Migration parameters for a backfill of Friedland clay in the KBS-3 concept

SR-Can – data and uncertainty assessment

Michael Ochs, BMG Engineering Ltd

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SKB

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Summary

SKB is currently preparing license applications related to the deep repository for spent nuclear fuel and an encapsulation plant. The present report is one of several specific data reports feeding into the interim reporting for the latter application; it is concerned with the derivation and recommendation of radionuclide migration input parameters to PA models for a backfill consisting of pre-compacted Friedland Clay. Recommended values for the following parameters as well as the associated uncertainties are derived and documented for all relevant elements and oxidation states:

*   diffusion-available porosity (ε),

*   effective diffusivity (D_e),

*   distribution coefficient (K_d).

In general, the derivation of data and associated uncertainties was based on the results of a very similar data derivation project completed recently for sorption by MX-80 (SKB TR-04-18 /Ochs and Talerico 2004/). Because of the conditional nature of K_d, this parameter was derived specifically for the conditions expected to be relevant for PA consequence calculations. Where possible, K_d values were evaluated for the specific porewater composition and solid/water ratio representative for Friedland Clay compacted to a dry density of 1,780 kg/m^3. Where experimental data or sorption models of sufficient quality were not available, the reference K_d selected in TR-04-18 was scaled to the sorption capacity of Friedland Clay. Values proposed for D_e and ε are based on the relations given in TR-04-18, which allow to calculate these parameters as a function of density. Associated uncertainties were quantified for a given set of PA conditions and were further estimated as a function of variability in these conditions.

Sammanfattning

SKB färdigställer för närvarande ansökningshandlingar för ett slutförvar för använt kärnbränsle samt en inkapslingsanläggning. Den här rapporten är en av ett antal med specifika data som går in till analysen som ligger till grund för ansökan. Den diskuterar framtagning och rekommendationer av radionuklidtransportparametrar för en återfyllnad som består av block av högkompakterad Friedland lera. Rekommenderade värden för följande parametrar tillsammans med tillhörande osäkerheter har tagits fram och dokumenterats för alla relevanta element och oxidationsförhållanden:

- Porositet tillgänglig för diffusion (ε).

- Effektiv diffusivitet (D_e).

- Fördelningskoefficient (K_d).

In princip, har data och osäkerheter tagits fram baserat på ett liknande projekt som genomfördes nyligen för sorption i MX-80 (SKB TR-04-18 /Ochs and Talerico 2004/). Eftersom K_d är beroende på rådande förhållanden, har värden tagits fram för de förutsättningar som är relevanta för analysen. Om möjligt, så har Kd värden utvärderats för specifika porvattenkemier och fast fas/vätska förhållanden som är representative för Friedland lera kompakterad till en torrdensitet av 1 780 kg/m^3. I de fall där experimentella data eller sorptionsmodeller med tillräcklig kvalitet saknas har de referensvärden som valts i TR-04-18 skalats om till sorptionskapaciteten för Friedland lera. De förslagna värdena för D_e och ε är baserade på de relationer som finns angivna i TR-04-18, vilka gör det möjligt att beräkna dessa parametrar som en funktion av densitet. De associerade osäkerheterna kar kvalificerats för en given uppsättning av förhållanden och har ytterligare uppskattats för variabiliteten is dessa förhållanden.

Contents

1   Overview and general remarks

This report summarises the migration parameters and associated uncertainties derived for a backfill of pre-compacted Friedland Clay (see Appendix A) corresponding to the KBS-3 concept. The derived migration parameters are:

- effective diffusivity (D_e),

- diffusion-available porosity (ε),

- distribution coefficient (K_d).

These parameters as well as the associated uncertainties were derived for 26 radionuclides. In case of redox-sensitive elements, each relevant oxidation state was evaluated separately. Data and uncertainty estimates are given in section 2, a general discussion regarding the validity range of the derived data in terms of bentonite properties and density, as well as in terms of geochemical conditions is given in section 3.

For the present selection of radionuclide migration parameters for a backfill of Friedland Clay, significant efforts were made to select the scientifically best and most defendable values, and to clearly define the associated uncertainties. To this end, different contributions to the overall uncertainties were quantified separately. Relevant uncertainties can stem from

- uncertainties in the source data (experimental error),

- uncertainties in applying the source data to the expected in-situ conditions for PA (errors introduced in the parameter transfer),

- difficulties in defining the expected in-situ conditions for PA (parameter uncertainty due to uncertainties in the underlying conditions).

It follows directly form this list that the critical points for minimising uncertainties in selected radionuclide migration parameters are

- to obtain the best possible description of the solution chemistry under the in-situ conditions of interest; and

- to be able to rely on data sources that allow to closely match these solution conditions (well-matched experimental data or reliable thermodynamic sorption models).

The goal of the present data evaluation was the selection of parameters applicable to the conditions in compacted Friedland Clay. While diffusion parameters may be derived directly for compacted conditions, K_d values from batch experiments need to be converted to compact conditions. This was done by fully taking into account the dependency of K_d on the calculated, expected in-situ porewater composition of the compacted clay.

The distribution of uncertainties among the relevant sources also allowed to document all data derivation procedures with a high degree of transparency and traceability. This is obviously important to increase confidence, but will also facilitate any subsequent updates or changes (due e.g. to modifications in the expected groundwater composition, etc.).

2   Data derivation and uncertainty estimates

The methods and underlying scientific arguments for deriving porosity (ε), effective diffusivity (D_e) and distribution coefficients (K_d) for the relevant radionuclides are based on and consistent with the approaches described in detail in SKB TR-04-18 /Ochs and Talerico 2004/, which is concerned with data for compacted MX-80 bentonite. The respective descriptions are not repeated here. Case-specific issues are briefly discussed, in particular the reasons behind K_d data selection and derivation for individual radionuclides. For all cases where K_d values and uncertainties were derived specifically for Friedland Clay compacted to 1,780 kg/m^3 and equilibrated with reference groundwater, detailed data derivation tables are given in Appendix C.

2.1   Porosity

Physical porosity is calculated using the following simple relationship:

$$\varepsilon = 1 - (\rho/\rho_s) \tag{2.1}$$

where ρ is the dry density and ρ_s the specific density of bentonite. For ρ and ρ_s, values of 1,780 kg/m^3 and 2,780 kg/m^3 were used, respectively.

For a dry density of 1,780 kg/m^3, a diffusion-available porosity of 0.36 is proposed for all elements, except for anions. The proposed value is equal to the physical porosity.

See section 2.2.2 for the diffusion-available porosity of anions.

2.2   Effective diffusivity

No diffusion data at all are available for Friedland Clay. Therefore, derivation of D_e for all radionuclides is based on the experimental data and model results for various clays shown in Figure 5-4 of TR-04-18.

2.2.1   HTO, methane, radon

Based on an analysis of D_e values obtained for HTO in different bentonites, the following regression equation ($r^2 = 0.94$) is proposed in TR-04-18 to calculate D_e as a function of dry density:

$$D_e = 6.7785E{-}9 \times e^{-2.5671E{-}3 \times \rho} \tag{2.2}$$

Data for Kunigel-V1 and MX-80 agree closely with this relation. Kunigel-V1 has a content of expandable clay minerals of ca 45–50% and is in this respect similar to Friedland Clay. Therefore, equation (2.2) was also directly applied to Friedland Clay, together with the corresponding uncertainty scaled to a density of 1,780 kg/m^3:

For a dry density of 1,780 kg/m^3, a D_e of $7.0 \times 10^{-11} \pm 4.65 \times 10^{-11}$ m^2/s is recommended for HTO, methane and radon (25°C).

The uncertainty represents the statistical standard error for the estimation of D_e by equation (2.2) in comparison to the experimental data in Figure 5-4 of TR-04-18. To take into account a temperature increase from ambient conditions to max. 50°C, /Schwyn 2003/ doubles the selected value; i.e., in this case a value of 1.4×10^{-10} m^2/s would result.

A comparison with data for the Opalinus Clay formation shows that the above result is very reasonable: /NAGRA 2002/ gives a dry density of 2,310 kg/m^3 for the Opalinus Clay at the Mont Terri location. Using equation (2.2) gives a D_e for HTO of 1.8×10^{-11} m^2/s. This is in excellent agreement with the value of 1–2×10^{-11} m^2/s given in /NAGRA 2002/.

2.2.2 Anions

As explained in detail in TR-04-18, D_e and diffusion-available porosity have to be evaluated together in the case of non-sorbing anions. Based on the K_d values proposed in section 2.3, this includes chloride, iodide, pertechnetate, all oxidation states of Se, as well as simple organic acids. The carbonate species CO_3^{2-} and HCO_3^- are also included in this group.

Based on an analysis of D_e values obtained for non-sorbing anions (chloride, iodide and pertechnetate) in different bentonites, the following regression equation ($r^2 = 0.92$) is given in TR-04-18 to calculate D_e as a function of dry density[1]:

$$D_e = 5.30087E–10 \times e^{-2.561E–3 \times \rho} \tag{2.3}$$

As in the case of HTO, the good agreement between values calculated by eq. (2.3) and data as well as model calculations for Kunigel-V1 (see Figure 5-4 of TR-04-18) is taken to support the direct application of this relation to Friedland Clay. The uncertainties proposed in TR-04-18 for D_e of anions in MX-80 at a dry density of 1,590 kg/m^3 are considered to apply to Friedland Clay as well, after scaling to a density of 1,780 kg/m^3.

For a dry density of 1,780 kg/m^3, a D_e of 5.6×10^{-12} m^2/s is recommended for anions (25°C). As upper and lower limit, 1.7×10^{-11} m^2/s and 1.7×10^{-12} m^2/s are proposed, respectively. Using the relation $\varepsilon_{anion} = (1 - (\rho/\rho_s))/2.5$ (equation 5.9 in TR-04-18), the corresponding diffusion-available porosity is calculated as 0.14, with 0.20 as upper and 0.10 as lower limit.

2.2.3 Cs

Following the arguments given in TR-04-18, a D_e(Cs) of $3 \times D_e$(HTO) is chosen in combination with the physical porosity to account for effects of enhanced cationic diffusion. Uncertainties are defined as in TR-04-18.

2.3 K$_d$ values

2.3.1 General considerations

The general approach for deriving K_d values is identical to the approach documented in detail in TR-04-18. The respective descriptions and discussions are not repeated here. The considerations specific to the data derivation for Friedland Clay are briefly described below. Subsequently, a brief discussion is given on the K_d derivation for each radionuclide and oxidation state.

Data sources

The data derivation in TR-04-18 was done for MX-80 bentonite. In comparison to MX-80, Friedland Clay contains a lower proportion of expandable clays and has a significantly lower CEC. Where experimental data of sufficient quality were available for clay materials with a mineralogy similar to Friedland Clay, these were preferred over data for bentonites or pure montmorillonite. On the other hand, sorption data for illite were typically not given first priority,

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[1]   To reproduce the slight curvature of predictions by an electric double layer model /Ochs et al. 2001/ for chloride diffusion in MX-80, a polynomial function is also proposed. As no diffusion data are available in case of Friedland Clay for comparison, the simpler function is proposed here.

as Friedland Clay does not contain a significant fraction of this mineral (the mixed-layer mineral fraction consists of smectite and a non-expandable, muscovite-like mineral, rather than smectite/illite).

Conditions and uncertainties

The reference conditions considered for the present data derivation are very similar to the ones considered for and documented in TR-04-18. The same reference groundwater (saline Beberg water BFI01 /Laaksoharju et al. 1998/) was used (see also TR-04-18, Appendix A). The corresponding porewater composition representative for Friedland Clay at a density of 1,780 kg/m^3 was calculated using the bentonite model by /Wieland et al. 1994/, with dissolved carbonate corresponding to a pCO$_2$ of 10$^{-2.6}$ atm imposed by the host rock formation. The composition of the resulting reference porewater RPW-FC is very similar to the composition of the reference porewater (RPW) calculated for MX-80 (TR-04-18).

As in TR-04-18, data uncertainties are defined for three levels:

Level 1: Uncertainties in the selected source data.

Level 2: Uncertainties introduced by transferring the data from source conditions to the application conditions relevant for Friedland Clay in contact with a reference groundwater.

Level 3: Uncertainties introduced through variability in the reference conditions.

Uncertainties for levels 1 and 2 were defined through the same methodology that had been used for the data derivation in case of MX-80 (cf TR-04-18). The derivation of uncertainties for level 3 differed from the approach documented in TR-04-18:

- In TR-04-18, K$_d$ values as well as the corresponding level 1- and level 2-uncertainties were derived in case of each radionuclide for three sets of conditions to trace out the influence of variable conditions on the overall uncertainty in K$_d$.

- For the present data derivation, K$_d$ values and the corresponding level 1- and level 2-uncertainties were derived for only one set of reference conditions (Friedland Clay/RPW-FC). The influence of variable conditions on the overall uncertainty in K$_d$ was evaluated in analogy to the results given in TR-04-18 for each radionuclide. Note that this is only possible because the two systems are sufficiently similar.

- Following TR-04-18, as the most relevant variations in conditions were considered:
  – An increase in the salinity of the groundwater, similar as in the scenario MX-80/HSPW considered in TR-04-18.
  – No exchange of CO$_2$ between bentonite and host rock, thereby decreasing the importance of the carbonate buffer system and lowering porewater pH to about 6.6 (scenario MX-80/ RPWC considered in TR-04-18).

Uncertainties in the expected in-situ redox conditions are handled by deriving K$_d$ for each relevant oxidation state of every radionuclide, as in TR-04-18. If variable redox conditions need to be taken into account, the overall uncertainty in K$_d$ for a given redox-sensitive radionuclide encompasses the entire data range for all relevant oxidation states.

2.3.2 Derivation of data and uncertainties for individual radionuclides

Americium

The only available study where Am sorption on minerals relevant for Friedland Clay was investigated systematically as a function of conditions is the work of /Gorgeon 1994/ (see TR-04-18 for a more detailed discussion).

For the present derivation of K_d, the data measured by /Gorgeon 1994/ on smectite and illite were considered. A comparison of these datasets shows that the sorption of Am at pH 7.3 is nearly identical for both minerals as well as for 0.1 and 1 M $NaClO_4$. The data derivation for Friedland Clay is based on a K_d value of 63 L/g obtained by /Gorgeon 1994/ at pH 7.3–7.5. Conversion to application conditions is based on CF-total 3, because the experiments by /Gorgeon 1994/ had been carried out in the presence of carbonate. However, it was shown in TR-04-18 that the influence of speciation on conversion is small in comparison to the overall uncertainties.

Caesium

The K_d value given in section 4 is based on the thermodynamic sorption model by /Wanner et al. 1996/. The good agreement of K_d values calculated by this model with K_d values derived by the CF-UF approach and their consistency with independent diffusion data has been shown in TR-04-18. The selected K_d value may be slightly conservative, as it neglects potentially stronger sorption of Cs on high affinity sites (frayed edge sites, FES) of illite, which makes up 4% of Friedland Clay.

Carbon

Following the argumentation given in TR-04-18, a K_d value of zero is selected for methane as well as for simple organic acids. Removal of inorganic ^{14}C from solution will occur through isotope exchange rather than sorption; and no K_d value is selected for inorganic C, therefore.

Cerium, holmium and samarium

As in TR-04-18, K_d values for these elements were derived using Eu as analogue element. As most representative experimental dataset for the present conditions in terms of solution and sorbent composition, the isotherm data measured by /Lauber et al. 2000/ on samples of Opalinus Clay were selected.

The data derivation for Friedland Clay is based on a K_d value of 50.1 L/g obtained at pH 8.0 /Lauber et al. 2000/. Conversion to application conditions is based on CF-total 3, because the experiments by /Lauber et al. 2000/ had been carried out in the presence of similar levels of dissolved carbonate. To transfer this value to pH 7.3, CF-pH was obtained from sorption edge data of Eu on SWy-1 montmorillonite /Bradbury and Baeyens 2002/, which show pH dependent sorption up to pH 9. This is in contrast to data on illite /Wang et al. 1998, Poinssot et al. 1999/, which suggest more or less constant sorption of Eu above pH 7 (i.e., a CF-pH of ≈1). Because of the predominance of smectite in Friedland Clay, pH-dependent sorption was assumed.

This approach would lead to reference K_d values for trivalent lanthanides that are notably higher than the corresponding values for Am. This would not be expected based on findings for bentonites or pure clay minerals and on the chemistry of these elements in aqueous solutions. While the data by /Lauber et al. 2000/ are of high quality, the Opalinus Clay contains a significant amount of calcite and illite. It may be that the high calcite content contributed to the high sorption of Eu. On the other hand, sorption of Eu on illite seems to very similar to sorption on montmorillonite /Poinssot et al. 1999, Bradbury and Baeyens 2002/. Unfortunately, no data on Am sorption on Opalinus Clay are available for a direct comparison.

Therefore, two alternative approaches were used to investigate the influence of data derivation methods and original data sources on the end result:

- K_d was derived directly from the value given in TR-04-18 for MX-80/RPW, using only the difference in CEC between the two substrates as scaling factor. The original underlying data source is a sorption isotherm of Eu on MX-80 in artificial porewater at pH 7.6 /Bradbury and Baeyens 2003a/.

- K_d was calculated for the relevant conditions with the thermodynamic sorption model by /Bradbury and Baeyens 2002/.

The results of these approaches are very close to the selected value (see Appendix C). Based on the discussion given above for Eu sorption by Opalinus Clay, the value calculated with the thermodynamic model is recommended. It has been confirmed in TR-04-18 that model calculations and application of the CF-approach to data on pure montmorillonite (SWy-1) give nearly identical results.

Chlorine and iodine

It is assumed that these elements exist exclusively as chloride and iodide under the relevant conditions. As in TR-04-18, a K_d value of zero is proposed for both of these anions.

Curium

As in TR-04-18, the K_d value derived for Am is used directly, together with the respective uncertainties. No additional UF-analogue is introduced.

Lead

Because of the lack of more relevant source data than the ones used for TR-04-18, the K_d value for Pb is directly based on the value selected in TR-04-18. The only relevant scaling factor is CF-CEC = 0.29. Uncertainties are scaled accordingly. Because of the similarity of porewater composition and the nearly identical speciation of Pb (calculated with the data in /Yui et al. 1999/) in both solutions, no additional uncertainties are introduced.

Neptunium

Data are given separately for IV- and V-valent oxidation states:

Np(IV) No relevant and reliable data were found for Np(IV). The K_d value derived for Th is taken for Np(IV), based on analogy considerations. No CF-spec is applied, due to the inconsistency in the underlying thermodynamic databases (analogous situation as for Pu(IV), see the discussion in the respective section below).

Therefore, the K_d value derived for Th is applied directly to Np(IV). To take additional uncertainties due to analogue considerations into account, UF-starting K_d was increased by a factor of 2 (see TR-04-18 for explanations).

Np(V) In addition to the datasets for Np(V) sorption on SAz-1 montmorillonite by /Turner et al. 1998, Bertetti et al. 1998/ and on smectite extracted from Wyoming bentonite /Gorgeon 1994/, the following datasets are considered: /Stammose et al. 1992/ measured sorption of Np(V) on purified FoCa-7 clay, which consists of 7% kaolinite and a mixed-layer kaolinite/smectite component. /Yamaguchi et al. 1991/ measured Np(V) sorption on Kunibond, a Ca-bentonite based on Kunigel-V1, at different levels of dissolved carbonate. The data from both studies agree extremely well with the data by /Turner et al. 1998, Bertetti et al. 1998/, even though the scatter is significantly higher in the experiments by /Yamaguchi et al. 1991/. All the above studies show good evidence that the influence of carbonate below pH 8 and of moderate variations in clay mineralogy on the sorption of Np(V) is not very significant. Therefore, the data by /Turner et al. 1998, Bertetti et al. 1998/ are taken as basis for deriving K_d, using CF-total 3 to transfer the data to the conditions relevant for Friedland Clay (see TR-04-18).

Nickel

The K_d value given in section 4 (1.47 m^3/kg) is calculated with the thermodynamic sorption model by /Bradbury and Baeyens 1997/. The calculated K_d value agrees well with values scaled from Opalinus Clay as well as from purified SWy-1 reference montmorillonite. On the other hand, a much smaller K_d value would result if sorption data for MX-80 would be used as source data (Table 2-1). The surprisingly low sorption of Ni on MX-80 in comparison to SWy-1 (even after correcting for differences in speciation) has also been observed and discussed in TR-04-18. It is, therefore, consistent with these observations to recommend a higher K_d for Friedland clay (this report) than for MX-80 (TR-04-18) in the case of Ni.

Niobium

Due to the lack of reliable experimental data, the K_d value for Nb is directly based on the value selected in TR-04-18. The only relevant scaling factor is CF-CEC = 0.29. Uncertainties are scaled accordingly. Because of the similarity of porewater composition and the predominance of uncharged Nb(OH)$_5$(aq) under the relevant conditions, no additional uncertainties are introduced.

Palladium

No other sorption data than the studies already discussed in TR-04-18 were found. The K_d value for Pd is, therefore, directly based on the value selected in TR-04-18. The only relevant scaling factor is CF-CEC = 0.29. Uncertainties are scaled accordingly. Because of the similarity in conditions, no additional uncertainties are introduced.

Table 2-1. K_d values for Ni on different clays scaled to Friedland Clay by using CEC only (because of the similarity in pH, the effect of differences in Ni speciation is small in comparison to the effect of sorption site density).

Parameter	Source data	Application
	MX-80[a]	Friedland Clay
CEC (meq/100 g)	79	25
pH	7.25	7.32
K_d (L/g)	0.28	0.07
	SWy-1[b]	Friedland Clay
CEC (meq/100 g)	87	25
pH	7.3	7.32
K_d (L/g)	2.63	0.76
	Opalinus Clay[c]	Friedland Clay
CEC (meq/100 g)	12	25
pH	7.24	7.32
K_d (L/g)	0.93	1.94

[a] Reference sorption value for MX-80 /Bradbury and Baeyens 2003a/.

[b] Sorption edge data for Swy-1 montmorillonite /Bradbury and Baeyens 1997/.

[c] Reference sorption value for Opalinus Clay /Bradbury and Baeyens 2003b/.

Plutonium

K_d values are derived separately for each of the possible oxidation states:

Pu(III) For Pu(III), only one relevant set of sorption data was found. Sorption of Pu was measured by /Shibutani et al. 1998/ under reducing conditions on Kunigel-V1 bentonite (ca 45% smectite content, CEC = 60.1 meq/100g) as a function of pH. Their data are in very good agreement with the data for Am by /Gorgeon 1994/ up to pH 8. Unfortunately, the concentration of pCO$_2$/dissolved carbonate and other ligands that may dissolve from bentonite impurities is not specified in /Shibutani et al. 1998/.

   Therefore, a K_d for Pu(III) is derived based on the source data by /Gorgeon 1994/ for Am(III); the K_d value derived for Am is directly taken in this case, for the following reason: When differences in the calculated speciation of Pu(III) and Am in RPW-FC are accounted for (by applying CF-spec 3 in each case), a K_d of 3.9 is resulting for Pu(III). In comparison to experimental K_d values of ca 50 L/g measured by /Lauber et al. 2000/ on Opalinus clay (CEC = 12 meq/100g), this value seems to be too low. Further, correction for solution speciation is generally problematic (see TR-04-18 for a more detailed discussion).To take additional uncertainties due to analogue considerations into account, UF-starting K_d was increased by a factor of 3 (see TR-04-18 for explanations).

Pu(IV) No relevant and reliable data were found for Pu(IV). The K_d value derived for Th is taken for Pu(IV), based on analogy considerations. No CF-spec is applied, due to the inconsistency in the underlying thermodynamic databases. For Th, /Hummel et al. 2002/ selected a stability constant for a ternary Th-hydroxo-carbonato complex, which dominates speciation under the conditions relevant for the present application. On the other hand, no data for a ternary Pu(IV) complex is given in either /Hummel et al. 2002/ and /Guillaumont et al. 2003/. While /Hummel et al. 2002/ argue that experimental observations can be explained by considering Pu(IV)-hydroxides and –carbonates separately, /Guillaumont et al. 2003/ acknowledge the existence and importance of a ternary Pu(IV)-hydroxo-carbonato complex, but do not recommend any data because of the insufficient experimental basis.

   Therefore, the K_d value derived for Th is applied directly to Pu(IV). To take additional uncertainties due to analogue considerations into account, UF-starting K_d was increased by a factor of 2 (see TR-04-18 for explanations).

Pu(V) No relevant data were found. The selected K_d is taken directly as the value derived for Np(V). To take additional uncertainties due to analogue considerations into account, UF-starting K_d was increased by a factor of 2 (see TR-04-18 for explanations).

Pu(VI) No relevant data were found. The selected K_d is taken directly as the value derived for U(VI). To take additional uncertainties due to analogue considerations into account, UF-starting K_d was increased by a factor of 2 (see TR-04-18 for explanations).

Protactinium

No data in addition to the information already discussed in TR-04-18 were found. The K_d value for Pa is, therefore, directly based on the value selected in TR-04-18. The only relevant scaling factor is CF-CEC = 0.29. Uncertainties are scaled accordingly. Because of the similarity in conditions, no additional uncertainties are introduced.

Radium and strontium

The K_d value given for these elements in section 4 is calculated with the thermodynamic model /Wieland et al. 1994/ used for calculating Friedland Clay porewater chemistry. Following / Fletcher and Sposito 1989/ the same selectivity coefficient as for Ca^{2+} is used for Sr^{2+} and Ra^{2+}. The calculated value agrees within a factor of 2 with K_d values derived from measurements of Sr sorption on Opalinus Clay /Lauber et al. 2000/ (K_d for Friedland Clay: 0.0027 L/g, using only CEC as scaling factor).

Radon

Following TR-04-18, a K_d of zero in combination with diffusion parameters for HTO are proposed in analogy to methane.

Selenium

K_d values are derived separately for each relevant oxidation state.

Se(-II)   Se in this oxidation state exists largely as HSe^- in relevant aqueous solutions. As in TR-04-18, a K_d of zero in combination with diffusion parameters for anions are proposed.

Se(IV)   Tetravalent Se exists largely as SeO_3^{2-} (selenite) in relevant aqueous solutions. Selenite sorption to various bentonites and montmorillonite is discussed to some detail in TR-04-18. No new reliable data were found (in case of the measurements by /Lauber et al. 2000/ on Opalinus Clay, the existence of Se(0) in addition to Se(IV) cannot be excluded).

   The K_d value for Se(IV) is, therefore, directly based on the value selected in TR-04-18. The only relevant scaling factor is CF-CEC = 0.29. Uncertainties are scaled accordingly. Because of the similarity in conditions, no additional uncertainties are introduced.

Se(VI)   Hexavalent Se exists largely as SeO_4^{2-} (selenate) in relevant aqueous solutions. As in TR-04-18, a K_d of zero in combination with diffusion parameters for anions are proposed.

Silver

No new data were found. Following TR-04-18, an overall K_d range of 0-4.4 m^3/kg (after scaling to the CEC of Friedland Clay) is proposed, with no mean or median.

Technetium

K_d values are proposed separately for each relevant oxidation state.

Tc(IV)   No new data were found. Following the approach in TR-04-18, the K_d value for Tc(IV) is, therefore, directly based on the analogy with Th. To account for the additional uncertainty due to the difference in speciation between Th(IV) and Tc(IV), UF-starting K_d is increased by a factor of 3 (in comparison to the normal UF).

Tc(VII)   Tc(VII) exixts as the pertechnetate anion (TcO_4^-) in normal aqueous solutions. As in TR-04-18, a K_d of zero in combination with diffusion parameters for anions are proposed.

Thorium

As most representative dataset for the present conditions in terms of solution and sorbent composition, the isotherm data measured by /Lauber et al. 2000/ on samples of Opalinus Clay were selected initially. The corresponding data derivation for Friedland Clay was based on a K_d value of 63.0 L/g obtained at pH 8.0. Conversion to application conditions was based on CF-total 3, because the speciation of Th under both source and application conditions is nearly entirely dominated by a hydroxo-carbonato complex. Under such conditions, the formation of ternary Th-carbonato-suface complexes can be expected (i.e., Th complexation with carbonate may not necessarily compete with sorption; see TR-04-18 for a more detailed discussion). To transfer the source K_d value to pH 7.32, CF-pH was obtained from sorption edge data of Th on SWy-1 montmorillonite /Bradbury and Baeyens 2003a/.

However, this approach leads to a surprisingly high K_d value for Th on Friedland Clay in comparison to

1. K_d values derived for Am and lanthanides on Friedland clay;

2. the K_d value that had been derived for Th on MX-80 in TR-04-18.

This can be traced to the observation that the same experimental K_d (63 L/g) is measured under comparable conditions for Opalinus Clay with a CEC of 12 meq/100g and MX-80 bentonite with a much higher CEC of about 80 meq/100g. Precipitation of solid Th phases seems to be extremely unlikely due to the low initial concentrations, but at the same time there is no good explanation for the similarity in uptake.

Following the above discussion, the K_d value of 18.2 L/g is selected, together with the corresponding uncertainties. While this may be conservative in the light of the data measured on Opalinus Clay, it is consistent with the value derived for MX-80 in TR-04-18 and is viewed as best possible value for Friedland Clay.

Tin

Only the IV-valent oxidation state is relevant, except under extremely reducing (unrealistic) conditions. /Lauber et al. 2000/ measured strong Sn(IV) sorption ($K_d > 125$ m^3/kg) on Opalinus Clay, but in the presence of comparatively high background concentrations of Sn (stemming from the substrate itself). /Bradbury and Baeyens 2003ab/ present unpublished data (sorption edge measurements on SWy-1 montmorillonite and illite in 0.1 M NaClO$_4$) that suggest K_d values > 300 m^3/kg. However, they do not report all experimental details, including initial Sn concentration.

Following the arguments given in TR-04-18, the K_d value for Sn(IV) is, therefore, directly based on the analogy with Th(IV). To account for the additional uncertainty due to the difference in speciation between Sn(IV) and Th(IV), UF-starting K_d is increased by a factor of 3 (in comparison to the normal UF).

Uranium

Data are given separately for IV- and VI-valent oxidation states:

U(IV)   No relevant and reliable data were found for U(IV). The K_d value derived for Th is taken for U(IV), based on analogy considerations. No CF-spec is applied, due to the inconsistency in the underlying thermodynamic databases (analogous situation as for Pu(IV), see the discussion in the respective section above).

Therefore, the K_d value derived for Th is applied directly to U(IV). To take additional uncertainties due to analogue considerations into account, UF-starting K_d was increased by a factor of 2 (see TR-04-18 for explanations).

U(VI)   In addition to the datasets for U(VI) already discussed in TR-04-18, the data by /Stammose et al. 1992/ were considered. They measured sorption of U(VI) on purified FoCa-7 clay (7% kaolinite, 93% mixed-layer kaolinite/smectite, CEC = 69 meq/100 g) in the presence of atmospheric levels of CO_2. Their data show very good agreement with the data by /Pabalan and Turner 1997/, which suggests a relatively uniform trend of U(VI) sorption to various clay mineral substrates as a function of pH and in the presence of significant levels of carbonate. As it offers a more substantial set of data, the study by /Pabalan and Turner 1997/ is taken as basis for deriving K_d, using CF-total 3 to transfer the data to the conditions relevant for Friedland Clay (see TR-04-18).

Zirconium

No data were found in addition to the information already discussed in TR-04-18. The K_d value for Zr is, therefore, directly based on the value selected in TR-04-18. The only relevant scaling factor is CF-CEC = 0.29. Uncertainties are scaled accordingly. Because of the similarity in conditions, no additional uncertainties are introduced.

Note that the value selected in TR-04-18 is based on analogy with Th, but under the assumption that the formation of $Zr(OH)_5^-$ complexes at pH > 6 /Hummel et al. 2002/ would directly compete with the formation of Zr-surface complexes. Because of the nearly identical pH in the calculated MX-80 and Friedland Clay porewaters, this assumption also applies to the present situation.

3 Validity ranges of selected data

3.1 Bentonite composition and density

K_d

The derived migration parameters were derived for Friedland Clay of a given composition (Appendix A) at the specified reference density of 1,780 kg/m^3. Because of the strong dependency of K_d on porewater composition, these data are strictly valid for these conditions only. However, it is not likely that a limited variation of the buffer density (e.g., within a range of about 1,500–1,900 kg/m^3) will have a significant influence on porewater composition or K_d, in particular when $p\text{CO}_2$ is imposed by the host rock formation (see below). Similar calculations carried out in TR-04-18 for MX-80 as a function of bentonite composition suggest that the resulting variability of porewater composition will be within the variability that is caused by uncertainties in the groundwater composition and $p\text{CO}_2$.

Porosity

For all elements except non-sorbing anions, the same value is proposed for diffusion-available and total porosity. As shown in Figure 5-3 in TR-04-18, total porosity depends on clay density, but is not significantly influenced by clay composition. Total porosity is calculated as $\varepsilon = 1 - (\rho/\rho_s)$. In the same manner, diffusion-available porosity for non-sorbing anions is given by $\varepsilon_{anion} = (1 - (\rho/\rho_s))/2.5$.

D_e

For all elements except non-sorbing anions and Cs, D_e for HTO is used. Measured D_e values plotted in Figure 5-4 of TR-04-18 for four different bentonites as a function of density show a clear dependency of D_e on density, which can be expressed as:

$$D_e = 6.7785\text{E–}9 \times e^{-2.5671\text{E–}3 \times \rho}$$

Similarly, the dependency of D_e for non-sorbing anions can be expressed as a function of density; this relation is estimated to be valid for a density range of ca 1,000–2,000 kg/m^3:

$$D_e = 5.30087\text{E–}10 \times e^{-2.561\text{E–}3 \times \rho}$$

For Cs, no explicit relation of De vs. density is given, but it is adopted from TR-04-18 that the same dependency on density as for HTO may be used, with D_e for Cs being larger by a constant factor of 3.

Very little quantitative information is available regarding the dependency of D_e on bentonite composition. Based on Figure 5-4 of TR-04-18, it can be estimated, however, that the variation of D_e among significantly dissimilar bentonites (assuming all other experimental conditions being the same) is within a factor of ca 5; i.e. within experimental error.

3.2 Geochemical conditions (groundwater composition, pCO$_2$, redox conditions)

K_d values were selected for specific sets of bentonite porewater compositions. These porewater compositions are the result of clay-groundwater interaction and correspond to particular combinations of i) clay composition and density and ii) geochemical conditions (groundwater composition, pCO$_2$). It is pointed out that changes in groundwater composition do not translate directly to corresponding changes in porewater composition, due to the buffering effect of clay. An approximate estimation of the possible effects of variations in the groundwater composition was done in TR-04-18 in the case of MX-80; it is expected that the effect will be very similar in the case of Friedland Clay. The effect of redox conditions was addressed by separately evaluating each relevant oxidation state in case of redox-sensitive elements.

As discussed, K_d values can be very sensitive with regard to porewater composition. Therefore, the validity of the selected data is bounded by the ranges of conditions covered by the porewater compositions considered:

- RPW-FC (pH 7.3, pCO$_2$ $1\times10^{-2.6}$ atm, I= 0.25 M), this report:

  K_d values are derived specifically for this set of conditions calculated for Friedland Clay in this report.

- RPWC (pH 6.5, pCO$_2$ 1×10^{-1} atm, I = 0.29 M), TR-04-18, and

- HSPW (pH 7, pCO$_2$ $1\times10^{-2.6}$ atm, I = 0.76 M), TR-04-18:

  The resulting variation of K_d is estimated based on the results obtained for these conditions in TR-04-18 (i.e., assuming the same CF-pH and CF-spec).

These values reflect an increase of salinity in the groundwater up to seawater conditions as well as a significant variation in dissolved carbonate (closed and open conditions with respect to CO$_2$). It is generally not advisable to extrapolate K_d values to conditions outside these ranges. Salinity is somewhat of an exception to this, because of the comparative "inertness" of Na and Cl; it is not expected that an increase of salinity to ca 1 M will have a significant effect on K_d (except for Cs, Sr, Ra).

In general, not enough diffusion data are available as a function of conditions to allow a sound assessment of the effects of variable conditions. In particular, no diffusion data are available for Friedland Clay. It was estimated in TR-04-18 that the effect of high salinity (up to 1M) on D_e of non-sorbing anions will not be significant in compacted MX-80. For sorbing elements, it is expected that the uncertainty of D_e as a function of conditions will not be relevant in comparison to the corresponding uncertainty in K_d.

Temperature

The selected data are valid for 25°C. An increase to 50°C is expected to lead to a twofold increase of D_e. Based on the data available to date, it is not possible to assess the influence of temperature on K_d with any certainty. However, no significant effects are expected for an interval of ca 10–50°C. No effect on porosity is expected for this temperature range.

4　Data summary

Table 4-1. Summary of D_e and ε values.

Radionuclide (Redox State)	D_e (m²/s)	Upper D_e limit (m²/s)	Lower D_e limit (m²/s)	ε (−)	Upper ε limit (−)	Lower ε limit (−)
Ag(I)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Am(III)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
C, carbonate spieces	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
C, methane	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
C, organic acids	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
Ce(III)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Cl(−I)	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
Cm(III)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Cs(I)	2.1×10^{-10}	2.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Eu(III)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Ho(III)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
I(−I)	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
Nb(V)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Ni(II)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Np(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Np(V)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pa(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pa(V)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pb(II)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pd(II)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pu(III)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pu(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pu(V)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Pu(VI)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Ra(II)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Rn(−)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Se(−II)	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
Se(IV)	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
Se(VI)	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
Sm(III)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Sn(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Sr(II)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Tc(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Tc(VII)	5.6×10^{-12}	1.7×10^{-11}	1.7×10^{-12}	0.14	0.20	0.10
Th(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
U(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
U(VI)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−
Zr(IV)	7.0×10^{-11}	1.1×10^{-10}	2.9×10^{-11}	0.36	−	−

Table 4-2. Summary of K_d values and validity ranges.

Radionuclide (Redox State)	Selected K_d and uncertaintiies for reference porewater (RPW-FC)			Additional uncertainties for saline porewater/low pH	
	K_d selected (m³/kg)	Upper K_d limit (m³/kg)	Lower K_d limit (m³/kg)	Upper K_d limit (m³/kg)	Lower K_d limit (m³/kg)
Ag(I)	–	4.40	0	4.40	0
Am(III)	17.7	110	3	110	0.5
C, carbonate spieces	isotope exchange	–	–	–	–
C, methane	0	–	–	–	–
C, organic acids	0	–	–	–	–
Ce(III)	10	60	2	60	0.2
Cl(–I)	0	–	–	–	–
Cm(III)	18	110	3	110	0.5
Cs(I)	0.03	0.2	0.004	0.2	0.001
Eu(III)	10	60	1.7	60	0.2
Ho(III)	10	60	1.7	60	0.2
I(–I)	0	–	–	–	–
Nb(V)	0.9	13.2	0.06	13.2	0.06
Ni(II)	1.47	8.80	0.24	8.80	0.05
Np(IV)	18.2	322	1.0	322	0.7
Np(V)	0.007	0.041	0.0011	0.041	0.0005
Pa(IV)	0.9	13.2	0.06	13.2	0.06
Pa(V)	0.9	13.2	0.06	13.2	0.06
Pb(II)	22	134	3,5	134	1.7
Pd(II)	1.5	22	0.1	22.0	0.1
Pu(III)	17.7	276	1.1	276	0.2
Pu(IV)	18.2	322	1.0	322	0.7
Pu(V)	0.007	0.065	0.0007	0.065	0.0003
Pu(VI)	0.9	9.0	0.1	42	0.1
Ra(II)	0.0013	0.0078	0.0002	0.0078	4.3E–05
Rn(–)	0	–	–	–	–
Se(–II)	0	–	–	–	–
Se(IV)	0.01	0.12	0.001	0.26	0.001
Se(VI)	0	–	–	–	–
Sm(III)	10	60	1.7	60	0.2
Sn(IV)	18.2	510	0.7	510	0.4
Sr(II)	0.0013	0.0078	0.0002	0.0078	4.3E–05
Tc(IV)	18.2	510	0.7	510	0.4
Tc(VII)	0	–	–	–	–
Th(IV)	18.2	202	1.6	202	1.0
U(IV)	18.2	322	1.0	322	0.7
U(VI)	0.9	5.7	0.15	26.6	0.15
Zr(IV)	1.2	30	0.03	83	0.03

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Clay characteristics

Table A-1. Impurities and accessory minerals in Friedland Clay /Karnland 2004/.

Component	Friedland (wt-%)	±	
Feldspars	3	1	
Gypsum	0.8		from chemical analysis
Illite	4	2	
Kaolin	10	5	
Mica (muscovite)	9	5	
Mixed layer *	44	5	* 33% 10Å, 67% expandable layers
C organic	0.6		from chemical analysis
Pyrite	0.62		from chemical analysis
Quartz	28	3	
CEC (meq/100g)	22(a)	2	

(a) This value became available after calculations had been completed using a CEC of 25 meq/100 g. The effect is negligible.

Calculated porewater composition

Parameter		RPW-FC
Na	(mol/L)	9.6170E-02
K	(mol/L)	1.0100E-01
Ca	(mol/L)	1.9583E-02
Mg	(mol/L)	5.7216E-03
CO_3	(mol/L)	1.2607E-03
Cl	(mol/L)	1.5570E-01
SO_4	(mol/L)	3.3953E-02
dissolved SiO_2	(mol/L)	1.0610E-04
pH		7.316
log $p\,CO_2$	(atm)	-2.6
		(open)
solids in equilibrium		quartz
		calcite
		gypsum
Ionic strength	(mol/L)	0.25

Data derivation tables for K$_d$ values

The same table format as in TR-04-18 is used, further explanations are provided there.

Data derivation tables are given for the following radionuclides :

- Americium
- Ceasium
- Europium
- Neptunium (Np(V) only)
- Nickel
- Radium and strontium
- Thorium
- Uranium (U(VI) only)

Table C-1. Predicted K$_d$ value for Am(III).

Am(III)		Conditions		Conversion (CF) & Uncertainty (UF) Factor
		Data source (a)	**Application**	**CF**
Solution		**0.1 M NaClO4**	**RPW-FC**	**RPW-FC**
Substrate		**Smectite**	**Friedland Clay**	**Friedland Clay**
CEC	(meq/100g)	79	25	0.32
pH		7.3	7.32	1
log p CO$_2$	(atm)	-3.5 (b)	-2.6	
CF-total 1				0.316
Speciation (c)				
CF-spec. 3		1.000	0.885	0.885
CF-total 3				**0.280**
				UF
Experimental K$_d$	(L/g)	**63.1**		
Predicted K$_d$ (CF-total 3)	(L/g)		*17.7*	
UF-starting K$_d$				1.6
UF-CEC				1.4
UF-speciation				1.4
UF-batch -> compacted				2.0
UF-total				6.2
K$_d$ upper limit	(L/g)		*109.747*	
K$_d$ lower limit	(L/g)		*2.843*	

(a): Na-smectite at 0.1 M NaClO$_4$ /Gorgeon, 1994/. Speciation calculated with data by /Guillaumont et al., 2003/

(b): assuming equilibrium with air as limiting condition

(c): Speciation calculated with data by /Guillaumont et al., 2003/

RPW-FC: Reference porewater (saline Beberg groundwater equilibrated with Friedland Clay)

Table C-2. Predicted K_d value for Cs(I).

Cs(I)		Conditions	Conversion (CF) & Uncertainty (UF) Factor
		Application	**CF**
Solution		**RPW-FC**	**RPW-FC**
Substrate		**Friedland Clay**	**Friedland Clay**
CEC	(meq/100g)	25	
pH		7.32	
ionic strength	(M)	0.25	
log $p\,CO_2$	(atm)	-2.6	
			UF
K_d sorption model (a)	(L/g)	**0.026**	
UF-model			3.0
UF-batch -> compacted			2.0
UF-total			6.0
K_d upper limit	(L/g)	0.1539	
K_d lower limit	(L/g)	0.0043	

(a): Model of /Wanner et al, 1996/ for bentonite

RPW-FC: Reference porewater (saline Beberg water equilibrated with Friedland Clay)

Table C-3. Predicted K_d value for Eu(III) using the CF-approach.

Eu(III)		Conditions		Conversion (CF) & Uncertainty (UF) Factor
		Source data (a)	Application	CF
Solution		Opalinus Clay	RPW-FC	RPW-FC
Substrate		SOPW2 (a)	Friedland Clay	Friedland Clay
CEC	(meq/100g)	12	25	2.08
pH		8	7.316	0.24 (b)
log $p\,CO_2$	(atm)	-4.2	-2.6	
CF-total 1				0.494
Speciation				
CF-spec 3 (c)		0.629	0.59	0.936
CF-total 3				0.463
				UF
Experimental K_d	(L/g)	50.1		
Predicted K_d (CF-total 3)	(L/g)		23.2	
UF-starting K_d				1.6
UF-pH-conversion				2.5
UF-speciation				1.4
UF-batch -> compacted				2.0
UF-total				11.1
K_d upper limit	(L/g)		258.469	
K_d lower limit	(L/g)		2.080	
K_d sorption model			10.04	
K_d scaled from MX-80 (TR-04-18)			2.3	

(a) Opalinus Clay sample (OPA), synthetic OPA porewater, pre-equilibrated (batch 4), see Lauber et al. /2000/

(b) from Eu sorption data on Swy-1 montmorillonite /Bradbury and Baeyens, 2002/

(c): calculated with the thermodynamic data given in /Hummel et al., 2002/

RPW-FC: Reference porewater (saline Beberg groundwater equilibrated with Friedland Clay)

Table C-4. Predicted K_d value for Eu(III) using the thermodynamic sorption model by /Bradbury and Baeyens 2002/.

Eu(III)		Conditions	Conversion (CF) & Uncertainty (UF) Factor
		Application	**CF**
Solution		**RPW-FC**	**RPW-FC**
Substrate		**Friedland Clay**	**Friedland Clay**
CEC	(meq/100g)	25	
pH		7.32	
ionic strength	(M)	0.25	
log $p\,CO_2$	(atm)	-2.6	
			UF
K_d sorption model (a)	(L/g)	**10.035**	
UF-model			3.0
UF-batch -> compacted			2.0
UF-total			6.0
K_d upper limit	(L/g)	60.21	
K_d lower limit	(L/g)	1.67	

(a): Model of /Bradbury and Baeyens, 2002/ for Na- and Ca-Swy-1 montmorillonite

RPW-FC: Reference porewater (saline Beberg water equilibrated with Friedland Clay)

Table C-5. Predicted K_d value for Np(V).

Np(V)		Conditions		Conversion (CF) & Uncertainty (UF) Factor
		Data source (a)	Application	CF
Solution		0.1 M NaNO$_3$	RPW-FC	RPW-FC
Substrate		SAz-1	Friedland Clay	Friedland Clay
CEC	(meq/100g)	120	25	0.208
pH		7.3	7.316	1
log $p\,CO_2$	(atm)	–	-2.6	
CF-total 1				0.208
Speciation				
CF-spec 3 (b)		1.00000	0.984649	0.985
CF-total 3				0.205
				UF
Experimental K_d	(L/g)	**0.032**		
Predicted Kd (CF-total 3)	(L/g)		**0.007**	
UF-starting K_d				1.6
UF-CEC				1.4
UF-speciation				1.4
UF-batch -> compacted				2.0
UF-total				6.2
K_d upper limit	(L/g)		0.041	
K_d lower limit	(L/g)		0.0011	

(a): Np(V) sorption on SAz-1 Na-montmorillonite in 0.1 M NaNO$_3$ /Turner et al, 1998; Bertetti et al, 1998)

(b): Calculated using the thermodynamic data given in /Guillaumont et al, 2003/

RPW-FC: Reference porewater (saline Beberg water equilibrated with Friedland Clay)

Table C-6. Predicted K_d value for Ni(II).

Ni(II)		Conditions	Conversion (CF) & Uncertainty (UF) Factor
		Application	**CF**
Solution		**RPW-FC**	**RPW-FC**
Substrate		**Friedland Clay**	**Friedland Clay**
CEC	(meq/100g)	25	
pH		7.32	
ionic strength	(M)	0.25	
log $p\,CO_2$	(atm)	-2.6	
			UF
K_d sorption model (a)	(L/g)	**1.47**	
UF-model			3.0
UF-batch -> compacted			2.0
UF-total			6.0
K_d upper limit	(L/g)	8.7958	
K_d lower limit	(L/g)	0.2443	

(a): Calculated withn the sorption model of /Bradbury and Baeyens, 1997/; TDB: /Hummet et al, 2002/
RPW-FC: Reference porewater (saline Beberg water equilibrated with Friedland Clay)

Table C-7. Predicted K_d value for Ra(II) and Sr(II).

Ra(II)/Sr(II)		Conditions	Conversion (CF) & Uncertainty (UF) Factor
		Application	**CF**
Solution		**RPW-FC**	**RPW-FC**
Substrate		**Friedland Clay**	**Friedland Clay**
CEC	(meq/100g)	25	
pH		7.316	
ionic strength	(M)	0.254	
log $p\,CO_2$	(atm)	-2.6	
			UF
K_d sorption model (a)	(L/g)	**0.0013**	
UF-model			3.0
UF-batch -> compacted			2.0
UF-total			6.0
K_d upper limit	(L/g)	0.0078	
K_d lower limit	(L/g)	0.0002	

(a): Model of /Wieland et al, 1994/ for bentonite, assuming the same selectivity for Sr and Ra as for Ca /Fletcher and Sposito, 1989/

RPW-FC: Reference porewater (saline Beberg water equilibrated with Friedland Clay)

Table C-8. Predicted K_d value for Th(IV). The value derived from MX-80 was selected.

Th(IV)		Conditions		Conversion (CF) & Uncertainty (UF) Factor	Conditions		Conversion (CF) & Uncertainty (UF) Factor
		Data source (a)	Application	CF	Data source (c)	Application	CF
Solution		SOPW2 (a)	RPW-FC	RPW-FC	SBPW	RPW-FC	RPW-FC
Substrate		Opalinus Clay	Friedland Clay	Friedland Clay	MX-80	Friedland Clay	Friedland Clay
CEC	(meq/100g)	12	25	2.08	79	25	0.32
pH		8	7.32	0.83 (b)	7.6	7.32	0.91 (b)
log $p\,CO_2$		-4.2	-2.6		-3.5	-2.6	
CF-total 1				1.733			0.289
Speciation							
CF-spec 3 (d)		1.000000	0.9999976	0.9999976	0.99999985	0.99999764	0.99999779
CF-total 3				1.733			0.289
				UF			UF
Experimental K_d	(L/g)	63			63		
Predicted K_d (CF-total 3)	(L/g)		109.335			18.210	
UF-starting K_d				1.6			1.6
UF-pH conversion				2.5			2.5
UF-speciation				1.4			1.4
UF-batch -> compacted				2.0			2.0
UF-total				11.1			11.1
K_d upper limit	(L/g)		1212.986			202.027	
K_d lower limit	(L/g)		9.855			1.641	

(a) Opalinus Clay sample (OPA), synthetic OPA porewater, pre-equilibrated (batch 4), see Lauber et al, /2000/

(b) from Th sorption edge on SWy-1 montmorillonite /Bradbury and Baeyens, 2003a/
(c) K_d values from Th(IV) sorption isotherm on MX-80 in synthetic bentonite porewater, SBPW /Bradbury and Baeyens, 2003a/

(d): TDB from /Hummel et al, 2002/
RPW-FC: Reference porewater (saline Beberg groundwater equilibrated with Friedland Clay)

Table C-9. Predicted K_d value for U(VI). The value derived from SAz-1 was selected.

U(VI)		Conditions		Conversion (CF) & Uncertainty (UF) Factor	Conditions		Conversion (CF) & Uncertainty (UF) Factor
		Data source (a)	Application	CF	Data source (b)	Application	CF
Solution		0.1 M NaNO$_3$	RPW-FC	RPW-FC	0.1 M NaClO$_4$	RPW-FC	RPW-FC
Substrate		SAz-1	Friedland Clay	Friedland Clay	FoCa-7	Friedland Clay	Friedland Clay
CEC	(meq/100g)	120	25	0.208	69	25	0.362
pH		7.32	7.316	1	7.3	7.316	1
log pCO$_2$	(atm)	-3.5	-2.6		-3.5	-2.6	
CF-total 1				0.208			0.362
Speciation							
CF-spec 3 (c)		1.0000	1.0000	1.000	1.0000	1.0000	1.000
CF-total 3				0.208			0.362
				UF			UF
Experimental K_d	(L/g)	4.4			17		
Predicted K_d (CF-total 3)	(L/g)		0.917			6.159	
UF-starting K_d				1.6			2.5
UF-CEC				1.4			1.4
UF-speciation				1.4			1.4
UF-batch -> compacted				2.0			2.0
UF-total				6.2			9.8
K_d upper limit	(L/g)		5.695			60.650	
K_d lower limit	(L/g)		0.148			0.626	

(a): U(VI) sorption on SAz-1 montmorillonite in 0.1 NaNO$_3$ /Pabalan and Turner, 1997/

(b): U(VI) sorption on purified FoCa-7 clay in 0.1 NaClO$_4$ /Stammose et al, 1992/

(c): TDB from /Guillaumont et al, 2003/

RPW-FC: Reference porewater (saline Beberg water) equilibrated with Friedland Clay