

Appendix 2

Long Term Test of Buffer Material- in situ Co^{2+} diffusion experiment

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Introduction

Bentonite has been proposed as buffer material in several concepts for high level nuclear waste repositories. The favourable bentonite properties are closely linked to the interaction between groundwater and the main mineral montmorillonite. An experiment series, called “Long Term Test of Buffer Material” (LOT) are carried out at Äspö Hard Rock Laboratory. The main objectives of LOT are to validate models for clay performance at standard KBS-3 repository conditions and to quantify clay alteration processes under adverse conditions such as very saline groundwater, high pH, high potassium concentration in clay pore water, high temperature and temperature gradient across the buffer. Several other test concerning copper corrosion, bacteria survival and cation diffusion are also carried out in conjunction with the buffer performance test. The LOT programme comprises seven test parcels which are exposed to KBS-3 repository conditions for 1 to >>5 years. Each test parcel (Fig 1) contains a heater a copper tube and pre- compacted bentonite blocks. The test parcel is placed in a vertically drilled 4-m deep borehole 450 m below ground level in Äspö Hard Rock Laboratory. When the bentonite is fully water saturated by groundwater entering the borehole through water carrying rock fissures , the copper tube is heated to simulate the temperature increase due deposition of radionuclide decay energy.

The influence of sorption and ion exclusion on the effective and apparent diffusivity of radionuclide containing cationic and anionic species in compacted bentonite has been studied extensively in laboratory (Muurinen 1994, Eriksen and Jansson 1996, Yu and Neretnieks 1997). Modelling diffusion and sorption are discussed in several papers (Molera Marimon 2002, Bourg et al 2003, Ochs et al 2001, 2003). Diffusion experiments with Cs⁺, Sr²⁺ and Co²⁺ have been carried out in bentonite compacted to 1800 kg/m³ dry density and saturated with Äspä ground water using the CHEMLAB probe (Jansson and Eriksen, 1998). LOT offers the possibility of in situ studies of radionuclide migration in compacted bentonite under

conditions quite different from those in laboratory; larger scale, initially dry bentonite subjected to water saturation with natural ground water, high temperature and temperature gradient across the buffer during the experiment.

The migration of the cations Cs^+ and Co^{2+} were studied in earlier 1-year LOT tests (Karnland et al 2000, Jansson et al 2003).

In this paper we describe a 6 year migration study within the LOT test parcel A2. Scooping calculations of expected concentration profiles of Cs^+ and Co^{2+} showed that Cs^+ would not be contained within the bentonite and only Co^{2+} was used in the test.

Experimental

A 4-m deep hole was drilled vertically into the rock 445 m below ground level in the Äspö hard rock laboratory. The test parcel A-2 containing a copper tube with 100 mm outer diameter surrounded by 38 cylindrical blocs with 300 mm diameter of Wyoming MX-80 bentonite pre-compacted to give a density of 2000 kg/m^3 when fully water saturated is shown schematically in Figure 1. Two identical 20 mm long bentonite plugs with 20 mm diameter and the same density as the parcel blocs were prepared in laboratory. A 5-mm diameter hole was drilled into the centre of each plug and a few cubic millimetres of dry bentonite containing sorbed Co^{2+} with $1 \text{ MBq } ^{60}\text{Co}$ as tracer was placed at the bottom of the hole. The top part of the hole was refilled with inactive bentonite and compacted to the plug density. The plugs were inserted into two diametrically opposite holes in the fifth bentonite block from the bottom of the test parcel immediately before lowering the parcel into the borehole. The hole was thereafter sealed with a concrete plug and the bentonite blocks left to be water saturated with ground water. The test parcel was equipped with a number of thermocouples, humidity and pressure gauges to monitor the evolution of temperature, water saturation and pressure in the bentonite. When scoping calculations as well as humidity gauges indicated that the bentonite was fully water saturated, the temperature in the parcel was increased by heating the central copper tube to 130°C by internal electric heaters. The heating was done to simulate the increase in canister temperature due to heat generation by decaying radionuclides within the spent fuel,

At the end of the test period the parcel was removed from the bore hole by over-core drilling and the ^{60}Co containing blocks transported to a radiochemistry laboratory for profile analysis. The experimental time schedule is given in Table 1.

PARCEL A2

5-years
T~130°C
additives

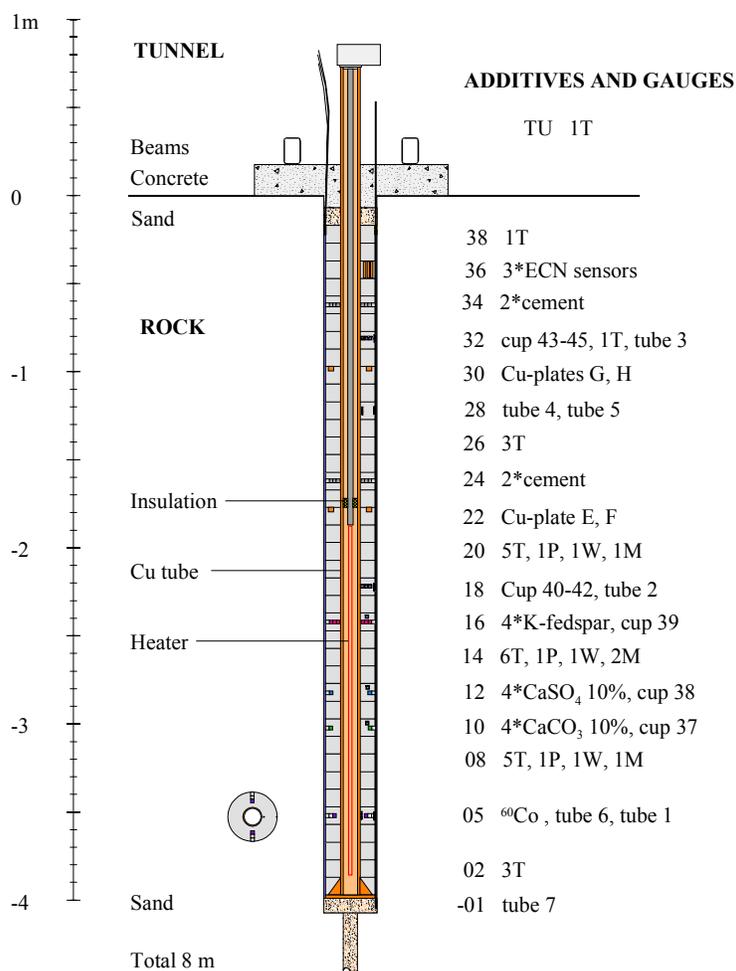


Figure1. Schematics of Lot- parcel 2.

Table 1. Time schedule for LOT-2 test.

| Installation | Heater | | Lift up | Sampling |
|--------------|------------|------------|------------|-----------------|
| | on | off | | |
| 1999-10-29 | 2000-02-02 | 2005-12-05 | 2006-01-16 | 2006-02-(08-22) |

Analyses

A rectangular part containing the ^{60}Co was sawn out of block five and sliced into 15 laminae and each lamina cut into small pieces, 2,5-3,5 g each, giving a total number of approximately 1300 samples. Block 5 after transport to the radiochemistry laboratory and schematics of the sampling layout are shown in Figure 2.

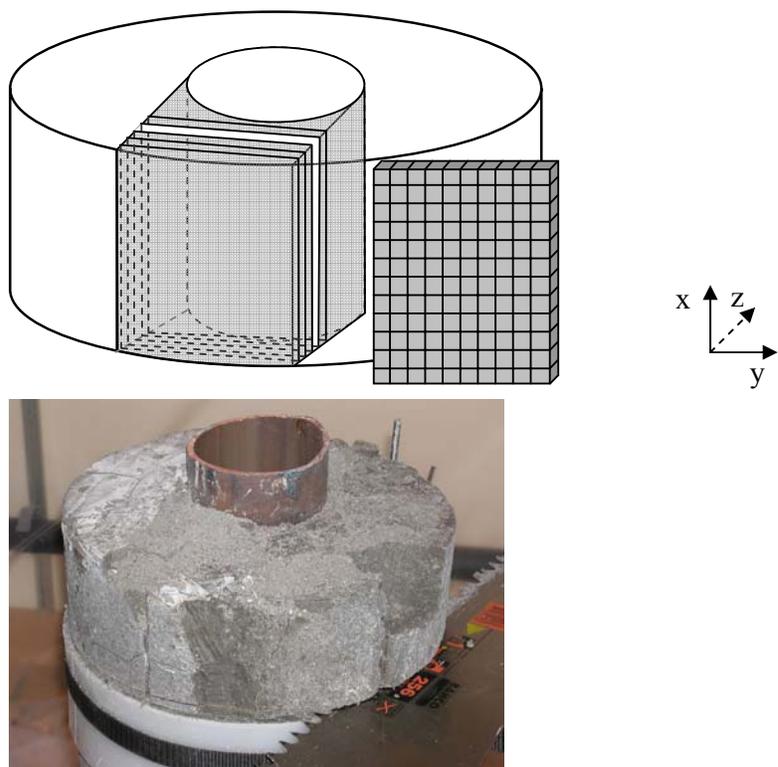


Figure 2 Block 5 after transport to radiochemistry laboratory. Schematics of sample layout .

All samples were dried overnight in an oven at 70°C and then weighed. The gamma activity was measured using a germanium detector and multi-channel analyzer. Every piece was measured until 10000 pulses were reached or for maximum one hour. The mid-point of the sample with maximum specific activity (cps/g), assumed to be the position where the diffusant was originally placed, is used as reference point for determining the geometric activity distribution.

Densities of $20*20*20$ mm samples from blocks 4 and 2 at differing distances from the copper tube were determined by weighing the samples in air and in paraffin oil.

Water ratios (water loss/dry density of bentonite) were determined for samples from blocks 4 and 6

Results and discussion.

The pressure build up due to water saturation and temperature at different distances from the copper tube in block 14 are plotted as function of time in Figures 3 and 4 respectively. Stable water ratio and temperature conditions were reached after approximately one year.

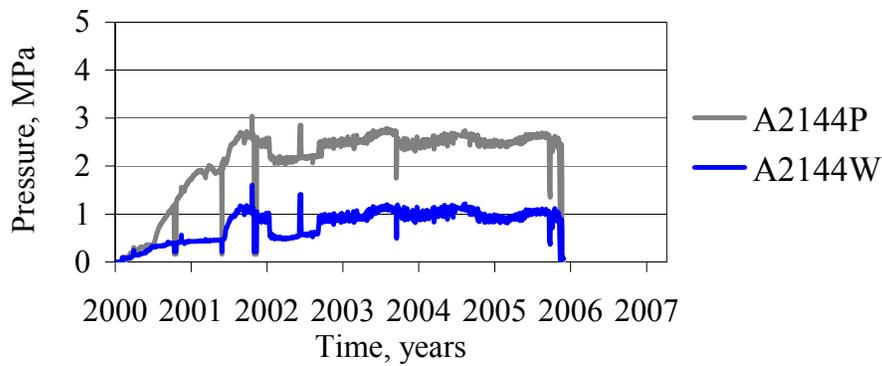


Figure 3. Pressure build up in block 14 on saturation with ground water. Last figure denotes distance in cm from copper tube.

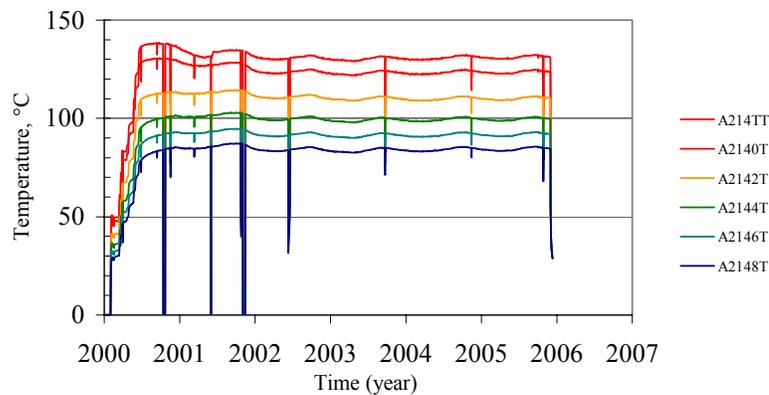


Figure 4. Temperature recordings in block 14 as function of time. Last figure denotes distance in cm from copper tube.

Water to solid ratios of samples from blocks 4 and 6 and wet densities of samples from block 4 are given in Table 2. The wet density decreases slightly and the water to solid ratio in block

4 increases with distance from the hot copper tube. The water to solid ratio in samples from block 6 is somewhat lower than the ratio in samples at the same distances from the copper tube in block 4.

The dry density and water filled porosity of the samples are calculated using equations /1/ and /2/ respectively-

$$\rho_d = \rho_w / (1 + R) \quad /1/$$

$$\varepsilon = \rho_w - \rho_d \quad /2/$$

ρ_w, ρ_d density of wet and dried bentonite sample respectively

R water to solid ratio

ε porosity

Assuming the mean value of samples from blocks 4 and 6 to be representative for the activity -containing block 5 we obtain $\rho_d = 1.53 \pm 0.05 \text{ g}\cdot\text{cm}^{-3}$ and $\varepsilon = 0.44 \pm 0.02$.

Taking the density of bentonite to be $2.73 \text{ g}\cdot\text{cm}^{-3}$ the porosity of dry compacted bentonite is given by equation /3/

$$\rho_d = 2.73(1 - \varepsilon) \quad /3/$$

Using equation /4/ we calculate the porosity of bentonite compacted to dry density $1.53 \text{ g}\cdot\text{cm}^{-3}$ to be 0.44 clearly showing that the compacted bentonite in block 5 was fully water saturated during the diffusion period.

Table 2. Water to solid ratios and wet densities measured at different distances from copper tube in blocks 4,6 and block 4 respectively.

| Distance from copper tube (mm) | 0-20 | 20-40 | 40-60 | 60-80 | 80-100 |
|-------------------------------------------------------|-------|-------|-------|-------|--------|
| Water ratio Block 6 | 0.248 | 0.255 | 0.263 | 0.274 | 0.290 |
| Water ratio Block 4 | 0.294 | 0.301 | 0.306 | 0.314 | 0.325 |
| Wet density ($\text{g}\cdot\text{cm}^{-3}$) Block 4 | 1.945 | 1.952 | 1.942 | 1.926 | 1.915 |

The specific activity (cps/g) is plotted as a function of distance along the x,y,z axes in

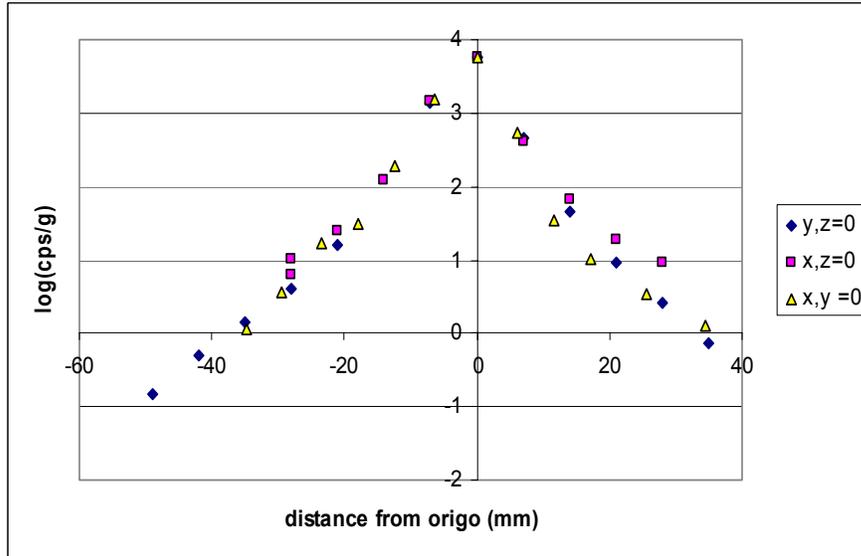


Figure 5. Specific activity of samples along x,y,z axis (see Figure 2) .

The specific activity of all samples from Block 5 is plotted in Figure 6 as a function of distance from the point on maximum specific activity.

The experimental data clearly show that the ^{60}Co activity was contained within block five. The radionuclide transport can therefore be treated as diffusion from a finite source into an infinite medium. Assuming the source to be a sphere with diameter a and initial concentration C_0 is given by equation /4/ Crank (1975).

$$C(r,t) = \frac{1}{2} C_0 \left[\operatorname{erf} \frac{a+r}{2\sqrt{D_a t}} + \operatorname{erf} \frac{a-r}{2\sqrt{D_a t}} \right] - \frac{C_0}{r} \sqrt{\left(\frac{D_a t}{\pi} \right)} \left[e^{-\frac{(a-r)^2}{4D_a t}} - e^{-\frac{(a+r)^2}{4D_a t}} \right] \quad /4/$$

where D_a is the apparent diffusivity.

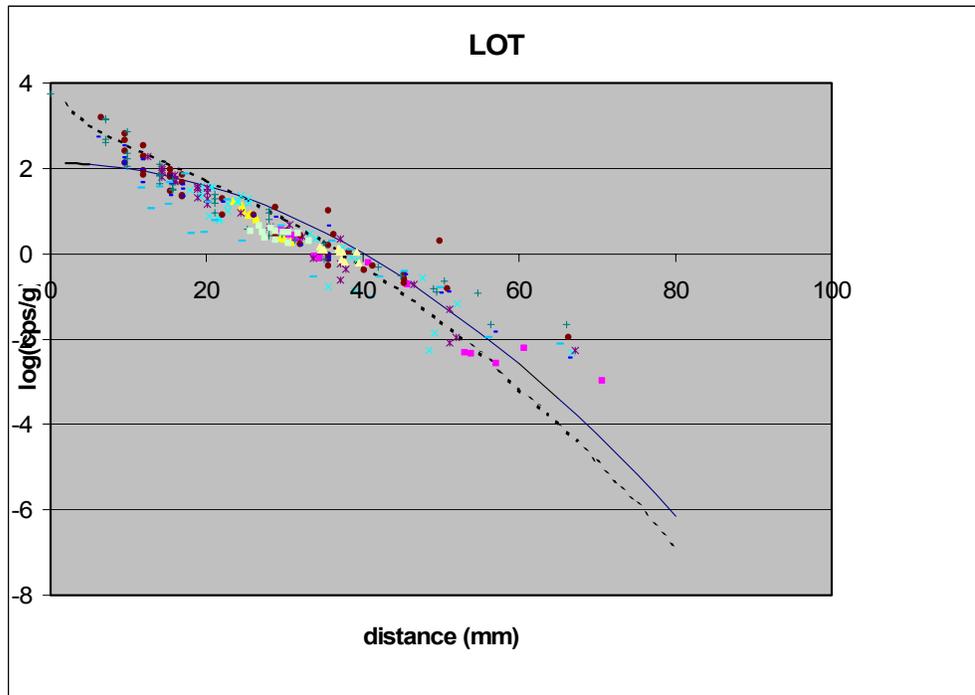


Figure 6. Specific activity of samples from block 5 plotted against distance from maximum specific activity. — $D_a=5 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $a=2 \text{ mm}$, ---- $D_a=5 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $a=2 \text{ mm}$, partial precipitation of Co as $\text{Co}(\text{OH})_2$ in pore water for $r < a$.

The specific activity as a function of distance from the point of maximum activity calculated with $a=2 \text{ mm}$ and $D_a=5 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ is plotted in Figure 6.

The calculated activity distribution clearly underestimates the measured specific activity at short distances from the maximum. The pH in the pore water at the end of the test period was according to Muurinen(2006) approximately 8.3 close to the copper heater and 7.2 at the bentonite rock interface. The variation of pH with distance from the copper surface with time is not known, but the pH in the pore water at the initial position of the Co-source may have, due to slow equilibration with the ground water, been ≥ 8.3 during a considerable part of the test period.

One possible explanation for the difference between calculated and measured specific activity close to the position of maximum activity is precipitation of Co as $\text{Co}(\text{OH})_2$.

Assuming the pore water concentration for $r < a$ to be solubility constrained and constant during the test period the specific activity $C(r,t)$ distribution for $r > a$ is given by equation /5/, Crank(1975)

$$C(r,t) = C(a) \frac{a}{r} \operatorname{erfc} \left[\frac{r-a}{2\sqrt{D_a t}} \right] \quad /5/$$

As seen from Figure 6 the fitted specific activity distribution for $a=2$ mm and $D=5 \cdot 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ corresponds better to the experimental observations.

When comparing data from the present diffusion test with data obtained in laboratory experiments it should be emphasized that several processes ; water saturation, ion exchange between bentonite pore water and surrounding ground water and heating of the water saturated bentonite , have taken place during the test period.

The in situ diffusion system studied is complicated with a large temperature gradient and according to pore water analysis also an increase in pH from approximately 7.2 at the bentonite/bedrock interface to 8.3 close to the copper tube surface . The time evolution of pH in the pore water is not known and pH has probably been in the range 8-8.3 , a range with great influence on Co^{2+} sorption and solubility (Bradbury et al, 2005; Marimon ,2002.) during a considerable part of the test period.

The apparent diffusivity D_a in porous media encompassing diffusion in pore water and complete immobilization of sorbed species is, assuming the physical constrictivity to be unity, given by equation /6/

$$D_a = \frac{D_w}{\tau^2} \frac{\varepsilon}{\varepsilon + K_d \rho} \quad /6/$$

- D_w diffusivity in pore water
- τ^2 tortuosity of pore system
- ε porosity
- ρ dry density of compacted bentonite
- K_d sorption coefficient

Marimon (2002) measured the apparent diffusivity of Co^{2+} at 20°C in bentonite compacted to $1.2\text{-}1.8 \text{ g cm}^{-3}$ dry density and equilibrated with electrolytic solution with different ionic

strength at pH 8.2 . Using Equation 6 we estimate D_a to be $(3.4 \pm 1.7) \cdot 10^{-10}$ at dry density 1.53 g cm^{-3} and 20° C .

The temperature profile in the LOT-2 parcel is shown in Figure 7. As can be seen the temperature in block 5 varies from approximately 120°C close to the copper tube heater to approximately 70°C at the bentonite/rock interface. The temperature at the position of maximum specific activity is approximately 95°C .

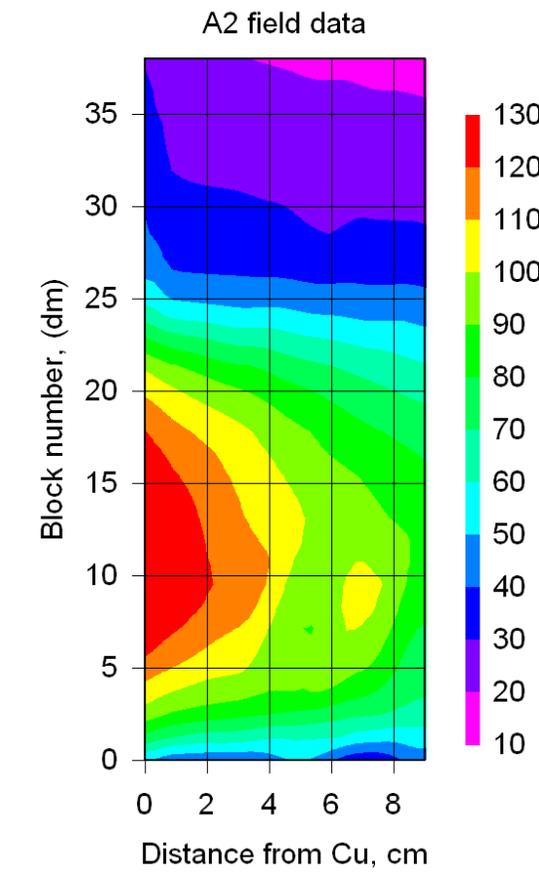


Figure 7. Temperature profile in the LOT-2 parcel.

Jansson et al (2003) have measured the apparent diffusivity of Co^{2+} in bentonite compacted to 1.8 g cm^{-3} dry density at $20, 70$ and 90°C . Extrapolating these data to 95°C and assuming the overall activation energy for the diffusion process (diffusion in the pore water and sorption on the bentonite) to be the same for 1.53 g cm^{-3} and 1.8 g cm^{-3} dry density we find the the

ratio $\frac{D_a(95^\circ C)}{D_a(20^\circ C)}$ to be 4.2 +/-0.5 and thus the expected apparent diffusivity in the LOT-

2 experiment to be $(1.4\pm 0.8)10^{-9} \text{ cm}^2 \text{ s}^{-1}$ which is within a factor 2-3 in agreement with the experimentally observed diffusivity.

Conclusions

The apparent diffusivity is in good agreement with data from previous in situ experiments and taking into consideration differences in compaction, pH of equilibrating electrolyte solutions and temperature also within a factor 2-3 with data from laboratory experiments.

References

- Bradbury, M., Baeyens, B., 2005. Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonate: Linear free energy relationships and estimates of surface binding constants for some heavy metals and actinides. *Geochimica. et Cosmochimica. Acta* 69, 875-892.
- Bourg, I.C., Bourg, A.C.M., Sposito, G., 2003. Modelling diffusion and absorption in compacted bentonite: a critical review.. *J. Contam. Hydrol.* 61, 293-302.
- Crank, J., 1975. *The Mathematics of Diffusion*, 2nd ed.; Oxford Univ. Press, Oxford
- Eriksen, T.E., Jansson M.; 1996. Diffusion of I⁻, Cs⁺ and Sr²⁺ in compacted bentonite – anion exclusion and surface diffusion. SKB Technical report TR-96-16
- Jansson, M., Eriksen, T.E., 1998. CHEMLAB – in situ diffusion experiments using radioactive tracers. *Radiochim. Acta* 82, 153-156.
- Karnland, O., Sanden, T., Johannesson, L-E., Eriksen, T.E, Jansson, M., Wold, S., Pedersen, K., Motamedi, M., Rosborg, B., 2000. Long term test of buffer material – final report on the pilot parcel. SKB Technical Report TR-00-22.
- Marimon, M.M On the Sorption and Diffusion of Radionuclides in Bentonite Clay, 2002. Doctoral Thesis, Department of Chemistry, Nuclear Chemistry, KTH.
- Muurinen, A., 1994. Diffusion of anions and cations in compacted sodium bentonite. Espoo Technical Research Center of Finland, Vtt Publication 168.
- Muurinen, A., 2007 Personal communication.
- Ochs, M., Lothenbach, B., Shibata, M., Sato, H., Yui, M., 2001. An integrated sorption – diffusion model for the calculation of consistent distribution and diffusion coefficients in compacted bentonite. *J. Contam. Hydrol.* 47, 283-296.

Ochs, M., Lothenbach, B.; Shibata, M., Sato, H., Yui, M., 2003. Sensitivity analysis of radionuclide migration in compacted bentonite ; a mechanistic model approach, J. Contam. Hydrol., 61, 313-328.

Pusch,R., Muurinen ,A., Lehtikoinen, J., Bors,J., Eriksen ,T, 1999. Microstructural and chemical parameters of bentonite as determinants of waste isolation efficiency. European Commission.Nuclear Science Technology Project Report EUR 18950 EN.

Shahwan,T., Erten, H.N, Unugur, S., 2006. A characterization study of some aspects of the adsorption of aqueous Co^{2+} ions on a natural bentonite clay. J.Colloid and Interface Sci., 300, 447-452..

Yu, J.W, Neretnieks,I.,1997, Diffusion and sorption properties of radionuclides in compacted bentonite. SKB Technical Report TR-97-12.