SKI Report 2007:17

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Spent Fuel Dissolution and Source Term Modelling in Safety Assessment

Report from a Workshop at Sigtunahöjden Hotel and Conference, Sigtuna, Sweden May 17-19, 2006

Synthesis and extended abstracts

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Foreword

SKI is preparing to review the license applications being developed by the Swedish Nuclear Fuel and Waste Management Company (SKB) for a final repository for the geological disposal of spent nuclear fuel (SFL-2) in the year 2009. As part of its preparation, SKI is conducting a series of technical workshops on key aspects of the Engineered Barrier System (EBS) and spent fuel. This workshop concerns the assessment of the spent fuel performance and near-field radionuclide retardation mechanisms in the engineered barriers. This will provide a basis for the review of SKB's source term modelling in future safety assessment work. Previous workshops have addressed the overall concept for long-term integrity of the EBS (SKI report 2003:29), the manufacturing, testing and QA of the EBS (SKI report 2004:26), the performance confirmation for the EBS (SKI report 2004:49), long-term stability of the buffer and the backfill (SKI report 2005:48) and corrosion properties of copper canisters (SKI Report 2006:11).

The goal of ongoing review work in connection of the workshop series is to achieve a comprehensive overview of all aspects of SKB's EBS and spent fuel work prior to the handling of the forthcoming license application. This report aims to summarise the issues discussed at the spent fuel and source term modelling workshop and to extract the essential viewpoints that have been expressed. The report is not a comprehensive record of all the discussions at the workshop and individual statements made by workshop participants should be regarded as opinions rather than proven facts. Results from the EBS workshops series will be used as one important basis in future review work.

This reports includes apart from the workshop synthesis, questions to SKB identified prior to the workshop, and extended abstracts for introductory presentations. Part of the preparation of the synthesis in this report has been done by Mike Stenhouse (Monitor Scientific LLC).

Workshop Synthesis Report

1 Introduction

In safety assessment (SA) for the final disposal of spent nuclear fuel, considerable attention is devoted to near-field safety features such as the rate of radionuclide release from spent nuclear fuel, radionuclide solubility limits near the fuel and radionuclide sorption on buffer materials. The KBS-3 concept relies on a complete isolation of the fuel within corrosion resistant copper canisters, but if isolation for some reason will fail the retardation and slow release of radionuclides becomes entities of key significance. In addition, these near-field safety features are important to demonstrate that safety does not depend on the single safety function of complete isolation.

This report describes a workshop that was organised by the Swedish Nuclear Power Inspectorate (SKI) for assessment of the handling of near-field radionuclide retention processes by the Swedish Nuclear Fuel and Waste Management Company (SKB). The general objective with this type of meeting is to improve the knowledge and awareness of recent developments and to provide preliminary review comments. A number of SKB reports provided the general background for the workshop discussions:

- Werme L. O., Johnson L. H., Oversby V. M., King F., Spahiu K., Grambow B., Shoesmith D. W., Spent fuel performance under repository conditions: A model for use in SR-Can, SKB TR-04-19, The Swedish Nuclear Fuel and Waste Management Company, 2004.
- Duro L., Grivé M., Cera E., Gaona X., Domènech C., Bruno J., Determination and assessment of the concentration limits to be used in SR-Met, Enviros Spain S.L., June 2005 (to be published in SKB's report series) [1]
- Ochs M., Talerico, C. SR-Can. Data and uncertainty assessment. Migration parameters for the bentonite buffer in the KBS-3 concept SKB TR-04-18, The Swedish Nuclear Fuel and Waste Management Company, 2004.

The first report addresses the release of radionuclides from spent fuel, the second report the concentration limits related to radionuclide solubility and the third buffer radionuclide sorption and migration parameters.

The above mentioned reports comprise a basis for the handling of the spent fuel, solubility and sorption processes in new complete safety assessment SR-Can. The discussion and analysis of these background reports at the workshop therefore provide an essential element of preparation for the planned review of SR-Can. The review comments provided in this report are nonetheless of a preliminary character since the SR-Can report was not available at the time of the workshop and details about the incorporation of various potential safety features into the entirety of safety assessment were not known.

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[1] SR-Met was intended to be a separate SKB report to demonstrate safety assessment methodology, but later it was decided that this work should be included in the SR-Can report. This report will be a supporting reference for SR-Can instead of SR-Met.

SKB plans to submit a license application for construction of a spent nuclear fuel repository in 2009. In support of this licensing application SKB will produce a safety assessment denoted SR-Site. The review comments expressed in connection with SR-Can and the SR-Can background reports are expected to be utilised in the preparation of the main safety assessment SR-Site. In addition, review of SR-Can along with e.g. discussions at the workshop plays an important role in the preparation prior to the licensing, in the sense that a number of independent experts get an updated and detailed knowledge about SKB's experiments, modelling approaches, documentation, safety assessment reasoning, etc.

The report sets out the detailed objectives and format of the workshop in Section 2. Section 3 provides a high-level overview of processes that need to be taken into account. In Section 4, there is a brief discussion about the chemical and physical environment near the engineered barriers. Section 5 gives a more detailed description of spent fuel processes that affect the radionuclide releases. In Section 6, the key issues for radionuclide chemistry and the estimation of concentration limits for various radionuclides are discussed. Section 7 discusses radionuclide sorption and migration in the buffer and Section 8 presents overall conclusions from the workshop.

Several appendices provide more details of the workshop – Appendix A lists the participants, Appendix B lists the questions that were provided to SKB ahead of the workshop, and Appendix C provides extended abstracts of the presentations made by SKI's experts at the workshop.

2 Workshop structure

2.1 Objectives

The detailed objectives of the workshop were to:

- identify critical issues in connection with SKB's handling of radionuclide chemistry, and the derivation of solubility concentration limits for safety assessment,
- preliminarily evaluate SKB's models and data for expressing the reaction of spent nuclear fuel and groundwater,
- review SKB's handling of radionuclide sorption and transport in the bentonite buffer,
- in a limited way, address a few topics related to the estimation of chemical conditions within the repository near-field environment.

Since the scope of these issues is very large in relation to what could be handled during the three days of the workshop, the viewpoints expressed in this report should be interpreted as examples of issues that may be brought up in the context of scientific and regulatory review, rather than the result of a comprehensive review.

2.2 Workshop format

The workshop was attended by SKI and SSI staff and external experts covering the full range of issues (see Appendix A for a list of participants).

On the first day, the experts independent from SKB were invited to give presentations covering the background for each of the issues, including their current understanding of SKB's approach to the topic (Appendix C includes extended abstracts of these presentations). The participants split into two working groups, one covering spent fuel and sorption issues and the other focusing on radionuclide chemistry and the derivation of concentration limits for radionuclides. These groups discussed the list of question that had been provided to SKB ahead of the workshop (see Appendix B) and some supplementary questions were suggested.

On the second day, SKB and their consultants participated in order to give presentations addressing the list of questions provided. This was followed by an informal hearing with SKB, drawing on the supplementary questions that had been prepared.

In a final session on the third day, the participants discussed the responses that SKB had given in preparation for the production of this synthesis report. The report has been developed on the basis of the workshop discussions with additional material provided by the participants after the workshop.

Viewpoints presented in this report are those of one or several workshop participants and do not necessarily coincide with those of SKI.

3 Overview of processes

The processes discussed at the workshop only have a safety significance after containment of the copper canister has been lost due to, e.g. corrosion, mechanical failure or a through-going initial defect. In Figure 1, this is illustrated by a small pin-hole in the canister through which groundwater can access the cast iron insert. Groundwater may enter the void space within the canister and access the fuel elements containing the radionuclides. The radionuclides may subsequently escape from the canister through diffusion and may pass through the bentonite buffer. They can then be transported through the host rock to the surface environment.

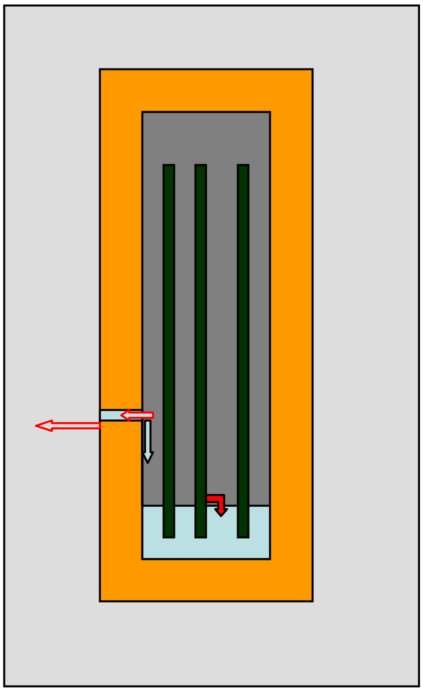

Figure 1. The copper canister surrounded by bentonite clay. There is a cast-iron insert inside the copper cylinder in which the fuel elements are placed. If the isolation is broken (indicated by a pin-hole in the copper shell) groundwater may access the interior of the canister (indicated by the blue arrow). Radionuclides from the fuel elements may be dissolved in the intruding groundwater and can subsequently escape from the engineered barriers through diffusion (indicated by red arrows).

The radionuclides are generally only very slowly released to the surrounding bedrock environment in spite of a loss of the canister containment. There are several mechanisms that contribute to the long-term safety since they mitigate peak-releases and allow additional time for radioactive decay. The most important ones discussed at the workshop are:

- Slow release of radionuclides from the spent fuel, which can be related to the relatively inert UO_2 – fuel matrix.
- Low concentration limits for some of the radionuclides. If the concentration for a radioelement is increased above a certain level, it will precipitate through the formation of solid secondary phases (e.g. oxide or hydroxide phases).

- Sorption of radionuclides on the compacted bentonite within the buffer surrounding the copper canister.

These mechanisms are discussed in chapters 5, 6 and 7 of this report.

The efficiency of all the above-mentioned processes will to a large extent depend on the chemical environment, especially the pH and redox-conditions. The evaluations of the chemical conditions inside a defect canister and inside the bentonite buffer are therefore subjects of key concern. This topic is discussed in chapter 4.

Additional mechanisms that may contribute to slow radionuclide release include:

- Sorption on corrosion products from the iron insert. This mechanism is at least during early stages after canister failure expected to be of none or limited importance.
- Containment provided by fuel cladding. The degradation processes of the cladding have not been addressed in recent safety assessment work and the condition of the cladding may be difficult to investigate prior to disposal.
- Co-precipitation of radionuclides. This process requires formation of new solid phases through major element reactions and is generally difficult to quantify.
- Slow release from a defect canister due to slow diffusion from the inaccessible canister interior and limited access of continuous aqueous pathways. The state of the defect canister will evolve through corrosion processes, so that the potential contributions to long-term safety will gradually diminish. In any case, predictions of defensible and realistic release rates from the canister interior would be hard to obtain.

It is more complex to demonstrate the safety significance of these processes and they have therefore had a limited role in previous safety assessments. They will not be addressed any further in this report. It should be noted, however, that the use of these additional safety features could in principle be further elaborated if sufficient and favourable information became available.

Two types of characteristic radionuclide behaviour can be distinguished. One type of nuclide is relatively inert in groundwater with a limited interaction with solid phases e.g. I-129, Cl-35. These nuclides are few in number and are only affected by the slow release from the fuel and not by sorption or solubility limits. They tend to dominate the dose contribution in previously published safety reports (SITE-94, SR97).

The other type of nuclide interacts extensively with solid phases and will adsorb on various materials and will form separate secondary phases if their concentration is increased above a certain level. Examples within this category include actinides such as uranium and plutonium isotopes. For such radioelements, there is a certain competition between the fuel, sorption and solubility safety functions. However, since a limited degree of redundancy between safety functions is important for the confidence of the overall safety case, reliable and significant safety functions should be examined even if the dose impact appears to be small.

4 Near-field chemical and physical conditions

There were no SKB presentations at the workshop exclusively dedicated to this subject, but it was incidentally brought up in various contexts. Paul Brown made a presentation during the first day of the workshop covering uncertainties in connection with the equilibrium assumption and the significance of geochemical processes of vastly different reaction rates. A brief summary of some essential issues is provided below, since the near-field chemical conditions have a strong impact on radionuclide retention processes. Examples of significant processes that may affect the near-field evolution are provided in Figure 2.

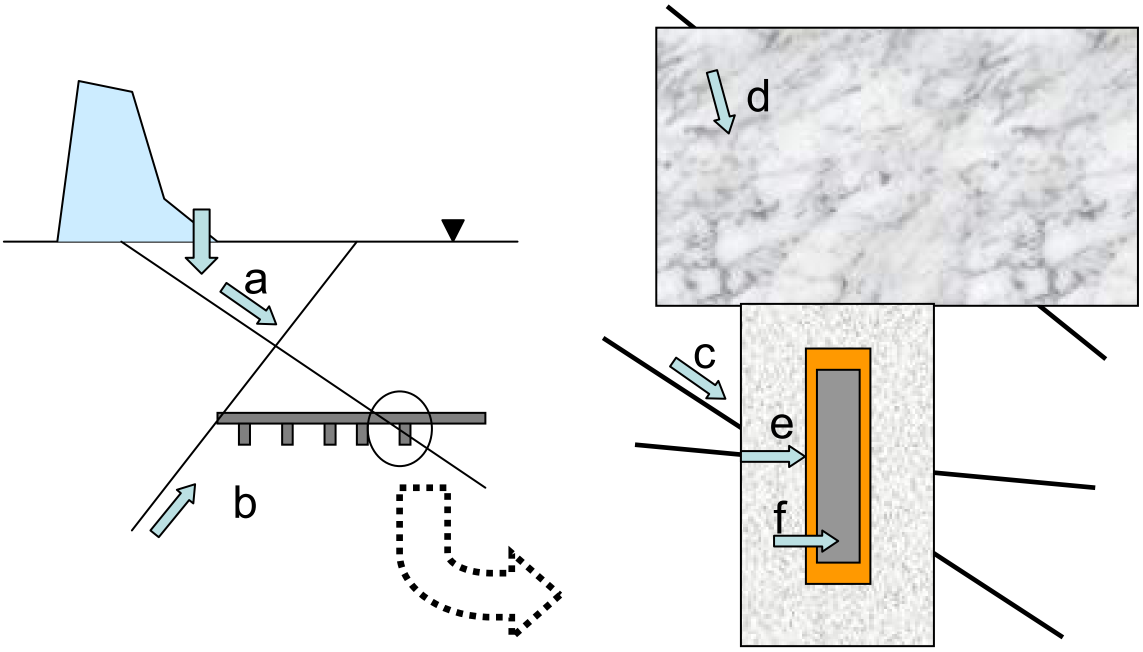

Figure 2. The chemical environment in the near-field is to a large extent governed by the prevailing natural groundwater conditions. It must be considered that the groundwater composition is not constant but will change in response to infiltration from the surface (a) or flow from segments of the bedrock below the repository (b). The composition of groundwater may be modified due to mixing with relatively immobile groundwater (c), reaction with backfill materials (d), buffer materials (e) and the canister (f).

The initial change of groundwater composition is associated with the consumption of remaining oxygen after sealing of repository tunnels, but this phase is not expected to coincide with periods of radionuclide release. Analysis of presently measured groundwater composition at investigated sites suggest that composition is to a large extent governed by previous mixing of groundwater of various origins and to some extent water-rock interaction.

The subsequent change involves inflow of groundwater originating from the surface environment, which may gradually lower the salinity level of the groundwater. During periods of climate change, groundwater composition and salinity may change more extensively due to a) inflow of very dilute glacial melt-water, b) uplift of very saline groundwater from great depth and c) inflow of seawater. Regions outside the most transmissive parts of the bedrock will resist changes due to lower flow rates and mixing with relatively immobile water (e.g. water in the rock-matrix). These regions will consequently be more slowly affected by climate events.

SKB's approach to account for the variable and rather uncertain evolution of groundwater composition is at least partly described in Duro et al. (2005). The uncertainties are covered by definition of 4 groundwater types:

- Forsmark reference water (based on measured composition at about 500 m depth)
- Saline groundwater (based on a measured composition in a deep Laxemar bore hole at about 1500 m depth)
- Ice-melting groundwater composition (based on a water sampled at the Grimsel site)
- Buffer equilibrated groundwater (Forsmark groundwater after equilibration with MX-80 bentonite)

During the workshop, SKB was asked why Forsmark groundwater was considered but not groundwater from Laxemar, where SKB also has ongoing site investigations. SKB acknowledged that this needs to be further considered, but also suggested that differences between Laxemar and Forsmark groundwater most probably could be considered to be minor.

Once the groundwater enters the bentonite buffer, there will be a reaction and equilibration with the mineral phases which results in a modification of the water composition, e.g. exchange of Ca for Na, and equilibration with reactive minerals such as calcite and pyrite. Finally, contact with the insert is expected to result in corrosion of iron, decomposition of water and formation of hydrogen.

$Fe(s) + 4H_2O = Fe_3O_4(s) + 4H_2$

As described in Duro et al. (2005) the redox state of groundwater near the fuel is assumed to be controlled by:

- equilibrium with a maximum pressure of H_2 of 10 MPa (limited by the hydrostatic pressure)
- equilibrium with a lower pressure of H_2, $pH_2 = 10^{-6.3}$ atm
- equilibrium with atmospheric oxic conditions ($pO_2 = 0.2$ atm).

There was a discussion about how certain the availability of hydrogen would be in the context of safety assessment time scales. One participant asked if SKB had considered greater damage to the canister (e.g. caused by mechanical failure due to an earthquake) or large defects, and whether or not such greater damage or defects would mean that hydrogen would be more rapidly lost as compared with the previously anticipated pin-hole scenario. SKB responded that the buffer would also contribute to the retention of hydrogen. The difference with the pin-hole case would not be so significant on the really long-term, since a small pin-hole would gradually evolve to a larger defect due to corrosion processes.

SKB was then asked about the corrosion rate that should be used for the insert and the expected life-time of the insert. After first contact with the groundwater, SKB estimated the life-time to be on the order of 100 000 years. A relatively low corrosion rate would be favourable in the sense that hydrogen would be available for a longer time, but a low rate could possibly be less favourable from other perspectives. In such cases, SKB pointed out the importance of a consistent use of a particular assumption throughout the assessment, even if that assumption may be more conservative from some perspectives and less conservative from others. One participant recommended that SKB use constant corrosion rates for the cast-iron insert, but suggested that the uncertainty introduced by this assumption should be covered by analysing implications of both higher and lower corrosion rates as alternatives.

During the workshop, it was suggested that the formation of the corrosion product magnetite (Fe_3O_4) is solely associated with microbial activity. SKB disagreed noting that magnetite is typically formed during anaerobic corrosion of iron. According to SKB, the equilibrium system is very well characterised (e.g. Garrels and Christ, 1965). In some of SKB´s experiments, so called green rust has been formed in addition to magnetite. There was a discussion about this and when asked about the nature of green rust, SKB responded that this material has the stoichiometry of 2Fe(II) + Fe(III), while magnetite has the stoichiometry of Fe(II) + 2Fe(III). Green rust is apparently very sensitive to even traces of oxidants.

The handling of groundwater concentration variability seems to have been more comprehensively discussed and analysed in the context of radionuclide concentrations limits (Duro et al., 2005) and sorption (Ochs and Talerico, 2004), as compared to spent fuel degradation (Werme et. al., 2004). A potential implication on the spent fuel performance of the groundwater concentrations of Cl^- and Br^- was mentioned as an example.

The impact of temperature has not been addressed in any of the technical reports covering spent fuel performance, sorption and migration parameters, and radionuclide concentration limits. Duro et al. (2005) used the reference temperature of 15°C for estimation of concentration limits and suggested that reaction enthalpy is not sufficiently well characterized for an analysis of temperature influence for the whole possible temperature range up to 100°C.

5 Spent fuel degradation

5.1 General

Spent fuel degradation occurs primarily when the fuel pellets come in contact with groundwater. The various spent fuel degradation mechanisms were addressed in SKB presentations by Virginia Oversby and Kastriot Spahiu. Among a whole range of issues, in particular instant release fractions, and the role and availability of reductants for the matrix dissolution were discussed. Christophe Jégou made a presentation during the first day of the workshop providing an overview of general mechanisms for spent fuel alteration.

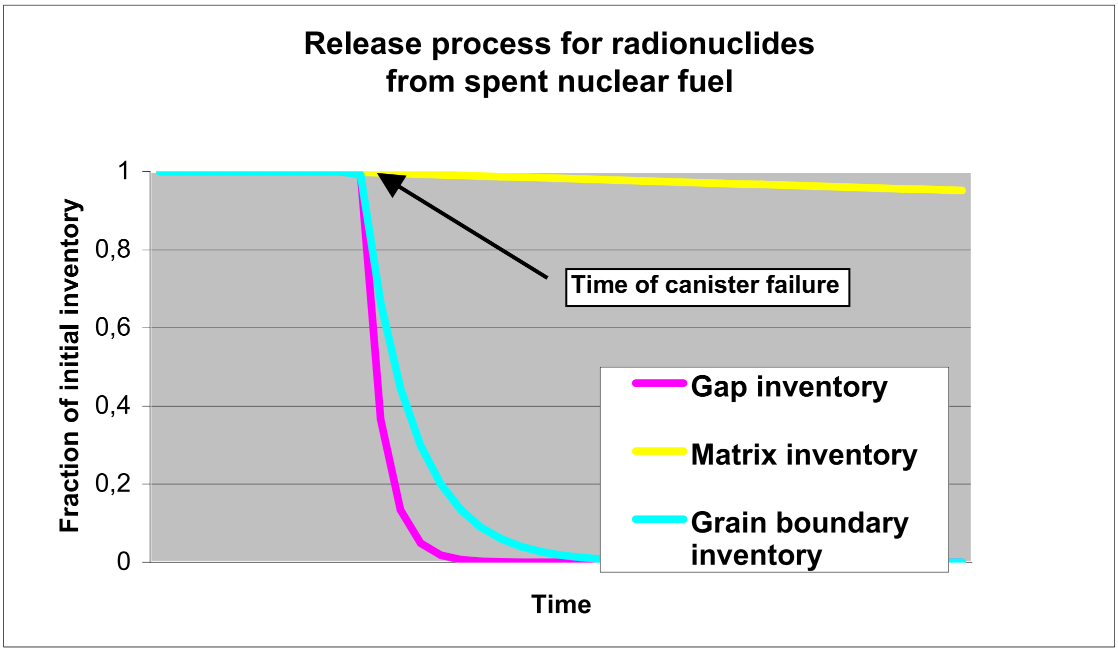

Figure 3. The release of radionuclides from spent nuclear fuel after canister failure and contact with groundwater can occur through various mechanisms, some of which are rapid such as gap release, while others are slower such as the dissolution of the UO_2-matrix.

Figure 3 shows a simplified conceptual model for release of radionuclides from spent fuel as presented by e.g. Jégou (see Appendix C). The radionuclide inventory can be distributed into three parts:

- Gap inventory
- Grain boundary inventory
- Matrix inventory

The gap inventory contains the radionuclides on the outside of the fuel pellets directly accessible for dissolution in intruding groundwater. The matrix inventory contains the radionuclides included in the fuel pellets in solid solution with the UO_2-phase. It is generally assumed that these radionuclides will be released at a rate which is proportional to the conversion of UO_2(s). The grain boundary inventory is presumably of an intermediate accessibility as radionuclides have to diffuse through the network of grain boundary pore-space before reaching the mobile groundwater in contact with the fuel.

Figure 4 illustrates the principle used for incorporating the spent fuel radionuclide release in safety assessment. Both the gap release and grain boundary release are assumed to be instantly accessible in the instant release fraction, i.e. no credit is taken for the presumably slower release of radionuclides deeply embedded in the grain boundaries of the fuel pellets. The matrix inventory is assumed to be released at a constant release rate due to a constant UO_2-matrix conversion until the whole inventory is depleted. This is most likely a great simplification in relation to an expected realistic evolution, but it can be justified on the basis of conservatism.

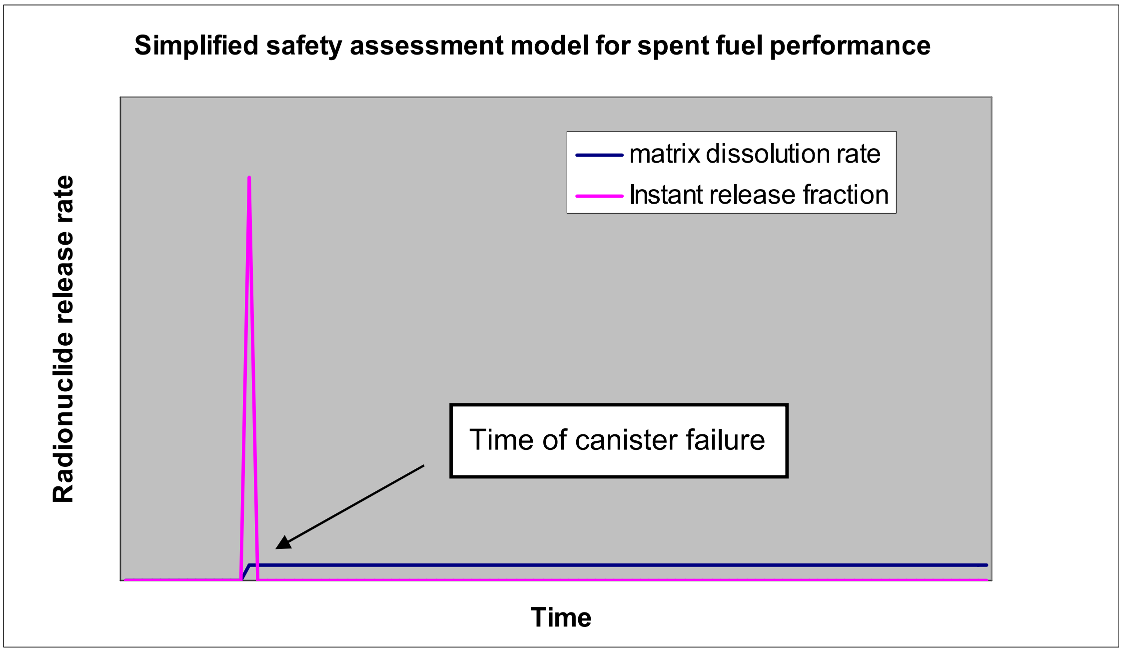

Figure 4. In safety assessment spent fuel radionuclide release mechanisms are greatly simplified by subdivision of the inventory into an instantly accessible fraction termed the instant release fraction, and a matrix inventory characterised by a constant release rate.

5.2 Instant release fractions

In the SR-Can safety assessment, instant release fractions (IRFs) are represented by triangular distributions (shape of probability distribution function). Virgina Oversby presented recommended IRFs and supporting data for the nuclides C-14, Cl-36, Se-79, Sn-126, Tc-99, Pd-107, I-129 and Cs-135. In general there are limited data in support of IRFs, since experimental work with spent fuel samples is very difficult and expensive. It is in particular difficult to characterise the nature of these elements within the fuel (e.g. chemical form) and this makes it necessary to correlate with other properties that can be more easily measured, e.g. fission gas release (a correlation is used for e.g. Cl-36, I-129, Cs-135). SKB suggested that it would in general be unproductive to carry out an extensive experimental programme to characterise IRFs, since the overall significance for long-term safety is small in most cases. However, additional efforts may be warranted in special cases, e.g. measurement of the release of Se and Sn.

There is also the problem of a considerable variability in IRFs which means that various sources of experimental data need to be evaluated in terms of how well they can be expected to represent the spent nuclear fuel from the Swedish nuclear power plants (currently stored at the CLAB facility). Variability is primarily related to fuel-type (e.g. BWR-fuel, CANDU-fuel, MOX-fuel) and burn-up (as MWd/kg U), but other factors are also important (irradiation history, linear power etc.). The utilised probability distributions should account both for variability and uncertainty and may need to be cautiously selected (i.e. tendency to overestimate the IRFs) to compensate for lack of knowledge and data. There is currently no consensus around an exact definition of the instant release fraction.

Jégou discussed two approaches for defining IRFs and selecting their numerical values (Appendix C):

- A "realistic" option based on experimental measurements of the gap + grain boundary releases in relation to the initial fuel characterization (the approach used by SKB in SR-Can and Werme et al., 2004).
- A second, pessimistic option involving a redefinition of the source terms by postulating that the rapid release inventory in fact includes all the radionuclides situated outside the UO_2 grains.

The second approach conservatively ignores the leaching resistance of segregated phases containing fission products (notably metals) and the fact that there may be a limited accessibility to water-limiting release of nuclides outside the UO_2 grains. For the long-term evolution of fuel after disposal, the second, pessimistic option raises the issue of including in the rapid release inventory a zone such as the rim, characterized by a high density of fission products not necessarily in solid solution in UO_2, due to restructuring especially for intermediate and high burn-up fuel (e.g. opening of the grain boundaries over the long term). Table 1 shows the instant release fractions used in SR-Can, and for a comparison other recent pessimistic values reported by Johnson et al. (2005).

Table 1. Instant release fractions for a few key radionuclides in % of total inventory. The second column includes the data in SKB report TR-04-19 by Werme et al. (2004) which are judged to be representative of the current Swedish fuel at the CLAB facility. The range corresponds to lower and upper values in SR-Can with the central value given within the brackets. The other columns contain IRFs recommended by Johnson et al. (2005) with best estimates first and pessimistic values within the brackets. The values correspond to fuel with various burn-up values given in the column heading (given as MWd/kg U). The values in these columns (3 to 6) include all fission products in the rim region (in addition to the gap and grain boundary inventory).

	SKB report TR-04-19	Burn-up 37	41	48	60
^{14}C	0.1 to 10 (5)	10	10	10	10
^{36}Cl	1 to 10 (5)	5	5	10	16
^{79}Se	0 to 0.1 (0.03)	1 (1)	1 (2)	3 (4)	6 (10)
^{90}Sr	Not relevant for long term	1 (1)	1 (2)	3 (4)	6 (10)
^{99}Tc	0 to 1 (0.2)	1 (1)	1 (2)	3 (4)	6 (10)
^{107}Pd	0 to 1 (0.2)	1 (1)	1 (2)	3 (4)	6 (10)
^{126}Sn	0 to 0.01 (0.003)	1 (1)	1 (2)	3 (4)	6 (10)
^{129}I	0 to 5 (2)	3 (3)	3 (3)	4 (6)	10 (15)
^{135}Cs	0 to 5 (2)	2 (2)	2 (2)	4 (6)	10 (15)
^{137}Cs	Not relevant for long term	2 (2)	2 (2)	4 (6)	10 (15)

During the workshop, the two approaches were discussed and compared with the aim to evaluate whether or not SKB had presented sufficient evidence to support their selection of IRFs. Based on an evaluation of e.g. the IRFs for Tc-99 and Pd-107, it could not be ruled out that SKB's treatment of the IRFs is optimistic especially for fractions of the fuel with slightly higher burn-up, which suggests that a more comprehensive justification would be needed. Even if no dramatic consequences can be expected considering the generally low average burn-up of the Swedish spent nuclear fuel, a fuller discussion of mechanisms would be helpful in the context of the SR-Site safety assessment (to be published in 2009). In addition, SKB would most probably be recommended to consider new experimental work and/or more conservative IRFs if higher burn-up fuel would have to be accounted for in future safety assessment.

There was also a question about the reasons why SKB had a separate pessimistic distribution for certain nuclides (since the probability distribution should normally contain the pessimistic values). SKB responded that the pessimistic distributions should reflect poor handling of nuclear fuel representative of a non-design basis scenario. There was also a discussion about the uncertainty of the IRF for I-129, which has previously been identified as an important safety assessment parameter. However, SKB responded that it would therefore not be worth any extensive efforts to further characterize this entity, since the influence is relatively limited in any case.

A controversial issue in the context of instant release fractions seems to be whether of not the IRFs as well as the nuclides embedded in the UO_2-fuel matrix can be considered entirely stable over the full assessment time period. It has been suggested that long-term alpha irradiation (fuel evolution in the absence of water) is liable to occur at low temperatures ("athermal diffusion"). This could result in an increase in the rapid release inventories when water eventually comes into contact with the fuel after a future canister failure. Several approaches have been used to examine this issue, of which the most conservative implies a non-negligible impact on IRFs (for intermediate and high burn-up fuel; see Jégou, Appendix C). On the other hand, SKB claims that further segregation of fission products does not occur over long time periods. This conclusion is based on e.g.:

- Olander's calculations (Olander, 2004);
- Consideration of the difference in the nature of the damage caused by alpha recoil;
- Oklo evidence;
- Studies of self-annealing properties of uraninite and thoranite.

Even if effects could be bounded for the fuel with present burn-up, it would be valuable for SKB to provide a general justification of the present approach with constant IRFs. This implies a need to further examine the credibility of the various proposed mechanisms and sources of information in order to reach a conclusion on whether or not diffusion accelerated by alpha self-irradiation can be neglected for practical purposes in all conceivable cases.

Another issue which is closely related to the stability of the IRFs is whether the helium (He) generated over long timeframes by alpha decay can affect the physical integrity of the fuel. The formation of helium bubbles in the fuel grains can lead to micro-cracking (see Jégou, Appendix C), which would in turn affect the availability of fission products. The extent of this process depends on the burn-up of the fuel. However, SKB concludes that this process should not be important for fuels with burn-up currently generated within the Swedish programme. This conclusion is based on a calculation of He build-up after 1,000 years and after 100,000 years ($8x10^{18}$ atoms/g and $3.1x10^{19}$ atoms/g, respectively), compared with experiments involving spent fuel implanted with $2x10^{20}$ atoms/g He^+, which showed no redistribution of fission products Xe or Nd. SKB was recommended to consider the usefulness of natural analogues concerning the potential effects of He.

5.3 Matrix dissolution

The long-term dissolution of the UO_2-matrix may be governed by two separate mechanisms, one for oxidizing conditions (at the fuel groundwater interface) due to the influence of radiolysis (from alpha, beta or gamma radiation), and one for reducing conditions where release would be controlled by uranium solubility and mass-transfer. Due to the much higher solubility of uranium under oxidising conditions, the former mechanism driven by the radiolysis production rate of oxidants is expected to be higher. Release of fission products and other actinides incorporated in the UO_2-fuel matrix is assumed to be proportional to matrix conversion.

In earlier experiments with spent nuclear fuel, oxidants either from radiolysis or from atmospheric contamination typically play a dominant role, which suggests that the observed dissolution rates are too high for the long-term safety assessment time scale (during which oxidant concentrations and radiation levels are typically much lower). However, spent fuel performance in some recent safety assessment has been assumed to be controlled by the oxidant production from alpha radiolysis (radiolysis from beta and gamma radiation can be assumed to have been decreased to a negligible level at times of canister failure). It is not clear that such oxidant production at a very low level would actually affect spent fuel performance, and considerable efforts have been spent within the SKB programme to demonstrate that there are credible oxidant scavenging mechanisms other than reaction with the UO_2-matrix that inhibit their effect on matrix conversion. These mechanisms include reaction with hydrogen (generated from canister insert corrosion) or iron.

Kastriot Spahiu presented results from SKB's recent experimental studies with spent nuclear fuel. These experiments show that under the presence of H_2 and Fe(s), dissolution rates in flow cells are 3-4 orders of magnitude lower than those under oxidising conditions. Furthermore, there is an absence of measured molecular oxidants which imply a consumption of oxidants generated by alpha radiolysis. For reaction resistant hydrogen, it has been suggested that metallic ε-particles, naturally occurring within spent fuel, have a key role in activating the oxidant consumption at the fuel surface. However, there is at present only a limited demonstration of the involved mechanisms of oxidant consumption (see Jégou, Appendix C).

In order to simulate the alpha radiation level of fuel with an age of several thousand years (with very low radiation from beta and gamma emitters), experiments have been carried out with UO_2(s) doped with 1-10% U-233. The dissolution rates of these doped materials are similar for UO_2(s) with 1-5% doping and only moderately elevated at 10%, which suggests that there might be a threshold for the influence of alpha radiolysis.

SKB has looked at the synthesis of all evidence to estimate the long-term (matrix) dissolution rate and has selected and cited 3 lines of evidence (Werme et al., 2004):

- UO_2 doped with U-233 (experiments at VTT Technical Research Centre of Finland); advantages include homogeneous distribution; a disadvantage is that there are no impurities, *cf.* spent fuel contains 3-4% fission products plus higher actinides. The effect of such impurities is difficult to predict. The results indicate total dissolution in 13±6 million years.
- Spent fuel dissolution in brine (Karlsruhe experiment, FzK); results indicate total dissolution in 2.5 million years.
- Electrochemical model (EM; King and Shoesmith, 2004); results indicate total dissolution in 10 -100 million years.

Thus, results for the matrix dissolution rate may be summarised as:

- VTT: 10^{-7}/year
- FzK: $4x10^{-7}$/year
- EM: 10^{-8}/yr to 10^{-7}/year.

In the SR-Can safety assessment, SKB uses a triangular distribution of fractional matrix conversion rates from 10^{-6}/year to 10^{-8}/year with 10^{-7}/year as the central value.

Jégou (Appendix C) suggests that the proposed range of conversion rates in SR-Can is reasonable and realistic. There are several conceptual uncertainties connected to the estimation of long-term conversion rates, but the fact that the suggested rates are consistent with a broad range of experimental data and modelling work indicates a level of robustness in SKB's probability distribution. The covered range was judged to account for both the gains recently established by the demonstration of the role of Fe and H_2 reductants, as well as a level of conservatism needed to account for the remaining uncertainties. However, the workshop discussions focussed around what was perceived as a lack of an explicit model that formalises SKB's understanding of the fuel alteration processes in the long-term. Workshop participants felt that it would be insufficient to rely on an extrapolation of measured short-term laboratory rates (even if they were representative of repository conditions) to the time scale of up to one million years. There might be a need to more fully account for various mechanisms that could potentially give a time-dependent fuel alteration, either explicitly by direct incorporation in a kinetic model, or implicitly with a justification of why time dependence can be neglected from a particular point of view. Using matrix conversion rates expressed as a fraction per year means that the reactive surface area of the fuel is not explicitly dealt with (heterogeneous reactions are normally reported in moles per surface area and time unit). A time-dependent alteration could partially be related to an increase in surface area with time and/or a decrease in the reactivity of the surface sites.

Regarding the benefits of high partial pressures of hydrogen, SKB was asked on what grounds they can assume that hydrogen will be available for reaction at the fuel-groundwater interface for the whole assessment period. SKB noted that there is a need for a better understanding of H_2 migration through the buffer. The issue of hydrogen availability is linked to an understanding of the near-field evolution and especially the assessment of how the canister insert will corrode after the initial groundwater access (see Section 3.).

The other mechanism of spent fuel alteration with fully reducing conditions (after radiolysis can no longer play a role), involves an assessment of uranium solubility and mass transfer within a defect canister. Sinks for dissolved uranium would speed up the uranium mass transfer and consequently the UO_2-matrix dissolution. Two such processes are coffinite formation and sorption of uranium on canister and canister corrosion product surfaces. Workshop participants suggested that the potential destabilisation of the UO_2-matrix due to coffinitization would be difficult to analyse. SKB responded that the risk associated with coffinite would be very low, since formation of coffinite is associated with the presence of U(VI). This result has been indicated by both field and laboratory investigations. It was suggested that there is a need to address the more general question of destabilisation of the UO_2-matrix due to all feasible sinks of uranium of which the most important could well be formation of silicate phases.

One question that was asked in the discussion with SKB was if measures had been implemented to avoid microbial activity during the experiments with spent nuclear fuel. SKB responded that the experiments at the Studsvik facility had involved the use of nitric acid which would inhibit microbes. SKB also suggested that residues from microbial activity in any case could be clearly seen (e.g. Savannah River experiments). However, it was also suggested microbial activity would not always give such visible residues, while still influencing the experimental conditions.

There was a question about whether or not SKB would be able to get any results from CHEMLAB experiments with spent nuclear fuel before submission of a license application. Such experiments, representing in-situ conditions in the deep crystalline bedrock at the Äspö laboratory, could be very valuable considering the limited potential for contamination and interference with atmospheric conditions. SKB responded that the time table for such experiments is still uncertain.

5.4 MOX-fuel

MOX-fuel is not routinely used in Swedish nuclear power plants, but small amounts need to be handled and eventually disposed of. One fraction originates from a trade with Germany and another fraction will come from the Oskarshamn power plant (produced in order to handle Pu from an old reprocessing contract). The treatment of the long-term performance of MOX-fuel was not covered by any of the SKB presentations, but the subject came up in discussions during the workshop.

There was a discussion about the differences compared with ordinary fuel, e.g. MOX-fuel grains comprise a Pu/U agglomerate similar to the rim of normal fuel. These grains exhibit a higher porosity and may be associated with more extensive fission product release. MOX-fuel has similarities with high burn-up fuel and it would be reasonable to expect that higher IRFs would be needed and possibly a higher matrix conversion rate. The SR-Can safety assessment does not seem to include MOX-fuel, but SKB still needs to address the problem in the planned licence application. More data from MOX-leaching experiments would be needed or possibly bounding calculations. SKB mentioned that the burn-up of the MOX-fuel currently stored in CLAB is low. There was also a discussion about how SKB would mix MOX-fuel with ordinary fuel within the canisters and within a repository and what implication such mixing would have for heat generation.

6 Calculation of concentration limits due to radionuclide solubility

As the radionuclides are released from the fuel, after the initial water ingress into a canister, they may form secondary phases. This limits concentration levels and thus the driving force for diffusion to the surrounding groundwater. The concentrations may provide an important safety function for several key radionuclides. Lara Duro made a presentation on the determination and assessment of the concentration limits to be used by SKB in SR-Can, which is discussed below. During the first day, Heino Nitsche presented some challenges and issues with neptunium thermodynamic data. He concluded that some data reported in the scientific literature e.g. neptunium (V) hydrolysis data, are the subject of controversy and may suffer from experimental artefacts. A common problem is a lack of characterisation of solid phases, e.g. ambiguous results can be expected if solid phase characteristics are not clear (amorphous – crystalline).

SKB provided two preliminary reports in support of the treatment of concentration limits and solubility in SR-Can:

- Duro L., Grivé M., Cera E., Gaona X., Domènech C., Bruno J., Determination and assessment of the concentration limits to be used in SR-Met, Enviros Spain S.L., June 2005 (to be published in SKB's report series)
- Duro L., Grivé M., Cera E., Domènech C., Bruno J., Update of a thermodynamic database for radionuclides to assist solubility limits calculation for PA, Enviros Spain S.L., June 2005 (to be published in SKB's report series).

During the preparation for the workshop, only the first of the two reports was distributed to the participants. The initial impression was that SKB had to address a severe lack of technical justification for their estimations of concentration limits. However, much of this criticism turned out to be invalid once the second report was identified. To facilitate this problem, Paul Brown provided a complementary review of the database after the workshop (see Appendix C). His conclusion is that the overall quality of the database is good and that the second report is useful in underpinning the results presented in the first report dealing with the determination of the concentration limits in SR-Can. However, he suggested that an attempt should be made to assign uncertainty limits and that the significant figures listed seem too large. Furthermore, there appeared to be an inconsistency in the inclusion of different types of data. Thermodynamic data for solid compounds are included for the sake of completeness, while some aqueous complexes are excluded since they were expected to be of minor significance.

SKB's assessment of concentration limits for SR-Can is based on an updated approach in relation to one used for the former safety assessment SR-97 (Bruno et al., 1997). Concentration limits have been derived for the following radioelements: C, Cs, Sr, Ra, Sn, Se, Zr, Nb, Tc, Ni, Pd, Ag, Sm, Ho, Th, Pa, U, Np, Pu, A, Cm. Lara Duro explained the main developments in response to previous criticism which included:

- TDB consistency
- The consideration of buffer-interacted groundwater and groundwater subsequently interacted with the canister
- Uncertainty assessment.

The near-field water composition was derived from near-field SR-Can modelling. This is further discussed in Section 4. Error propagation in the TDB, uncertainty assessment and sensitivity analysis have not yet been fully completed but are part of an ongoing project.

The selection of solubility-limiting phase is a critical step in the calculations of concentration limits for safety assessment. A three-step approach was devised, which includes 1) calculations with the Meduse code to identify the most stable phase, 2) expert judgment on the selection of solid phase considering kinetic constrains, and comparison with laboratory and natural analogue data, 3) punctual solubility calculations with addition of element until equilibrium with the selected phase is reached. Sensitivity analyses reveal that the most critical groundwater chemistry variables are mostly pH, and for some nuclides Eh and ligand concentrations such as CO_3^{2-} and Cl^-.

The main conceptual uncertainties included the nature of the solid phases (crystalline – amorphous, mixed phases), groundwater composition that depends on scenario selection (e.g. glacial water, saline uplift) and whether or not sulphate reduction would be occurring. The numerical uncertainties included P and Fe concentrations, thermodynamic data uncertainty (mainly the effect of temperature), activity corrections and uncertainties connected to the use of a particular geochemical code (HYDRA-MEDUSA, PHREEQEC). Table 2 summarises the main uncertainties that were judged to be most important for each element.

SKB described how elemental solubilities were calculated for cases with different groundwater composition. Main highlights of calculations were:

- concentration of Ra determined by modelling is much less than that in natural groundwater, primarily because mixed phases are not being taken into consideration,
- concentration of U determined by modelling is less than that observed experimentally,
- concentration of Th determined by modelling is greater than that in natural groundwater.

SKB noted that the final application of this work will be the provision of pdfs for a probabilistic assessment. Using this approach, groundwater composition is the input for assessment calculations rather than solubility, so the pdfs will reflect uncertainty in groundwater composition and especially the range of pH values. Workshop participants felt that this was a good step forward, but wondered if uncertainty in thermodynamic data should not also be included in the overall uncertainty distribution. SKB responded that the aim of the modelling is not to provide realistic predictions of groundwater composition, but rather to provide upper concentrations limits. There is therefore no need to explicitly account for all sources of uncertainty with modelling tools.

SKB also pointed out that comparisons had been made with radionuclide concentrations measured in laboratory experiments and natural analogues. In this context, there was a strong consensus among the workshop participants that the diagrams provided in SKB's report Duro et al. (2005) were very useful (comparison of modelled concentrations with natural and experimental measurements). However, SKB suggested that more work would be needed to explain the order-of-magnitude differences between some of the derived concentration limits and their corresponding natural groundwater concentrations.

A question from the workshop participants was to what level mathematical/statistical modelling work was used in support of the reported sensitivity analyses and if a comparison had been made with previous results reported in the literature. SKB responded that sensitivity analyses were based on chemical reasoning and some additional calculations. Work related to error propagation was ongoing at the time of the workshop.

Table 2. Uncertainties regarded as most important for different radioelements in the estimation of concentration limits for the SR-Can safety assessment (Duro et al., 2005).

Element	Associated uncertainty
C	Reduction to $CH_4(g)$
Sr and Ra	SO_4^{2-} to HS^- reduction, possibility of co-precipitation with other carbonates
Sn	SO_4^{2-} to HS^- reduction
Se	Formation of native Se^0; SO_4^{2-} to HS^- reduction
Zr	Crystallinity of the solid phase
Nb	Scarcity of thermodynamic data
Tc	Formation of metallic Tc^0
Ni	SO_4^{2-} to HS^- reduction
Pd	Formation of metallic Pd^0
Ag	Formation of metallic Ag^0; SO_4^{2-} to HS^- reduction
Sm, Ho, Am, Cm	Effect of phosphates in water; Stability of the solid hydroxo-carbonate
Th	Crystallinity of the solid phase, uncertain thermodynamic data for aqueous carbonates
Pa	Scarcity of thermodynamic data
U	Formation of silicates
Np	Crystallinity of the solid phase
Pu	Effect of phosphates in water, stability of the solid hydroxo-carbonate; SO_4^{2-} to HS^- reduction

7 Sorption and migration of radionuclides through the bentonite buffer

In discussion between SKI and SKB prior to the workshop, it was decided that no specific SKB presentation would be urgently needed on this topic. However, Mike Stenhouse prepared a review of SKB's main supporting reference for the handling of buffer sorption and migration of radionuclides (Ochs and Talerico, 2004). This review was presented during the first day of the workshop (see Appendix C) and was discussed briefly with SKB during the second day. Since SKB did not have access to the experts with the most detailed knowledge in the area, a few detailed written questions were sent to the first author of the report (Ochs) after the workshop.

Since the dominant transport mechanism for radionuclides released from the canister is diffusion through compacted bentonite, the challenge of the database recommendations is to ensure consistency between distribution coefficients (K_d values), effective diffusion coefficients (D_e) and apparent diffusion coefficients (D_a), according to equation [1]:

$$D_a = D_e / (\varepsilon + K_d \rho) \qquad [1]$$

where ρ = dry density of bentonite (kg/m^3) and ε = available (diffusion) porosity (--).

In fact, the recommendations provided by Ochs and Talerico (2004) were not the final ones used by SKB for the SR-Can safety assessment (formal decision provided in SKB's SR-Can data report, 2006). Rather, the work by Ochs and Talerico (2004) allowed final selections to be made based on the groundwater speciations determined in the data report (SKB, 2006).

The review on behalf of SKI also took note of the consensus of the NEA Sorption Working Group, which concluded that porewater composition is the important governing link between K_d and D_e/D_a.

A number of questions were posed, centred round several key issues:

- Selection of the solid phase (compacted bentonite);
- Determination of the aqueous phase (calculated bentonite porewater composition);
- Rationale for selecting supporting experimental data;
- The use of analogue elements;
- Treatment of uncertainties.

In terms of the compacted bentonite and its component mineral phases, the selection process was normalized to a bentonite dry density of 1590 kg/m^3 and solid density of 2760 kg/m^3 [2]. The latter value is slightly different from previous assessments but was considered to be more

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[2] Three types of bentonite are currently being considered for the buffer by SKB.

reasonable for the disposal conditions specified by SKB, as well as being based on comparisons with various Japanese bentonites, all of which have solid densities > 2700 kg/m^3 (Ochs, 2006).

The reference bentonite composition quoted in Appendix B of Ochs and Talerico (2004) *appeared* to have been derived from a number of different sources, although linked to a single citation. However, the specified composition is the same as that provided in the studies of Wanner *et al.* (1992) and Wieland et al. (1994), to ensure internal consistency among calculated porewater compositions and the underlying bentonite composition. Thus, the bentonite-water interaction model proposed by Wanner et al. (1992) and Wieland et al. (1994) is based on, and consistent with, the bentonite composition reported by these authors.

Since the chemistry of bentonite porewater was derived by modelling the interaction of Swedish groundwater(s) with the compacted bentonite, a key input for this process was to identify specific groundwater compositions. It was noted that the reference groundwater compositions used by Ochs and Talerico (2004) were different from those selected by Duro *et al.* (2005) to determine upper limit elemental concentrations, in particular for highly saline conditions. However, Ochs [2006] commented that the work reported in Ochs and Talerico (2004) had been carried out at an early stage, before site-specific water compositions had been selected. Thus, the primary water composition selected as the basis for the sorption recommendations was the saline Beberg water taken from SR97 (Yu and Neretnieks, 1997; also cited in Laaksoharju et al.,1998). Thereafter, adjustments were made to this reference water for pH (by addition of NaOH) and salinity (by adding NaCl) to provide what was considered to be a range of groundwater compositions bounding expected groundwater chemistries.

Ochs (2006) rightly argues that any differences in specific groundwater compositions (compared with those selected in Duro et al., 2005) are insignificant when compared to the uncertainties in other parameters, in particular the controlling source of $p\mathrm{CO}_2$ in the buffer (whether bentonite-groundwater interactions or host rock). Further, the highly saline and non-saline waters were selected primarily to investigate the sensitivity of radionuclide migration parameters to groundwater composition.

As discussed in Ochs and Talerico (2004), the bentonite porewater compositions were calculated using the bentonite-water interaction model of Wanner et al. (1992) and Wieland et al. (1994). This model treats ion-exchange and surface-complexation reactions only.

A question was raised concerning the uncertainty in the evolution of bentonite porewaters and how to derive the porewater composition as a function of time. Ochs (2006) considered that the possible range of scenarios (for future evolution of the buffer) was covered adequately in the porewater compositions provided.

The systematic approach adopted by Ochs and Talerico (2004) to provide K_d values was to adopt a D_e value for tritiated water (HTO) and, thereafter, derive values of K_d for different elements based on chemical speciation under the specified conditions of bentonite porewater composition. The combination of D_e and K_d was then used to calculate D_a for comparison with corresponding D_a values obtained experimentally. Exceptions to this approach included anions and Cs^+. A D_e value for anions, together with uncertainty range, was evaluated separately and independently of diffusion porosity, but then linked to the most consistent value of ε. A similar process was carried out for Cs^+.

The selection of supporting experimental data was restricted to a relatively limited number of sorption/diffusion data in the literature, selected on the basis of what was considered to be high-quality experimental data, and representative of conditions that are relevant, or as close as possible, to those of SR-Can. The question was raised whether this range of supporting experimental data was sufficient to bound all possible conditions relevant to the SR Can safety assessment. Ochs (2006) noted that one of the problems with previous reviews of data was that the various sources of uncertainty were not treated in a consistent way, and that this was one of the primary motivations for carrying out the sorption study in as consistent a manner as possible. Thus, one of the fundamental characteristics in the approach adopted was to clearly define and characterize the parameter space representing possible in situ conditions. Thereafter, in the context of key conditional parameters, pH, carbonate concentration and salinity/ionic strength were selected as the basis for K_d derivation.

With regard to the use of analogues, the question was asked whether thorium is the best analogue for zirconium. Ochs (2006) commented that the basis for this selection was that both elements exist only in the +IV-valent state in normal aqueous solutions, and as an uncharged tetra-hydroxo species [$M(OH)_4^0$] around pH=7.

In terms of uncertainties, Ochs and Talerico (2004) carried out a detailed evaluation to provide a systematic analysis of different types of uncertainty, taking into account the sensitivity of K_d values to different parameters. It appeared that some uncertainties, for example cation exchange capacity (CEC) had been treated in a more quantitative manner than other factors, such as scatter in experimental data and scaling/conversion factors. Ochs (2006) responded that, while the available K_d database is not sufficient to calculate statistical uncertainties, the quantitative basis for the assumed uncertainty was the same throughout, i.e. based on typical experimental scatter.

Also, in the specific case of surface complexation and the role of pH, it was felt that the contribution to uncertainty of the impact of pH at the sorption edge may have been underestimated, with variability at least an order of magnitude. Ochs (2006) commented that the observed uncertainties in recommended K_d values were in line with this, in fact, spanning more than an order of magnitude.

Finally, a few editorial problems (wrong diagram, analogue conversion process for Am(III) to Pu(III), mistake in a K_d derivation, missing references) that contributed to some confusion in understanding the sorption study, were resolved by Ochs (2006).

8 Quality assurance and the handling of uncertainties

There was no SKB presentation exclusively devoted to this subject, but the topic was brought up several times during the discussions. Günther Meinrath made a presentation during the first day about the importance of assigning a measure of uncertainty when providing results from chemical measurement. Specified uncertainty levels should be taken into account when utilising such data. It was emphasised that there are multiple sources of uncertainty to evaluate and the assessment of them should be used to communicate a level of reliability of the measurement. The existence of internationally agreed conventions, which govern the treatment of uncertainty, was also brought up.

There was a discussion about how uncertainties are accounted for e.g. in spent fuel experiments. It is apparent that rigorous evaluations of the measurement uncertainty budget, which are sometimes conducted in international trade, are seldom made in this area of science. However, basic measures to ensure measurement reliability are implemented such as the use of duplicates/triplicates in ICP-MS analysis. Workshop participants suggested that QA in the context of ISO 9001 should be carried out. It should be clearly stated how measurement errors should be calculated and how uncertainty should be evaluated. At the same time, it would be unreasonable to discard all old data gathered before ISO 9001 was established. For old data, there should at least be some discussion about uncertainty. It was also suggested that modelling work should include propagation of errors (which implies that uncertainties have to be estimated when providing data for modelling). Error bars should, if possible be used when plotting experimental or modelling results.

A general question was to what extent a more detailed evaluation of uncertainties could be expected to improve the outcome from safety assessment. It was argued that the spent fuel parameters for safety assessment should be based on a broad experimental programme, which includes a series of experiments. This would mean that the reliability of a single measurement is not so critical. At the same time, if parameters are derived from small concentration differences, the potential for errors is quite large. SKB mentioned that dissolution rates were calculated based on the largest difference between consecutive points (measurements of concentration as a function of time together with analytic uncertainty), which provides an over-estimate.

9 Discussion and conclusion

During the last day of the workshop, there was a discussion among the independent experts and the SKI/SSI staff about the impressions from the responses given by SKB. The participants felt that they had a rather good overview of SKB's basis for handling safety functions associated with the fuel, sorption and radionuclide solubility in SR-Can. Comments brought up by the reviewers during the workshop discussion and in their extended abstract would be useful to follow up in future stages of the review of SKB's programme. However, since the relative importance of safety functions in SR-Can would depend on how the information is put together in the entire safety assessment, it was too early to draw any conclusions regarding the sufficiency of data and the methods applied in the background reports. It was suggested that the workshop should be followed up by additional review activities one after the publication of SR-Can so that the reviewers can draw conclusions based on a better knowledge of their context.

The value of the new experimental information in the fuel area (especially the H_2-effect) and the methodological developments in the sorption and radionuclide solubility area were acknowledged. Nevertheless, regarding SKB's presentations covering the fuel area, the workshop participants would have liked to have had a more comprehensive description of the philosophy behind the experimental data gathering and less detailed information about the dataset itself and the experimental methods. There is a need to provide a structure for how data, assumptions and models should be tied together and what the impact are of the data and conceptual uncertainties, which have been identified and discussed within the scientific community.

The implications of conceptual uncertainties related to the spent fuel performance were regarded as limited or moderate considering that the Swedish spent nuclear fuel has a rather low burn-up. However, there is still a need to further evaluate those implications since the spent fuel performance is a key aspect of the long-term safety. This would be even more important if higher burn-up fuel or additional MOX-fuel were to be produced in the future.

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Appendix A: Participants

External Experts

Mike Stenhouse	Monitor Scientific LLC
Heino Nitsche	Nitsche Consulting
Christophe Jégou	CEA
Günther Meinrath	RER consultants
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Lars Werme
Kastriot Spahiu
Patrik Sellin
Virgina Oversby (consultant)
Jordi Bruno (Enviros)
Lara Duro (Enviros)
Mats Jonsson (KTH)

Appendix B: Questions to SKB

List of issues distributed to SKB prior to the workshop

Comment: There is no need to provide detailed answers to all questions on this list of issues. Issues on this list are only intended to stimulate fruitful discussions during the hearing with SKB. Other issues may also be brought up.

1. Instant release fractions

Exact definition of instant release and justification of inclusion/exclusion of various sources (e.g. rim micro-structure, segregated phases)?

How to handle lack of data?

Degree of conservatism in SR-Can data?

More information about thermal history and features of BWR fuel?

2. Spent fuel alteration

Mechanistic model to demonstrate understanding of e.g. hydrogen inhibiting effect?

Minimum hydrogen level for inhibiting effect?

Sufficiency of available hydrogen in the long-term?

Other groundwater chemistry factors which needs to be considered?

Accounting for specific surface area in estimating the annual release fraction?

Relationship with structural degradation of fuel pellets?

Approach for incorporating variability and possibly time-dependence for annual release fractions in safety assessment?

Alteration by UO_2-solubility e.g. pump-effect and coffinite formation?

3. Spent fuel other

Systematic compilation and characterisation of assumptions used for SR-Can model?

Additional experimental studies to be accounted for?

Use of in-situ CHEMLAB experiments?

Any significant fuel inventory uncertainties?

Accounting for variability due to fuel-type, burn-up, linear power density, fuel damage etc.?

Handling of MOX-fuel?

Alteration of fuel during long-term storage?

Formation of fuel colloids?

4. Radionuclide solubility

How are uncertainties in model calculations accounted for?

Selection of solubility limiting phases?

How is variability in concentration limits accounted for (as opposed to only using mean values)?

Definition of ranges of groundwater composition that must be accounted for?

Influence of kinetics in the consideration of radionuclide solubility?

Influence of co-precipitation?

What are requirements on thermodynamical data to make sufficiently reliable predictions of solubilities?

How are measurement uncertainty accounted for? Do SKB participate in proficiency tests and round-robin studies?

5. Radionuclide sorption

How is radionuclide sorption modelled and used?

Are these models flexible and able to use for predictions if the aquatic chemistry changes?

Limitations imposed by using Kd-concept?

Definition of ranges of groundwater composition that must be accounted for?

6. Evolution of environmental conditions

How are redox equilibrium estimated and used in the simulations and estimations?

Evidence that magnetite will be the main corrosion product?

Are there any slow and irreversible processes contributing to the chemical evolution of the repository environment?

Do any of these provide significant uncertainties in the context of the safety assessment?

7. Others

General definition of sufficient quality for using data in safety assessment?

Appendix C: Extended Abstracts

Mike Stenhouse : Review of Transport Properties for Radionuclides in the Near-Field of a Repository for Spent Fuel

Heino Nitsche: Challenges and Issues with Neptunium Thermodynamic data

Christophe Jégou: Discussion on the main hypotheses and results developed in report SKB TR-04-19

Paul Brown: The Uncertainty of the Equilibrium Assumption

Paul Brown: Comments on "Update of a thermodynamic database for radionuclides to assist solubility limits calculations for PA" by Duro et al. (2005a)

Günther Meinrath: The implications if internationally agreed criteria for measurement data for performance assessment of nuclear waste repositories

*** The extended abstracts for each workshop paper will follow this ***

Review of Transport Properties for Radionuclides in the Near-Field of a Repository for Spent Fuel

Mike Stenhouse, Monitor Scientific LLC, Denver, Colorado, U.S.A.

1. Introduction

This extended abstract presents the main findings of a review of SKB TR-04-18: "*Data and uncertainty assessment: Migration parameters for the bentonite buffer in the KBS-3 concept*", prepared by Michael Ochs and Caterina Talerico (2004)[1] as part of the SR-Can safety assessment. The work is placed in the context of a previous compilation of migration parameters provided for compacted bentonite for SR-97 in Andersson (1999). Thereafter, the methodology of O&T (2004) is discussed and their results presented and compared with the previous compilation.

COMP#23 is the near-field migration code used by SKB to calculate radionuclide migration by diffusion through the buffer. It assumes constant values of effective diffusivity (D_e, m^2/s), diffusion-available porosity (ε) and distribution coefficient (K_d, m^3/kg) in each compartment.

For the buffer, under conditions where sorption is linear, C_p, the concentration of the diffusing species, is given by the following equation:

$$\frac{\partial C_p}{\partial t} = D_e / (\varepsilon + K_d \rho) \partial^2 C_p / \partial x^2 = D_a \partial^2 C_p / \partial x^2 \qquad [1]$$

where ρ is the dry density of bentonite (kg/m^3), and D_a is the apparent diffusion coefficient (m^2/s), i.e., $D_a = D_e/\varepsilon + \rho K_d$.

1.1 Background

The previous recommendations for SKB for the SR 97 safety assessment were provided by Andersson (1999). The main sources of data in this latter report for the key transport parameters for compacted bentonite were from Yu and Neretnieks (1997) and Ochs (1997).

In the review of the sorption data for compacted bentonite, Stenhouse (2000) noted the lack of a reference porewater composition for compacted bentonite by Yu and Neretnieks (1997). For his report, Ochs (1997) determined the pH of bentonite porewater at just below 7, based on geochemical modelling and the assumption that the bentonite-porewater is a *closed system* with regard to CO_2 availability. On the other hand, Bruno *et al.* (1999) favoured a porewater composition that reflected more the composition of incoming groundwater, and calculated (thermodynamic modelling) a pH of close to 9. Muurinen and Lehikoinen (1998) also preferred this latter approach, determining a final porewater of around 9 and 8.8 for interaction of bentonite with fresh and saline waters, respectively. Thus, while acknowledging the lack of consensus on how such a reference porewater composition should be established, Stenhouse (2003) considered the lack of a reference porewater a major omission in the work of Yu and Neretnieks (1997).

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[1] Hereafter referred to as O&T (2004).

In his compilation, Andersson (1999) took into account the conclusions of Ochs (1997) in providing the final recommendations for SR 97, adopting a conservative approach in recommending K_d values for sorption of radionuclides on compacted bentonite that were considered reasonable in the review.

In terms of an understanding of sorption processes, significant amount of work on the interpretation of K_d values has been done since the previous recommendations. In particular, the NEA Sorption Working Group appear to have reached a consensus about the key aspects of K_d measurement. Particular emphasis is attached to the aqueous phase chemistry, and members of this Group believe that if the solution chemistry is characterized adequately, then the K_d result can be interpreted in a meaningful way (NEA, 2004), *i.e.*, porewater composition is the main governing link between K_d and D_e/D_a. In terms of bentonite porewater chemistry, the outstanding issue is how geochemical conditions and bentonite properties should be taken into account for the calculation of the buffer porewater composition.

2. Current Approach / Philosophy

The work of O&T (2004) takes into account the conclusions of the previous review of Ochs (1997) but, in response to other peer review comments of the SR 97 and SFL 3-5 safety assessments, in particular concerning the use of expert opinion as well as the quantification of uncertainties (SKI/SSI, 2000), provides a different, more transparent methodology for determining migration parameters for compacted bentonite. Thus, given this different approach for the most recent compilation, values of K_d and D_e by O&T (2004) are not strictly comparable with previous compilations, as discussed below.

O&T (2004) note that their recommendations concerning data and uncertainty are based on an approach that follows a standardized outline and instructions provided by SKB. This approach has been adopted presumably in response to review comments provided by the regulators (SKI/SSI, 2001). These instructions are included in different sections of the report, as appropriate.

In their discussion of diffusion data, which is an extension of Och's previous discussion (Ochs, 1999), O&T (2004) note that diffusion coefficients need to be extracted from raw experimental data, which requires the use of some form of model. Under these, circumstances, interpretation of experimental results must be treated with caution. For this reason, the authors' approach for most radionuclides, with the exceptions of anions and Cs, is 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 are used to generate an apparent diffusion coefficient (D_a) using Equation [1], which is compared with experimental determinations of D_a, where available, as a final "consistency check".

The key arguments posed by O&T (2004) as a basis for adopting a D_e for HTO, combined with K_d measurements using batch sorption are:

- Lack of D_e data for reactive elements, *i.e.*, ones that sorb strongly on compacted bentonite;
- D_e values for HTO are not sensitive to the specific chemical conditions and, therefore, are more relevant than element-specific data obtained under one set of conditions.

- In terms of sorption, the key component of bentonite is the smectite montmorillonite, so that the latter mineral can be taken as representative of the sorption properties of bentonite, given the allowance for similar porewater chemistry.

The approach of O&T (2004) is to derive K_d values that are representative of porewater compositions that have been calculated for this work. Sorption K_d measurements involving compacted bentonites are difficult to interpret because typically values must be 'extracted' (de-convoluted) from the underlying diffusion measurements. Direct measurements of K_d on compacted bentonties are virtually non-existent. In addition, porewater compositions are difficult to characterise, so that comparisons with, or scaling to, reference bentonite porewaters for SR-Can are also difficult.

A key finding used by O&T (2004), as a basis for their treatment of sorption data, is the similarity in measurement results of surface area (BET value) of loose and compacted (2,000 kg/m^3) bentonites – both MX-80 and Montigel bentonites. Kato *et al.* (1995) also favour no reduction in sorption-available surface area for bentonites on compaction. Consequently, O&T (2004) conclude that K_d values obtained from batch sorption experiments can be applied to compacted bentonite, "*provided that differences in solution composition are accounted for".* Any discrepancies between K_d values for batch experiments and compacted bentonite can be resolved as long as the chemistries of the solution or porewaters are accounted for, including compaction (solid/liquid ratio) (Ochs et al., 2003; Bradbury and Baeyens, 2003).

2.1 Sources of Data

O&T (2004) apply a restrictive constraint on what sorption source data to use in their derivation or 'scaling' process involving K_d values. Data sources must fulfil two basic requirements:

- Data must correspond to, or allow the derivation of, parameters to the compacted state of 1,590 kg/m^3;
- Data must correspond to, or allow the derivation of, parameters applicable to the relevant geochemical conditions, in particular porewater composition corresponding to the compacted state

Accordingly, primary data preferences focus on systematic sets of high-quality data where parameters have been provided as a function of conditions. For diffusion source data, the primary preferences are:

- Diffusion data as function of density in pre-equilibrated bentonite;
- Diffusion data as function of density for MX-80;
- Diffusion data as function of density for other bentonites.

For sorption source data, the corresponding primary preferences are:

- Large systematic data set or isotherm modelling for bentonite type MX-80 or similar bentonite;
- Representative sorption modelling;
- Few but systematic data for MX-80;

- Few systematic sorption data for other bentonites.

As a result of these constraints, the sources of data used by O&T (2004) are relatively limited. In reviewing possible diffusion data, however, O&T (2004) note that most diffusion data have been measured using compacted bentonite, with the range in the degree of compaction encompassing the reference compaction of 1,590 kg/m^3. Furthermore, diffusion measurements on other bentonites indicate a similar dependence of diffusion coefficient on density.

The main sources of data used by O&T (2004) were:

- Data provided for the Swiss HLW disposal programme (Bradbury and Baeyens, 2003), including sorption data obtained using a synthetic porewater;
- Yu and Neretnieks (1997);
- Diffusion data from the Japanese HLW programme, provided by Sato and co-workers, *e.g.*, Sato *et al*. (1995).

2.2 Conversion Process

The sequence of steps in the conversion process carried out by O&T (2004) are:

- Definition of conditions under which transport parameters were to be considered;
- Derivation of diffusion-related physical parameters, *i.e.*, D_e and ε for the reference dry density of bentonite. This derivation process covers all elements except anions and Cs, and for a number of different porewater compositions. Thereafter, the derivation process addresses:
  - D_e values and ε for anions;
  - D_e values and ε for Cs.
- Derivation of K_d values for each element.

This approach follows closely that of Bradbury and Baeyens (2003), who carried out a similar derivation of data for the Swiss national HLW programme supervised by Nagra.

The starting points for establishing 'reference' conditions are:

- Selected buffer material, MX-80, reference density (ρ) 1,590 kg/m^3, composition provided;
- Groundwater compositions (Laaksoharju *et al*., 1998).

Thereafter, O&T (2004) established a range of bentonite porewater compositions based on the initial groundwater compositions. It is not clear from the report, however, how many of the groundwaters provided by Laaksoharju *et al*. (1998) were used in this way by O&T (2004).

The conversion, or derivation, process involving K_d values relies on the following factors, applied to experimental sorption data:

- (1) Allowance for different sorption capacity of solid phase between source data and reference conditions, via use of cation-exchange capacity (CEC): *CF-CEC.*

- (2) Allowance for pH differences affecting the extent of sorption between source data experiments and reference conditions: use of data for radionuclide sorption on sorption edges, primarily accounting for hydrolysis: via *CF-pH*.
- (3) Allowance for differences in speciation between experimental/modelling conditions (data source) and reference conditions. Such allowance was determined by speciation modelling to identify potential competition between ligands and sorption sites for each radionuclide. This competition was interpreted in two ways;
  - Assuming that carbonato complexes compete with sorption sites: *CF-spec2*;
  - Assuming that carbonato complexes do *not* compete with sorption sites, reflecting substantial evidence that such complexes sorb themselves: *CF-spec3*.

2.3 Use of Analogues

Chemical analogues have been widely used in the past for cases where there is a lack of experimental/modelling data for a specific element. O&T (2004) also make use of analogues and, in cases where analogues are invoked, have a slightly different derivation procedure, to be consistent with the derivation procedure carried out for other elements.

3 Uncertainties

O&T (2004) identify, and attempt to quantify, several sources of uncertainty in deriving transport parameter values for buffer migration, *viz.*

- Uncertainty associated with the original (experimental/modelling) data;
- Uncertainty in converting the source data to conditions representative of the KBS-3 near-field;
- Uncertainty in knowledge of future conditions.

As discussed previously, the main uncertainty affecting near-field conditions concerns pCO_2 and, hence, *pH*, and whether the buffer is assumed to be closed with respect to pCO_2 exchange with the host rock. Under closed conditions, pCO_2 is controlled by bentonite-groundwater interactions. Under open conditions, pCO_2 is dictated by external pCO_2 in the host rock. To cover this uncertainty, O&T (2004) model porewater compositions under both conditions.

Uncertainty factors are provided by O&T (2004) for each of the above conversions, to be used to multiply or divide the best estimate in order to obtain an overall range, *viz.*
- UF-CEC: 1.4
- UF-pH: 2.5
- UF-spec: 1.4.

In addition, uncertainty factors are provided to reflect uncertainty in:

- Conversion of batch sorption data to conditions in compacted bentonite: UF-batch => compacted: 2.0
- Data sources. Given the restricted number of sources that were used to derive K_d values, an uncertainty factor of 1.6 was adopted, *i.e.*, UF-K_d-starting data: 1.6.
- Use of analogues: UF-starting K_d: 2.5.

As a result of the above analysis and quantification of uncertainties, overall upper and lower limits are provided for each best estimate K_d value.

4. Overall General Comments

Table 1 provides a comparison of D_a values calculated using the recommendations of O&T (2004) with D_a values calculated based on SR 97 data for D_a, ε, and K_d values. Note that in both cases, D_a values have been calculated for this review, and are not provided in either report. Thus, D_a values have been calculated in the case of SR 97 safety assessment calculations using *realistic* K_d values provided in Lindgren (1999), and, in the case of SR-Can, best estimate values of K_d.

The comparison indicates that, although the primary D_e value used by O&T (2004) is more conservative that the D_e values used in SR 97, best estimate K_d values and, hence, D_a values calculated using these K_d values, are, in most cases, less conservative than the corresponding SR 97 data. However, the upper and lower limits applied to best estimate K_d values by O&T (2004), based on these authors' analysis and quantification of uncertainties, yield a relatively wide range in K_d values, typically more than one order of magnitude and often two orders of magnitude.

The recommendations of O&T (2004) must be considered as a work-in-progress in the sense that additional guidance will be necessary prior to safety assessment calculations, in particular:

- Which reference porewater composition to use as the basis for K_d value for central, or reference, scenario.
- Which K_d value(s) to use – whether best estimate or lower limit in range of K_d value.

Perhaps a weakness in the overall evaluation of recommended or derived transport properties, is the use of what O&T (2004) refer to as "soft terminology" in the final qualification of their K_d ranges, *i.e.*, in terms of 'extremely likely', 'very likely', 'likely', or 'probable'.

4.1 Evolution of Porewater Composition

Evolution of bentonite porewaters is accounted for by starting with a range of groundwater compositions covering a broad range of compositions, including what are considered to be extreme cases, and then deriving (thermodynamic modelling) corresponding bentonite porewater compositions based on interaction of bentonite with these individual groundwater compositions.

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Table 1: Comparison of Migration Parameters for SR-Can and SR 97

Radio-nuclide	***SR 97 Lindgren (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 RPW^2**	**RPWC^2**	**D_a (m^2/s)^3 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-}		3.00E-11	**7.32E-11**	Isotopic exchange			
Cl(-I)	0	1.00E-12	**2.44E-12**	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)	0.2	3.00E-12	**7.32E-12**	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)	0.01	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: ^1D_a values calculated using dry density 1590 kg/m^3; porosity 0.41.
^{2} RPW = Reference bentonite porewater (open system);
^{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.

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Challenges and Issues with Neptunium Thermodynamic Data

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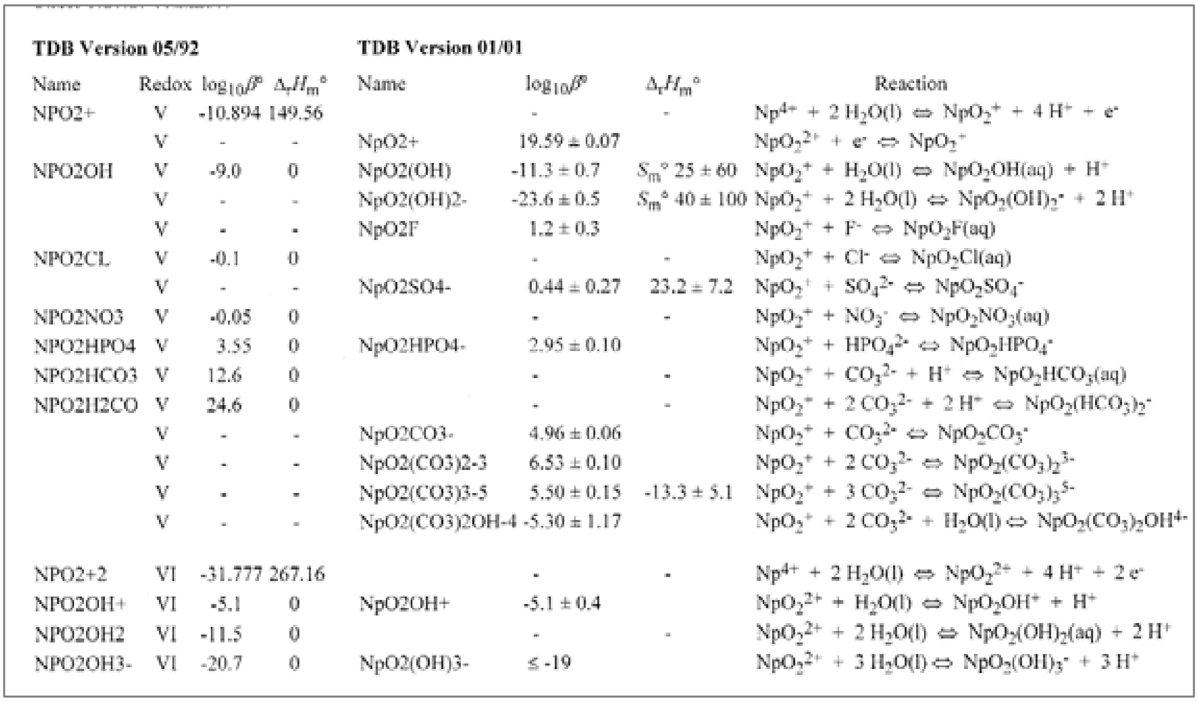
Thermodynamic data are commonly used to assess solubility and speciation of materials for performance assessment of geologic nuclear waste repositories. Although several extensive thermodynamic databases (Lemire 2001; Hummel 2002) have been compiled, many data required to predict potential retention, release and migration rates of radionuclides from a geologic nuclear waste repository are either insufficiently or not at all known. For such cases, estimates and extrapolations are used from data of either homologous elements or elements that display oxidation states and ionic radii similar to the element for which data are unavailable. Furthermore, ongoing research will produce new and improved thermodynamic data, thus requiring continuous updating of existing thermodynamic database. I would like to use the currently accepted numbers for the neptunium(V) hydrolysis and the solubility-controlling phases, Np_2O_5, $\text{NaNpO}_2\text{CO3}$, and NpO_2 as examples to demonstrate this point.

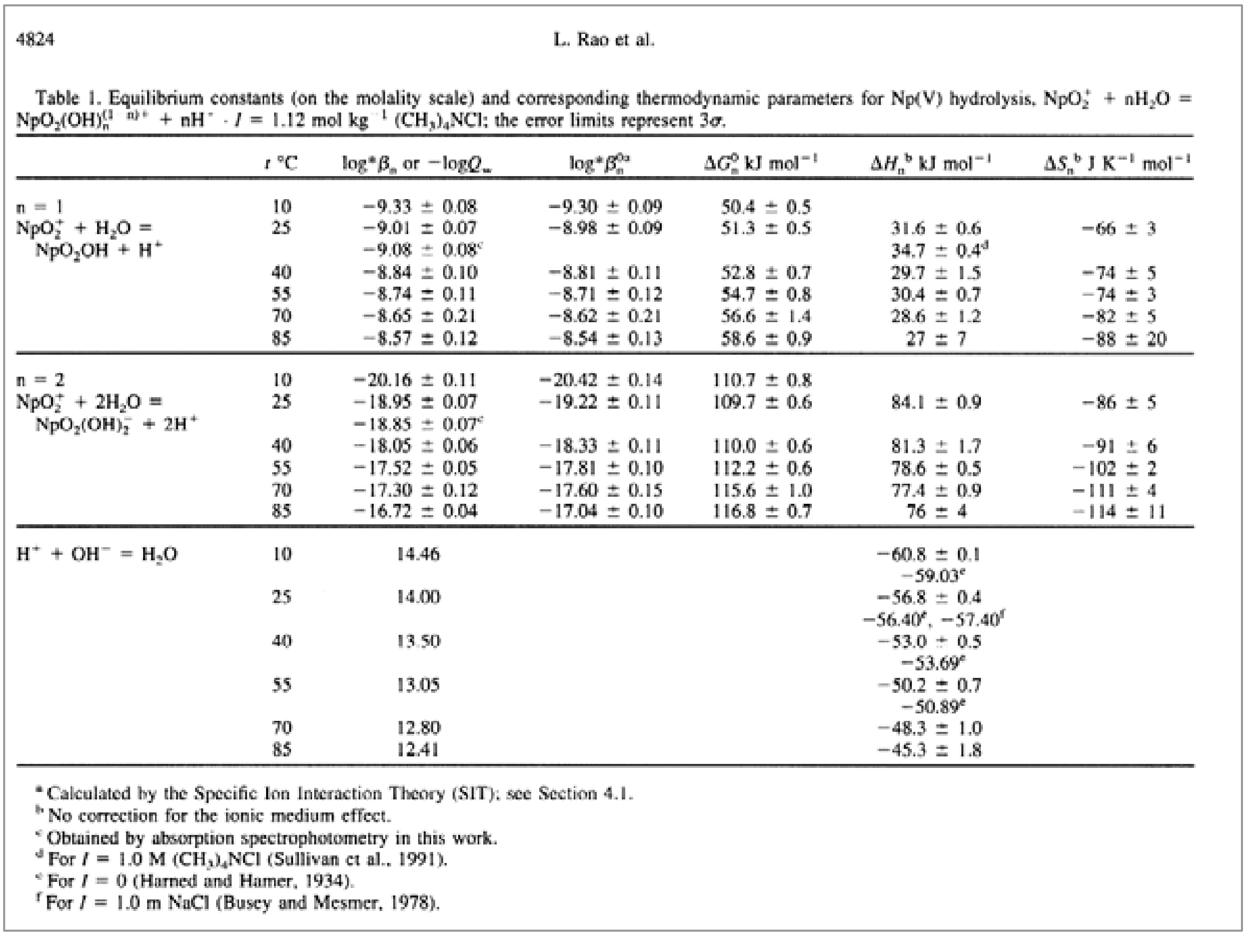
Neptunium(V) Hydrolysis

The currently accepted neptunium(V) hydrolysis values of $\beta_{1,1} = -(11.3 \pm 0.\ 7)$ and $\log \beta_{1,2} = -(23.6 \pm 0.5)$ for the first and second neptunium(V) hydrolysis constant, respectively are shown in Table 1.



TDB Version 05/92				TDB Version 01/01			
Name	Redox	$\log_{10}\beta°$	$\Delta_r H_m°$	Name	$\log_{10}\beta°$	$\Delta_r H_m°$	Reaction
NPO2+	V	-10.894	149.56		-	-	$Np^{4+} + 2\,H_2O(l) \Leftrightarrow NpO_2^+ + 4\,H^+ + e^-$
	V	-	-	NpO2+	19.59 ± 0.07		$NpO_2^{2+} + e^- \Leftrightarrow NpO_2^+$
NPO2OH	V	-9.0	0	NpO2(OH)	-11.3 ± 0.7	$S_m°$ 25 ± 60	$NpO_2^+ + H_2O(l) \Leftrightarrow NpO_2OH(aq) + H^+$
	V	-	-	NpO2(OH)2-	-23.6 ± 0.5	$S_m°$ 40 ± 100	$NpO_2^+ + 2\,H_2O(l) \Leftrightarrow NpO_2(OH)_2^- + 2\,H^+$
	V	-	-	NpO2F	1.2 ± 0.3		$NpO_2^+ + F^- \Leftrightarrow NpO_2F(aq)$
NPO2CL	V	-0.1	0		-	-	$NpO_2^+ + Cl^- \Leftrightarrow NpO_2Cl(aq)$
	V	-	-	NpO2SO4-	0.44 ± 0.27	23.2 ± 7.2	$NpO_2^+ + SO_4^{2-} \Leftrightarrow NpO_2SO_4^-$
NPO2NO3	V	-0.05	0		-	-	$NpO_2^+ + NO_3^- \Leftrightarrow NpO_2NO_3(aq)$
NPO2HPO4	V	3.55	0	NpO2HPO4-	2.95 ± 0.10		$NpO_2^+ + HPO_4^{2-} \Leftrightarrow NpO_2HPO_4^-$
NPO2HCO3	V	12.6	0		-	-	$NpO_2^+ + CO_3^{2-} + H^+ \Leftrightarrow NpO_2HCO_3(aq)$
NPO2H2CO	V	24.6	0		-	-	$NpO_2^+ + 2\,CO_3^{2-} + 2\,H^+ \Leftrightarrow NpO_2(HCO_3)_2^-$
	V	-	-	NpO2CO3-	4.96 ± 0.06		$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$
	V	-	-	NpO2(CO3)2-3	6.53 ± 0.10		$NpO_2^+ + 2\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$
	V	-	-	NpO2(CO3)3-5	5.50 ± 0.15	-13.3 ± 5.1	$NpO_2^+ + 3\,CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$
	V	-	-	NpO2(CO3)2OH-4	-5.30 ± 1.17		$NpO_2^+ + 2\,CO_3^{2-} + H_2O(l) \Leftrightarrow NpO_2(CO_3)_2OH^{4-}$
NPO2+2	VI	-31.777	267.16		-	-	$Np^{4+} + 2\,H_2O(l) \Leftrightarrow NpO_2^{2+} + 4\,H^+ + 2\,e^-$
NPO2OH+	VI	-5.1	0	NpO2OH+	-5.1 ± 0.4		$NpO_2^{2+} + H_2O(l) \Leftrightarrow NpO_2OH^+ + H^+$
NPO2OH2	VI	-11.5	0		-	-	$NpO_2^{2+} + 2\,H_2O(l) \Leftrightarrow NpO_2(OH)_2(aq) + 2\,H^+$
NPO2OH3-	VI	-20.7	0	NpO2(OH)3-	≤ -19		$NpO_2^{2+} + 3\,H_2O(l) \Leftrightarrow NpO_2(OH)_3^- + 3\,H^+$

Recently, Rao and coworkers (Rao 2004) published a paper titled “Hydrolysis of Neptunium(V) at Variable Temperatures (10-85°C).” This paper appeared to be a most comprehensive and long-awaited clarification of neptunium thermodynamics, including standard formation enthalphies, Gibbs free energies, and standard entropies that were derived for a combination of absorption spectroscopic, potentionmetric titration and micro-calorimetric measurements. The thermodynamic date that were derived in this publication derived are shown in Table 2.



4824 L. Rao et al.

Table 1. Equilibrium constants (on the molality scale) and corresponding thermodynamic parameters for Np(V) hydrolysis. $NpO_2^+ + nH_2O = NpO_2(OH)_n^{(1-n)+} + nH^+$ · I = 1.12 mol kg^{-1} $(CH_3)_4NCl$; the error limits represent 3σ.

	t °C	log*β_n or −logQ_w	log*β_n^{0a}	ΔG_n^0 kJ mol^{-1}	ΔH_n^{b} kJ mol^{-1}	ΔS_n^{b} J K^{-1} mol^{-1}
n = 1	10	−9.33 ± 0.08	−9.30 ± 0.09	50.4 ± 0.5		
$NpO_2^+ + H_2O =$	25	−9.01 ± 0.07	−8.98 ± 0.09	51.3 ± 0.5	31.6 ± 0.6	−66 ± 3
$NpO_2OH + H^+$		−9.08 ± 0.08^c			34.7 ± 0.4^d	
	40	−8.84 ± 0.10	−8.81 ± 0.11	52.8 ± 0.7	29.7 ± 1.5	−74 ± 5
	55	−8.74 ± 0.11	−8.71 ± 0.12	54.7 ± 0.8	30.4 ± 0.7	−74 ± 3
	70	−8.65 ± 0.21	−8.62 ± 0.21	56.6 ± 1.4	28.6 ± 1.2	−82 ± 5
	85	−8.57 ± 0.12	−8.54 ± 0.13	58.6 ± 0.9	27 ± 7	−88 ± 20
n = 2	10	−20.16 ± 0.11	−20.42 ± 0.14	110.7 ± 0.8		
$NpO_2^+ + 2H_2O =$	25	−18.95 ± 0.07	−19.22 ± 0.11	109.7 ± 0.6	84.1 ± 0.9	−86 ± 5
$NpO_2(OH)_2^- + 2H^+$		−18.85 ± 0.07^c				
	40	−18.05 ± 0.06	−18.33 ± 0.11	110.0 ± 0.6	81.3 ± 1.7	−91 ± 6
	55	−17.52 ± 0.05	−17.81 ± 0.10	112.2 ± 0.6	78.6 ± 0.5	−102 ± 2
	70	−17.30 ± 0.12	−17.60 ± 0.15	115.6 ± 1.0	77.4 ± 0.9	−111 ± 4
	85	−16.72 ± 0.04	−17.04 ± 0.10	116.8 ± 0.7	76 ± 4	−114 ± 11
$H^+ + OH^- = H_2O$	10	14.46			−60.8 ± 0.1	
					−59.03^e	
	25	14.00			−56.8 ± 0.4	
					−56.40^e, −57.40^f	
	40	13.50			−53.0 ± 0.5	
					−53.69^e	
	55	13.05			−50.2 ± 0.7	
					−50.89^e	
	70	12.80			−48.3 ± 1.0	
	85	12.41			−45.3 ± 1.8	

[a] Calculated by the Specific Ion Interaction Theory (SIT); see Section 4.1.
[b] No correction for the ionic medium effect.
[c] Obtained by absorption spectrophotometry in this work.
[d] For I = 1.0 M $(CH_3)_4NCl$ (Sullivan et al., 1991).
[e] For I = 0 (Harned and Hamer, 1934).
[f] For I = 1.0 m NaCl (Busey and Mesmer, 1978).

The reported formation constants for the first and second neptunium(V) hydrolysis complex with log $\beta_{1,1}$ = − (8.89 ± 0.01) and log $\beta_{1,2}$ = − (18.95 ± 0.07), respectively, are lower by several orders of magnitude when compared to currently accepted values of $\beta_{1,1}$ = − (11.3 ± 0. 7) and log $\beta_{1,2}$ = − (23.6 ± 0.5) that are published in several current data compilations. Applying the newly published data by Rao et al. would mean that at 25°C in an aqueous solution at a pH of nine, approximately 50 percent each of neptunium(V) would each exist as the first hydrolysis species, NpO_2OH, and as unhydrolyzed dioxoneptunyl(V) cation, NpO_2^+. However on closer examination of the spectrophotometric data at 25 °C, a severe inconsistency with existing data must be noted. Rao et al. report measuring a shift in the absorption spectrum of NpO_2^+ from 980.4 nm to 991 nm with increasing hydroxyl ion concentration, reproduced here as Figure 1. The authors state "by using much lower concentrations of Np(V) and smaller additions of (CH3)4NOH, spectra with better resolution were obtained as shown in Figure 5B. From spectra 1 to 8, the peak of the free NpO_2^+ (aq) at 980.4 nm decreased with the increase in the concentration of hydroxide, and a peak at 991 nm appeared and reached maximum intensity in Spectra 5. As the concentration of hydroxide was further increased (from spectra 5 to 8), the intensity at 991 nm decreased and broad bands appeared at longer wavelengths. The spectra are similar to those observed by Tananaev (1990) and Sevost'yanova and Khalturin (1976)."

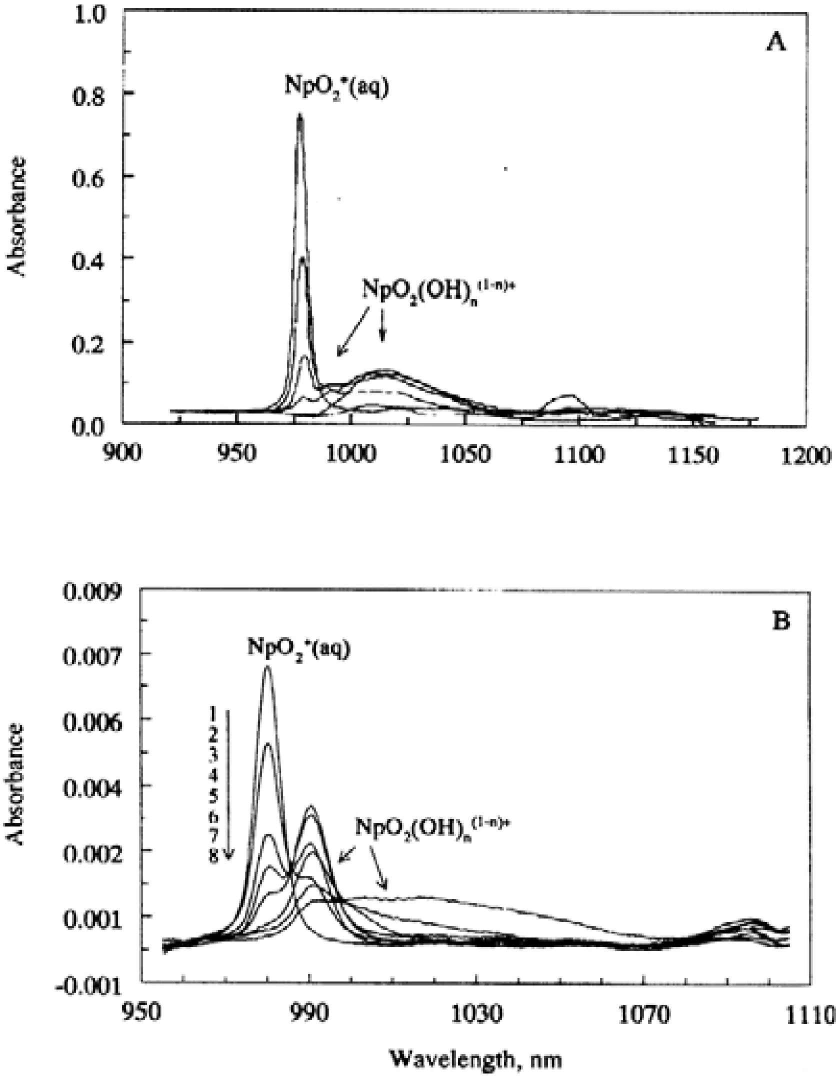


Fig. 5. Absorption spectra of Np(V). $I = 1.12$ mol kg^{-1} $(CH_3)_4NCl$, t = 25°C, optical path 1.0 cm. (A) $C_{Np} = 1.8 \times 10^{-3}$ mol dm^{-3}, C_{OH} = 0–1.0 mol dm^{-3}; (B) $C_{Np} = 1.75 \times 10^{-5}$ mol dm^{-3}, C_{OH} (mol dm^{-3}) for Spectra 1–8: 1e-7, 6.6e-6, 2.67e-5, 4.0e-5, 5.6e-5, 1.0e-4, 1.35e-4, 2.0e-4.

Although it was known from the literature since the early 1990's that the addition of hydroxide ions to an acidic Np(V) solution does not cause a shift to the absorption band of the free NpO_2^+ at 980 nm and results, at best, in line broadening of the band of the free ion. Rao et al. showed in Figure 5 of their publication a spectral shift of this band from 980 to about 991nm with the addition of hydroxide. This is a severe problem with their published experiments and a clear indication that the authors must have experienced contamination from carbonate in their experiments, thus putting in question the reported results of their study.

Nitsche, Standifer and Silva (Nitsche 1990) [1] state "We must emphasize the complete absence of an absorption band at 991 nm in the carbonate-free NpO_2^+ solutions when we increased the pH to 8.5. Sevost'yanova and Khalturin utilized this peak at 991 nm for hydrolysis studies by absorption spectroscopy. Our results do not confirm their finding. Only the addition of small amounts of carbonate to our NpO_2^+ solution (5.56 x 10^{-5} M) of constant pH 8.5 ± 0.02 produced the band at 991 nm. The band grew with increasing carbonate concentration, and the NpO_2^+ - NpO_2OH peak at 980 nm decreased." Nitsche et al show in their publication that the shift of the Np(V) absorption band from 980.4 nm to 991.1 nm is solely due to the addition to carbonate. A reproduction of these absorption spectra are shown in Figure 2.

HEINO NITSCHE ET AL.

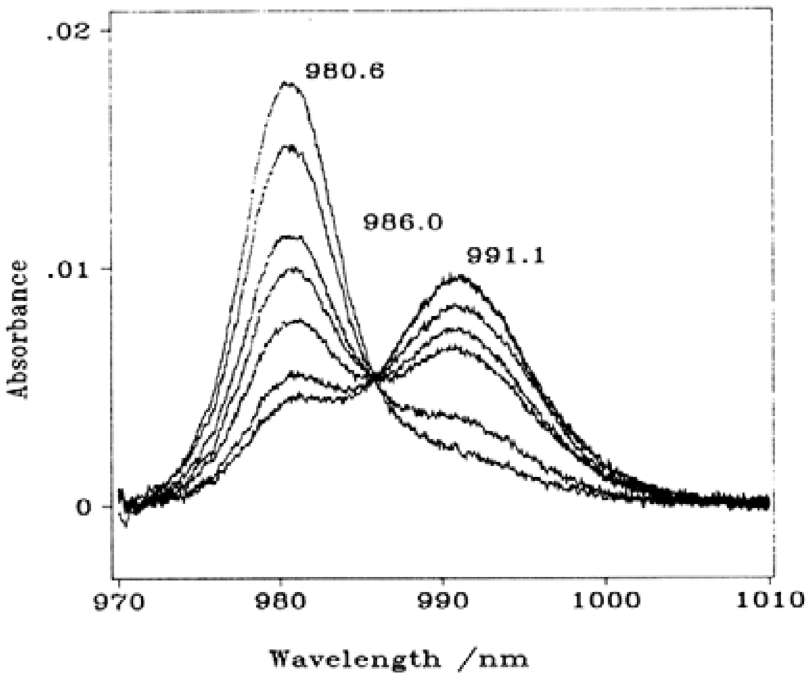


FIGURE 1. Absorption spectra of neptunium(V) carbonate solutions; [Np] = 5.56×10^{-5} M, $[CO_3^{2-}] = 3.39 \times 10^{-6}$ to 1.45×10^{-4} M.

Neck, Kim and Kanellkopolous (Neck 1992) also investigated neptunium(V) hydrolysis and carbonate complexation by spectrophotometry and state[2] "Fig. 4b demonstrates the influence of carbonate contamination on the absorption spectrum of Np(V). The first spectrum shows a saturated Np(V) solution at pH = 9.9 under inert argon atmosphere. When the quartz cuvette was opened, atmospherical CO_2 entered the solution immediately. Simultaneously the NpO_2^+ peak at 982 nm decreased and a new band at 993 nm arised. In fact the absorption band at 993 nm is not caused by hydrolysis reactions as claimed by Sevost'yanova and Khalturin

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[1] page 205

[2] Page 29

(Sevost'yanova 1976), but obviously by Np(V) carbonate complexation.” Figures 4a/b of their publication are reproduced here as Figure 3.

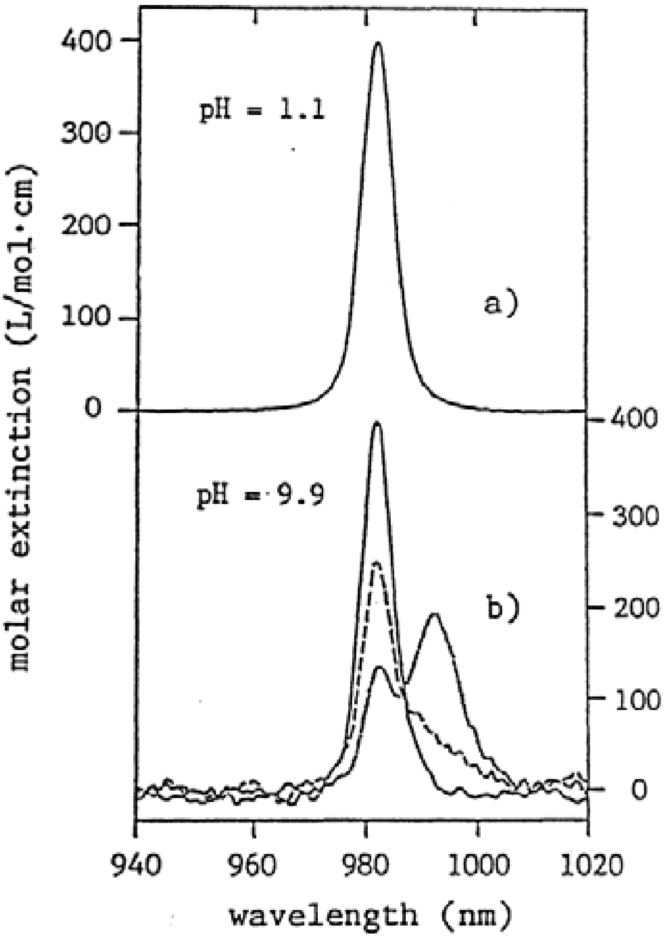

Fig. 4. Absorption spectra of Np(V). a) pH = 1.1, $c_{Np} = 6.7 \cdot 10^{-4}$ M in 0.1 M $HClO_4$. b) pH = 9.9, $c_{Np} = 3.3 \cdot 10^{-5}$ M in 0.1 M $NaClO_4$. —— cuvette under CO_2-free Ar atmosphere; - - - cuvette opened for 5 min; ...... cuvette opened for 10 h.

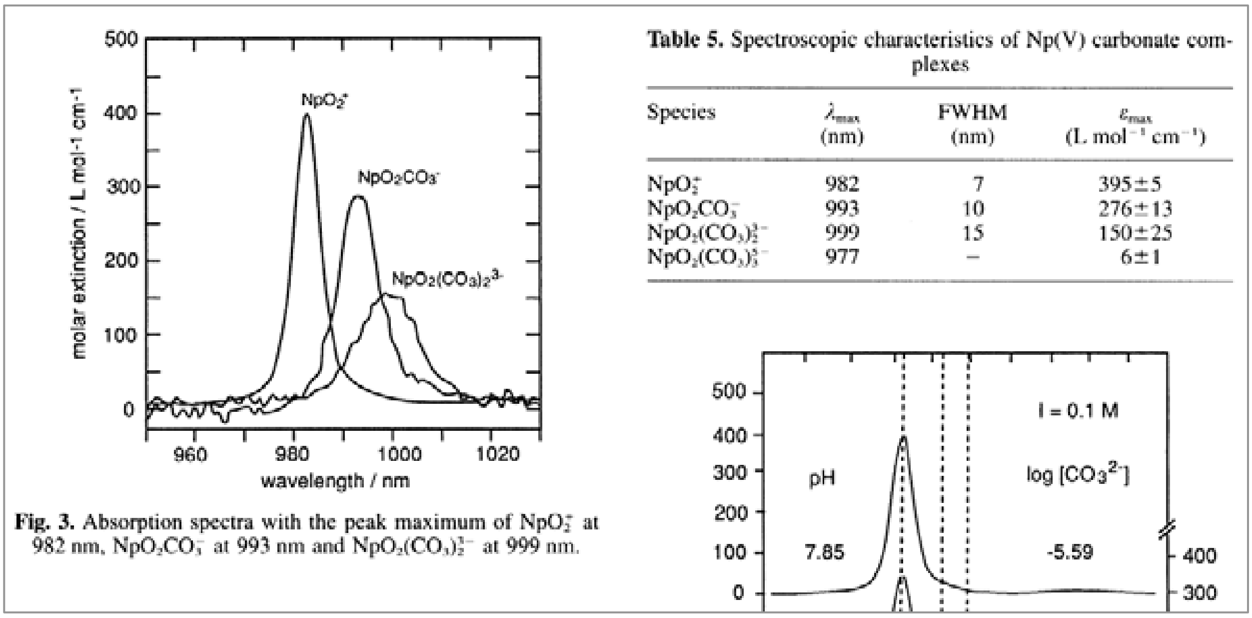

Fig. 3. Absorption spectra with the peak maximum of NpO_2^+ at 982 nm, $NpO_2CO_3^-$ at 993 nm and $NpO_2(CO_3)_2^{3-}$ at 999 nm.

Table 5. Spectroscopic characteristics of Np(V) carbonate complexes

Species	λ_{max} (nm)	FWHM (nm)	ε_{max} (L mol^{-1} cm^{-1})
NpO_2^+	982	7	395±5
$NpO_2CO_3^-$	993	10	276±13
$NpO_2(CO_3)_2^{3-}$	999	15	150±25
$NpO_2(CO_3)_3^{5-}$	977	–	6±1

The neptunium absorption spectra of Rao et al. clearly show that their room temperature data were hampered by carbonate contamination. Considering the good agreement of these data with the potentiometric titration data as well as the calorimetric data, it is most likely that all their experiments may have been compromised by carbonate contamination, thus putting the data of the entire paper in question. The statement "..excellent agreement (of the absorption data) with the values from potentiometry" by Rao et al.[3], demonstrates this dilemma and does not lend credibility to the published data.

However, the currently accepted values for the first and second Np(V) hydrolysis constants are not free of controversy, and should be considered, at best as lower limits. The OECD, Nuclear Energy Agency (NEA) review states[4]"…..None of these studies is as clear-cut as it might be wished. The solubility studies suffer from lack of characterisation of the solids. Such studies only indicate the relative stabilities of the solids and solution species…." And later on page 760, the NEA review comments on the solubility-controlling solids that form the basis for the recommended neptunium(v)-hydrolysis constants: "Two different solids were assumed, one being found in contact with 0.1 M $NaClO_4$ or with 1 M $NaClO_4$ that had not aged more than a few days. The second, more stable solid was formed in contact with 3 M $NaClO_4$ solutions or after 20-30 days in contact with 1 M $NaClO_4$….. The solids were not analysed for possible incorporation of sodium ions, however the parallel solubility curves for the two solids strongly suggest they have similar stoichiometries." It is established knowledge that solubility studies involving unknown or insufficiently-characterized solid phases, that may even be amorphous, are only of limited thermodynamic value. These discrepancies between existing data on neptunium(v) hydrolysis clearly demonstrates that a new experimental approach is needed to unequivocally determine these constants.

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[3] page 4826

[4] section 8.1.3, page 103

Neptunium Solubility Controlling Phases under Oxic Conditions

Neptunium(IV) dioxide, NpO_2

Wolery et al. (Wolery 1995; Wolery 2000) report EQ/36 modeling calculations on the Np(V)/J13 groundwater system measured by Nitsche et al. at 25°C and near neutral pH and determined that the experimentally observed concentration of $\sim 10^{-3}$ M were highly supersaturated with respect to the formation of NpO_2(cr). They suggested that the formation of NpO_2 was kinetically limited and were not observed due to the relatively short experimental duration of several months.

Roberts et al. (Roberts 1999; Roberts 2003) report the formation of crystalline NpO_2 from initially NpO_2^+(aq) solution in laboratory solubility experiments at 200°C. The elevated temperature was chosen to overcome slow reduction and/or precipitation kinetics. The paper suggest further experimental work to asses the time scale for the formation of NpO_2(cr) from dissolved NpO_2^+ or from meta-stable Np(V) solids at temperatures below 200°C. The authors determined a first-order rate constant for the precipitation of NpO_2(cr) at this temperature. Furthermore, the calculations indicate that indeed NpO_2(cr) is likely to form at temperatures between 50 and 100°C within about 100 years, depending on the activation energy.

Thermodynamic calculations using the following NEA data

	$\Delta_f G^o$(298.15 K) (kJ/mol) NEA Review (Lemire 2001)
NpO_2^+	- 907.76 ± 5.63
NpO_2(cr)	- 1021.73 ± 2.51
Np_2O_5(cr)	- 2031.57 ± 11.22
H_2O	- 237.14 ± 0.04

indicate that the conversion of either aqueous Np(V) or crystalline dineptunium pentoxide to crystalline neptunium dioxide may be possible according to equations (1) and (2):

$$NpO_2^+(aq) + 0.5\ H_2O \leftrightarrow NpO_2(cr) + 0.25\ O_2(g) + H+; \quad (Eq.1)$$

$$\Delta_r G^o(298.15\ K) = 4.60 \pm 6.16\ (kJ/mol).$$

$$Np_2O_5(cr) \leftrightarrow 2\ NpO_2(cr) + 0.5\ O_2(g); \quad (Eq.\ 2)$$

$$\Delta_r G^o(298.15\ K) = 11.89 \pm 12.30\ (kJ/mol).$$

Within the uncertainties of the results, the standard Gibbs energies of reaction may indeed have negative values, thus indicating that these reactions may be spontaneous, and the solids listed on the right side of equations 1 and 2 may form and become the thermodynamically stable phases.

Np_2O_5 and $NaNpO_2CO_3$

Two experimental neptunium solubility studies in J-13 well water at 25°C, 60°C and 90°C from oversaturation (Nitsche 1993; Nitsche 1993; Nitsche 1994; Efurd 1998) and from undersaturation (Efurd 1998) exist. Steady state neptunium concentrations were reached after approximately 40-100 days for Nitsche et al., and approximately after 400 days for Efurd et al. Nitsche et al. identified the solids formed at 90°C at pH 6 and 7 as crystalline Np_2O_5 and all other precipitates as $NaNpO_2CO_3 \cdot xH2O$, Efurd et al. identified the solids as crystalline $Np_2O_5 \cdot xH_2O$, however they remark in their publication that " X-ray diffraction data showed only a few broad Bragg reflections for neptunium solids formed at low temperature, while increased temperature induced sharper peaks at 90°C." Later on the authors state "…. we cannot exclude the presence of amorphous neptunium(V) hydroxide by X-ray diffraction." Nitsche et al. identified Np_2O_5 as the solubility-controlling solid only at 90°C and two pH values, and judging from Fig. 2 of the Erfurd et al. paper, the assignment of Np_2O_5 as the steady-state solid from the interpretation of the X-ray powder diffraction pattern appears doubtful (here only the most pronounced 90°C-powder pattern is shown; the pattern does not agree well with the Np_2O_5 literature reference pattern and the agreement will even worsen for the lower temperature solids, as it is indicated by the authors). It is unclear if the assignment of the steady-state neptunium solids XRD patterns to crystalline Np_2O_5 is indeed scientifically justifiable and defensible.

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Discussion on the main hypotheses and results developed in report TR-04-19

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Abstract

This paper discusses the main hypotheses and results developed in report TR-04-19 on the long-term behavior of spent fuel after disposal, in relation with the SR-Can safety assessment. This review was requested by SKI in order to prepare for the workshop on "Source-term modeling for KBS-3 repository concept" in May 2006. It is also based on several reference documents listed at the end of this document.

1. Initial release fractions

Any assessment of the initial release fractions must take into account the available experimental data and knowledge concerning spent fuel a few years after removal from the reactor, but also the possible variations in these inventories over time.

1.1 Initial release in spent fuel on removal from the reactor [1,2,3,4]

Even before attempting to consider possible variations over time, we must admit that for most of the long-lived radionuclides (^{36}Cl, ^{129}I, ^{99}Tc, etc.) we know very little about the initial rapid release inventories (chemical form of the segregated phases, distribution coefficient with the matrix, leaching behavior depending on the dissolved phase and on the redox conditions (e.g. Tc), difficulties of analyzing long-lived radionuclides in trace amounts in solution, etc.). Moreover, the limited experimental data available and the disparities among the fuel samples studied (fuel type, irradiation history and linear power, type of samples leached, etc.) generally require conservative approaches (e.g. taking the FGR as the upper limit).

Recent work has attempted to take experimental data and available knowledge into account in estimating the initial rapid release inventories versus burnup (for fuel a few years after removal from the reactor). The following compares the values taken from technical report TR-04-19 and this work (the most pessimistic approach is considered here). Given the burnup distribution of the Swedish fuel (with the exception of 17 fuel elements exceeding 50 GWd/t), the main values to be considered range up to 48 GWd/t. More detailed information concerning the thermal history (linear power values, etc.) of the Swedish fuel would have been a welcome addition to report TR-04-19, along with information on the specific features of boiling water reactor fuel.

	37 [3]	41 [3]	48 [3]	60 [3]	Rapport TR-04-19
^{14}C	10	10	10	10	0.1 to 10 (5)
^{36}Cl	5	5	10	16	1 to 10 (5)
^{79}Se	1 (1)	1 (2)	3 (4)	6 (10)	0 to 0.1 (0.03)
^{90}Sr	1 (1)	1 (2)	3 (4)	6 (10)	Not relevant for long term
^{99}Tc	1 (1)	1 (2)	3 (4)	6 (10)	0 to 1 (0.2)
^{107}Pd	1 (1)	1 (2)	3 (4)	6 (10)	0 to 1 (0.2)
^{126}Sn	1 (1)	1 (2)	3 (4)	6 (10)	0 to 0.01 (0.003)
^{129}I	3 (3)	3 (3)	4 (6)	10 (15)	0 to 5 (2)
^{135}Cs	2 (2)	2 (2)	4 (6)	10 (15)	0 to 5 (2)
^{137}Cs	2 (2)	2 (2)	4 (6)	10 (15)	Not relevant for long term

There are significant differences between the recent **pessimistic** values reported by Johnson *et al.* (optional approach) and those mentioned in report TR-04-19: the former are generally higher than the latter. It is important to examine the reason for these differences, which in some cases reflect rather different approaches and options.

First of all, there is no real discrepancy concerning isotopes such as ^{1} **C** and ^{36}**Cl**, and the proposed values are relatively high in both cases. These high values and subjective choices are attributable to the current and generally acknowledged lack of data and knowledge. For example, no data are available for ^{36}Cl release from LWR fuel.

The comparison is not relevant for ^{9} **Sr** and ^{13} **Cs** (with half-lives of about 30 years) over the time scales that concern us here.

For ^{99} **c,** ^{1} **Pd** and ^{129}**I** the values proposed by Johnson *et al.* are near the upper limits of report TR-04-19 for the lowest burnup; the most notable differences appear above 41 GWd/t, for ^{99}Tc and ^{107}Pd in particular (2 to 3% increase). The source of these differences lies in the different approaches adopted to determine the rapid release inventories. Two options can be considered:

- A "realistic" option is based on experimental measurements of the gap + grain boundary releases in relation with the initial fuel characterization (the approach used in TR-04-19).
- The second option involves redefining the source terms themselves by postulating that the rapid release inventory in fact includes all the radionuclides situated outside the UO_2 grains. The drawback of this approach is that it ignores the leaching resistance of segregated phases capable of containing fission products (notably metals) and fails to take into account the accessibility to water (inclusions in the grains, RIM porosity…), leading to a conservative assessment.

  From the standpoint of the possible release after disposal, the second approach raises the issue of including in the rapid release inventory a zone such as the rim, characterized by a high density of fission products **not necessarily in solid solution in UO_2** due to restructuring (submicron grains and closed porosity). This particular microstructure occurs for a local burnup in the rim of about 50–60 GWd/t, i.e. for a mean burnup generally exceeding 40 GWd/t. The issue of taking the rapid release FP inventory of the rim into account is thus relevant for the Swedish fuel elements with a burnup above 40 GWd/t. Although in fuel a few years after removal from the reactor this "rapid release" inventory is not accessible to water (closed porosity, etc.), its activity must be taken into account in the definition of the rapid release inventory postulated in the second approach. **here is**

currently a lack of long term leaching data for the rim to support and substantiated this hypothesis, but it cannot be completely ruled out due to the uncertainties on the evolution of the rim microstructure opening of the grain boundaries over the long term in the period preceding water ingress refer to the following section Unlike the authors of report TR-04-19, Johnson *et al.* proposed also the second approach (optional approach).

Report TR-04-19 also states that the rapid release inventories for **^{9}Se and ^{126}Sn** were revised in accordance with leaching data. The inventory reduction based on Wilson's work is justified under the first approach mentioned above.

1.2 Fuel evolution prior to water ingress [4,5,6]

Report TR-04-19 mentions potential variations of spent fuel in the absence of water (fission product relocation and changes in the microstructure over time) only for the "rapid release activity" source term. It would appear important to note that the potential spent fuel variations over long periods prior to water intrusion are liable to involve not only the rapid release source term but also the fuel matrix source term. The concept of an annual release fraction for the fuel matrix is discussed in greater detail below in the section covering the matrix. In any event, the spent fuel evolution mechanisms and processes prior to water ingress have been investigated by several studies in recent years not only by the CEA [4] but also under several European contracts (SFS, NF-PRO). It is important today to review these studies and reexamine them in the light of the specific features of the Swedish fuel (UOX fuel with low burnup).

Discussions of fuel stability over time focus today mainly on two areas of investigation: accelerated diffusion by alpha self-irradiation, and the evolution of the fuel surface area over time due to helium accumulation.

1.2.1 Accelerated diffusion due to alpha self-irradiation [5,6]

The diffusion of fission products over time from the grains to the grain boundaries due to persistent long-term alpha irradiation (fuel evolution in the absence of water, or closed-system fuel evolution) is liable to occur at low temperatures ("athermal diffusion") and result in a significant increase in the rapid release inventories when water comes into contact with the package: rapid release inventory data obtained experimentally with unaged spent fuel thus cannot be extrapolated over the long term.

Concerning the influence of accelerated diffusion due to alpha self-irradiation, several approaches and theoretical models have been developed to quantify the fission product diffusion coefficient under alpha irradiation. **A broad range of basic hypotheses have been postulated, and do not always address the same processes**; moreover, they generally concern U and O mobility, and little is known about the effects of accelerated diffusion of FP. For example, the Thermal Spike approach proposed by Olander [5] reduces the accelerated diffusion due to alpha self-irradiation to an "athermal" component based only on electron energy deposits from the helium atom, resulting in very low diffusion coefficients (10^{-30} m^2/s). From a conceptual standpoint it is difficult to limit the "athermal" component only to electron energy deposits by the helium particle. Clearly the ballistic interactions of recoil nuclei with the lattice are likely to induce atom mobility that is also purely athermal. Nevertheless, even taking into account the ballistic component also yields low values for the diffusion coefficient, ranging from 10^{-28} to 10^{-30} m^2/s [6] over long time periods, although these values are not necessarily negligible compared with the electronic component of the alpha particle alone (Olander's basic hypothesis). **Beyond the notion of athermal diffusion, the more general expression "diffusion accelerated by alpha self irradiation" diffusion involving defects, ballistic collisions, etc is probably more appropriate**

Most of the theoretical approaches developed to date to estimate diffusion accelerated by alpha self-irradiation give low diffusion coefficients, although when the models are applied to in-reactor operation they are unable to account for the experimental data either. **hese considerations simply reveal insufficient knowledge of the processes involved, leading Ferry *et al* [6] to develop conservative approaches** The most conservative approaches (extrapolation of reactor data) result in a diffusion coefficient of about 10^{-25} m^2/s during the first few decades, and decreasing thereafter with the fuel alpha activity. These values impact the "rapid release activity" source term—in particular at high and intermediate burnup (an increase by a few percent in the grain boundary inventories of the restructured zones).

1.2.2 Effect of helium production on the spent fuel surface area [4]

The fuel surface area variation over time is related to the formation of gases—notably helium—by alpha decay. Helium solubility remains limited in UO$_2$ and the formation of helium bubbles in the fuel grains can lead to higher pressure resulting in microcracking of the grains (not the plastic deformation expected at lower temperatures). Helium mobility is limited after disposal, but can reach a few tenths of a micrometer if diffusion is assumed to be accelerated by alpha self-irradiation. Microcracking can enhance helium release into the grain boundaries, possibly affecting their long-term stability. The tensile strength of the grain boundaries on removal from the reactor is highly dependent on the irradiation conditions (burnup, temperature, and presence or absence of fission gases); the grain boundaries are generally embrittled in the reactor to an extent that depends significantly on the presence or absence of fission gases and metallic precipitates. The importance of these phenomena over the long term has not been satisfactorily quantified to date, especially in high burnup fuel and in the rim for intermediate burnup levels.

1.3 Conclusion

The choice of values for the rapid release inventory thus depends largely on the approach adopted (two main options) :

- an essentially experimental approach (data on release in solution, measurement of gas fractions released, fuel characterization) on unaged fuel samples (a few years after removal from the reactor),
- or an approach that seeks to take into account the long-term uncertainties and is often viewed as conservative.

Based on current knowledge, the rapid release data (first approach) proposed in report TR-04-19 **are generally optimistic in the context of a safety assessment**. It must not be forgotten, however, that the impact of the processes controlling the evolution of the inventories and source terms over time, if they occur, will be limited considering the relatively low burnup of the Swedish fuel.

2. Spent fuel matrix alteration

2.1 General considerations on the Rapid Release Fraction used for performance assessments

Before discussing the choice of a value for the annual release fraction, it is important to reconsider the contents of this parameter—which, although very practical for a performance assessment, is liable to mask uncertainties. Clearly the spent fuel matrix alteration process involves a surface, and more specifically a water/matrix reaction interface. If R, the alteration rate, is expressed in $g \cdot m^{-2} \cdot d^{-1}$, the release fraction is thus implicitly related to a reactive surface area as follows:

$$RRF = RS/m_{matrix} \text{ (per day)}$$

Numerous studies have attempted to quantify the value of the R parameter for different types of materials: sintered UO_2 pellets with or without actinide doping, Simfuel, and spent fuel. Although "model" experiments on unirradiated dense sintered samples are capable of satisfactorily controlling the S parameter, this is not the case for experiments involving spent fuel. A large number of experimental findings for different materials are discussed in report TR-04-19 without actually addressing the concept of the reactive surface area. Spent fuel is likely to exhibit much different accessibility to water at the grain boundaries than the unirradiated "model" materials. Moreover, even if gains are possible on the value of the intrinsic parameter R depending on the alteration conditions (inhibiting effect of hydrogen, decreasing concentration of oxidizing agents over time, etc.), to what extent are these gains not likely to be called into question by a variation in the reactive surface area of the spent fuel on a repository time scale? These issues should have been addressed and discussed in addition to the available experimental leaching results. It is clear that the low burnup values of the Swedish fuel tend to be favorable and should limit the problem of microcracking at the grain boundaries due to helium accumulation; moreover, processes may also lead to a reduction in the reactive surface area (precipitation of secondary phases, diminishing reactive site density, etc.) as shown by several authors. It remains difficult today to assign weights to these processes over the long term.

2.2 Spent fuel alteration in air

Although these alteration conditions are not representative of a reductive repository environment, the available data in aerated media for unaged spent fuel are very instructive and can situate the upper limit.

Several studies on spent fuel segments under oxidizing conditions have shown a continuous decrease in the alteration rates (to 10^{-5} year for strontium) after 7 years of leaching. Recent experiments (CEA data) have demonstrated that the grain boundary inventories had been released in fragments sampled from the core of fuel segments leached for 7 years (without any contribution from the rim), meaning that water gained access to the entire surface of the grains of the rod core. Despite the likely increase in the reactive surface area over time, however, the annual release fraction was observed to decrease. This result can be explained only by a reduction of R and of the intrinsic fuel reactivity. These remarks corroborate the recent conclusions of B. Hanson [7] and imply that studies will be necessary in the future to better understand fuel reactivity variations (evolution of donor/acceptor sites, etc.) in the presence of oxidants depending on the fuel chemistry. *The decreased reactivity is a positive factor considering the possible increase in the reactive surface area over time.* In any event, the value of 10^{-5} should be considered as an upper limit since the repository conditions (reducing medium, low flux, etc.) will be favorable to a diminishing alteration rate.

2.3 Effect of alpha radiolysis on oxidizing dissolution of the UO_2 matrix after disposal

2.3.1 Alpha radiolysis in "anoxic" media without allowance for the environment [8,9]

Considerable work has been carried out throughout the world in recent years on UO_2 alteration mechanisms under alpha radiolysis alone using different experimental approaches (electrochemical and chemical methods on actinide-doped UO_2, external irradiation, etc.). Significant progress has been made, notably the demonstration of two types of behavior for uranium release in solution depending on the alpha activity of the fuel samples (leading to the notion of a threshold varying with the environmental conditions). Continuous uranium release—attributed to alteration controlled by radiolysis (oxidizing dissolution)—is observed for the highest flux levels (not representative of repository conditions) whereas at low flux levels representative of a repository the alteration is controlled by solubility (constant uranium concentration over time). In the case of solubility-controlled alteration, various steady-state conditions can be obtained depending on the alpha activity, generally exceeding that of an undoped UO_2 control sample. For example, steady-state conditions are obtained at about 5×10^{-9} mol/L for a UO_2 batch doped with 10% ^{233}U, compared with 2×10^{-9} to 10^{-9} mol/L for an undoped control sample [9]. Moreover, the contribution of acid rinses results in significantly (5- to 10-fold) higher concentrations; it is thus generally impossible to rule out uranium dissolution/reprecipitation and/or sorption processes compatible with a steady-state concentration over time in the homogeneous solution.

Can solubility control guarantee the absence of any radiolysis effect and ensure systematic similarity with the behavior of undoped UO_2? It is still difficult to answer this question, and the difficulty today is still to determine to what extent data based on uranium chemistry in solution can guarantee that fuel matrix alteration and the release of fission products cease at low flux levels in the absence of hydrogen and iron. Only electrochemical (in situ) or chemical approaches including an alteration tracer appear capable of resolving this issue. In this regard, tests seeking to incorporate an alteration tracer in UO_2 that is more soluble than uranium in solution and well integrated in the UO_2 matrix will be important for the future, even if they have been inconclusive to date (Sr-doped UO_2 by SCK-CEN or CEA). Tests in which variations in the $^{235}U/^{238}U$ isotopic ratios are monitored are also very important, and **constitute major progress** even it is not possible to avoid problems with uranium sorption that make it more difficult to determine the alteration rate.

A review of published data shows that it is still difficult to specify an optimum alteration rate R at low alpha particle flux values for simple systems (pure carbonated water and anoxic conditions) given the nature of the tests carried out and of the alteration monitoring.

2.3.2 Effect of the environment (hydrogen, iron (Fe(II)), etc.) on radiolysis [8,10]

The experiments reported in the literature on complex systems allowing for environmental parameters (reductive media, presence of canister corrosion products) have generally attempted to accurately quantify the fuel matrix oxidation under alpha radiolysis. Considering that a very low leach rate was expected, a substantial experimental effort was successfully carried out by various authors (trace analyses and XPS analyses, monitoring of $^{235}U/^{238}U$ isotopic ratios).

Experiments carried out in the presence of hydrogen, combining solution chemistry and characterization of the UO_2 pellet surface by XPS, are very demonstrative and convincing. They clearly show a lack of surface oxidation and solubility near that of UO_2 for a UO_2 batch with the alpha flux expected in a geological repository (10% ^{233}U); this unequivocally demonstrates the beneficial effect of hydrogen on fuel matrix alteration. The action of hydrogen thus appears capable of accounting for low alteration rates (10^{-8}/year) as mentioned in report TR-04-19. Nevertheless, the effect of hydrogen warrants some comments with regard to taking it into account in performance assessment calculations:

- The mechanism responsible for the inhibiting effect of hydrogen is still undetermined (Consumption of oxidants? A hydrogen activation mechanism? The role of the UO_2 surface and metallic phases?) and requires additional studies to substantiate its inclusion in performance assessment calculations.

- Allowing for hydrogen in performance assessment calculations also requires that hydrogen be present in sufficient quantities at the reaction interface. This implies carrying out parameter studies not only to determine the threshold values relating the alpha flux and the minimum hydrogen concentration capable of inhibiting alteration, but also to guarantee that these thresholds will be met after disposal. Hydrogen is a mobile element: what data are currently available concerning hydrogen mobility in a repository and in the surrounding environment? (For example, studies of H_2 migration around natural uranium deposits could perhaps provide further data in this area.)
- The acquisition of kinetic data on the effects of low-flux alpha radiolysis constitutes another pertinent area of investigation in addition to hydrogen studies. The effects of alpha radiolysis expected in a geological repository will clearly be limited or even negligible [9] but determining a long-term alteration rate at low flux would probably consolidate these low alteration rates irrespective of the presence or absence of hydrogen. The hydrogen effect could then be considered an additional safety factor during the phase in which it is produced by canister corrosion.

Iron, to a lesser extent than hydrogen, also appears to affect fuel matrix alteration by consuming oxidizing species. Its availability at the reaction interface (iron mobility or immobility, existence of a redox gradient, etc.) is also a major parameter [12] likely to result in significant variations in the alteration rate ranging from 10^{-6}/year to several orders of magnitude lower. Nevertheless, the range proposed in SR-Can covers this uncertainty.

Technical report TR-04-19 incorporates most of the existing work and very clearly highlights the difficulty of obtaining kinetic data, especially at low flux levels. The report takes into account the fact that tests under static conditions often raise many problems including the sample oxidation history samples (immediate release), the initial surface condition (crystal defects, etc.), uranium sorption on the reactor walls, etc. The proposed alteration rates are generally considered conservative by the authors since they are based on a balance and a quantity of uranium determined at the end of the experiment and applied to the complete duration of the experiment. The conservatism is probably subject to qualification because the uranium balances most often ignore the quantity of uranium reprecipitated on the spent fuel samples, which in turn depends on the possible redox gradients.

In the present state of knowledge [11], the proposed release fractions—between 1 ^{6} and 1 per year for the spent fuel matrix after disposal—are reasonable and realistic heir robustness is supported by the fact that they were determined by examining a broad and exhaustive experimental data set, resulting in a final variation over two orders of magnitude his uncertainty range of two orders of magnitude is reasonable and takes into account not only the gains obtained on the environmental conditions hydrogen, iron, etc but also the uncertainties experimental uncertainties on the release fractions calculated from the uranium balances, possible surface area variations, etc he choice of an intermediate value 1 per year is a more questionable decision mean value, "splitting the difference?" : a sensitivity study covering the range from 1 ^{6} to 1 would certainly be preferable

The absence of any explicit time-dependence of the alteration rate is worth noting, and in fact reflects the absence of a true, relatively general kinetic law of alteration capable of integrating key environmental parameters (oxidant scavengers, etc.) and variations over time (oxidant concentrations, surface area, etc.). Paradoxically, although the alteration mechanisms of spent fuel are relatively well known and are the subject of an international consensus, writing a law remains a particularly intractable task, notably with allowance for radiolysis (too many reaction schemes and too much detail, lack of data on alpha radiolysis even in pure water, etc.). Several models have attempted to index the alteration rates over time (alteration rates dependent on the alpha activity, etc.) but the values assigned to some constants generally lack any sound theoretical basis, resulting in highly variable and unrealistic alteration rates (i.e. in disagreement with experimental findings). These difficulties are aptly summarized by Shoesmith and Johnson [12]. The Matrix Alteration Model (MAM) recently developed under the SFS European [13] project includes the effects of radiolysis and represents a significant step forward, but environmental constraints must still be taken into account. The MAM cannot yet describe time-dependent alteration rates in the range from 10^{-6} to 10^{-8} per year adopted for the SR-Can model. Integrating the environmental constraints could eventually imply that radiolysis would no longer be taken into account (no oxidants because of hydrogen and low flux levels), yielding a law based on uranium solubility at the reaction interface.

2.3.3 Control of alteration by UO_2 solubility

The absence of a long-term radiolysis effect (no redox disequilibrium)—whether due to the presence of hydrogen or to insufficient flux levels—will significantly diminish fuel alteration, which can be described locally by a deviation from thermodynamic equilibrium. The alteration will not cease under these conditions, however, as problems of U(IV) sorption on environmental materials cannot be ruled out (pump effect?) and the presence of silicon also raises the perspective of forming more stable compounds such as coffinite, found in the natural environment. The investigation of coffinite is a complex subject and the experimental determination of coffinite solubility (+ thermodynamic properties) involving the very difficult synthesis of this material is still an objective.

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The Uncertainty of the Equilibrium Assumption

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The technical report issued by SKB entitled “Interim main report of the safety assessment SR-Can” [SKB, 2004] identifies a number of timescales which are relevant for performance assessment of the KBS-3 disposal concept for spent nuclear fuel. It has been estimated that in the case of spent nuclear fuel an assessment period of longer than 10,000 years is necessary since a period of approximately 100,000 years is required before the radiotoxicity (but not necessarily the chemical toxicity) of the spent fuel is comparable with that of the natural uranium used to produce the fuel. Thus, relevant time-dependent chemical, physical and biological processes are those that occur over the period of time before natural radiotoxicity levels are reached. The identified time-dependent processes include:

- The fundamental timeframe relevant for the development of radiotoxicity;
- Long-term geological processes, many of which occur over millions of years;
- Climate change. It is unclear the extent to which human-induced climate change may affect historical climate cycles;
- The different timeframes over which biological evolution occurs;
- The natural development of ecosystems, recognised to undergo considerable change in a timeframe of 1,000 years;
- Societal change;
- Thermal evolution of the repository;
- Re-saturation of the materials in the disturbed zone of the repository; and
- Re-establishment of the natural chemical conditions of the host rock.

In a geochemical context, however, the time-dependent processes can be more simply characterised. In this context, they include:

- Fast processes which are assumed to proceed to chemical equilibrium and can be modelled using equilibrium chemical equations;
- Slow processes which are assumed to proceed at a rate which is in quasi-steady-state, and therefore, can be modelled by chemical rate equations; and
- Very slow processes which are assumed to be slow enough as to have a negligible effect in describing the geochemistry of the system.

In terms of the disposal of nuclear fuel, where the timeframe is of the order of 100,000 years, few processes are likely to be very slow. Since fast processes are governed by chemical equilibrium they are also considered to be reversible. On the other hand, slow processes are governed by chemical rate equations and are often non-reversible. Non-reversible physical, and potentially biological, processes can also impact on the geochemical evolution of the nuclear repository. By their very nature, that is, irreversible, these processes have the potential to change the geochemical evolution of the repository and invoke different quasi-steady states.

The premise of performance assessment is that a slow and chemically irreversible process occurs, that is, the corrosion of canisters containing the spent nuclear fuel leading to exposure of the fuel to groundwater and its subsequent dissolution. Many of the dissolution mechanisms of the nuclear fuel will also be governed by slow, and potentially, irreversible processes. Additionally, other slow processes within the near-field of the repository including long-term geological interactions, dissolution of back-fill and thermal evolution are also likely to occur irreversibly. In their technical report entitled "Determination and assessment of the concentration limits to be used in SR-Met", Duro et al. [2005] recognise that one important uncertainty in their assessment is the composition of the interacting groundwater due to potential interactions from (i) the buffer, (ii) intrusion of oxidising groundwater and (iii) saline uplift. Further, they also indicate that their assessment does address "contact of water with the fuel and "weathering" of the fuel, that is, the transformation of the elements present in the fuel due to the effect of water". Each of the above processes identified by Duro et al. [2005] is likely to occur slowly and potentially irreversibly. They considered variability of the interacting groundwater by including an assessment of different groundwater compositions. However, the base assumption involved the assessment of concentration limits using an equilibrium solubility approach. It is not clear how, if at all, slow kinetic processes of either precipitation or dissolution, or those associated with other factors, were addressed in their assessment and how such processes affect the uncertainty of their predictions.

Conversely, although the dissolution of radionuclides from spent fuel may largely be governed by slow processes, the upper limit of their concentration is likely to be controlled to a large extent by application of the Ostwald step rule. This rule postulates that the precipitate with the highest solubility, that is, the least stable solid phase will precipitate first [Duro et al., 2005]. Thus, the precipitation of amorphous and less crystalline phases are often likely, the majority of which may be controlled by equilibrium. Moreover, many slow precipitation and dissolution reactions are governed by multiple rate equations, the effect of which is to drive the precipitation/ dissolution towards equilibrium.

This presentation will examine the affect of slow, and more importantly irreversible, processes on the geochemical evolution of the near-field of the repository. Moreover, it will present a synopsis on whether such processes add considerable uncertainty to the performance assessment of the repository and will question whether the equilibrium assumption in concentration limit control is valid.

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Questions for SKB

1. The premise of performance assessment is that a slow and chemically irreversible process occurs, that is, the corrosion of canisters containing the spent nuclear fuel leading to exposure of the fuel to groundwater and its subsequent dissolution. How have other equally important slow and irreversible processes been addressed in the safety assessment SR-Can? How do such processes affect the geochemical evolution of the repository?

2. It is a given that a large number of time-dependent chemical, physical and biological processes will occur in the timeframe of the safety assessment (100,000 years). Many of these processes will induce slow and irreversible reactions to affect the geochemical evolution of the repository. What affect will such reactions have on the uncertainty of the predictions made within the safety assessment?

Comments on "Update of a thermodynamic database for radionuclides to assist solubility limits calculations for PA" by Duro et al. (2005a) – Paul Brown.

The following comments are arranged in terms of the format used in the original document used by Duro et al. (2005a). That is, comments are provided in terms of individual elements (radionuclides). However, a number of overall comments need to be made.

Overall, the derived database will be a very useful document that fulfils the objective of underpinning the calculation of solubility limits outlined in the subsequent document "Determination and assessment of the concentration limits to be used in SR-Can" by Duro et al. (2005b). The database appears to have been carefully constructed, with existing databases, particularly the NAGRA-PSI database, being supplemented only where necessary. The overall quality of the database appears quite good.

The authors clearly outline the need to update their database in relation to the newly released volumes of the NEA-TDB thermochemical series, for selenium and nickel (Olin et al., 2005; Gamsjäger et al., 2005 – Volumes 6 and 7). Given that there would appear to be some differences in the thermochemical data derived by Duro et al. and those in the NEA-TDB reviews for nickel and selenium, the outlined update should be undertaken. This is also the case in relation to the NEA-TDB thermochemical review of zirconium (Brown et al., 2005 – Volume 8) and, as such, the database for this element should also be updated.

The use of extrapolation or theoretical methods appears to be judicial. Such methods are implemented when it is largely suspected that a chemical species is likely to have some relevance in conditions of importance to the performance assessment. This is particularly true in the derivation of enthalpy and entropy data.

It is suggested that the authors assign uncertainty limits to more, if not all, of their derived thermochemical parameters. It is understood that this is often a difficult task and that scientific judgement will frequently need to be employed. Nevertheless, uncertainty limits will aid in assessment of the certainty of the concentration limits derived in the subsequent document (Duro et al., 2005b). An additional concern is that for many of the data reported, the number of significant figures listed seems too large.

There would appear to be an inconsistency in the inclusion of different types of thermochemical data. The data for a number of solid compounds has been included for the sake of completeness (e.g. $Sm_2(SO_4)_3$) whereas a number of aqueous species are not included because they do not have an influence on the chemical speciation (e.g. $Th_6(OH)_{15}^{9+}$). It could be argued that all species should be included in the database to guard against inappropriate conclusions in relation to the importance of individual species and for completeness.

The complete database does not seem to be listed in any of the reports. The spreadsheet lists some of the data but the compilations given in the spreadsheet do not seem complete. To adequately review the data, all selected thermochemical data should be listed in an Appendix to the Duro et al. (2005a) report.

The following comments are provided to assist the authors in this comprehensive compilation and aid as an improvement in the consistency of the database and its supporting documentation.

Cesium

It is not clear how the data in Bard et al. (1985) were derived. As such, it is not clear whether or not Duro et al. (2005a) have been thermodynamically consistent in their use of the data from the earlier source. For example, in utilising the Gibbs energy data given in Bard et al. (Cs^+: $\Delta G_f = -282$; CsOH(aq): $\Delta G_f = -439.3$; and H_2O: $\Delta G_f = -237.178$), a value for log K for the reaction $Cs^+ + H_2O = CsOH(aq) + H^+$ of -13.98 is derived. The value of -15.64 given by Duro et al. (2005a) appears too negative. If the stability constant had been determined for the above reaction then the derived log K needs to be maintained. Other examples of this apparent inconsistency appear elsewhere in this section.

The wrong sign for some of the solubility data appears to be in some of the tables. For example, should the negative logarithm of the solubility constant given for $Cs_2CO_3(s)$ be positive?

The constant listed for CsI(aq) appears too positive. A quick review of the literature indicates a value more in line with those of the other Cs halides would be more appropriate (i.e. log K = -0.03).

Strontium and Radium

No comments can be given since the original NAGRA-PSI database has been used for these elements in its entirety.

Tin

It is agreed that the Sn(II) hydrolysis species $Sn_3(OH)_5^+$, $Sn_4(OH)_4^{4+}$ and $Sn_6(OH)_8^{4+}$ are doubtful and that they should not be included in the database. They were included in the original report due to Sn being above Pb in the periodic table and these species form in the hydrolysis of Pb(II).

It is not clear what data has been selected for the Sn(II) nitrate species. Are these data from the theoretically or experimentally determined values?

It is suggested that a more appropriate method to calculate the Sn(IV) chloride stability constants would be to use the SIT utilising the available U(IV), Np(IV), Pu(IV) or Zr(IV) chloride interaction coefficients as analogues where possible. As reported, the uncertainty values given for these constants appears too low given that they have been estimated from data obtained in 5 M ionic strength.

The data reported for Sn(IV) complexes do not appear sensible. These appear to be too low. Similar data for other tetravalent cations are much higher.

Selenium

The database should be updated with respect to the NEA-TDB volume for selenium. Since a review of these data may lead to changes in the database, it does not seem appropriate to make other comments at this time.

Zirconium

The database should be updated with respect to the NEA-TDB volume for zirconium. Since a review of these data may lead to changes in the database, it does not seem appropriate to make other comments at this time. However, in this context, an additional paper by Ekberg et al. (2004) may be relevant for the higher monomeric species. Further, the paper of Källvenius et al. (2002) was not published in that form and is replaced by the above cited paper (i.e. Ekberg et al. (2004)).

Niobium

The use of the last significant figure as a measure of uncertainty is likely to be underconservative. It is suggested that the uncertainties will be much higher than such an estimate.

Are the data listed in the table of Nb data corrected to zero ionic strength? If so, as they appear to be, how have the values been calculated?

Technetium

No comments are made.

Nickel

The database should be updated with respect to the NEA-TDB volume for nickel. Since a review of these data may lead to changes in the database, it does not seem appropriate to make other comments at this time.

Palladium

It is agreed that it is difficult to appropriately assign stability constant data for PdI_2 and PdI_3^- since no data are available and a step change in stability is likely to occur between the two complexes. However, the two species are likely to occur if both PdI^+

and PdI_4^{2-} occur. Therefore, would it not be possible to estimate constants for these two species by interpolation of the existing Pd chloride and bromide data?

Silver

What is the relevance of the reaction leading to the formation of $Ag(NO_2)_2^-$? If this reaction was important, would there not be a similar reaction leading to the formation of $AgNO_2$?

Samarium and Holmium

It would appear sensible to discuss these two elements together even though the difference in their ionic radii is somewhat larger than that between say, americium and curium. Undoubtedly, their chemical reactions are quite similar leading to analogous behaviour in their thermochemical behaviour. However, having said that, some of the data given appear somewhat puzzling. The ionic radius of Ho is smaller than that of Sm. As a consequence, it would be expected that the stability of Ho complexes would be greater than that for Sm. For many of the data selected, the opposite is the case (e.g. data with NO_3^-, $H_2PO_4^-$ (to produce H_2PO_4 species), SO_4^{2-} and Cl^-).

Should not the polymeric hydrolysis species, $Ln_2(OH)_2^{4+}$ and $Ln_3(OH)_5^{4+}$, not also be included in the database for completeness. Baes and Mesmer (1976) indicated that these species are likely to form and data is available in the literature for at least the former species. Given the likely Ln concentration, potentially these species would not be important but the speciation program should be used to demonstrate this.

Americium and Curium

In relation to the stability constant for $AnHCO_3^{2+}$, it is not completely clear what is meant by "as a function of CO_3^{2-}". Does this refer to the following reaction: $An^{3+} + CO_3^{2-} + H^+ = AnHCO_3^{2+}$?

How good is the correlation used for obtaining the phosphate stability constant data? The correlation should be presented to give the reader some confidence in the reliability of the An data.

The stability constant given for AnF_3 does not appear realistic even though three separate studies have essentially obtained the same value. The third stepwise constant (logarithm) for AnF_3 is 5.02 whereas the second overall constant is 5.80. On this basis, the third constant seems too high since the stepwise constant is far greater than either of the first two stepwise constants.

Thorium

The reasoning for the exclusion of $Th_6(OH)_{15}^{9+}$ is not convincing. Ekberg et al. (2000) demonstrated that this species is an important species at Th concentrations as low as 10^{-5} M. Furthermore, their reported constants for this species were in very good agreement with the earlier data of Baes et al. (1965), obtained in the same medium, as they were for the formation of the other polymeric species, $Th_4(OH)_8^{8+}$. The two sets of data together give five separate measurements over the temperature range 0 to 95°C, giving confidence to the enthalpy data derived for the complexes. The importance of the $Th_6(OH)_{15}^{9+}$ species, however, in the work of Ekberg et al. may be due to the absence of the $Th_4(OH)_8^{8+}$ species in perchlorate media.

The data obtained by Ekberg et al. (2000) used both potentiometric and solvent extraction techniques to obtain the stability constant data. As such, stability constant data for the monomeric species are also presented over the temperature range 15 to 35°C, and therefore, enthalpy data are also presented for these species. These data differ somewhat from those calculated by Duro et al. (2005).

Again, how good is the correlation for determining the Th nitrate complex formation constant? Has the value for the corresponding Zr nitrate complex been included in the correlation? Further, could not similar correlations be included for Th phosphate complexes?

Protactinium

How reliable is the data for protactinium? A large amount of data for protactinium is given in Brown and Wanner (1987). Use of this latter data is not considered appropriate and, as such, the only available data that is somewhat useful is that quoted by Duro et al. (2005a). However, it is suggested that the quoted uncertainties for the various thermochemical data are too low.

Uranium

To what does 02BRO relate in the discussion of the polymeric hydrolysis species of U(VI)?

The hydrolysis of U(IV) was reported by Ekberg et al. (2001) from 15 to 35°C. These data obtained in 1 M perchlorate, in relation to the stability constant of UOH^{3+} reported at 25°C, are in good agreement with the selected constant of Duro et al. (2005a) when the differences in ionic strength are considered. The enthalpy of the species, namely 50 ± 1 kJ/mol is also in good agreement with the value selected by Duro et al. (2005a). These data were not reviewed in the TDB update (Guillaumont et al., 2003). Data are also presented by Ekberg et al. (2001) for the stability constant of $U_4(OH)_{12}^{4+}$ over the same temperature range.

Is the stability constant reported in Table 16-6 for the NAGRA-PSI database for $UO_2F_4^{2-}$ -11.7 ± 0.7? There appears to be an error written in the table as given.

Neptunium

How probable is it that similar An(IV) hydroxycarbonate species, such as $Np(OH)_3CO_3^-$ etc., form for other elements? Stability constant data for such species have not been given for other tetravalent cations, but potentially these species may form, particularly considering that these type of species form for An(VI) cations.

On what basis can the aqueous Np phosphate complexes be eliminated from the databases, whereas the solid $Np(HPO_4)\cdot nH_2O$ should be included? This does not seem to make chemical sense.

Again, it would be nice to provide the correlations used to derive the thermochemical data of the sulfate species.

Plutonium

Similar comments as given above for neptunium.

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The implication of internationally agreed criteria for measurement data for performance assessment of nuclear waste repositories

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The values obtained from measuring the amount of substance in certain matrices may serve as a basis for important decisions. Important decisions are decision that affect others. Hence, such data may be questioned. In order to be abe to communicate the quality of the data and their role in a decision process, the values obtained by measurement should be reproducible. Furthermore, the analyst should be able to communicate a measure of the reliability of a measurement value. This measure should be understood over space and time. It is common in case of physical measurements to provide a complete measurement uncertainty budget with a measurement value. In chemistry, most measurement values are given as mean value. In the past decade, the experience from international trade disputes has shown that values obtained from chemical measurements urgently require a quality measure in order to be able to support the growing demand for quality on a global scale. Examples are food safety, drug abuse (doping), pharmaceutical product safety and cross-border environmental issues. Information from scientific measurement processes is only one component of a decision-making.

A measurement is a comparison. A comparison cannot be made with arbitrary accuracy and precision. Hence, it is necessary to state the level of credibility a measurement value has. The common focus of parties with discrepant interest is on the true value of a measurand, e.g. the true value of an active agent in a pharmaceutical product or the alcohol content in a driver's blood. Such information can only be meaningful if the measurement value can be related to a reference which ensures that subsequent re-analysis will be comparable to the previous study (e.g. an analysis of blood samples A and B in an EPO doping investigation). It is the task of an experimenter to ensure the comparability with the reference (e.g. by calibration with appropriate materials) and to evaluate the possible range of discrepancy that follows from the limited accuracy and precision of the many comparisions usually involved in a chamical analysis.

There exists an international framework within which these measurments can be done. This metrological framework is a direct result of the French Revolution. Meanwhile 57 states are members of the Meter Convention. The international metrological network ensures comparability by providing stable references and ensures equivalence of measurement results by continuous laboratory intercomparisions. The Meter Convention is a mere convention, that is an agreement between the member states. However, its procedures and protocols are structured in a way to allow decision even in situations of conflicting interest.

Within this framework, a variety of intercomparisons and proficieny tests are performed. These intercomparisons (e.g. within the IRMM's IMEP program or the BIPM's Key Comparisions) show that values of chemical measurements scatter much wider that previously appreciated.

The tools developed to allow a realistic assessment of the quality of a measurement value are multiple. Cause-and-effect diagrams, stochastic simulation and statisticial techniques are among them. The application of these tools revealed a tendency to overestimate the reliability of chemical measurements which is dramatic. The large discrepancies in the results from chemical measurements, e.g. in thermodynamic data of relevant chemical species applied in the numerical evaluation of environmental states, have been recognised for a long time. Instead of requiring a realistic assessment of the associated influence quantities, 'experts' have reduced the variance in the observations by discrediting data with the aim to forward data sets with less variance.

Providing a meaningful estimate for the measurement uncertainty has meanwhile become an essential requirement for those values from chemical measurements affecting other people. The ISO 'Guide to the Expression of Uncertainty in Measurement' (a document valid for all measurements, not only for chemical quantities) is also signed by the IUPAC. ISO 17025 gives detailed requirements for testing laboratories. A new ISO standard for the determination of pH values will for the first time specify the evaluation of a realistic measurement uncertainty budget for pH measurement.

The implications of these developments for performance assessment are manifold and in many respects cannot yet clearly specified. However, the importance of accounting for a realistic amount of measurement uncertainty in the data evaluation and prediction procedures commonly performed in PA of nuclear waste repositories is evident. The picture emerging from a predictive simulation run will be less obvious if each prediction is accompanied by a (presumably large) margin of uncertainty. Decision-making will become more complicated if the ability to destinguish between various options on basis of the numerical simulation output will be reduced. However, the apparent discrepancies (e.g. in thermodynamic data of nuclear waste components and their specific chemical forms) will vanish and economic and time resources can be allocated more efficiently.

It seems evident that a public will not accept that the alcohol level in a driver's body will be assessed by more stringent criteria than the risk potential of radioactive material to be disposed in the geosphere for hundredthousands of years.

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