulsed Field Gradient NMR. *Phys. Rev. Letters*, 88(105505), pp 1–4.
- Stallmach F, Kärger J, 2003.** Stallmach and Kärger reply to: Using NMR to measure Fractal Dimensions. *Phys. Rev. Letters*, 90(039601), pp 1.
- Steeffel C, Carroll S, Zhao P, Roberts S, 2003.** Cesium migration in Hanford sediment: a multisite cation exchange model based on laboratory transport experiments. *J. Contam. Hydrol.*, 67, pp 219–246.

- Stenhouse M, 1995.** Sorption databases for crystalline, marl and bentonite for safety assessment. Nagra Technical Report NTB-93-06, National Cooperative for the Disposal of Radioactive Waste (NAGRA), Switzerland.
- Strawn D, Sparks D, 1999.** The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite. *J. Colloid Interface Sci.*, 216(2), pp 257–269.
- Stumm W, Morgan J, 1996.** *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3 ed., Wiley, New York.
- Stumpf T, Bauer A, Coppin F, Kim J, 2001.** Time-resolved laser fluorescence spectroscopy study of the sorption of Cm(III) onto smectite and kaolinite. *Environ. Sci. Technol.*, 35(18), pp 3691–3694.
- Stumpf T, Bauer A, Coppin F, Fanghänel T, Kim J, 2002.** Inner-sphere, outer-sphere, and ternary surface complexes: a TRLFS study of the sorption process of Eu(III) onto smectite and kaolinite. *Radiochimica Acta.*, 90(6), pp 345–349.
- Stumpf T, Fanghänel T, 2002.** A time-resolved laser fluorescence spectroscopy (TRLFS) study of the interaction of the interaction of trivalent actinides (Cm(III)) with calcite. *J. Colloid Interface Sci.*, 249(1), pp 119–122.
- Sturchio N, Banner J, Binz C, Heraty L, Musgrove M, 2001.** Radium geochemistry of ground waters in Paleozoic carbonate aquifers, midcontinent, USA. *Applied Geochemistry*, 16(1), pp 109–122.
- [50] Suksi S, Siitari-Kauppi M, Hölttä P, Jaakola T, Lindberg A, 1989.** Sorption and diffusion of radionuclides (C, Tc, U, Pu, Np) in rock samples under oxic and anoxic conditions. YJT Report YJT-89-13, Nuclear Waste Commission of Finnish Power Companies.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Sylwester E R, Hudson E A, Allen P G, 2000.** The structure of uranium(VI) sorption complexes on silica, alumina, and montmorillonite. *Geochim. Cosmochim. Acta*, 64(14), pp 2431–2438.
- [74] Tachi Y, Shibutani T, Yoshikawa H, 1999.** Sorption Behavior of Neptunium on Rocks under Reducing Conditions. JNC Technical Report  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- [53] Tewehy J, Weed H, Coles D, Ramspott L, Maclean S, 1978.** Studies of radionuclide availability and migration at the Nevada Test Site relevant to radioactive waste disposal. In: WISAP Task 4, 2nd Contractor Information Meeting Proceedings, PNL Report PNL-SA-7352, Pacific Northwest Laboratory, Washington.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- [54] Ticknor K, 1994.** Sorption of nickel on geological materials. *Radiochimica Acta*, 66/67, pp 341–348.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Tipping E, 1996.** Hydrochemical modelling of the retention and transport of metallic radionuclides in the soils of an upland catchment. *Environmental Pollution*, 94(2), pp 105–116.
- [55] Torstenfelt B, Andersson K, Allard B, 1982a.** Sorption of strontium and cesium on rocks and minerals. *Chemical Geology*, 36, pp 123–137.
- [58] Torstenfelt B, Ittner T, Allard B, Andersson K, Olofsson U, 1982b.** Mobilities of radionuclides in fresh and fractured crystalline rock. SKB TR-82-26, Svensk Kärnbränslehantering AB.

- Torstenfelt B, Eliasson T, Allard B, Andersson K, Höglund S, Ittner T, 1983a.** Radionuclide migration into natural fracture surfaces of granitic rock. In: D.G. Brookins ed., *Scientific Basis for Nuclear Waste Management – VI*, Elsevier, New York.
- Torstenfelt B, Allard B, Johansson W, Ittner T, 1983b.** Iron content and reducing capacity of granites and bentonite. SKB TR-83-36, Svensk Kärnbränslehantering AB.
- [59] Torstenfelt B, Rundberg R, Mitchell A, 1988.** Actinide Sorption on Granites and Minerals as a Function of pH and Colloids/ Pseudocolloids, *Radiochimica Acta*, 44/45, pp 111–117.  
(Note: Secondary reference – data obtained from JNC Sorption Database)
- Trivedi P, Axe L, 2000.** Modeling Cd and Zn sorption to hydrous metal oxides. *Environ. Sci. Technol.*, 34, pp 2215–2223.
- Trivedi P, Axe L, 2001a.** Predicting divalent metal sorption to hydrous Al, Fe, and Mn oxides. *Environ. Sci. Technol.*, 35, pp 1779–1784.
- Trivedi P, Axe L, 2001b.** Ni and Zn sorption to amorphous versus crystalline iron oxides: macroscopic studies. *Environ. Sci. Technol.*, 35, pp 1779–1784.
- Trotignon L, Beaucaire C, Louvat D, Aranyossi J-F, 1999.** Equilibrium geochemical modeling of Äspö groundwaters: a sensitivity study of thermodynamic equilibrium constant. *Applied Geochemistry*, 14, pp 907–916.
- Turner D, Pabalan R, Prikryl J, Bertetti F, 1999.** Radionuclide sorption at Yucca Mountain, Nevada – A demonstration of an alternative approach for safety assessment. *Mat. Res. Soc. Symp. Proc.*, 556(1999), pp 583–590.
- Turner D, Pabalan R, 1999.** Abstraction of mechanistic sorption model results for safety assessment calculations at Yucca Mountain, Nevada. *Waste Management*, 19(1999), pp 375–388.
- US EPA, 1999.** Understanding variation in partition coefficient,  $K_d$ , values. Volume II: Review of geochemistry and available  $K_d$  values for cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium ( $^3\text{H}$ ), and uranium, Office of Air and Radiation, EPA 402-R-99-004B, United States Environmental Protection Agency (EPA).
- Vandergraaf T, Ticknor K, Melnyk T, 1993.** The selection of a sorption data base for the geosphere model in the Canadian nuclear fuel waste management program. *J. Contam. Hydrol.*, 13(1993), pp 327–345.
- Villalobos M, Leckie J, 2001.** Surface complexation modeling and FTIR study of carbonate adsorption to goethite. *J. Colloid Interface Sci.*, 235(1), pp 15–32.
- Viswanathan H, Robinson B, Valocchi A, Triay I, 1998.** A reactive transport model of neptunium migration from the potential repository at Yucca Mountain. *Journal of Hydrology*, 209(1–4), pp 251–280.
- Waite T, Davis J, Payne T, Waychunas G, Xu N, 1994.** Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochim. Cosmochim. Acta.*, 58(24), pp 5465–5478.
- Waychunas G, Fuller C, Davis J, 2002.** Surface complexation and precipitate geometry for aqueous Zn(II) sorption on ferrihydrite I: X-ray absorption extended fine structure spectroscopy analysis. *Geochim. Cosmochim. Acta*, 66(7), pp 1119–1137.
- Waychunas G, Fuller C, Davis J, Rehr J, 2003.** Surface complexation and precipitate geometry for aqueous Zn(II) sorption on ferrihydrite: II. XANES analysis and simulation. *Geochim. Cosmochim. Acta*, 67(5), pp 1031–1043.

- Weber W, McGinley P, Katz L, 1991.** Sorption phenomena in subsurface systems: concepts, models and effects on contaminant transport. *Water Resour. Res.*, 25(5), pp 499–528.
- Wehrli B, Sulzberger B, Stumm W, 1989.** Redox processes catalyzed by hydrous oxide surfaces. *Chemical Geology*, 78, pp 167–179.
- Wehrli B, Ibric S, Stumm W, 1990.** Adsorption kinetics of vanadyl(IV) and chromium(III) to aluminium oxide: evidence for a two-step mechanism. *Colloids Surf.*, 51, pp 77–88.
- Wersin P, Hochella M, Persson P, Redden G, Leckie J, Harris D, 1994.** Interaction between aqueous uranium(VI) and sulfide minerals: Spectroscopic evidence for sorption and reduction. *Geochim. Cosmochim. Acta.*, 58(13), pp 2829–2843.
- [60] Wernli B, Bajo C, Bischoff K, 1985.** Determination of the sorption coefficients of uranium(VI) in Grimsel and Boettstein granite (Report written in German: “Bestimmung des Sorptionskoeffizienten von Uran(VI) an Grimsel- und Böttsteingranit”), EIR-543, Swiss Federal Institute of Reactor Research, Wuerenlingen, Switzerland.
- (Note: Secondary reference – data obtained from JNC Sorption Database)**
- Westall J, 1995.** Modeling of the speciation of metal ions with heterogeneous environmental sorbents. *Mat. Res. Soc. Symp. Proc.*, 353, pp 937–950.
- White C, Wilkinson S, Gadd G, 1995.** The role of microorganisms in biosorption of toxic metals and radionuclides. *Int. Biodeterior. Biodegrad.*, 35(1–3), pp 17–40.
- Widestrand H, Byegård J, Ohlsson Y, Tullborg E-L, 2003.** Strategy for the use of laboratory methods in the site investigations programme for the transport properties of the rock. SKB R-03-20, Svensk Kärnbränslehantering AB.
- Wilmot R, Galson D, 2000.** Expert Judgement in Safety assessment. SKI report 2000:04, Swedish Nuclear Power Inspectorate.
- Wilmot R, Galson D, Hora S, 2000.** Expert Judgements in Safety assessments. Report of an SKI/SSI Seminar. SKI report 2000:35, Swedish Nuclear Power Inspectorate.
- Wood S, 1990.** The aqueous geochemistry of the rare-earth elements and yttrium: 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chemical Geology*, 82, pp 159–186.
- Wu C-H, Lin C-F, Lo S-L, Yasunaga T, 1998.** Adsorption/desorption kinetics of  $\text{MoO}_4^{2-}$  onto  $\gamma\text{-Al}_2\text{O}_3$  by the pressure-jump technique. *J. Colloid Interface Sci.*, 208, pp 430–438.
- Wu C-H, Lin C-F, Lo S-L, Yasunaga T, 1999.** A review paper on the kinetic study of the pressure jump technique. *Proc. Natl. Sci. Coun. ROC(A)*, 23(4), pp 466–478.
- Yamaguchi T, Nakayama S, 1998.** Diffusivity of U, Pu and Am carbonate complexes in a granite from Inada, Ibaraki, Japan studied by through diffusion. *J. Contam. Hydrol.*, 35(1–3), pp 55–65.
- Zachara J, Smith S, Liu C, McKinley J, Serne R, Gassma P, 2002.** Sorption of  $\text{Cs}^+$  to micaceous subsurface sediments from the Hanford site, USA. *Geochim. Cosmochim. Acta.*, 66(2), pp 193–211.
- Zukin J, Hammond D, Ku T-L, Elders W, 1987.** Uranium-thorium series radionuclides in brines and reservoir rocks from two deep geothermal boreholes in the Salton Sea Geothermal Field, southeastern California. *Geochim. Cosmochim. Acta.*, 51(10), pp 2719–2731.
- Östhols E, Bruno J, Grenthe I, 1994.** On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline  $\text{ThO}_2$  in  $\text{CO}_2\text{-H}_2\text{O}$  media. *Geochim. Cosmochim. Acta.*, 58(2), pp 613–623.

## Water classification of the Simpevarp area used as reference groundwaters in this investigation

Table A-1. Chemical composition of the groundwater types used in the diffusivity and sorption measurements for the Simpevarp and Laxemar sub areas and the Forsmark site /Byegård et al. 2005/. Concentrations are given in mg/l.

	Type I (HSH02 0–200 m) Fresh water	Type II (KFM02A 509–516 m) Groundwater with marine character	Type III (KSH01A 558–565 m) Present ground-water at repository level	Type IV (KLX02 1,383–1,392 m) Brine type water of very high salinity
Li <sup>+</sup>	0.016	0.051	0.58	4.85
Na <sup>+</sup>	127	2,120	3,230	7,450
K <sup>+</sup>	2.16	33.3	12.4	32.6
Rb <sup>+</sup>	(0.0252) <sup>A</sup>	0.0628	0.0424	0.178
Cs <sup>+</sup>	(0.00117) <sup>A</sup>	0.00179	0.00137	0.0186
NH <sub>4</sub> <sup>+</sup>	(0.0947) <sup>A</sup>	0.04	0.04	0.56
Mg <sup>2+</sup>	1.43	232	44.7	1.2
Ca <sup>2+</sup>	5.21	934	2,190	14,800
Sr <sup>2+</sup>	0.0695	7.95	32.3	253
Ba <sup>2+</sup>	(1.29) <sup>A</sup>	0.188	0.188	0.024
Fe <sup>2+</sup>	(0.364) <sup>C</sup>	1.20	0.686	3.45
Mn <sup>2+</sup>	0.02	2.12	0.46	1.11
F <sup>-</sup>	3.03	0.9	0.967	(1.6) <sup>D</sup>
Cl <sup>-</sup>	21.5	5,150	8,800	36,800
Br <sup>-</sup>	(0.2) <sup>B</sup>	22	71	509
SO <sub>4</sub> <sup>2-</sup>	8.56	510	221	1,210
Si <sub>(tot)</sub>	6.56	5.2	4.7	2.6
HCO <sub>3</sub> <sup>-</sup>	252	124	12	42
S <sup>2-</sup>	(0.01) <sup>B</sup>	0.05	0.05	0.05
pH	8.58	7.1	7.45	6.8
Approximate Ionic Strength	5.86×10 <sup>-3</sup>	1.88×10 <sup>-1</sup>	3.16×10 <sup>-1</sup>	1.44

A) No measurements available, data imported from KSH01 #5263.

B) Based on detection limit.

C) Based on the Fe-tot measurement.

D) No measurements available, data imported from KLX02 #2731.

## Appendix B

### Water compositions used for sorption experiments as reported in source literature references

Table B-1. Water compositions used for sorption experiments as reported in references. Concentrations are given in mg/l.

Name: Ref #	Aq293 [1],[2],[3]	Aq1105 [1],[2],[3]	Allard_SGW (See note below)	Bajo_SGW [7]	Baston_SSW [10],[11],[12]	Baston_EDW [10],[11],[12]	Baston_EDW2 [10],[11],[12]	Berry_SGW [14]
Li <sup>+</sup>								
Na <sup>+</sup>	42	288	65	930	9,900	29	11	3,449
K <sup>+</sup>	5	10	3.9	87	380	11	11	149
Rb <sup>+</sup>								
Cs <sup>+</sup>								
Mg <sup>2+</sup>	8	15	4.3	16	1,300	2.40	0.05	56
Ca <sup>2+</sup>	33	25	18	140	380	4.10	2.8	2,245
Sr <sup>+</sup>								
Ba <sup>2+</sup>								
Fe <sup>2+</sup>				0.02	0.20	0.20	0.003	
Mn <sup>2+</sup>								
F <sup>-</sup>	1	2		3	0.64	0.41	0.78	
Cl <sup>-</sup>	93	500	70	1,675	18,000	20	1.2	5,672
Br <sup>-</sup>								
SO <sub>4</sub> <sup>2-</sup>	7	12.5	9.6	248	2,100		0.55	125
Si <sub>(aq)</sub> <sup>+</sup>			12	10	4.70	6.20	14	
HCO <sub>3</sub> <sup>-</sup>	94	124	123	305	140	10	10	3,000
PO <sub>4</sub> <sup>2-</sup>								
pH	8.00	8.00	8.0 – 8.2	7.6	8.0 – 10.0	8.0 – 10.0	9.6	
Eh (mV)								
Ionic strength	5.4×10 <sup>-3</sup>	1.7×10 <sup>-2</sup>	4.85×10 <sup>-3</sup>	5.9×10 <sup>-2</sup>	6×10 <sup>-1</sup>	1.6×10 <sup>-3</sup>	7.4×10 <sup>-4</sup>	2.75×10 <sup>-1</sup>

Notes: References where Allard\_SGW synthetic groundwater has been used are: [5],[17],[21],[22],[32],[41],[43],[47],[49],[50],[55],[65],[67],[68]

**Table B-2. Water compositions used for sorption experiments as reported in references. Concentrations are given in mg/l.**

Name: Ref #	ÁG_SGW [15]	ÁFA_SGW [15]	Erdal_SGW2 [20]	Erdal_SGW3 [20]	SSW [25],[69]	LPVA2a [26]	LPVA2b [26]	Allard_pH 7 [27]	Allard_pH 8 [27]
Li <sup>+</sup>	1.3	0.75				0.14	0.04		
Na <sup>+</sup>	2,400	1,735	6	7.5	10,537	2,080	1,990	52	56
K <sup>+</sup>	10	12.7	2.9	4.8	380	29	26.8	3.9	3.9
Rb <sup>+</sup>	0.026	0.056							
Cs <sup>+</sup>	0.001	0.005				0.005	0.034		
Mg <sup>2+</sup>	50	85.6	1.5	2	1,272	239	230	4.3	4.3
Ca <sup>2+</sup>	2,540	1,310	9.3	9.6	398	785	760	18	18
Sr <sup>+</sup>	35	21.4			13.30	6	3.3		
Ba <sup>2+</sup>	0.14	0.08				< 0.5	< 0.8		
Fe <sup>2+</sup>				0.4		0.08	0.82		
Mn <sup>2+</sup>						3.1	2.4		
F <sup>-</sup>				0.3	1.40	1.1	1.1		
Cl <sup>-</sup>	8,350	5,400		2.3	18,951	5,060	4,800	41	55
Br <sup>-</sup>		22			65	17	17		
SO <sub>4</sub> <sup>2-</sup>	170	305		5.1	2,649	510	491	9.6	9.6
Si <sub>(tot)</sub>	16	20		7.9		9.4	9	6.4	12
HCO <sub>3</sub> <sup>-</sup>	17	57		55	139	51	58.1	123	123
PO <sub>4</sub> <sup>2-</sup>						< 0.01	< 0.01		
pH	7.5	7.5		8.0–8.2	7.7	7.5	7.74	7.0	8.0–8.2
Eh (mV)									
Ionic strength	3×10 <sup>-1</sup>	1.9×10 <sup>-1</sup>	≈ 1.2×10 <sup>-3</sup>	1.5×10 <sup>-3</sup>	6.2×10 <sup>-1</sup>	1.8×10 <sup>-1</sup>	1.7×10 <sup>-1</sup>	4×10 <sup>-3</sup>	4.4×10 <sup>-3</sup>



**Table B-3. Water compositions used for sorption experiments as reported in references. Concentrations are given in mg/l.**

Name: Ref #	OIso pH 7 [27]	OIso pH 9 [27]	OIBr [27]	OIBr 1:10 [27]	BT_Stu [29],[58]	BT_Str [29],[58]	BT_Fi6 [29],[58]	BT_Fi7 [29],[58]	BT_Fi8 [29],[58]
Li <sup>+</sup>									
Na <sup>+</sup>	4,800	9,500	10,000	1,000	90	49	959	274	320
K <sup>+</sup>	21	21	< 5	< 5	2.8	0.59	16	16.0	12
Rb <sup>+</sup>									
Cs <sup>+</sup>									
Mg <sup>2+</sup>	56	0.084	< 0.1	0.21	9	0.23	69	16	12
Ca <sup>2+</sup>	4,000	2.7	17,000	1,700	31	14	554	134	37
Sr <sup>+</sup>	35	0.044							
Ba <sup>2+</sup>									
Fe <sup>2+</sup>									
Mn <sup>2+</sup>									
F <sup>-</sup>	1.2	1.2					0.97	1.75	2.3
Cl <sup>-</sup>	14,600	14,600	46,000	4,600	57	35.00	2,407	477	387
Br <sup>-</sup>	105	105							
SO <sub>4</sub> <sup>2-</sup>	4.2	4.2			36	4.90	205	45	42
Si <sub>(tot)</sub>	2.5	3.2	7	0.7	11	5.50	17	13	12
HCO <sub>3</sub> <sup>-</sup>	10	102	1.8	0.18	195	86	123	280	263
PO <sub>4</sub> <sup>2-</sup>									
pH	7.2	9	7.1	6.4	7.3	8.9	7.7	8.1	8.3
Eh (mV)									
Ionic strength	5.2×10 <sup>-1</sup>	4.1×10 <sup>-1</sup>	1.73	1.7×10 <sup>-1</sup>	7.1×10 <sup>-3</sup>	3.1×10 <sup>-3</sup>	9×10 <sup>-2</sup>	2.3×10 <sup>-2</sup>	1.8×10 <sup>-2</sup>

**Table B-4. Water compositions used for sorption experiments as reported in references. Concentrations are given in mg/l.**

Name: Ref #	Kuimala_GW1 [33]	Kuimala_GW2 [33]	KI_KR4 [34]	OL_KR5 [34]	Laske_SGW [35]	Laske_S-PREP [35]	Maclean_SGW [36]	BW [38]
Li <sup>+</sup>								
Na <sup>+</sup>	2,420	190	18	3,330	85	850	6.7	1,400
K <sup>+</sup>	22	2	0.87	15	234	2,340	1.5	42
Rb <sup>+</sup>								
Cs <sup>+</sup>			< 0.005	0.008				
Mg <sup>2+</sup>	262	5	3	67	40	400	1.5	97
Ca <sup>2+</sup>	995	22	13	2,100	600	600	8.3	77
Sr <sup>+</sup>								
Ba <sup>2+</sup>								
Fe <sup>2+</sup>	0.24	0.07	0.52	0.23				
Mn <sup>2+</sup>			0.21	0.36				
F <sup>-</sup>	1	1						< 1
Cl <sup>-</sup>	5,260	185	3.2	9,200	40	400	2.1	1,000
Br <sup>-</sup>			0.03	58				
SO <sub>4</sub> <sup>2-</sup>	688	50	2	3.3	1,440	1,440	2.7	
Si <sub>(tot)</sub>	7	14					26.2	
HCO <sub>3</sub> <sup>-</sup>	12	223	58.2	4.2			47.7	
PO <sub>4</sub> <sup>2-</sup>								12
pH	7.25	8.4	8.2	7	6.2	6.2	7.7	8
Eh (mV)			-61	-157				
Ionic strength	2×10 <sup>-1</sup>	1.1×10 <sup>2</sup>	2×10 <sup>-3</sup>	3.1×10 <sup>-1</sup>	5.1×10 <sup>-2</sup>	1.2×10 <sup>-1</sup>	1.2×10 <sup>-3</sup>	5.7×10 <sup>-2</sup>

**Table B-5. Water compositions used for sorption experiments as reported in references. Concentrations are given in mg/l.**

Name:	N_GW_SITE1	N_GW_SITE2	HC4	Relyea 30 NaCl [44]	Relyea 30 NaHCO <sub>3</sub> [44]	Relyea 30 CaCl <sub>2</sub> [44]	Relyea 5130 NaCl [44]	Tewehy_GGW [53]
Ref #	[40]	[40]	[42]	[44]	[44]	[44]	[44]	[53]
Li <sup>+</sup>								
Na <sup>+</sup>	1,875	1,600	65	672	652	1.21×10 <sup>5</sup>	4	6.7
K <sup>+</sup>	32.4	33		14			9	1.5
Rb <sup>+</sup>								
Cs <sup>+</sup>								
Mg <sup>2+</sup>	285	156		0.05			1.4	1.5
Ca <sup>2+</sup>	600	205	65	0.20	0.2		537	8.3
Sr <sup>+</sup>								
Ba <sup>2+</sup>								
Fe <sup>2+</sup>	2.8	0.70						
Mn <sup>2+</sup>								
F <sup>-</sup>	1.8	1.8						
Cl <sup>-</sup>	4,731	4,672	100	1,100	43	1.83×10 <sup>5</sup>	916	2.1
Br <sup>-</sup>								
SO <sub>4</sub> <sup>2-</sup>	400	360	100			36		2.7
Si <sub>(100)</sub>	8.6	7.1						
HCO <sub>3</sub> <sup>-</sup>	86	78	100	14	1,216	11	11	48
PO <sub>4</sub> <sup>2-</sup>								
pH	7.6	7.7	8					7.9
Eh (mV)								
Ionic strength	1.6×10 <sup>-1</sup>	1.3×10 <sup>-1</sup>	1×10 <sup>-2</sup>					1.2×10 <sup>-3</sup>

**Table B-6. Water compositions used for sorption experiments as reported in references. Concentrations are given in mg/l.**

Name: Ref #	Ticknor_GW1 [54]	Ticknor_GW2 [54]	Ticknor_GW3 [54]	Ticknor_GW4 [54]	Ticknor_GW5 [54]	Ticknor_GW6 [54]	Ticknor_GW7 [54]	Ticknor_GW8 [54]
Li <sup>+</sup>								
Na <sup>+</sup>	3,930	1,890	3,860	1,910	3,890	1,880	3,900	1,900
K <sup>+</sup>	15.4	14	14.5	14.6	15.4	13.9	15.2	14.6
Rb <sup>+</sup>								
Cs <sup>+</sup>								
Mg <sup>2+</sup>	0.1	0.2	47.2	46.1	0.6	0.2	47.6	45.8
Ca <sup>2+</sup>	0.45	1,830	0.49		0.46	1,780	0.77	1,810
Sr <sup>+</sup>								
Ba <sup>2+</sup>								
Fe <sup>2+</sup>								
Mn <sup>2+</sup>								
F <sup>-</sup>	2.8	2.5	3.1	1.5	1.5	1.6	1.4	1.7
Cl <sup>-</sup>	5,300	5,300	5,400	5,500	5,200	5,300	5,500	5,500
Br <sup>-</sup>								
SO <sub>4</sub> <sup>2-</sup>	1,010	1,000	1,000	1,010	1,000	990	980	980
Si <sub>(tot)</sub>	7.9	8.6	7.8	8.4	7.6	7.9	7.9	8.0
HCO <sub>3</sub> <sup>-</sup>					25.6	25.1	26.4	21.3
PO <sub>4</sub> <sup>2-</sup>								
pH								
Eh (mV)								
Ionic strength	1.8×10 <sup>-1</sup>	2.1×10 <sup>-1</sup>	1.8×10 <sup>-1</sup>	1.4×10 <sup>-1</sup>	1.7×10 <sup>-1</sup>	2.1×10 <sup>-1</sup>	1.8×10 <sup>-1</sup>	2.2×10 <sup>-1</sup>

**Table B-7. Water compositions used for sorption experiments as reported in references. Concentrations are given in mg/l.**

Name: Ref #	BT_SGW [59]	Wernli_SGW [60]	OL_KR5_3 [76]	OL_KR5_4 [76]	Allard 1:10 [76]
Li <sup>+</sup>					
Na <sup>+</sup>	45	931	2,800	3,030	6
K <sup>+</sup>	5.3	87	13.9	15	0.39
Rb <sup>+</sup>					
Cs <sup>+</sup>					
Mg <sup>2+</sup>	1.76	16	57	69	0.43
Ca <sup>2+</sup>	11.5	140	1,650	2,140	1.8
Sr <sup>+</sup>					
Ba <sup>2+</sup>					
Fe <sup>2+</sup>	0.01	0.02			
Mn <sup>2+</sup>					
F <sup>-</sup>	2.1	3			
Cl <sup>-</sup>	6.4	1,673	7,580	9,200	4.1
Br <sup>-</sup>					
SO <sub>4</sub> <sup>2-</sup>	18.1	248	10.9	3.7	1.6
Si <sub>(tot)</sub>	31.8	10	6.6	5.4	1.6
HCO <sub>3</sub> <sup>-</sup>	143	305		7.3	12
PO <sub>4</sub> <sup>2-</sup>					
pH			7.9	8.4	8.1
Eh (mV)					
Ionic strength	3.8×10 <sup>-3</sup>	5.9×10 <sup>-2</sup>	2.6×10 <sup>-1</sup>	3.1×10 <sup>-1</sup>	4.5×10 <sup>-4</sup>