SKI Report 2008:17

Research

Review of SR-Can: Evaluation of SKB's handling of spent fuel performance, radionuclide chemistry and geosphere transport parameters

External review contribution in support of SKI's and SSI's review of SR-Can

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ISSN 1104-1374
ISRN SKI-R-08/17-SE

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FOREWORD

The work presented in this report is part of the Swedish Nuclear Power Inspectorate's (SKI) and the Swedish Radiation Protection Authority's (SSI) SR-Can review project.

The Swedish Nuclear Fuel and Waste Management Co (SKB) plans to submit a license application for the construction of a repository for spent nuclear fuel in Sweden 2010. In support of this application SKB will present a safety report, SR-Site, on the repository's long-term safety and radiological consequences. As a preparation for SR-Site, SKB published the preliminary safety assessment SR-Can in November 2006. The purposes were to document a first evaluation of long-term safety for the two candidate sites at Forsmark and Laxemar and to provide feedback to SKB's future programme of work.

An important objective of the authorities' review of SR-Can is to provide guidance to SKB on the complete safety reporting for the license application. The authorities have engaged external experts for independent modelling, analysis and review, with the aim to provide a range of expert opinions related to the sufficiency and appropriateness of various aspects of SR-Can. The conclusions and judgments in this report are those of the authors and may not necessarily coincide with those of SKI and SSI. The authorities own review will be published separately (SKI Report 2008:23, SSI Report 2008:04 E).

This report covers issues related to spent fuel performance, radionuclide chemistry and geosphere transport parameters.

Bo Strömberg (project leader SKI)   Björn Dverstorp (project leader SSI)

FÖRORD

Denna rapport är en underlagsrapport till Statens kärnkraftinspektions (SKI) och Statens strålskyddsinstituts (SSI) gemensamma granskning av Svensk Kärnbränslehantering AB:s (SKB) säkerhetsredovisning SR-Can.

SKB planerar att lämna in en ansökan om uppförande av ett slutförvar för använt kärnbränsle i Sverige under 2010. Som underlag till ansökan kommer SKB presentera en säkerhetsrapport, SR-Site, som redovisar slutförvarets långsiktiga säkerhet och radiologiska konsekvenser. Som en förberedelse inför SR-Site publicerade SKB den preliminära säkerhetsanalysen SR-Can i november 2006. Syftena med SR-Can är bl.a. att redovisa en första bedömning av den långsiktiga säkerheten för ett KBS-3-förvar vid SKB:s två kandidatplatser Laxemar och Forsmark och att ge återkoppling till SKB:s fortsatta arbete.

Myndigheternas granskning av SR-Can syftar till att ge SKB vägledning om förväntningarna på säkerhetsredovisningen inför den planerade tillståndsansökan. Myndigheterna har i sin granskning tagit hjälp av externa experter för oberoende modellering, analys och granskning. Slutsatserna i denna rapport är författarnas egna och överensstämmer inte nödvändigtvis med SKI:s eller SSI:s ställningstaganden. Myndigheternas egen granskning publiceras i en annan rapport (SKI Rapport 2008:19; SSI Rapport 2008:04).

Denna rapport redovisar granskning av frågor kopplade till använt bränsle, radionuklidkemi och transportparametrar för berget.

Bo Strömberg (projektledare SKI)　　　Björn Dverstorp (projektledare SSI)

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1 Introduction

SR-Can covers the containment phase of the KBS-3 barriers as well as the consequences of releases of radionuclides to the rock and eventually the biosphere (after complete containment within fuel canisters has partially failed). The aim of this report is to provide a range of review comments with respect to those parameters related to spent fuel performance as well as radionuclide chemistry and transport. These parameter values are used in the quantification of consequences due to release of radionuclides from potentially leaking canisters. The report does not cover modelling approaches used for quantification of consequences. However, modelling used to derive parameter values is to some extent addressed (such as calculation of maximum radionuclide concentration due to formation of solubility limiting phases).

Figure 1 gives an overview of the data used for the consequence assessment in SR-Can. Parameter values contained in the red boxes are addressed in this report, while parameters with green boxes are addressed in other contexts of the SR-Can review, e.g. parameters from the hydrology and biosphere assessment are addressed in the SIG-review (international expert review group devoted to site investigations). The groundwater chemistry is to a limited extent addressed as a critical input for the estimation of e.g. radionuclide solubility and K_d values to account for sorption.

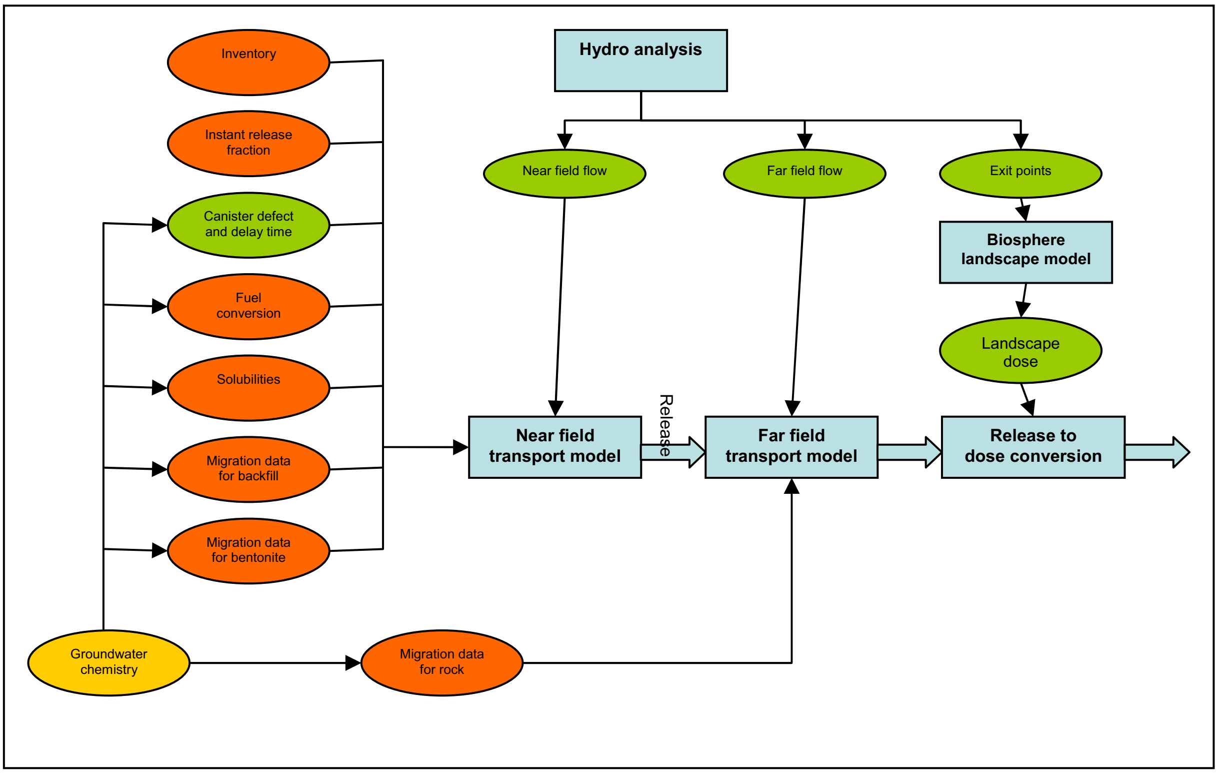

Figure 1: Overview of the data used for the consequence assessment in SR-Can. Parameter values contained in the orange ovals are addressed in this report, while the other boxes are addressed in other contexts of the SR-Can review (figure reproduced from SKB SR-Can TR-06-09, page 400).

The suggestions presented here complement and extend the review findings reported in SKI Report 2007:17 (SKI, 2007), covering a previous workshop held in 2006 about spent fuel dissolution and source term modelling in safety assessment. Some of the supporting material for SR-Can which was available at that time was reviewed as part of the earlier workshop, e.g. migration parameters for the buffer (SKB TR-04-18) and spent fuel performance parameters (SKB TR-04-19). Additional items reported here include a more detailed assessment of mechanisms of spent fuel alteration, migration parameters for rock materials (K_d and D_e values), some details of actinide chemistry and the 4n+2 radionuclide decay chain, as well as co-precipitation of radionuclides with major element phases. The decision to focus on the latter was based on the observations in SR-Can, that neglecting co-precipitation of Th-230 may be non-conservative, and that accounting for co-precipitation of Ra-226 with Ba may significantly lower calculated doses. Considering the relatively limited resources available for this review, it is apparent that some of the issues included in this review have been scrutinised only to a very limited extent. It is therefore recommended that additional review resources be devoted to this area over the next few years.

An appropriate handling of uncertainties will be especially important in the context of SR-Site, but efforts in this area should be apparent also in the SR-Can. It is necessary to systematically identify and characterise the various sources contributing to uncertainty. In the SKI regulations and guidelines SKI FS 2002:1 (in 9§ and Appendix), it is stated that uncertainties should be discussed and examined in depth when selecting calculation cases, calculation models and parameter values as well as when evaluating calculation results. In this report, SKB's approaches for handling uncertainties related to the relevant safety assessment parameters are discussed.

Sensitivity analysis, also required according to the above-mentioned regulation and guidelines, is strongly related to the handling of uncertainties. It is a tool for prioritising the efforts needed in the handling of uncertainties. Within the area of spent nuclear fuel and radionuclide chemistry, it is for instance important to ensure the availability of reliable information for those nuclides that contribute the most to the calculated dose within various scenario calculation cases. The basis for assessing geochemical and transport behaviour of top (dose-contributing) nuclides such as Ra-226 and I-129 are addressed in the report, but not the calculations which support the ranking of the nuclides (since this assessment may also depend on e.g. how the biosphere is represented). A description of alternative / complementary approaches for uncertainty and sensitivity analyses is summarised in an Appendix to this report.

Section 2 of this report contains the general review statements of the group as well as a summary of the findings in the Appendix dealing with approaches for uncertainty and sensitivity analyses. Section 3 includes an assessment of SKB's parameters for spent fuel performance, an analysis of solubility and co-precipitation mechanisms and their couplings to geochemical conditions and thermodynamic data for nuclides such as U, Pu, Th, Np and Ra, and finally a review of retention and migration parameters for the buffer and backfill. Section 4 discusses the far-field retention and migration parameters for the bedrock at the two candidate sites. Section 5 summarises the main conclusions of this review.

2 General Review Statements

2.1 Overview

Based on the more detailed review comments provided in Sections 3 and 4 on the treatment of certain processes and the provision of certain parameters for SR-Can, some general review statements are provided below, either as text or bullet points, in separate sub-sections according to specific topics. While the primary documents dealing with parameter values for assessment calculations were examined in detail, this does not constitute a comprehensive review, which would involve the review of a substantial number of supporting documents. Thus, several comments or criticisms may well have been addressed in these supporting documents.

Because it is impossible to accurately model simultaneously all the processes that are likely to occur in a repository, safety assessment (SA) and SA calculations inevitably represent a compromise between the modelling of 'reality' and the need to carry out more simple modelling using a broad series of assumptions in order to simplify the calculations for probabilistic analysis. The challenge for the reviewer, therefore, is to ensure that the assumptions made and the modelling carried out, form an adequate basis for providing a reasonable representation of the evolution of the repository under a variety of conditions.

2.2 Uncertainty Analysis

SKB's treatment of uncertainties in SR97 was a topic for criticism in the review of this previous assessment, and it is clear that SKB has worked hard to address these criticisms. Nevertheless, there are still areas of work where the treatment of uncertainties would benefit from a more quantitative assessment.

In an effort to convey the general expectations of the regulator in terms of the handling of data, Appendix A of this report has been prepared to provide some relevant examples of approaches to the treatment and propagation of measurement errors and how they may impact the interpretation of results, particularly those generated by thermodynamic modelling. The highlights from this Appendix are presented here.

One goal of any piece of research or experimental work should be to interpret data as objectively as possible, and statistics plays an important role in this process. Thus, data that are used primarily as a basis for some interpretation should be supported by an appropriate statistical treatment.

Graphs are often used to present data and support some underlying interpretation, and box and whisker plots are useful in this regard by conveying a sense of the overall spread of data and their distribution, e.g. Figure 9-42 in the Main Report (SKB, 2006a). Diagrams that show the actual distribution can also be helpful, but it is important to avoid ambiguities created by the presentation format, e.g. distributions of calculated solubility limits of certain metal ions as column graphs, the nature of which is sensitive to interval/bin size.

With this perspective, SKB's Main Report for SR-Can (SKB, 2006a) and the Data Report (SKB, 2006b) do not contain many data with stated uncertainties. Rather the vast majority of data are tabulated as mean values only, which makes it difficult to judge the data objectively.

Correlation is a word that has been used in many of the supporting data reports, but its use throughout the various documents has not been consistent, often being confused with *dependence*, as discussed in Appendix A. Thus, in SKB (2006b), the general impression is given that data have not been analysed carefully for their internal relationships, whether correlation and/or dependence. An example of this criticism is provided in the Appendix, where an independent statistical treatment of a dataset leads to a conclusion that is different from that presented by SKB.

The determination of solubility limits is one area of work where uncertainty analysis is important to complement any recommendations made. To demonstrate the importance of these techniques, calculations are provided in Appendix A of solubility limits of two actinides (Np and Am) showing the effects of uncertainties in either water composition or thermodynamic data (i.e., stability constants). The solid phases considered to be solubility limiting are the same as those considered in the SKB work (Duro et al., 2006a). Furthermore, the thermodynamic databases used are the same. Although water composition and thermodynamic data were considered in this case, it is acknowledged that it is not always easy to decide which factors should be included in the handling of uncertainties.

While details of the analysis are provided in the Appendix, Table 1 shows one comparison of the results obtained based on uncertainty in thermodynamic data combined with a single water composition (SKB reference groundwater), with the results of Duro et al. (2006a) for the same reference water. The uncertainty intervals for the calculated solubilities are wider when considering stability constants relative to those produced from the assessment of water composition as the uncertain parameter (see Appendix A). The mean values correspond well with those stated by Duro et al. (2006a) but this is expected. What is more interesting is that the actual range in solubilities determined here, due to only uncertainties in stability constants, is more than two orders of magnitude. Therefore, it must be assumed that *one cannot get closer than this to an estimate of the calculated solubility of these phases based on the data currently available*. Doubt may arise as to the uncertainty intervals selected in this study (i.e., directly from the NEA database, for actinides and other stability constants where possible, otherwise a value of ±0.5 log unit has been used), in which case, efforts should be made to obtain more realistic uncertainty intervals for the other species, then redo the calculations.

Table 1: Statistical data for the selected solid phases (all concentrations in mol/dm^3), based on uncertainties in thermodynamic data combined with a single water composition (SKB reference groundwater).

Solid phase	**min. conc.**	**max. conc.**	**mean**	**skewness**	**[a] mean**
$NpO_2 \cdot 2H_2O$(am)	5.0E-11	2.8E-8	1.2E-9	-0.14	1E-9
$AmCO_3OH$(am)	7.0E-7	2.0E-4	1.8E-5	-0.32	8.7E-6

[a] from Duro et al. (2006a), SKB reference groundwater composition.

Interpretations and conclusions can be judged by others only on the basis of appropriate information about the certainties involved. The important point to emerge from the work reported in Appendix A is that expert judgment may not always prevail in estimations of uncertainty and sensitivity.

2.3 Handling of Uncertainty and Sensitivity Analysis

A general problem in safety assessments is related not only to uncertainty analyses but also to the *handling* of uncertainties. In this situation, it is appreciated that the use of a sufficiently conservative assumption or parameter value must be an option for the implementer, otherwise there will never be a full safety assessment. A full safety assessment will contain several thousand parameter values, most of which have only a minor or negligible impact on the outcome. Methods must be available, therefore, for such parameters to be handled in a reasonably simple way. On the other hand, there will also be a range of difficult-to-measure and highly critical parameter values, for which details concerning uncertainty sources should be evaluated and reported.

There is no way to know the distinction between those parameters of negligible consequence to the outcome and highly critical parameters, without conducting sensitivity analysis. Under such circumstances, sensitivity analysis plays an important role, as discussed below and in various sections of this report, for example in connection with sorption-related K_d values for radionuclides. Thus, for some radionuclides (radioelements), whether the K_d value changes by a factor of 10 or 100 may have no impact on the assessment calculations, in which case efforts should be concentrated on those radionuclides for which such changes do have an appreciable impact. However, it is important for reviewers that such information is reported, in order to improve an understanding of what K_d values need to be determined accurately and which do not.

In the same way, for assessment calculations, decisions may be made to bound the values of one or more parameters, based on one or more assumptions, the argument being that it is not necessary to know the value accurately, but rather, to know that, under the defined conditions, a parameter is never greater or lesser than, the bounding limits. Such decisions are a necessary part of SA but, given these circumstances, it is important from a reviewer's perspective to ensure that these bounding limits are firstly acceptable, i.e. based on conservative assumptions and conservative input parameters and secondly, not overly conservative, to the extent of masking an understanding of the system.

Again, the justification between establishing the need for parameter values based on accurate data and perhaps recommending only bounding limits, should be demonstrated via sensitivity analysis. Given the number of parameters that require such bounding limits for SA calculations, sensitivity analysis takes on significant importance and *such analysis needs to be reported in detail as a major component of the overall safety assessment*. As part of SR97, Lindgren and Lindström (1999) carried out transport calculations that explored a series of sensitivities, and it is hoped that a similar, even more in-depth exercise will be repeated for SR-Can.

2.3.1 Approaches to Sensitivity Analysis – Example for Ranking Parameters

As a basis for ranking parameters, two types of sensitivity analysis methods were used in the work involving solubilities reported in Appendix A: *variance* analysis and *binary search tree* analysis. The concepts of the two approaches are explained below and the results regarding the solubility calculations are shown in Section A10 (Appendix A).

Variance analysis

Variance analysis is made by holding one of the investigated parameters at a fixed value while the others are varied, typically within an interval 2 log units wide, for a given number of iterations, e.g. 20. The variance is then calculated, and the next parameter of interest is held at a fixed value. The parameter (species in the case of solubility determination) that gives the smallest variance when held constant is deemed the most important and so on. At the beginning of the calculations, a random matrix is created. It contains random values for the different parameters, each sampled within a given uncertainty range.

There is one row for each investigated parameter. The rows combined form a matrix with as many rows as there are investigated parameters and as many columns as the selected iteration number. In the first iteration, the first parameter is held at its mean value and the others receive values according to the first column of the matrix. In the next iteration, the values are taken from the second column and so on for the given number of iterations. The second parameter is then held at a fixed value and the others receive values according to the columns of the random matrix. This approach gives the same variance for the unimportant parameters, thus making the selection criterion simple. The selection criterion is usually that the difference between two successive variances must be at least one thousandth of the last one. The important parameters are then transferred to the uncertainty analysis.

Binary search tree

The theory behind the binary search tree is rather simple, and the approach is more commonly used in optimisation problems. The inputs to the model are seen as a vector containing the different parameter values. It is known, *a priori*, that only a few of these are important. Therefore, by using a binary search tree, the number of iterations needed to identify the important parameters may be less than the total number of parameters.

The method illustrated in Figure 2 may be described in the following way. The calculations are made two times, one with every investigated parameter at their maximum value, and one with the minimum value. The results are then compared to investigate whether there is a significant difference. If so, the input vector is divided into two parts, where each becomes the basis for further calculations. The same approach is used at the next level of the search tree, except that at this level, the values in half of the original vector are changed while the rest are held fixed. If there is no significant change this time, it is concluded that there are no important parameters in that part of the vector and it is not investigated further. If the change is significant, the new vector is divided into two parts and the method described above is applied to both parts. Finally, all of the important parameters are identified.

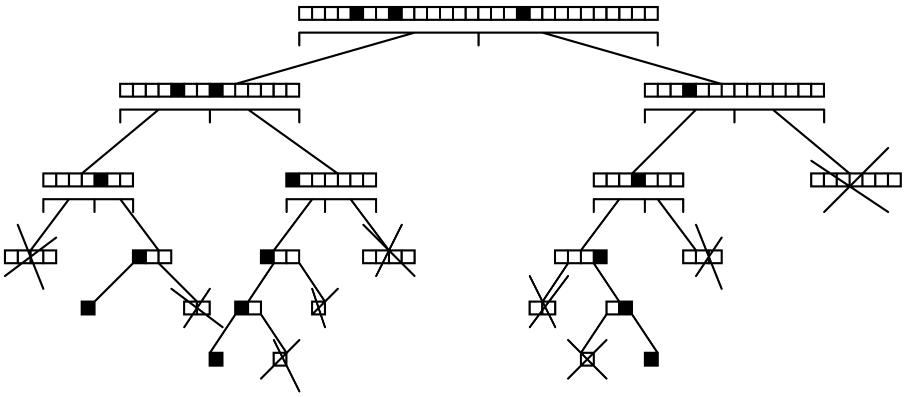

Figure 2: Binary search tree for a 28-cell input vector with three important parameters (filled boxes).

Consider the case in which two iterations are made at each level, i.e. high and low values for the parameters. The number of iterations needed to investigate which parameters influence the result may then be significantly reduced if the method indicated in Figure 2 is used. As seen for the case described above, the number of iterations is only slightly reduced compared with the "one factor at a time" approach. However, as the number of parameters grows, the greater the profit will be of using a binary search tree. For the cases described in this section, the number of parameters is usually about two hundred, with between one and six being important. Thus, the approach is very effective in the sense that it requires only a few iterations, usually reduced to about a third of the number of parameters.

2.4 Treatment of Source Term

The following review statements are offered here on source term issues:

- **Inventories**: With regard to inventories, it is important from the standpoint of securing international acceptance, to update SKB's initial inventories, taking into account the most recent work in this area – the international (OECD) benchmark program to compare UOX inventory calculation codes.
- **Instant Release Inventories in Contact with Water**: There is a current lack of experimental data on this topic for most relevant radionuclides to justify defining the instant release inventory based on parameters related to reactor irradiation history and experimental data on initial characterisation and leach testing. Given this lack of data, there is a risk of proposing instant release fractions that are too optimistic. An alternative approach is an attempt to integrate the various uncertainties concerning the mechanisms of long-term fuel evolution. In particular, there is a case for redefining the instant release fraction, to take into account long-term fuel degradation mechanisms such as changes in the long-term stability of grain boundaries under the effects of helium accumulation, irradiation damage, increased surface area of fuel, and the influence of the closed porosity of the rim. At the very least, it would be valuable to compare the impacts of using SKB's estimates of instant release fraction with those from an approach that takes into account mechanisms for the long-term degradation of fuel such as those discussed above.
- **Fuel matrix alteration**: While the release fractions proposed by SKB are reasonable and realistic, the supporting rationale – model based on empirical data – is rather weak. The available reports do not place sufficient emphasis on understanding the

mechanisms supporting SKB's predictive model or even acknowledge the range of models on matrix alteration currently available internationally. On the other hand, it is acknowledged that certain environmental parameters, such as the influence of hydrogen generated from canister corrosion and the effects of secondary phases containing U(IV) on uranium release, can be considered additional safety-related factors.

2.5 Treatment of Radionuclide Migration in the Near Field

2.5.1 Radionuclide Solubility

It is beyond the scope of this report to provide a comprehensive review of the solubility of all elements. Rather, some selected observations of relevance to the SA are summarised below as examples of solubility issues.

Actinides– Temperature Dependence

Given that temperatures up to 100 °C can be expected near spent fuel canisters in the repository, the resultant effect on radionuclide speciation and solubility is an important issue and should be addressed directly. Although data gaps at elevated temperature are likely, the lack of data cannot be used to justify neglecting this issue. Thus, examples from the literature could be used to address this problem in a general way and as a basis for developing a strategy to properly deal with this issue.

Selected Actinides – Plutonium (III) Phosphate

Duro et al. (2006a) identified the importance of dissolved phosphate for the solubility of Pu(III), given the ability of this ligand to form stable solid phases with Pu(III). The lack of phosphate measurements for Pu(III)solubility is also acknowledged. Thus, an experimental programme to determine the solubility of Pu(III) phosphate in the saline reference water is highly recommended. In the absence of reliable data, Duro et al. (2006a) made recommendations based on a correlation with An(III). While such a correlation may well be justified, a more detailed explanation of the selection process is recommended.

Actinide(IV) Polymer / Intrinsic Colloid / Eigencolloid Formation

With regard to An(IV) solubility and in particular Pu(IV) solubility, colloid formation, either via the formation of intrinsic/eigen/real colloids or as pseudocolloids via the attachment of soluble plutonium species to groundwater colloids, may potentially play a significant role in radionuclide transport. Recent publications indicate that discrepancies in measured solubility constants can be accounted for by the formation of Pu(IV) polymer/eigencolloids (Neck et al., 2007), and that Pu(IV) polmers are actually nanoclusters of crystalline PuO_2 (Soderholm et al., 2007). Given these recent developments, SKB should describe how it plans to address this issue for plutonium and other tetravalent actinide species in its solubility assessment.

Actinides - Thorium Chemistry

The treatment of thermodynamic data for thorium has been examined as one example of the application of these data in the derivation of solubility limits, since this radioelement is a significant contributor to dose over long time frames, i.e. up to 1,000,000 years.

A solubility limit is a complex heterogeneous equilibrium between a (solubility-limiting) solid phase and various solution species. With currently accepted models, determination of the solubility limits for Th requires knowledge of:

- Solubility product of the solubility-limiting solid phase;
- Relevant hydrolysis reactions of Th; and
- Complexation behaviour of Th with carbonate, a readily available ligand in natural groundwater systems.

Information on the above quantities is limited, however, since few studies have been performed on the Th-H_2O-CO_2 system. Thus, given the wide range of hydrolysis species and associated hydrolysis constants proposed for Th in the literature, the choice of species must be considered subjective and substantial uncertainty ought to be attached to the solubility limit determined for Th. However, such an uncertainty is not expressed or discussed in the relevant SKB report (Duro et al., 2006a). The situation concerning ranges of species and associated thermodynamic data for Th reactions with carbonate is even worse. Even a relatively cursory examination of the supporting experimental work in the literature indicates a lack of traceability and controls for laboratory experiments, which allow an independent reviewer to make sound judgements.

Thus, the current picture of Th complexation in solution and Th solid phase formation under natural groundwater conditions are inconsistent. Under these circumstances, a simple value for a solubility product for an element such as provided in Duro et al. (2006a) is inappropriate without substantial discussion. Certainly, some statement on a meaningful uncertainty range is an absolute necessity.

Co-precipitation of Alkaline Earth Metals

The modelling performed by Duro et al. (2006b) to determine the solubility controlling phases was constrained by what are considered to be a number of conceptual uncertainties, all of which can influence the predicted solubility of the alkaline earth metals, Sr, Ba and Ra; in particular:

- The formation of amorphous phases was accepted, with precipitation of such phases favoured over crystalline phases.
- The precipitation of only pure solid phases.
- The systems being studied were not considered to be in equilibrium with respect to the sulfate/sulfide redox couple, due mainly to the lack of evidence for sulphate-reducing bacteria (SRB).

Evidence from seawater and uranium mill tailings studies suggests that the alkaline earth metals are likely to form an amorphous but mixed sulfate phase in the near field of the repository, which will control the solubility of Sr, Ba, and Ra. Published data further suggests that dissolved Ra, and possibly Ba, will be undersaturated with respect to their respective pure mineral phases, $RaSO_4$ and barite ($BaSO_4$), with Ra undersaturated by many orders of magnitude. Thus, the decision by Duro et al. (2006b) to use the pure sulfate mineral phases of these two elements as solubility controlling phases is conservative and reasonable.

On the other hand, although the solubility controlling mineral phase selected by Duro et al. (2006b) for Sr is celestite ($SrSO_4$), the actual phase that forms may be an amorphous form of $SrSO_4$(s) that may be up to 1.5 log units more soluble. Thus, the choice of celestite may not be conservative and, therefore, it is suggested that SKB carry out sensitivity analyses using a more soluble $SrSO_4$ phase.

In addition, two other assumptions in this area made by SKB may not be valid:

- The absence of microbial activity around the canister; and
- The sulfide concentration in bentonite porewaters is controlled by the buffer.

There still remains some uncertainty concerning the lack of microbial activity in the vicinity of canisters. Given that the presence of SRB may increase the sulfide concentration in porewater, SKB should conduct studies in sulfide biogeochemistry as a means of assessing the potential effect that sulfide could have with regard to canister corrosion as well as enhanced concentrations of alkaline earth metals in near field porewater.

2.5.2 Radionuclide Migration through the Buffer

For conditions (most scenarios) where the buffer remains intact surrounding waste canisters, radionuclides will migrate through the buffer by diffusion following release from the canister. The relevant parameters necessary to model this diffusion are the effective diffusion coefficient (D_e), the diffusion porosity (ε), the sorption coefficient (K_d), and the bulk density of the medium (compacted bentonite) (ρ).[1]

A first step in the making various recommendations on parameter values is to define a reference bentonite and reference groundwater compositions. While this has been done, the timing of the work was such that there are differences between the reference solid and waters used by Ochs and Talerico (2004) who made the buffer migration parameter recommendations, and the Data Report (SKB, 2006b). Presumably, for SR-Site, the same reference bentonite and groundwater data will be used throughout the different pieces of work.

The most significant differences noted were the percentage of minor constituents in the bentonite and the properties of the buffer. In the Data Report, calcite is not present, but contributes 0.7% to the reference bentonite of Ochs and Talerico (2004), which, under the assumption of closed conditions, is responsible for the $p\text{CO}_2$. Modelling of bentonite-water interactions is a key step in the derivation of bentonite porewater compositions which, in turn, need to be characterised properly in order to make adequate recommendations on the extent of sorption (K_ds). For this reason, the decision of the SR-Can as documented in the Data Report (SKB, 2006b) to select K_ds representative of porewater compositions of a bentonite-water system that is open to the host rock is sensible.

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[1] Discussed further in Section 3.3.

An additional factor that is used to help in the estimation of K_ds is the cation exchange capacity (CEC) and this parameter has values differing by ~15%. While the resultant impacts on parameter values recommended and carried through to safety assessment calculations may be minor, such inconsistencies are unfortunate.

The decision to adopt a single value of the effective diffusion coefficient (D_e [HTO]) and porosity for most elements (anions and Cs excepted) corresponding to the specified dry density of compacted bentonite, appears reasonable and was also adopted for previous assessments. However, an uncertainty of at least an order of magnitude either way should be attached to a uniform value of D_e, given the range in experimental data for the D_e values of different elements (e.g. Figure 9, Brandberg and Skagius, 1991), unless arguments are provided to the contrary.

The parameter D_e is expressed in terms of D_W, the diffusion coefficient in free water, as:

$$D_e = D_W(\varepsilon.\delta/\tau^2) \qquad [1]$$

where ε is the porosity, δ the constrictivity, and τ the tortuosity of the medium. A constant D_e implies that the factor ($\varepsilon.\delta/\tau^2$) remains constant for different nuclides, which seems logical since this factor is fundamentally a geometric property of the medium through which diffusion occurs. However, the fact remains that anions and Cs are usually treated differently, as also done in this assessment, because of ‘electrical effects’ surrounding these negative and positive ions. Thus, smaller (secondary) effects due to the size of nuclide species may also affect the magnitude of this composite ‘geometric’ parameter causing the variability in measured D_es for different elements as summarised by Brandberg and Skagius (1991).

Thereafter, the focus of most of the effort was in recommending sorption parameters (K_ds) for each element that are representative of in situ conditions, i.e. porewaters of compacted bentonite, equilibrated with different groundwaters. Ideally, it would be preferable to have experimental data that could be used directly rather than requiring ‘extrapolation’, i.e. solution chemistries are the same as under repository conditions. To this end, it is hoped that results from the current laboratory experimental programme may help to address the lack of site-specific data.

In terms of diffusion, anions are treated in a slightly different way, to take into account anion exclusion. The approach used by Ochs and Talerico (2004) to determine self-consistent combinations of D_e and ε for anions, is acceptable. Similarly, the treatment of Cs, which has been shown to exhibit enhanced diffusion, is considered justified.

Ochs and Talerico (2004) have put considerable emphasis on documenting in detail the derivation process for K_ds for each element and make the overall process (conversion of K_ds from batch sorption experiments to values representative of repository conditions) transparent. The basic premise used is that the nature of the solid phase is the same for batch sorption experiments as compacted bentonite – only the solid/liquid ratio is different, which, in turn, affects solution chemistry. Data are cited to support this premise.

While transparent, the multi-step derivation process is relatively complicated and, to a large extent, subjective, although supported in part by experimental data. However, those experimental parameters that affect measured K_ds are taken into account in the derivation process. Apart from the thermodynamic modelling carried out to support speciation considerations, the authors have clearly attempted to identify, separate, and treat consistently, the various contributions to uncertainty, while acknowledging that the available datasets are not sufficient to allow the calculation of statistical uncertainties. Thus, uncertainty estimates on final recommendations are essentially subjective. This situation could probably be improved if uncertainties are treated according to international convention (ISO, 1995; EURACHEM, 2000). These widely-accepted documents address the treatment of uncertainty in terms of specification of the parameter(s) being measured, identification of sources of uncertainty, quantification of uncertainty, and calculation of combined uncertainty. GUM[2] also focusses on general rules for evaluating and expressing uncertainty for varying levels of accuracy as well as different disciplines.

K_d values were recommended for "saline" and "highly-saline" waters only. However, the Data Report (SKB, 2006b) uses identical values for non-saline conditions, which should be conservative, although the impacts of differences in K_d values by a factor of 10 or even 100 should be explored by sensitivity analysis, particularly for natural series radionuclides, where the effects of retardation are not necessarily intuitive.

As a precursor to making recommendations for different elements, it would have been helpful to have an indication, based on previous safety assessment calculations, of which radionuclides are key contributors to dose under different circumstances (scenarios). In addition, for those radioelements that are key contributors, it would be helpful to have some form of complementary sensitivity analysis carried out by SKB, which shows the impact of, for example, factor of 10 changes in K_d values. Such analyses would help to focus the review effort, not to mention any supporting laboratory experiments.

In terms of the data input to assessment calculations, the only parameter that is directly comparable with previous assessments is the apparent diffusion coefficient (D_a), which is calculated from the various parameters recommended above. As shown in Section 3.3, resultant D_a values are generally less conservative for SR-Can than for the previous SA. D_a is reduced by about a factor of 4 for Cs and 2 for cations Sr and Ra, while for most of the remaining nuclides, D_a is reduced by a factor of about 10. In the case of Tc(IV), however, the decrease is by a factor of ~2,500!

Differences in recommendations of a factor of 10 or more between assessments do not necessarily relate to an improved understanding for the current assessment, which, therefore, emphasises the call for some supporting sensitivity analysis to identify the key radionuclides and associated diffusion parameters on which to focus an experimental effort.

2.5.3 Radionuclide Migration through the Backfill

Review comments here are based on information provided in the Data Report (SKB, 2006b), Process Report (SKB, 2006d) and Initial State Report (SKB, 2006f), as the primary document TR-06-85 (Ochs, 2006b) supporting data recommendations was not available for review. Again, issues concerning the potential for backfill erosion under specific circumstances are beyond the scope of this report and are discussed elsewhere (SKI, 2008),

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[2] **G**uide to the Expression of **U**ncertainty in **M**easurement (ISO,1995).

It is appreciated that the nature of the backfill has not yet been decided by SKB and that substantial work is ongoing in this area to provide key data. *Given the current lack of experimental data on either diffusion or sorption for Friedland clay, one of the clays being considered as backfill component, this work is considered essential.*

Given the current choices, the main issues associated with radionuclide migration through the backfill are:

- Can diffusion and sorption data for bentonite be applied to the backfill mixture, which comprises 30% bentonite and 70% crushed rock?
- In the absence of data for an alternative material to bentonite, Friedland clay, can diffusion data for bentonite be applied to the substitute clay?

With regard to basic diffusion parameters (effective diffusion coefficient, porosity) and in the absence of experimental diffusion data, allowances for compaction density should be able to reduce uncertainties. The major uncertainty concerning diffusion appears to be whether anion exclusion will occur, and, although data exist to suggest that it does occur in bentonite-sand mixtures, some supporting experimental data would help clarify the situation regarding the two current options for backfill.

Some confusion concerning porosity values has been noted in the review of some of the text and tables. However, the ‘correct’ values appear to be included in the relevant data input tables.

With regard to sorption and K_d recommendations, the lack of supporting experimental sorption data is acknowledged. Presumably, experiments are being conducted to rectify this situation. The Data Report (SKB, 2006b) indicates that for the bentonite/crushed rock mixture, K_d estimates for bentonite were scaled according to surface area (N_2-BET) and percentage weights of each component. This must be regarded as only a first approximation, since porewater composition was shown to have the greatest control on K_d values measured experimentally. There is no guarantee that the porewater composition in an intimate, homogeneous, compacted mixture of bentonite and crushed rock will reflect only bentonite-water interactions. Thus, in the absence of experimental data to support the assumption that the porewater composition of a bentonite/crushed-rock mixture reflects that of bentonite alone, *it is not conservative to use sorption data that are representative of the bentonite alone.*

The K_d recommendations for sorption on Friedland clay (Ochs, 2006b), as described in the Data Report, appear to have been derived in a similar way to the corresponding data for compacted bentonite, and so are more reliable.

2.6 Treatment of Radionuclide Migration in the Far Field

2.6.1 Matrix diffusion

In the far field, radionuclides will migrate mainly by advection, but will undergo a complementary process whereby radionuclides (and other species) can diffuse into and through the rock matrix and micro-fracture network adjacent to the main flow channels. This process, matrix diffusion, is a significant retardation mechanism for radionuclides migrating through the geosphere. In addition to diffusion, radionuclides can adsorb on additional rock/mineral surfaces that are accessible via diffusion.

The extent of matrix diffusion depends on the pore space in the rock matrix that is connected, i.e. accessible to diffusion, as well as the diffusion rate and ability of radionuclides to adsorb. Connected pore space, or penetration depth, is a key issue concerning matrix diffusion (see below).

Thereafter, the approach taken to derive effective diffusion coefficients (D_es) of radionuclides in the far field is via measurement of a formation factor combined with literature values of diffusion coefficients of ions in free water, i.e. unrestricted. The formation factor is a geometric factor that incorporates the porosity and characteristics (constrictivity, tortuosity) of the pores. Importantly, the formation factor can be determined by electrical methods, both in the laboratory and in the field. The recommendations on matrix diffusion parameters leading to estimates of D_e were based primarily on field (in situ) electrical measurements.

It has to be noted that the in situ electrical method involving downhole logging of resistivity combined with electrical conductivity measurements of ‘porewater’ in the laboratory, is relatively new and, consequently, requires broad acceptance by the scientific community. Liu et al. (2006) state that similar values of the formation factor have been found on samples using different measurement techniques, both electrical and more traditional methods. Given such an important issue, it was important to be able to review these experimental measurements, but they are not included in the report or, to our knowledge, supporting documents cited. On the other hand, a drawback of laboratory measurements is that the samples of rock used are not representative of in situ conditions, and this consideration has to be included in the overall evaluation.

Site-specific in situ measurements were conducted at three sites, all sub-areas of the two regions being considered for repository construction and development. Complementary porosity measurements were carried out in the laboratory on borehole samples.

Measurement errors are not quoted or discussed explicitly for either the laboratory or in situ measurements of the formation factor and porosity in the three areas of Sweden described previously, nor in the literature values compiled. It would have been useful to have an idea of the basic measurement error of the electrical conductivity measurements. This is currently a field of intense international collaboration (e.g. PTB, 2007). However, the authors note that the natural variability in the formation factor is much greater than the inherent measurement uncertainties, and the resultant data appear to support this argument. This variability is not necessarily a concern as the argument is also made that the nature of a flowpath through the geosphere will result in the averaging of properties. Such an argument is reasonable.

Recommendations were made to SKB on formation factors and porosities for the three sub-areas considered. Recommendations on formation factors are based on the arithmetic means of the datasets, although the Data Report (SKB, 2006b) records the geometric means. This discrepancy is relatively minor, however, resulting in, at most, a factor of 2 difference. Associated high and low values of formation factor appear to have been selected arbitrarily and rather subjectively, particularly in view of the observed variability. Thus, sensitivity analysis should be carried out to investigate the impact of the upper and lower values recommended, compared with the 95% confidence intervals (lognormal space).

Although Liu et al. (2006) consider the effects of anion exclusion to be negligible for the conditions under study, the SR-Can team in the Data Report made the decision to retain the previous factor of 10 reduction in the formation factor (hence, D_e value), while acknowledging that an appropriate factor is closer to 2-3. Again, sensitivity analysis should be used to support the decision to retain the larger factor.

While Liu et al. (2006) do not provide a specific recommendation for the maximum penetration depth of solutes diffusing into the matrix, they do conclude that "*the porous system of the rock matrix is connected on all scales relevant for the performance assessment*" (SKB, 2006b, p. 71). Subsequently, the SR-Can team adopted a triangular distribution of penetration thickness to be used in the SA (SKB, 2006b), which ranges from 3 cm to 5 m (there is some confusion whether the value is 5 m or 10 m). This is clearly a topic for sensitivity analysis, particularly for non-sorbing nuclides, to establish the impact of penetration depth on retardation and, hence, peak flux out of the repository.

In terms of comparisons with the previous assessment, resultant formation factors and, hence, D_e values are essentially the same, although recommended porosities are a factor of 5 lower. The situation regarding formation factor/D_e is surprising given that in situ formation factors have been used for the first time as the basis for formation factor recommendations, yet formation factors are typically lower than laboratory measurements. Similarly, given that a factor of 10 reduction in porosity has been retained for anions from SR97, this means that the extent of matrix diffusion will be greater than in the previous assessment. Thus, since measurements of porosity are carried out only in the laboratory, an argument could be made, primarily in the interests of self-consistency, for using a combination of laboratory formation factor and porosity measurements to generate the required diffusion coefficients.

The key difference between previous recommendations of formation factor and those provided in Liu et al. (2006) for SR-Can is that in situ measurements were used as the basis for the current recommendations. The arguments in favour of in situ measurements are logical since such measurements reflect in situ temperature and stress conditions better than laboratory measurements. However, a diagram used to support the differences between in situ and laboratory measurements also does not show any trend in in situ measured formation factors with depth, which would be expected if stress were an important variable. Thus, this apparent discrepancy needs further investigation.

2.6.2 Radionuclide Sorption in Far Field

The recommendations for sorption parameters, provided by Crawford et al. (2006), are used in conjunction with the matrix diffusion parameters discussed in the previous sub-section. The parameter K_d continues to be used as the sorption parameter in assessment calculations, and the reasons for this are still valid. The challenge continues to be that recommendations take into account all the key parameters that are known to affect K_d measurements, and this sensitivity is recognised and considered by the authors of the report.

Only a subset of radioelements has been updated since the previous assessment, based on a sampling and analysis strategy supporting site investigations. Hopefully, the laboratory programme and/or updating of recommendations will be extended to include all sorbing nuclides that contribute significantly to dose in assessment calculations.

The authors have provided much greater transparency concerning their K_d derivation process than in previous assessments, although the strategy has been to restrict the experimental datasets to those that used rock types similar to those of Swedish rocks at the investigation sites, combined with experimental conditions (aqueous phase) as close as possible to Swedish conditions. This strategy resulted in more restricted datasets than had been used previously and there is the possibility of selection bias with using a relatively small number of experimental datasets. One such bias was noted for radium.

Crawford et al. (2006) discuss likely experimental biases in the sorption data considered, i.e. common to all datasets. In particular, consideration of the effects of crushing rock samples thereby exposing a greater number of sorption sites is logical. While previous K_d recommendations for other national programmes have probably taken such a bias into account, the authors address it in a systematic way. This consideration resulted in the recommendation of a correction factor, to reduce laboratory K_ds by a factor of 10 in extrapolating to in situ conditions.

On the same theme, while the general trend in specific surface area as a function of volumetric mean grain size was convincing (and the basis for the factor of 10), the specific surface areas of Swedish rock types analysed was shown to be about a factor of 5-10 lower than those of Finnish rocks, for which a substantial number of sorption data were selected. It is not clear that this systematic difference was accounted for in those cases that were dominated by Finnish rocks.

K_d values were recommended for non-saline and saline waters, represented by chloride concentrations ≤ 400 mg/l and > 400 mg/l, respectively. The authors identify, discuss and address the important sources of uncertainty adequately, some of which are due to experimental errors and some due to the differences between experimental and site-specific conditions. It is hoped that SKB's laboratory programme will help provide data that address at least some of the key uncertainties.

3 Radionuclide Release and Migration in the Near Field

3.1 Spent Fuel Source Terms – Main Hypotheses and Results Developed in SR-Can

The text in this sub-section supplements a previous SKI review[3] of document TR 04-19 "*Spent Fuel Performance under Repository Conditions: A Model for Use in SR-Can*" (Werme et al., 2004), and provides a review of additional documents (SKB, 2006a, 2006c), but is still largely based on the data in Werme et al. (2004). The purpose of the review described here is to highlight the main uncertainties concerning the source term definitions (instant release inventories and spent fuel matrix) and to present the current state of knowledge concerning the definition of the instant release inventories and their long-term evolution. The text also seeks to define additional actions for consolidating the work carried out under SR-Can.

3.1.1 Initial Inventories

It is important to update the initial inventories and incorporate the most recent work on inventory calculations. An international (OECD) benchmark program to compare the performance of various UOX calculation codes was carried out recently (presented at the PHYSOR'06 conference, with the final document submitted to the OECD in March 2007). Taking this work into account in SR-Can (for which no additional calculations have been carried out) would have a major effect in terms of international acceptance of the data.

3.1.2 Instant Release Inventories in Contact With Water

The definition of the instant release inventories remains the most controversial subject in recent years at an international level. Two main options can be considered to define the instant release inventories:

- One option is to define the instant release inventories and their uncertainties based on parameters related to reactor irradiation conditions (linear power, fission gas release, etc.) and on experimental data (initial characterisation and leach testing) obtained on fuel after a few years of cooling.
- The second approach seeks to integrate the uncertainties on the mechanisms of long-term fuel evolution; this implies redefining the instant release inventories to allow for contributions that are not currently taken into account in the preliminary approximation, and tends to increase the source term.

With regard to the first approach, and irrespective of any discussion concerning the possible evolution of the instant release inventories over time, it is important to note the lack of

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[3] For a better overall understanding, the previous review (SKI, 2007) should be read prior to reading the current review.

experimental data available for relevant radionuclides (^{129}I, ^{36}Cl, ^{99}Tc, ^{79}Se, ^{126}Sn, ^{107}Pd, etc.) and for "light-water" reactor fuel, i.e. the case of Swedish fuel. Taking into account the limited available data on CANDU (low burnup and high linear power) and PWR fuel or choosing parameters such as the gas release fraction for SR-Can reflects a real lack of data *and statistics* for light-water reactor fuel.

For example, an element such as ^{79}Se is sometimes considered to exhibit volatile behaviour, whereas, based on minimal leaching data, the radioelement is considered within the scope of SR-Can to be non-segregated in the free spaces. Differences in the estimated selenium instant release inventory exceeding two orders magnitude can then arise depending on the selections made (0.03% for SR-Can compared with several percent in Johnson et al. (2004)). For another example concerning ^{36}Cl (an activation product of ^{35}Cl), no data are available for light-water reactor fuel, and a factor of three is applied to the gas release fraction based on the few data obtained with CANDU fuel. The gas release fraction thus no longer appears to be a penalising or conservative factor.

Although numerous experimental studies have been carried out in recent years at an international level — including Sweden — to quantify the "matrix" source term, very few studies have attempted to specify the instant release inventories in view of the difficulties encountered, for example in analysing long-lived fission products in solution. This is unfortunate, as the "instant release inventories" source term could become a design basis criterion for a spent fuel package in a nuclear waste repository. This difficulty concerns not only the quantification of the instant release inventories during spent fuel leaching experiments, but also the validation of the initial inventories (comparison between neutronic calculations and solution analysis results following complete dissolution of fuel rods). Although this approach is sometimes described as "realistic", it nevertheless involves a dose of subjectivity (including the definition of the uncertainties) and does not take into account possible long-term fuel modifications.

The second approach attempts to redefine the instant release inventory by allowing for the uncertainties concerning the possible long-term fuel evolution mechanisms (radionuclide migration toward the "free space" under alpha self-irradiation, stability of the grain boundaries and closed porosity, increased surface area, etc.). This implies that an inventory not initially subject to instant release (i.e. not directly accessible to water) in the fuel could become so over the long term when water comes into contact with the package after several thousand years in a closed system. Clearly, in this context the definition of the instant release inventories will depend to a large extent on the state of knowledge and understanding of the mechanisms capable of modifying these inventories. Leaching data obtained with non-aged fuel will be difficult to extrapolate over the long term if these mechanisms are of significant magnitude.

The risk with this approach would be to propose instant release values that are too unfavourable and too conservative. This approach should therefore be considered **as incremental with the current state of knowledge**, but is fully appropriate for investigating the long-term behaviour of a waste package and is suitable for the time scales involved.

The fuel, which is not at thermodynamic equilibrium, is subject to radioactive decay that is capable of modifying the instant release inventories over time. Two processes have been the subject of several studies in recent years:

- The diffusion, enhanced by alpha self-irradiation, of radionuclides from the UO_2 matrix toward the exterior of the grains;
- The long-term stability of the grain boundaries under the effects of helium accumulation and irradiation damage in the ceramic material.

Both processes would be capable of modifying the instant release inventories over time.

It is now generally acknowledged that radionuclide diffusion enhanced by alpha self-irradiation will be negligible (diffusion coefficient decreasing from $\sim10^{-27}$ m^2/s to $\sim10^{-29}$ m^2/s) and will not significantly affect the long-term instant release inventories (Ferry and Piron, 2007). The highest limit proposed by Johnson et al. (2004) for the definition of the instant release inventories can therefore be revised downward. The roughly 5% increase in instant release inventories obtained with an athermal diffusion coefficient of about 10^{-25} m^2/s thus appears too penalising.

Concerning helium accumulation in the ceramic, a model recently developed under the European NF-PRO project (Ferry et al., 2007) is based on low helium mobility under alpha self-irradiation and a low helium solubility limit in UO_2 grains. These hypotheses are now supported by numerous experimental findings. This implies that the "only" process liable to modify the mechanical stability of the ceramic is the formation of helium bubbles a few nanometres in diameter inside the grains (or helium accumulation in pre-existing fission gas bubbles) with increasing pressure in the bubbles leading to intra-granular rupture. Rupture will occur above a critical pressure that depends on the tensile strength and porosity of the ceramic (Ferry et al., 2007) and will propagate to the grain boundaries, thereby increasing the surface area by several orders of magnitude and resulting in instant release.

The model demonstrated that after 10,000 years, the critical pressure will not be reached in the bubbles in the case of spent fuel with a mean burnup of 47 GWd/t. While reassuring, this result cannot yet be applied to the rim because the model does not take into account the strong radial heterogeneity of high-burnup spent fuel (high local burnup, different microstructure and mechanical properties, etc.). Nor does the model allow for local or extended defects capable of modifying helium mobility. At the present time, therefore, radionuclides localised in the rim and especially in closed porosity cannot be excluded from the instant release inventories for high burnup fuel. The contribution of the rim to the instant release inventories is based on the estimated rim thickness and on fission gas behaviour, and constitutes a major difference between the two approaches.

Considering that athermal diffusion appears to be negligible, the closed porosity of the rim in the case of high burnup fuel remains a significant source of uncertainty in relation to the stability of grain boundaries and the sub-micron structure of the rim. It is important to note that uncertainties concerning the rim do not imply that the rim can dissolve more rapidly than the rest of the matrix as mentioned on p. 58 of TR-06-22 (SKB, 2006c), but simply that a fraction of the radionuclide inventory initially inaccessible to water can become accessible over time. Although the conceptual differences between the two approaches result in different instant release values, especially for UOX fuel at high burnup (> 40 GWd/t) and for long-lived radionuclides (^{129}I, ^{36}Cl, ^{79}Se, ^{135}Cs, etc.), the discrepancies today tend to diminish, and the burnup of most of the Swedish fuel elements is less than 40 GWd/t (see Figure 3).

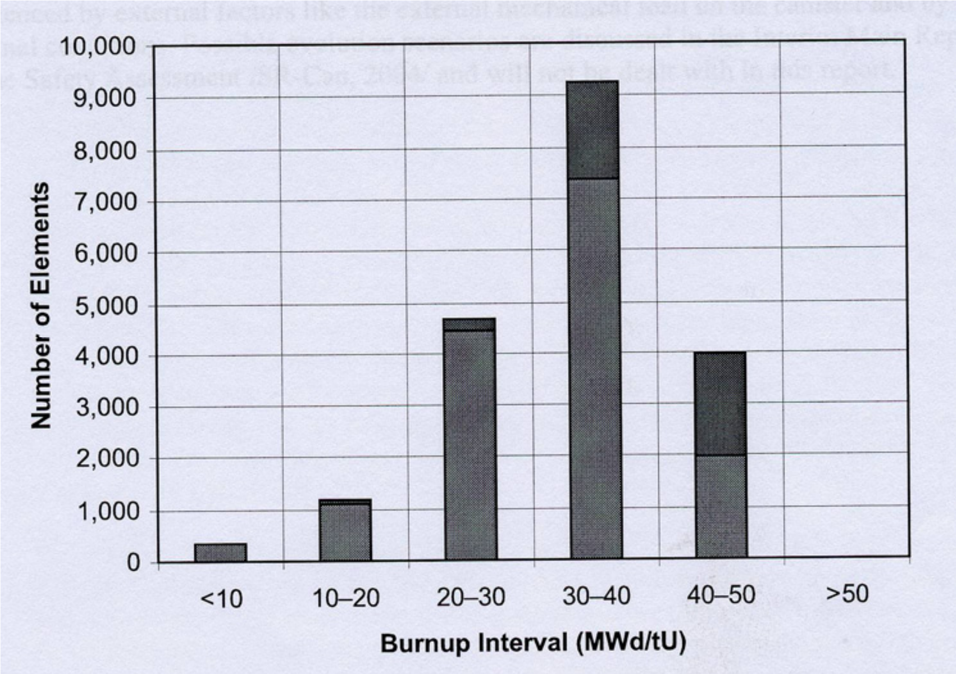

Figure 3: Distribution of spent fuel elements versus burnup

It would be interesting to incorporate the differences between the two approaches into integration calculations to estimate their real impact on ultimate dose release. The instant release inventories using the second approach are currently being revised (within the European NF-PRO project) and will then be usable as a basis for these calculations. Unlike the actinides, with their low solubility limits under reducing conditions, changes in the source term for long-lived fission products can clearly have an impact.

3.1.3 Fuel Matrix Alteration

With regard to fuel matrix alteration, it is important to emphasise that the proposed release fractions — between 10^{-6} and 10^{-8} per year for the spent fuel matrix after disposal — are reasonable and realistic. Conversely, the rationale concerning uncertainty management and the reasons for this choice are currently weak (p. 45, SKB (2006b)):

> *"....the model is based on empirical data from a number of experiments performed under redox conditions similar to those expected in a repository at the time when water contacts the fuel".*

If a predictive model claims long-term validity, it cannot be supported only on the basis of experimental data. This is a general comment on the approach adopted by SR-Can (and also applies to the instant release inventories). The available reports do not place sufficient emphasis on the alteration (or evolutionary) mechanisms and on understanding these mechanisms to substantiate the design options. This is relatively surprising for the "matrix" source term, since numerous modelling approaches have been developed in Sweden by SKB (the driving force in this area) and under European contracts (SFS[4] in particular).

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[4] SFS: Spent Fuel Stability under repository conditions.

Although every model has its limits and is based on debatable hypotheses, it is important to refer to them in order to specify and reiterate the confidence level on the selected options. Several different levels of modelling are available today concerning the matrix (scientific models covering oxidising dissolution in various degrees of detail and more operationally oriented); they have been a subject of discussion and have reached a degree of international consensus, and it would be unfortunate not to refer to this consensus within the scope of a briefing document.

Beyond the description and the rationale, and again to support the selected options, it now appears that the effect of alpha radiolysis of water on oxidising dissolution of the fuel matrix will have little or no impact on alteration at low flux levels (after 10,000 years). This implies not only that some environmental parameters — including the presence of hydrogen produced by canister corrosion — can be considered as additional safety-related factors, but also that the effects of secondary phases containing U(IV) (coffinite, etc.) on the stability of the fuel matrix merit further investigation.

3.2 Radionuclide Solubility Limits

3.2.1 Specific Issues on Actinide Solubility

Temperature dependence of actinide solubility and speciation

Duro et al. (2006a) state (p. 15):

> "*The reference temperature has been fixed at 15°C, which is the average expected in groundwater at the repository depth*".
>
> "*Due to the presence of the waste, it is foreseen that temperature can reach up to 100°C. This thermal effect can have some effect on the solubility of the radioelements of interest. Solubility calculation at temperatures different from 25°C require data on reaction enthalpy. This type of data is not always available for all the aqueous complexes and solids relevant in our study (for explanations see Duro et al. 2005/). These data gaps are not very relevant to assess a change of temperatures from 25°C to 15°C, but it can importantly affect the calculations at 100°C.*"

The approach described above is less than ideal. The authors insightfully recognise that temperatures up to 100°C can be expected near the waste package, which in turn may substantially affect radionuclide solubility and even speciation. This is a highly important issue that cannot be dismissed by stating "*given the difficulty in assessing the temperature effect at 100°C, we have preferred to report only solubilities calculated at 15°C.*" It is advisable that this very important issue of changing radionuclide solubility with increasing temperature is properly addressed. Examples from the literature could be used to address the general nature of this problem and to devise a strategy on how to properly deal with this issue. Ignoring it is not acceptable for such a key issue in safety assessment.

Plutonium (III) Phosphates

The authors identify the importance of dissolved phosphate for the solubility of Pu(III) (Duro et al., 2006a, pp. 86-87):

> "*One of the main uncertainties in the assessment of the behaviour of Pu is the concentration of phosphate in the system (see discussion in Chapter 5). Phosphates have been identified to form stable Pu(III) solid phases leading to lower Pu concentrations. Therefore, a phosphate of Pu(III) might be the predominant aqueous species in neutral and reducing waters if phosphates were present. The lack of phosphate measurements in the reference groundwater, thus, might pose a limitation in the assessment of a proper solubility limit for this element*."

This lack of phosphate measurements for the Pu(III) solubility is clearly recognized. The value for solubility of $PuPO_4 \cdot xH_2O$, is used which is in reasonable agreement with the value for the $AmPO_4 \cdot xH_2O$, $\log K^0 = -5.23$. However, given the much lower solubility of the $PuPO_4 \cdot xH_2O$ solid when compared with $Pu(OH)_4(am)$, $Pu(OH)_3(cr)$, and $PuO_2(OH)_2 \cdot 2H_2O$, as shown in Duro et al. (2006a, Figure 6.52), this phosphate may be the truly solubility-limiting solid for plutonium under reducing conditions. The existing solubility data for this solid were not accepted by the NEA Data Base "because of possible experimental shortcomings" (OECD/NEA, 2001, p. 415). It is highly recommended to measure the Pu(III) phosphate solubility in the saline reference water and determine its exact composition and crystallinity. Formation of (a) mixed phase solid(s) cannot be excluded. This would further change the thermodynamic approach for plutonium solubility.

Three Pu(III) and one Pu(V) aqueous phosphate complexes are reported by Duro et al. (Duro 2005, pg. 147, Table 18-7). The complex stability constants for these species were derived through estimates "*from correlation with An(III)*". Unfortunately, there are very little data on An(III) phosphate species in the literature, and a more detailed explanation about the selection process should be given before these data are accepted into the SKB data base.

Actinde(IV) Polymer/Intrinsic/Eigencolloid Formation

It is surprising that polymer/eigencolloid formation as a source term for plutonium, especially Pu(IV), is not considered in Duro et al. (2006a). The authors state (Duro et al., 2006b, p. 176):

> "*Metal ions with high charge, such as Al^{3+}, Fe^{3+}, Pu^{4+}, Th^{4+} etc, are strongly hydrolysed at pH values prevailing in groundwaters. If present in large concentrations, the hydrolysis products contain several metal ions (polynuclear) and by aggregation they can form colloidal particles. In the case of plutonium, the formation of colloids is practically irreversible. However, the concentration levels needed for the formation of actinide colloids will never be reached in the geosphere.*"

Colloid formation, either via the formation of intrinsic/eigen/real/ colloids or as pseudocolloids via the attachment of soluble plutonium species to groundwater colloids, may potentially play an important role in plutonium transport. This topic has now been researched for nearly 30 years in conjunction with plutonium solubility, speciation and transport, and plutonium has been observed in groundwaters near nuclear event sites. Pu(IV) polymer/eigencolloids can form at low pH values and low concentrations, and it has recently been demonstrated to account for the large discrepancy in measured solubility constants for Pu(IV) (Knopp et al., 1999; Neck et al., 2007). A very recent publication shows that Pu(IV) polymers are not polymeric at all, but exist as nanoclusters of crystalline PuO_2 (Soderholm et al., 2007). These finding clearly demonstrate that the plutonium "community" needs to revise its present understanding that Pu(IV) polymer formation occurs through the condensation of the hydrolytic species, $[Pu(OH)]^{(4-n)+}$, to yield hydroxo-bridged species, Pu-OH-Pu, that further condense with time to produce amorphous or poorly crystalline mixed Pu oxide hydroxides.

SKB should delineate how it plans to address this issue for plutonium and other tetravalent actinide species in its solubility assessment.

3.2.2 Treatment of Thorium Chemistry in SKB Report TR-06-09

Thorium as a fission product is of minor importance in terms of the total radiation generated in nuclear waste. As an estimate for its abundance in used nuclear fuel, Table 4-2 in SKB TR-06-09 (SKB, 2006a) gives an inventory of Th-234 of 1.17×10^{10} Bq per ton of uranium using a burn-up of 38 MWd per kg uranium, after forty years of operation. However, because Th-234 has beta-decay with a lifetime of only 24.1 days, the main activity contribution is expected to be due to Th-230. The activity given for Th-234 in Table 4-2 is comparable to that of Pu-238 (9.45×10^{13} Bq) and Pu-240 (1.18×10^{13} Bq).

Nevertheless, thorium is a relevant element in the spent nuclear fuel, with major contributions to total dose over a period of more than 1,000,000 years after discharge from a reactor. Thus, the treatment of thermodynamic data for Th and application of these data in the derivation of solubility limits are of considerable interest. With currently accepted models, the solubility limit is established from the solubility-limiting solid phase (which does not necessarily need to be the thermodynamically most stable phase) and the relevant metal ion complexes in aqueous solution under given physicochemical conditions. The solubility product determines the concentration of uncoordinated (hydrated) metal ions, while the solution species stabilise the metal ion in solution by forming additional species with the metal ion. Thus, a solubility limit is an intricate heterogeneous equilibrium between a solid phase and various solutions species – the heterogeneous equilibria are coupled by the uncoordinated (hydrated) metal ion. Thus, for a critical assessment of the solubility limit, both equilibria need to be analysed carefully.

Carbonate is a readily available ligand in natural aqueous systems for actinides like thorium. The carbonate species, CO_3^{2-}, is a hard acid within the Pearson hard and soft acids and bases (HSAB) concept while actinides are hard bases. In aqueous solution, i.e. natural groundwaters, hydroxide competes with carbonate for actinide ions. The concentration ratio of hydroxide and carbonate depends on, among other minor factors like ionic strength, the CO_2 partial pressure (pCO_2). The CO_2 partial pressure in groundwaters varies considerably between 0.03 % (atmospheric CO_2 partial pressure) and 10 %. Higher CO_2 partial pressures may occur due to dissolution of carbonate rock in the subsurface by acidic groundwaters. The main reason for increased CO_2 partial pressures in groundwaters is biological activity, mainly plant roots which release CO_2 into the upper soil layers. Recharging groundwater, e.g. from meteoric events, percolates through these upper soil layers absorbing CO_2. The CO_2 partial pressure of a groundwater can be estimated from the ratio of HCO_3^- and pH according to Eq. 2:

$$\lg [HCO_3^-] = \lg K + \lg pCO_2 + pH \qquad [2]$$

where lg X is the decadic logarithm of X and K is a constant. Hence, an estimation of the solubility limits of Th requires knowledge of three thermodynamic quantities:

- The solubility product of the solubility limiting Th solid phase;
- The relevant hydrolysis reactions of Th; and
- The complexation behaviour of Th with carbonate.

Our knowledge of each of these three quantities is, however, rather poor, as very few studies have been performed in the system Th-H_2O-CO_2 and the stoichiometry and magnitude of the stability of Th hydrolysis species remains unclear (see below). Solubility studies suffer because of the formation of a solid with poorly crystalline structure and varying solubility. Th(IV) is partially hydrolysed at very low pH, at a value around 1. In solubility studies, the observed slope in the solubility curve (log [Th] vs. -lg $[H^+]$) differs clearly from a value of -4 which is expected for solid $Th(OH)_4$ or ThO_2. Colloid formation is commonly credited as the reason for this observation.

In the SKB report TR-06-17 (Duro et al., 2006b) dealing with the thermodynamic database, the authors state (p. 81):

> "*This fact has lead to the different solubility values recommended in the literature for the solubility of* $Th(OH)_4(s)$*. This issue has received special attention during the last years and several publications have dealt with the determination of a solubility product able to explain the concentrations of this element in equilibrium with the solid hydroxide in the whole range of pH, what has resulted in very discrepant values*".

In the following paragraph, the authors also state:

> "*According to the revision in the NAGRA-PSI 01/01 database there are several authors.....confirming that the solubility of thorium is well described by using a solubility product constant* $\log K^o_{s,4} = -8.5$*…*".

Given such widely varying solubilities, the procedure by which a consistent solubility product is derived, or at least greater justification for the selected value, should be provided.

Ample thermodynamic data on Th hydrolysis species are available in the literature, the preferred experimental method of determination being potentiometric titration. Nevertheless, the reported hydrolysis constants and hydrolysis species are rather variable. There is currently no trackable way to resolve the wide variety of Th hydrolysis species proposed in the literature, proposed mainly on the basis of 'best-fit' models with no attempt to identify and apply criteria to model selection (e.g. statistical χ^2 or F tests). Any selection of species is, therefore, necessarily subjective, and a solubility limit will carry a large modelling uncertainty. However, such a large uncertainty is neither expressed nor discussed in TR-06-17 (Duro et al., 2006b) or TR-06-32 (Duro et al., 2006a).

The situation concerning variability in underlying data is even less satisfactory for thermodynamic data relating to the interaction of Th with carbonate. The early work of Joao et al. (1987) reports a formation constant for $Th(CO_3)_5^{6-}$ in NH_4NO_3 medium at high ionic strength from solvent extraction. Later work by Östhols et al. (1994) and Felmy et al. (1997) introduced mixed Th hydroxycarbonato species. Therefore, solubility limits of Th are evaluated on the basis of the pure carbonato species $Th(CO_3)_4^{4-}$ and $Th(CO_3)_5^{6-}$ together with the mixed species $Th(OH)_3CO_3^-$ and $Th(OH)_2(CO_3)_3^{4-}$. The reason for introducing such species is not discussed in Duro et al. (2006b) but could be a result of curve-fitting optimisation. It should be noted that the species $Th(OH)_2(CO_3)_3^{4-}$ is, under curve-fitting aspects, equivalent to $Th(CO_3)_4^{4-}$. This is a consequence of Eq. 2, giving a linear relationship between pH and $lg[CO_3^{2-}]$ under a fixed CO_2 partial pressure.

It should be noted that in addition to the four carbonato/hydroxycarbonato species, seven pure hydrolysis species have been proposed. Three of these are oligomeric metal species. Given the rather large scatter of Th solubilities and the strong interference of colloids, these eleven species will pose almost no constraints on the interpretation of almost any solubility data observed. This statement holds more true, as Duro et al. (2006b) assign rather large errors (the value following the '±' sign is not clearly defined) of up to ±2.0 on a logarithmic scale.

Duro et al. (2006b) base their recommendations largely on the Swiss NAGRA thermodynamic database. A more recent study by Altmaier et al. (2005) on the solubility of Th in carbonate solutions was cited but neither discussed nor taken into account for the SKB database. These latter authors propose $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)(CO_3)_4^{5-}$ species in addition to the $Th(OH)_2CO_3°$, $Th(OH)_3CO_3^-$ and $Th(OH)_4(CO_3)^{2-}$ species. Diagrams show that the solubilities of Altmaier et al. (2005) differ clearly from the data reported by Östhols et al. (1994).

Thus, the current picture of Th complexation in solution and Th solid phase formation under conditions of natural aqueous systems, is rather inconsistent. A large part of the literature concerning thermodynamic data of actinide behaviour in aqueous solution focus on supporting the quality of the data set while not addressing relevant influences from measurement uncertainties (Meinrath & Schneider, 2007). Clearly, a simple value for a solubility limit for an element as given in TR-06-09 (SKB, 2006a) is inappropriate without a more detailed discussion. A statement on a meaningful uncertainty range (as a confidence range or, better, as a complete uncertainty budget, as discussed in Appendix A) should be provided.

By way of example, Figure 4 shows a speciation calculation based on the data of Altmaier et al. (2005), where the values immediately following the '±' sign in Altmaier et al. (2005) are used as 68 % confidence limits. Clearly, there are significant differences in the resultant speciation at the 68% and 95 % confidence limits, when compared to the median values. ThO_2(cr) from SKB TR-06-17 (Duro et al., 2006b) is assumed as the solid phase with its respective solubility product. The large uncertainty of $\lg {}^*K_s$ (1.80 ± 1.3) is not taken into consideration. The CO_2 partial pressure is assumed to be 0.03% (atmospheric). The speciation differs somewhat from the assumptions given in Duro et al. (2006b).

$ThCO_3(OH)_3^-$ is stated in TR-06-17 (Duro et al., 2006b) as the only dominant species, but the CO_2 partial pressure in the reference groundwater was not specified. At higher CO_2 partial pressures, carbonato species may become more prominent. This question, however, is too complex do be addressed in this report. A more detailed discussion might be warranted.

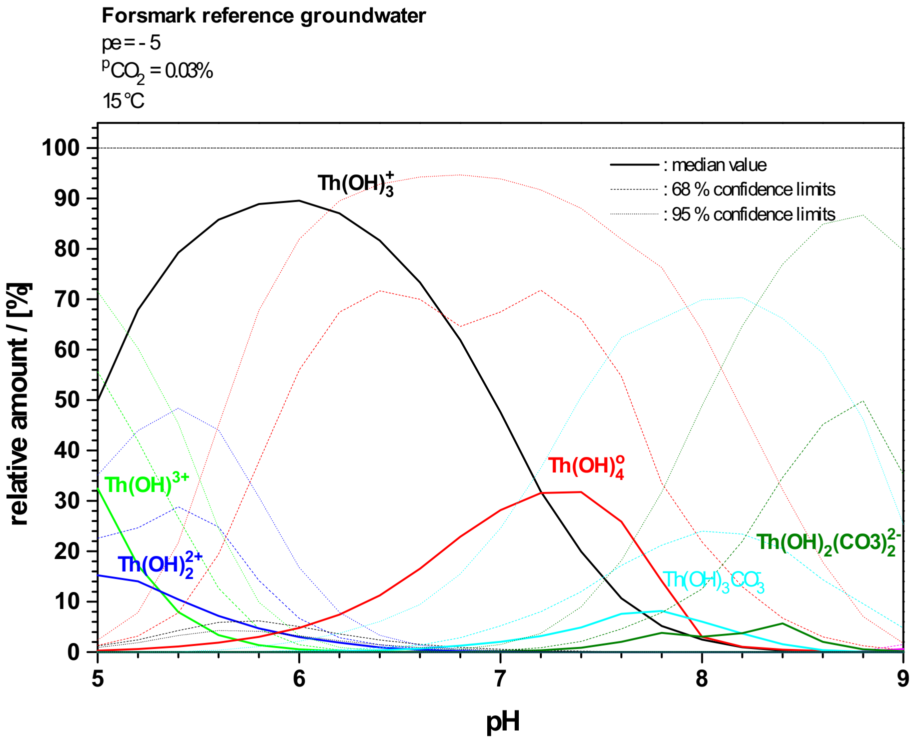

Figure 4: Th(IV) species distribution simulated using the LJUNGSKILE code (Ödegaard-Jensen et al. (2004)). The diagram gives the median values (solid lines), 68 % confidence limits (dashed lines) and 95 % confidence limits (dotted lines). At pH 7, the dominating species is either Th(OH)3+, Th(OH)4° or Th(OH)3CO3-. The latter is the predominant species given in TR-06-17 with a maximum contribution (95 % confidence) of about 20 %. The upper 68 % and 95 % confidence limits coincide.

3.2.3 Co-precipitation of Alkaline Earth Metals

SKB has noted that taking into account co-precipitation of Ra-226 would have a strong impact on dose calculations, so that the issue of whether co-precipitation occurs is an important one to address.

There are a number of aspects of the repository that are likely to affect the geochemical behaviour of the alkaline earth metals. The inventory of BWR fuel given in TR-06-09 (SKB, 2006a; Table 4.2) indicates that Sr-90 and Cs-137 have high activities 40 years after operation. In addition, in the scenario of a growing pinhole failure in the canister, Ra-226 has the highest long-term near field release. Considering that Cs-137 decays to Ba-137, the chemical inventory in the near field of the repository will contain Sr, Ba and Ra.

The groundwater chemistry scenarios in the vicinity of the repository indicate that the solubility of the alkaline-earth metals, Sr, Ba and Ra, is likely to be controlled by sulfur, present as sulfate. The modelling carried out by Duro et al. (SKB, 2006b) supports this statement indicating that these metals will be controlled by the solubility of celestite ($SrSO_4$), barite ($BaSO_4$) and $RaSO_4$(s), respectively.

The modelling performed by Duro et al. (SKB, 2006b) to determine the solubility controlling phases was subject to a number of constraints, which are particularly important in assessing the likely behaviour of the alkaline-earth metals in the repository following canister failure. These constraints include (SKB, 2006b):

- The formation of amorphous, or less crystalline, phases has been accepted. As indicated by Duro et al. (SKB, 2006b), the Ostwald Step Rule postulates that the phase with the highest solubility will precipitate first. Nucleation of more soluble phases is kinetically favoured over less soluble phases due to a higher surface area to particle mass ratio. Thus, the precipitation of amorphous phases will be favoured over crystalline phases.
- It is assumed that precipitation of only pure solid phases occurs. That is, mixed metal precipitation, such as co-precipitated phases like $(Ba,Ra)SO_4$, is not considered. The modelling that was performed to determine the solubility limiting phases only considered the near field of the repository, where the only mineral phases likely to be present are those that either result from the corrosion of the canister (SKB, 2006b) or are produced from precipitation of the radionuclides in, or decay products from, the fuel inventory.
- The system is not considered to be in equilibrium with respect to the sulfate/ sulfide redox couple. It was argued that in the absence of sulfur reducing bacteria (SRB), the reduction of sulfate to sulfide is a very slow process and since no clear evidence has been demonstrated for the presence of SRB, the establishment of equilibrium for this redox couple is unlikely.

All of these constraints are considered to be conceptual uncertainties (see Appendix A) by Duro et al. (SKB, 2006b) in the solubility calculations they performed. All three constraints (uncertainties) have an important bearing on the predicted solubility of the alkaline-earth metals, Sr, Ba and Ra. It has been well established in the literature, however, for different scientific fields (Baraniak et al., 1999; Martin et al., 2003; Sinclair et al., 2005; van Beek et al., 2007) that co-precipitation of the alkaline-earth metals occurs and that these precipitates are often amorphous. Further, it has also been shown that the aqueous concentration of the metals can increase substantially in the presence of SRB.

Radiobarite Formation in Seawater

The behaviour of Ba and Ra in seawater has been recently studied by van Beek et al. (2007) in surface waters (20 m depth) of the Sargasso Sea (Atlantic Ocean) down to depths below 4000 m. Both dissolved and particulate concentrations of Ba and Ra were found to be consistent with previous studies of seawater (Ku et al., 1980; Bishop, 1988; Kim et al., 2003; Foster et al., 2004) in the world's oceans. Barite is considered as the main carrier of Ba and Ra in non-lithogenic sediments, the main form of sediments above 4000 m. In addition, acantharians are known to occur in the near surface regions (above 150 m) of the Sargasso Sea. Acantharians are protozoa that make their skeleton from celestite. Thus, particulates carrying Sr, Ba and Ra in the ocean consist of a source mixture from both celestite and barite.

Barium and ^{226}Ra show similar behaviour in both the water column and in particulates as a function of depth, as is shown in Figure 5, having a ratio of 2.4 ± 0.3 dpm/μmol in seawater and 2.8 ± 0.4 dpm/μmol in particulates. The $^{228}Ra/^{226}Ra$ ratio in particulates was also found to be almost identical to the ratio in the seawater at the same water depth. Barium is almost absent from particulates in the upper water column (20 m) but increases considerably just below this depth, suggesting that the dissolution of celestite from the acantharians provides a mechanism for barite formation in shallow waters (van Beek et al., 2007).

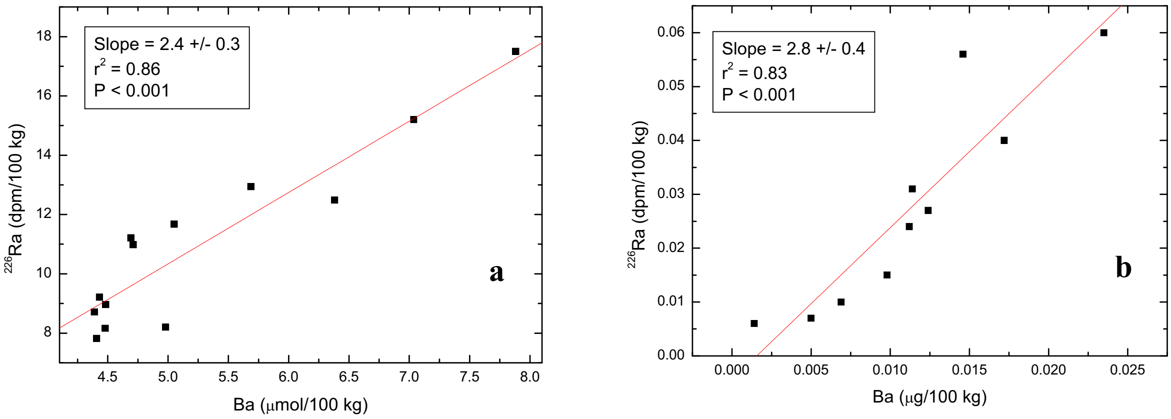

Figure 5: Relationship between Ba and ^{226}Ra concentrations in (a) seawater and (b) sinking particulates in the Sargasso Sea (20-4250 m) (from van Beek et al., 2007).

The relationship between Ba, ^{226}Ra and ^{228}Ra in particulates and seawater tends to suggest that exchange occurs relatively rapidly between seawater and the particulates. In general, the concentration of Sr, Ba and Ra associated with the particulates tends to decrease with increasing depth, suggesting that the sulfate minerals in which they are contained are dissolving. This is supported by an increase in the dissolved concentration of Ba and ^{226}Ra with increasing depth. The close similarity between the seawater and particulate ^{228}Ra/^{226}Ra ratios tends to suggest that the sulfate containing particulates lack crystallinity, supporting rapid exchange between dissolved and particulate Ra. The sulfate particulates are therefore likely to be amorphous. However, the presence of Sr in the particulates, at concentrations similar to those of Ba, leads to a phase which is undersaturated with respect to barite. Further, the ratio of 4.6 nmol ^{226}Ra/mol Ba in seawater indicates that Ra is also undersaturated with respect to $RaSO_4$(s) by many orders of magnitude.

Radiobarite in Uranium Mill Tailings

The behaviour of Ba and ^{226}Ra in uranium mill tailings has been studied by a number of workers (Martin et al., 2003; Sinclair et al., 2005; and references therein). Martin et al. (2003) demonstrated a strong correlation between the bottom water and porewater concentrations of Ba and ^{226}Ra, as illustrated in Figure 6. The ^{226}Ra/Ba ratio is two orders of magnitude higher than found in seawater due to the larger inventory of ^{226}Ra in the tailings. Conversely, Sinclair et al. (2005) found no relationship between ^{226}Ra and either Ba or Sr. It was believed that ^{226}Ra was associated with a non-barite host phase in the tailings studied in this latter work which was used to explain the lack of a relationship.

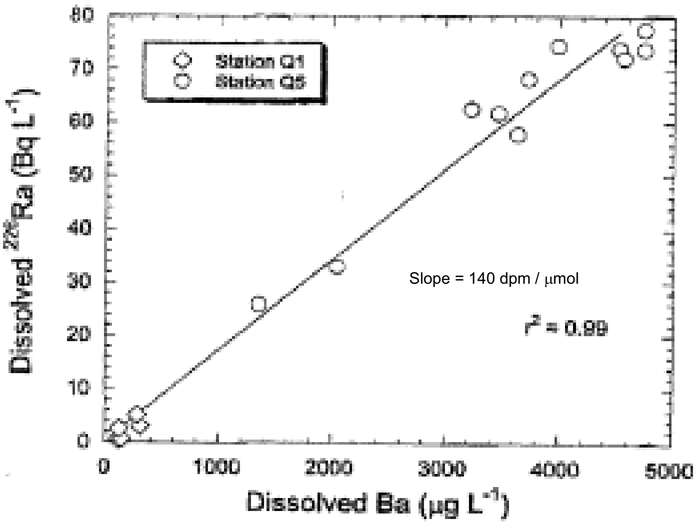

Figure 6: Relationship between ^{226}Ra and Ba concentrations in bottom water and porewater in uranium mill tailings (from Martin et al., 2003).

Solubility calculations carried out by Martin et al. (2003) indicated that Ba was oversaturated with respect to barite in the porewaters of the tailings by about 1.5 log units. Sinclair et al. (2005) found a similar behaviour and found evidence for microcrystalline barite in the tailings, as shown in Figure 7. These results indicate that the Ba concentration is controlled by a poorly ordered, amorphous barite phase. Where Ra is available in the porewaters, its concentration is also controlled by the same phase. In the tailings studied by Martin et al. (2003), even though the ^{226}Ra/Ba ratio is two orders of magnitude higher than was found in seawater, Ra still remains undersaturated with respect to $RaSO_4$(s).

The study of Martin et al. (2003) also demonstrated that under reducing conditions SRB are effective in dissolving barite, thereby increasing considerably the dissolved Ba and ^{226}Ra concentration. This field based evidence for the microbial-driven release of Ba and Ra is consistent with laboratory studies which have demonstrated Ra release associated with both U mill tailings and (Ba,Ra)SO_4 treatment sludges (Martin et al., 2003). Thus, dissolved concentrations of Ba and ^{226}Ra will be controlled by the solubility of an amorphous barite phase unless there is sufficient SRB activity to cause sulfate reduction.

Inference for the Near Field Solubility of Alkaline Earth Metals

Evidence from seawater and uranium mill tailings studies suggests that the alkaline earth metals are likely to form an amorphous but mixed sulfate phase in the near field of the repository which will control the solubility of Sr, Ba and Ra. Although the phase will not be a pure mineral, published data suggests that dissolved Ra and possibly Ba will be undersaturated with respect to their respective pure mineral phases, $RaSO_4$ and barite, in the case of Ra by many orders of magnitude. Thus, the decision by Duro et al. (SKB, 2006b) to use the pure sulfate mineral phases of these two elements to control the solubility is conservative, and a sound choice. Conversely, ^{90}Sr has a high activity in the BWR fuel 40 years after operation and Sr is also present in the reference groundwater. Duro et al. (SKB, 2006b) indicate that Sr will be controlled by celestite, however, it is plausible that the actual phase that forms is an amorphous form of $SrSO_4$(s) that may be up to 1.5 log units more soluble. If such a phase were to form, it is quite possible, therefore, that a different mineral phase could control the solubility of Sr, potentially strontianite ($SrCO_3$(c)). However, this is not expected to have much effect on the overall solubility of Sr in the reference groundwater. Nevertheless, the choice of pure celestite to control the solubility of Sr by Duro et al. (SKB, 2006b) may not be conservative and it is suggested that sensitivity analyses are conducted by SKB using a more soluble $SrSO_4$ phase.

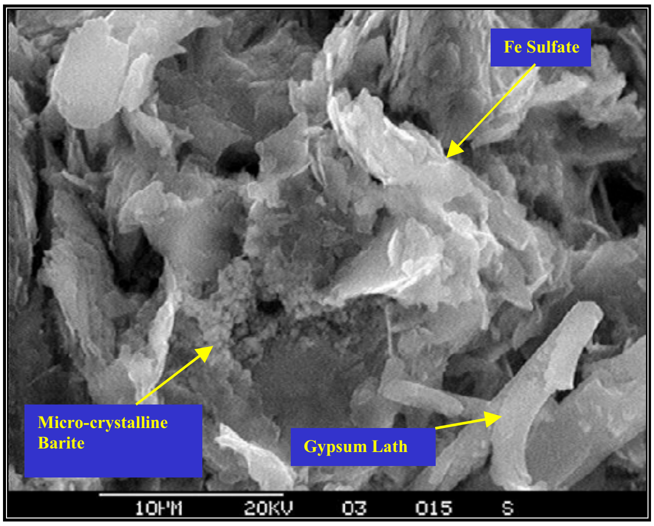

Figure 7: Scanning electron microscope image of uranium mill tailings indicating the presence of a poorly crystalline barite phase (from Sinclair et al., 2005).

There is also clear evidence from uranium mill tailings studies (Martin et al., 2003) that in the presence of SRB barite can dissolve releasing Ba and Ra. It has been argued by SKB (2006a) that microbial activity is unlikely on or very near the copper surface of the canister over the time the interface between the canister and buffer is wet because the full swelling pressure has developed. It is also suggested (SKB, 2006a) that while pyrite is present in the buffer, it maintains a concentration limit on sulfide, largely preventing it from entering and passing through the buffer, thereby minimising the corrosion of the canister from sulfide present in the groundwater.

Sulfide concentrations in groundwater are frequently below the detection limit (ca. 2×10^{-7} mol/L ≡ 0.01 mg/L), but concentrations near 10^{-4} mol/L have been measured in groundwater from the Laxemar area and near 10^{-5} mol/L in the Forsmark area (SKB, 2006a). This latter concentration is much larger than those predicted by Duro et al. (SKB, 2006b) for Forsmark groundwater, namely 1.27×10^{-11} mol/L, although the measured data may be related to a differing redox condition than that modelled by Duro et al. (2006b). In the absence of microbial activity, SKB (2006a) has determined that the rate of corrosion is likely to be less than 1 mm in 100,000 years. This calculation is based on two assumptions: (a) microbial activity is absent and (b) pyrite in the buffer will control the sulfide concentration. Neither of these assumptions may be correct. Sinclair et al. (2005) demonstrated the formation of an amorphous form of mackinawite (FeS(s)) in uranium mill tailings even in the presence of pyrite, indicating a much higher dissolved concentration of sulfide than if it was in equilibrium with pyrite. There are also some studies (for example, Roffey, 1990) that indicate the presence of microbial activity in a radioactive waste repository setting.

The modelling undertaken by Duro et al. (2006b) indicates that the sulfide concentration is much larger for a saline water intrusion (0.0356 mol/L). Modelling indicated that this concentration would not be affected by the presence of pyrite or FeS(s) and both of these mineral phases would be undersaturated. The saline water intrusion scenario in SR-Can (SKB, 2006a), however, assumed the groundwater to be in equilibrium with amorphous FeS(s). This latter assumption is in accord with the laboratory and modelling results of Sinclair et al. (2005), where the *pe* was -3.76 and barite was undersaturated. Nevertheless, there would appear to be remaining uncertainty with respect to the potential sulfide concentrations that could develop in the near field of the repository, either as a result of saline intrusion or from microbial activity. SKB should focus on sulfide biogeochemistry to obtain additional information on the potential effect that (a) sulfide could have with respect to canister corrosion and/or (b) reducing groundwater may have in dissolving alkaline earth sulfates.

3.3 Radionuclide Migration through the Buffer

Once a canister fails, non-volatile radionuclides will eventually be released from the fuel matrix into solution. Assuming that the bentonite buffer remains in place up to and beyond the time of canister failure[5], radionuclides will migrate through the buffer by diffusion, whereby the concentration of the diffusing species, C_p, is given by the following equation under conditions where sorption, if it occurs, is linear:

$$\partial C_p / \partial t = D_e / (\varepsilon + K_d \rho_d) \partial^2 C_p / \partial x^2 = D_a \partial^2 C_p / \partial x^2 \qquad [3]$$

where D_e is the effective diffusion coefficient [m^2/s], K_d is the distribution coefficient for sorption [kg/m^3], ε is the diffusion porosity [-], ρ_d is the dry density of bentonite (kg/m^3), and D_a is the apparent diffusion coefficient [m^2/s], i.e.

$$D_a = \frac{D_e}{\varepsilon + \rho_d K_d} \qquad [4]$$

COMP#23 is SKB's near-field migration code used to calculate radionuclide diffusion through the buffer. The code assumes constant values of effective diffusivity (D_e, m^2/s), diffusion-available porosity (ε) and distribution coefficient (K_d, m^3/kg) for each near-field compartment. Sorption and K_d measurements are discussed further in Section 4.2.

Eq. 4 shows that D_a is a 'lumped' or composite parameter. For strongly-sorbing radionuclides, D_a is difficult to measure directly experimentally, because of the long times required for radionuclides to diffuse through a sample of compacted bentonite. Thus, Eq. 4 indicates the need for a consistent set of data. In general, diffusion coefficients (and associated K_d values) need to be extracted from raw experimental data using some form of model. Under these circumstances, interpretation of experimental results must be treated with caution. Most importantly, a consistent set of data must be used for each radionuclide.

There is not yet a consensus concerning how buffer porewater composition should be determined. Because porewater composition in compacted bentonite cannot be measured in situ, and there are doubts concerning the representativeness of extracted porewaters, chemical

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[5] Erosion of the buffer under certain conditions is discussed elsewhere (SKI, 2008).

composition must be determined by geochemical modelling using some form of bentonite–water interaction model. For such modelling, there are essentially two approaches which result in a different pH for the resultant porewaters. The buffer system is treated either as:

- A closed system, as assumed by Ochs (1997) for SR97 and Ochs and Talerico (2004) for SR-Can, in which case the $p\mathrm{CO}_2$ is controlled 'internally' by bentonite-water interactions, or
- An open system, in which case the $p\mathrm{CO}_2$ is controlled by the corresponding level in the host rock.

The primary effect of the $p\mathrm{CO}_2$ is in the equilibrium pH obtained: around 7 in the case of a closed system, and at least 1 unit higher when the system is not closed and CO_2 is allowed to escape. Such differences in pH can significantly affect the extent of sorption, particularly of those radionuclides that sorb by surface complexation.

SKB's primary report dealing with diffusion of radionuclides through the buffer and associated recommendations concerning diffusion parameters, is provided by Ochs and Talerico (2004). Buffer diffusion data are also discussed in the Data Report for Sr-Can (SKB, 2006b). Review comments were provided in SKI (2007) following a 2006 Workshop from which a number of questions, primarily for clarification, were submitted to SKB on the diffusion report of Ochs and Talerico (2004). Responses to these questions (Ochs, 2006a) were subsequently received by SKI and so comments provided here are intended to supplement the previous review.

With a view to obtaining a self-consistent set of input parameters, the approach of Ochs and Talerico (2006) for most radionuclides, with the exception of anions and Cs (discussed below), was to apply element-specific K_d values in conjunction with the effective diffusion coefficient, D_e, for tritiated water (HTO). Thereafter, D_e, ε and K_d were used to generate an apparent diffusion coefficient (D_a) via equation [3], which could be compared with experimental determinations of D_a, where available, as a "consistency check".

The arguments made by Ochs and Talerico (2004) as a basis for adopting a D_e for HTO to be used for most nuclides, are reasonable and supported, where possible, by additional data, although it could be argued that experimental measurements of D_e for different radioelements are 'lost data'. However, reference to previous assessments indicates that D_e values for different nuclides, based on experimental measurements, range over about an order of magnitude, anions excepted. Thus, the focus of the effort by Ochs and Talerico (2004) is rightly on the selection of appropriate K_d values.

With regard to sorption and the experimental determination of K_d values for the sorption of radionuclides on bentonite to support diffusion data, a key issue has been how representative the K_d values obtained using bentonite in batch sorption experiments are of repository conditions, where the bentonite is compacted. With regard to differences in measured K_d values between compacted and dispersed bentonite being due to the aqueous rather than the solid phase, the authors cite a variety of sources in which the same specific surface area (N_2-BET value) is obtained for both aggregates, as evidence for identical sorption properties of the solid phase. The difference, then, is primarily one of solid/water ratio, with the ratio being substantially smaller in the former case. However, the consensus of researchers involved in sorption experiments, represented by the NEA Sorption Working Group (NEA, 2005), is that this difference in solid/water ratio is reflected by differences in the chemical composition of the porewater, rather than behaviour of the solid phase. The focus, therefore, is on an accurate characterisation of bentonite porewaters *under repository conditions*.

Variations in porosity and D_e (HTO) as a function of bentonite density have been well demonstrated. For anions, selection of a self-consistent dataset for D_e and ε was shown to be "ambiguous". Thus, Ochs and Talerico (2004) select the "best" D_e value plus uncertainty without considering ε or α (capacity factor), then select the best ε and α to go with the selected D_e value. The reduction in diffusion porosity for anions is based on Swiss experiments that were conducted specifically to separate out the effects of D_e and porosity in the interpretation of their data, and so are directly relevant to the choices made – reduction in porosity by a factor in the range 1.8-3.5. Ochs and Talerico (2004) use these values to determine bounding limits of porosity, with a selected recommended factor of 2.5 leading to a porosity of 0.17.

There are clear improvements in the 'derivation' of parameters relevant to diffusion through the bentonite buffer, mainly in terms of documentation and transparency, both of which allow an assessment of SKB's treatment of uncertainties. For example, one issue that arose from the previous assessment was the lack of a reference bentonite porewater composition used as a basis for one source of K_d recommendations. In the current report (Ochs and Talerico, 2004), several reference groundwater compositions (scenario-specific) are used to determine resultant bentonite porewater compositions. While there are some differences in groundwater compositions between this work and that of Duro et al. (2006a), the differences are small and attributed to the different timeframes for carrying out each piece of work in the context of the finalisation of reference waters. Presumably, the subsequent safety assessment SR-Site will be able to avoid such inconsistencies.

The supporting data and their interpretation, which are provided as the basis for recommending porosity and D_e (HTO) values corresponding to the reference dry density of bentonite are well documented. The corresponding uncertainties (regression analysis) are significantly less than those associated with K_d recommendations for different nuclides. The challenge has clearly been to recommend K_d values that are representative of bentonite porewater composition under repository conditions. In an effort to provide greater transparency than in previous assessments, Ochs and Talerico (2004) provide clear details of their K_d derivation process.

A relatively small number of batch sorption datasets were used as the basis for the different K_d recommendations. The rationale for using such a restricted number was to try to match bentonite compaction and porewater composition as closely as possible or, where compaction and porewater composition were not the same, to have sufficient documented experimental information to be able to establish trends as a function of compaction density as well as allowing extrapolation of the K_d data obtained in the sorption experiments to expected in situ conditions.

The extrapolation procedure of Ochs and Talerico (2004) is, in fact, rather 'convoluted' but well documented and transparent. The procedure takes into account those differences in conditions under which sorption experiments were carried out, that are likely to affect measured K_d values significantly, viz.

- Solid phase: cation exchange capacity (CEC), this parameter being used as the proxy for sorption capacity;

- Aqueous phase: pH, speciation, presence of competing ligands, in particular carbonate.

The predicted influence of each of the above 'parameters' was treated separately in terms of a conversion factor. In the case of carbonate, it should also be noted that two possibilities are considered: that carbonato species compete with sorption sites for nuclides, or do not compete, the latter reflecting the possibility that radionuclide-carbonato species themselves can sorb.

Ultimately, conversion factors were combined together to yield an overall conversion factor. Differences in speciation between sorption experiment conditions and predicted repository conditions were evaluated via thermodynamic modelling. However, in common with the calculations carried out by Duro et al. (2006a), no errors were attached to the stability constants.

Beyond the thermodynamic modelling, the authors have clearly attempted to identify, separate and treat consistently the various contributions to uncertainty, while acknowledging that the available datasets are not sufficient to allow the calculation of statistical uncertainties. Accordingly, uncertainties are attached to each aspect of the extrapolation or 'conversion' process in terms of factors[6] associated with K_d values, viz.

- CEC: factor of 1.4 on K_d value;
- pH: factor of 2.5 on K_d value;
- Speciation and competitive ligands: factor of 1.4 on K_d value.

Although well documented, the above uncertainties are semi-quantitative at best, but subjective for the most part. In particular, given the sensitivity of K_d values of many radioelements (those that form surface complexes) to a small change in pH, in conjunction with the consideration of whether the bentonite system is open or closed, the uncertainty factor attributed to pH appears low - a factor of ~10 is more appropriate.

There are significant differences between the reference MX-80 bentonite composition specified by Ochs and Talerico (2004; Appendix B) and that quoted in SKB (2004). In particular, with regard to minor components, SKB (2004) specifies for the reference bentonite a calcite component of 0%, pyrite 0.07%, and 0.2% for organic carbon whereas Ochs and Talerico (2004) specify corresponding values of 0.7%, 0% and 0%.

The composition specified by Ochs and Talerico (2004) was chosen to "*ensure internal consistency among the calculated porewater compositions and the underlying bentonite composition*". Also, the "*bentonite-water interaction model……is based on and consistent with the corresponding bentonite composition reported* [by the authors of the model]*"*. Nevertheless, given the effort to establish bentonite porewater composition as accurately as possible as a basis for making K_d recommendations, it is surprising that a different reference bentonite composition was used as a starting point. This issue should be resolved for the next assessment.

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[6] These factors are used to multiply/divide each best estimate K_d value.

There is also a difference in CEC value as cited in SKB (2004) compared with Ochs and Talerico (2004), Appendix B. The difference between the two values is ~12-15%, which seems to be an appreciable difference, given the focus on CEC as one of the conversion factors applied to K_d values.

As with other parameters, it is important to be able to assess via sensitivity analysis, how different K_d values (order-of-magnitude changes) affect radionuclide release from the near field. Such analyses then aid the decision-making process on what radionuclides to focus on for experimental work.

The subjective treatment of uncertainties in the work by Ochs and Talerico (2004) ultimately leads to an overall assessment of the recommended K_d values for each radioelement (best estimate, together with upper and lower limits) in terms of what is described as 'soft terminology' using the descriptors "*extremely likely*", "*very likely*", "*likely*" and "*probable*" to indicate the (subjective) degree of confidence of the authors that recommended ranges will cover all data for a given set of conditions.

Table 2 contains a comparison of buffer migration parameters determined using the recommendations of Ochs and Talerico (2004) for SR-Can with those of Lindgren and Lindström (1999) for SR97. Given the different methods of deriving different parameters, the only parameter that should be compared directly is D_a. With regard to the selections of Ochs and Talerico (2004), the SR-Can opted for the open bentonite system that could equilibrate with the host rock (**RPW** porewaters; see Table 2).

Clearly, from Table 2, the current data for SR-Can are less conservative than those for SR97, with differences (typically a reduction) of at least an order of magnitude in recommendations for most elements relative to the previous assessment, these recommendations having been provided some seven years previously. More specifically, D_a is decreased by about a factor of 4 for Cs and 2 for cations Sr and Ra, while for most of the remaining nuclides, D_a is reduced by a factor of about 10. In the case of Tc(IV), however, the decrease is by a factor of ~2,500!

Given the observed reductions in recommendations by at least an order of magnitude, and in some cases by more than two orders of magnitude, *such reductions do not necessarily reflect an improved understanding of the bentonite-porewater system but rather a different derivation process including different underlying experimental data.* This observation, therefore, underscores the call for the reporting of sensitivity analyses based on changing diffusion-related parameters by a factor of 10 or even 100. While some general statements are made in the report (Ochs and Talerico, 2004) concerning sensitivity analysis, no specific analysis was carried out as part of the work reported.

In an ideal situation, it would be preferable to have experimental data that could be used directly to support migration parameter selections, rather than require "extrapolation". To this end, it is hoped that results from the current laboratory experimental programme may help to address the lack of site-specific data.

Table 2: Comparison of Buffer Migration Parameters for SR-Can and SR 97

Radio-nuclide	***SR 97 Lindgren and Lindström (1999)*** **Saline, reducing conditions**			***Ochs and Talerico (2004)*** **Saline, reducing conditions**			
	K_d **Realistic** (m^3/kg)	D_e (m^2/s)	D_a[1] (m^2/s)	K_d (m^3/kg) **Best Estimates**		D_a (m^2/s)[3]	
				RPW[2]	**RPWC[2]**	**RPW[2]**	**RPWC[2]**
Ag(I)	0	2.00E-10	**4.88E-10**	**(0)**	(0)	***(2.79E-10)***	*(2.79E-10)*
Am(III)	3	7.00E-11	**1.47E-14**	**61**	11	***1.24E-15***	*6.86E-15*
CO_3^{2-}	0	3.00E-11	**7.32E-11**	**Isotopic exchange**			
Cl(-I)	0	1.00E-12	**2.00E-11**	**0**	0	***5.88E-11***	*5.88E-11*
Cm(III)	3	7.00E-11	**1.47E-14**	**61**	11	***1.24E-15***	*6.86E-15*
Cs(I)	0.05	6.00E-10	**7.51E-12**	**0.11**	0.1	***1.71E-12***	*1.88E-12*
Ho(III)	1	2.00E-10	**1.26E-13**	**8**	1	***9.43E-15***	*7.55E-14*
I(-I)	0	3.00E-12	**6.00E-11**	**0**	0	***5.88E-11***	*5.88E-11*
Nb(V)	0.2	5.00E-10	**1.57E-12**	**3**	3	***2.52E-14***	*2.52E-14*
Ni(II)	0.1	1.00E-09	**6.27E-12**	**0.3**	0.06	***2.51E-13***	*1.25E-12*
Np(IV)	3	1.00E-09	**2.10E-13**	**63**	40	***1.20E-15***	*1.89E-15*
Pa(IV)	0.3	7.00E-10	**1.47E-12**	**3**	3	***2.52E-14***	*2.52E-14*
Pd(II)	0.01	1.00E-10	**6.13E-12**	**5**	5	***1.51E-14***	*1.51E-14*
Pu(III)	3	3.00E-10	**6.29E-14**	**100**	30	***7.55E-16***	*2.52E-15*
Ra(II)	0.01	5.00E-10	**3.07E-11**	**0.005**	0.005	***1.43E-11***	*1.43E-11*
Se(IV)	0.003	7.00E-11	**1.35E-11**	**0.04**	0.09	***1.57E-13***	*6.98E-14*
Sm(III)	1	2.00E-10	**1.26E-13**	**8**	1	***9.43E-15***	*7.55E-14*
Sn(IV)	3	7.00E-11	**1.47E-14**	**63**	40	***1.20E-15***	*1.89E-15*
Sr(II)	0.01	5.00E-10	**3.07E-11**	**0.005**	0.005	***1.43E-11***	*1.43E-11*
Tc(IV)	0.1	5.00E-10	**3.14E-12**	**63**	40	***1.20E-15***	*1.89E-15*
Th(IV)	3	7.00E-11	**1.47E-14**	**63**	40	***1.20E-15***	*1.89E-15*
U(IV)	1	5.00E-10	**3.14E-13**	**63**	40	***1.20E-15***	*1.89E-15*
Zr(IV)	2	5.00E-11	**1.57E-14**	**4**	11	***1.89E-14***	*6.86E-15*

NOTES:[1] D_a values calculated using dry density, ρ_d, 1590 kg/m^3; porosity, ε, 0.41 (0.05 for Cl^-, I^-).

[2] RPW = Reference bentonite porewater (open system), selected by the SR-Can team;

[2] RPWC = Reference bentonite porewater (closed system).

[3]: D_a values calculated using D_e of 1.20E-10 m^2/s for all elements except anions and Cs; porosity 0.43.
D_e for anions 3.00E-11 m^2/s; porosity for anions 0.17;
D_e for Cs 3.00E-10 m^2/s; porosity 0.43.

3.4 Radionuclide Migration through the Backfill

The reports reviewed for this section include relevant portions of the Process Report for the buffer and backfill (SKB, 2006d), the Data Report (SKB, 2006b), and the Initial State Report (SKB, 2006f). The primary document for migration parameter data recommendations (Ochs, 2006b) was not available at the time of the review.

It is understood that the choice of backfill for the tunnels has not yet been decided. Thus, two options for backfill materials are discussed in SR-Can:

- Friedland clay;
- 30%/70% (by weight) bentonite/ballast mixture.

According to the Initial State Report (SKB, 2006f), the ballast component of the latter mixture comprises crushed rock. Radionuclide migration through the backfill will occur via advection and diffusion. Whether or not diffusion is the dominant process for radionuclide migration is beyond the scope of this review. However, given that diffusion of radionuclides will occur, diffusion parameters are required for safety assessment calculations.

Clearly, considerable uncertainty surrounding the backfill properties exists, particularly when neither diffusion nor sorption data are available for either option above, and experimental data are definitely advisable to support any decisions and/or selections made. As a starting point, thermodynamic modelling of porewaters resulting from an intimate mixture of bentonite and crushed rock is recommended.

Under these circumstances, therefore, the key issues concerning data input are:

- Can relevant diffusion data (D_e [HTO]) for bentonite be used to determine corresponding data for Friedland clay?
- Can relevant diffusion and sorption data for bentonite be used to determine corresponding data for the bentonite/crushed rock mixture?

With regard to the two material options listed above, the major component that is common to both is smectite. The Process Report states (SKB, 2006e; p170) "*In both types of proposed backfill, the content of smectite is about 20%.....*". In fact, the smectite content of the bentonite/crushed rock mixture is closer to 25% (MX-80), while the Initial State Report states (SKB, 2006e; p.69) "*A detailed mineralogical characterisation of the swelling component is not possible.*" Thus, the potential differences in smectite composition will have an impact, albeit relatively small in comparison with other uncertainties, on the uncertainty in D_e value as a result of the weighting process (discussed below).

In terms of basic diffusion parameters, in situ density will influence effective diffusion coefficient and porosity values. From considerations of the dry density of both Friedland clay and the bentonite/rock mixture, together with measurements of swelling pressure, anion exclusion and enhanced Cs diffusion are expected to occur. While measurements of diffusivity for different compositions of a bentonite-sand mixture appear to support this conclusion, as SKB notes in the relevant Process Report (SKB, 2006f), the behaviour of a bentonite-rock mixture may not be the same as for bentonite-sand, and the extent to which anion exclusion and enhanced Cs diffusion occur may also differ. It should also be noted that statements earlier in the same section of the Process Report (SKB, 2006f) appear to contradict the above experimental findings, viz.

> "*It can generally be assumed that the EDL-effects on enhanced cation diffusion and anion exclusion will decrease with decreasing content of expandable 2:1 minerals and increasing pore size. In sand-bentonite mixtures EDL-effects are expected to be negligible (except at sufficiently high bentonite/sand ratios).*"

Volume weighting, in combination with the D_e (HTO) for bentonite, is applied to the bentonite-rock mixture to obtain D_e for backfill, which reflects the important geometric factor ($\varepsilon.\delta/\tau_2$).

There is some confusion concerning porosity values in the Data Report. The central porosity of Friedland clay is cited as 0.41 in Table A-14 (SKB, 2006b) but in the text (p. 95) a value 0.36 is quoted. Also, with regard to bentonite/crushed rock, the Data Report states (SKB, 2006b; p.96): "*As the physical porosity of the pre-compacted bentonite/ballast blocks, a central value of 0.23 is given* [in the Initial State Report]." In fact, the value of 0.23 in the Initial State Report (SKB, 2006f; p. 65) is the void ratio. However, the central porosity is cited correctly in Table A-15. Regarding the inconsistencies in porosity values quoted in Tables A-14 and A-15, the text of the Data Report and Tables A-17 and A-18, it is presumed that Tables A-17 and A-18 are correct, i.e. provide a self-consistent dataset concerning diffusivities and K_d values.

With regard to sorption data for the bentonite-rock option, as shown in the work concerning sorption in the buffer, while various factors are important, the porewater composition needs to be characterised in detail as a basis for estimating K_d values. Thus, the scaling of K_d values according to surface area (N_2-BET) and percentage weight of each component, without consideration of porewater composition in the same way as for compacted bentonite porewaters, can only be regarded as a first approximation.

Also, as a basis for being conservative in estimating K_ds for the bentonite/crushed rock mixture, the Data Report states (SKB, 2006b; p. 96) "*….there is no prerequisite that the mineral surfaces in the rock are as available as the mineral surfaces in the bentonite*." However, given that the weight ratio is 0.3:0.7 in favour of crushed rock, the perhaps more convincing argument could be made that the mineral surfaces in the bentonite will be less available than those of the crushed rock component. Ultimately, the "real" answer will depend on the in-place homogeneity of the mixture. Certainly, the "most conservative" approach described by SKB is not as described – the most conservative treatment would be to ignore the sorption properties of the bentonite and scale according to relative weights. However, this is judged to be overly conservative and not supported by the experimental sorption data available on this topic.

The K_d estimates for sorption on Friedland clay (Ochs, 2006b) appear to have been derived in a similar way to the corresponding data for compacted bentonite, i.e., based on specific porewater compositions derived for solid/water ratios representative of the clay compacted to the reference density, and so are much more acceptable.

4 Radionuclide Migration in the Far Field

4.1 Matrix Diffusion

SKB's primary report dealing with matrix diffusion and associated recommendations concerning matrix diffusion parameters for candidate sites at Oskarshamn and Forsmark, is provided by Liu et al. [2006]. These authors discuss the provision of formation factors (related to matrix diffusion, as discussed below) under laboratory and in situ conditions as well as laboratory measurements of porosity, from which effective diffusion coefficients may be derived. Matrix diffusion data are also discussed in the Data Report for Sr-Can (SKB, 2006).

Matrix Diffusion Process

Matrix diffusion has been recognised for several decades as a mechanism for retarding radionuclide migration in the far field or geosphere, where advection is the dominant transport mechanism. A rock such as granite contains not only fractures through which groundwater flows, but also, on the microscopic scale, a matrix comprising a network of microfractures and connected pores in which the water is essentially stagnant (see Figure 8). Such pore volume can be accessed by molecular diffusion. For matrix diffusion to be an important retardation mechanism, however, there must be a significant difference between the permeability of fractures and that of the rock matrix.

Furthermore, if radionuclides diffusing into accessible pores are able to sorb on mineral surfaces, the potential for retention by sorption on the innermost surfaces of the rock is substantially greater, by several orders of magnitude, than sorption only on fracture surfaces surrounding flow channels. However, sorption is not a pre-requisite for retardation. Indeed, radionuclides that do not sorb, or sorb poorly, are able to diffuse further into the rock than strongly-sorbing radionuclides.

Sorption aside, the extent of matrix diffusion depends on the volume of rock adjacent to flow channels that is accessible, i.e. the connected pore space. Thereafter, diffusivity depends on the overall geometry of the network of connected pores and, for those radionuclides that are able to sorb, the total surface area of rock (minerals) in contact with water in these pores, as well as the ability of radionuclide solutes to access these pores.

The resultant retardation may allow sufficient time for substantial radioactive decay of radionuclides to occur, depending on the half-life of the radionuclide being considered and, for many radionuclides, may be sufficient to reduce their activity to negligible levels before reaching the biosphere.

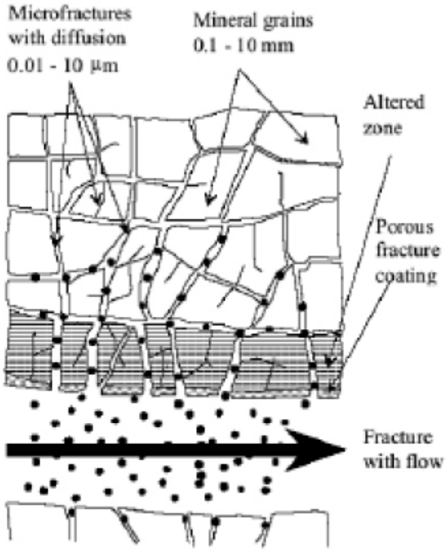

Figure 8: Conceptualised view of matrix diffusion (from Rasilainen, 1997).

A range of evidence exists at different spatial scales to support matrix diffusion, including laboratory and field measurements, as well as field observations. Numerous laboratory experiments using both non-sorbing and sorbing tracers, have demonstrated the ability of radionuclides to diffuse into the matrix of different types of crystalline rock. Field tracer tests using non-sorbing and sorbing tracers, have also been conducted throughout the world, including several sites in Sweden (Finnsjön, Stripa and Äspö) and Switzerland (Grimsel) (RETROCK, 2005). Such tests offer the opportunity to investigate the role of matrix diffusion on a larger scale than in the laboratory. Laboratory experiments normally involve sample thicknesses of a few centimetres whereas field experiments involve length scales of tens of centimetres up to metres.

Geological evidence from natural analogue sites also supports matrix diffusion. For example, at Poços de Caldas in south-eastern Brazil, colour changes visible in outcrops indicate the spreading of redox fronts adjacent to fracture zones. Such colouration is due to brownish-reddish iron oxyhydroxides indicative of oxidising zones. Comparison of the extent to which coloured rock is distributed along, and adjacent to, fractures gives a good indication of the relative differences in penetration of oxidising groundwaters due to advection (along fractures) and diffusion (away from the fractures and into the rock matrix) – at least an order of magnitude greater in the case of the former (Nagra, 1993).

A more relevant example is shown in Figure 9, at the underground research laboratory site at Äspö in Sweden. In this case, the fine-grained rock matrix (advection negligible) indicates discolouration due to hematite formation adjacent to microfractures. This hematite formation is attributed to oxidation of iron-rich minerals by diffusing oxygen-rich groundwaters.

Treatment of Matrix Diffusion

Matrix diffusion in safety assessments is treated in a similar way in most countries where crystalline rock is being considered as host rock, including Finland, Sweden, and Switzerland, whereby the diffusion of radionuclides through the rock matrix is considered to follow Fick's law, i.e., the mass flux is proportional to the radionuclide (solute) concentration gradient.

Figure 9: Micrograph of rock sample collected at Äspö, showing the effects of matrix diffusion on a mm scale – oxidising water diffusing into the rock matrix.
NOTE: The dark colouration around the fracture and microfractures is due to hematite. Total sample width is 1.2 mm (from Mazurek et al., 1997).

The diffusivity of a species diffusing through the rock matrix depends on its ability to diffuse as well as the geometry of the matrix through which it is diffusing. The equation used as a basis for determining the appropriate matrix diffusion coefficient is:

$$D_e = D_W \bullet F \qquad [5]$$

where D_e = Effective diffusion coefficient of a species [$m^2\ s^{-1}$];
D_W = Diffusion coefficient of same species in free (unconfined) water [$m^2\ s^{-1}$];
F = Formation factor [-].

The formation factor, F, is an overall geometric factor that takes into account porosity as well as constrictivity (cross-sectional area of pores) and tortuosity (true length of pathway) of the pores.

Eq. 5 shows that D_e, the effective diffusion coefficient for any (radionuclide) species, can be obtained via knowledge of the formation factor and the diffusion coefficient of the species in free water. Importantly, the formation factor can be determined from electrical measurement methods related to resistivity of the rock and resistivity of the porewater.

For those solutes (radionuclides) that sorb, the relevant diffusion coefficient is D_a, the apparent diffusion coefficient, which is derived from D_e, *viz.*

$$D_a = \frac{D_e}{\phi + \rho_d K_d} \qquad [6]$$

where ϕ = matrix porosity [-];
ρ_d = dry density of rock [$kg\ m^{-3}$];
K_d = distribution coefficient [$m^3\ kg^{-1}$].

Eq. 6 is the same as that used previously for diffusion through the bentonite buffer. The denominator of the above equation is often referred to as the capacity factor, α, of the rock, i.e., the capability of the rock for the retention of radionuclides.

Laboratory and Field Measurements of Diffusivity

Both laboratory and in situ measurements are discussed in the report by Liu et al. (2006). Since the in situ electrical method is relatively new and not universally accepted, the authors provide a discussion of the method(s) and an assessment of the associated assumptions.

In particular, while it is widely acknowledged that electrical conductivity can be used to measure diffusion properties in bulk water, this might not be the case for a volume of rock that contains a network of narrow pores. The report states: "*A number of different types of test have been performed to check these concerns. It has been found that very similar values of the formation factor are found on the same samples when using 1) through-diffusion, 2) electrical conductivity in an AC field, 3) electrical conductivity in a DC field, and 4) through-migration of ions subject to a DC electric field.*" Given such an important argument, it would have been beneficial to see a comparison of formation factors using electrical and more traditional techniques in this report.

Another major concern, also acknowledged by the authors, is that electrical methods based on the application of an *alternating* current do not necessarily reflect the movement of ions, but may also be due to the conduction of electricity across, for example, metal oxide minerals. Again, a comparison of values obtained by different measurement techniques would help allay this concern.

Another key assumption with in situ measurements has to be made because the salinity of porewaters is not determined directly and so cannot be proven to be of a specific value. Rather, it is assumed that the porewaters are in equilibrium with freely flowing groundwater (fractures) at a corresponding depth. While the report states that measurements from core material from the same location support this assumption, this evidence is not provided in the report.

In the laboratory, a key concern regarding diffusion measurements is how representative the resultant diffusion parameters are of in situ conditions. Clearly, the stress condition of rock samples will change significantly when extracted from the subsurface and used for laboratory measurements. Even if attempts are made to re-stress samples that were previously de-stressed, it is hard to argue that in situ conditions have been fully restored in such cases. In addition, some mechanical damage to the pore structure cannot be avoided during excavation. Thus, porosity and diffusion measurements carried out in the laboratory might be expected to yield higher values than those obtained from in situ measurements and this is the case, up to an order of magnitude in some cases (but see later comment in Section 4.1.8).

The primary sources of site-specific data relevant to matrix diffusion in Swedish bedrock come from three areas of Sweden: Forsmark, Simpevarp, and Laxemar, viz.

- **Forsmark**: dominated by intrusive igneous rocks. Five boreholes in this area were used to provide geological interpretation of the area, while two of the five boreholes provided key laboratory and in situ data.
- **Simpevarp**: The area is considered to be lithologically heterogeneous, consisting of a complex mixture of granite and metavolcanic rocks. Two boreholes provided key laboratory and in situ data.
- **Laxemar**: A single borehole was used to provide laboratory and in situ data, although in this case, laboratory measurements are not discussed in the report.

The first region and the other two regions are subareas of Östhammar and Oskarshamn, respectively, two municipalities that are currently the subject of site investigations in connection with a deep repository. In this respect, the measurements can be considered to be site-specific.

For all the above regions, in situ formation factors were determined via in situ or downhole rock resistivity measurements combined with "*in situ groundwater electrical conductivity measurements*". Strictly, the electrical conductivity measurements are not carried out in situ but are made on groundwater samples extracted from fractures at specific depths. Laboratory resistivity measurements also made use of rock samples taken from the same boreholes used for in situ logging.

To supplement the site-specific measurements, additional formation factor and porosity data based on laboratory diffusion measurements, were provided from previous compilations in the literature concerning crystalline rocks in Finland, Sweden, Switzerland and the United Kingdom.

Discussion of Errors and Uncertainties

Measurement errors are not quoted or discussed explicitly for either the laboratory or in situ measurements of formation factor and porosity in the three areas of Sweden described previously. It would have been useful to have an idea of the basic measurement error of the electrical conductivity measurements, although it is understood that these errors are relatively small.

The argument is made consistently throughout the report that the natural variability in the formation factor is much greater than the inherent measurement uncertainties, and the resultant data appear to support this argument. For example, Figure 10 shows a compilation of all formation factors measured for a single borehole in the Simpevarp region (Löfgren, 2004), indicating significant variability. The diagram also reflects an additional complication – in this case, an absence of in situ measured formation factors less than ~10^{-5}, although laboratory-derived formation factors below this value exist. This artificial threshold is due to the resistivity limits of the logging tool.

Similarly, no measurement errors are included in the compilations of literature data concerning porosities and diffusivities (bulk and effective diffusion coefficients). For the latter, however, diagrams were presented summarising the variation in values for the formation factor determined using different non-sorbing tracers. These diagrams provide the mean and standard deviation of the measurements carried out using the different tracers, with the overall range of results seen to be at least one order of magnitude even at one standard deviation.

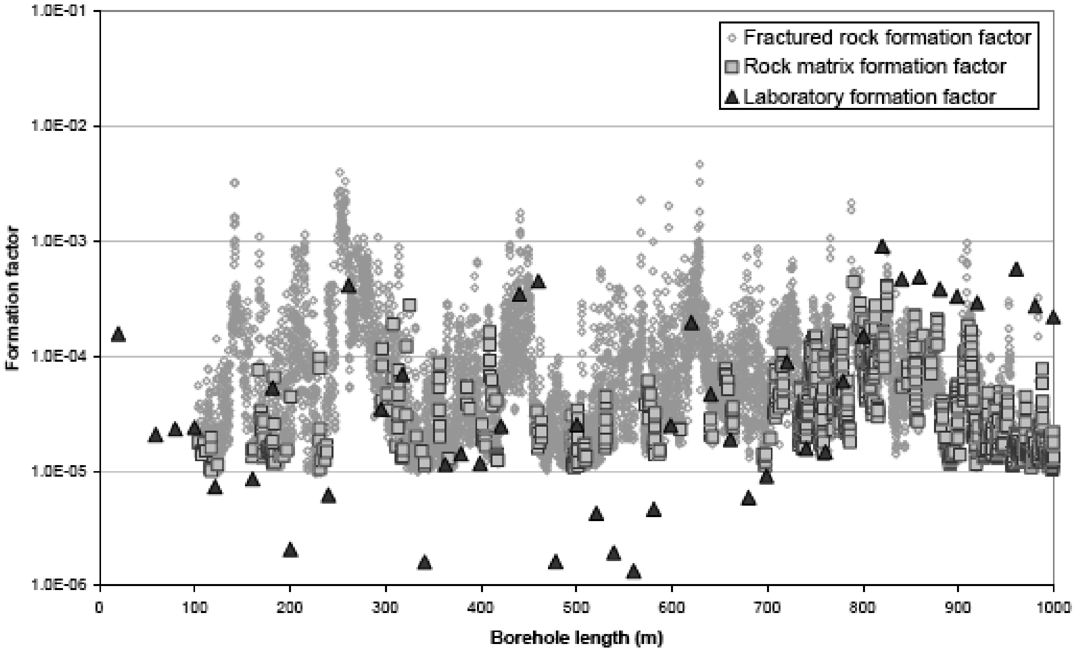

Figure 10: Formation factor log from borehole (KSH01A) in Simpevarp (from Löfgren, 2004).

NOTE: Data from depths less than 200 m are not used for the final recommendations as the salinity of porewaters at these shallow depths is expected to be low, which may affect the measurements.

Beyond measurement errors, factors that can affect formation factor data are discussed by the authors, including rock type, rock stress, rock heterogeneity, the damaged zone around boreholes used for down-hole measurements, sample size, and the characteristics (size, charge) of the different tracers used, as well as subjective sampling (biased towards a relatively high-quality rock matrix). These factors all contribute to the large variability in formation factor values observed from the measurements carried out, as discussed above. Similarly, large variations in the formation factor have been observed in in situ measurements of rock samples down the length of a borehole at the Stripa mine, indicating substantial heterogeneity on a scale of tens of centimetres even in a single borehole (Birgersson and Neretnieks, 1988).

Thus, Liu et al. (2006) make the valid argument that the natural variability in formation factors, several orders of magnitude over scales of a few tens of centimetres to metres, far outweighs the uncertainties associated with the measurements themselves. The additional argument is made in the report that the nature of the flowpath will result in an averaging out of properties as the spatial scale increases. This argument also appears valid.

Presentation of Data

The formation factors obtained in situ and in the laboratory are presented as log_{10} values on the x-axis, but with the y-axis scale presented as the normal score (increments of the standard deviation of the log-transformed values) rather than frequency. A normalised frequency curve is, however, included in each plot.

The plots are not easy to read/interpret and it would be useful to include more of the traditional normalised frequency plots such as that shown in the report for one borehole (see Figure 11). This particular plot is one of the 'better' ones (with minimal tails), judging from similar plots provided in other reports referenced, which have substantial 'tails'.
The authors state that the data are "*well described by a log normal distribution with mean μ and standard deviation σ in ^{e}log space*". However, this comment is arguable – the actual plots presented do not appear to be that well described by such distributions.

The lognormal plots for formation factors for granitic rock and crystalline rock measured by through diffusion in the laboratory show much better distributions than the formation factors measured in situ. The authors point out that the in situ dataset includes all depths and rock types encountered, and, while this variability might be expected to degrade the quality of the lognormal distribution, the actual diffusion pathways are likely to encounter such variability. There is also the additional complication for in situ measurements, as discussed in Section 4.1.5, of an artificial threshold in formation factors due to the sensitivity limit being reached by the logging tool.

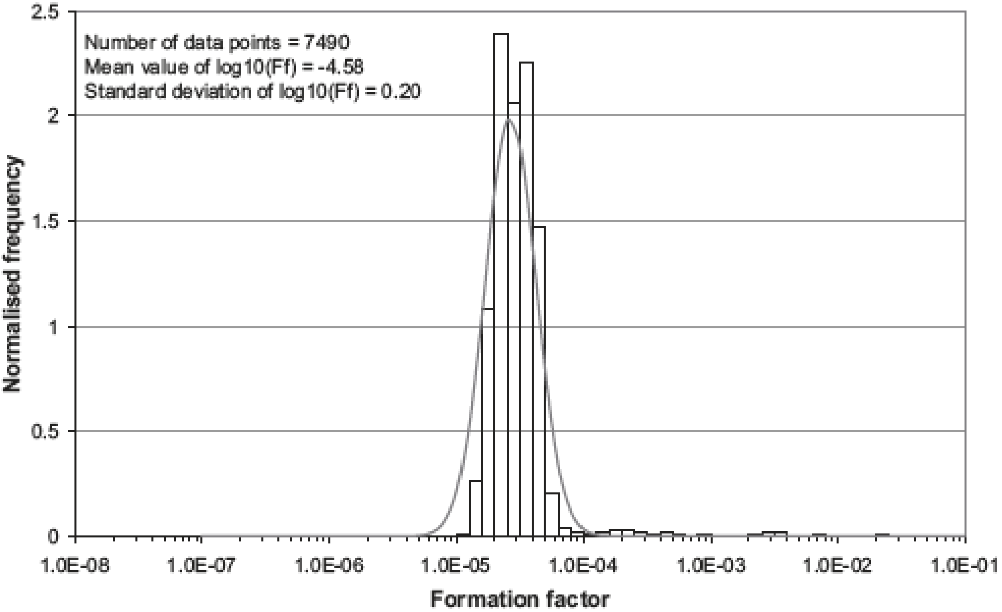

Figure 11: Lognormal vs. frequency plot for formation factors for one borehole (abstracted from Liu et al., 2006, p. 67).

Clearly, the distributions presented in Liu et al. (2006) may benefit from some subdivision into depths or rock types, given that formation factors (and porosities) can vary by orders of magnitude from one rock type to another. However, at the present time, the overall distributions show significant deviations from the straight line that is indicative of a lognormal distribution. On the other hand, the regression coefficient for most of the lines shown is typically > 0.9, so the visual presentation may be misleading in terms of apparent versus actual sample density. Again, results from sensitivity studies involving formation factors and resultant diffusivities need to be carried out to demonstrate the importance of outliers.

With regard to porosity measurements from all three sites, the authors demonstrate a much better fit using a lognormal distribution and compare this with a corresponding poor fit of a normal distribution (Liu et al., 2006; p. 63, Figures 5-13 and 5-14). Several porosity measurements were excluded from the datasets used as a basis for the recommendations. These exclusions were due to the decision to avoid strongly altered rock (Forsmark) or a highly-localised and heterogeneous rock type (Laxemar). Exclusion of these porosity measurements resulted in lower average porosities and is judged to be conservative.

Recommendations by Liu et al. (2006)

Liu et al. (2006) recommend the following parameter inputs to PA:

- **Formation factors**: For each site, the arithmetic mean of the in situ measurements to be used for the base case. With regard to the range of values reflecting uncertainty (discussed further below), the recommended low value is a factor of 3 less and the recommended high value is a factor of 3 higher, than the arithmetic mean.
- **Porosities**: For each site, the recommended central value for the base case is the arithmetic mean of laboratory-measured porosities, divided by a factor of 3. The arguments in favour of this selection are that the arithmetic mean is higher than the geometric mean, and also laboratory-measured porosities tend to be higher than those measured in situ because of the de-stressing effect. The recommended high value is the arithmetic mean of laboratory-measured values for each site, while the recommended low value is the arithmetic mean divided by 5.

It seems somewhat inconsistent to present all data for formation factors and porosities using lognormal distributions, yet provide recommendations based on the arithmetic mean. In fact, in terms of the formation factor, there is negligible difference (between arithmetic and geometric means) for Laxemar and only a factor of 2 difference for Forsmark and Simpevarp. Given the variability with rock type and rock heterogeneity, a factor of 2 appears negligible.

The recommendations for high and low values for each range appear rather subjective and arbitrary, particularly for the high values and particularly in view of the observed variability. Thus, at the very least, sensitivity analysis should be carried out to assess the importance of the upper and lower limits to the values measured. For comparison with the recommended range, such sensitivity analysis may well have been carried out, but it would be helpful to know/see specific results.

Effective diffusion coefficients are obtained by multiplying the formation factor by the diffusivity of species in free solution. The values for diffusivity of different species in free water have not changed since SR97. *One exception is the value quoted for the diffusivity of iodide in free water, which is in error – it should be $2.0 \cdot 10^{-9}$ m^2 s^{-1} rather than $0.83 \cdot 10^{-9}$ m^2 s^{-1}.* The value “0.83” has been carried through as far as the Data Report (SKB, 2006b; Table A-40).

The authors comment that the recommendations are relevant to unaltered rock some distance from fractures and that the diffusive properties of altered rock adjacent to fractures would enhance the uptake of radionuclides. This conclusion is supported by a comparison of formation factors obtained primarily on rock matrix, with those obtained primarily for fractured rock. The latter have a slightly greater mean log_{10} values. Essentially ignoring the more-porous altered rock component is judged to be conservative, and based on the comparison discussed above, is not overly conservative.

Liu et al. (2006) also provide what is described as a "*subjective treatment of uncertainties*" that can affect formation factor and porosity measurements. Given that it is impossible to know whether formation factor measurement values are 'correct', this subjective treatment is judged to be reasonable.

The Data Report (SKB, 2006b) states that the SR-Can team adopted the above recommendations, with an additional consideration of anion exclusion. However, according to the Data Report, Table A-41 contains recommendations for the three sites as the mean value ($\log_{10}F$) ± one standard deviation, not the arithmetic mean. Furthermore, the recommended mean lognormal porosity values given in Table A-42 do not match the recommendations of Liu et al. (2006). The recommended standard deviations ($\log_{10}\varepsilon$) agree with the summary values cited by Liu et al. (2006) in Table 5-7, but the recommended mean ($\log_{10}\varepsilon$) values are each 0.4 greater than the corresponding values given in Table 5-7.

The possible effect of anion exclusion on diffusivity, due to a narrower diffusion pathway resulting from repulsion from negative charges on mineral surfaces, is considered to be negligible for saline waters and, therefore, is not addressed further. The SR-Can team, however, retain the reduction of the previous assessment by a factor of 10 for anions, although the team acknowledges that recent evidence appears to indicate that this factor is too high. This decision is judged not to be overly conservative but again, sensitivity studies need to be carried out to establish the impacts of a factor of 10 reduction in diffusivity for anions rather than 2-3.

A key question is the extent of diffusion into the rock matrix – what thickness of rock adjacent to a fracture should be included in the modelling of matrix diffusion? To provide some perspective to the question of penetration depth, previous work by the authorities is acknowledged here (SKI, 1991), which determined that for sorbing nuclides, the effect of a penetration depth (for diffusion) of the order of 10^{-3} m is very similar to that from unlimited penetration. There is no comparative discussion, however, about the influence of penetration depth for non-sorbing nuclides, but the situation will not be the same.

While Liu et al. (2006) do not provide a specific recommendation for maximum penetration depth of solutes diffusing into the matrix, they do conclude that "*the porous system of the rock matrix is connected on all scales relevant for the performance assessment*" (SKB, 2006b, p. 71). Subsequently, the SR-Can team adopted a triangular distribution of penetration thickness to be used in the SA (SKB, 2006b). The minimum value of this triangular distribution is 3 cm, which is comparable to the thickness of samples used for diffusion measurements in the laboratory, while both central and maximum values are set to the same value, based on "*half the spacing of hydraulically conductive fractures*" (SKB, 2006b; p. 193). The typical spacing is cited in SKB (2006b; p. 193) as 10 m, which would appear to suggest a value of 5 m for the central and maximum values. However, a value of 10 m is then cited in the former report (SKB, 2006b; p. 194). At the very least, sensitivity analyses are recommended to establish the impact of penetration depth for non-sorbing radionuclides on releases to the biosphere.

Comparison with Previous Safety Assessment

For the SKB 91 safety assessment, an effective diffusion coefficient of $1 \cdot 10^{-13}$ m^2 s^{-1} was proposed for all elements in Finnsjön granite with a diffusion porosity of 0.5% (Brandberg and Skagius, 1991).

For the subsequent safety assessment SR97, Ohlsson and Neretnieks (1997) cite a value of ~1 × 10^{-13} m^2 s^{-1} for the effective diffusivity of HTO. This value was based on a free water diffusivity of 2.4 × 10^{-9} m^2 s^{-1} for tritiated water and a formation factor in the range 4-5 × 10^{-5} for Swedish fresh rock, i.e., unaltered rock, which is expected to have a lower porosity than weathered rock. The assumed porosity for Swedish rock was 0.5% (Ohlsson and Neretnieks, 1997), similar to the 1991 recommendation.

For SR97, Andersson (1999) used a value for the formation factor of 4.2 × 10^{-5} for a porosity of 0.5%, based on through diffusion experiments using 1-2 cm samples of Äspö diorite (Johansson et al., 1996). He also concluded that the formation factor has "*an order of magnitude natural variability*". At that time, Andersson (1999) also emphasised the need for sensitivity analysis.

With regard to recommendations on porosity in SR-Can, the central values are a factor of 5 less than the previous recommendations. In the same way, the recommended central values in SR-Can for the formation factor of Forsmark and Simpevarp are essentially the same as the SR97 safety assessment. However, since porosity is included in the formation factor (= $\phi \bullet \delta / \tau^2$), this comparison implies that the geometry factor characterising the pore structure (δ / τ^2) is a factor of ~5 greater for SR-Can compared with the previous assessment.

Using the free water diffusivity for tritiated water of 2.4 × 10^{-9} m^2 s^{-1}, together with the average (4 × 10^{-5}) of the recommended central values of formation factors for Forsmark and Simpevarp, the effective diffusivity of tritiated water is calculated to be ~10^{-13} m^2 s^{-1}, i.e. similar to SR97. However, since D_a is the parameter used in SA calculations and since for non-sorbing species, $D_a=D_e/\phi$, the decrease in recommended porosity by a factor of 5 equates to an increase in the apparent diffusion coefficient by the same factor, i.e., the rate of diffusion into the rock matrix is greater than for SR97, which appears to be less conservative than for previous assessments.

The key difference between previous recommendations for the formation factor and those provided in Liu et al. (2006) for SR-Can is that in situ measurements were used as the basis for the current recommendations. The arguments made on behalf of using such in situ data are that the measurements are made at ambient (rock) temperature, and that perturbations to the natural system are minimal in terms of water chemistry, rock stresses and disturbances of the rock around boreholes. Such conditions are not reproduced for the laboratory measurements. While these arguments are convincing, additional work needs to be done to gain widespread acceptance that in situ electrical measurements indeed reflect diffusion of ions in porewaters and are not influenced by conducting minerals in the rock.

Interestingly, Liu et al. provide a diagram that shows the difference between laboratory measurements of formation factors and in situ measurements (see Figure 12). While this diagram does indeed show a clear order-of-magnitude difference between the two methods, the mean of in situ measurements averaged over consecutive 100 m sections plotted as a function of depth shows essentially no deviation from a horizontal line, i.e., no significant relationship with stress (given that rock stress increases with depth). This apparent contradiction needs to be investigated further and it may be that the key issue concerning sampling conditions is the effect of mechanical damage to core material used in the laboratory.

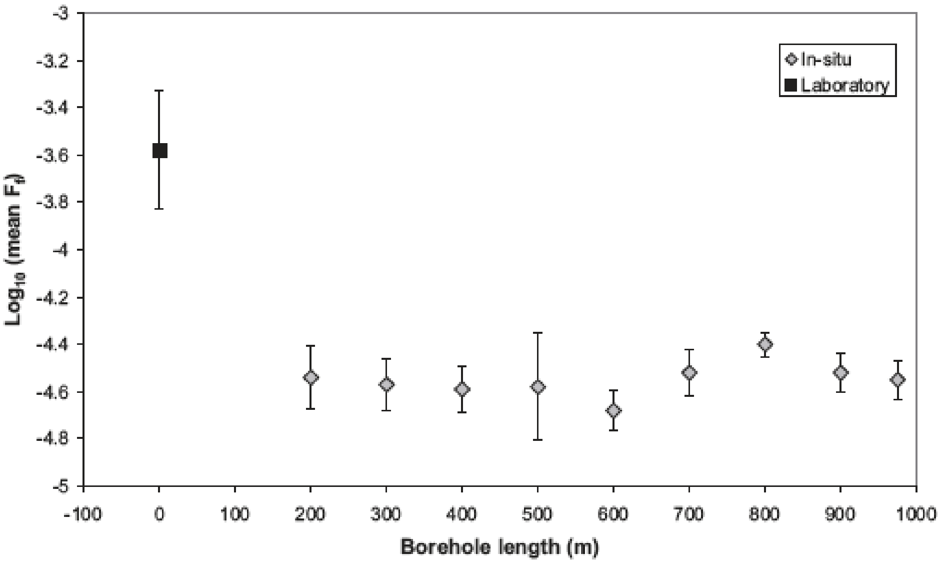

Figure 12: Mean value and standard deviation (*log_{10}*) of formation factors at different depths (from Liu et al., 2006).

Summary Remarks

The recommendations provided by Liu et al. (2006) and for the most part accepted by the SR-Can team, result in *effective diffusivities* that are essentially the same as those in previous assessments, but resultant apparent diffusion coefficients are a factor of 5 higher. The basic difference lies in the use of in situ measurements of formation factors, which yield lower values than those obtained in the laboratory. A question remains as to the true reason for the order-of-magnitude lowering of formation factors obtained by in situ measurement, possibly due more to mechanical damage to core material used in the laboratory rather than de-stressing of samples.

Despite the substantial variability of in situ formation factors, due mainly to a mixture of rock types and rock heterogeneity, it appears reasonable that an averaging process will take place along the transport pathways of radionuclides released from the repository. Thus, the provision of mean values for formation factors of all types of rock measured in situ is judged to be reasonable.

Examination of the data recommendations provided by Liu et al. (2006) and accepted by the SR-Can team, indicate that the key difference in terms of sensitivity is the reduction in recommended porosity, by a factor of 5. Given that the SR-Can team also retains a factor of 10 reduction in porosity for anions from SR97, this means that the extent of matrix diffusion will be greater than in the previous assessment.

Given that measurements of porosity are carried out only in the laboratory, an argument could be made for using a combination of laboratory formation factor and porosity measurements to generate the required diffusion coefficients, primarily in the interests of self-consistency. This is not a criticism of the in situ measurements of formation factors, but rather a desire for a self-consistent dataset.

4.2 Radionuclide Sorption in the Far Field

The primary SKB document used to provide recommendations for the sorption of radionuclides in the far field was prepared by Crawford et al. (2006). The sorption recommendations, to be used in combination with advection and matrix diffusion, are provided independently of the report on matrix diffusion, but the recommendations from both reports are used in combination to provide the modellers with the parameter values necessary to model radionuclide migration through fractures and the rock matrix.

Sorption, a surface-based process, in this case involving interaction of aqueous radionuclide species with surfaces of adjacent rock (minerals), is represented by K_d, the distribution coefficient, typically quoted in units of m^3/kg. While originally formulated as a thermodynamic parameter, it is now universally acknowledged that K_d values are empirical and highly sensitive to environmental conditions. The chemical adsorption mechanisms that are generally encompassed by K_d values are ion exchange and surface complexation.

Beyond the realm of K_d values and their application, thermodynamic sorption models are being developed and used more and more frequently to help in the understanding of sorption mechanisms and the conditions that control sorption. However, these models continue to be applied under relatively constrained conditions and cannot yet be coupled to safety assessment models, due in part to a lack of supporting thermodynamic data for different radioelements.

Specific conditions that can severely impact the values of K_d measured in the laboratory include:

- **Chemistry of the aqueous phase** (pH, Eh, ionic strength, available complexants, competing species), which affects the speciation of radionuclides being considered;
- **Nature of the sorbing surface** (types of mineral, surface area).

For example, those radionuclides that sorb primarily by ion exchange are affected particularly by ionic strength of the aqueous phase as well as competing ions and sorption capacity of the sorbent, reflected in terms of the cation exchange capacity (CEC). The sorption behaviour of radionuclides that sorb primarily by surface complexation is particularly sensitive to solution pH, while the sorption of radionuclides that exhibit multiple oxidation states can vary enormously depending on the dominant oxidation state under different redox conditions.

K_d values are normally measured in batch sorption experiments that allow multiple sets of data to be obtained relatively quickly while varying experimental conditions, in order to determine those parameters that are sensitive to the sorption of specific radionuclides. Experimentally, K_d values are usually based on activity measurements, but only of the aqueous phase alone, often resulting in measurement errors that are typically large for those nuclides that sorb strongly, when residual activities in the liquid phase are close to the instrumental,detection limit and, therefore, difficult to measure.

Given the sensitivity of K_d values to experimental and environmental conditions, the challenge, therefore, is to ensure that K_d values / ranges of values that are recommended for different radionuclides, are representative of the conditions expected in the far field around the repository.

For the previous safety assessment (SR97), K_d values were recommended by Carbol and Engkvist (1997), and for the current assessment, these recommendations have been updated, but only for a subset (8) of radioelements, due to timing constraints. Presumably, recommendations for the full suite of radioelements will eventually be updated. The selection of the eight radioelements, Ni, Sr, Cs, Ra, Th, U, Np and Am, was based on a recommended strategy adopted for SKB's site-selection programme, as discussed by Wiedestrand et al. (2003). It is interesting to note that this latter publication describes a site-specific laboratory sampling and measurement programme that addresses matrix diffusion and sorption in the far field.

The previous recommendations (Carbol and Engkvist, 1997), offered as realistic and conservative estimates and accepted for safety assessment calculations (Andersson, 1999), were based essentially on expert judgement, taking advantage of additional sorption data that had been compiled since the earlier (1991) assessment. Review of these recommendations (SKI, 2000) concluded that the realistic estimates were generally consistent and supported by good scientific arguments (expected chemical behaviour, analogy to other elements). Recommended ranges also appeared to be reasonable for the most part, although it was recommended that sensitivity analysis be used to explore the impact of the lower limit of each range.

As was the case with Ochs and Talerico (2004), Crawford et al. (2006) also provide greater transparency than in previous assessments, concerning their K_d derivation process. All experiments considered in this work are documented in terms of experimental conditions and sorption data, although measurement errors are available only in a few cases. Given relatively few data obtained for the sorption of most of the radionuclides on Swedish site-specific rock (exceptions are Sr and Cs), these authors focussed their selection of supporting sorption data on experiments using rock types that are similar to those of Swedish rocks at the investigation sites, and with experimental conditions (aqueous phase) as close as possible to Swedish conditions. However, differences exist in terms of solid and aqueous phases, between Swedish conditions and the experimental conditions associated with the compiled sorption data, and the resultant variability in K_d values is relatively high.

In all but one case, recommended K_d values were given for:

- Non-saline waters (represented by chloride concentration < 400 mg/l);
- Saline waters (represented by chloride concentration > 400 mg/l).

Chloride was shown to be a useful proxy for ionic strength, at least in the aqueous solutions used in laboratory batch sorption experiments. In one case, for Sr, K_d values were recommended for three different salinities represented by chloride concentration:

- Non-saline (Cl < 400 mg/l);
- Weakly saline (400 mg/l ≤ Cl < 4,000 mg/l); and
- Strongly saline (Cl ≥ 4,000 mg/l).

The authors identify, discuss and address the important sources of uncertainty adequately, some of which are due to experimental errors and some due to the differences between experimental and site-specific conditions. It is hoped that the laboratory programme identified by Wiedestrand et al. (2003) will help to cover at least some of the key uncertainties.

A key bias identified and discussed in detail by Crawford et al. (2006) concerned the use of crushed rock in laboratory sorption experiments. These authors argue that the actual crushing of rock into smaller fragments results in additional mineral surfaces available for sorption, and provide a diagram supporting this argument (see Figure 13). While previous K_d recommendations for other national programmes have probably taken such a bias into account, Crawford et al. (2006) address it in a systematic way.

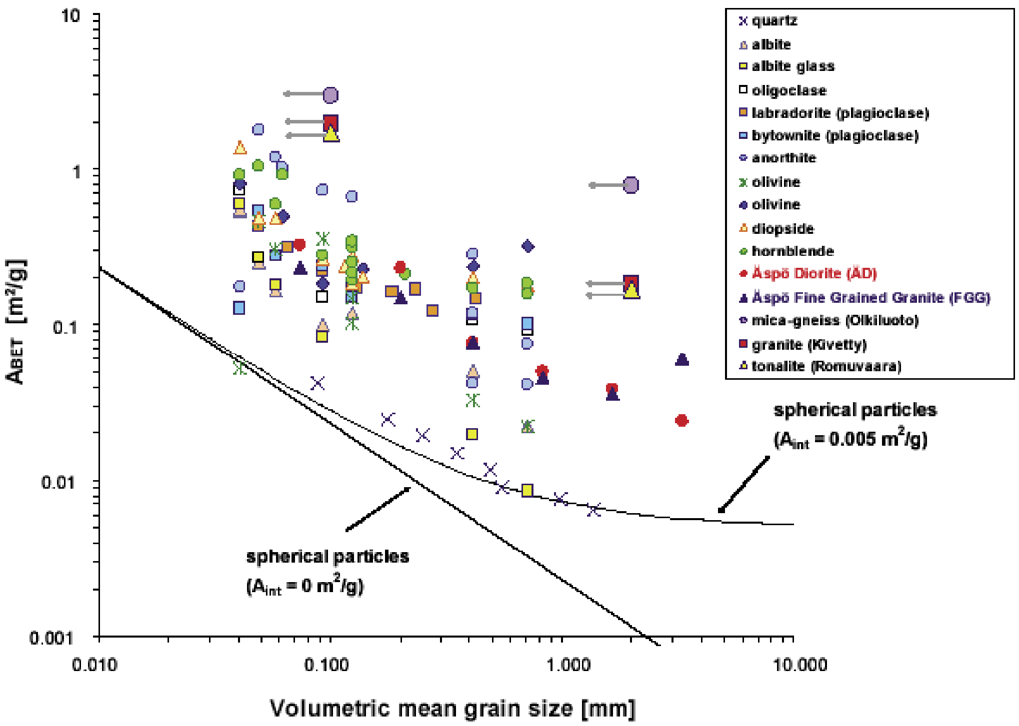

Figure 13: Plot of specific surface area (BET measurements) versus volumetric mean grain size for different granitic minerals.
NOTE: Sources of data: Brantley and Mellott (2000), Höltta et al. (1997), Byegård et al. (1998), and Kulmala and Hakanen (1995). Curves indicate theoretical surface area of uniform spherical grains with (curve) and without (line) internal sorption surfaces (Figure 4-3 from Crawford et al., 2006). Samples with horizontal, left-pointing arrows signify particle size measurements ≤ grain size specified.

While the general trend in specific surface area as a function of volumetric mean grain size is reasonable, an interesting feature from Figure 13 is that the specific surface areas of Swedish rock types analysed is about a factor of 5-10 lower than those of Finnish rocks, for which a substantial number of sorption data were selected. This observation suggests that for the few elements for which the bulk of data was used as a basis for K_d estimation are from Finland, an extra 'correction' factor is needed.

Other important sources of uncertainty in laboratory batch sorption measurements discussed by Crawford et al. (2006) concern:

- The changes of sorption with time and the associated implications, i.e. whether due to sorption kinetics leading to equilibrium sorption, diffusion into internal pores, or alteration/weathering of rock samples during experiments.

- The lack of stress on samples used in batch sorption experiments relative to repository conditions, which can affect the porosity available (increase laboratory measured K_ds).
- The use of synthetic solutions rather than site-specific groundwaters. The former typically have no trace ions or natural colloids present, either of which could affect the extent of sorption.

Crawford et al. (2006) compiled sets of 'raw' sorption data for each of the 8 elements selected for the study. The raw data compiled are associated with laboratory batch experiments that are closest to Swedish site-specific conditions in terms of types of rock used as sorbent, together with the provision of details about the aqueous phase. Rock samples were favoured over individual minerals and the arguments presented by the authors on behalf of the selection of rocks rather than minerals are reasonable. Thereafter, the authors generated a reduced dataset that continued to reflect the best combinations of rock types and aqueous solution chemistries, but also provided documentation on additional important experimental details.

The selected data sets are, in most cases, only a subset of the raw data, so that the possibility of a bias in the selected data exists owing to the restricted number of experimental datasets. This 'problem' is illustrated by consideration of the *sorption data selected for radium* under saline conditions. The main source of sorption data is Finnish work (Huitti et al., 1996), which contributes over half (24) of the 41 K_d measurements. These data indicate relatively high K_d values overall compared with other data in the set, and many of the values are quoted as "*>XX*", i.e. the detection limit was reached. Further examination of the experimental details reveals that the aqueous solution contained a relatively high sulphate concentration ($\sim 5 \bullet 10^{-3}$ M) together with artificial amounts of Ba^{2+} added at concentrations 10^{-7} M or $< 10^{-7}$ M. A concern here, therefore, is whether precipitation/co-precipitation of Ra^{2+} might occur, which would result in apparently high "K_d values", although surface-based sorption would not be the mechanism responsible in this case.

The reference waters (Types I, II, II and IV) defined for Sr-Can by Byegård et al. (2005) are shown in Figure 14 together with waters that were used in the batch sorption experiments described in the supporting Excel spreadsheets. Crawford et al. (2006) note the difficulty in ascribing K_d values to specific salinities and demonstrate this with a plot of K_d for Cs as a function of chloride concentration (ionic strength). The variability in K_d for any given chloride concentration is considerable, extending over several orders of magnitude, with only a modest decreasing linear trend apparent over about five orders of magnitude in chloride concentration.

In terms of consistency, a possible complication arises from combining the current recommendations with those of Carbol and Engkvist (1997), owing to different definitions of non-saline/saline waters in each case – for the latter, non-saline water has a chloride concentration < 500 mg/l, while the chloride concentration for saline waters is taken as between 500 mg/l and 6,500 mg/l). However, this inconsistency is judged to be minor compared to other factors affecting K_d values.

The recommendations of Crawford et al. (2006) are provided in terms of a best estimate K_d for saline and non-saline waters (three waters defined for Sr) *under laboratory conditions*. This best estimate is the median of the $\log_{10}$-transformed dataset. These authors also provide a "*subjectively estimated uncertainty range*" in the form of inter-quartile 25%-75% range, as well as lower and upper bounds for the overall variability of each element. Thereafter, correction factors are "tentatively supplied" to account for the main biases:

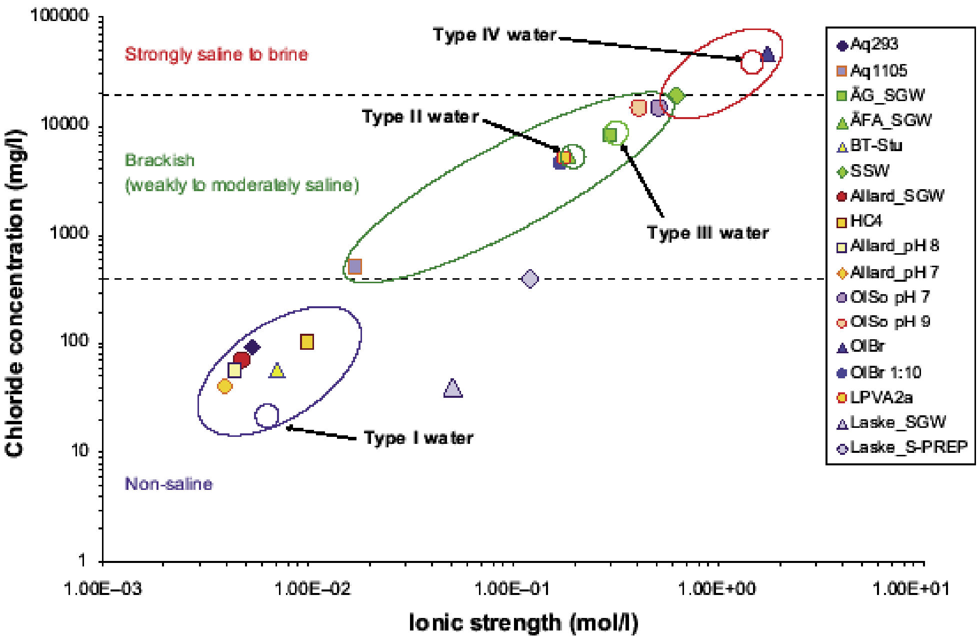

Figure 14: Plot of chloride concentration versus ionic strength of different waters used in batch sorption experiments. The four reference water types selected for SR-Can are also shown in the figure (Figure 5-1 from Crawford et al., 2006).

- Crushed rock versus intact rock: multiply recommended K_ds by 0.1;
- Time-dependent sorption behaviour: given current lack of understanding of such behaviour, multiply by 1.
- Reduction of stress on samples in the laboratory: multiply by factor between 0.1 and 1;
- Chemical effects, e.g. competitive ligands: element-specific but taken as 1 for the base case scenario.

It is interesting to know if the calculations within SR-Can take into account the above correction factors, in particular the factor relating to stress.

In their conclusions, the authors state: "*Although much of the literature data presented……. 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.*"

Nevertheless, the dataset for each element is provided in the report as a lognormal distribution, which at least provides a basis for statistical treatment of the data. Given the empirical nature of K_d and its susceptibility to changes in environmental conditions, the ranges in recommended K_d values provided by the authors appear too small. This same criticism was also attached to the recommendations of Carbol and Engkvist (1997). Because K_d is so susceptible to experimental conditions and because not all variables are necessarily included in the datasets selected as a basis for the K_d recommendations, it would be advisable to keep the ranges of recommended K_d values as broad as possible. Thus, there is a good argument for retaining the best estimate as being equivalent to the mean $\log_{10}K_d$ with a range of K_d values corresponding to:

- Mean $log_{10}K_d$ ±2σ, i.e. a 95% confidence interval based on the K_d data selected.

At least ±1σ (68% confidence interval) should be considered as the minimum range, while the range corresponding to the 95% confidence interval should be explored via sensitivity analysis.

Table 3 provides a comparison of K_d values and corresponding ranges according to the above suggestion, with the recommendations of Crawford et al. (2006). In fact, the comparisons shown in the Table indicate essentially no difference (typically less than a factor of 2) in best estimate K_ds. Of course, the 95% confidence intervals quoted here provide a greater variation in K_d value than the 25-75% inter-quartile range quoted in Crawford et al. (2006).

It is fair to say that the recommended best estimates for K_ds for most elements have not changed significantly over the past 15 years – the trends in sorption behaviour remain the same. What has improved, however, is a more systematic methodology used to select or derive K_ds together with, in some cases, a better mechanistic understanding of the sorption behaviour of certain elements.

Table 3: Comparison of K_d values based on means $\log_{10} K_d$ ± 2 standard deviations with specific recommendations of Crawford et al. (2006).

Element	**Mean Log_{10} K_d^***	**K_d value (m^3/kg)**	**Crawford et al. K_d**	**1 σ (std. dev.)**	**Corresponding range K_d±2σ (m^3/kg)**	**Crawford et al. range (25-75% interquartile) (m^3/kg)**
Ni – NS*	-0.938	1.2E-01	1.2E-01	0.417	1.7E-02 to 7.9E-01	5.5E-02 to 3.0E-01
Ni – S*	-1.813	1.5E-02	1.0E-02	0.422	2.2E-03 to 1.1E-01	8.0E-03 to 2.8E-02
Sr – NS	-1.823	1.5E-02	1.3E-02	0.624	8.5E-04 to 2.7E-01	6.5E-03 to 4.1E-02
Sr – WS*	-2.359	4.4E-03	5.0E-03	0.371	7.9E-04 to 2.4E-02	2.5E-03 to 8.6E-03
Sr – SS*	-4.0	1.0E-04	9.8E-05	0.475	1.1E-05 to 8.9E-04	4.7E-05 to 2.2E-04
Cs – NS	-0.778	1.7E-01	1.8E-01	0.787	4.4E-03 to 6.3E00	4.9E-02 to 7.2E-01
Cs - S	-1.425	3.8E-02	4.2E-02	0.756	1.2E-03 to 1.2E-00	1.0E-02 to 1.4E-01
Ra – NS	-0.058	8.7E-01	2.1E00	0.725	3.1E-02 to 2.5E+01	9.9E-02 to 2.3E00
Ra - S	-0.253	5.6E-01	1.3E00	0.778	1.6E-02 to 2.0E01	1.4E-01 to 1.9E00
Th - all	0.183	1.5E00	1.0E00	0.378	2.7E-01 to 8.7E00	7.9E-01 to 2.4E00
U (IV)	0.569	3.7E00	6.3E00	0.998	3.7E-02 to 3.7E+02	1.1E00 to 1.3E+01
U(VI)	-2.234	5.8E-03	6.3E-03	0.602	3.6E-04 to 9.3E-02	1.5E-03 to 1.6E-02
Np (IV)	-0.061	8.7E-01	9.6E-01	-0.676	3.9E-02 to 2.0E01	3.2E-01 to 2.8E00
Np(V)	-1.695	2.0E-02	1.8E-02	-0.469	2.3E-03 to 1.7E-01	1.1E-02 to 4.4E-02
Am - all	0.926	8.4E00	1.3E+01	0.631	4.6E-01 to 1.5E+02	3.2E00 to 2.1E+01

NOTE: Values of mean $\log_{10}K_d$ and 1σ are also taken from Crawford et al. (2006).
NS = non-saline waters; S = saline; WS = weakly saline; SS = strongly saline.

Table 4 contains a comparison of the recommended (best estimate) K_d values provided by Crawford et al. (2006) with the values use in SR97 (Lindgren and Lindström, 1999). Provided the correction factor of 0.1 is used in conjunction with the best estimates, the current K_d 'best estimates' are more conservative than those of the previous SA, typically by at least an order of magnitude. The key exception is the K_d value for Ra under saline groundwater conditions (underlined in Table 4). In this case, with the correction factor applied, the K_d value is an order of magnitude higher than the value used in the previous SA. The possibility of a potential bias in the underlying experimental data supporting this recommendation was commented on earlier in this section.

Table 4: Comparison of new K_d recommendations for SR-Can with those of SR97.

	"Reasonable estimate", K_d (m^3/kg) [1]		**"Best estimate" K_d x 0.1 [2] (m^3/kg)**	
Element	***Non-saline (Beberg, Ceberg)***	***Saline (Aberg)***	***Non-saline***	***Saline***
Ni(II)	0.1	0.02	0.012	0.001
Sr(II)	0.01	0.0002	0.0013	0.000031
Cs(I)	0.5	0.05	0.018	0.0042
Ra(II)	0.1	0.02	0.13	0.21
Th(IV)	5.0	5.0	0.1	0.1
U(IV)	5.0	5.0	0.63	0.63
U(VI) [3]	0.01	0.005	0.00063	0.00063
Np(IV)	5.0	5.0	0.096	0.096
Np(V) [3]	0.01	0.005	0.0018	0.0018
Am(III)	3.0	3.0	1.3	1.3

[1]: Source Lindgren and Lindström (1999).

[2]: Source Crawford et al. (2006). As recommended by these authors, a correction factor has been applied to their 'best estimate' values (multiply by 0.1) to allow for surface area effects of crushed rock enhancing sorption. The Data Report (Table A-43, SKB, 2006b) includes this recommendation.

[3]: Source Table A.2.6.2, Andersson (1999).

5 Conclusions of Review

The following are the key highlights and comments generated in the course of the review provided as bullet points:

General

- Inconsistencies exist between recommendations provided in technical reports and those quoted in the Data Report. One of the reasons for such inconsistencies has been the timing of different pieces of research. It is hoped that the timing of contributions to SR-Site will be such that these inconsistencies can be avoided.
- Sensitivity analyses need to be carried out and reported in a number of areas to support some of the assumptions or decisions made in the assessment calculations. The likelihood is that SKB has performed many of the sensitivity analyses identified in different parts of this report, but these need to be reported, preferably to complement the recommendations provided.

Source Term

- It would be beneficial for SKB to develop a more mechanistic approach for fuel matrix alteration, as a basis for supporting its rationale on recommending radionuclide release fractions, although the actual values proposed by SKB are reasonable.
- The various uncertainties concerning the mechanisms of long-term evolution of spent fuel calls for a relatively conservative approach, in particular by redefining what is included in the instant release fraction.

Solubilities in the Near Field

- Quoted errors on thermodynamic data should be factored into uncertainty analysis when developing recommendations for solubility limits. An example is provided in Appendix A to show how this might be achieved.
- The effect of elevated temperature on radionuclide speciation and solubility is an important issue and should be addressed directly, despite the general lack of thermodynamic data at higher temperatures. Examples in the literature could be used to develop a strategy to deal with these gaps.
- Given the importance of phosphate in the context of Pu(III) solubility, SKB should devise an experimental programme to determine the solubility of Pu(III) phosphate in the saline reference water. At the very least, recommendations based on a correlation with An(III) should be supported with a more detailed justification.
- With regard to the solubilities of actinide(IV) and in particular Pu(IV), and given recent findings in this area, SKB should develop a plan to address the issue of actinide(IV) polymer/intrinsic colloid/eigencolloid formation and/or nanoclusters.
- The difficulties associated with the ranges of possible complexes of actinides and the application of thermodynamic data does not seem to be acceptable as a basis for determining/recommending a single value for a solubility product, as demonstrated in this report with reference to thorium chemistry.
- With regard to the solubility controlling phases of some elements, in particular, alkaline earth metals Sr, Ba and Ra, the possibility of solubility-controlling mixed

mineral phases should be considered by SKB as well as the presence of microbial activity and the resultant influence on sulfide concentration in bentonite porewaters.

Radionuclide Migration through the Buffer

- Buffer porewater compositions were determined using one form of the bentonite-interaction model, but other models do exist. As a means of lending confidence to the porewater compositions assumed in SR-Can, therefore, it would be a useful exercise to make comparisons with the results generated from at least one other type of model.
- There are clear improvements in the 'derivation' of parameters relevant to the diffusion of radionuclides through the bentonite buffer, mainly in terms of documentation and transparency, both of which allow an assessment of SKB's treatment of uncertainties.
- Although well documented, the uncertainties attached to key parameters, in particular K_d partition coefficients, are semi-quantitative at best, and subjective for the most part. In particular, given the sensitivity of K_d values of most radioelements to a change in pH, in conjunction with the consideration of whether the bentonite system is open or closed, the uncertainty in K_d value for some radioelements as a result of a small change in pH appears low. A factor of ~10 may have merit.
- As with other parameters, it is important to be able to assess via sensitivity analysis, how different K_d values (order-of-magnitude changes) affect radionuclide release from the near field. Such analyses then aid the decision-making process on what radionuclides to focus on for experimental work.
- In comparison with the previous assessment, there are differences (typically a reduction) of at least an order of magnitude in D_a values for most elements relative to the previous assessment, these recommendations having been provided some seven years previously. The reduction with respect to Tc(IV) is by ~2,500. Such reductions represent a less conservative approach and do not necessarily reflect an improved understanding of the system. Therefore, the reporting of sensitivity analyses based on changes in diffusion-related parameters by a factor of 10 or even 100 is strongly recommended as a basis for identifying those radionuclides for which more supporting experimental data should be obtained.

Radionuclide Migration through the Backfill

- In the absence of diffusion and sorption data for both the bentonite/rock and Friedland clay backfill options, it is hoped that SKB has an ongoing experimental programme to support this lack of data.
- With regard to sorption data for a bentonite/rock backfill, and as shown in the work concerning sorption in the buffer, while various factors are important, the porewater composition needs to be characterised in detail as a basis for estimating K_d values. Thus, the scaling of K_d values according to surface area (N_2-BET) and percentage weight of each component, without consideration of porewater composition in the same way as for compacted bentonite porewaters, must be regarded only as a first approximation.
- As a basis for being conservative in estimating K_ds for a 30% bentonite: 70% crushed rock backfill, the Data Report states (SKB, 2006b; p. 96) "*….there is no prerequisite that the mineral surfaces in the rock are as available as the mineral surfaces in the bentonite*." Given that the weight ratio is 0.3:0.7 in favour of crushed rock, perhaps the more convincing argument could be made that the mineral surfaces in the bentonite

are less available than those of the crushed rock component, in which case scaling K_d values according to sorption on bentonite does not appear to be conservative.

Matrix Diffusion

- The key difference between previous recommendations for the formation factor and those provided in Liu et al. (2006) for SR-Can is that in situ measurements were used as the basis for the current recommendations. While the arguments in favour of in situ measurements are convincing, additional work needs to be done to gain widespread acceptance that in situ electrical measurements indeed reflect diffusion of ions in porewaters and are not influenced by conducting minerals in the rock.
- Despite the substantial variability of in situ formation factors, due mainly to a mixture of rock types and rock heterogeneity, it appears reasonable that an averaging process will take place along the transport pathways of radionuclides released from the repository. Thus, the provision of mean values for formation factors of all types of rock measured in situ is judged to be reasonable.
- The recommendations concerning matrix diffusion (formation factors) result in *effective diffusivities* that are essentially the same as those in previous assessments, but resultant apparent diffusion coefficients are a factor of 5 higher. The key difference in terms of sensitivity is the reduction in recommended porosity, by a factor of 5. Given that a factor of 10 reduction in porosity for anions is retained from SR97, this means that the extent of matrix diffusion will be correspondingly greater than in the previous assessment.
- Given that measurements of porosity are carried out only in the laboratory, an argument could be made for using a combination of laboratory formation factor and porosity measurements to generate the required diffusion coefficients, primarily in the interests of self-consistency. This is not a criticism of the in situ measurements of formation factors, but rather a desire for a self-consistent dataset.
- The situ measurements of formation factors typically yield lower values than those obtained in the laboratory. A question remains as to the true reason for the order-of-magnitude lowering of formation factors obtained by in situ measurement, possibly due more to mechanical damage to core material used in the laboratory rather than de-stressing of samples.

Radionuclide Sorption in the Far Field

- Greater transparency concerning the K_d derivation process is provided for SR-Can compared with previous assessments. All experiments considered in this work are documented in terms of experimental conditions and sorption data, although measurement errors are available only in a few cases. Given relatively few data obtained for the sorption of most of the radionuclides on Swedish site-specific rock (exceptions are Sr and Cs), selection of supporting sorption data focussed on experiments using rock types that are similar to those of Swedish rocks at the investigation sites, and with experimental conditions (aqueous phase) as close as possible to Swedish conditions. However, differences exist in terms of solid and aqueous phases, between Swedish conditions and the experimental conditions associated with the compiled sorption data, and the resultant variability in K_d values is relatively high.
- A key bias identified and discussed in detail concerned the use of crushed rock in laboratory sorption experiments. The argument is made that the actual crushing of

rock into smaller fragments results in additional mineral surfaces available for sorption, and this is addressed in a systematic way. While the general trend in specific surface area as a function of volumetric mean grain size is reasonable, supporting data also indicate that the specific surface areas of Swedish rock types analysed is about a factor of 5-10 lower than those of Finnish rocks, for which a substantial number of sorption data were selected. This observation suggests that for the few elements for which the bulk of data was used as a basis for K_d estimation are from Finland, an extra 'correction' factor is needed.

- A relatively restricted number of datasets used as the basis for providing recommendations raises the possibility of bias in the final selections. This issue is demonstrated by the sorption data for radium under saline conditions, for which the recommended K_d is larger than that for non-saline conditions.
- Given the empirical nature of K_d and its sensitivity to changes in environmental conditions, the ranges in recommended K_d values appear to be too small. Because K_d is so susceptible to experimental conditions and because not all variables are necessarily included in the datasets selected as a basis for the K_d recommendations, the ranges of recommended K_d values should be kept as broad as possible.
- It is fair to say that the recommended best estimates for K_ds for most elements have not changed significantly over the past 15 years – the trends in sorption behaviour remain the same. What has improved, however, is a more systematic methodology used to select or derive K_ds together with, in some cases, a better mechanistic understanding of the sorption behaviour of certain elements.

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Appendix A: Examples of Approaches to Handling Uncertainties and Sensitivity Analysis

A1 Introduction

It is common that scientific reports submitted by implementers are reviewed by independent experts on behalf of the public and other stakeholders, particularly where there is potential for an environmental, health and/or safety impact, such as in assessing the performance of high level radioactive waste repositories. Experts are reliant on the availability of data that can be judged. The quest for data which can be critically and independently assessed is not only in the interest of expert review panels, because the findings of the panels are, in turn, critically evaluated, e.g. by independent non-government organisations. Such organisations would indicate any overly benevolent assessment on the basis of inadequately presented data. Thus, quality and fitness-for-purpose of submitted data are essential – for both the implementers and the review panels.

Values obtained by measurement cannot be obtained with arbitrary accuracy and precision. In many cases, the obtained values need to be interpreted in terms of some model to extract the information contained within the data. The interpretation of datasets may be acceptable on a conventional basis. However, it is an essential part of science to objectively assess data and their interpretation as far as possible. Statistics plays an important role in this assessment process.

"*It is the prime task of any statistics intended for scientific use to convince yourself and others that the data have been interpreted fairly*" (Efron, 1986). There seems to be no other equivalent method that avoids major pitfalls in data interpretation such as underestimation and/or overinterpretation of experimental data. Data accompanied by a statistical interpretation also documents to what extent the presenter of the data carried out an evaluation of the data free from prejudice, willful thinking and human error – even though these goals are ideals for which typically approximation only is possible.

The question to what extent experimental data can be assessed objectively has been a challenge to all scientists over many centuries. However, there is no single, straightforward procedure, but the field of statistics has provided helpful guidance since the introduction of the theory of error in the early 19th century and the rise of statistics in the beginning of the 20th century. Statistics has become the common language for communicating data and data interpretation issues. Presentation of data without some relevant details of their measurement and their interpretation does not ease the task of reviewers who scrutinise the data. A few examples are given below using a few selected abstracts from the recent SKB's Main Report of the SR-Can project *Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation.* (SKB, 2006a).

A2 Graphical representation of distributed data

A positive example of data presentation is given by box-and-whisker plots, e.g. Figure 9-42 on p. 265 of the Main Report (SKB, 2006a). From such plots the spread of the data as well as the rough shape of the distribution can be appreciated. The information in box-and-whisker plots can be further increased if those data being located beyond the ends of the whiskers are also indicated individually (so-called refined boxplots). Furthermore, the total number of individual data on which the box-and-whisker plots are constructed is useful information.

A further method to present distributed data is to show the distribution itself. Binned distributions, e.g. Figure 9-43 on p. 265 can be ambiguous because the general shape of the distribution may be highly variable with bin size and selection of bin boundaries. This statement is especially true for the distributions of calculated solubility limits of certain metal ions provided in the Data Report for SR-Can (SKB, 2006b).

A3 Numerical representation of distributed data

All measured data and data obtained by modelling on the basis of uncertain input data also carry an uncertainty. Conventionally, such data are presented in the general form

$$A = \{B \pm b\}\ [X] \tag{A1}$$

where A is a quantity, B and b are real numbers and $[X]$ is a physical unit. The symbol "±" may carry several notions.

a) The first notion is that of $\{b\}$ being a standard deviation of $\{B\}$. In that case it is implicitly assumed that A is normally distributed with $\{B\}$ as the best estimate for the mean value, and that $\{b\}$ is the standard deviation. Thus $\{b\}$ is a measure of the reliability of the estimate $\{B\}$. This information is incomplete without stating the total number of observations on which eq. A1 is based.

b) The second notion is that of a 68% confidence limit. The notion is only equivalent to the previous notion if the degrees of freedom (*df*) in the determination is > 30, otherwise the reliability of the mean $\{B\}$ is overestimated. In the case of $df < 30$, the general form of the equation has to be

$$A = \{B \pm t_{df,\alpha/2}\, b\}\ [X] \tag{A2}$$

where $t_{df,\alpha/2}$ is the value of Student *t* test at *df* degrees of freedom and confidence level $\alpha/2$, α being the significance level for the two-sided test. Student *t* test values are tabulated in most mathematical and statistical handbooks. The degrees of freedom should be stated.

c) The third notion is that of a confidence limit higher than 68%. This must be stated explicitly together with the degrees of freedom at the respective confidence level $\alpha/2$.

d) The complete uncertainty budget can also be given. The complete uncertainty budget is required by the ISO *"Guide to the Expression of Uncertainty in Measurement"* (GUM) (ISO, 1995) as the conventional way to communicate data reliability. The general form is

$A = \{B\}\ [X]$ with a combined standard uncertainty of $u_c = b\ [X]$ (A3)

For data that are intended to support decisions involving nuclear waste disposal, this internationally-agreed form should be favoured when reporting data reliability.

In addition, ranges, as given e.g. in Tables A12 and A13 of the Data Report (SKB, 2006b), are not easy to interpret. For example, what is the distribution of the data? Are the extreme values close to the main body of data or at some extreme position? Clearly, the task of a statistic is to represent the total body of a set of data. A statistic, e.g. the mean value, the median and a confidence range, does have preferential properties, e.g. consistency, sufficiency etc. A range is not suitable as a statistic, since this implies that important information in a dataset is lost if the dataset is reduced to its range only. There are, however, situations where ranges may be a basis for statistical data interpretation (Lord, 1947).

SKB's Main Report for SR-Can (SKB, 2006a) and the Data Report (SKB, 2006b) do not contain many data with stated uncertainties. Rather, the vast majority of data tabulated in SKB (2006b) are given as mean values only. Thus, it is almost impossible to judge such data using objective criteria.

A4 Comment on Correlation and Dependence

Many data are obtained as data pairs (bivariate data, or XY data), where a quantity *X* is obtained conditional upon another quantity *Y*. Such data are commonly interpreted by some theoretical or empirical relationship, i.e. a numerical function depending on one or more theoretical parameters. A feature of the data pairs and the parameters of the relationship function is correlation. Another feature is dependence. The relationship between correlation and dependence is not simple. It is unclear, however, what is meant by 'correlation' in the SKB assessment reports. High correlation is a feature which implies that an extreme value of one parameter is preferentially found with an extreme value of the other parameter. Correlation requires that values of both quantities form a relationship (see below). The situation is different with dependence. If two quantities or parameters are dependent, this dependence may indicate an internal, e.g. physical, relationship. This physical relationship does not come into existence as a result of the investigation – it is part of the world's structure. Therefore, the statement in SKB (2006b), §3.2.6:

> "*As shown in a study by /Stroes-Gascoyne et al. 1994/, the release of C-14 could not to be correlated with neither burn-up nor power rating. It was argued by Johnson and Tait /Johnson and Tait 1997/ that this is reasonable since the predominant source for C-14 is nitrogen impurities introduced during the manufacturing process and are not associated with the burn-up history.*
>
> *The instant release fraction of I-129, Cl-36 and Cs-135 are all proportional to the fission gas release and should hence be correlated*".

indicates that the terms 'correlation' and 'dependence' have been confused.

From a scrutiny of the Data Report TR-06-25 (SKB, 2006b) the general impression obtained is that data have not been analysed carefully for their internal relationships, be it correlation and/or dependence. There are ample misconceptions about the relationship between correlation and dependence in the literature. Among the most important misconceptions is the assumption that parameters *X* and *Y* are independent only if they are uncorrelated. There are, in fact, examples where the lack of correlation does imply independence. However, there is no general requirement for this assumption. Figure A-1 gives an example of uncorrelated data with obvious dependence. A similar misconception is the assumption that small correlations imply weak dependence. This assumption is a weaker form of the previous one but, in fact, a weak correlation does not allow any statement to be made regarding dependence.

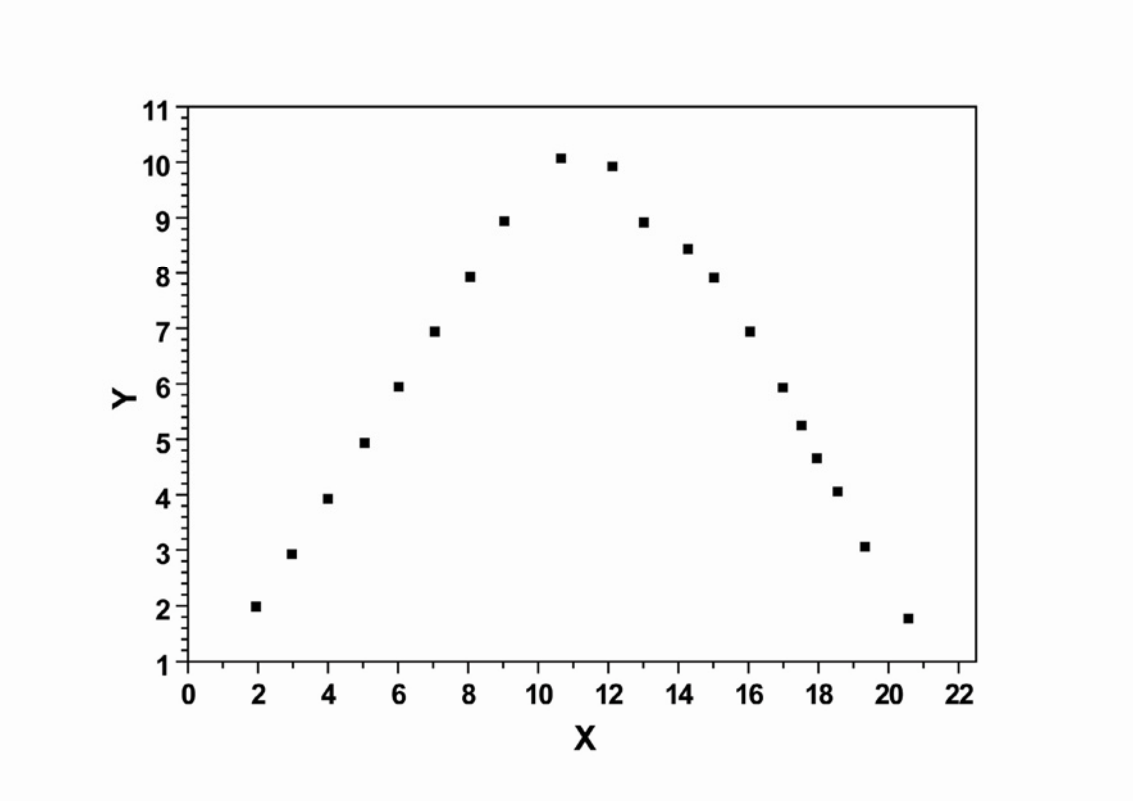

Figure A-1: Uncorrelated dataset which is not independent.

A5 Linear relationships: Example from TR-09-06

The most fundamental linear relationship between measurement values or parameters is

$$y = a\,x + b + \varepsilon \qquad [A4]$$

where *y* is the dependent quantity and *x* is the independent quantity. This functional relationship is the simplest and most used of all statistical regression models. A random variable *Y* is related to the variable *X* according to Eq. A4 where *a* gives the slope, *b* the intercept with the ordinate and ε denotes a random disturbance.

With regard to SKB's discussion of liquefaction and in the absence of specific information given in the report, it must be assumed that the extrapolations discussed in the Main Report (SKB, 2006a, p. 359) are obtained via linear regression of the experimental swelling pressure data. The following discussion is based on this assumption. The data on which Figure 9-101 is based were also unavailable from the Data Report SKB (2006b). Therefore, the values were read directly from the enlarged insert of the diagram. The result is given in Figure A-2. The optimum linear regression line based on five degrees of freedom has a slope $a = -0.1(3) \pm 0.015$ (1σ) and an intercept $b = 5.3(7) \pm 0.069$. These values compare with values of $a = -0.1389$ and $b = 5.3715$ given in Figure 9-101 of SKB (2006a). Note that the second decimal point is uncertain – thus, there is no reason to state four significant figures.

The use of linear regression implies that the data of Figure 9-101 satisfy a series of assumptions, e.g. the independent and identical distribution of the residuals e, which are used as estimators for the disturbances ε (see e.g. Bates and Watts, (1988)). On this basis, marginal confidence limits for slope and intercept can be evaluated. It becomes evident that Figure 9-101 (where only mean values of slope and intercept are given) holds too many significant figures and that, within the significant figures, the slopes and intercepts from the original figure and Figure A-2 are equivalent. Figure A-2 also shows the 95% confidence band of the regression line as well as the 95% confidence band for predicting a new, eighth, data point, e.g. at the intercept of the regression line with abscissa ($y = 0$) (see below).

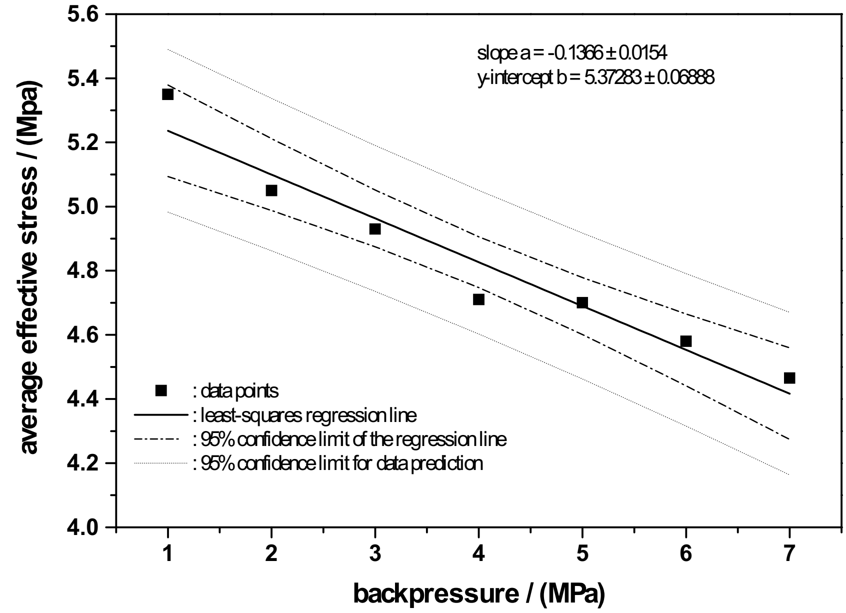

Figure A-2: A representation of the data in Figure 9-101 of SKB (2006a).

In order to investigate the correlation between backpressure and average effective stress, the variance-covariance matrix is evaluated. From these data, a covariance of -0.14286 is obtained, which results in a product-moment correlation $\rho = -0.89$. Hence, both parameters are highly correlated and the correlation is negative. Thus, a large value of backpressure is likely to be observed with a low value of the average effective stress.

The joint and marginal 95% confidence regions of slope a and intercept b as calculated in this study are shown in Figure A-3.

On this basis, the confidence band of the slope can be extrapolated to $y = 0$. An estimate for backpressure P at zero average effective stress is $31 < P < 54$ with 95% confidence. This confidence range of P is obtained under the assumption that the requirements of linear regression are fulfilled and that the relationship is indeed linear over the backpressure range of interest. For extrapolation, the confidence limits for the regression line have been applied, otherwise the uncertainty boundaries would have been even larger.

The assumption of a linear relationship over the entire backpressure range of interest is highly debatable, however. Accordingly, the conclusions in SKB (2006a), that the expected backpressure will be slightly higher than the groundwater pressures for the reference glacial cycle (about 30 MPa), cannot be taken as a conservative assumption, since a slight non-linearity in the pressure relationship may drastically change that assumption.

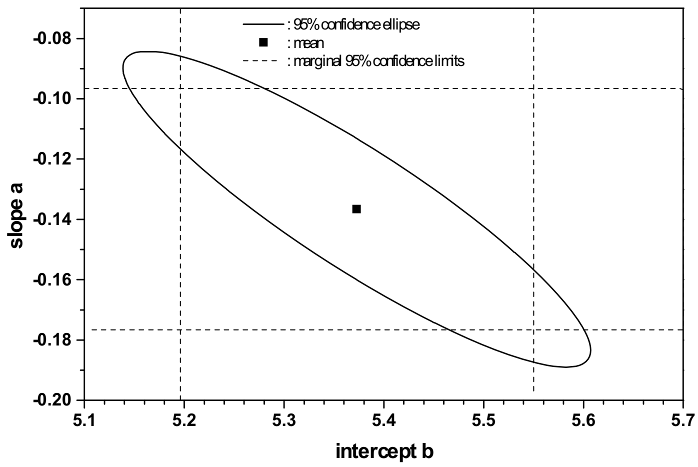

Figure A-3: Joint and marginal 95% confidence regions of slope *a* and intercept *b*.

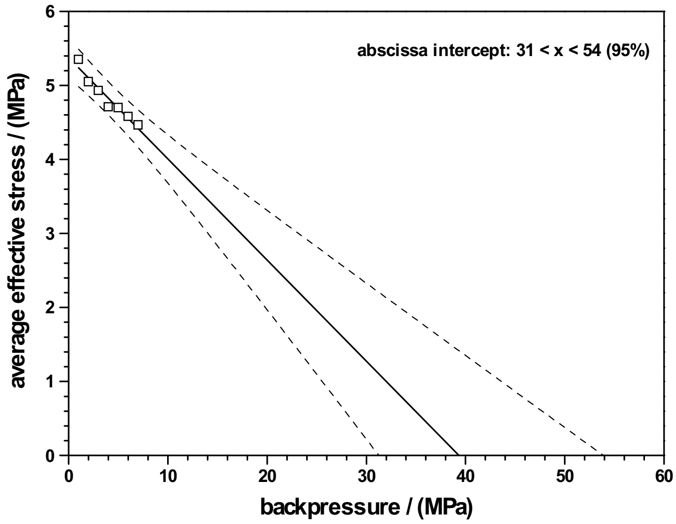

Figure A-4: Expected backpressure at zero average effective stress extrapolated from seven measurement values at low backpressure on the assumption of linear behaviour over the associated pressure range.

A6 Uncertainty in Complex Situations

The importance of sensitivity and uncertainty analysis is widely acknowledged in the literature, especially with respect to nuclear waste disposal (Ades and Lu, 2003; Denison and Garnier-Laplace, 2004; Dettinger and Wilson, 1981; Eisenberg et al., 1987; Ewing et al., 1999; Finkel, 1994; Hamed and Bedient. 1999, Jaquet et al., 1998, Nitzsche et al., 2000). These references are just a selection of communications dealing with the methodology, importance and limitations of uncertainty analysis. The following discussion refers to uncertainty and sensitivity analysis of the two solid phases deemed to be solubility limiting for Np and Am in Duro et al. (2006), $NpO_2{\cdot}2H_2O$ and $AmOHCO_3$.

The calculations are divided into uncertainties in the solubility originating from changes in either water composition or stability constants. It should be emphasised that in all calculations performed here, the same database is used as was used in the calculations reported in SKB (2006a) and that the speciation code used in both cases is PHREEQC. Thus, any deviation between results is due to different methods of handling the uncertainty calculations. In the calculations presented here, we have used the computer programs SENVARWIN and UNCCONWIN (see Ekberg and Ödegaard-Jensen (2004) and references therein); these are not the only codes of this type available. The important point to stress is which factors should be contained in a sensitivity and uncertainty analysis. In this case we have selected the water composition and the thermodynamic stability constants. If the calculations were made at an elevated temperature, the uncertainties in the enthalpy of reaction would also have to be taken into account (Ekberg et al., 1996).

A7 Types of Uncertainty

A7.1 Water Composition

The origin of uncertainties in water composition may be different. The most obvious is the measurement uncertainty, which may affect the determined concentration up to 90% (for example, see the results reported from the International Measurement Evaluation Programme (IMEP) for trace elements in water (IRRM, 2007), especially if one also includes the problems of sampling water from a specific location. The way to discern these uncertainties is through repeated sampling and analysis, thereby obtaining a spread of values.

It is not straightforward how to handle the other type of uncertainty in water composition, i.e. uncertainty arising from the fact that changes in water composition may occur over time either as the result of a natural slow phenomenon, such as changes in ground water flow directions or as the result of a rather sudden change, e.g. glaciation. There are several ways to handle this type of uncertainty, one way being to identify the potential for such changes and to try to foresee the nature of the water composition, then estimate the solubility in that particular water. This is usually called scenario, or “what if”, analysis. In this case it must be appreciated that changes in water composition do not occur as a discrete event but will take place continuously between one scenario and another. Therefore, some intermediate compositions may be overlooked if only the base waters of the scenarios are used for calculations. Usually these effects are very small if the different selected waters are more or less orthogonal, i.e. spanning the entire uncertainty range once and only once.

An alternative way of making the uncertainty analysis of water composition is to try to make an orthogonal system of the different scenario waters, i.e. determine the highest and lowest concentration possible of each of the water constituents, then assign a distribution to this interval and treat the resultant vector with a normal sampling method. Here, this latter approach has been adopted, while Duro et al. (2006a) selected the scenario approach (i.e. using only those water qualities as defined in the specified scenarios).

The UNCCONWIN program investigates how uncertainties in water composition affect the solubility of a solid phase. Each element concentration is given as a uniformly distributed interval, indicated by the user, from which samples are taken using the Latin Hypercube Sampling (LHS) technique. Other factors that can be selected are different iteration criteria, e.g. number of LHS intervals, and which database to use. A simple sensitivity analysis is also carried out. This is achieved by simply giving one of the investigated parameters a high and a low value, while the others are kept at their mean value, and then running PHREEQC once for each case. This procedure is repeated for all the parameters, and the difference in solubility for each case is compared. The parameter that gives rise to the greatest difference is considered to be the most important and so on. This approach will obviously only give a rough estimate of the internal ranking since only first-order effects are taken into account. However, the sensitivity analysis is usually used only as an indicator in this case, and no further calculations depend on its result.

The result of an UNCCONWIN uncertainty calculation consists of two parts, viz.

- A file containing some statistical estimators such as the mean solubility, minimum and maximum solubility and a confidence interval for the mean; and
- Plots of the calculated frequency function and the cumulative distribution function (cdf) for the solubility.

As there are relatively few samples, owing to the LH sampling, the plots will be somewhat jagged, but they will at least give a hint of the distribution of the solubility.

The water data were taken from Table 3-1 in Duro et al. (2006a) where the highest and lowest concentrations for each element were determined as input to the UNCCONWIN program. To be conservative, and obtain as high uncertainties as possible under the given circumstances, a uniform distribution was given for each element. The resulting solubility distributions for Np and Am are given in Figures A-5 and A-6, respectively. Corresponding statistical estimators are given in Table A-1.

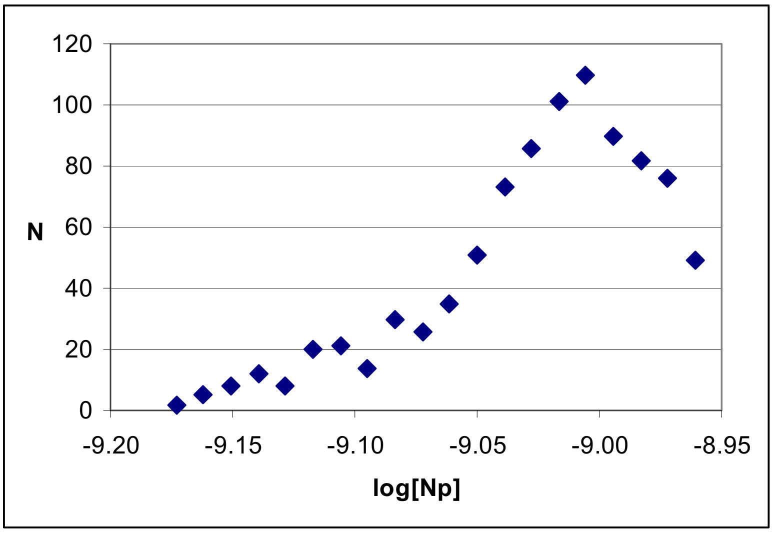

Figure A-5: Distribution function of the Np concentration, based on uncertainties in groundwater composition.

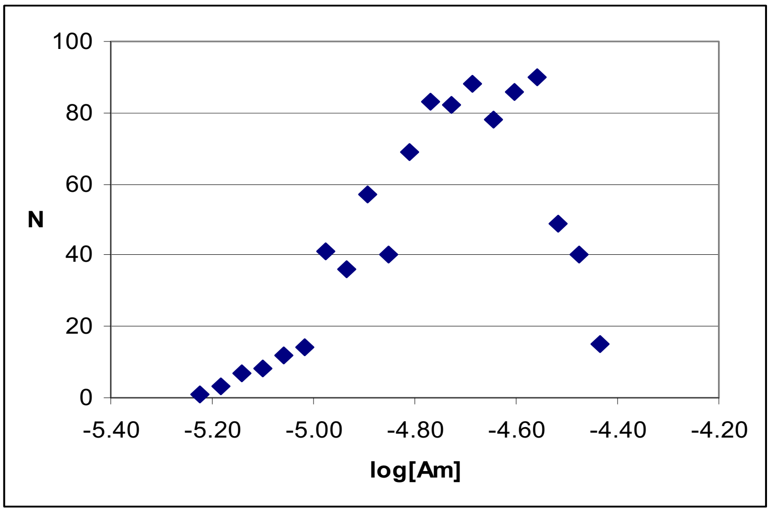

Figure A-6: Distribution function of the Am concentration, based on uncertainties in groundwater composition.

Table A-1: Statistical data for the selected solid phases, concentrations in mol /dm^3, based on uncertainties in groundwater composition.

Solid phase	**Min. conc.**	**Max. conc.**	**mean**	**skewness**	[a] **min./max.**	[a] **mean**
$NpO_2 \cdot 2H_2O$(am)	6.6E-10	1.1E-9	9.5E-10	-0.91	5.1E-10 / 1.7E-5	1.0E-9
$AmCO_3OH$(am)	5.6E-6	3.9E-5	1.9E-5	-0.48	1.1E-7 / 9.1E-6	8.7E-6

[a] from Duro et al. (2006); "min./max." cover *all* water chemistries considered; "mean" is value for SKB reference groundwater composition and "*recommended concentration limit (RCL)*".

As shown in Table A-1, comparison of the mean results obtained in this study for the solubility limiting concentrations, with those given by Duro et al. (2006a), shows good agreement. In the case of Np, the spread of solubilities presented here is significantly smaller than that presented by Duro et al. (2006a), while for Am, the situation is the opposite. The reason for these differences is probably due to the fact that Np is a redox-sensitive element but *pe* is not a variable in the UNCCONWIN calculations. Redox will be treated as an uncertain parameter in the thermodynamic section instead. This is a fault in the current version of the program. In the case of Am, one may observe that the concentrations given here are higher and the spread larger than those reported by Duro et al. (2006). This difference is probably due to the fact that with the approach used by Duro et al. (2006), only a sub-set of the full uncertainty space actually spanned by the given waters is used. Several possible combinations of water compositions do not appear in the Duro report. Thus the approach used here, with a continuous change between the end member concentrations of each element, is more realistic.

Results from the associated sensitivity analysis are shown in Table A-2. The results are tentative since the approach is not fully developed to work with LHS, but serves as a good estimate.

As can be expected, not only anions turn out to be important elements in the sensitivity analysis but also some cations are important since they may bind the important anions, thus making them less accessible. It should be stressed that every sensitivity and uncertainty analysis is subject to the specific case investigated, i.e. the ranges of the different variables selected. Thus, one might get “odd” results from such an analysis simply because one element had a much larger uncertainty interval than a chemically more important one. *Therefore, expert judgement may not always prevail in estimations of uncertainty and sensitivity, i.e. expert judgment may not lead to the “correct” answer.*

Table A-2: Results from the sensitivity analysis

$AmCO_3OH(am)$	$NpO_2{\cdot}2H_2O(am)$
Si	Cl
Ca	CO_3
Cl	Ca
CO_3	Na

A7.2 Thermodynamic data

The uncertainties in thermodynamic data may have several sources, but it is generally agreed that data such as stability constants for chemical reactions are rather heavily encumbered by these uncertainties. This is well reflected in the NEA-TDB data collections where data are generally given with an associated uncertainty estimated from available data or using expert judgement. Clearly, different methods of data collection put different emphasis on obtaining reasonable uncertainty intervals, but the important fact remains that no data should be published without reasonable uncertainty intervals that allow modellers to make estimations on how significantly these uncertainties affect their calculations.

In this case study, the same solid phases as selected above are used together with the reference water described in Duro et al. (2006a). Since no uncertainties have been given in the database used by Duro et al. (2006a) the uncertainties given in the NEA-TDB books on neptunium and americium (Silva et al., 1995; Lemire et al., 2001; Guillamont et al., 2003) have been used as far as possible.

However, there are far too many data in the databases (with defined uncertainties) to allow for uncertainty analysis directly. Thus, we first have to screen away stability constants that do not affect the solubility calculations. This is done using two different approaches as described below. For the sake of completeness, the results of both approaches will be presented even though normally only one method is used.

A8 Sensitivity Analysis

The SENVARWIN package is a combination of a statistical sampling and evaluation program. The solubilities are calculated by the thermodynamic equilibrium program PHREEQC, similar to the UNCCONWIN program.

The calculation frame, which is given by the user, comprises the choice of solid phase, water composition and database. It is also necessary to give some iteration criteria. The calculations are then made in two steps, first a preliminary sensitivity analysis and then an uncertainty analysis, the results of which are also used for the stepwise regression, which serves as the final sensitivity analysis. (For a more detailed description of the program, see Ekberg, (1995), Ekberg and Ödergaard-Jensen (2004), and references therein).

A preliminary sensitivity analysis may be performed in two ways, as discussed in detail in Section 2.3.1:

- Variance analysis; or
- Binary search tree analysis.

A9 Uncertainty Analysis

In the uncertainty analysis, Monte Carlo sampling is made without any restrictions, i.e. the values of the parameters are selected randomly within each interval, at each iteration. This approach makes it possible to detect any synergistic effects between two or more species. The calculations are usually made with 1000 to 2000 samples, thus giving enough values to cover the parameter space sufficiently well. Every solubility calculation is saved in a file which is later used for the final sensitivity analysis.

The results of the uncertainty calculations are a plot showing the calculated density function of the solubilities and some statistics. The calculated statistics are the mean, the variance, the skewness, a 95% confidence interval for the mean based on the solubilities being lognormally distributed and a 95% confidence interval for the solubility population based on an arbitrary distribution.

The final sensitivity analysis is made from the solubility calculations in the uncertainty analysis, thus requiring no further PHREEQC runs. It is assumed that the sensitivity to one parameter is described by the regression coefficients, a_0 through a_n, in a linear model, such as:

$$Y = a_0 + a_1 x_1 + \dots\dots\dots\ a_n x_n \qquad \text{(A5)}$$

where x_1 through x_n represent the input parameters, e.g. the logarithm of stability constants or enthalpies of reaction, and Y represents the output result, i.e. solubilities. Such an approach yields very small regression errors in the cases used here and may therefore be applicable.

A10 Results

As stated earlier, the input uncertainties in this case are pH, *pe* and temperature together with the stability constants for all species in the database. Since the work of collecting all these uncertainties lies outside the scope of this demonstration, the calculation is restricted to intervals one log unit wide, sampled from a uniform distribution. Where conveniently accessible, the uncertainties in the NEA-TDB books have been used. However, it was clear that the estimate of intervals one log unit wide is generally a good one.

The distribution function for the Np and Am cases are given in Figures A-7 and A-8, respectively.

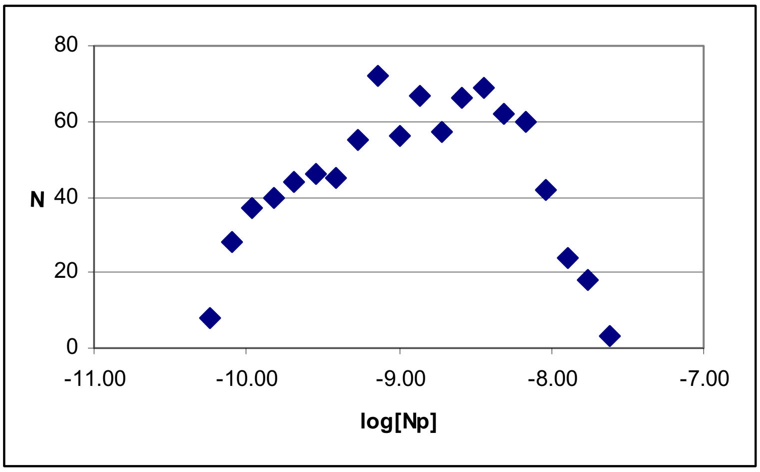

Figure A-7: Solubility distribution function for the Np case.

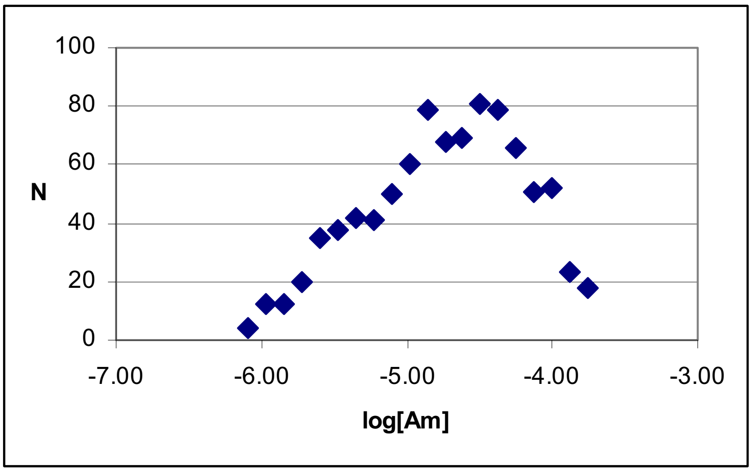

Figure A-8: Solubility distribution function for the Am case.

Table A-3: Statistical data for the selected solid phases (all concentrations in mol/dm^3), based on uncertainties in thermodynamic data combined with the SKB reference groundwater composition.

Solid phase	**min. conc.**	**max. conc.**	**mean**	**skewness**	**[a] mean**
$NpO_2{\cdot}2H_2O$(am)	5.0E-11	2.8E-8	1.2E-9	-0.14	1.0E-9
$AmCO_3OH$(am)	7.0E-7	2.0E-4	1.8E-5	-0.32	8.7E-6

[a] recommended values from Duro et al. (2006), SKB reference groundwater composition.

Clearly, the uncertainty intervals for the calculated solubilities are wider when considering the stability constants relative to those produced from the assessment of water composition as the uncertain parameter. The mean values correspond well with those stated by Duro et al. (2006) but this is expected. What is more interesting is that the actual range in solubilities due to only uncertainties in stability constants is more than two orders of magnitude. Therefore, it must be assumed that *one cannot get closer than this to an estimation of the calculated solubility of these phases based on the data currently available*. Naturally, doubt may arise as to the uncertainty intervals selected in this study, in which case efforts should be made to obtain more realistic uncertainty intervals, then the calculations should be redone. Sensitivity analysis can be used to show which constants need to be determined more accurately to decrease the predicted solubility.

Table A-4: Results from the sensitivity analysis using the variance analysis method. The species are listed in order of importance

$AmCO_3OH$(am)	**NpO_2:$2H_2O$(am)**
$AmOSi(OH)_3^{2+}$	$NpCO_3(OH)_3^-$
$Am(CO_3)_2^+$	CO_3^{2-}
CO_2	$Np(OH)_4$
CO_3^{2-}	CO_2
$AmHCO_3^{2+}$	$CaHCO_3^+$
$CaHCO_3^+$	$MgSO_4$

The results from the variance analysis (Table A-4) show that some of the “odd” results from the UNCCONWIN calculation have reasonable explanations. Species containing Ca and Mg are shown to be very important for the solubilities. In the results given in Table A-4, pH, *pe* and temperature as well as the solubility constant for the solid phase are not included. Therefore, it is expected that the results from the final regression will differ from those given in Table A-4. In addition, if the relationships are not linear, i.e. there are synergistic or antagonistic correlations between constants, there will be a significant deviation and the variance analysis will be the most reliable.

The results from the stepwise regression are shown in Table A-5.

Table A-5: Results from the sensitivity analysis using the binary search tree method

$AmCO_3OH$(am)	**NpO_2:$2H_2O$(am)**
solid	solid
pH	$Np(OH)_4$
CO_2	CO_3^{2-}
pe	$NpCO_3(OH)_3^-$
	CO_2

In the cases presented in this work, there is a clear difference between the binary search tree analysis and the variance analysis. The latter is the more thorough, so from a sensitivity analysis point of view is the most trustworthy. However, the finding of the solubility constant for the solid phase as a key parameter is certainly valid. There are similarities between the methods, but the *pe* for Am obtained in the binary search tree analysis is surprising. Since redox potential does not affect Am directly, there must be other redox-sensitive elements that are important.

A11 Conclusions

Uncertainty is an intrinsic element of science, and data have to be interpreted with the associated uncertainties in mind. A careful analysis is required to avoid both underestimation of the reliability of a measurement value and overinterpretation of measurement results (Ellison et al., 1997).

Statistics is one element of careful data analysis. For many experimental designs, statistics (i.e. mean value, and confidence limit) are available having advantageous properties (i.e. sufficiency, efficiency and optimality), and therefore, are preferred over other choices for summarising a dataset in a concise way. Often, a statistic is optimal only under some constraints (i.e. independently and identically distributed residuals). Hence, a careful analysis of a given dataset requires more than just an application of some standard recipes for obtaining a mean value or a regression line (Ripley and Thompson, 1987; Thompson. 1994).

Interpretations and conclusions can be judged by others only on the basis of appropriate information about the uncertainties involved. The ISO *Guide to the Expression of Uncertainty in Measurement* (GUM) (ISO, 1995) is the internationally agreed convention for the communication of uncertainty in measurement.

Analysis of datasets by ordinary linear regression is a common ‘routine’ method for bivariate data where a linear relationship is assumed to exist. However, within the framework and validity of ordinary linear regression, a theory of error exists which may provide valuable conclusions about the limits of the interpretation. The common error analysis, provided by the theory of error for linear regression, given on the basis of information provided in the Main Report (SKB, 2006a) illustrates a situation where the mean value-based conclusion in this report becomes rather questionable, if not invalidated, by the assessment of a (purely statistical) estimation of a confidence limit for the regression line. It must be emphasised that this error analysis is not an assessment of a complete measurement uncertainty budget as required by GUM (ISO, 1995). Furthermore, alternative methods (bivariate least squares analysis, orthogonal regression, robust regression) exist which may be more suitable as estimation tools for extrapolation (Meinrath and Schneider, 2007).

A thorough uncertainty and sensitivity analysis of solubility estimations is a rather tedious task but certainly needs to be made. It has been shown here that the water composition uncertainty is not as important as the effects of uncertainties in stability constants. The latter were not considered in the estimation of the concentration limits recommended by Duro et al. (2006). The fact that water composition uncertainties have a much smaller impact than stability constants is not new and has been reported previously in the literature (Ekberg, 2002). The uncertainty in the concentration limits estimated here, based on the selected input uncertainties, gives a range of about 2.5 orders of magnitude. This result indicates that solubility estimations smaller than two orders of magnitude are probably unrealistic and that a safety analysis for a nuclear waste repository should take this into account. Alternatively, a more thorough investigation of the actual uncertainties in thermodynamic data could be made to justify a smaller interval.

A complete uncertainty and sensitivity analysis carried out for all possible solid phases is recommended. Whether such an analysis will reveal that some stability or solubility constants should be determined more accurately to allow for adequate solubility estimates remains to be seen. This is naturally dependent on how important the concentration limit is for the safety assessment. The striking fact is, however, that no real discussion of these uncertainties has been made in either the report by Duro et al. (2006) or the previous uncertainty report by Bruno et al. (1997). Previous comments in relation to the latter report indicated that the work carried out by Bruno et al. (1997) contained too little uncertainty analysis and it was recommended that the available literature be studied, thereby enabling an appropriate uncertainty analysis to be undertaken. From the more recent report, it is clear that the literature has not been studied and that an appropriate uncertainty analysis has not been undertaken. This places some doubt on the probable range in concentrations of important radionuclides within the repository.

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