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Workshop on spent fuel performance and radionuclide chemistry

Rånäs 2010: Assessment of some outstanding issues

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SSM perspective

The safety assessment for final disposal of spent nuclear fuel has to compre-hensively address the stage when containment barriers have failed and when radionuclide releases occur to the surrounding groundwater at repository depth. Essential processes for estimating risk/dose related to this scenario involve the release of radionuclide from the spent fuel surfaces due to radio-lytic oxidative dissolution of the UO2-matrix, interaction between radionu-clides and geologic media as well as secondary phases, and formation of intrinsic actinide colloids. This report describes the outcome of a workshop about these processes that were held at Rånäs Castle north of Stockholm 7-9/6-2010.

Objectives

The objective of this workshop was to bring together experts in the areas of radionuclide chemistry and spent nuclear fuel and track recent scientific developments in these areas.

Results

This report in particular summarizes scientific progress related to the following issues:

- an assessment of the Swedish Nuclear Fuel and Waste Management Co.'s approach for determination of solubility limits for essential radioelements,
- the influence of iron on actinide solubility (and formation of mixed cationic-ligand species)
- the formation of polymer-Pu(IV) colloids and its connection with plutonium solubility under reducing conditions
- an assessment of data spread and experimental uncertainty associated with radionuclide Kd-values
- the long-term erosion of the bedrock environment in which a nuclear fuel repository is hosted.

The last subject is not directly related radionuclide behaviour, but substantial erosion of the bedrock in relation to the repository depth would potentially induce dramatic changes in groundwater flow and chemical conditions, which in turn affect radionuclide migration and exposure.

Need for further research

The priorities of different research issues connected to radionuclide chemistry depend on assumptions and treatment in safety assessment. There is thus a need to return to the issues brought up in this report in the context of the planned review of the Swedish Nuclear Fuel and Waste Management Co.'s safety assessment SR-Site.

Project information

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1. Introduction

The safety assessment for final disposal of spent nuclear fuel in geological media needs to comprehensively integrate knowledge and information from many disciplines connected to the biosphere, the near-surface environment, the bedrock environment, the engineered barriers and the spent fuel itself. Some issues can be dealt with individually but most are strongly coupled with each other. This means that a multidisciplinary, integrative and iterative approach is needed for following the progress in safety assessment, in which experts covering many vastly different areas meet and interact with each other. This provides a basis for understanding the importance and safety significance context of individual issues.

The Swedish Radiation Safety Authority (SSM; and previously the Swedish Nuclear Power Inspectorate and the Swedish Radiation Protection Authority) has in recent years covered the spent fuel and radionuclide chemistry area through research projects and a series of small workshops with external experts (Paul Brown, Christian Ekberg, Hanna Hedström, Christophe Jégou, Günther Meinrath, Heino Nitsche, Mike Stenhouse) covering different aspects of this general area. Previously three meetings have been held that are documented in a series of SSM and SKI research reports (SKI, 2007, Stenhouse et al., 2008; Meinrath et al., 2009). This report is a summary of the outcome of the forth meeting, which is likely to be the last within this context. The Swedish Nuclear Fuel and Waste Management Company (SKB) have announced that they will submit a license application in early 2011 for construction of a final repository. This means that the type of informal review and information gathering explored during these workshops will be replaced with a formal regulatory review and licensing procedure.

The general objectives of this meeting were to follow scientific progress in relevant areas and review various aspects of SKB’s previous treatment of spent fuel and radionuclides in safety assessment in a similar manner as previous meetings (SKI, 2007; Stenhouse et al., 2008, Meinrath et al., 2009). It should be noted that reviews during a regulatory preparations phase are preliminary in character focussing on competence development, identification of research priorities and understanding of the safety assessment context.

This report starts with a discussion about various issues connected to spent fuel performance for retaining radionuclides after contact with groundwater (Chapter 2). The report then goes on to discuss SKB’s previously reported speciation calculations for radionuclides (Chapter 3). A general concern is decoupling of processes that may affect each other. In this chapter, there is also discussion about recently reported interactions between iron and actinides in solution. In Chapter 4, there is a discussion about recently published research on intrinsic actinide colloids and in particular plutonium colloids. An additional subject is the difficulties of handling the large variation in reported K_d-values for interaction between granitic rock and various radionuclides (Chapter 5). The handling of uncertainties is of key importance especially since reported K_d-values may not necessarily be representative for the expected natural bedrock situation. The long-term erosion and uplift of the bedrock may in extremely long time scales bring the fuel closer to the surface and may also change the geochemical host environment, which is discussed in Chapter 6. Finally, there was a working group session in which the connection between the analysed specific topics and the upcoming licensing situation was briefly discussed (Chapter 7) and there are also some concluding remarks (Chapter 8).

2. Spent fuel long-term performance

2.1 Radionuclide inventory, instant release fractions and their uncertainties for spent UOX fuel

The inventory uncertainties are probably rather small for most fission products (< 10%) and actinides (< 20%). Uncertainties associated with some of the long-lived activation products such as ^{14}C and ^{36}Cl in fuel and structural materials are probably more considerable since they arise from uncertainties in the concentrations of the precursor in the unirradiated materials. For the fission product ^{79}Se there remain significant uncertainties in the inventories as a result of continuing uncertainty in the half-life (perhaps a factor of 3-4).

Regarding the instant release fraction (IRF) of dominant fission products (e.g. Cs, I, Sr), uncertainties are most probably relatively small at least for spent fuel with a burnup below 40-50 GWd/t. For the light activation products ^{14}C and ^{36}Cl, the data on IRF are much more limited and indirectly derived since there are no reliable leaching data for light water reactor fuel. The uncertainties can thus be expected to be more considerable.

The uncertainties related to IRFs may become more important if average spent fuel burn-up will be gradually increased above the level of 40-50 GWd/t. High burn up conditions are associated with structural alteration of the fuel properties which may considerably affect IRF. In addition, there is a very limited amount of experimental data from experiments with high burn-up fuel. An important question is therefore whether currently used IRF values will be retained for spent fuel with a burn-up of up to 60 GWd/t. Since realistic values for high burn-up cannot be easily obtained, it is essential that there is a feasible approach to derive and justify pessimistic IRF values for such fuel.

2.2 Structural evolution of spent fuel

The spent fuel instant release fractions and matrix conversion rates are affected by the physical state of the spent fuel. However, surface-controlled spent fuel matrix conversion is most often only reported as the annual release fractions in which surface area is only implicitly considered. Models and experiments may consider relatively fresh undamaged fuel, while actual repository conditions at the time of canister failure could possibly be better represented by a damaged and aged fuel with a greater surface area. This possibility needs to be considered in the assessment of radionuclide release from a failed spent fuel canister.

The physical state of the spent fuel is most considerably affected by the heating and cooling in the reactor. Thermal stresses associated with rapid temperature change and a temperature gradient from the center of a pellet to the edge may result in various degrees of fuel cracking. Fuel subjected to adverse reactor conditions may have a considerably larger surface area. The surface area of a fuel pellet depends of its geometric surface area, the surface roughness factor as well as the fracturing frequency. An estimate of the actual surface area suggests a variation between about 10 cm^2/g up to about 55 cm^2/g with the most probable value around 30 cm^2/g.

The state of fuel would gradually change at the time of contact with groundwater and onwards, but possibly it would also change with time in a sealed perfectly tight fuel canister. The most likely mechanism to affect an isolated fuel is the production of radiogenic helium. A detailed analysis has been carried out by the CEA, which considered the helium bubble diameter, fuel fracture strength and the generation rate of helium as a function of time. The analysis suggests that the critical bubble pressure would not be reached in 10 000 years. Considering that the He generation rate decrease with time, it is not evident that such a critical pressure would be reached at all in the safety assessment time scale. An overview is provided by Ferry et al. (2006).

Radionuclides incorporated in the fuel matrix may during the contained storage phase be transported towards the grain boundaries by alpha self-irradiation enhanced diffusion or “athermal diffusion” (Poinssot et al., 2002). The significance of these processes has been discussed over a number of years mainly through consideration of the value for the diffusion coefficient that is appropriate to represent this process. Similarly as for helium bubble formation, “athermal diffusion” is expected to decrease with time due to the decreasing alpha activity.

Recent studies have evaluated the impact of alpha decay effects on further microstructural changes and have concluded that the distribution between the instant release fraction (IRF; see also Section 2.1 of this report) and the matrix is likely to be more stable over time than previously envisaged. This probably also applies for high burn-up fuels. Consequently the values proposed by CEA and NAGRA to evaluate the IRF are now significantly lower than those proposed few years ago for high burn-up fuels (55 to 60 GWd/t). The pessimistic values proposed by SKB for ^{129}I, ^{135}Cs and ^{137}Cs are now close to the range of values proposed by Nagra and CEA for high burn-up fuels. Nevertheless, there are still significant differences for ^{79}Se and ^{126}Sn of one to two orders of magnitudes, which need to be discussed and justified. It should be noted that for high burn-up fuels the mobility of activation products under irradiation such as ^{36}Cl are not necessary negligible prior to water access.

2.3 Models for long-term dissolution/conversion of the spent fuel matrix in contact with groundwater

The dissolution of the UO_2 matrix after contact with groundwater may occur either under the reducing conditions of the groundwater or under oxidizing conditions at the fuel surface induced by radiolysis. The first case was not discussed at the workshop in any detail but should generally be much more favorable due to very low solubility of the uranium matrix under reducing conditions. However, some issues regarding transport mechanisms for mobilised tetravalent uranium and the thermodynamically most stable form of uranium under various groundwater conditions should be considered.

Radiolysis induced dissolution would be driven by the oxidant production under the prevailing radiation field and groundwater chemistry conditions. In radiolysis, fuel conversion would not necessarily be identical to what could be expected in fully oxidizing conditions, but the rate would be determined by the oxidant supply rate to the fuel surface. The main experimental uncertainty is that fresh spent fuel is unlikely to be representative of oxidant production under repository conditions due to the very high radiation dose rates with a high γ- and β contribution. Over the time scale canister failures are envisaged (10^3 to 10^5 years), the γ- and β-radiation dose rates from the aged fuel are expected to have decreased by several orders of magnitudes, while the α-radiation dose will only have decreased by one to two orders of magnitude (Figure 1). Experiments with α-doped natural UO_2 provide one means to examine this influence, but other uncertainties related to the structural difference between aged spent fuel and α-doped natural UO_2 are possibly introduced. In any case, results from experiments with α-doped natural UO_2 (with an α-dose rate at about 80 Gy/h) confirm that radiolytic oxidants are consumed for conditions of hydrogen concentrations at 10^{-2} M and below (Carbol et al., 2009).

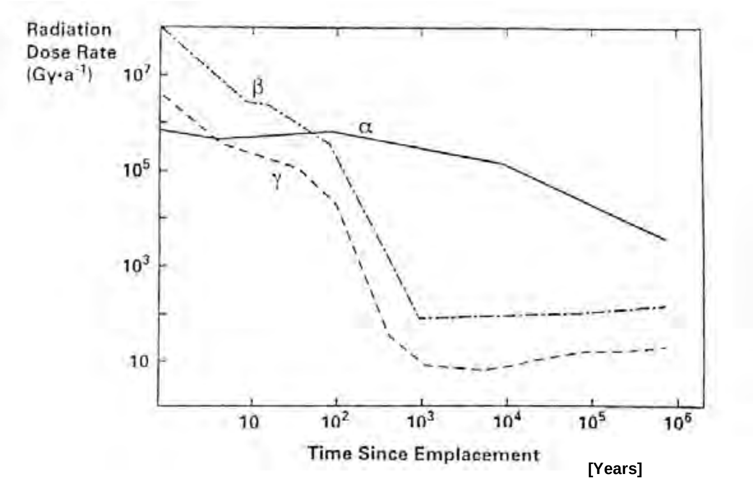


Figure 1. Evolution of α-, β-, γ-radiation field of spent nuclear fuel as a function of time after the emplacement of the fuel.

Experimental results suggest that elevated partial pressures of hydrogen will considerably suppress spent fuel matrix dissolution (Spahiu et al., 2004). This is shown by an almost constant concentration of strontium (as a tracer for matrix conversion) in reaction vessels with 5 MPa hydrogen, while strontium levels quickly increase in the case of spent fuel leaching under anoxic conditions without hydrogen. In a failed spent fuel canister, hydrogen is expected to mainly originate from the anoxic corrosion of a cast iron insert. The activation of hydrogen means that radiolytic oxidants will be consumed before they have a chance to oxidise the fuel surface. Alternatively, uranium which has already been oxidised to the pentavalent or hexavalent oxidation state may be reduced back to its original tetravalent state. The detailed mechanism of the hydrogen activation is, however, not straightforward to experimentally examine and is still not fully understood. For low-LET radiation (i.e. γ- and β-radiation) oxidizing species would most probably be consumed by the homogenous reaction with molecular hydrogen through a series of reactions with radicals (Pastina and LaVerne, 1999; Pastina and LaVerne, 2001). Significant contribution of radicals will occur provided that molecular oxidants are not in excess (i.e high-LET radiation is low in relation to low-LET radiation). Under condition of high-LET radiation (i.e. α-radiation) catalytic activation of hydrogen should have the potential to consume molecular oxidants such as O_2 and H_2O_2.

The detailed mechanism of the hydrogen activation on radioactive UO_2 surfaces is still uncertain. One alternative is that the so called ε-phases of the spent fuel activate hydrogen (nanoparticles of an alloy of Mo-Tc-Ru-Pd in the fuel), and another that the UO_2-fuel surface itself has the capability to activate hydrogen. Broczkowski et al. (2005) examined the influence of hydrogen on a measured corrosion current (intended to represent a spent fuel corrosion rate) both in the absence and presence of ε-phase metal particles. The results indicate that the presence of ε-phases have a key role in affecting the corrosion rate dependence on hydrogen partial pressure. Moreover, Trummer et al. (2009) found that additions of Pd (as a model substance for ε-phases) facilitated catalytic reduction of U(VI) in the presence of hydrogen.

A wide range of experimental results suggest that the presence of hydrogen inhibits matrix dissolution. However, this effect needs to be demonstrated for a sufficient range of groundwater conditions in order to ensure that no groundwater component may jeopardize this reaction. The reliance of the ε-phases suggests that catalyst poisoning needs to be examined.

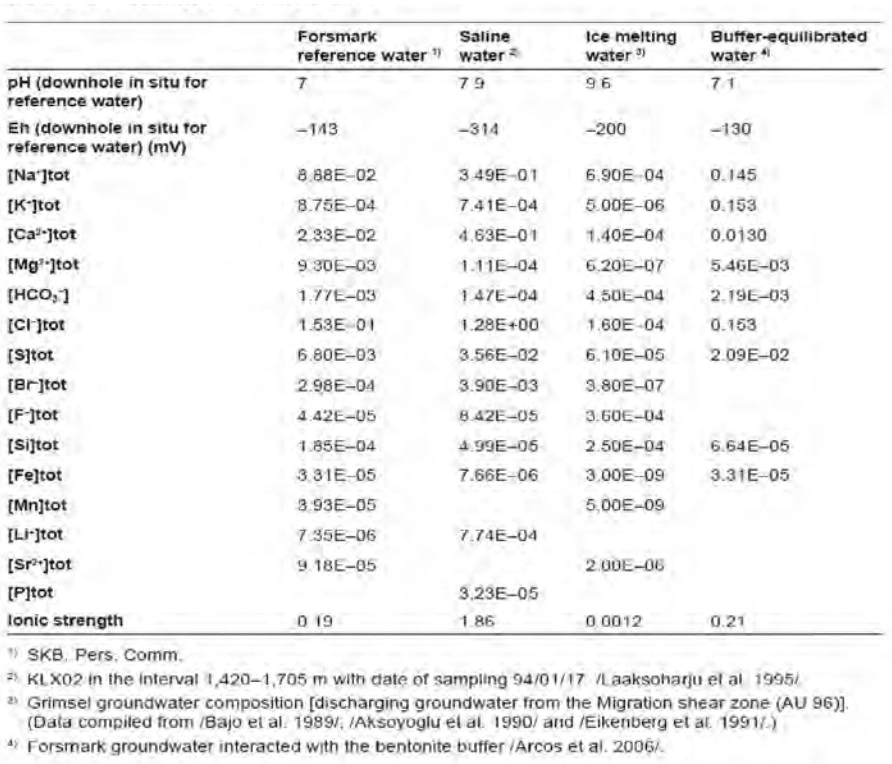
A good approach to examine model uncertainty is to conduct benchmarking exercises where independent modelling teams apply and compare different modelling concepts. The recently completed MICADO project is a good example of using this approach on issues related to matrix dissolution rates of spent nuclear fuel in the long-term (Grambow et al., 2010). Although this work is not a replacement for careful experimental studies, it provides a means to identify modelling assumptions that can have the most pronounced influence on spent fuel performance in post-closure safety assessment.

3. Radionuclide solubility in safety assessment

3.1 Geochemical model database and methodology

The composition of the Forsmark reference groundwater is reproduced in Table 1 together with the scenarios of saline water, ice melting water and buffer equilibrated water. This table indicates the major ions whose species stability and solubility constants must be included in the geochemical database utilised to determine solubility limits of radionuclides. Obviously, the database must also include the stability and solubility constants of all relevant radionuclides.

Table 1: Composition of groundwater composition scenarios for the Forsmark site (reproduced from Duro et al., 2006).



	Forsmark reference water [1]	Saline water [2]	Ice melting water [3]	Buffer-equilibrated water [4]
pH (downhole in situ for reference water)	7	7.9	9.6	7.1
Eh (downhole in situ for reference water) (mV)	–143	–314	–200	–130
$[Na^+]$tot	8.88E–02	3.49E–01	6.90E–04	0.145
$[K^+]$tot	8.75E–04	7.41E–04	5.00E–06	0.153
$[Ca^{2+}]$tot	2.33E–02	4.63E–01	1.40E–04	0.0130
$[Mg^{2+}]$tot	9.30E–03	1.11E–04	6.20E–07	5.46E–03
$[HCO_3^-]$	1.77E–03	1.47E–04	4.50E–04	2.19E–03
$[Cl^-]$tot	1.53E–01	1.28E+00	1.60E–04	0.153
[S]tot	6.80E–03	3.56E–02	6.10E–05	2.09E–02
$[Br^-]$tot	2.98E–04	3.90E–03	3.80E–07	
$[F^-]$tot	4.42E–05	8.42E–05	3.60E–04	
[Si]tot	1.85E–04	4.99E–06	2.50E–04	6.64E–05
[Fe]tot	3.31E–05	7.66E–06	3.00E–09	3.31E–05
[Mn]tot	3.93E–05		5.00E–09	
$[Li^+]$tot	7.35E–06	7.74E–04		
$[Sr^{2+}]$tot	9.18E–05		2.00E–06	
[P]tot		3.23E–05		
Ionic strength	0.19	1.86	0.0012	0.21

[1] SKB, Pers. Comm.

[2] KLX02 in the interval 1,420–1,705 m with date of sampling 94/01/17 /Laaksoharju et al. 1995/

[3] Grimsel groundwater composition [discharging groundwater from the Migration shear zone (AU 96)]. (Data compiled from /Bajo et al. 1989/, /Aksoyoglu et al. 1990/ and /Eikenberg et al. 1991/.)

[4] Forsmark groundwater interacted with the bentonite buffer /Arcos et al. 2006/.

SSM have been provided with two sets of information in relation to the database adopted by SKB. These are (a) a PHREEQC database and (b) two databases in Excel workbooks (the first is in the absence of uncertainty limits for the stability and solubility constants and the second contain such limits). The methodology adopted by SKB in the Excel workbook calculation of solubility limits is illustrated in Figure 2. The figure shows that the calculation of the solubility limit of a single radionuclide is performed in three steps: (a) determination of the free major ion concentrations from the total major ion concentrations (for example, as listed in Table 1) and the stability and solubility constants chosen for selected species formed by reaction of major ion cations and anions at a temperature of 25 ºC and a given pH and Eh (see for example Table 1); (b) calculation of the free radionuclide concentrations from assessment of the radionuclide solubility limiting phases and the free major ion concentrations (the solubility limiting phase that leads to the lowest free radionuclide concentration will produce the solubility limit for that radionuclide; and (c) adjustment to the total radionuclide concentration from the free radionuclide concentration and the selected stability constants for species formed between the radionuclide and the major ions. All constants are adjusted for the ionic strength of the groundwater.

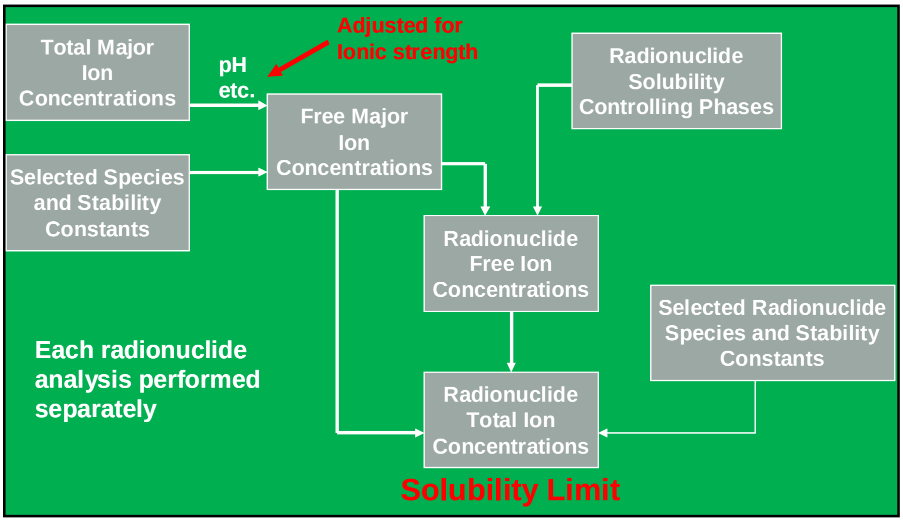


Figure 2: Schematic of the methodology used by SKB to determine the solubility limits of radionuclides

As indicated, the database utilised for such solubility limit calculations must include stability and solubility constants for all major ions and all relevant radionuclides. Thus, in terms of major ions, the database should include information for the cations, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Li^+, Sr^{2+}, H^+, the anions, CO_3^{2-}, Cl^-, SO_4^{2-}, S^{2-}, Br^-, F^-, OH^-, (PO_4^{3-} in the saline scenario) and SiO_2. However, the Excel workbook provided by SKB does not contain data for all of these ions. There is no data given for the cations, Mg^{2+}, Mn^{2+} and K^+, the anions, F^-, Br^- and S^{2-} (although the latter is indicated in the workbook) or the neutral SiO_2. Furthermore, it is not clear how PO_4^{3-} is included in the saline water scenario. Moreover, there is only 21 species considered for the reactions between the major ions. The likely presence of aluminium is not considered in either the database or in the groundwater composition although at circumneutral pH the aluminium concentration that would be present is likely to be very low but at higher and lower pH, the dissolution of aluminosilicate minerals may lead to increased aluminium in solution.

On the other hand, the PHREEQC database contains stability and solubility constants for a very much larger set of species and includes data for all major ions including aluminium. However, it is not entirely clear which of the databases has been utilized by SKB but it is suspected that it is the database in the Excel workbooks as this appears to be the only situation where the treatment of the stability and solubility constant uncertainties has been carried out.

Following determination of the free major ion concentrations, the solubility limit for each radionuclide is determined independently. Furthermore, the free major ion concentrations are not corrected for the reactions between the radionuclides and the major ions, either in terms of the formation of complexes in solution or the precipitation of mineral phases. Also, no assessment is done whatsoever for the potential interaction between the major ions of the groundwater and stable isotopes (e.g. Ba, Pb etc.) that may form from the decay of the radioactive waste (the reactions of stable isotopes and their potential influence on radionuclide solubility do not appear to have been considered by SKB in either the Excel workbook or PHREEQC methodologies). As a consequence of the deficiencies listed above, the methodology adopted by SKB for the determination of the solubility limits of radionuclides may be flawed. As a result, the uncertainties in the solubility limits may be considerable. For the Excel workbook case, individual elements and many species (for both major ions and radionuclides) have been excluded without reason. It is inappropriate to exclude species on the basis of expert judgment. Species may be unimportant under certain conditions but may become important if the modelled conditions change.

A number of deficiencies in the database and methodology adopted by SKB were outlined in a previous SSM report (Meinrath et al., 2009). These deficiencies include serious issues associated with the methodology adopted as well as important issues related to the exclusion from the database of various species for both major ions and radionuclides (with some major ions not being considered at all). Of equal importance, however, is the likelihood that in the calculation of the radionuclide solubility limits that the physico-chemical properties of the groundwater appear to have been fixed during the calculations. Reactions between ions and water and those of redox sensitive elements are likely to induce changes in pH and/or Eh (pe). Moreover, solubility results obtained using PHREEQC can vary by many orders of magnitude even given the identical total concentration information for all elements, the only difference being the initial oxidation state of an individual radionuclide input into the model. It is clear that there is a need for all these issues to be addressed.

Table 2 outlines the solubility limits reported in Duro et al. (2006) and those from their Excel spreadsheet for each of the 19 radionuclides considered. For the majority of radionuclides, the agreement between the two methodologies is quite good (being about or less than a factor of two). This is important given the much simpler methodology utilised in the Excel workbook. However, for a number of radionuclides either the calculated solubility limits are significantly different or the solubility controlling phases are not the same. These differences highlight additional deficiencies in the calculation of solubility limits that need to be addressed by SKB. More importantly, it is not clear why SKB appear to have chosen to adopt the simple Excel workbook methodology. The use of PHREEQC to perform these solubility limit calculations is more robust and permits the use of the full range of species that potentially may form in aqueous solution.

Table 2: Comparison of the solubility limits determined by SKB for 19 radionuclides using either a PHREEQC (Duro et al., 2006) or Excel workbook methodology

SOLUBILITY LIMITS (mol/kg)				
Radionuclide	Duro et al.	Phase	Excel	Phase
Sr	6.70E-04	$SrSO_4$	6.84E-04	$SrSO_4$
Ra	9.80E-08	$RaSO_4$	1.71E-07	$RaSO_4$
Ni	5.50E-05	$NiCO_3$	4.39E-05	$NiCO_3$
Sn	8.60E-08	SnO_2	6.09E-08	SnO_2
Se	1.40E-10	FeSe	1.21E-10	FeSe
Ag	**4.40E-06**	**AgCl**	**4.76E-13**	**Ag**
U	**9.50E-09**	**$UO_2.2H_2O$**	**4.69E-07**	**$UO_2.2H_2O$**
Zr	9.70E-09	$Zr(OH)_4$	1.23E-08	$Zr(OH)_4$
Nb	2.40E-05	Nb_2O_3	2.74E-05	Nb_2O_3
Pa	3.00E-07	Pa_2O_5	3.29E-07	Pa_2O_5
Np	1.00E-09	$NpO_2.2H_2O$	1.01E-09	$NpO_2(am)$
Pu	1.30E-07	$Pu(OH)_4$	6.99E-08	$Pu(OH)_4$
Am	**8.70E-06**	**$AmOHCO_3$**	**2.83E-06**	**$NaAm(CO_3)_2.5H_2O$**
Cm	8.70E-06	$CmOHCO_3$	5.15E-07	$CmOHCO_3$
Tc	4.40E-09	$TcO_2.1.6H_2O$	4.21E-09	$TcO_2.1.6H_2O$
Pd	2.90E-06	$Pd(OH)_2$	3.94E-06	$Pd(OH)_2$
Sm	**4.40E-07**	**$Sm_2(CO_3)_3$**	**2.33E-07**	**$SmOHCO_3$**
Ho	1.20E-06	$Ho_2(CO_3)_3$	2.52E-06	$Ho_2(CO_3)_3$
Th	7.90E-07	$ThO_2.2H_2O$	1.02E-06	$ThO_2.2H_2O$

3.2 Influence of iron on actinide solubility

Complexation of different nuclides important for a final repository for spent nuclear fuel has attracted interest from the chemical community over the last few decades. Fairly reliable data exist for many cationic elements and their reactions with anionic species. However, there are relatively few studies on the behaviour and formation of mixed cationic-ligand species. In the case of solids, the situation is better since co-precipitation and solid solutions have been a recognised field for a reasonably long time.

However, when studying the literature in more detail it becomes evident that even the rather simple systems containing only hydolysis reactions can behave in a rather surprising way. Earlier investigations have shown that hydrolysis in systems containing two or more metal ions does not always follow the same pattern as that of the individual systems (Davydov et al., 1982, Davydov et al., 1986, Davydov et al., 1992, Davydov et al., 1994). In more recent work, performed at the Swedish University of Agricultural Sciences

(SLU) in Uppsala and Chalmers University of Technology in Gothenburg, it was shown that mixed metal complexes can have a significant effect on the solubility of both thorium and uranium. In addition, it is expected that these effects will also be important for other metals like plutonium and neptunium, although this has not yet been established. In work by Torapava et al. (2010), on the hydrolysis of solutions containing iron and thorium, it was shown that a mixed iron-thorium species was formed, with the structure shown in Figure 3.

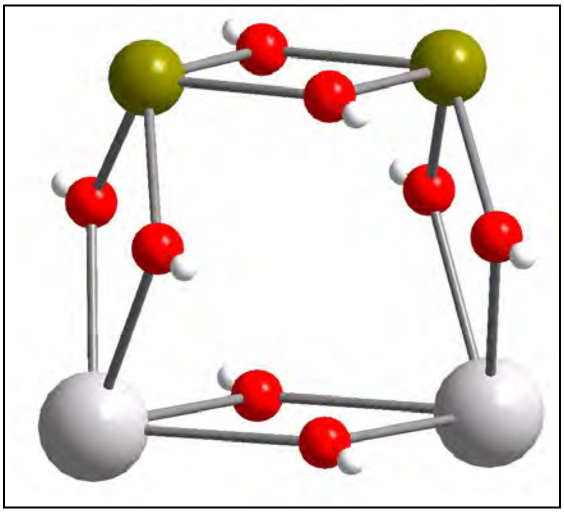


Figure 3. Ball and stick model of the $[Th_2Fe_2(\mu^2\text{-}OH)_8(H_2O)_{12}]^{10+}$ complex (Torapava et al., 2010).

The study consisted of a series of thorium and iron mixtures. The desired concentrations were obtained by mixing stock solutions of thorium and iron(III) and setting the pH in the solution to the desired value by adding sodium hydroxide. The concentration range for thorium was 0.02 – 0.05 M and the iron concentration range was 0.02 – 0.1 M. The pH range was pH 2.0-4.8. A precipitate later identified as ferrihydrate occurred in the lower pH range up to about pH 2.9. After that no precipitation occurred, despite the fact that at these concentrations iron should precipitate at about a pH of 2.3 and thorium at a pH of about 3. No quantitative estimation of the solubility increase was made but the solutions were stable for several months. In a different series made in a similar way it was seen that at a pH higher than 5 a precipitate was formed which was investigated using powder diffraction. It was neither ThO_2, $Th(OH)_4$ nor FeOOH.

Additional experiments were performed at Chalmers on samples at pH 4 and 9. In this case the sample pH was set in both the thorium and iron solutions separately. The iron solution was allowed to equilibrate and was then centrifuged, filtered and subsequently added to the saturated thorium ($Th(OH)_4$) solution with the solid phase present. In the case of the higher pH the solubility was doubled and in the lower pH case it was increased by a factor of about 1.5. At this point, however, it must be realised that these experiments were not optimally designed.

New experiments will be performed where an addition of iron(III) will be made at different intervals until a stable thorium concentration in the solution is reached. It is expected that the solubility of thorium will increase dramatically.

Scoping studies on mixed metal complex formation have also been made with iron(III) and uranium(VI) showing a six-fold increase in the solubility at a pH of 4. Although only very preliminary results, they indicate that neptunium and plutonium may also show similar behaviour. There is a need to investigate this further and to obtain both the thermodynamic data and reliable identification of these new solubility limiting phases of actinides in an iron rich environment.

4. Intrinsic actinide colloids

This section discusses current knowledge on the solubility of Pu species related to aqueous solutions with reducing properties such as water from the Forsmark site (SKB 2008). A similar examination of the knowledge basis and relevance of tetravalent thorium and neptunium and trivalent americium is recommended to be undertaken in the future.

4.1 Pu(IV) polymer-Pu(IV) colloid

Until recently, it was believed that the solubility of plutonium in reducing groundwaters was essentially controlled by two solid phases, trivalent plutonium(III) hydroxide, $Pu(OH)_3$, and/or tetravalent Pu(IV) amorphous hydrous oxide, PuO_2(am, hyd). PuO_2(am, hyd) was considered an amorphous non-crystalline solid and is closely related to the formation and existence of polymeric tetravalent Pu, often called Pu(IV) polymer or Pu(IV) colloid. For the sake of clarity, it will be referred to as Pu(IV) colloid in the remainder of this text.

A good summary of the history of Pu(IV) colloid was recently given by Soderholm and co-workers (Soderholm et al., 2007). Over the last 10 years it has been shown that Pu(IV) colloid may be responsible for the large difference in the measured solubility constants of Pu (Knopp et al., 1999; Neck et al., 2007b). There are good indications that it may be responsible for the migration of plutonium over long distances in the environment (Kersting et al., 1999; Novikov et al., 2006). Pu(IV) colloid forms even in acidic solutions and at low concentrations of plutonium. Laboratory studies, conducted over the past 60 years, have demonstrated that it exists as a colloidal solution, showing a characteristic optical absorption spectrum that is different from true dissolved ionic Pu^{4+} solutions (Cleveland, 1970). The formation of Pu(IV) colloid was believed to occur via the condensation of $[Pu(OH)_n]^{(4-n)+}$ through an olation reaction to yield hydroxo-bridged species (Johnson and Toth, 1978):

$Pu\text{-}OH + Pu\text{-}OH_2 = Pu\text{-}OH\text{-}Pu + H_2O$

Common belief was that the Pu hydroxo-bridged oligomers condense with time to produce poorly crystalline mixed Pu(IV)-oxide-hydroxides. X-ray powder diffraction patterns, both from solution and from dried or precipitated solids, exhibit poorly defined, broad peaks that are generally consistent with the known PuO_2 fluorite structure (Rai and Ryan, 1982; Thiyagarajan et al., 1990). Furthermore, X-ray absorption fine structure (EXAFS) measurements (Conradson, 1998; Rothe et al., 2004) were evaluated with a distribution of Pu-O bond lengths that are interpreted as Pu-O, Pu-OH, and $Pu\text{-}OH_2$ linkages in accordance with the existence of Pu(IV) colloid formed through olation and dehydration reactions.

There is evidence that Pu(IV) colloid exists in solution in the form of nanocrystalline PuO_2 that can grow in size due to cluster formation. The Pu-O clusters may be directly formed by an oxolation reaction. As Pu(IV) solutions begin to hydrolyze, oxolytic species are formed immediately through an oxolation instead of olation reaction :

2 Pu-OH → Pu-O-Pu + H_2O

Oxolation reactions occur with higher-valent, harder cations such as W(VI), Mo(VI) and result in a wide range of well defined magic number clusters (R.E. Wilson, ANL 2010, private communication; Henry et al., 1992). As such, the Pu(IV) colloid solution may be interpreted as a solution containing solely crystalline PuO_2 crystallites of different size. Small-angle neutron scattering and X-ray diffraction of Pu(IV) solutions measurements exhibit well-defined Bragg diffraction lines for the Pu polymer in aqueous and organic phases. All of the lines could be identified as PuO_2-like linear aggregates with a chain diameter of about 5 nm (Thiyagarajan et al., 1990) Electron micrographs of dried solutions showed evidence of small PuO_2-like clusters with a diameter of about 2 nm (Lloyd and Haire, 1978). Laser-induced breakdown detection (LIBD) experiments on the samples used in the above-mentioned EXAFS measurements of Rothe et al. characterized the mean particle size in the range from smaller than 5 nm (detection limit) to about 12 nm.

Recently, Soderholm and coworkers (Soderholm et al., 2007) isolated single crystals from an initially alkaline peroxide solution that was acidified and passed through an anion-exchange column without retardation of the Pu, typical of a sample containing Pu(IV) colloid. After repeated cycles of heating to near dryness and reconstituting with HCl, the eluate was treated with aqueous LiCl and allowed to evaporate, producing red crystals. Single-crystal diffraction data established the structure of this compound with the composition $Li_{14}(H_2O)_n[Pu_{38}O_{56}Cl_{54}(H_2O)_8]$. The bond-length distribution of the 36 independent PuO bonds within a cluster, taken together, resulted in the cluster average distance of 2.30 Å, which is near to the value measured for bulk PuO bonds of 2.33 Å. There was no evidence of Pu-OH bonding in the cluster! However, the cluster size appears to be anion dependent: Pu-Cl clusters consisted on average of about 38 atoms, whereas a study with nitrate indicated that Pu-NO_3 clusters are made of about 90 atoms (R.E. Wilson, ANL 2010, private communication).

4.2 $Pu(OH)_3$ solubility and existence in reducing groundwater conditions

An excellent summary of this subject and the development of a first-time thermodynamic interrelation between $Pu(OH)_3$ solid with $Pu(IV)O_2$ and Pu(IV) colloid was given by Neck and coworkers (Neck et al., 2007a). The selected data and interpretation made in the following are largely abstracted from this publication.

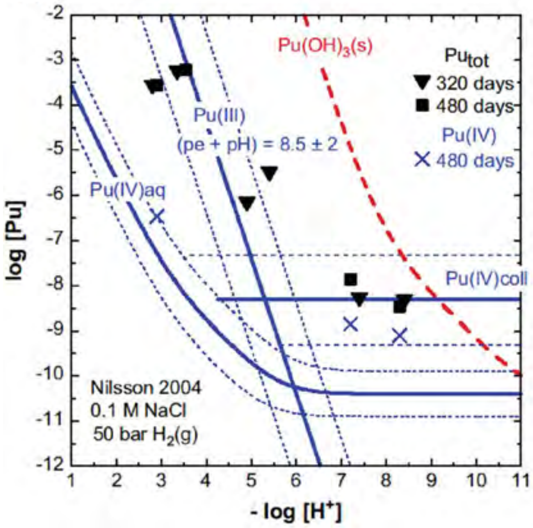


Figure 5. Solubility of Pu(IV) hydrous oxide determined by Nilsson (2004) after 320 and 480 days in 0.1 M NaCl solutions under a pressure of 50 bar H_2(g) after the transformation of the initial Pu(III) hydroxide precipitate. The calculated Pu(III) concentration refers to the experimental redox conditions of (pe + pH) = 8.5 ± 2.

Nilsson (2004) determined the solubility of $Pu(OH)_3$(s) at ambient temperature in 0.1 M NaCl under a pressure of 50 bar H_2(g) in an autoclave containing Pt wire as a catalyst. The X-ray amorphous $Pu(OH)_3$(am) that precipitated from the Pu(III) stock solution was expected to remain stable. However, the Pu concentrations measured after centrifugation (analyzed for $[Pu]_{tot}$ = [Pu(III)] + [Pu(IV)] after 150, 320 and 480 days and for [Pu(IV)] after 480 days) were much lower than expected for $Pu(OH)_3$(s) (Figure 5), and the redox potentials measured after 480 days were much higher than expected for P(H_2(g)) = 50 bar (Figure 6). Nilsson concluded from the change in color of the originally blue $Pu(OH)_3$(s) solid to a green precipitate that the solid had changed to amorphous hydrous plutonium dioxide of the composition $PuO_{2+/-x}$(am, hyd). Neck concluded that the redox potential was not controlled by the reaction 0.5 $H_2(g) = H^+ + e^-$ that should have resulted in (pe + pH) =- 0.85 (Figures 5 and 6, red dotted lines).

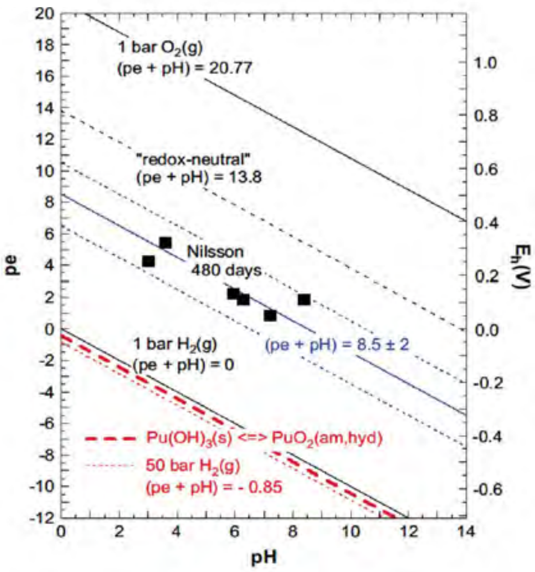


Figure 6. Redox potentials determined by Nilsson (2004) after 320 and 480 days in 0.1 M NaCl solutions under a pressure of 50 bar H_2(g) after the transformation of the initial Pu(III) hydroxide precipitate. The calculated Pu(III) concentration refers to the experimental redox conditions of (pe + pH) = 8.5 ± 2. The dotted line (pe + pH) = -0.85, calculated for P(H_2(g)) = 50 bar is in the stability field of $Pu(OH)_3$(s) slightly below the fat dashed stability line at (pe + pH) = - 0.4. The expected solubility curve for the initial $Pu(OH)_3$(s) precipitates shown for comparison also as fat dashed line.

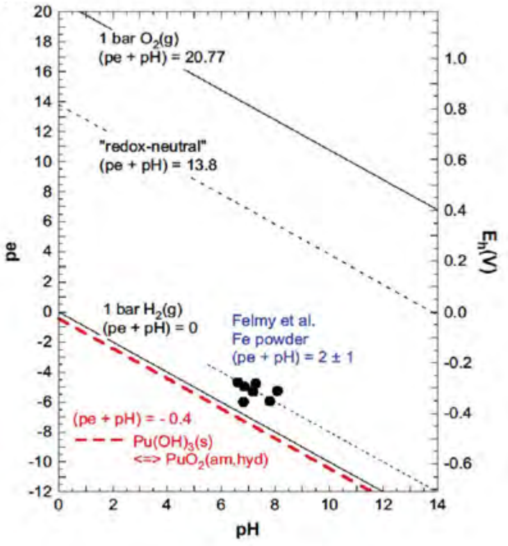


Figure 7. Redox potentials in suspensions containing Fe powder (Felmy et al., 1989). The fat-dashed line at (pe + pH) = - 0.4 represents the stability line of $Pu(OH)_3$(s) with regard to its transformation into PuO_2 (am,hyd). The solid lines at (pe + pH)=0 and 20.77 define the stability field of water, the dashed line at (pe + pH) = 13.8 is calculated for redox-neutral aqueous solutions.

Neck et al. (2007a) calculated the solubility of $Pu(OH)_3(s)$ from thermodynamic data and concluded that $Pu(OH)_3(s)$ is only stable under very reducing conditions, (pe + pH) = -0.4 +/- 1.0, which is close the reduction line of water (H^+), shown in figure 7, as the dashed red line and the solid black line located slightly above it, respectively. The authors reinterpreted the data of Nilsson and concluded that the solubility is consistent with a Pu(III) concentration for the experimental value of (pe + pH) = 8.5 ± 2 with an additional contribution from Pu(IV) colloid (Figures 5 and 6).

Neck et al. (2007a) used the concentration line, shown in Figure 5 that was recently experimentally determined as log Pu(IV) colloid = -8.3 +/- 1.0 from a solubility study of Pu(IV) hydrous oxide (Neck et al., 2007b). This concentration was determined by comparing the concentrations of unfiltered solubility samples with those that were filtered with 10 kDa ultrafilters (1.5 - 2 nm Pu(IV) colloids). The Pu(IV) colloid concentration remained constant at a value from pH 8 to 13. This is consistent with the observation of Fujiwara et al. (2001) who measured a concentration of log Pu(IV) colloid = -9 after 2 nm filtration of solutions with pH values ranging from 7-9. The equilibrium value of dissolved mononuclear Pu(IV) species, $Pu(OH)_4$, was determined to be log $Pu(OH)_4$ = - 10.3 ± 0.2 which is in agreement with the value determined by Rai et al. (1999), log $Pu(OH)_4$ = -10.4 ± 0.5. The difference between the ultrafiltered samples (about 2 nm) and the mononuclear species is $10^{1.3}$ i.e, about 95 percent of the 2 nm filtered still contains plutonium species which are not in the form of monomeric $Pu(OH)_4$ but exist most likely as very small Pu(IV) colloid particles that may even be crystalline. This is surprising and novel knowledge which may change our understanding of Pu(IV) solution chemistry insofar as the ionic fraction of “dissolved” plutonium may be only a small percentage of the 2 nm filtered plutonium fraction. This is an important finding because the transport of plutonium in reducing aqueous solutions may primarily occur through the movement of Pu(IV) colloids.

4.3 Solubility of plutonium under reducing conditions

In the absence of carbonate and phosphate ions, and other complexing groundwater components, the solubility of plutonium under reducing conditions is controlled by $Pu(OH)_3(s)$ which, in turn, is in equilibrium with its different hydroxide complexes $Pu(OH)_n^{3-n}$. However, depending on the actual redox potential the equilibrium between Pu(III) and Pu(IV) has to be considered:

$$Pu(OH)_3(s) = PuO_2(am, hyd) + H_2O + H^+ + e^-$$

Using the available thermodynamic constants for this equilibrium, the stability relation (pe + pH) = -0.4 +/- 1.0 can be calculated for the existence of $Pu(OH)_3(s)$.This value is represented by the red dashed line in Figure 7, which is very close to the lower stability field of water, as represented by the (pe +pH) = 0 line, also shown in Figure 7 as the lowest black line.

If the redox conditions of the water are not negative enough, i.e, (pe + pH) > -0.4, the equilibrium between dissolved Pu(III) and Pu(IV) can lead to Pu(IV) concentrations that exceed the solubility of Pu(IV) hydrous oxide and, thus, will lead to the precipitation of PuO_2(am, hyd), until all $Pu(OH)_3$(s) is dissolved. This could be a likely scenario for Forsmark groundwaters with (pe + pH) = 4.58. This potential plutonium solubility scenario should be investigated in detail.

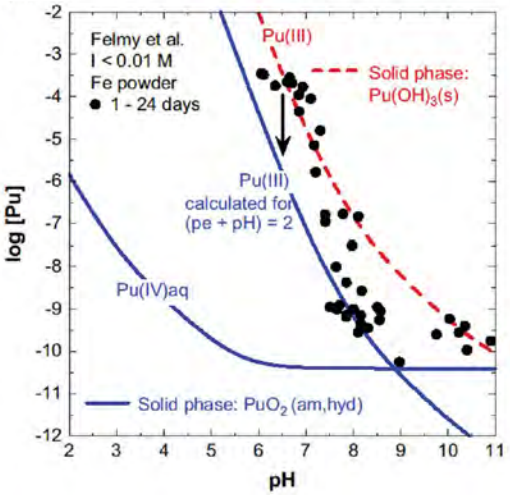


Figure 8. Solubility study of Felmy et al. (1989) with $Pu(OH)_3$(s) at 23 °C and I < 0.01 M. Experimental Pu concentration measured after 1.8-nm filtration and calculated solubility; the dashed line is calculated for solubility control by $Pu(OH)_3$(s), the solid lines for solubility control by PuO_2(am,hyd) at (pe + pH) = 2 ±1.

$Pu(OH)_3$(s) solubility in the presence of iron

Redox potentials in suspensions of corroding iron are in the range (pe + pH) = 2 ± 1 which is substantially above the stability line of $Pu(OH)_3$(s). Under these conditions, the $Pu(OH)_3$(s) precipitate is metastable and should convert into PuO_2(am, hyd). The results of a solubility study by Felmy et al. (1989) of $Pu(OH)_3$(s) dissolution in the presence of iron powder are shown in Figure 8. This figure also shows equilibrium concentrations for Pu(III), together with the Pu(IV) and Pu(III) solution concentrations that were calculated for (pe + pH) = 2 (Neck et al., 2007a). The experimental concentration, determined by Felmy et al., are between the red dashed line in Figure 8, representing the equilibrium of Pu(III) (aq) with $Pu(OH)_3$(s), and the blue solid line, representing the equilibrium between Pu(III) and Pu(IV) aqueous species that are in equilibrium with the PuO_2(am, hyd) solid phase. It is noteworthy that several data points show a tendency to the lower curve representing PuO_2(am, hyd) which could be expected after transformation of $Pu(OH)_3$(s) into PuO_2(am, hyd).

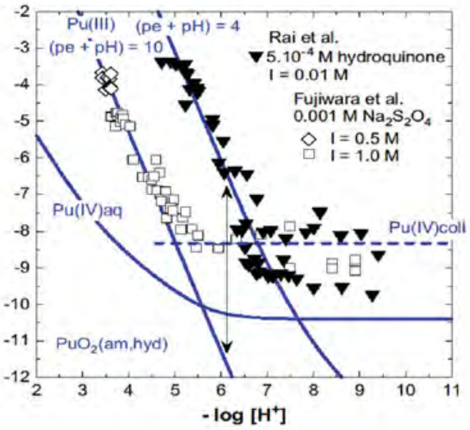


Figure 9. The effect of (pe + pH) on the solubility of Pu(IV) hydrous oxide under reducing conditions. Solubility data of Fujiwara et al. (2001) at (pe + pH) = 10 ±1 (in 0.5 and 1.0 M $NaClO_4$ + 0.001 M $Na_2S_2O_4$) and Rai et al. (2002) at (pe + pH) = 4.0 ±0.5 (in 5.2 x10^{-4} M hydroquinone solutions at I = 0.01 M).

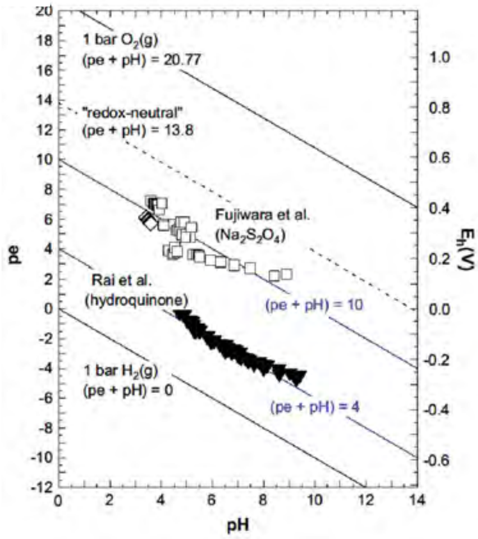


Figure 10. Experimental pH and redox potentials for the studies of Fujiwara et al. (2001) and Rai et al. (2002).

Reductive dissolution of PuO_2(am, hyd) using sodium dithionite and hydroquinone

The dissolution of PuO_2(am, hyd) in the presence of $Na_2S_2O_4$ was investigated by Fujiwara et al. (2001) and in the presence of iron and hydroquinone by Rai and coworkers (Rai et al., 2002). The experimentally determined redox potentials and solubilities are shown in Figures 9 and 10 together with the corresponding calculation of Neck et al. for (pe + pH) = 4 and 10. According to the thermodynamic calculation for the equilibrium of the reaction

PuO_2(am, hyd) + $e^- + 4H^+ = Pu^{3+} + 2H_2O$,

the increase of (pe + pH) from 4 to 10 leads to a decrease of Pu(III) concentration of about six orders of magnitude (see arrow in Figure 9).

4.4 Summary of findings regarding Pu geochemical behaviour

- There is evidence that Pu(IV) colloid exists in solution in the form of nano-crystalline PuO_2 that can grow in size due to cluster formation.

- Experiments have shown that about 95 percent of the 2 nm filtered plutonium(IV) solutions contain plutonium species which are not in the form of monomeric $Pu(OH)_4$ but exist most likely as very small Pu(IV) colloid particles that may even be crystalline.

- This is an important finding because the transport of plutonium in reducing aqueous solution may primarily occur through the movement of Pu(IV) colloids.

- $Pu(OH)_3$ (s) is only stable under very reducing conditions, i.e., (pe + pH) < -0.4.

- Forsmark groundwater with (pe + pH) = 4.58, will most likely favour the precipitation of PuO_2 (am, hyd) in equilibrium with Pu(III) and Pu(IV) solution species.

- $Pu(OH)_3$(s) is metastable and should convert into PuO_2(am, hyd) in the presence of corroding iron.

- Reductive dissolution of PuO_2(am, hyd) using sodium dithionite and/or hydroquinone leads to an equilibrium between PuO_2(am, hyd) and Pu(III) (aq). The increase of (pe + pH) from 4 to 10 leads to a decrease of Pu(III) concentration of about six orders of magnitude.

5. Sorption phenomena

The phenomenon of sorption plays an important role in nature. It describes interaction of solution constituents with the immobile surrounding (e.g. container walls or geological material) at concentrations far below the solubility limit. Thereby the nature of the detailed processes causing sorption is not specified and is largely unknown and/or speculative.

Despite being a poorly defined process, sorption phenomena also play an important role in reactive transport modelling. Sorption processes are capable of retaining material that otherwise would be transported with the solution. Thus, solution constituents are retarded with respect to the movement of the solution. Sorption therefore contributes to the barrier effect of the geological formation in the performance of a nuclear waste repository after the release of radionuclides from the waste containers into the geosphere. This is illustrated in Figure 11.

Sorption phenomena have been described by the widely practised K_d approach. This approach assumes an analogy to the well-known liquid-liquid equilibria between two immiscible phases. In the K_d approach, one liquid phase is replaced by a sorbing solid phase. Equilibrium is then described on a mass to mass basis normalised to the amount, m, of solid equilibrated with a given volume, V, of the liquid phase.

$$K_d = Q/q \tag{1}$$

where Q is the mass of solute sorbed on the solid phase, and q is the mass of solute retained in solution. Since the mass of a dissolved substance in solution is proportional to its molar concentration times volume:

$$K_d = C \ / Q \tag{2}$$

The mass sorbed on the solid has to be inferred from the concentration in solution observed after establishment of a steady state:

$$Q = (C_0 – C) V \tag{3}$$

resulting in;

$$K_d = ((C_0 – C) / C) (V m^{-1}) \tag{4}$$

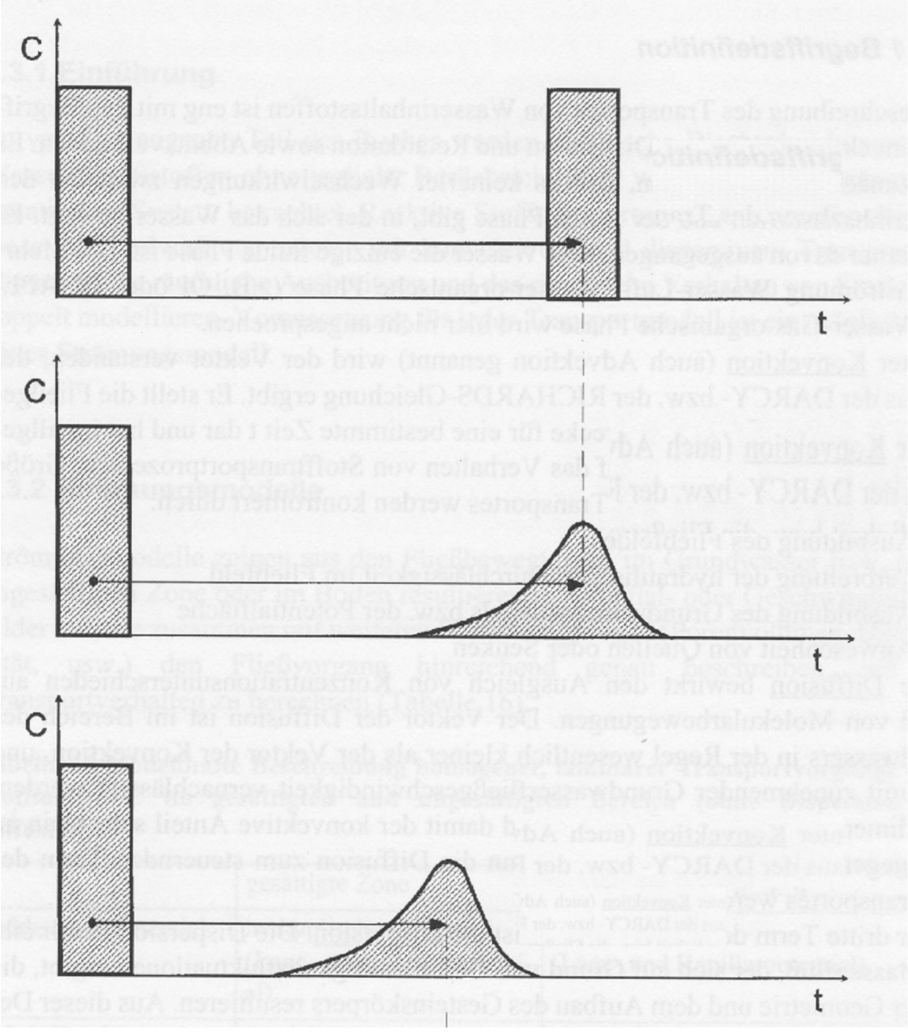


Figure 11. Effect of advection (top), advection and dispersion/diffusion (middle) and advection, dispersion, diffusion and retardation on the concentration profile in a transported medium.

This approach does not allow any inference on the processes likely to be involved in the observed sorption phenomenon. The resulting values of the quantity K_d are considered to be reproducible if:

- the physical conditions are comparable (E_H, pH, temperature, etc.);
- the observed concentration reduction is not caused by other processes (precipitation, microbial interaction, volatilisation etc.) other than surface interactions;
- the solid material is comparable; and
- the solution composition is comparable.

This brief summary amounts to the statement that K_d values cannot be expected to be highly reproducible measurands with a low margin of variability in repetitious experiments. An overly large scatter of data presumably obtained under comparable conditions, however, would severely limit the reliability of the K_d approach in the demonstration of the safety features of a nuclear waste repository.

The workshop participants generally agreed with the statements on the available sorption data in SKB reports R-06-75 (Crawford et al., 2006) and R-08-84 (Crawford, 2008) being widespread and inconsistent. From the database accompanying Report R-06-75, selected K_d values for Am(III) interaction with granite/granodiorite were given. These data with their minimum and maximum limits are given in Figure 12 as empirical cumulative distribution functions and interpreted by their closest fitting normal distributions. From a Kolmogorov-Smirnov test, both distributions were found to be normally distributed with a probability > 99%. The spread of the data over both distributions is about 3.5 orders of magnitude. Thus it becomes evident that the observed spread is not caused by individual outliers or an inhomogeneous data structure.

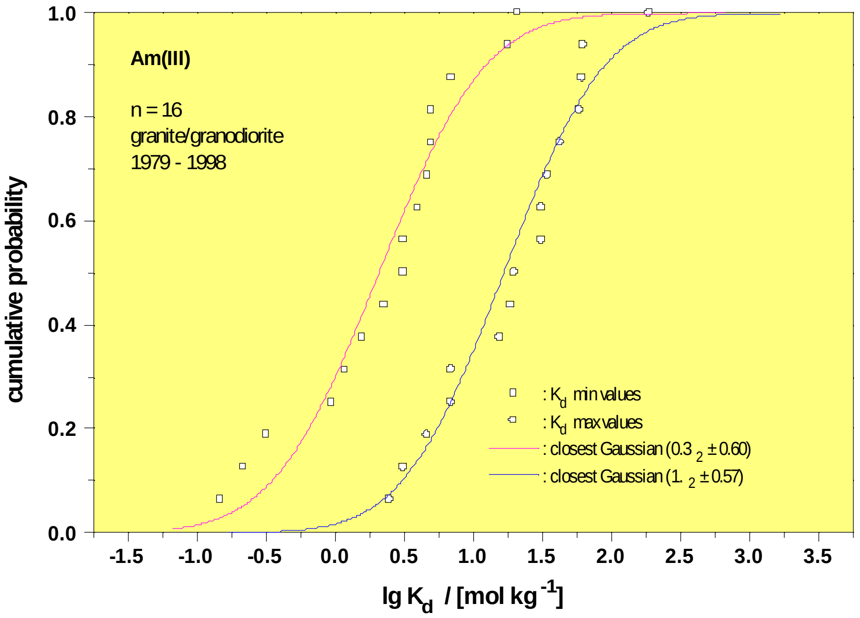


Figure 12. Graphical presentation of selected sorption data from 16 different literature sources as empirical cumulative distributions. Range over both distributions is 3.5 orders of magnitude.

The observation from extended transport simulation calculations reported in (Crawford, 2008) that the transport time of a solute particle increases linearly with K_d illustrates the detrimental effect of large uncertainty ranges in the relevant K_d values from literature on the quality of numerical transport simulations in the demonstration of the safety features of a nuclear waste repository in the respective host materials.

On basis of the extensive review material provided in the database to report R-08-84 (Crawford, 2008), and information provided by reports R-06-75 and R-08-84 (Crawford et al., 2006; Crawford, 2008), led the panel to make the following comments and suggestions:

The panel of reviewers previously have addressed the need to assess a reasonable margin of uncertainty with each K_d value reported (Meinrath et al. 2009). A suggestion has been made on basis of cause-and-effect analysis according to the convention established by ISO and other scientific-technical organisations in the 'Guide to the Expression of Uncertainty in Measurement´. From this suggestion it becomes evident that values evaluated for K_d may easily go astray if the experimental conditions are inappropriate. The ratio V/m (see equation 4, above) cannot be arbitrarily shifted from a value of 1 because at lower values the solid material will not be covered appropriately with the liquid phase. It also cannot be arbitrarily increased because the container walls and other interfering effects will become non-negligible. Thus the individual laboratory's ability to assess the amount of substance C_0 and C becomes crucial. An excellent measuring capability of a complete measurement uncertainty of ± 5% (95 % confidence limit) may limit the smallest measurable K_d to about 0.01 $m^3\ kg^{-1}$ (Meinrath and Schneider, 2007) Similar fundamental limits may apply to the technical accessible upper limits. The reviewers note that no attempt has been made in (Crawford et al., 2006) or (Crawford 2008) to set quantitative criteria for the magnitude of uncertainties associated with the literature data. A reassessment of the respective literature data on the basis of reasonable estimates of uncertainty may reveal outlying and/or physically unreasonable data.

In agreement with the statements in (Crawford, 2008) the importance of secondary minerals in cracks and fissures of the granitic material is emphasized. Because a larger share of the K_d data in the database of report R-06-75 (Crawford et al., 2006) is from 1990 and before, the importance of preserving such secondary minerals in the pre-treatment of the samples and the practical performance of the experiments may not have been appropriately considered.

Most geological materials are made up from several minerals in varying amounts, e.g. granite from mica, quartz and feldspar. The establishment of mineral-specific databases has been proposed previously (Delakowitz et al., 1996). A closer look to the material collected in the past 14 years may improve the current unsatisfactory state.

The approach taken by Crawford (2008) to normalise the K_d to experimentally assessed surfaces and trying to quantify the effect of crushing by extrapolation is seen with much interest. The need for appropriate assessment of the regression line and critical analysis of alternative data interpretations is emphasized here.

6. Long-term erosion in the vicinity of the waste repository

It has since long been recognised that disposed spent fuel in a final repository could in exceptionally long time scales arrive at ground surface due to natural denudation of the bedrock. The time scale of such development is most probably well beyond what is normally considered in safety assessment, but there is still an ongoing interest and discussion about the topic in the international community. The Nuclear Energy Agency (NEA) in Paris has had a leading role in analysing the scientific and ethical issues connected to extreme timescales. The context is summarized by NEA in its most recent published report on this topic (NEA, 2009) as:

"*Geological repositories are sited to provide protection of man and the environment from the hazard associated with long-lived radioactive waste by containing and isolating the waste. Though the sites and engineered barrier designs are generally chosen for their long-term stability and predictability, repository evolution is nonetheless subject to unavoidable uncertainties that generally increase with time. Furthermore, radiological exposure modes, which are closely related to human habits, can be predicted with confidence only in the very short term. The decreasing demands on system performance as a result of the decreasing hazard of the waste partly offset the increasing demands that uncertainties place on safety assessment. Nevertheless, while some hazard may remain for extremely long times, increasing uncertainties mean that there are practical limitations as to how long anything meaningful can be said about the protection provided by any system against the hazard. These limitations should be acknowledged by the safety cases.*"

It is considered that safety assessment predictions over the long-term (> 1 Ma) become highly speculative, but at the same time significant hazards still exist and consequently high consequences could still be possible. In analysing issues that may be of significant concern over this time frame, the issues of (a) uplifting and (b) erosion should be carefully considered. These phenomena could ultimately lead to direct exposure of the radionuclides that are still remaining after the phases of complete and partial isolation of the fuel (during which some degree of reliance on e.g. sorption, low solubility and slow groundwater flow is still possible). Physical and chemical dispersion phenomena would however affect the state of the fuel and it therefore seems implausible that at any time a living being would be exposed to an intact spent fuel (SF) or high level waste (HLW) package. It would be more plausible if exposure were to occur through uplifting or erosion that it would be in relation to fragments and residues of the fuel scattered or diluted over a larger area than the footprint of the repository. In the case of HLW, the most significant radionuclide would probably be exposure to Tl-209 that would be in secular equilibrium with its parent Np-237. For spent nuclear fuel, the exposure issue relates to Bi-214 from the decay chains of U-238, Pu-238 and U-234 and remains almost indefinitely. In very long time frames, however, the major source of Bi-214 results from the decay chain of natural uranium (U-238).

Erosion and uplifting were considered to a limited extent as geosphere processes in SKB's latest safety assessment SR-Can (SKB, 2006), but the reviewers recommended that glacial erosion should be further analysed not least since it could affect the selection of an appropriate repository depth (Dverstorp et al., 2008). Glacial erosion should also be discussed as a key process that would affect the ultimate fate of the repository and a comparison with the hazard from a natural uranium ore of similar size as the repository would be of key interest.

Natural analogues can provide significant information in relation to behaviour of radioactive material in geological settings over very long time periods. Such information may include erosional history and migration of radionuclides in the geosphere. One such natural analogue which has been studied in detail is the Koongarra uranium deposit in Northern Australia (SKI, 1992; Figure 13).

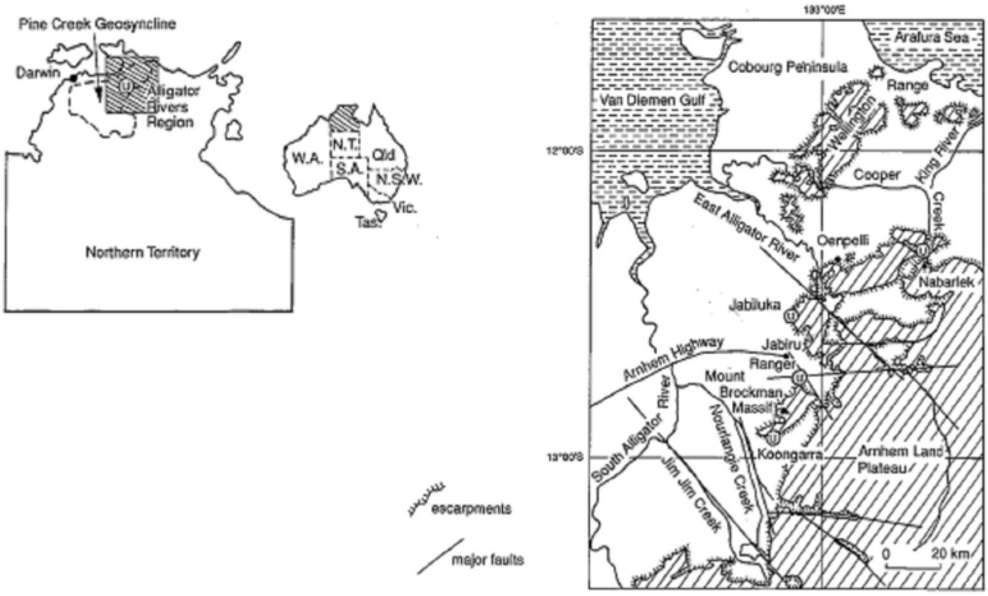


Figure 13. Map indicating the location of the Koongarra uranium deposit in the Northern Territory of Australia (reproduced from the Alligator Rivers Analogue Project report, Volume 1).

The Koongarra deposit lies beneath the sandstone escarpment of the Mount Brockman Massif (Figure 14). A distinct and extensive primary hydrothermal alteration halo exists that extends up to 1.5 km from the ore with uranium occurring in an inner dispersion fan approximately 50 m from the ore (Figure 14). Geomorphological and paleoclimatic controls are likely to have played a substantial role in the development of the dispersion fan. In particular, escarpment retreat and valley denudation will have played important roles (Figure 15).

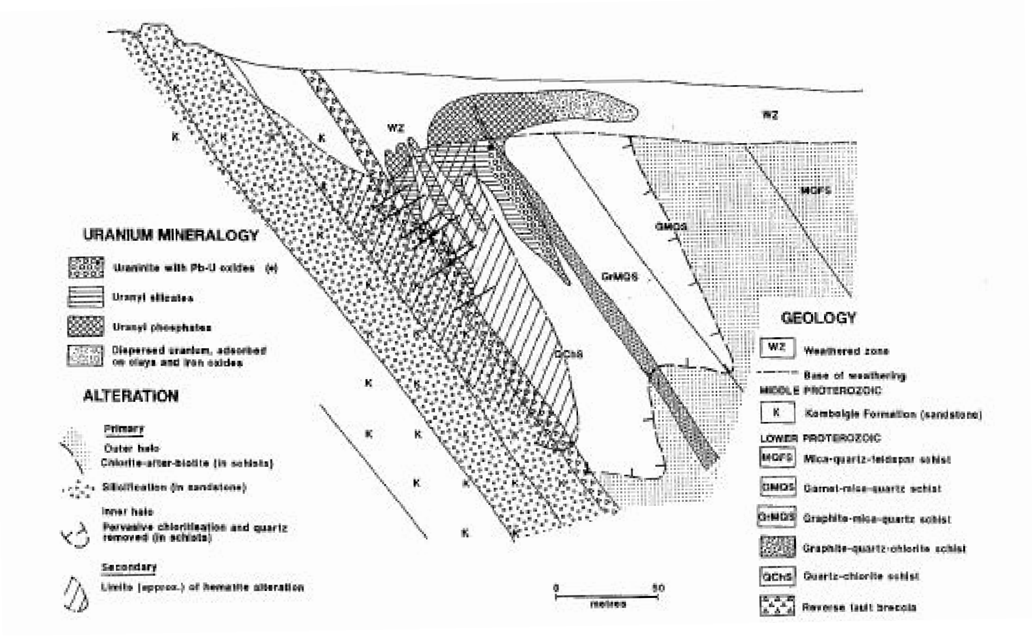


Figure 14. Simplified cross-section through the Koongarra ore body indicating the geology, distribution of U minerals and alteration (reproduced from Alligator Rivers Analogue Project report, Volume 1).

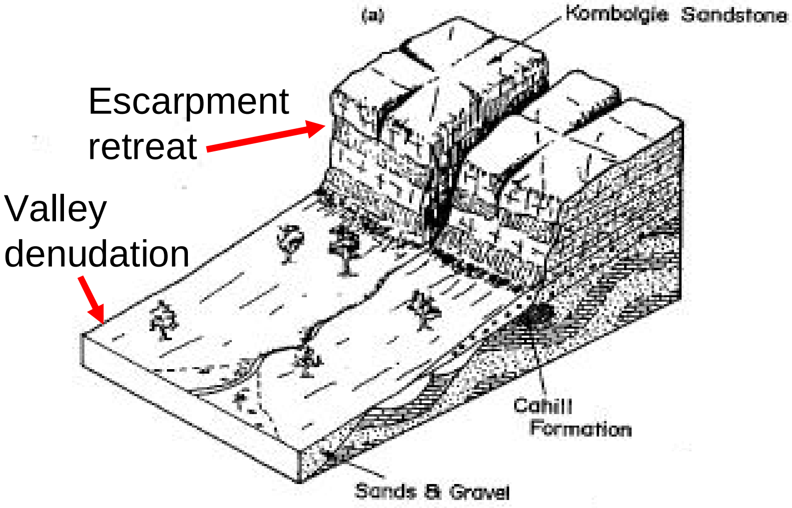


Figure 15. Schematic representation of Kombolgie Sandstone escarpments and underlying Cahill Formation indicating escarpment retreat and valley denudation (adapted from Alligator Rivers Analogue Project report, Volume 3).

In relation to the development of the dispersion fan, escarpment retreat is of secondary importance to valley denudation but it is a necessary precursor. Indications are that the rate of escarpment retreat varied from between 20 and 200 m per million years. The rate of retreat was dependent on the rock mass geometry and structural geology. Rates of valley denudation were estimated from a number of studies (Roberts et al., 1991; Duggan, 1988; Hart et al., 1987). A rate of 22 mm/ka was determined from both washload rates in the Magela Creek as well as suspended sediment and solute yields in Koongarra Creek. A lower value of 12 mm/ka was determined from sediment and solute yields in Magela Creek, however, it was believed that this latter value was too low by a factor of about two since the data were obtained during "abnormal" climatic years. Consequently, the rate of denudation is of the order of 22 mm/ka. This suggests that it would take approximately 5 million years for the valley to be eroded 100 m. The rates of erosion are similar to rates calculated for other Australian catchments as well as that elsewhere in the world in similar climatic conditions.

It is certain, however, that erosion rates will have changed over time as a consequence of changing climatic conditions. During drier periods, denudation rates would have decreased. Conversely, intense monsoonal periods would have led to enhanced rates of chemical weathering. Nevertheless, the mean catchment estimate of 22 mm/ka would appear to be the best estimate and can be used as a guide to the rate of erosion in the Koongarra region over the last few million years.

Regardless of the geomorphological events that took place, the formation of the dispersion fan necessitates that the ore body was located in an oxidising weathering environment. Nevertheless, the most direct control on the dispersion fan is the site-specific denudation rate. These will control the "arrival" of the ore body in the oxidising environment that is suitable to induce the radionuclide mobilisation that has resulted in the formation of the dispersion fan.

It is proposed that the Swedish repository at the Forsmark site will be built at a depth of 500 m. The landforms on the coast of the Baltic Sea are still emerging from the subsident state as a result of the last glaciation ("glacial rebound"). The rate of rise on the Finnish coast is approximately 8 mm/a. Such a rate of rise may induce geological stress in the region of the repository. This landform rise, however, is cyclic in nature and unlikely to affect the rate of erosion that will occur of the landform.

If one compares the Forsmark site with the Koongarra uranium ore deposit, a future repository at a depth of 500 m would not be exposed for 25 million years. The granitic environment may erode more slowly than the geological environment at Koongarra since the rock is more competent. However, it is also possible that future glaciation periods may temporary and locally lead to a rate of erosion that may be greater than that determined for Koongarra. In any case, it is recommended that a more thorough assessment of the impact of erosion be estimated in the context of the Swedish waste repository.

7. Working group discussions

7.1 Group 1: Spent fuel issues

Paul Brown (Chairman), Jinsong Liu (Secretary), Hanna Hedström and Christophe Jégou

The issues discussed within Group 1 are directly related to the properties of the spent fuel. Other issues indirectly related to the properties of the spent fuel, such as radionuclide chemistry and colloid formation from dissolution of the nuclides in the spent fuel, among others, were discussed within Group 2 of the workshop participants.

The following issues were discussed within Group 1:

Criticality

Criticality refers to the phenomenon when more than one neutron is produced with the consumption of one neutron in the chain reactions of fission. In practice the coefficient (the number of neutrons produced when one neutron is consumed) is usually taken to be slightly less than one, e. g. 0.95 as a criterion for criticality. The criticality criterion will be implemented during the packing (geometrical arrangement) of the spent fuel in the canister. There is, however, a risk that the geometrical arrangement of the spent fuel will be altered after a canister breach and mobilization of radionuclides in the spent fuel, and criticality can be achieved. There are no further comments on this issue by the group. This issue will be reviewed again within the frame of the long-term safety review during a future licensing process.

Instant release fraction (IRF)

The IRF relates to those radionuclides that will be released within an extremely short period after the breach of a canister. Most of these radionuclides are either gases or in very volatile phases.

The group realises that values of IRF proposed by SKB in the SR-Can report were significantly lower for most of the nuclides than those of the French CEA (Commissariat á L'Energie Atomique) values. Regarding SKB's recommended values in SR-Can, the long-term evolution of spent fuel appear not to have been taken into account. Recent research results from CEA and the EU MICADO project show that the microstructure of the spent fuel could be more stabile during long-term evolution of the spent fuel than previously considered, and as a consequence CEA and the Swiss NAGRA have recently revised their data of IRF. The values of IRF are now generally close to SKB's values. There are, however, still significant differences for some nuclides, e.g.^{79}Se, ^{107}Pd and ^{126}Sn, and this should be further explored. The reason for the discrepancy might be that SKB considers some of these nuclides to be present in non-volatile phases.

The group also considers that the relation between IRF values and the solubility limit of the relevant nuclides is not clear in SKB´s treatment. The solubility limit can be reached only after a significant amount of any nuclide has been released.

As for the IRF values of some activation products such as ^{36}Cl, uncertainties are large due to a lack of good assessment of the initial inventory, but SKB, NAGRA and CEA all have proposed similar values for it. The group considers that the value is likely to be pessimistic for safety assessment purposes. It is noted by the working group that previous approaches for obtaining the IRF values seldom consider the chemical conditions under which the IRF's are supposed to be released.

Regarding athermal diffusion of fission products within the spent fuel particles, a conservative estimate was made several years ago by CEA and the results showed that the process is not important for the values of the IRF except for ^{36}Cl and ^{14}C due to the potential mobility of these two nuclides. The group wonders if this point will be considered in the SR-Site report. Most of the nuclides in the IRF are either gases or very volatile. The group wonders if their release rate can be significantly changed when the buffer is partially or completely eroded in some of the deposition holes. This question is closely related to gas transport through an intact buffer versus through an eroded buffer.

Matrix performance

The group considers that the values of the matrix dissolution rate (10^{-6} to 10^{-8}) proposed might be realistic for UO_2 fuel, but may not be appropriate for MOX fuel. Many experimental data obtained under reducing conditions confirmed that the dissolution rates of the UO_2 fuel are low. The group considers, however, that the mechanisms for H_2 gas to inhibit the effect of water radiolysis need to be better understood. The mechanism for homogeneous systems (in solution) has been proposed to be the reaction of the H_2 with radicals. Since the radicals are more readily formed under beta and gamma radiolysis, the inhibition effect will be more profound in homogeneous systems under beta and gamma radiation. For heterogeneous systems, the mechanism of surface catalysis has been proposed. There is still much uncertainty relating to the mechanistic interpretation of the experimental data for heterogeneous systems.

The group still wonders if the enhancement of copper corrosion by the gamma-radiolysis of water (during the early period of repository evolution) is important.

The group considers as well that there seems to be a lack of leaching data of spent fuel in the presence of Fe^{2+}, but Fe^{2+} may have an effect on water radiolysis.

Criteria for screening nuclides

The group wonders how some of the stable isotopes will be treated in future safety cases. One example is ^{137}Ba (a daughter of ^{137}Cs) which may have an effect on sulphate concentration through the solubility of barite. The effect of this particular element might not be so significant since sulphate is a major species in the groundwater. Nonetheless, a better consideration of stable isotopes might be needed for the solubilities of nuclides that are controlled by major groundwater species like sulphate.

The group has discovered that the dose evolution diagrams (the diagram that shows the dose rate changing with time for total dose and the doses for respective individual radionuclides) varies considerably between different sources. A valid explanation for this has to be found.

Regarding the selection of radionuclides to be included in the safety analysis calculations, it seems to the group that some nuclides are taken into account simply because they are readily measured. The question could then be the opposite: are there any important radionuclides omitted simply because it is difficult to measure them? The group would also like to point out that data for certain nuclides are just obtained indirectly by analogue with other nuclides. The uncertainties accompanying this should be thoroughly analysed in future reviews.

Inventory data

The group is aware that several partners have proposed to initiate an EU project to deal with the issue of inventory data. This project will be mainly an experimental project and will use leaching results to determine the inventory.

The group would like to point out that the most important factor that influences the inventory is not the burn-up but rather the thermal history of the spent fuel. It is not easy to obtain the information of the linear power, and on the other hand it is much easier to get burn-up information. In the French program it has been tried to find correlation between label activity and burn-up. The group would also like to point out that the data for ^{36}Cl used in several waste management programs come from the leaching experiment of CANDU fuel and not from UO_2 or MOX fuel. The group wonder if the differences (if any) between that in CANDU fuel and that in UO_2 or MOX fuel can be better analysed in SR-Site.

The group has realised that there are different values of the half-live of ^{79}Se in the literature (Jiang et al., 1996), a value of $(1.13 \pm 0.17) \times 10^6$ a is given, while in “the 7th edition of the Karsluhe chart of the nuclides”, the value is 4.8×10^5 a). The group wonders how this discrepancy will be treated in the SR-Site report.

Uranium mine natural analogue

The group believes that in SR-Can there has not been an enough utilisation of the results and arguments obtained from natural analogue studies for the treatment of issues related to spent fuel. There are many sites that may be of potential use like, Koongara in Australia, Oklo in Gabon and Cigar Lake in Canada. Potential behaviour of uranium nuclides in oxidising and reducing groundwater could be illustrated through natural analogue studies.
The group wonders if erosion of the bedrock under glacial conditions and possible consequences for surface expose of uranium minerals has been suf-

ficiently studied in SKB’s previous safety reports. The group would like to point out that the clay halo in the Cigar Lake uranium deposit can be an analogue to the bentonite buffer in the deposition hole in a final repository.

Physical properties of the spent fuel

There have been several presentations concerning the physical properties of the spent fuel during the workshop and more information can be found in other relevant parts of this report.

Influences of the burn-up

The instant release fraction (IRF) of spent fuel is expected to increase with an increase of the burn-up. The influences are however more limited than previously considered as has been revealed by the results from recent studies by CEA and NAGRA. New evidence has been obtained from these studies which show that the microstructure of the rim zone of the fuel pellet is more stable in the long term than previously believed. On the other hand, there is an increase of the fission gases when the burn-up is higher than 45 MWd/kg U.

When the burp-up is high there is an increase of the amount of trivalent species in the fuel that are difficult to oxidise. This may explain some observations indicating that the matrix is more stable for high burn-up fuel.

MOX fuel

The group would like to point out that the long-term stability of MOX fuel has not been demonstrated. The IRF related to MOX fuel could be much higher than that related to UO_2 fuel since there is no evidence of the long-term stability of the microstructure of MOX fuel. Moreover, models for matrix alteration of MOX fuel are still lacking. Nevertheless, when the amount of Pu increases the matrix may become more difficult to oxidise.

7.2 Group 2: Radionuclide chemistry issues

Christian Ekberg (Chairman), Bo Strömberg (Secretary), Günther Meinrath and Heino Nitsche

The issues discussed within Group 2 were those only indirectly related to the properties of the spent fuel such as radionuclide solubility limits, sorption of released radionuclides and colloid formation from dissolution of the nuclides in the spent fuel.

The following issues were discussed within Group 2:

Radionuclide solubility

Low solubility can be an important safety function for most radionuclides which will limit dispersion from the canister and deposition hole area. How important this safety function will actually be depends on the spent fuel release of radionuclides under repository conditions, but in any case the low solubility provides a redundant safety function for some of the nuclides with the highest radiotoxicity, e.g. the actinides. SSM’s review of SKB’s solubility calculations will focus on three topics, 1) the influence of groundwater chemistry on radionuclide solubility, 2) review of utilized thermodynamic data, and 3) methodology of speciation calculations.

Regarding the first topic, the review group is concerned that a too limited approach is implemented by just focusing on three “water types”. It might therefore be reasonable to explore a wider range of groundwater conditions with independent modelling tools. The idea is to thoroughly explore groundwater chemistry parameter space for a few cases and then attempt to define combinations of groundwater chemistry parameter values that are not covered by the three water type approach. If such combinations are found they would either have to be dismissed (as unrealistic groundwater chemical conditions) or further explored as a basis for assessing radionuclide solubility. Any necessary independent modelling work could be carried out with appropriate modelling tools.

The thermodynamic database utilized by SKB will have to be examined and reviewed. The first activity in this area could be to compare the SKB database with another database which also utilizes the PHREEQC format (e.g. HATCHES). Any large deviations found should be further examined. A few calculation runs could also be made with the alternative database to see the consequence of such deviations. The second approach for thermodynamic data review would be to focus on a selected set of radionuclide solubility determinations. Using independent modelling tools, the most sensitive thermodynamic data would then be determined for each case. The values of these datasets would then be thoroughly scrutinized to ascertain that traceability, data handling and experimental methods for establishing the data are sound and appropriate. The final item of the thermodynamic data review would then be to evaluate to what extent recent data updates have an influence and if any recently published material would have a significant impact on the review findings.

Incorporation of radionuclides into secondary phases by co-precipitation
Barium is a component of spent nuclear fuel (inactive barium as well as radiobarium) and once it is released it will be precipitate when it comes into contact with sulphate containing groundwater (as barite). In this crystal structure divalent radionuclide such as radium-226 will be captured by co-precipitation. Divalent strontium may also be integrated into the crystal lattice of barite. Another type of co-precipitation will be incorporation into ferric precipitates that may form in the repository surroundings. Nuclides of any charge may also be incorporated in such materials. These type of retention mechanisms may conservatively either not be addressed at all in the safety case or possibly only addressed for radium. No detailed review planning can be made at present.

Sorption of radionuclides on granitic rock and bentonite clay
Sorption on rock is a difficult issue since rock is a complex material composed of variable ranges of minerals with vastly different sorption properties and groundwater chemical conditions. These factors are not explicitly addressed with the lumped parameter K_d-concept which is utilised in almost all safety assessment work in the area of geological disposal of radioactive wastes. Regarding groundwater chemistry, almost the same arguments could be raised for sorption as was mentioned above for the radionuclide solubility calculations, namely the safety case could consider an appropriately wide and diverse array of groundwater chemical composition. Regarding the min-

eralogy and solid composition, a significant issue is if sorption on clay minerals in the rock or fracture filling minerals or only that on intact rock in the rock matrix will be considered. Sorption of radionuclides on bentonite clay (buffer and backfill) was regarded as an easier task, since the bentonite is a much better defined material.

The review of sorption could be a task requiring substantial effort. In order to focus the review, independent consequence calculations and/or sensitivity analysis provided with the safety case, can be used to identify K_d-values that significantly affect the dose/risk assessment. Derivation and traceability for those K_d-values will have to be checked carefully. The amount of effort required for this review task depends on the level of detailed quantitative uncertainty assessment provided with the safety case. Even if quantitative uncertainty assessment is a feasible tool for confidence building, it was noted within the group that it cannot fully replace the expert judgement that can be provided by sorption experts with decades of experience in evaluating sorption properties for radionuclides. The group considers that SSM should affiliate such an expert in the context of future licensing reviews.

The influence of colloids

The issue of colloids can be split up in two areas; intrinsic colloids and pseudo colloids. The second area is probably the more difficult one to deal with and will require substantial resources. The literature on intrinsic plutonium colloids have been covered well by efforts connected to the present workshop. The results confirm that tetravalent plutonium will indeed be colloidal. Some complementary work will be needed to check the literature about uranium colloids (if they exist) and thorium, neptunium and americium colloids. The critical aspects of colloids are their shape, their charge and their size distribution. Colloidal stability will be quite sensitive to pH conditions. At the pH_{zpc} (zero point charge) colloids will not interact with solid phases and will thus be mobile. If pH conditions change the colloids would be attracted to negatively charged mineral surfaces or positively charged iron colloids (depending on the direction of the pH change). The critical questions from a safety assessment point of view will be if the colloids will be stable, to what extent the colloids would interact with solid material in the bedrock and if there is any reasonable scenario in which colloids could pass all the way to the biosphere (and thus contribute to dose). It was regarded that the best preparation for future reviews is to get a good overview of the current scientific literature. The members of the group felt that intrinsic colloids will probably not be such an important issue from a safety point of view, but there may still be open scientific issues requiring careful attention.

Pseudo colloids are other colloids in the groundwater that may enhance the transport of radionuclides if the nuclides become attached to them. Important groundwater colloids may be iron colloids (e.g. formed by canister corrosion), clay and silica colloids. Since buffer erosion (and backfill erosion) is regarded as an important process, it is expected that also bentonite colloids may be important under special circumstances. It should be noted that bentonite colloids have been thoroughly covered by other SSM efforts (see Apted et al., 2010), but these did not focus on the interactions between colloids and radionuclides. An effort to look at the influence of pseudo colloids on radionuclides should be coordinated with efforts directed to bentonite erosion and colloids formation. An essential first task is to get a good overview of the information in the scientific literature about interactions between colloids and radionuclides. A critical question is if the radionuclides attached to colloids anywhere along the flowpath in the geosphere will desorb when the colloids move to an area with no radionuclides in its surroundings. If this is the case the radionuclides will not reach the biosphere as colloids. The largest safety implication is the case of irreversible sorption of radionuclides to colloids. Another critical issue is to what extent the colloids will themselves interact with the bedrock. Filtration and "straining" of colloids has been discussed as a process that would decrease the importance of the possible colloid pathways. It is difficult to plan the review of this issue, since the safety case handling of colloid issues is presently not known.

Matrix diffusion

Matrix diffusion was not covered in any detail in this group since no expert in this area was available. It was noted, however, that it is an area to be thoroughly addressed in future reviews. Apart from experts in matrix diffusion as such, it might be necessary to find an additional expert to review SKB's electrical conductivity measurements. The electrical conductivity measurements are utilized to a large extent to determine matrix transport properties.

Thermodynamic sorption models

It is not know if thermodynamic sorption models will be used as a support in upcoming safety assessment work, but if this is the case additional experts may be needed to cover this area.

8. Final remarks

The main objective of the workshop reported here was to evaluate and discuss various aspects related to the treatment of spent fuel performance and radionuclide chemistry in the safety case for the final disposal of spent nuclear fuel. Preliminary SKB material has been considered and compared with other scientific work in these areas. The viewpoints expressed in this report are not necessarily indicative of deficiencies in the SKB programme, since the review approach is retrospective and only preliminary material has been considered. The following items were discussed in particular:

Regarding instant release fractions, the uncertainties are rather small for low- and intermediate burn-up fuel except for some of the long-lived activation products such as ^{14}C and ^{36}Cl and the fission product ^{79}Se. The uncertainites for high burn-up fuel (up to 60 GWd/ton U) can be more considerable. It is essential that at least a conservative approach for assignment of IRFs can be justified for this type of fuel.

The uncertainty of matrix dissolution models also need to be carefully examined. The best approach is to use a combintation of modelling results and experimental leaching data to justify fractional release rates. Conceptual modelling uncertainties should be given large emphasis in a similar manner as was done in the recently completed Micado project (Grambow et al., 2010).

Hydrogen generation in the vincinity of the spent fuel surface has the potential to substantially supress the influence of radiolytically produced oxidants. Fractional release rates can potentially be lowered accordingly, but this requires a comprehensive analysis since the understanding of the underlying mechanism is currently somewhat deficient. It needs to be understood if there is a threshold effect that depends on the amount of hydrogen, the amplitude of the radiation field, the chemistry of solution, and the catalytic effect of the fuel surfaces. It would also be valuable to know if the UO_2 surface itself has the abiltiy to activate hydrogen since this would imply less reliance ot the ε-phases. Moreover, the availability of hydrogen next to the fuel surfaces needs to be analysed and considered for the range of scenarios included in the safety assessment.

Geochemical modelling work with the aim to further explore concentration limits for key radioenlements has recently been reported by SKB. A review of this work suggests that there may be considerable uncertainties assoicated with the simplified Excel calculations. The uncertainties are mainly related to a reduction of the dataset utilized with omission of some species and components. There is an uncertainty introduced by not fully accounting for the interaction between groundwater componenets with radionuclides and stable isotopes from the spent fuel. The selection of species, elemental components and their interactions need to be further explained. Moreover, the applied method to account for variation in groundwater composition has to be scrutinized in more detail since the end-member approach may be too limited.

SKB will need to demonstrate treatment of Pu(IV) polymer colloids. New research results indicate that Pu(IV) in the aqueous phase under repository conditions may be in colloidal crystalline form (nanocrystals), which will affect transport properties because there are then no ionic species. This represents a significant change in the scientific understanding of the geochemical behavior of this element.

The workshop has scrutinized literature K_d values presented by SKB. It is clear that the range of literature K_d values for certain radionuclides is unsatisfactorily wide. A plausible explanation is that the level of uncertainty for certain nuclides is mainly influenced on what is straightforward to measure. The uncertainty related to some activation products maybe particularly important in the safety case. It is therefore essential to assess the data reliability and examine the associated uncertainty effects. More concrete measures to improve the knowledge and understanding of the area may be to find methods to better account for the representative reactive surface area for sorption and related to this, to sufficiently consider secondary minerals of a sample, including fracture filling minerals such as chlorite and iron hydroxides.

It has long been recognised that disposed spent fuel in a final repository could in exceptionally long time scale arrive at the ground surface due to natural denudation of the bedrock. The time scale of such development is most probably well beyond what is normally considered in safety assessment, but there is still a renewed interest of the topic in the international community. The hazard of what is remaning of the fuel is mainly related to radionuclides in the decay chain of U-238 at times well beyond 1 million years. This situation arises because of diminishing inventory of fission products and other actinides with time. Since engineered barrier performance can hardly be accounted for over such an extreme time scale, the situation is therefore analoguous to that of surface near uranium ore. A good case study should be the Koongarra uranium deposit in Northern Australia. Investigations at this site show that uranium approaching the ground surface due to the natural denudation of the bedrock is dispersed from the primary ore in the shallow part of the rock. This shallow part of the uranium ore is called the dispersion fan. For Swedish conditions, it is important that glacial erosion, which is expected to dominate the natural denudation of the bedrock, is carefully investigated.

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

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

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