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**Porosity, sorption and diffusivity data complied for the SKB 91 study**

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POROSITY, SORPTION AND DIFFUSIVITY DATA COMPILED FOR
THE SKB 91 STUDY


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# Summary

The SKB 91 study is an integrated safety analysis of the KBS-3 concept of a repository located in the Finnsjön area. For this study, values of important transport parameters in the bentonite backfill and in the rock are proposed. $K_d$-values, diffusivities and diffusion porosity for different elements in compacted MX-80 bentonite are based on experimental data found in the literature. With regard to sorption, both a best estimate and a conservative value is given. Because sorption on bentonite is very much dependent on the conditions prevailing and experimental data are limited and not necessary representative for the conditions expected in the repository, the proposed best estimate values may include large uncertainties.

Data proposed for rock are matrix diffusivities, matrix porosity and diffusivity in mobile bulk water. These values are based on experimental results on Finnsjö rock.

# Content

# 1. Introduction

## 1.1 Background

The Swedish Nuclear Fuel and Waste Company, SKB, are performing a new integrated safety analysis of the KBS-3 concept for the final storage of spent fuel. The primary aim of the study, SKB 91, is to illustrate the importance of site-specific geological parameters on the safety of the repository. For this purpose the Finnsjön area has been selected as the repository site.

## 1.2 Purpose

One important part of the safety analysis is to calculate the nuclide transport through the different barriers surrounding the waste. Two of the barriers are the bentonite backfill surrounding the waste canisters and the rock surrounding the repository.

The purpose with this study is to propose values for important transport parameters in the bentonite backfill and in the surrounding rock. These values should be representative for the selected repository design and location, and should be based on experimental data reported in the literature.

## 1.3 Scope

Two different groundwaters, one saline and one fresh, representative for the Finnsjön area are considered in the safety analysis [Papp et al., 1990]. The composition of these waters are given in Table 1.

The bentonite backfill is a sodium bentonite, Wyoming MX-80, compacted to a density of 2000 kg/m³. The parameters for which values are requested are:
- effective diffusion porosity,
- pore diffusivity (definition is given in Chapter 2), and
- sorption capacity in terms of a $K_d$-value.

Both oxidising (Eh = +250 mV) and reducing (Eh = -200 mV) conditions are of interest in the pH-interval 7 - 9. The elements for which values are requested are:

Se, Sr, Zr, Tc, Pd, Sn, I, Cs, Ce, Sm, C (organic and inorganic), Cl, Ni, Nb, Am, Pu, Np, U, Pa, Th, Ra, Rn, Pb.

The species assumed to exist under the conditions specified are given in Table 2 for some of the elements [Bruno and Selin, 1991]. It should be noted, however, that the speciation given in Table 2 is determined without considering the chemical reactions between groundwater and bentonite.

Parameters in the rock barrier for which data are requested are:
- effective diffusion porosity in the rock matrix,
- pore diffusivity, and
- diffusivity in fractures in the rock.

Data should as far as possible be site-specific, and be representative for the two different groundwaters in Table 1 and the above listed element.

All data are requested for low temperatures, i.e. temperatures not affected by heat transfer from the spent fuel.

Table 1      Groundwater composition, ppm, Finnsjön [Papp et al., 1990].

| | Fresh | Saline |
|---|---|---|
| Ca | 76.0 | 1600.0 |
| Na | 23.0 | 120.0 |
| Mg | 6.3 | 1700.0 |
| K | 3.2 | 13.0 |
| Fe | 9.0 | 0.016 |
| Si | 6.0 | 6.0 |
| Cl | 61.0 | 5500.0 |
| Br | 0.3 | 29.0 |
| F | 0.6 | 1.2 |
| $NO_3$ | 0.5 | - |
| $SO_4$ | 8.9 | 380.0 |
| $HCO_3$ | 220.0 | 48.0 |
| Ionic strength | 0.0084 M | 0.308 M |
| pH | 6.9 | 7.0 |
| Eh(mV) | red/ox -200/650 | red/ox -200/650 |

Table 2      Dominating species of some of the elements of interest according to Bruno and Selin [1991].

| Nuclide | Dominating species | | | |
|---|---|---|---|---|
| | Fresh | | Saline | |
| | Ox. | Red. | Ox. | Red. |
| U | $UO_2(CO_3)_2^{2-}$ $UO_2(CO_3)_3^{4-}$ | $U(OH)_4$ | $UO_2(CO_3)_2^{2-}$ $UO_2(CO_3)_3^{4-}$ | $U(OH)_4$ |
| Pu | $PuO_2^+$ $PuSO_4^+$ | $Pu^{3+}$ | $PuO_2^+$ $PuSO_4^+$ | $Pu^{3+}$ |
| Np | $NpO_2^+$ $NpO_2CO_3^-$ | $Np(OH)_4$ | $NpO_2^+$ $NpO_2Cl$ | $Np(OH)_4$ |
| Am | $AmCO_3^+$ $Am^{3+}$ | $AmCO_3^+$ $Am^{3+}$ | $AmCO_3^+$ $Am^{3+}$ | $AmCO_3^+$ $Am^{3+}$ |
| Th | $Th(OH)_4$ | $Th(OH)_4$ | $Th(OH)_4$ | $Th(OH)_4$ |
| Ra | $Ra^{2+}$ | $Ra^{2+}$ | $Ra^{2+}$ | $Ra^{2+}$ |
| Sn | $Sn(OH)_4$ | $Sn(OH)_4$ | $Sn(OH)_4$ | $Sn(OH)_4$ |
| Tc | $TcO_4^-$ | $[TcO(OH)_2]_2$ | $TcO_4^-$ | $[TcO(OH)_2]_2$ |

## 2.  Definitions

### 2.1  Porosity

The total porosity in porous and fractured media is composed of a *flow porosity*, a *diffusion porosity* and a *storage porosity*.

The *flow porosity* represents those fractures and pores through which the dominant mode of fluid and aqueous species transport is by fluid flow. This porosity contributes to the permeability of the medium.

The *diffusion porosity* represents those pores through which the dominant mode of transport is by diffusion. This porosity consists of connecting pores with stagnant water, which often also are connected with pores where fluid flow dominates, i.e. the flow porosity.

The *storage porosity* represents those pores which are connected to diffusion pores or flow pores but have a dead end. These pores contribute to the capacity of the pore system to hold the dissolved species, but they contribute little or nothing to the transport of the species.

The porosity that is of interest in this study is the diffusion porosity. It is, however, experimentally very difficult to determine the diffusion porosity and storage porosity separately.

### 2.2  Sorption capacity, $K_d$

The equilibrium between the concentration of species in the pore solution and sorbed on the solid surface can be described by an adsorption isotherm. At low concentrations of the species in solution, the equilibrium is usually linear and defined by a distribution coefficient, $K_d$.

$K_d$ is based either on the mass or volume of solid material as follows:

$$K_d \text{ [m}^3\text{/kg or m}^3\text{/m}^3] = \frac{\text{concentration of species in solid [g/kg or g/m}^3]}{\text{concentration of species in solution [g/m}^3]}$$

The distribution of species between solid and solution can also be based on the surface area of the solid. This distribution coefficient is generally denoted $K_a$, and has the unit [m]. The relation between the mass or volume based distribution coefficient and the surface based distribution coefficient is the specific surface available for sorption per mass or volume of the solid material.

It must be pointed out that $K_d$ or $K_a$ coefficients for a certain species are specific for the conditions under which they are measured. The values are often independent of the species concentration, if it is low, but may be strongly dependent on other conditions such as concentration of competing species, pH of the solution and redox conditions.

## 2.3    Diffusivity

The rate of transfer of a diffusing substance through a cross-sectional area of an isotropic material is, according to Fick's first law, proportional to the concentration gradient measured normal to the area. In case of diffusion in a fluid this is mathematically expressed as:

$$N = - D_v \cdot A \frac{dc}{dx} \tag{1}$$

where  $N$ = flow rate of diffusing species, [g/s]
$D_v$ = diffusivity of species in fluid, [m$^2$/s]
$A$ = cross-sectional area through which diffusion occurs, [m$^2$]
$c$ = concentration of species, [g/m$^3$]
$x$ = diffusion distance, [m].

In a porous material where diffusion occurs in the pore fluid the flow rate of diffusing substance is:

$$N_p = -D_p \cdot A \cdot \varepsilon_p \cdot \frac{dc_p}{dx} \tag{2}$$

where $D_p$ is the diffusivity in the pore solution, $\varepsilon_p$ is the diffusion porosity of the material and $c_p$ is the concentration of the species in the pore solution.

The pore diffusivity, $D_p$, is lower than the diffusivity in an unconfined fluid, $D_v$. This is because of the tortuous winding of the pores, which increases the length of the diffusion path, and because the pores may be constricted in some parts. The relation between the pore diffusivity and the diffusivity in an unconfined fluid is:

$$D_p = D_v \cdot \frac{\delta}{\tau^2} \tag{3}$$

where $\delta$ is the constrictivity and $\tau^2$ is the tortuosity of the pores.

By introducing the diffusion porosity in Equation 3, the following relation between the effective diffusivity, $D_e$, and the diffusivity in unconfined fluid, $D_v$, is obtained.

$$\frac{D_e}{D_v} = \frac{D_p \cdot \varepsilon_p}{D_v} = \frac{\varepsilon_p \cdot \delta}{\tau^2} \tag{4}$$

The ratio on the right hand side in Equation 4 is called the formation factor.

Fick's second law, or the diffusion equation, describes the concentration of a diffusing species as a function of time and space. For diffusion of a sorbing species in a porous material this is mathematically given by:

$$\varepsilon \frac{\partial c_p}{\partial t} + \rho \frac{\partial q}{\partial t} = D_e \frac{\partial^2 c_p}{\partial x^2} \qquad (5)$$

where $\varepsilon$ is the sum of the diffusion porosity and the storage porosity, $\rho$ is the bulk density of the solid material and q is the concentration of the diffusing species in the solid.

If the concentration on the surface of the solid is locally in equilibrium with the concentration in the pore fluid and the equilibrium is linear, the concentration in the solid can be expressed as:

$$q = K_d \cdot c_p \qquad (6)$$

A combination of Equations 5 and 6 gives:

$$\frac{\partial c_p}{\partial t} = \frac{D_e}{\varepsilon + K_d \cdot \rho} \frac{\partial^2 c_p}{\partial x^2} = D_a \frac{\partial^2 c_p}{\partial x^2} \qquad (7)$$

where $D_a$ is the apparent diffusivity, which includes the retardation effects caused by the sorption on the solid material. If the species does not sorb on the solid material, i.e. $K_d$ is zero, and the storage porosity is negligible compared to the diffusion porosity, the apparent diffusivity, $D_a$, is equal to the pore diffusivity, $D_p$.

For sorbing species there are experimental indications of an additional diffusion mechanism, surface diffusion, acting in parallel with pore diffusion. Surface diffusion increases the transport rate of sorbing species in porous materials. Another mechanism which may affect the diffusional transport in clay materials is anion exclusion. Clay particle surfaces are negatively charged. Anionic species are thereby repelled from the clay surface, and their concentration increases away from the surface. This means a smaller porosity available for diffusion of anions in the clay.

To summarise, the following three diffusivities are normally used to describe diffusional transport in porous materials:

-       pore diffusivity,
-       effective diffusivity, and
-       apparent diffusivity.

The relation between the different diffusivities are given by the equations above.

3.     **Result of literature review**

3.1     Introduction

Different sources have been used to find literature relevant for this study. These are the SKB internal bibliographical data base and the international bibliographic data bases CHEMABS and INIS. The NEA Sorption Data Base has also been checked for sorption data on bentonite and montmorillonite.

3.2     Porosity, sorption and diffusivity data for bentonite

The water content of a 100% saturated Wyoming bentonite (MX-80) with a bulk density of 2000-2100 kg/m$^3$ is 20-25% [Pusch, 1983]. Muurinen et al [1987] reported a water content of 40% in MX-80 bentonite for a wet density of 2000 kg/m$^3$, and 25% for a dry density of 2100 kg/m$^3$, which then corresponds to a bulk density of 2350 kg/m$^3$. The porosity of the bentonite based on the water content could be seen as a total porosity.

The porosity accessible for species other than those dissolved from the bentonite itself can be estimated from measurements of the effective diffusivity and the apparent diffusivity of the species if it does not sorb on the bentonite. Diffusion experiments with Cl$^-$ in MX-80 bentonite (dry density 2100 kg/m$^3$) show that the accessible porosity for Cl$^-$ is 0.3% compared to the total porosity of 25% [Muurinen et al., 1987]. Eriksen [1982] has measured both effective diffusivity and apparent diffusivity for the ions Cl$^-$ and I$^-$ in MX-80 bentonite with a bulk density of 2100 kg/m$^3$. From these values the accessible porosity can be calculated, and is found to be about 5% for both species. These results indicate that the effective porosity for anions in bentonite is significantly lower than the porosity given by the water content in the clay.

In the following part of this section experimentally determined sorption and diffusivity data for bentonite found in the literature are presented.

*Selenium*

No data on diffusivity of Se in bentonite have been found. As far as sorption is concerned, K$_d$-values for sorption of Se on Ca-bentonite are given in a compilation of sorption data made by Oscarson et al. [1984]. At a pH of 7, ionic strength of about 0.09 M and Eh of -160 mV, a K$_d$-value of 0.003 m$^3$/kg is reported.

*Strontium*

Data on experimentally determined sorption and diffusivity data in bentonite contacted with synthetic groundwater are given in Table 3. The synthetic groundwater is of the "Allard"-type with a total salt concentration of 306 ppm, a total carbonate concentration of 123 ppm and ionic strength of 0.0085 M. The pH of the water is about 8.2. All data are from experiments under oxidising conditions. One K$_d$-value is determined in compacted bentonite. The other values are from batch experiments. The K$_d$-value measured in the compacted clay sample is lower than what is found in the batch experiments, most probably due to the smaller surface available to sorption in this case. The apparent diffusivity, D$_a$, is in all cases determined from the concentration profiles in the compacted bentonite sample. The obtained values are in fair agreement with each other.

Table 3      Sorption and diffusivity data for strontium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | Liquid to solid [ml/g] | $K_d$ [m³/kg] | $D_a$ [m²/s] | Density [kg/m³] | Ref. |
|---|---|---|---|---|---|
| 50 | 0.5 | 2.7 | $3.3 \cdot 10^{-11}$ | 2350[1] | Neretnieks et al., 1978a |
| 25 | Compacted | 0.6 | $2.3 \cdot 10^{-11}$ | 2100[1] | Eriksen et al., 1981 |
| 70 | | | $4.1 \cdot 10^{-11}$ | 2100[1] | |
| 25 | 0.25-1 | 0.6-1.3 | | | |
| 25 | | | $1 \cdot 10^{-11}$ | 2100[1] | Eriksen et al., 1982 |
| | | | $1.4 \cdot 10^{-11}$ | | |
| 20 | | 2.9 | $1.8 \cdot 10^{-12}$ | 1900-2300[2] | Torstenfelt et al., 1983 |
| 20 | | | $2 \cdot 10^{-11}$ | 2000[2] | Torstenfelt et al., 1986 |

[1] Wet density
[2] Probably dry density

Kahr et al. [1985] have reported values of the apparent diffusivity, $D_a$, in compacted MX-80 bentonite samples ranging from $1.0 \cdot 10^{-12}$ m²/s to $4.89 \cdot 10^{-11}$ m²/s. The lowest value was obtained in a sample with a water content of 7%, and the highest value in a sample with a water content of 29%. In a sample with a water content of 19%, $D_a$ was determined to be between $2.9 \cdot 10^{-11}$ to $3.17 \cdot 10^{-11}$ m²/s.

Muurinen and co-workers [1985, 1986] measured the sorption and diffusion of strontium in sodium-bentonite contacted with solutions with different salt concentrations. Their results are summarised in Table 4. At high salt concentrations they obtained a much lower $K_d$-value than at low salt concentrations. This is explained by the mechanism of sorption, which is ion-exchange. A higher salt concentration in the solution means more cations that compete about the available sorption sites and consequently a lower $K_d$ for strontium. The estimated apparent diffusivity is not varying much between the different experiments. It should be noted that the values are determined assuming that an additional transport mechanism, surface diffusion, occurs. The determined effective diffusivity is high.

The effect of competing cations is also shown by $K_d$-values for strontium sorption on montmorillonite, reported by Releya [NEA sorption data base]. $K_d$-values in the presence of $Na^+$ at a concentration of 650 to 670 ppm are in the range 0.5 to 1.9 m³/kg. When a water with only small amounts of $Na^+$ but a $Ca^{2+}$-concentration of about 540 ppm were used in the sorption experiment, $K_d$-values of about 0.03 to 0.05 m³/kg were obtained. This shows that sorption of $Sr^{2+}$ is sensitive to the concentration of $Ca^{2+}$.

$K_d$-values for strontium and sodium bentonite at different ionic strength in the solution, taken from a compilation of sorption data made by Oscarson et al., [1984], are given in Table 5.

Table 4     Sorption and diffusivity data, Na-bentonite and oxidising conditions [Muurinen et al., 1985, 1986].

| Liquid | $K_d$ [m³/kg] | $D_a$ [m²/s] | $D_e$ [m²/s] | Dry density [kg/m³] |
|---|---|---|---|---|
| NaCl, 1 M (23000 ppm $Na^+$) | 0.003[a] | | | |
| NaCl, 0.6 M (13800 ppm $Na^+$) | 0.007[a] | $6.9 \cdot 10^{-12}$ | | 1740 |
| NaCl, 0.5 M (11500 ppm $Na^+$) | 0.01[a] 0.008[b] 0.027[c] | $6.0 \cdot 10^{-12}$ | $2.9 \cdot 10^{-10}$ | 1750 |
| NaCl, 0.1 M (2300 ppm $Na^+$) | 0.087[a] 0.191[c] | $8.7 \cdot 10^{-12}$ | $2.9 \cdot 10^{-9}$ | 1750 |
| NaCl, 0.01 M (230 ppm $Na^+$) | 1.465[a] 1.204[b] | | | |
| NaCl, 0.001 M (23 ppm $Na^+$) | 1.465[a] | $9.1 \cdot 10^{-12}$ | | 1740 |
| Groundwater, total salt = 10000 ppm | 0.05[a] | $7.8 \cdot 10^{-12}$ $9.5 \cdot 10^{-12}$ | | |

[a] batch method
[b] compacted sample
[c] sample in diffusion experiment

Table 5     $K_d$-values for strontium and Na-bentonite [Oscarson et al., 1984].

| Major species in solution | Ionic strength [M] | pH | $K_d$ [m³/kg] |
|---|---|---|---|
| NaCl | 0.01 0.02 0.1 0.2 | | 10 2 0.11 0.03 |
| NaCl + NaOAc | 0.01 0.1 1 4 | 7 7 7 7 | 3.7 0.12 0.0038 0.00047 |
| NaCl | 0.03 5.1 | | 1.1 0.0014 |

*Zirconium*

No sorption or diffusivity data for zirconium and bentonite have been found in the literature. Allard et al., [1977] have, however, reported $K_d$-values for sorption of zirconium on a mixture of bentonite (10%) and quartz (90%) to be in the range 0.05 to 1 m³/kg.

*Technetium*

Results from sorption and diffusion experiments in MX-80 bentonite contacted with synthetic groundwater of "Allard" type are given in Table 6. Some results are from experiments where Fe(s) was added to the clay in order to try to measure the diffusion of technetium in the reduced state (Tc(IV)). For Tc in the oxidised form no sorption was found, while some sorption is reported for Tc in the reduced form. The addition of reducing agents (Fe(s)) resulted in somewhat lower values of the apparent diffusivity, $D_a$. In one experiment with long contact time, a significantly lower $D_a$-value was obtained.

$K_d$-values for technetium contacted with a 0.16 M NaNO₃-solution at a pH of 7 to 8 have been reported by Ito et al. [1988]. For oxidising conditions a $K_d$-value of 0.0004 m³/kg was obtained. To simulate reducing conditions a 0.1 M NaBH₄ was added to the solution. In this case a $K_d$-value of 0.047 m³/kg was measured.

Table 6      Sorption and diffusivity data for technetium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M.

| Oxidation state | $K_d$ [m³/kg] | $D_a$ [m²/s] | Density[1] [kg/m³] | Ref |
|---|---|---|---|---|
| Tc(VII) | | $5.3 \cdot 10^{-11}$ | 2000 | Torstenfelt et al., 1981 |
| Tc(IV) | | $3.0 \cdot 10^{-13}$ | | |
| Tc(VII) | 0 | $1.4 \cdot 10^{-12}$ | 1900-2300 | Torstenfelt et al., 1983 |
| Tc(IV) | 0.05 | $3.0 \cdot 10^{-13}$ | | |
| Tc(VII) | | $1.2 \cdot 10^{-12}$ | 2000 | Torstenfelt et al., 1986 |
| Tc(VII) | | $6.7 \cdot 10^{-13}$ | | |
| Tc(IV) | | $1.5 \cdot 10^{-13}$ | | |
| Tc(IV) | | $8.4 \cdot 10^{-14}$ | | |
| Tc(IV) 36 days[a] | | $5.4 \cdot 10^{-13}$ | 2000 | Albinsson et al., 1990 |
| 90 days[a] | | $1.1 \cdot 10^{-14}$ | | |
| 552 days[a] | | $1.7 \cdot 10^{-16}$ | | |

[1] Probably dry density      [a] Contact time in experiment

*Iodine*

Results from sorption and diffusion experiments in MX-80 bentonite contacted with synthetic groundwater of the "Allard" type is given in Table 7. In the experiment reported by Eriksen et al. [1981] the apparent diffusivity, $D_a$, and the effective diffusivity, $D_e$, were

evaluated independently of each other from experimental data. The determined apparent diffusivity, $D_a$, differs between the two investigations by as much as a factor of 100.

Table 7       Sorption and diffusivity data for iodine in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M.

| $K_d$ [m$^3$/kg] | $D_a$ [m$^2$/s] | $D_e$ [m$^2$/s] | Density [kg/m$^3$] | Ref |
|---|---|---|---|---|
| | $4 \cdot 10^{-12}$ | $2.1 \cdot 10^{-13}$ | $2100^{1)}$ | Eriksen et al., 1981 |
| 0.001 | $3.2 \cdot 10^{-14}$ $1.2 \cdot 10^{-13}$ | | $1900-2300^{2)}$ | Torstenfelt et al., 1983 |

$^{1)}$ Wet density
$^{2)}$ Probably dry density

Values of the apparent diffusivity, $D_a$, reported by Kahr and co-workers [1985] show a dependence of the water content of the sample. In compacted samples of MX-80 bentonite with a water content of 7% a $D_a$-value of $4.9 \cdot 10^{-12}$ m$^2$/s was measured. The maximum $D_a$-value, $2.24 \cdot 10^{-10}$ m$^2$/s, was obtained in a sample with a water content of 31%. In samples with a water content of 19-20%, values from $1.13 \cdot 10^{-10}$ m$^2$/s to $2.2 \cdot 10^{-10}$ m$^2$/s were determined.

In a compilation of sorption data for bentonite [Oscarson et al., 1984] a $K_d$-value of $1.4 \cdot 10^{-6}$ m$^3$/kg is reported for iodine at a pH of 9.9. $K_d$-values determined by Releya [NEA sorption data base] for iodine on montmorillonite contacted with solutions containing sodium, calcium, chloride and carbonate, range from 0.0005 to 0.0017 m$^3$/kg.

*Cesium*

Sorption and diffusivity data from experiments with MX-80 bentonite contacted with synthetic groundwater (Allard type) are given in Table 8. Similar to the experiments with strontium diffusion in MX-80 bentonite, the results from experiment with cesium diffusion indicate high apparent diffusivities considering the measured $K_d$-values.

In Table 9, $K_d$-values and apparent diffusivities, $D_a$, for cesium in MX-80 bentonite contacted with solutions of different salinity are given [Muurinen et al., 1985 and 1986]. The $K_d$-values are decreasing with increasing sodium concentration in the solution. This is because the sorption mechanism for cesium is ion exchange, and the sodium ions in the solution are competing with the cesium ions about the sorption sites on the surface. The difference in apparent diffusivities are about one order of magnitude, and most values are lower than the values reported in MX-80 contacted with "Allard" groundwater (see Table 8). It should, however, be noted that the $D_a$-values in Table 9 also include a surface diffusion mechanism. The determined effective diffusivity is high.

Table 8    Sorption and diffusivity data for cesium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | $K_d$ [m³/kg] | $D_a$ [m²/s] | Density [kg/m³] | Ref. |
|---|---|---|---|---|
| 50 | 0.34[1] | | | Neretnieks et al., 1978a |
| | | $5.4 \cdot 10^{-11}$ | 2350[b] | |
| 25 | 0.645[a] | $7.5 \cdot 10^{-12}$ | 2100[b] | Eriksen et al., 1981 |
| 70 | | $4.0 \cdot 10^{-11}$ | 2100[b] | |
| 25 | 1.37-1.46 | | | |
| 25 | | $1.5 \cdot 10^{-12}$ | 2100[b] | Eriksen et al., 1982 |
| | | $3 \cdot 10^{-12}$ | | |
| 20 | 1.4[2] | $1.2 \cdot 10^{-12}$ | 1900- | Torstenfelt et al., 1983 |
| | | $2.0 \cdot 10^{-12}$ | 2300[c] | |
| 20 | | $2.4 \cdot 10^{-12}$ | 2000[c] | Torstenfelt et al., 1986 |

[a] Compacted sample
[b] Wet density
[c] Probably dry density

[1] Initial concentration < 8 mg/l
[2] Initial concentration = $10^{-9}$ M

Kawaguchi and co-workers [1989] have measured $K_d$-values for cesium in Na-bentonite contacted with solutions containing sodium concentrations from $1.45 \cdot 10^{-3}$ M (33.3 ppm $Na^+$) to 0.466 M (10718 ppm $Na^+$). The $K_d$-values decreased from 2.12 to 0.007 m³/kg with the increase in sodium concentration. They also measured sorption in Na-bentonite contacted with distilled water and obtained $K_d$-values between 1.72 and 2.12 m³/kg. In addition, diffusion measurements were performed in compacted Na-bentonite samples contacted with distilled water. In samples with a density of 1850 kg/m³ and a water content of 35%, the apparent diffusivity, $D_a$, was estimated to about $6.5 \cdot 10^{-12}$ m²/s. This value is comparable to the values obtained in MX-80 bentonite saturated with synthetic groundwater of "Allard" type (see Table 8).

Apparent diffusivities reported by Kahr et al. [1985] in MX-80 bentonite range from $7.3 \cdot 10^{-14}$ to $4.3 \cdot 10^{-12}$ m²/s when the water content in the compacted samples increase from 7% to 21%.

$K_d$-values between 1.1 to 1.7 m³/kg for cesium sorption on bentonite and Na-montmorillonite at pH 8 - 9 and ionic strength 0.0055 to 0.03 M are given by Oscarson et al., [1984].

| Table 9 | Sorption and diffusivity data for Cs. Na-bentonite and oxidising conditions [Muurinen et al., 1985 and 1986]. |
|---|---|

| Liquid | $K_d$ [m³/kg] | $D_a$ [m²/s] | $D_e$ [m²/s] | Dry density [kg/m³] |
|---|---|---|---|---|
| 0.001 M NaCl (27 ppm Na⁺) | 2.66[a] | | | |
| 0.003 M NaCl (69 ppm Na⁺) | 1.8[a] | $2.5 \cdot 10^{-13}$ | | 1940 |
| 0.01 M NaCl (270 ppm Na⁺) | 1.025[a] 4.173[b] | | | |
| 0.02 M NaCl (460 ppm Na⁺) | 0.85[a] | $3.5 \cdot 10^{-13}$ | | 1910 |
| 0.1 M NaCl (2700 ppm Na⁺) | 0.334[a] 0.834[c] | $4.0 \cdot 10^{-12}$ | $4.5 \cdot 10^{-9}$ | 1750 |
| 0.2 M NaCl (4600 ppm Na⁺) | 0.21[a] | $8.5 \cdot 10^{-13}$ | | 1870 |
| 0.5 M NaCl (13500 ppm Na⁺) | 0.11[a] 0.33[b] 0.198[c] | $4.5 \cdot 10^{-12}$ | $1.5 \cdot 10^{-9}$ | 1750 |
| 0.6 M NaCl (13800 ppm Na⁺) | 0.09[a] | $6.9 \cdot 10^{-13}$ | | 1980 |
| 1 M NaCl (23000 ppm Na⁺) | 0.073[a] | | | |
| 1.2 M NaCl (27600 ppm Na⁺) | 0.05[a] | $6.5 \cdot 10^{-13}$ | | 2030 |
| Groundwater, total salt = 10000 ppm | 0.393[a] | $6.1 \cdot 10^{-13}$ $1.0 \cdot 10^{-12}$ | | |

[a] Batch experiment
[b] Compacted sample
[c] From sample in diffusion experiment

*Cerium*

Sorption data for cerium in bentonite are given in a compilation of sorption data made by Oscarson et al. [1984]. $K_d$-values reported range from 0.3 to 2.0 m³/kg in bentonite saturated with a solution containing sodium, calcium, chloride and carbonate with an ionic strength of 0.0055 M and pH 8.5.

*Carbon*

A $K_d$-value of 0 for inorganic carbon ($HCO_3^-$) in Na-montmorillonite is given by Allard et al. [1981].

The effective diffusivity of dissolved $CH_4$ in bentonite saturated with synthetic groundwater of "Allard" type has been reported by Neretnieks et al. [1978b]. The bentonite was compacted to a density of 2350 $kg/m^3$, and the measurement was performed at 50°C. The effective diffusivity, $D_e$, was determined to $3.9 \cdot 10^{-11}$ $m^2/s$.

*Chloride*

Muurinen and co-workers [1987] have performed measurements of the sorption and diffusion of chloride in MX-80 bentonite. The bentonite was contacted with a synthetic groundwater (MS-9) with concentrations of the major components as follows: $Na^+ = 271.5$ ppm, $Ca^{2+} = 17.9$ ppm, $Cl^- = 70.5$ ppm, $HCO_3^- = 600$ ppm. No sorption of chloride was measured in the experiments. The apparent diffusivity, $D_a$, and the effective diffusivity, $D_e$, were independently determined from the experiments. The results are given in Table 10 together with results from diffusion measurements in MX-80 bentonite contacted with synthetic groundwater of "Allard" type [Eriksen et al., 1981]. This latter synthetic groundwater has lower concentrations of sodium and carbonate than the MS-9 water. Also in this experiment $D_a$ and $D_e$ were independently determined. The two investigations report similar values of the effective diffusivity, $D_e$, for the same wet density of the bentonite, while the apparent diffusivity, $D_a$, differs.

Kahr et al [1985] report values of the apparent diffusivity, $D_a$, in compacted MX-80 bentonite to be $1.2 \cdot 10^{-10}$ and $2.22 \cdot 10^{-10}$ $m^2/s$ for a water content in the sample of 20 and 31%, respectively.

Table 10  Diffusivity in compacted MX-80 bentonite contacted with synthetic groundwater.

| Density [kg/m³] | | $D_a$ [m²/s] | $D_e$ [m²/s] | Ref |
|---|---|---|---|---|
| Dry | Wet | | | |
| 1200 | 1750 | $1.5 \cdot 10^{-10}$ $2.0 \cdot 10^{-10}$ | $1.1 \cdot 10^{-11}$ | Muurinen et al., 1987 |
| 1500 | 1950 | $7.0 \cdot 10^{-11}$ $9.4 \cdot 10^{-11}$ | $2.8 \cdot 10^{-12}$ | |
| 1800 | 2100 | $5.1 \cdot 10^{-11}$ $5.2 \cdot 10^{-11}$ | $2.0 \cdot 10^{-13}$ | |
| 2100 | 2350 | $3.0 \cdot 10^{-11}$ | $8.5 \cdot 10^{-14}$ | |
| | 2100 | $6 \cdot 10^{-12}$ | $3.1 \cdot 10^{-13}$ | Eriksen et al., 1981 |

*Nickel*

Some $K_d$-values for nickel and Na-montmorillonite are reported by Oscarson et al. [1984]. The values are for pH ranging from 6.1 to 6.8 at various ionic strength of the solution, but are from different experimental investigations. At an ionic strength of 0.002 M $K_d$-values of 0.098 and 0.13 $m^3/kg$ are given. From another investigation $K_d$-values of 0.014 and 0.0013 $m^3/kg$ are given for an ionic strength in the solution of 0.3 and 1.0 M, respectively. These results indicate a dependence of the ionic strength on the sorption at pH below 6.8.

*Niobium*

In a compilation of sorption data for bentonite made by Oscarson et al. [1984], $K_d$-values are given for niobium and bentonite saturated with a synthetic groundwater with an ionic strength of 0.0055 M and a pH of 8.3-8.7. The reported values for a solution to solid ratio of 10 ml/g range from 0.18 to 0.51 m³/kg, and for a solution to solid ratio of 20 ml/g $K_d$-values from 0.51 to 1.7 m³/kg are reported.

*Americium*

Sorption and diffusivity data for americium and MX-80 bentonite, contacted with a synthetic groundwater of "Allard" type are given in Table 11. The results show high sorption of americium and consequently low apparent diffusivity, $D_a$. A higher carbonate concentration in the solution does not seem to give higher apparent diffusivity.

Table 11          Sorption and diffusivity data for americium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | $K_d$ [m³/kg] | $D_a$ [m²/s] | Density[1] [kg/m³] | Ref. |
|---|---|---|---|---|
| 25 | 6.2-6.6[a] | | | Allard et al., 1982 |
| 25 | | $4 \cdot 10^{-15}$ $1.4 \cdot 10^{-14}$ | 1900-2000 | Torstenfelt et al., 1982a |
| 25 | | $2.0 \cdot 10^{-15}$ $7.3 \cdot 10^{-15}$ $2.8 \cdot 10^{-15[*]}$ $9.5 \cdot 10^{-15[*]}$ | 1900-2300 | Torstenfelt et al., 1983 |
| 20 | | $1.3 \cdot 10^{-14}$ $2.8 \cdot 10^{-16[*]}$ | 2000 | Torstenfelt et al., 1986 |

[1] Probably dry density          [a] Batch experiment
[*] 600 ppm $HCO_3^-$ added to the solution

$K_d$-values for americium and montmorillonite reported by Releya [NEA sorption data base] range from 0.23 to 53.1 m³/kg for a solution to solid ratio of 30 ml/g. The highest values were obtained when the montmorillonite was contacted with a solution containing low concentrations of chloride (43 ppm) and high concentrations of carbonate (1216 ppm). The cation in solution was sodium (652 ppm) and pH ranged from 7 to 9. The lowest $K_d$-values, less than 2.5 m³/kg, were obtained when a solution containing mainly chloride (916 ppm) and calcium (537 ppm) was used in the experiment.

In the compilation of sorption data for bentonite made by Oscarson et al. [1984], $K_d$-values for americium in the system montmorillonite and groundwater are reported as 0.16 m³/kg at pH 5 and pH 8, and 1.4 and 9.2 m³/kg at pH 9.9 in Na-montmorillonite and Ca-montmorillonite, respectively.

Morgan and co-workers [1987] have measured the sorption of americium onto Wyoming bentonite contacted with demineralised water. For a liquid to solid ratio of 100 ml/g a $K_d$-value of 2.1 $m^3/kg$ is given.

*Plutonium*

Sorption and diffusivity data for plutonium and MX-80 bentonite, contacted with synthetic groundwater of "Allard" type are given in Table 12. In one diffusion measurement a fraction of the plutonium was found to move faster in the bentonite. The evaluated apparent diffusivity for this fraction is orders of magnitude higher than the values evaluated from the other experiments. In another of the diffusion experiments solid FeO was added to the bentonite. The lower diffusivity evaluated from this experiment compared to the others is, according to the authors, probably not caused by the addition of Fe(II).

Table 12    Sorption and diffusivity data for plutonium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | $K_d$ [$m^3/kg$] | $D_a$ [$m^2/s$] | Density[1] [$kg/m^3$] | Ref. |
|---|---|---|---|---|
| 25 | 3.5[*] | | | Allard et al., 1982 |
| 20 | | $6.9 \cdot 10^{-15}$ $3.0 \cdot 10^{-14}$ | 1900-2000 | Torstenfelt et al., 1982a |
| 20 | | $3.2 \cdot 10^{-15}$ $8.6 \cdot 10^{-15}$ | 1900-2300 | Torstenfelt et al., 1983 |
| 20 | | $3.2 \cdot 10^{-12*)}$ $1.9 \cdot 10^{-15}$ | 2000 | Torstenfelt et al., 1986 |
| 20 | | $3 \cdot 10^{-16**)}$ | 2000 | Albinsson et al., 1990 |

[1] Probably dry density    [*] A small fraction of the plutonium
[*] Batch experiment    [**] FeO added + nitrogen atmosphere, Pu(IV)

Idemitsu et al. [1989] have reported results from measurements of plutonium diffusivity in Na-bentonite contacted with distilled water and compacted to a density between 1200 to 1800 $kg/m^3$. When the experiment was terminated almost no movement of plutonium was detected. The apparent diffusivity, $D_a$, was estimated to be less than $10^{-14}$ $m^2/s$.

$K_d$-values for plutonium and montmorillonite, measured by Releya [NEA sorption data base], range from 0.58 to 11.5 $m^3/kg$ (one measurement gave 20 $m^3/kg$). The solutions contained sodium, calcium, chloride and carbonate with different concentrations, and pH ranged from 7 to 9. No obvious correlation between the composition of the solution and the measured $K_d$-value can be seen.

Morgan and co-workers [1987] have measured sorption of plutonium onto Wyoming bentonite contacted with demineralised water. For a liquid to solid ratio of 50 ml/g a $K_d$-value of 5.4 $m^3/kg$ is given.

*Neptunium*

Sorption and diffusivity data for neptunium and MX-80 bentonite, contacted with synthetic groundwater of "Allard" type are given in Table 13. Addition of Fe to the bentonite results in a decrease of the apparent diffusivity, $D_a$. Addition of Fe in combination with performing the experiment in a nitrogen atmosphere gives the lowest apparent diffusivity [Albinsson et al., 1990].

Table 13      Sorption and diffusivity data for neptunium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | $K_d$ [m³/kg] | $D_a$ [m²/s] | Density[1] [kg/m³] | Ref. |
|---|---|---|---|---|
| 25 | 0.05[a]<br>0.12[b] | | | Allard et al., 1982 |
| 20 | | $2.2 \cdot 10^{-13}$<br>$3.7 \cdot 10^{-13}$ | 1900-<br>2000 | Torstenfelt et al., 1982a |
| 20 | 5.0[c] | $4.5 \cdot 10^{-15c)}$<br>$1.6 \cdot 10^{-14c)}$ | 1900-<br>2300 | Torstenfelt et al., 1983 |
| 20 | | $8.2 \cdot 10^{-13}$<br>$4.2 \cdot 10^{-14c)}$<br>$2.1 \cdot 10^{-14d)}$ | 2000 | Torstenfelt et al., 1986 |
| 20 | | $9.2 \cdot 10^{-16e)}$ | 2000 | Albinsson et al., 1990 |

[1] Probably dry density      [c] 0.5% Fe(s) added to bentonite
[a] Batch, initial Np concentration $1.9 \cdot 10^{-7}$ M    [d] 1% $Fe_3(PO_4)_2(s)$ added to bentonite
[b] Batch, initial Np concentration $1.9 \cdot 10^{-9}$ M    [e] Fe added + nitrogen atmosphere, Np(IV)

$K_d$-values for neptunium and montmorillonite in NaCl solutions under oxidising conditions, given in the compilation of sorption data made by Oscarson et al. [1984], are 0.017 m³/kg at an ionic strength of 0.03 M and 0.09 m³/kg at an ionic strength of 5.1 M.

Releya [NEA sorption data base] have measured $K_d$-values under oxidising conditions in montmorillonite and obtained values ranging from 0.006 to 0.07 m³/kg. The lowest values were obtained when the montmorillonite was saturated with a solution containing high carbonate concentrations (1216 ppm) and low chloride concentrations (43 ppm).

Morgan et al. [1987] have reported $K_d$-values for neptunium in Wyoming bentonite contacted with demineralised water. For a liquid to solid ratio of 50 ml/g a value of 1.6 m³/kg is given.

*Uranium*

Sorption and diffusivity data for uranium and MX-80 bentonite contacted with synthetic groundwater of "Allard" type are given in Table 14. In some of the experiments [Torstenfelt

et al., 1986] a fast moving fraction was identified with apparent diffusivity about an order of magnitude larger than the rest of the uranium. Higher carbonate concentration in the solution does not significantly effect the diffusivity. In experiments where Fe was added to the bentonite and the experiment was performed in nitrogen atmosphere [Albinsson et al., 1990] lower diffusivities were measured.

Table 14      Sorption and diffusivity data for uranium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | $K_d$ [m³/kg] | $D_a$ [m²/s] | Density[1] [kg/m³] | Ref. |
|---|---|---|---|---|
| 25 | 0.093[a] | | | Allard et al., 1982 |
| 20 | | $5.8 \cdot 10^{-13}$ $3.4 \cdot 10^{-13[b]}$ $1.1 \cdot 10^{-13[c]}$ | 1900- 2000 | Torstenfelt et al., 1982a |
| 20 | | $8.2 \cdot 10^{-13}$ $1.9 \cdot 10^{-13[b]}$ $4.5 \cdot 10^{-14[c]}$ | 1900- 2300 | Torstenfelt et al., 1983 |
| 20 | | $3.4 \cdot 10^{-12}$ $6.4 \cdot 10^{-13}$ $8.5 \cdot 10^{-12[b]}$ $2.3 \cdot 10^{-13[b]}$ $8.3 \cdot 10^{-14[b]}$ $3.3 \cdot 10^{-11[c]}$ $1.6 \cdot 10^{-13[c]}$ | 2000 | Torstenfelt et al., 1986 |
| 20 | | $1.2 \cdot 10^{-14[d]}$ $2.8 \cdot 10^{-14[d]}$ | 2000 | Albinsson et al., 1990 |

[1] Probably dry density
[a] Batch experiment
[b] 600 ppm $HCO_3^-$ in solution
[c] 0.5% Fe(s) added to bentonite
[d] Fe added + nitrogen atmosphere, U(IV)

Muurinen and co-workers [1987] have measured sorption and diffusion of uranium in MX-80 bentonite saturated with synthetic groundwater under oxidising conditions. They concluded that there is no sorption at pH of 8 to 9 and initial concentrations of uranium above 0.05 ppm. The independently evaluated apparent diffusivity, $D_a$, and effective diffusivity, $D_e$, from the experiments are given in Table 15.

The apparent diffusivity of uranium in MX-80 bentonite under oxidising conditions and different water content in the bentonite are reported by Kahr et al. [1985]. They determined the apparent diffusivity, $D_a$, to be from $4.0 \cdot 10^{-15}$ m²/s at a water content of 7% to $3.56 \cdot 10^{-14}$ m²/s at a water content of 20%

Ames et al. [1983a] measured the sorption of uranium onto montmorillonite in 0.01 M NaCl-and 0.01 M $NaHCO_3$-solutions under oxidising conditions. For an initial uranium concentration of $10^{-4}$ M in 0.01 M NaCl a $K_d$ of 0.36 m³/kg was obtained. Decreasing the initial uranium concentration to $3.5 \cdot 10^{-7}$ M increased $K_d$ to 0.53 m³/kg. Corresponding $K_d$-

values for uranium in 0.01 M NaHCO$_3$-solution was found to be 0.086 m$^3$/kg for the high initial uranium concentration and 0.068 m$^3$/kg for the low initial uranium concentration.

Table 15      Diffusivity of uranium (UO$_2$(NO$_3$)$_2$) in MX-80 bentonite contacted with synthetic groundwater, oxidising conditions [Muurinen et al., 1987]

| Dry density [kg/m$^3$] | Wet density [kg/m$^3$] | D$_a$ [m$^2$/s] | D$_e$ [m$^2$/s] |
|---|---|---|---|
| 900 | 1480 | 8.4·10$^{-13}$ 3.8·10$^{-12}$ | 2.1·10$^{-12}$ |
| 1140 | 1660 | 1.6·10$^{-12}$ | 4.9·10$^{-13}$ |
| 1240 | 1680 | 1.2·10$^{-13a)}$ | 6.0·10$^{-14a)}$ |
| 1560 | 1960 | 4.3·10$^{-14}$ | |

$^{a)}$ UO$_2$Cl$_2$ added as tracer

Morgan et al. [1987] have reported K$_d$-values for uranium under oxidising conditions in Wyoming bentonite contacted with demineralised water. For a liquid to solid ratio of 50 ml/g a value of 0.046 m$^3$/kg is given.

*Protactinium*

Sorption and diffusivity data for protactinium and MX-80 bentonite, contacted with synthetic groundwater of "Allard" type are given in Table 16. The determined apparent diffusivity, D$_a$, is high considering the high sorption of protactinium onto bentonite.

Table 16      Sorption and diffusivity data for protactinium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | K$_d$ [m$^3$/kg] | D$_a$ [m$^2$/s] | Density[1] [kg/m$^3$] | Ref. |
|---|---|---|---|---|
| 25 | 5.0$^{a)}$ | | | Allard et al., 1982 |
| 20 | | 6.0·10$^{-13}$ | 1900-2000 | Torstenfelt et al., 1982a |
| 20 | | 6.2·10$^{-13}$ | 2000 | Torstenfelt et al., 1986 |

[1] Probably dry density      $^{a)}$ Batch experiment

*Thorium*

Sorption and diffusivity data for thorium and MX-80 bentonite, contacted with synthetic groundwater of "Allard" type are given in Table 17.

Kahr et al. [1985] report values of the apparent diffusivity, $D_a$, of thorium in compacted MX-80 bentonite under oxidising conditions to be $2.01 \cdot 10^{-14}$ $m^2/s$ for a water content of 20% in the bentonite, and $9.76 \cdot 10^{-14}$ $m^2/s$ for a water content of 30%.

Table 17      Sorption and diffusivity data for thorium in bentonite contacted with a synthetic groundwater with pH=8.2, total salt=306 ppm, total carbonate=123 ppm, ionic strength 0.0082 M. Oxidising conditions.

| Temp [°C] | $K_d$ [m³/kg] | $D_a$ [m²/s] | Density[1] [kg/m³] | Ref. |
|---|---|---|---|---|
| 25 | > 6.3[a] | | | Allard et al., 1982 |
| 20 | | $4.6 \cdot 10^{-15}$ $8.5 \cdot 10^{-15}$ | 1900- 2000 | Torstenfelt et al., 1982a |
| 20 | | $7.7 \cdot 10^{-15}$ | 2000 | Torstenfelt et al., 1986 |

[1] Probably dry density      [a] Batch experiment

## Radium

Ames and co-workers [1983b] have measured sorption of radium on montmorillonite in 0.01 M NaCl solutions. For a liquid to solid ratio of 20 ml/g and an initial radium concentration of about $10^{-9}$ to $10^{-7}$ M a $K_d$-value of 3.1 to 3.7 m³/kg was obtained at 25°C.

## Lead

A $K_d$-value for lead and Na-bentonite has been found in the compilation made by Oscarson et al., [1984]. From a measurement in a $NH_4NO_3$-solution at pH 5 a $K_d$ of 1 m³/kg is reported.

### 3.3      Porosity and diffusivity data for Finnsjö rock

The search in the literature for porosity and diffusivity data has been focussed on studies of rock from Finnsjön. A large number of experiments with non-sorbing tracers in Finnsjö granite have been performed, and results from these experiments are compiled below. Some results from experiments with sorbing species are also given, but no big effort has been made to find experimental data for all the elements of interest. The results compiled are all from experiments performed in rock samples in the laboratory. Diffusion experiments performed in a field-scale in the Stripa mine [Birgersson and Neretnieks, 1990] and in the laboratory in rock samples under mechanical stress [Skagius 1986], show that results from laboratory experiments are representative for field conditions.

The porosity of rock samples from Finnsjön has been measured by Öqvist and Jämtlid [1984]. The samples were from borehole Fi8 at depths ranging from 105.8 to 461.5 m. the porosity was estimated from the difference in weight between the sample dry and the sample saturated with water. This method will give the sum of the diffusion porosity and the storage porosity (see 2.1). The porosity of the samples ranged from 0.12 to 0.83%. Reported mean values of the porosity for each rock type are:

| Aplitegranite | 0.55% | Granodiorite | 0.23% |
| Gneissgranite | 0.12% | Granite | 0.50% |
| Gneiss | 0.23% | | |

Experimental studies of diffusion in rock materials also often include measurement of the porosity of the rock material. Data on the porosity and the diffusivity will therefore both be given in the following presentation, which is separated in two parts, diffusion experiments with non-sorbing species and diffusion experiments with sorbing species.

*Non-sorbing species*

The diffusivity of iodine in rock samples from Finnsjön has been studied by Skagius [1986], Ittner and co-workers [1988] and Gidlund and co-workers [1990]. Skagius [1986] has reported values of the effective diffusivity, $D_e$, and values of the porosity for granite samples with and without fissure coating materials. The samples were from boreholes Fi4, Fi5, Fi7 and Fi8, taken at depths between 72 and 362 m. Gidlund et al. [1990] have reported values of the effective diffusivity, $D_e$, and the porosity in samples from boreholes Fi6 and Fi11 where these holes intersect a fracture zone (Zone 2). Ittner et al [1988] give a value of the apparent diffusivity, $D_a$, for iodine in a granodiorite sample from the Finnsjön area. A summary of the reported results from the above mentioned investigations is given in Table 18.

Table 18      Summary of reported diffusivity and porosity data for rock samples from the Finnsjön area.

| Rock | $D_a$ [m$^2$/s] | $D_e$ [m$^2$/s] | $\varepsilon$ [%] | Ref |
|---|---|---|---|---|
| Granite | | $7.0 \cdot 10^{-14}$ to $4.4 \cdot 10^{-13}$ | 0.2 to 0.6 | Skagius, 1986 |
| Granite + fissure coating | | $3.0 \cdot 10^{-14}$ to $2.0 \cdot 10^{-11}$ | 1.1 to 7.4 | Skagius, 1986 |
| Tectonite | | $1.2 \cdot 10^{-13}$ to $4.3 \cdot 10^{-12}$ | 0.9 to 8.0 | Gidlund et al., 1990 |
| Granodiorite | | $2.8 \cdot 10^{-15}$ to $1.7 \cdot 10^{-12}$ | 0.2 to 3.1 | Gidlund et al., 1990 |
| Aplite (calcite) | | $6.6 \cdot 10^{-14}$ to $2.4 \cdot 10^{-12}$ | 0.3 to 4.5 | Gidlund et al., 1990 |
| Granodiorite | $1.9 \cdot 10^{-14}$ | | | Ittner et al.. 1988 |

The frequency distribution of the reported values of the effective diffusivity, $D_e$, and the porosity is shown in Figures 1 and 2, respectively. From Figure 1 it can be seen that the majority of the $D_e$-values lie in the range $1.0 \cdot 10^{-13}$ to $3.2 \cdot 10^{-13}$ m$^2$/s (log $D_e$ = -13 to -12.5). Figure 2 shows that most of the porosity values reported are below 0.5 %.

The porosity values reported are determined from the difference in wet and dry weight of the samples. This method gives the sum of diffusion porosity and storage porosity. If it is

assumed that the storage porosity is negligible compared to the diffusion porosity, the pore diffusivity, $D_p$, is given by the ratio of the effective diffusivity of the non-sorbing iodine and the porosity. The frequency distribution of the pore diffusivity ($D_p$), calculated from the reported values of the effective diffusivity ($D_e$) and the porosity, is shown in Figure 3. The major part of the data results in a pore diffusivity, $D_p$, in the interval $10^{-11}$ to $10^{-10}$ m$^2$/s.

The apparent diffusivity, $D_a$, of the granodiorite sample (Table 18) is equal to the pore diffusivity, $D_p$, with the same assumption as above; that the storage porosity is negligible compared to the diffusion porosity. The value is lower than the $D_p$-values in Figure 3.

Skagius [1986] and Gidlund [1990] have also reported results from measurements of the diffusivity of Uranin (Na-fluorescein) in rock samples from Finnsjön. In both studies, lower values of the effective diffusivity, $D_e$, were obtained using Uranin as a tracer.

Under oxidising conditions no sorption of technetium onto rock material is expected. Torstenfelt et al [1982b] have reported an effective diffusivity, $D_e$, for technetium in Finnsjö granite of $1.5(\pm 0.8) \cdot 10^{-12}$ m$^2$/s. This value lies in the upper range of the effective diffusivity values reported for iodine (see Figure 1).

Ittner and co-workers [1988] have measured the diffusivity of technetium in samples from boreholes Fi6, Fi7 and Fi8 in the Finnsjön area. The result is presented as an apparent diffusivity, $D_a$, which is equal to the pore diffusivity, $D_p$, assuming that the storage porosity is small compared to the diffusion porosity. The reported values range from $2.2 \cdot 10^{-14}$ to $3.0 \cdot 10^{-13}$ m$^2$/s, which is lower than the $D_p$-values from the iodine diffusion measurements depicted in Figure 3.
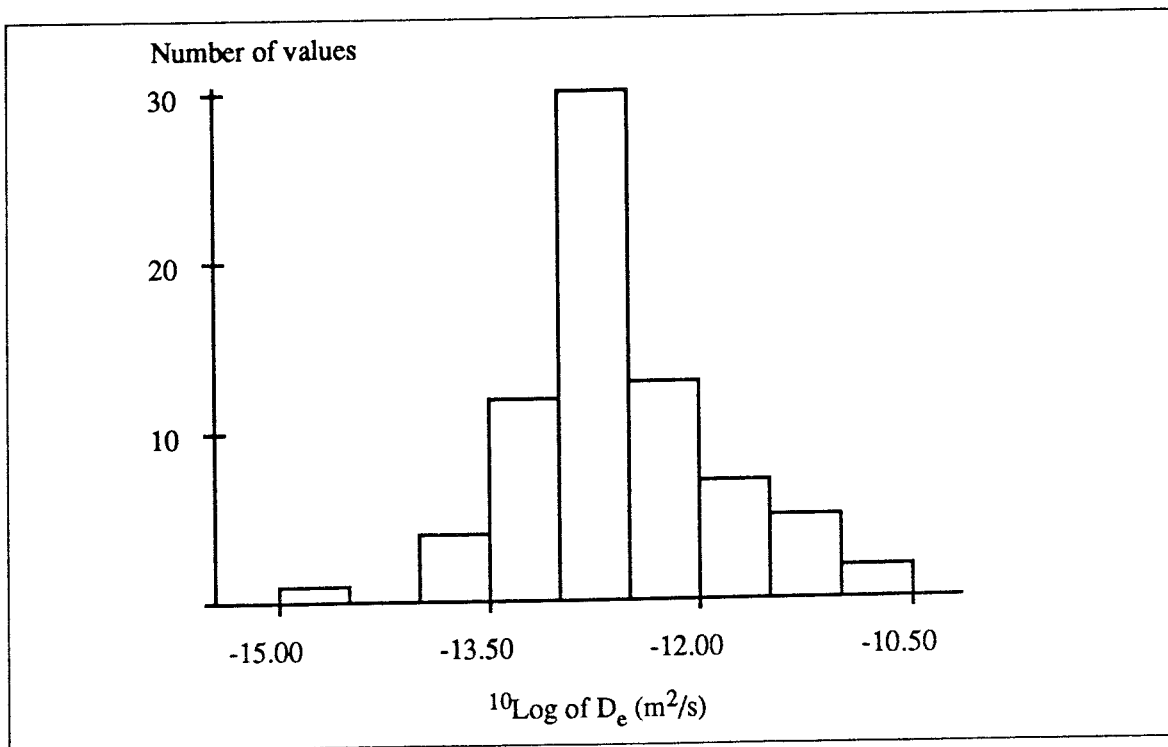


Figure 1 Frequency distribution of the logarithm of the effective diffusivity in Finnsjö rock. From iodide diffusion experiments.
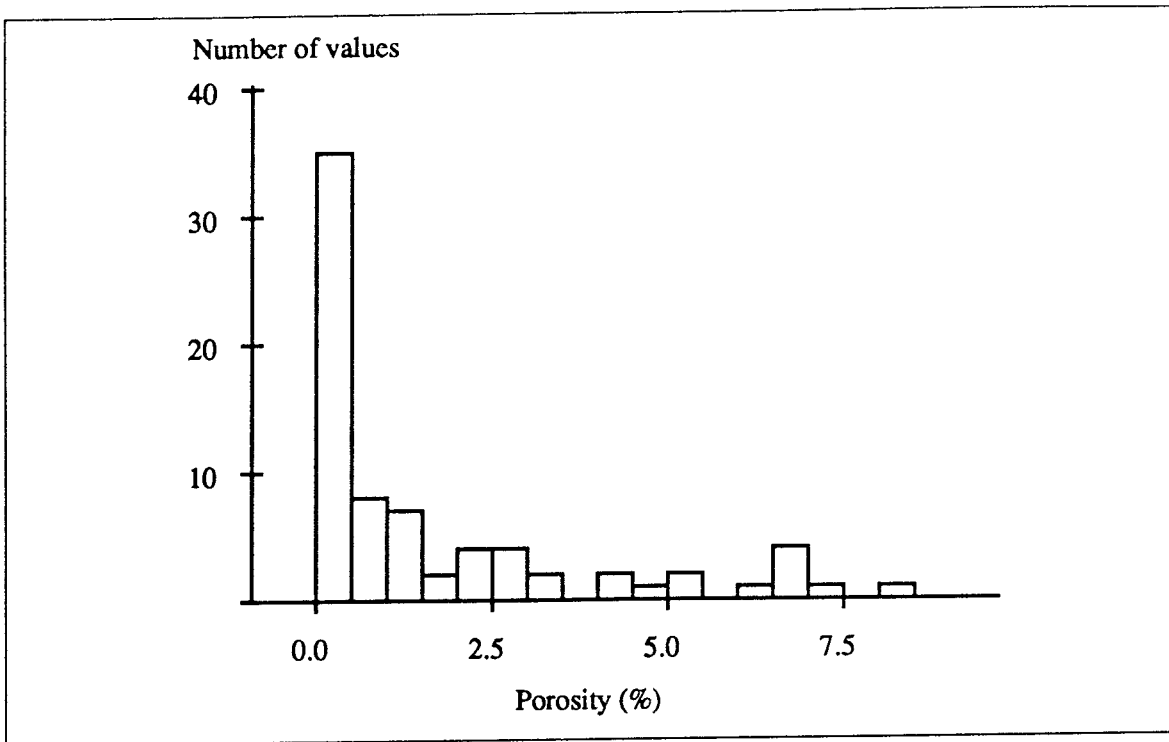
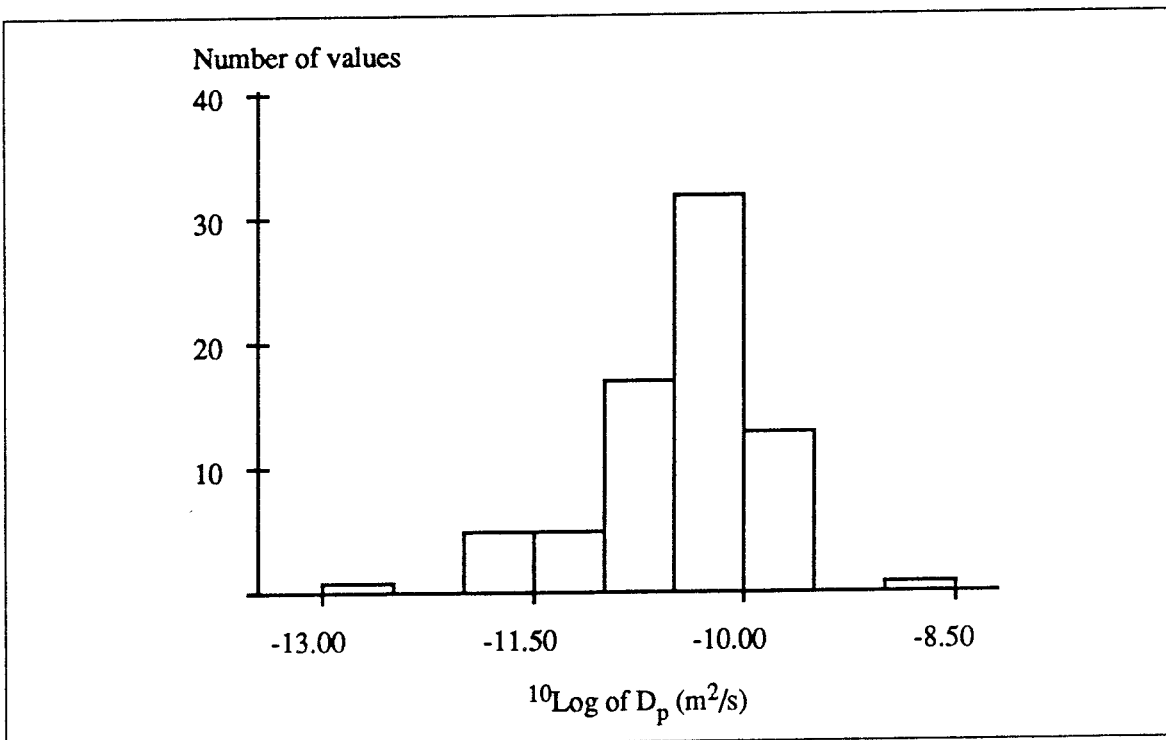Figure 2 Frequency distribution of matrix porosity in rock samples from Finnsjön.



Figure 3 Frequency distribution of the logarithm of pore diffusivity in rock from Finnsjön. From measured effective diffusivities and porosities.

*Sorbing species*

Skagius [1986] has measured the diffusion of strontium and cesium in granite samples from Finnsjön. The determined effective diffusivities were $2.2 \cdot 10^{-12}$ and $1.6 \cdot 10^{-12}$ m$^2$/s for strontium and cesium, respectively. These values lies in the upper range of the D$_e$-values reported from iodine diffusion experiments (Figure 1).

An effective diffusivity of $2.7(\pm 1.3) \cdot 10^{-10}$ m$^2$/s for cesium in Finnsjö granite is given by Torstenfelt et al [1982b]. This value is about one order of a magnitude higher than the highest value obtained in experiments with iodine diffusion.

Ittner and co-workers [1988] have measured the diffusion of strontium, cesium, neptunium plutonium and americium in rock samples from Finnsjön under oxidising conditions. The result is reported as apparent diffusivities. To be able to compare the result from this investigation with the results from the diffusion measurements with iodine, the relation between the apparent diffusivity and the effective diffusivity (see Eq.7) is used to calculate the effective diffusivity, D$_e$. K$_d$-values used are proposed by Allard for SKB 91 [Allard, 1991]. The result is shown in Table 19. All the calculated values of the effective diffusivity, D$_e$, lies in the upper range of the values reported for iodine diffusion in Finnsjö granite.

| Table 19 | Reported apparent diffusivities in Finnsjö granite [Ittner et al., 1988] and calculated effective diffusivities using sorption data according to Allard [1991]. |
|---|---|

| Nuclide | D$_a$ [m$^2$/s] | K$_d$ [m$^3$/kg] | D$_e$ [m$^2$/s] |
|---|---|---|---|
| $^{90}$Sr | $4.9 \cdot 10^{-13}$ | 0.05 | $6.6 \cdot 10^{-11}$ |
| $^{137}$Cs | $5.0 \cdot 10^{-12}$ | 0.05 | $6.8 \cdot 10^{-10}$ |
| | $1.2 \cdot 10^{-13}$ | | $1.6 \cdot 10^{-11}$ |
| | $2.2 \cdot 10^{-13}$ | | $3.0 \cdot 10^{-11}$ |
| | $8.3 \cdot 10^{-14}$ | | $1.1 \cdot 10^{-11}$ |
| | $1.4 \cdot 10^{-13}$ | | $1.9 \cdot 10^{-11}$ |
| $^{237}$Np | $3.3 \cdot 10^{-15}$ | 0.01 | $8.9 \cdot 10^{-14}$ |
| $^{239}$Pu | $1.6 \cdot 10^{-15}$ | 3.0 | $1.3 \cdot 10^{-11}$ |
| $^{241}$Am | $2.3 \cdot 10^{-14}$ | 3.0 | $1.9 \cdot 10^{-10}$ |
| | $2.8 \cdot 10^{-14}$ | | $2.3 \cdot 10^{-10}$ |
| | $3.9 \cdot 10^{-16}$ | | $3.2 \cdot 10^{-12}$ |

# 4. Data proposed for SKB 91

## 4.1 Bentonite

The groundwater-bentonite system is chemically and physically complex which means that experimentally determined data for the system are very dependent on the conditions prevailing during the experiment. Extrapolations to other conditions are difficult and may involve large uncertainties. Another uncertainty lies in the time-scale. Experimental data are from short-time experiments while the data used in a safety analysis should be relevant for very long time periods. It must therefore be pointed out that the estimates proposed in the following sections are best estimates based on the information found in the literature which in some cases is very limited.

### 4.1.1 Sorption data

In Table 20 a best estimate and a conservative $K_d$-value is proposed for the elements earlier specified. It should be noted that no consideration is taken to any presence of humic substances in the bentonite pore water. The values proposed are motivated below.

*Selenium*

In the bentonite pore water selenium will probably exist as an anion, and no or very little sorption should be expected. Based on experimental results a $K_d$-value of 0.003 m³/kg is proposed as a best estimate. As a conservative value 0 is proposed, in analogy with other anions such as $I^-$ and $TcO_4^-$.

*Strontium*

Strontium will prevail as $Sr^{2+}$ in the pore water, and the sorption mechanism is ion exchange. In fresh water with low concentrations of competing ions such as $Ca^{2+}$ and $Na^+$ a $K_d$-value of 0.5 m³/kg is proposed as a best estimate. Higher values have been measured in batch experiments and in compacted samples without any $Ca^{2+}$ present in the solution. The value proposed is about the same as has been measured in a compacted sample contacted with synthetic groundwater [Eriksen et al., 1981]. As a conservative value a five times lower $K_d$ is proposed.

In saline water with high concentrations of particularly $Ca^{2+}$, sorption of $Sr^{2+}$ will be reduced due to competition between these two divalent cations. A best estimate value of 0.01 m³/kg is proposed. This is lower than experimentally determined values in NaCl-solutions. It is also somewhat lower than what has been measured in a solution containing a lower $Ca^{2+}$-concentration than in the SKB 91 saline reference water. As a conservative value 0.001 m³/kg is proposed.

*Zirconium*

Zirconium is tetravalent and hydrolysed in the pH-range of the bentonite pore water. A strong sorption is therefore expected. Experimental data on bentonite/quartz (10/90) mixtures resulted in $K_d$-values up to 1 m³/kg. The value for pure bentonite would probably be higher.

A $K_d$-value of 2 m³/kg is therefore proposed as a best estimate, and 0.2 m³/kg as a conservative value.

## Technetium

Under oxidising conditions technetium prevails as $TcO_4^-$ and very little or no sorption is expected. A $K_d$-value of 0 is therefore proposed.

Under neutral to weak alkaline and reducing conditions the dominating species is an oxyhydroxide according to Bruno and Selin [1991] and sorption will occur. Differences in measured apparent diffusivities under oxidising and reducing conditions indicate a $K_d$-value of 1 m³/kg. A measured $K_d$ under reducing conditions is reported to be 0.05 m³/kg. Based on this limited information a best estimate of 0.1 m³/kg is proposed, and a conservative value of 0.01 m³/kg.

## Palladium

No experimental data on sorption of palladium have been found. Palladium will probably be present in the fresh reference water as a neutral hydroxide complex. In saline water also negatively charged chloride complexes can be formed. If hydroxide complexes dominate, sorption is to be expected. Due to the lack of experimental data and the fact that palladium could be present as anionic complexes a $K_d$-value of 0.01 m³/kg is proposed as a best estimate but conservatively no sorption is proposed.

## Tin

According to Table 2, tin will be hydrolysed in the reference waters. In analogy with thorium a best estimate of 3 m³/kg is proposed. Due to the lack of relevant experimental data a conservative value of 0.01 m³/kg is proposed.

## Iodine

Iodine is present as an anion in the reference waters and will most probably not sorb on the bentonite. A $K_d$-value of 0 is therefore proposed.

## Cesium

Cesium sorption on bentonite will be by ion exchange. In the SKB 91 fresh water with small amounts of competing cations a best estimate of 1 m³/kg is proposed for low cesium concentrations. As a conservative value 0.2 m³/kg is proposed.

In saline water less sorption will occur, and a best estimate of 0.05 m³/kg is proposed and as a conservative value 0.005 m³/kg.

*Cerium*

Cerium will probably be hydrolysed in the bentonite pore water and thus strongly sorbed onto the material. Based on experimental results a $K_d$ of 1 $m^3/kg$ is proposed as a best estimate. As a conservative value 0.2 $m^3/kg$ is proposed.

*Samarium*

No data on samarium have been found, but it is chemically similar to cerium. The same $K_d$-values as for cerium is therefore proposed.

*Carbon*

Sorption of both inorganic and organic carbon are expected to be very low and a $K_d$-value of 0 is proposed.

*Chloride*

Chloride is an anion in the waters and based on experimental data a $K_d$-value of 0 is proposed.

*Nickel*

Experimental data on nickel sorption are sparse. Data only at pH 6.8 and below have been found and they indicate a $K_d$ of 0.1 $m^3/kg$. Since nickel forms strongly sorbing hydroxide complexes at higher pH this value may be too low. However, nickel has a chemistry similar to cobalt. $K_d$-values for cobalt and montmorillonite have been reported in Anderson et al. [1983] to range from 0.1 to 3.2 $m^3/kg$ at pH 7 - 9. Muurinen et al. [1985] have reported $K_d$-values of 3.74 $m^3/kg$ for cobalt and bentonite, contacted with a synthetic groundwater with a total salt content of 10 g/l. Based on the experimental data on nickel and cobalt sorption a $K_d$-value of 0.5 $m^3/kg$ is proposed as a best estimate, and 0.1 $m^3/kg$ as a conservative value.

*Niobium*

Niobium will probably be hydrolysed in the reference waters. Based on experimental data a best estimate $K_d$ of 0.2 $m^3/kg$ is proposed. A conservative value of 0 is proposed because niobium may form anionic species such as $NbO_4^{3-}$ and $NbO_3^-$ [KBS-3, 1983].

*Americium*

Americium will exist as a cation and a positively charged carbonate complex in the pore water in the bentonite and will thus strongly sorb. Experimental data span over a wide range. Most of the $K_d$-data lies in the interval 1 to 7 $m^3/kg$ and a best estimate value of 3 $m^3/kg$ is proposed. As a conservative value 1 $m^3/kg$ is proposed.

*Plutonium*

As for americium, plutonium will be positively charged both in the saline and in the fresh reference waters. Plutonium is redox sensitive, but no major difference in sorption is expected between the two oxidation stages. Experimental data range from 0.6 to about 11 $m^3$/kg. As a best estimate the same $K_d$-value as for americium is proposed, 3 $m^3$/kg. Conservatively, a $K_d$-value of 1 $m^3$/kg is proposed.

*Neptunium*

Experimental data for oxidising conditions indicate a somewhat lower $K_d$ for systems with high carbonate concentrations. This is probably due to the formation of negatively charged carbonate complexes. In both reference waters the positively charged $NpO_2^+$ complex will also be present so the same $K_d$-value of 0.05 $m^3$/kg is proposed as a best estimate for both fresh and saline waters. As a conservative value for both water systems $K_d = 0.005$ $m^3$/kg is proposed.

Under reducing conditions the neutral tetrahydroxide is expected to dominate, which leads to a strong sorption. Experimental data on sorption under reducing conditions is sparse, but a value of 5 $m^3$/kg has been reported. Due to the very limited experimental information a $K_d$ of 3 $m^3$/kg is proposed as a best estimate. Conservatively, a $K_d$ of 0.1 $m^3$/kg is proposed.

*Uranium*

Under oxidising conditions uranium is present as negatively charged carbonate complexes. A low sorption is thus expected. Based on experimental data a $K_d$ of 0.05 is proposed as a best estimate. As a conservative value 0.005 $m^3$/kg is proposed.

Under reducing conditions the neutral tetrahydroxide dominates and the same $K_d$-values as for neptunium are proposed.

*Protactinium*

Protactinium is probably pentavalent under oxidising and tetravalent under reducing conditions, and is likely hydrolysed in the reference waters. Strong sorption is therefore expected and is supported by one experimental value of 5 $m^3$/kg. Due to the very limited experimental information a best estimate $K_d$ of 3 $m^3$/kg is proposed, and a conservative value of 0.1 $m^3$/kg.

*Thorium*

Thorium will be hydrolysed in both reference waters and will thus strongly sorb on the bentonite. This is supported by experimental data. A best estimate of 3 $m^3$/kg is proposed and a conservative value of 0.1 $m^3$/kg.

*Radium*

Radium will exist as $Ra^{2+}$ in the two reference waters. A $K_d$ of 3 m³/kg has been reported from an experiment in a NaCl-solution. Since ion exchange is the sorption mechanism, the presence of competing $Ca^{2+}$ ions will probably result in lower $K_d$-values. Since the chemistry of radium is similar to that of strontium the same values as for strontium is proposed.

*Radon*

Radon is a noble gas and is not expected to sorb.

*Lead*

One experimental $K_d$-value of 1 m³/kg has been found in the literature. Because of this limited experimental back up a $K_d$ of 0.5 m³/kg is proposed as a best estimate. Because lead probably will form carbonate and chloride complexes in the reference waters, which may be anionic, a conservative value of 0 is proposed.

## 4.1.2 Diffusivity and porosity data

The proposed effective diffusivity, $D_e$, pore diffusivity, $D_p$, and diffusion porosity $\varepsilon_p$ for the elements in MX-80 bentonite compacted to a density of 2000 kg/m³ are given in Table 21. The values of the effective diffusivity, $D_e$, are based on experimentally determined apparent diffusivity values, $D_a$, and the best estimate $K_d$-values given in Table 20.

The same diffusivity values are proposed for both the saline and the fresh reference waters. The difference in diffusivity of the elements between these waters is probably smaller than the uncertainty in the proposed values.

For the majority of the elements an effective diffusivity of $1 \cdot 10^{-10}$ m²/s is proposed. For plutonium the proposed effective diffusivity and best estimate $K_d$-value (Table 20) will result in an apparent diffusivity, $D_a$, of $2 \cdot 10^{-14}$ m²/s. This value is more than one order of magnitude higher than most of the experimentally determined apparent diffusivities of plutonium. For the transient phase of the diffusion it is therefore proposed to assume an apparent diffusivity, $D_a$, of $1 \cdot 10^{-15}$ m²/s. For stationary diffusion of plutonium the diffusivity and porosity values in Table 21 are proposed.

For the elements strontium, cesium and protactinium, high diffusion rates have been experimentally measured despite that they sorb onto the bentonite material. This fast transport can be due to an additional transport mechanism, surface diffusion [Muurinen et al., 1985, 1986]. If this is the case, a separate surface diffusivity should be considered for these elements. To make it more simple it is here proposed that a higher value of the effective diffusivity is used instead to compensate for effects of additional transport mechanisms. This leads to an effective diffusivity, $D_e$, that is higher than the diffusivity in unconfined fluid. It should, however, be pointed out that it may not be strictly correct to do this simplification.

No experimental diffusivity data are available for radium. Due to the chemical similarity between radium and strontium, the same effective diffusivity as for strontium is proposed for radium.

Table 20      Proposed $K_d$-values [$m^3$/kg] for bentonite and fresh and saline waters. Best estimate value, conservative value.

| Element | Fresh water | | Saline water | |
| --- | --- | --- | --- | --- |
| | Oxidising | Reducing | Oxidising | Reducing |
| Am | 3, 1 | 3, 1 | 3, 1 | 3, 1 |
| C (org.+ inorg.) | 0 | 0 | 0 | 0 |
| Ce | 1, 0.2 | 1, 0.2 | 1, 0.2 | 1, 0.2 |
| Cl | 0 | 0 | 0 | 0 |
| Cs | 1, 0.2 | 1, 0.2 | 0.05, 0.005 | 0.05, 0.005 |
| I | 0 | 0 | 0 | 0 |
| Nb | 0.2, 0 | 0.2, 0 | 0.2, 0 | 0.2, 0 |
| Ni | 0.5, 0.1 | 0.5, 0.1 | 0.5, 0.1 | 0.5, 0.1 |
| Np | 0.05, 0.005 | 3, 0.1 | 0.05, 0.005 | 3, 0.1 |
| Pa | 3, 0.1 | 3, 0.1 | 3, 0.1 | 3, 0.1 |
| Pb | 0.5, 0 | 0.5, 0 | 0.5, 0 | 0.5, 0 |
| Pd | 0.01, 0 | 0.01, 0 | 0.01, 0 | 0.01, 0 |
| Pu | 3, 1 | 3, 1 | 3, 1 | 3, 1 |
| Ra | 0.5, 0.1 | 0.5, 0.1 | 0.01, 0.001 | 0.01, 0.001 |
| Rn | 0 | 0 | 0 | 0 |
| Se | 0.003, 0 | 0.003, 0 | 0.003, 0 | 0.003, 0 |
| Sm | 1, 0.2 | 1, 0.2 | 1, 0.2 | 1, 0.2 |
| Sn | 3, 0.01 | 3, 0.01 | 3, 0.01 | 3, 0.01 |
| Sr | 0.5, 0.1 | 0.5, 0.1 | 0.01, 0.001 | 0.01, 0.001 |
| Tc | 0 | 0.1, 0.01 | 0 | 0.1, 0.01 |
| Th | 3, 0.1 | 3, 0.1 | 3, 0.1 | 3, 0.1 |
| U | 0.05, 0.005 | 3, 0.1 | 0.05, 0.005 | 3, 0.1 |
| Zr | 2, 0.2 | 2, 0.2 | 2, 0.2 | 2, 0.2 |

Experimental results show low diffusion rates of anionic species of the elements technetium (oxidising conditions), iodine and chlorine despite the fact that they do not sorb on the material. For these elements a lower effective diffusivity than for the majority of elements is therefore proposed. There are some other elements which will be anionic in the bentonite pore water, and which may behave similar to iodine, chlorine and technetium (oxidising conditions) for example carbon, niobium and selenium. Because no experimental evidence has been found on low diffusion rates for these elements an effective diffusivity of $1 \cdot 10^{-10}$ $m^2/s$ is proposed. This may be somewhat conservative.

From the effective diffusivity, $D_e$, the pore diffusivity $D_p$, can be calculated if the diffusion porosity $\varepsilon_p$ is known. The diffusion porosity may be less than the water content of the bentonite. Due to lack of experimental data it is assumed that the diffusion porosity for most elements is equal to the water content at the actual density of the bentonite buffer. Based on data in the literature it is proposed that a value of 25% is used.

For the elements iodine, chlorine and technetium (oxidising conditions) a lower diffusion porosity is proposed because one reason to the low diffusion rates of the corresponding anionic species may be a restricted accessible porosity.

Table 21      Proposed effective diffusivity, $D_e$, pore diffusivity, $D_p$, and diffusion porosity $\varepsilon_p$ in MX-80 bentonite with bulk density 2000 $kg/m^3$. Fresh and saline reference waters.

| Elements | Effective diffusivity, $D_e$ [$m^2/s$] | [$m^2/year$] | Pore diffusivity, $D_p$ [$m^2/s$] | [$m^2/year$] | Diffusion porosity $\varepsilon_p$ [%] |
|---|---|---|---|---|---|
| Se, Zr, Tc(red.) Sn, Ce, Sm, C, Ni, Nb, Am, Pu, Np, U, Th, Rn, Pb | $1 \cdot 10^{-10}$ | $3.2 \cdot 10^{-3}$ | $4 \cdot 10^{-10}$ | $1.3 \cdot 10^{-2}$ | 25 |
| Sr, Cs, Pa, Ra | $2.5 \cdot 10^{-8}$ | 0.79 | $1 \cdot 10^{-7}$ | 3.2 | 25 |
| Tc(ox.), I, Cl | $2.5 \cdot 10^{-12}$ | $7.9 \cdot 10^{-5}$ | $5 \cdot 10^{-11}$ | $1.6 \cdot 10^{-3}$ | 5 |

## 4.2    Finnsjö rock

Based on the experimental data compiled in Figures 1 to 3, the following values are proposed for the matrix of the rock in Finnsjön:

Effective diffusivity, $D_e = 1 \cdot 10^{-13}$ $m^2/s$, $3.2 \cdot 10^{-6}$ $m^2/year$

Pore diffusivity, $D_p = 2 \cdot 10^{-11}$ $m^2/s$, $6.3 \cdot 10^{-4}$ $m^2/year$

Diffusion porosity, $\varepsilon_p = 0.5\%$

These values are proposed for all elements, non-sorbing and sorbing. Experimental results give higher diffusivity values for sorbing species, which indicates that the proposed values may be on the conservative side (see Table 19). Values of the effective diffusivity for

sorbing species are, however, calculated using $K_d$-values which probably are associated with some uncertainty.

The same values are proposed for both the fresh and the saline reference waters. The difference in ionic strength between the waters may result in some difference in the diffusivity values. This difference is, however, expected to be small. For example, the diffusivities of ions in sea water are less than 10 % lower than their values at infinite dilution [Lerman, 1988]. The difference in diffusivity between different samples of Finnsjö rock (see Table 18) is expected to overshadow any difference due to water composition.

The diffusivity of species in mobile groundwater in the rock is lower than the diffusivity in an unconfined fluid due to the tortuosity and constrictivity of the fractures. These entities are very difficult to estimate and it is therefore proposed that conservatively assume a diffusivity in mobile water in rock equal to the diffusivity in unconfined fluid.

The diffusivity of various ions at infinite dilution in unconfined water is reported by Lerman [1988]. For cations the values given range from $1.53 \cdot 10^{-10}$ m$^2$/s for Th$^{4+}$ at 18°C to $1.77 \cdot 10^{-9}$ m$^2$/s for Cs$^+$ at 18°C. The only cation with a higher diffusivity than Cs$^+$ is H$^+$ with a diffusivity of $8.17 \cdot 10^{-9}$ m$^2$/s at 18°C. Anions exhibit similar values. Most anions have a diffusivity in the range $7 \cdot 10^{-10}$ to $1.7 \cdot 10^{-9}$ m$^2$/s except OH$^-$ for which a diffusivity of $4.5 \cdot 10^{-9}$ m$^2$/s is given.

These reported diffusivities for infinite dilution are also reasonable approximations for diffusivities in dilute solutions [Lerman, 1988]. As was mentioned above, reported diffusivities in sea water are less than 10% lower than their values at infinite dilution.

Based on the above given values of diffusivity of ions at infinite dilution the diffusivity in mobile water to be used in the SKB 91 study for both the fresh water and saline water is proposed to:

$$D_f = 2 \cdot 10^{-9} \text{ m}^2/\text{s}, \quad 6.3 \cdot 10^{-2} \text{ m}^2/\text{year}$$

To obtain the effective diffusivity of the species in the fractures the diffusivity given above should be multiplied by the fracture porosity of the rock.

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