



# SKB rapport R-97-15

October 1997

Review of a report on diffusion and  
sorption properties of radionuclides  
in compacted bentonite

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**REVIEW OF A REPORT ON DIFFUSION  
AND SORPTION PROPERTIES OF  
RADIONUCLIDES IN COMPACTED  
BENTONITE**

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

**REVIEW OF A REPORT  
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Keywords: sorption, diffusion, review, uncertainties, performance  
assessment

## ABSTRACT

The present report encompasses the discussion of data uncertainties of the revised report prepared by Yu and Neretnieks (1997). Uncertainties of the reference system, in particular the porewater chemistry relevant for compacted bentonite, are illustrated with the help of a thermodynamic model. Uncertainties regarding the chemistry of the critical elements considered by Yu and Neretnieks (1997) are reviewed, and ranges of validity with regard to the extrapolation of sorption and diffusion data are indicated, where appropriate. The data selection made by Yu and Neretnieks (1997) is reviewed for each critical element, and uncertainties associated with these data are discussed. Possibilities on how to handle such uncertainties are discussed, and very briefly, the use of thermodynamic models for sensitivity analyses is illustrated using Cs.

## SAMMANFATTNING

Den här rapporten innehåller diskussionen kring dataosäkerheterna i rapporten av Yu och Neretnieks (1997). Osäkerheterna i referenssystemet, i synnerhet den relevanta porvattenkemin för högkompakterad bentonit, illustreras med hjälp av en termodynamisk modell. Osäkerheterna i de kritiska elementens kemi, som behandlas av Yu och Neretnieks (1997), är granskad och validitetsområdet för sorptions- och diffusionsdata visas, där det är möjligt. Datavalet av Yu och Neretnieks (1997) är granskat för varje kritiskt element, och osäkerheterna kopplade till dessa data diskuteras. Möjligheterna att behandla dessa osäkerheter diskuteras och ett exempel på hur en termodynamisk modell skulle kunna användas visas, mycket kort, för Cs.

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## SUMMARY AND CONCLUSIONS

The present report encompasses the discussion of data uncertainties of the revised report prepared by Yu and Neretnieks (1997). According to an outline provided by SKB, the following topics are addressed in the present report:

- General comments
- Use in SR 97
- Dependencies on other parameters, ranges of validity, sensitivities
- Characterisation of uncertainties
- Quantification of uncertainties
- Correlations
- Treatment in safety assessment

In addition, comments on general concepts presented by Yu and Neretnieks (1997) are provided in an appendix.

Following is a summary of the comments on the selected sorption and diffusion data:

- Am: The  $K_d$  and  $D_a$  value selected are reasonable and consistent.
- C: The selected  $D_a$  value is reasonable for carbonate species, a value for methane should also be given.
- Ce, Sm: The selected data are reasonable.
- Cl, I: The selected  $D_a$  value is reasonable for ambient temperatures.
- Cs: Two different  $K_d$  values have been selected for 'fresh' and 'saline' systems, but only one  $D_a$  value. This approach is not consistent.
- Pb: The selected  $D_a$  value is consistent with a  $K_d \leq 0.5 \text{ m}^3/\text{kg}$ .
- Np: A lower  $K_d$  value should be selected to be consistent with the selected  $D_a$ .
- Ni: The selected range of data is reasonable.
- Nb: The selected range of data is reasonable.
- Pd: The selected range of data is probably conservative.
- Pu: The selected  $D_a$  value should be higher, and the conservative  $K_d$  value should be lower to account for uncertainties in Eh and pH.
- Pa: A much lower conservative  $K_d$  value and a corresponding  $D_a$  should be selected to account for uncertainties in Eh.
- Ra, Sr: The data selected for a 'fresh' system are not relevant.
- Se: The selected data are reasonable.
- Tc: Two different  $K_d$  values have been selected for reducing and oxidising conditions, but only one  $D_a$  value. This approach is not consistent.
- Th: The selected data are reasonable.
- Sn: The selected range of data is reasonable.
- U: The selected data are reasonable.
- Zr: The realistic value for  $K_d$  should be chosen from the compiled data, the conservative  $K_d$  should be lower due to the lack of data on the aqueous chemistry of Zr.



# 1 INTRODUCTION

## 1.1 Background of this review

Compacted bentonite is considered by SKB as backfill material for nuclear waste repositories. The approach of SKB for the final storage of spent nuclear fuel is defined in the KBS-3 concept. Integrated safety analyses of this concept, such as the SKB 91 study, are prepared by SKB in order to clarify the importance of different factors for the overall safety of a deep repository for spent nuclear fuel. For the SKB 91 study, a compilation (SKB TR 91-16) of porosity, sorption, and diffusivity data was carried out (Brandberg and Skagius, 1991). Based on the framework in this Technical Report, a more recent and extensive data compilation was carried out by Yu and Neretnieks (1997). This report is the subject of the present Discussion of Data Uncertainties.

## 1.2 Scope

The present report encompasses the discussion of data uncertainties of the material prepared by Yu and Neretnieks (1997). According to an outline provided by SKB, the following headlines are used to structure the present report:

- General
- Use in SR 97
- Dependencies on other parameters, ranges of validity, sensitivities
- Characterisation of uncertainties
- Quantification of uncertainties
- Correlations
- Treatment in safety assessment

# 2 REFERENCE SYSTEM

As discussed in the present report, the sorptive and diffusive properties of the key radionuclides treated in the report by Yu and Neretnieks (1997) depend on chemical parameters, such as Eh, pH, salinity, and so on. In other words, uncertainties regarding the parameters that are expected for the bentonite porewater under repository conditions will result in uncertainties of  $K_d$  and  $D_a$  values. It is useful, for this reason, to define the reference system that a data selection is based on.

## 2.1 BENTONITE CHARACTERISTICS

The reference system considered here is 100 % saturated Wyoming bentonite MX-80, compacted to a dry density of 2000 kg/m<sup>3</sup>, corresponding to a bulk (wet) density of 2250 kg/m<sup>3</sup> and a porosity  $\epsilon$  of 0.25. The mineral composition, including impurities, is given by Yu and Neretnieks (1997), based on data reported by Lehtikoinen et al. (1996).

It is worthwhile to point out that MX-80 bentonite contains several readily soluble impurities that will influence the porewater composition. At high degrees of compaction, porewater chemistry may be dominated by the dissolution of these impurities. The content of CaCO<sub>3</sub> was determined as 1.4 % (Müller-Vonmoos and Kahr, 1983), the content of NaCl (0.007 %) and CaSO<sub>4</sub> (0.34 %) was evaluated by Wanner et al. (1992), based on experiments carried out by Werme (1992) with untreated MX-80 bentonite. Lehtikoinen et al. (1996) report a sulphate content of 0.34 to 0.8 %, as well as other impurities (e. g. fluoride, phosphate, organic matter), but no NaCl impurities.

Further, Wieland et al. (1994) report surface chemical characteristics for MX-80, as well as ion exchange and surface hydrolysis ('edge-sites') constants. A few calculations were carried out for the present report using this 'bentonite model', and the relevant parameters are reproduced for convenience in Table 2-1 and Table 2-2.

**Table 2-1. Surface chemical parameters of Wyoming bentonite MX-80.**

Parameter	Value for MX-80	Reference
CEC	85 meq/100g	Wieland et al. (1994)
exchangeable Na <sup>+</sup>	81.7 %	Müller-Vonmoos and Kahr (1983)
exchangeable K <sup>+</sup>	0.3 %	Müller-Vonmoos and Kahr (1983)
exchangeable Mg <sup>2+</sup>	3.9 %	Müller-Vonmoos and Kahr (1983)
exchangeable Ca <sup>2+</sup>	14.1 % <sup>1</sup>	-
SOH site density	2.84 meq/100g	Wieland et al. (1994)

1 calculated by difference

**Table 2-2. Parameters of the bentonite model used in the present report.**

Surface species	$\log_{10} K^\circ$	Reference
<i>Surface site master species: Z<sup>-</sup></i>		
ZNa	20.0	Wanner (1986)
ZK	20.26	Fletcher and Sposito (1989)
Z <sub>2</sub> Mg	40.13 <sup>1</sup>	Wanner et al. (1992)
Z <sub>2</sub> Ca	40.2 <sup>1</sup>	Wanner et al. (1992)
ZCs		Wanner et al. (1996)
ZH	23.0	Wieland et al. (1994)
<i>Surface site master species: SOH</i>		
SOH <sub>2</sub> <sup>+</sup>	5.4	Wieland et al. (1994)
SO <sup>-</sup>	-6.7	Wieland et al. (1994)

<sup>1</sup> After conversion to the mole fraction model.

<sup>2</sup> For Ra<sup>2+</sup>, the ion exchange constant for Sr<sup>2+</sup> is used.

<sup>3</sup> Obtained for pre-treated MX-80 which had a CEC of 108 meq/100 g.

## 2.2 POREWATER COMPOSITION

The behaviour of many critical elements will depend on the composition of the porewater in the bentonite backfill. Accordingly, Yu and Neretnieks (1997) report the composition of groundwaters representative for the Äspö, Finnsjön and Gideå sites. For each groundwater, ionic strength, pH, and Eh are also given. Eh values range from about -200 to -300 mV, but relatively high concentrations of sulphate are reported at the same time. However, under the pH-Eh conditions of these groundwaters, a significant fraction of the sulphur present should exist as S(-II), i. e., as sulphide species (Stumm and Morgan, 1996). Apparently, these systems are not in equilibrium, or the measurements are erroneous (sulphide could be oxidised to sulphate during sampling, or the Eh readings may not correspond to all redox-couples present).

The porewater composition of compacted bentonite may be modelled by using the respective groundwater composition and the bentonite characteristics and surface reactions given in Table 2-1 and Table 2-2, respectively. Groundwater compositions were used as given in Table 2 of Yu and Neretnieks (1997). Bentonite porewater compositions were modelled by allowing some of these groundwaters to equilibrate with MX-80 bentonite at a dry density of 2000 kg/m<sup>3</sup>. The resulting porewater compositions are given below (Table 2-3).

An important result of this calculation is that the influence of fresh and saline groundwaters on porewater composition may be quite small if one considers the soluble impurities (such as CaSO<sub>4</sub> and NaCl) of the bentonite to be dissolved. In this case, the porewater chemistry is to a significant degree determined by the bentonite itself. Further, Yu and Neretnieks (1997) assume the porewater pH to be between 8 - 10, whereas the present calculations show that the pH may be around 7 or lower, based on the model of Wieland et al. (1994). It needs to be pointed out that the low pH values given in Table 2-3 are calculated under the assumption that the system is closed with respect to CO<sub>2</sub>. Allowing CO<sub>2</sub> to escape would lead to higher pH values (a decrease of pCO<sub>2</sub> to atmospheric conditions would result in a pH slightly above 8).

**Table 2-3. Calculated bentonite porewater composition for MX-80 (dry density = 2000 m<sup>3</sup>/kg) in contact with groundwaters from different sites in Sweden.**

Parameter	Input groundwater:	
	Äspö (KAS02)	Finnsjön (KFI07)
<i>dissolved total concentration (M)</i>		
Br	5.0E-04	–
Ca	5.8E-01	5.8E-01
Cl	1.9E-01	2.5E-02
CO <sub>3</sub>	7.9E-03	1.4E-02
F	7.9E-05	7.9E-05
Fe(II)	–	3.2E-05
SiO <sub>2</sub>	1.1E-04	1.1E-04
K	2.1E-02	2.0E-02
Mg	1.3E-01	1.3E-01
Na	5.7E+00	5.6E+00
SO <sub>4</sub>	5.2E-02	9.0E-02
<i>other parameters</i>		
pCO <sub>2</sub> (atm)	-1.35 <sup>(1)</sup>	-1.13 <sup>(1)</sup>
pH	6.79	6.84
I (M)	0.32	0.26

<sup>(1)</sup> Calculated assuming a closed system.

### 3 GENERAL COMMENTS

The report by Yu and Neretnieks (1997) encompasses a review of sorptive and diffusive properties of mainly ionic species of key elements for the SKB performance assessment. For each element considered, sorption is characterised by distribution coefficients ( $K_d$  values), and diffusion is

characterised by apparent ( $D_a$ ) or effective diffusivities ( $D_e$ ). For each element, values for performance assessment are proposed by Yu and Neretnieks (1997), based on a compilation of  $K_d$  values and diffusivities reported in the literature.

The data taken from the literature are all derived from laboratory experiments by a variety of researchers, the respective data sources are given by Yu and Neretnieks (1997). The laboratory experiments were carried out under a wide range of conditions with regard to

- the types of bentonites and clay minerals used,
- the composition of the solutions used, and
- the solid/water ratio and the degree of bentonite compaction employed in the sorption and diffusion experiments.

The data proposed by Yu and Neretnieks (1997) for performance assessment are based on the judgement of these authors. The proposed data refer to the reference system considered: 100 % saturated Wyoming bentonite MX-80, compacted to a dry density of 2000 kg/m<sup>3</sup>, corresponding to a bulk (wet) density of 2250 kg/m<sup>3</sup> and a porosity  $\epsilon$  of 0.25. The mineral composition, including impurities, is given by Yu and Neretnieks (1997), based on data reported by Lehtikoinen et al. (1996). However, no reference system is established regarding the expected conditions in the porewater of the bentonite buffer. In my opinion, these uncertainties are the most critical with respect to a selection of  $K_d$  and  $D_a$  values.

## 4 USE IN SR 97

The data discussed here will be used to model the migration of radionuclides through compacted bentonite, which is used as backfill material. I. e., these data will be applied to the near-field of a repository.

Both  $D_a$  and  $K_d$  values are 'lump-sum' parameters that may be used directly in transport models, given that the chemical boundary conditions of the model are compatible with the conditions under which the experimental data were generated. The behaviour of many of the critical elements discussed is strongly dependent on redox conditions, pH, dissolved carbonate and other solution parameters. This makes extrapolations to other conditions difficult, in particular if there are no models available to conduct a sensitivity analysis (see section 7.1). Many batch  $K_d$  values are, in addition, not directly relevant for compacted bentonite because the respective experiments were conducted with very dilute solutions (see section 5.2.1).

## 5 DEPENDENCIES ON OTHER PARAMETERS, RANGES OF VALIDITY, SENSITIVITIES

In the following sections, these issues are discussed for a range of parameters that are of importance for the migration of radionuclides in compacted bentonite:

- Dependencies on other parameters and ranges of validity are discussed together.
- No sensitivity analysis has been performed by Yu and Neretnieks (1997); but a check of consistency has been done, which is reviewed in the present report for each element.

### 5.1 TEMPERATURE

To date, very few sorption and diffusion experiments have been carried out at elevated temperatures. Therefore, it is difficult to quantify the effect of temperature on sorption and diffusion processes. In general, however, an increase in temperature will increase the thermal movement of any species. Therefore, sorption will decrease, and diffusion will increase with an increase in temperature. A rough estimation of temperature effects may be based on data compiled for Cs and Tc of Yu and Neretnieks (1997).

For Cs, the data reproduced in Table 5-1 and Table 5-2 show that an increase in temperature lowers the  $K_d$  value and increases the apparent diffusivity. However, it also becomes clear that chemical effects exert a similar or larger influence on Cs migration than temperature. A temperature increase from 25 °C to 80 °C lowers  $K_d$  by a factor of  $\approx 2$ ; a salt concentration of 55400 ppm instead of 11700 ppm in the solution lowers  $K_d$  by the same factor (Table 5-1). Similarly, Table 5-2 shows that the ionic form of the bentonite influences the  $D_a$  about as much as does the temperature. The decrease of Cs sorption by higher salt concentrations in the solution can be explained by a higher concentrations of cations able to compete with Cs for sorption sites, see section 6.4.5.

For the diffusion of Tc in Avonlea Na-bentonite (dry density  $\approx 1350$  kg/m<sup>3</sup>) under oxidising conditions, Sawatsky and Oscarson (1991) report a  $D_a$  of  $0.7 \cdot 10^{-10}$  m<sup>2</sup>/s at 25 °C and of  $\approx 1.9 \cdot 10^{-10}$  m<sup>2</sup>/s at 80 °C. On the other hand, for reducing conditions, they report a  $D_a$  of  $7 \cdot 10^{-12}$  m<sup>2</sup>/s at 25 °C and a dry density of 1300 kg/m<sup>3</sup>. Under oxidising conditions, Tc(VII) exists as  $\text{TcO}_4^-$  ion and does not undergo notable sorption. Tc(IV), prevailing under reducing conditions, hydrolyses and sorbs, presumably by surface complexation, onto clays. Apparently, temperature does not significantly

influence the diffusion of the non-sorbing species  $\text{TcO}_4^-$ , while the different chemistry exhibited by Tc(VII) and Tc(IV) has a large influence on diffusion.

It needs to be pointed out that both  $\text{Cs}^+$  and  $\text{TcO}_4^-$  are chemically not very reactive. Therefore, the effect that a physical parameter such as temperature has on the migration of these ions in bentonite is relatively large. In comparison, chemical effects are expected to play a much more important role for the behaviour of reactive elements, such as e. g. actinides and lanthanides. For redox-sensitive elements, temperature could possibly have a large influence by affecting their distribution between different redox-states. However, not enough reliable enthalpy data are available to judge this effect.

In summary, temperature may have some influence on sorption and diffusion of dissolved species in bentonite, but uncertainties associated with predicted chemical conditions in the buffer and with the speciation of many elements are probably much more relevant. With regard to the description of radionuclide behaviour at elevated temperatures, there is a serious lack of basic chemical data.

**Table 5-1.  $K_d$  values reported for Cs by Yu and Neretnieks (1997).**

Temperature (°C)	Salt concentration (ppm)	$K_d$ ( $\text{m}^3/\text{kg}$ ) (1)
25	55400	0.0356
80	55400	0.0167
25	11700	0.0780

(1) Initial Cs concentration is  $10^{-6}$  M, the solid is a Na-Ca-montmorillonite. Original source is Oscarson et al. (1987).

**Table 5-2.  $D_a$  values reported for Cs by Yu and Neretnieks (1997).**

Temperature (°C)	Bentonite	$D_a$ ( $\text{m}^2/\text{s}$ ) (1)
25	Na-form	$7.5 \times 10^{-12}$
70	Na-form	$4.0 \times 10^{-11}$
25	Ca-form	$3.4 \times 10^{-12}$
70	Ca-form	$4.0 \times 10^{-12}$

(1) Bulk density of the bentonite was  $2100 \text{ kg/m}^3$ , original source is Eriksen et al. (1981)

## 5.2 CHEMICAL CONDITIONS

In this section, the influence of chemical conditions on the sorption and diffusion behaviour of the elements considered in the report by Yu and Neretnieks (1997) is evaluated by:

- providing a general overview of the influence of redox conditions, pH, and solution composition on the behaviour of the key elements, and
- discussing the influence of relevant parameters on  $K_d$  and  $D_a$  values for each element.

### 5.2.1 Bentonite/water ratio

Many of the variations of solution composition discussed below are directly related to the bentonite/water ratio. Bentonites invariably contain small amounts of soluble impurities, including calcite, gypsum and NaCl. The dissolution of these impurities (see Table 2-3) leads to an increase of the concentration of dissolved major cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ...) and ligands (carbonate species, sulphate...), which has a significant influence on the migration behaviour of most elements (see discussion below).  $D_a$  values are determined at high bentonite/water ratios, and correspond to more or less realistic conditions in this respect.  $K_d$  values, on the contrary, often are determined in the presence of only small amounts of bentonite in dilute solutions, which can lead to apparent discrepancies when these  $K_d$  values are directly compared with  $D_a$  values (see discussion on Cs, Sr and Ra in section 6.4)

### 5.2.2 Redox conditions

Whether the sorption and diffusion behaviour of a key element is influenced by the redox conditions in the bentonite buffer will depend on the redox sensitivity of this element. Therefore, it is useful to divide the elements treated by Yu and Neretnieks (1997) into groups of redox-sensitive elements and elements with a stable oxidation state:

- |                                             |                                                                   |
|---------------------------------------------|-------------------------------------------------------------------|
| (1) Redox-sensitive elements:               | C, Np, Pa, Pd, Pu, Se, Tc, U                                      |
| (2) Elements with a stable oxidation state: | Am, Ce, Cl, Cs, I, Nb, Ni,<br>Pb, Ra, Rn, Sm, Sr, Th, Zr,<br>(Sn) |

Uncertainties regarding expected redox conditions will have a direct influence only on the elements in group (1). The oxidation state of the elements in group (2) is stable (Sn is included in this group, because it is expected to exist



only as Sn(IV) under relevant conditions, although Sn(II) may exist under extremely reducing conditions). However, the behaviour of these elements may be influenced indirectly, e. g. through redox-induced changes of dissolved ligand or metal concentrations in the porewater. Redox-sensitive elements in the bentonite-groundwater system include sulphur and organic plus inorganic carbon, according to the compositions given in Yu and Neretnieks (1997). Both of these elements can form different ligands, depending on the redox conditions.

Further, Yu and Neretnieks (1997) report dissolved Fe(II) to be present in the water from borehole KFI07 at Finnsjön. The pH and Eh of this water are given as 7.9 and -250 mV, respectively. Under these conditions, a slight increase in pH could cause the precipitation of Fe(III)-oxides or -hydroxides, which would possibly increase sorption of some radionuclides by creating reactive solid surfaces.

Finally, it needs to be pointed out that the redox potential refers only to the thermodynamic boundary conditions of a given system. Whether a certain species will actually undergo a redox reaction will depend on the presence of the reaction partners required for this reaction.

Expected dependencies of sorption and diffusion processes on redox conditions is discussed below for each element (or groups of elements, where appropriate) treated in the report of Yu and Neretnieks (1997).

### 5.2.3 Solution pH

#### General

As in section 5.2.2, the elements considered by Yu and Neretnieks (1997) may be divided into several groups, depending on whether their sorption and diffusion behaviour is dependent on pH or not. In general, this will depend on:

- (1) whether the solution speciation of a given element is pH-dependent or not,
- (2) whether a given element forms dissolved, solid or surface-bound compounds with species whose behaviour is pH-dependent.

Accordingly, the groups given below are made up to provide a general overview. Note that these groups represent only a very general characterisation of these elements, however. The influence of pH on the elements in group (1) is much larger than the influence of pH on the elements in group (2), in general.

- (1) Elements directly influenced by pH: Am, C(IV), Ce, Nb, Ni, Np, Pa, Pb, Pd, Pu, Se, Sm, Sn, Tc(IV), U, Zr
- (2) Elements indirectly influenced by pH: Cl, I, Ra, Sr
- (3) Elements not influenced by pH: Cs, Rn, Tc(VII), C(-IV)

Note that Tc is included in group (1) as well as group (3), depending on its redox state. Np, Pa, Pu, and U take on different oxidation states depending on the redox conditions, but all oxidation states exhibit a pH-dependent speciation as well as sorption and diffusion behaviour. Inorganic C(IV) is distributed between  $\text{CO}_2(\text{aq/g})$ ,  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$  according to pH, while methane (C(-IV)) is not influenced by pH.

### **Influence on sorption and diffusion**

It is important to point out that the sorption behaviour of an element is generally analogous to its speciation characteristics in solution:

- Elements that exist as hydrolysed cations in solution sorb onto clays mainly by forming surface complexes with surface-bound  $\text{OH}^-$  groups. The sorption of these elements in the circumneutral pH range is, therefore, highly dependent on pH. These elements are found in group (1) above and include Am, Ce, Nb, Ni, Np, Pa, Pb, Pd, Pu, Sm, Sn, U, Zr. The onset of hydrolysis for some of these elements (Ni, Pb) is around pH 5-6, and the sorption mechanism also changes from ion-exchange to surface complexation (Bradbury and Baeyens, 1995; Lothenbach et al., 1997) at the corresponding pH.
- On the other hand, elements that exist mainly as simple ions (Cs, Ra, Sr) sorb via ion exchange reactions. Under the conditions considered here, pH has practically no influence on their sorption behaviour, but salinity is very important (see next section).

The influence of pH on the diffusion behaviour is two-fold for an element whose speciation is influenced strongly by pH (see group (1) above):

- The species that are available for diffusion are directly dependent on the solution speciation of a given element under the respective porewater conditions.
- The  $K_d$  value is influenced by pH, and the apparent diffusivity  $D_a$  may be significantly changed as a function of  $K_d$ :

$$\frac{D_p}{D_a} = 1 + \frac{K_d \rho}{\varepsilon} \quad (1)$$

where  $D_p$  is the pore diffusivity,  $\rho$  is the dry density of the water-saturated bentonite and  $\varepsilon$  its porosity.

#### 5.2.4 Solution composition, salinity

Distribution coefficients and apparent diffusivities of the elements considered by Yu and Neretnieks (1997) will be influenced by the composition of the porewater in the compacted bentonite. The most important parameters in this respect, redox condition and pH, are discussed in the previous sections.

Apart from these parameters, the concentration of dissolved ligands in the bentonite porewater will be very important for the sorption and diffusion behaviour of metal ions. Important ligands include carbonate, sulphate/sulphide, phosphate, fluoride, and possibly organic ligands such as carboxylic acids or phenols stemming from the organic matter contained in the bentonite. To a lesser degree, the behaviour of some radionuclides that exist as anions under relevant conditions (carbonate species, selenide/selenite) may depend on the concentrations of major cations in the porewater.

In sites where saline groundwaters are important, the high concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  ions may influence the behaviour of some radionuclides. For most elements of interest here,  $\text{Cl}^-$  is not a very important ligand. At high concentrations, however, it will have some influence on the chemistry of e. g. trivalent actinides and lanthanides, Pb and Pd.  $\text{Na}^+$  will mainly enhance the migration of  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Ra}^{2+}$  by competing with these ions for the ion exchange sites available on the bentonite surfaces.

#### 5.2.5 Discussion of individual elements

In the following sections, the influence of redox conditions, pH and other solution characteristics on sorption and diffusion behaviour is discussed in some detail for each element (or each group of elements) treated in the report of Yu and Neretnieks (1997). To some degree, this discussion focuses on the conditions in the present reference system (see section 2), but the influence of the parameters must equally be considered in the interpretation and selection of sorption and diffusion data derived from laboratory experiments. Thus, the following discussion serves also as a base for the characterisation of uncertainties (section 6) associated with the values selected by Yu and Neretnieks (1997).

## Americium (Am), cerium (Ce), samarium (Sm)

In general, the chemistry of lanthanides and trivalent actinides is very similar. Most information on sorption and diffusion processes are available for Am, and a critically evaluated thermodynamic database is also available for this element (Silva et al., 1995). Therefore, Am is used here as a chemical analogue for Sm and Ce.

Am exists in aqueous solution exclusively in the +III oxidation state. Since hydrolysis and complexation with carbonate species is very important for the speciation and sorption behaviour of Am, pH is a critical parameter for the migration of Am in compacted bentonite. The influence of solution composition/salinity on Am speciation is illustrated in Table 5-3. The influence of Cl<sup>-</sup> is relatively small, but the SO<sub>4</sub><sup>2-</sup> stemming from the dissolution of gypsum contained in MX-80 bentonite has a significant influence. Formation of dissolved complexes will lower *K<sub>d</sub>* values to some degree.

Data for these elements are valid under all redox conditions, but only a very narrow range of validity can be expected with regard to pH and the concentration of dissolved ligands, in particular sulphate and carbonate.

**Table 5-3. Speciation of americium in different ground- and porewaters. Thermodynamic data are taken from Silva et al. (1995).**

Species	Äspö		Finnsjön	
	Groundwater <sup>1</sup>	Porewater <sup>2</sup>	Groundwater <sup>1</sup>	Porewater <sup>2</sup>
<i>distribution (%)</i>				
pH	7.7	7.9	6.8	6.8
Am <sup>3+</sup>	8.9	6.0	–	2.6
AmOH <sup>2+</sup>	40.6	3.2	1.4	1.6
Am(OH) <sub>2</sub> <sup>+</sup>	16.8	0.16	1.4	–
AmF <sup>2+</sup>	0.25	0.16	–	–
AmCl <sup>2+</sup>	3.1	2.0	–	0.12
AmCO <sub>3</sub> <sup>+</sup>	4.7	39.7	49.2	36.9
Am(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	0.36	1.5	44.5	2.9
Am(CO <sub>3</sub> ) <sub>3</sub> <sup>3-</sup>		–	3.4	–
AmSO <sub>4</sub> <sup>+</sup>	5.3	35.3	–	32.8
Am(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	0.17	12.0	–	23.0

<sup>1</sup> The composition is given in Table 2 of Yu and Neretnieks (1997).

<sup>2</sup> The composition is calculated for compacted bentonite, see Table 2-3.

## **Carbon (C)**

The following discussion is only concerned with inorganic C, including methane.

Under the redox conditions considered here (see section 2), inorganic C should be present mainly as carbonate species, although methane may become important at pH values  $\leq 7$  (Brookins, 1988). The most important carbonate species under the present conditions will be  $\text{HCO}_3^-$ , but dissolved  $\text{CO}_2$  may be as important as  $\text{CO}_3^{2-}$  at pH values of about 8 (about 1 % of total carbonate; cf. Stumm and Morgan, 1996). With decreasing pH, dissolved  $\text{CO}_2$  will become more important. This points to the possibility that part of the radiocarbon may diffuse as dissolved  $\text{CO}_2$  or  $\text{CH}_4$ . Both are neutral molecules and are expected to diffuse faster than anionic species.

However,  $\text{CO}_2$  is always in equilibrium with dissolved and solid carbonate species, and the migration of  $^{14}\text{C}$  will be retarded with respect to the migration of total C. Contrary to most other radioelements, C is a major constituent of the bentonite buffer. However,  $\text{CH}_4$  is chemically relative inert, and its  $^{14}\text{C}$  will probably not be distributed over all C-species.

Data for  $\text{CH}_4$  are valid for all solution conditions, given that  $\text{CH}_4$  is the dominant species. Under more oxidising conditions, C exists as carbonate; between pH  $\approx 7-9$ ,  $\text{HCO}_3^-$  can be expected to be dominant. The redox equilibrium of C(IV)/C(-IV) is pH dependent, but can be predicted well (Stumm and Morgan, 1996).

## **Chlorine (Cl) and iodine (I)**

Both elements are expected to occur only as dissolved anions ( $\text{Cl}^-$ ,  $\text{I}^-$ ) under the relevant conditions. Since  $\text{Cl}^-$  is ubiquitous in groundwater systems, the migration of radiochlorine may be somewhat retarded with respect to total chlorine.

Data are not expected to be vary as a function of the Eh-pH and solution conditions considered here (see section 2).

## **Caesium (Cs), Radium (Ra), Strontium (Sr)**

These elements are expected to exist predominantly as simple (non-hydrolysed) ions that are not influenced by pH or Eh. Dissolved ligands will also have very little influence on their speciation. Of critical importance for their migration in bentonite is the concentration of major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , but also  $\text{H}^+$  at low pH) in the porewater that will compete with  $\text{Cs}^+$ ,

Ra<sup>2+</sup> and Sr<sup>2+</sup> for ion exchange sites. Thus, it is commonly assumed that the sorption of Cs<sup>+</sup>, Ra<sup>2+</sup> and Sr<sup>2+</sup> will be higher in the presence of fresh groundwater in comparison with saline groundwater. This is frequently observed in batch experiments where only small amounts of bentonite are present. As shown by the data in Table 2-3, however, high concentrations of major ions in porewater of compacted bentonite will be derived from impurities of the bentonite itself.

Data are valid at pH values above ≈5 and under all redox conditions. Only a very narrow range of validity can be expected with regard to the concentration of major cations in solution.

### **Niobium (Nb)**

Nb will not be influenced by Eh, it exists only as Nb(V) in aqueous solution. Data on the aqueous chemistry of this element are very sparse, but according to Baes and Mesmer (1986), Nb will exist to about equal proportions as Nb(OH)<sub>5</sub><sup>0</sup> and Nb(OH)<sub>6</sub><sup>-</sup> (or NbO<sub>3</sub><sup>-</sup>) at pH ≈7.5. With increasing pH, the relative concentration of the anionic species will increase. Also, other dissolved constituents of the porewater will not be important for Nb in all likelihood.

Data are expected to be valid under all relevant redox conditions, but the speciation of Nb (i. e., its distribution between the dissolved neutral and negatively charged, and surface-bound species) will be sensitive to pH in the pH range considered here (section 2). Not enough information exists with regard to the influence of dissolved ligands.

### **Nickel (Ni)**

Eh has no influence on Ni, it exists only as Ni(II) in aqueous solution. The porewater pH is expected to have a large effect on the behaviour of Ni. Bradbury and Baeyens (1995) could show that above pH ≈7, Ni sorbs predominantly by surface complexation on bentonite, whereas at lower pH values, ion exchange becomes more important. According to the study of Bradbury and Baeyens (1995), sorption will be maximum at pH ≈8-10 and will decrease at higher pH values due to the increased formation of hydroxo complexes. Ni is also expected to form stable carbonato complexes (Berner, 1995), and high concentrations of dissolved carbonate may reduce Ni sorption significantly.

Data are valid under all redox conditions, but the range of validity is only small with regard to changes in pH. Stability constants for the formation of

complexes of Ni with other dissolved ligands are not well known, and no range of validity can be indicated in this respect.

### **Neptunium (Np), protactinium (Pa), plutonium (Pu), uranium (U)**

All of these actinide elements may exist in aqueous solution in different oxidation states. They also undergo hydrolysis, which has also a critical influence on their actual redox state. Thus, both pH and Eh will have a strong effect on the sorption and diffusion of these elements.

Pa and Np may exist in aqueous solution in the +IV and +V oxidation state. Both the redox chemistry and hydrolysis of Pa are not well known. Under the present conditions, it may exist exclusively as Pa(V). The chemistry of Np is known better, it exists probably as Np(IV) under the present conditions.

For U the oxidation states +IV and +VI are most important. Pu can take on oxidation states between +III and +VI in solution; some of these may coexist, depending on the pH.

For these elements, no generic range of validity is indicated.

### **Lead (Pb)**

Eh has no influence on Pb, it exists only as Pb(II) in aqueous solution. For the present application, it may be compared with Ni, as a first approximation. Pb sorbs through surface complexation on clays at neutral to slightly alkaline pH, and through ion exchange at lower pH (Lothenbach et al., 1997). Both hydrolysis as well as the formation of carbonato complexes will influence the sorption of Pb.

Data are valid under all redox conditions, but the range of validity is only narrow with regard to changes in pH and the concentrations of dissolved ligands.

### **Palladium (Pd)**

Under the present conditions, dissolved Pd exists primarily as uncharged Pd(OH)<sub>2</sub> species, although chloride complexes could be of minor importance under the present conditions. Since it hydrolyses more easily than Ni or Pb, it probably also sorbs more strongly through surface complexation.

### **Radon (Rn)**

Rn is a noble gas, it will not be influenced by chemical conditions. An increase in temperature is expected to increase its mobility.

### **Selenium (Se)**

In aqueous solution, Se can exist in the -II, +IV and +VI oxidation state, depending on redox conditions (Baes and Mesmer, 1986). Under the present Eh-pH conditions (section 2), Se exists most likely as Se(-II) or possibly as Se(IV). In the pH range considered here, Se(-II) exists probably as  $\text{HSe}^-$ , while Se(IV) can exist predominantly as  $\text{SeO}_3^{2-}$  or  $\text{HSeO}_3^-$  ion, depending on the pH (Baes and Mesmer, 1986). Thus, pH also influences the relevant redox equilibria.

Considering the uncertainties associated with the chemistry of Se, no generic range of validity is indicated.

### **Tin (Sn)**

Under the present conditions (section 2), dissolved Sn is expected to exist only as Sn(IV) (Brookins, 1988). The aqueous chemistry of Sn(IV) is not well known, but in the pH-range considered here, the only important species is probably the neutral  $\text{Sn(OH)}_4$  species (Amaya et al., 1997). Thus, the solution speciation of Sn is probably not influenced by Eh, pH and other solution conditions. Its sorption behaviour may be dependent on pH, however, due to the pH-dependent speciation of the edge surface of bentonite.

Due to the very limited sorption, diffusion and thermodynamic data available, no range of data validity can be given.

### **Technetium (Tc)**

The behaviour of Tc will be influenced very strongly both by Eh and pH. Under oxidising conditions, Tc(VII) exists as  $\text{TcO}_4^-$  ion and does not undergo notable sorption; its speciation is not influenced by pH. Tc(IV), prevailing under reducing conditions, hydrolyses and sorbs, presumably by surface complexation, onto clays.

Since the distribution between Tc(VII) and Tc(IV) is very sensitive with respect to Eh-pH conditions, no general range of validity can be indicated.



### **Thorium (Th)**

Th will not be influenced by Eh, it exists only as Th(IV) in aqueous solution. It hydrolyses strongly, but above pH  $\approx 5$ , it exists only as  $\text{Th}(\text{OH})_4^0$  species (Baes and Mesmer, 1986). However, at elevated concentrations of dissolved carbonate, comparable to the values in Table 2-3, Th-carbonate complexes become important (Östhols et al., 1994; Rai et al., 1995). Thus, both the sorption and diffusion of Th are independent of pH only in the presence of low carbonate concentrations. The study of LaFlamme and Murray (1987) indicates that high concentrations of dissolved carbonate may significantly reduce the sorption of Th at pH  $\approx 8-10$ .

Data are valid for all redox conditions, but in the presence of the dissolved carbonate concentrations considered here, no range of validity can be given with respect to pH.

### **Zirconium (Zr)**

Zr will not be influenced by Eh, it exists only as Zr(IV) in aqueous solution. Very little is known, however, about the aqueous chemistry of Zr under relevant conditions. Above pH  $\approx 6-7$ , Zr exists only as  $\text{Zr}(\text{OH})_5^-$  species (Baes and Mesmer, 1986). It is not known, however, whether Zr forms any important complexes with other relevant ligands.

Data are valid for all redox conditions, but with regard to the existing uncertainty of the aqueous chemistry of Zr under relevant conditions, no generic range of validity will be given.

## **6 CHARACTERISATION OF UNCERTAINTIES**

In the following sections, subjective uncertainties, as well as measurement uncertainties and dependencies on the methods used are discussed for the sorption and diffusion data selected by Yu and Neretnieks (1997). Most critical, in my opinion, are the subjective uncertainties associated with the selection process leading to the dataset given in Table 18 of their report. Therefore, the data proposed by Yu and Neretnieks (1997) are discussed in an element-by-element fashion in section 6.4: data selection. This discussion includes subjective, as well as other uncertainties.

## 6.1 MEASUREMENT UNCERTAINTIES

Measurement uncertainties can be evaluated based on the compiled data in cases where a large database of sorption and diffusion data is available. Very helpful in this respect is a check of consistency of sorption and diffusion data, as illustrated in Figure 9 in the report of Yu and Neretnieks (1997). This check is reviewed in this report for each element.

Measurement uncertainties relevant for diffusion experiments are discussed in the report of Yu and Neretnieks (1997). Uncertainties related to batch  $K_d$  measurements can be related to a number of experimental parameters and are difficult to evaluate for a single experiment, even if properly documented. In my opinion, the best methods to evaluate measurement uncertainties are:

- a comparison with a number of experimental data from similar systems,
- a comparison of sorption and diffusion data, and
- a check of experimental  $K_d$  values by an established sorption model, where possible.

## 6.2 DEPENDENCE ON METHOD USED

$D_a$  values in bentonite are measured at relatively high dry densities. Therefore, most of the experimental conditions are similar to the expected conditions in the bentonite backfill, where the data are applied. Problems inherent to specific experimental approaches are discussed in the report of Yu and Neretnieks (1997). In general, redox conditions are more difficult to control in long-term diffusion experiments than in batch experiments, and data for reduced species must be carefully evaluated.

The direct measurement of  $K_d$  values is carried out in batch experiments, typically at very low bentonite/water ratios. Thus, the application of such data to compacted bentonite necessarily involves an extrapolation to different conditions. As shown by the calculations presented in Table 2-3 and discussed in section 5.2.1, the porewater in compacted bentonite is to a large degree controlled through the bentonite itself. Soluble impurities contained in bentonite will lead to relatively high concentrations of dissolved salts. Thus, the direct application of data from a batch system corresponding to 'fresh' water to the intact bentonite is not valid.

## 6.3 DEPENDENCE ON THE REFERENCE SYSTEM

There are no spatial variabilities, but variabilities with regard to the porewater composition in compacted bentonite are critical and need to be taken into account, as discussed in sections 2.2 and 5.2.1. Also, the redox conditions

expected in the near field should be defined as good as possible. It is advisable to make efforts to separate these uncertainties from uncertainties related to the chemistry of an individual element. For example, uncertainties on the redox chemistry of a given element may not be very important below a certain Eh, given that the pH is higher than e. g. 7.5. If the pH-Eh range expected for the repository is not well known, on the other hand, it may be impossible to assume that the uncertainties of the redox chemistry of the above element can be neglected.

## 6.4 DATA SELECTION

As already pointed out before, a critical evaluation of the data proposed by Yu and Neretnieks (1997) is made difficult by the fact that no well defined reference system has been established as a basis for data selection. In particular, no information is given regarding the expected porewater composition. In view of the strong influence of solution conditions on the behaviour of most elements considered here (sections 5.2 and 5.2.5), it is difficult to select data for a poorly characterised system.

$K_d$  and  $D_a$  values depend on a very large number of parameters, and extrapolation to different conditions is often questionable if the underlying reference system and sorption and diffusion mechanisms are not known.

It is very unfortunate that only few experimental details are given in the tables containing the data compiled by Yu and Neretnieks (1997). While these tables provide a very good overview of the available data, the information provided is not enough to enable the reader to evaluate these data without consultation of the original references.

Once the decision is made to use 'realistic' and 'conservative' values to address uncertainties of selected data, it should be done in view of

- a given element's chemistry, and the respective dependencies on pH, Eh and other solution parameters,
- the amount and quality of available information ( $K_d$  and  $D_a$  values, thermodynamic data, models),
- uncertainties regarding the reference conditions.

Thus, an approach where conservatism is defined in a rigid manner for most elements (increase of  $D_e$  by a factor of 10) is not very helpful, in my view. Especially, since a conservative estimate for  $K_d$  is needed in order to calculate a conservative  $D_a$  value. As shown in section 2, the conditions in the porewater of compacted bentonite are relatively constant in comparison with the variations found in typical batch systems that employ a wide variety of solutions. Thus,  $D_a$  values are probably more reliable and a better

representation of reality, and should be used instead of  $K_d$  values to define 'realistic-conservative' boundaries.

Note that  $K_d$  values cannot be evaluated independently of the diffusion model used. If the traditional diffusion model defined by equation (1) is used, a relatively small  $K_d$  value needs to be selected, see e. g. Cs. It is known that there are discrepancies between sorption and diffusion experiments.

If higher  $K_d$  values would be selected for Cs, e. g. the values calculated with the model of Wanner et al. (1996) given in Table 6-4, an improved diffusion model needs to be used. Yu and Neretnieks propose the surface diffusion approach, where sorbed ions are expected to be mobile, and a surface diffusivity is evaluated for each element. The surface diffusion coefficient is multiplied with the respective  $K_d$  value, implying that (surface) diffusion increases with increasing sorption. On the other hand, the approach based on diffuse double layer theory developed by Kato et al. (1995) and Sato et al. (1995) may be used. In this model, no additional diffusion process needs to be invoked. Further, it is not necessary to consider sorbed ions as mobile, and the diffusion of Cs in compacted bentonite can be modelled by a integrated sorption-diffusion model (Ochs et al. 1997).

Obviously, there is a discrepancy between measured apparent diffusivity ( $D_a$ ) values and values predicted by 'traditional' diffusion theory. It is not correct, however, to state that there is experimental evidence for surface diffusion. There is only experimental evidence for the aforementioned discrepancy, but not for any particular process. At this state, it is not appropriate to include a surface diffusion coefficient in an adaptation (for compacted bentonite) of Fick's second law, without a detailed discussion of experimental evidence.

For the present review, use of the traditional diffusion model is assumed.

#### 6.4.1 Americium (Am)

Yu and Neretnieks (1997) state that Am is expected to exist mainly in the form of hydroxo- and carbonate complexes. To evaluate the speciation of Am in pore- and groundwater, the thermodynamic data for Am of the NEA-TDB (Silva et al., 1995) may be used. Such calculations show that complexes with sulphate are probably more important for Am under the conditions considered here (Table 2-3).

In terms of the literature surveyed by Yu and Neretnieks (1997), there are some relevant studies that could have been added to the current selection. Shibutani et al. (1994) report  $K_d$  values for Am on sodium bentonite, Stammose and Dolo (1990) report on the sorption of Am at trace levels on

clay minerals. Sato et al. (1993) determined apparent diffusivities in bentonite.

The speciation behaviour, as well as sorption data obtained for different pH values (e. g. data by Shibutani et al., 1994, and Stammose and Dolo, 1990) show that the sorption of Am is very sensitive with respect to pH. I. e., small variations in the porewater pH can cause a large change of  $K_d$  values. For example, Stammose and Dolo (1990) report  $K_d$  values of about 5 m<sup>3</sup>/kg at pH 6, and 39 m<sup>3</sup>/kg at pH 7.1.

Thus, the realistic and conservative  $K_d$  values selected should reflect possible variations in pH (as well as other uncertainties). In my opinion, the values 3 and 1 m<sup>3</sup>/kg selected by Yu and Neretnieks (1996) are much too close together to reflect any uncertainties (basically, these two values may be regarded as one).

The  $D_a$  value selected seems to be reasonable, and a  $K_d$  value of 3 m<sup>3</sup>/kg is compatible with the  $D_a$  (see  $D_e$  in Table 18 of Yu and Neretnieks). It is not expected that the  $K_d$  value will be <3 m<sup>3</sup>/kg under the present conditions.

#### 6.4.2 Carbon (C)

Based on the present information, it is not possible to select a  $K_d$  value different from zero. The selected  $D_a$  value is based on the findings of Oscarson and Hume (1994), which appear to be valid for the diffusion of carbonate species. This value is not valid for reducing conditions where methane may be formed. As pointed out in section 5.2.5, carbonate will exist as anionic species, for whom anion exclusion is important, but methane is always uncharged and displays a higher diffusivity (Neretnieks and Skagius, 1978). Thus, a  $D_a$  value for methane also needs to be given, based on e. g. the study of Neretnieks and Skagius (1978).

#### 6.4.3 Cerium (Ce)

Since very little data for Ce are reported, I suggest to use the data recommended for Am, since these elements are expected to behave very similarly. The data selected for Ce are more conservative, presumably due to the lack of data. It would be helpful to state this explicitly. Otherwise, it is not clear to the reader whether the data for Ce conservative, or whether the data selected for Am are somewhat optimistic. The selected  $D_a$  and  $K_d$  values are consistent.

#### 6.4.4 Chlorine (Cl)

$D_a$  values for  $\text{Cl}^-$  are not expected to depend on pH, Eh and other solution conditions to any significant degree. The value of  $2\text{E-}11 \text{ m}^2/\text{s}$  seems to be reasonable. A conservative value could be proposed for elevated temperatures.

#### 6.4.5 Caesium (Cs)

Yu and Neretnieks (1997) selected two sets of recommended sorption data, distinguishing between 'fresh' and 'saline' systems. However, the model calculations on bentonite-groundwater interactions carried out for the present review show that the composition of the porewater in compacted bentonite will be similar for both fresh and saline waters. Since Äspö groundwater already contains a high concentration of cations,  $K_d$  values do not differ much as a function of the bentonite/water ratio. On the other hand, Finnsjön groundwater is relatively dilute, and an increase of the bentonite/water ratio leads to an increase of the concentration of cations, due to the dissolution of impurities in the bentonite. This decreases the sorption of Cs (Table 6-4), as discussed in section 5.2.5. Batch  $K_d$  values obtained in dilute, low-ionic strength solutions in the presence of small amounts of bentonite are not relevant for compacted bentonite.

**Table 6-4.  $K_d$  values, pH and I calculated for different solid/water ratios of MX-80 bentonite in contact with fresh and saline groundwater. Model and bentonite parameters are given in Table 2-1 and Table 2-2.**

bentonite/water ratio	$K_d$ ( $\text{m}^3/\text{kg}$ )	pH	I (M)
<i>Äspö groundwater</i>			
2000 $\text{kg}/\text{m}^3$	0.096	6.8	0.33
2 $\text{g}/\text{L}$	0.076	7.4	0.23
<i>Finnsjön groundwater</i>			
2000 $\text{kg}/\text{m}^3$	0.15	6.8	0.26
2 $\text{g}/\text{L}$	0.32	7.1	0.024

Contrasting with the approach taken for the selection of sorption data, only one  $D_a$  value is selected for both fresh and saline waters. This approach is internally inconsistent and should be completely avoided (see also sections on Ra, Sr). It also leads to unnecessary, and probably wrong, interpretations. Figure 9 in the report of Yu and Neretnieks (1997) shows that the 'saline' and the selected  $D_a$  value are reasonably consistent, whereas surface diffusion is

invoked to explain the  $D_e$  obtained for the 'fresh'  $K_d$  value. However, the calculations presented above show that this apparent effect is an artefact created by the comparison of sorption data corresponding to a dilute solution with diffusion data corresponding to a porewater with high concentrations of other cations.

Such inconsistencies could be avoided by investigating the sensitivities of the system under consideration through modelling exercises. In particular for Cs, the model developed and tested by Wanner et al. (1996) could be used.

Both the 'realistic' and 'conservative'  $K_d$  value proposed for the fresh system by Yu and Neretnieks (1997) are too high, and are not relevant for compacted bentonite. The 'realistic' value proposed for the saline system is expected to be valid under the present conditions, and is consistent with the proposed  $D_a$  value.

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

$D_a$  values for I<sup>-</sup> are not expected to depend on pH, Eh and other solution conditions to any significant degree. The value of 2E-11 m<sup>2</sup>/s seems to be reasonable. A conservative value could be proposed for elevated temperatures.

#### **6.4.7 Lead (Pb)**

There are a number of studies missing that report sorption data for Pb on different montmorillonites: e. g. Schulthess and Huang (1990), Lothenbach et al. (1997), and others. The realistic  $K_d$  value selected by Yu and Neretnieks (1997) may not hold under all conditions considered here. The expected pH in the porewater is critical in this respect. Below pH ≈7, ion exchange starts to become the dominant adsorption mechanism, and competition by major cations for exchange sites may lower the  $K_d$  value of Pb (Ochs et al., 1997). The selected  $D_a$  value is reasonable for a  $K_d$  value ≤0.5 m<sup>3</sup>/kg.

#### **6.4.8 Neptunium (Np)**

The data selected by Yu and Neretnieks (1997) for Np cover uncertainties related to the expected redox state of this element. The  $D_a$  value selected for reducing conditions is appropriately higher than the  $D_a$  value selected for thorium. To be consistent, a somewhat lower  $K_d$  value should be selected for Np(IV) than for Th, as long as the reason for the higher diffusivity of Np(IV) is not known with certainty.

#### 6.4.9 Nickel (Ni)

Bradbury and Baeyens (1995) also presented a very large amount of systematic sorption measurements for Ni on montmorillonite that should have been considered by Yu and Neretnieks (1997). These data could corroborate the value selected by Yu and Neretnieks (1997). Under the present conditions, it is not expected that the  $K_d$  value decreases below the range indicated. The sorption data are compatible with the selected  $D_a$  value.

#### 6.4.10 Niobium (Nb)

There are indeed very few data published on the sorption of Nb onto clays. Accordingly, a conservative  $K_d$  value of 0 has been selected by Yu and Neretnieks (1997). As indicated by Figure 9 in their report, the recommended data seem reasonable. Data for London Clay, a sediment rich in smectites, have been published by e. g. Berry et al. (1988) and could be used for support.

#### 6.4.11 Palladium (Pd)

According to its tendency to hydrolyse, Pd(II) sorbs probably strongly on bentonite. The values selected by Yu and Neretnieks (1997) are probably conservative. However, in view of the lack of data, this is reasonable. It would probably worthwhile to investigate the behaviour of Pd, in order to verify the expected stronger sorption.

#### 6.4.12 Plutonium (Pu)

Only one  $K_d$  value is listed for Pu, but several studies on the sorption of Pu on e. g. Na-bentonite (Shade et al., 1984) and others have not been considered by Yu and Neretnieks (1997).

More importantly, it is not possible to select only one  $K_d$  and  $D_a$  value for the redox sensitive element Pu if data for reducing and oxidising conditions are considered separately for other such elements. In order to account for uncertainties regarding the expected redox conditions, the conservative  $K_d$  value should be about as low as the conservative value for U and Np (i. e.,  $\approx 0.005$ - $0.01$  m<sup>3</sup>/kg, depending on the expected uncertainties regarding pH and solution composition). Accordingly, the  $D_a$  value should be higher. This is also warranted considering some of the high  $D_a$  values compiled by Yu and Neretnieks (1997).



#### 6.4.13 Protactinium (Pa)

It is not warranted to select different data for 'fresh' and 'saline' systems. As already discussed in the section on Cs, the porewater in the compacted bentonite will be similar, independently of the input groundwater (at least for the groundwaters considered here).

On the other hand, the large uncertainty regarding the redox and hydrolysis behaviour of Pa need to be taken into account. It cannot be excluded that Pa exists as Pa(V) under the present conditions. This possibility should be covered with a  $K_d$  value of 0.001 m<sup>3</sup>/kg and a corresponding  $D_a$ .

#### 6.4.14 Radium (Ra) and strontium (Sr)

As pointed out correctly by Yu and Neretnieks (1997), Ra and Sr can be expected to behave very similar and are thus treated together here.

Regarding the data selection for these two elements, similar criticism applies as in the case of Cs. It is not warranted to select drastically different  $K_d$  values for compacted bentonite, since the dissolution of impurities will lead to a relatively high concentration of major cations even in the presence of dilute groundwater.

Thus, the  $K_d$  values selected for the 'fresh' system are not relevant and should be deleted. The  $K_d$  values for the saline system are compatible with the diffusion data and are expected to cover the range of uncertainties regarding the porewater composition.

#### 6.4.15 Radon (Rn)

In comparison with the measurements reported for methane by Neretnieks and Skagius (1978), the data selected for Rn seem to be reasonable.

#### 6.4.16 Samarium (Sm)

In the absence of experimental data, it is perfectly reasonable to rely on the analogy with cerium (see comments there). In addition, there are some sorption data available in the literature, e. g. by Baston and co-workers.

#### 6.4.17 Selenium (Se)

The selected data seem reasonable. It is appropriate to consider  $K_d = 0$  in view of the uncertainties regarding the chemistry of Se.

#### 6.4.18 Technetium (Tc)

The data compilation for Tc given by Yu and Neretnieks (1997) is extensive, and it is pointed out correctly that under reducing conditions, Tc is present as Tc(IV) which shows cationic behaviour, whereas under oxidising conditions, Tc(VII) is present as pertechnetate anion. It is further pointed out correctly by Yu and Neretnieks (1997) that the pertechnetate anion cannot be expected to sorb, and that diffusion coefficients for Tc may be one to two orders of magnitude higher in oxidising environments than in reducing environments.

Yet, the same  $D_a$  value is proposed for both oxidising and reducing conditions. This choice is not consistent with the chemistry of Tc, and not understandable considering the above (correct) discussion by Yu and Neretnieks (1997), and the fact that they propose different  $K_d$  values for oxidising and reducing conditions.

Yu and Neretnieks (1997) discuss some evidence that Tc(VII) may be (partly) reduced to Tc(IV) in the course of a diffusion experiment in compacted bentonite, which may have prompted them to make the aforementioned inconsistent recommendation. It is known that it is not always trivial to conduct experiments with Tc in a single oxidation state, but such experimental difficulties must not lead to the selection of the same data for Tc(VII) and Tc(IV).

Again, it is not a consistent approach to select different  $K_d$  values for oxidising and reducing conditions but only one  $D_a$  value for both conditions. While the data recommended by Yu and Neretnieks (1997) for reducing conditions seem to be reasonable, according to Figure 9 of their report, the proposed data for oxidising and reducing conditions are not consistent.

#### 6.4.19 Thorium (Th)

The recommended data seem to be reasonable and are expected to cover the uncertainties regarding the porewater composition. The realistic  $K_d$  value is compatible with the selected  $D_a$  value.

#### 6.4.20 Tin (Sn)

While both Sn and Th form tetrahydroxo complexes at neutral pH, Sn hydrolyses to higher-order hydroxo complexes with increasing pH, in contrast to Th. The aqueous chemistry of Sn(IV) is not very well known, however, and this uncertainty is reflected in the choice of the 'conservative'  $K_d$  value.

#### 6.4.21 Uranium (U)

Yu and Neretnieks (1997) give a fairly extensive data compilation for U, and the presentation of the data table could be greatly improved by listing data for U(VI) and U(IV) separately, whenever possible. Where studies do not allow this, it should be indicated. This would also provide the reader with a quick overview regarding the quality of the different literature sources.

Yu and Neretnieks (1997) propose two complete sets of data for reducing and oxidising conditions, resulting in reasonable  $D_e$  values. The  $K_d$  values for oxidising conditions are probably conservative.

#### 6.4.22 Zirconium (Zr)

Considering the lack of sorption data available, the value given for the quartz/bentonite mixture (1 m<sup>3</sup>/kg) should be selected as realistic value. This would also be compatible with the few diffusion data available. Until more diffusion data become available, the conservative  $K_d$  value should also be lowered to 0.05 m<sup>3</sup>/kg to account for the uncertainties regarding the aqueous chemistry of Zr.

## 7 FURTHER COMMENTS

### 7.1 QUANTIFICATION OF UNCERTAINTIES, TREATMENT IN SAFETY ASSESSMENT

It will probably be very difficult to quantify uncertainties, because many uncertainties are not statistical in nature but are due to a lack of data. The conditions in compacted bentonite cannot be measured directly, but have to be estimated or evaluated based on models. For a number of critical elements there is serious lack of basic data regarding their behaviour in aqueous solutions (redox potentials, hydrolysis constants).

A common method for dealing with such uncertainties is the use of 'realistic' and 'conservative' values. It is, however, difficult to define 'conservative' in a meaningful and consistent way. In general, 'conservative' values for an

element whose chemistry is not well known, and/or for which only few sorption and diffusion experiments have been carried out will be more pessimistic than values selected for well-known elements.

Stochastic analyses are probably not very meaningful, because many uncertainties are not statistical in nature, as pointed out above.

Representation of uncertainties as intervals would be possible, with intervals covering the range 'realistic' to 'worst-case'. The worst-case value could be used to check whether the safety relevance (defined by e. g. the resulting dose rate) would be affected. If so, more data should be acquired to reduce the spread of the respective interval. Thermodynamic speciation and sorption models could be helpful in defining the limits of such intervals by conducting systematic sensitivity analyses. A very brief example is given in the present report (Table 6-4), where the influence of different groundwater compositions on the sorption of Cs is evaluated. Similar modelling exercises may be conducted for other elements (Ochs et al., 1997).

## 7.2 CORRELATIONS

The sorption and diffusion behaviour of many critical elements is correlated through dependencies on e. g. pH and Eh (see section 5.2). The degree to which each element is influenced by such variables differs from element to element, which does not allow to quantify the respective correlations.

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