CHEMLAB

A probe for in-situ radionuclide experiments

Diffusion studies

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SKB

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Abstract

CHEMLAB is a borehole laboratory built into a probe, in which *in situ* experiments can be carried out under ambient conditions with respect to pressure and temperature with the use of natural groundwater from the surrounding rock.

The first CHEMLAB experiments, diffusion of cations and anions in compacted bentonite clay, have been carried out in borehole KA2512A at a depth of 320 m. in Äspö Hard Rock Laboratory. Diffusant solutions of Co^{2+}, Sr^{2+}, Cs^+, I^- and TcO_4^- with ^{57}Co, ^{85}Sr, ^{134}Cs, ^{131}I and 99Tc as tracers were used. The measured profiles for the radionuclides in the bentonite are in good agreement with profiles predicted from modelling based on apparent diffusivities and sorption coefficients obtained in laboratory experiments with clay compacted to corresponding dry density and synthetic ground water with the same composition as in borehole KA2512A.

Sammanfattning

CHEMLAB är ett borrhålslaboratorium inbyggt i en sond i vilken ett antal in-situ experiment kan genomföras under samma förhållanden som förväntas råda i ett djupförvar.

De första CHEMLAB experimenten, katjons- och anjonsdiffusion i kompakterad bentonitlera, har genomförts i borrhål KA2512A på 320 meters djup i Äspö Hard Rock Laboratory. Lösningar med Co^{2+}, Sr^{2+}, Cs^+, I^- och TcO_4^- med ^{57}Co, ^{85}Sr, ^{134}Cs, ^{131}I och ^{99}Tc som spårämnen användes i försöken. De uppmätta profilerna för radionukliderna i bentonitleran stämmer väl överens med förväntade profiler som modellerats från synbara diffusiviteter (*apparent diffusivities, D_a*) och sorptionskoefficienter som erhållits i laboratorieexperiment med lera kompakterad till motsvarande torrdensitet och jämviktad med syntetiskt grundvatten med samma sammansättning som grundvattnet i borrhål KA2512A.

Contents

1   Introduction

CHEMLAB is a borehole laboratory built into a probe, in which different experiments can be carried out under ambient conditions regarding pressure and temperature and with the use of the formation groundwater from the surrounding rock.

Before designing CHEMLAB a number of feasible experiments, deemed to be interesting to carry out in a borehole probe, were conceptually lined out. To be able to carry out those experiments CHEMLAB had to meet a number of specifications, such as flow paths, pump flows, acceptable dead-volumes, etc. The final design resulted in a quite complex system.

Experiments intended to be performed in CHEMLAB are /Jansson and Eriksen, 1996/;

- **Radionuclide diffusion in compacted bentonite clay**, where diffusive transport of radionuclides under relevant deep groundwater conditions is investigated.

- **Migration of redox sensitive radionuclides**, where retention in the transport of redox sensitive radionuclides (such as technetium) in a rock fissure is measured and demonstrated.

- **Migration from the clay buffer to the rock**, where the diffusion of radionuclides in a clay buffer, followed by a transition to a rock fissure containing flowing groundwater is studied.

- **Radiolysis experiments**, where the influence of water radiolysis on the mobility of redox sensitive radionuclides is studied.

- **Batch sorption experiments**, where the sorption of redox sensitive radionuclides to a rock surface is studied under relevant deep groundwater conditions.

- **Radionuclide solubility** of redox sensitive radionuclides, such as neptunium.

- **Spent fuel leaching**, which is maybe the easiest experiment to carry out of the outlined, but the trickiest when it comes to radiation protection.

This variety of different experiments requires different experimental set-ups especially with respect to flow paths in the probe. To be able to perform the planned experiments two pumps are needed, as well as tracer reservoirs and fraction collectors. The flows in CHEMLAB are controlled by six multi-channel valves. Since there is a limited diameter of a borehole, there is not very much radial space available and each component will be quite long instead. For instance each multi-channel valve, which can be seen in Figure 1-1, requires a good half-meter.
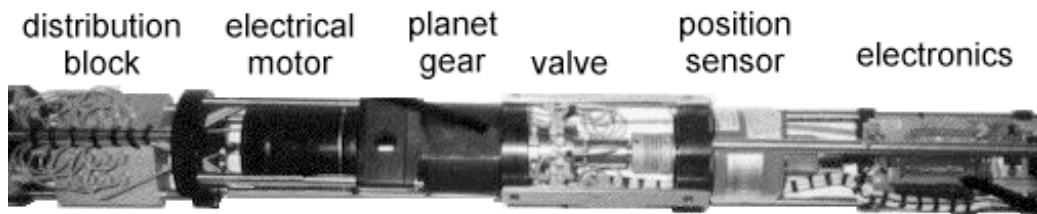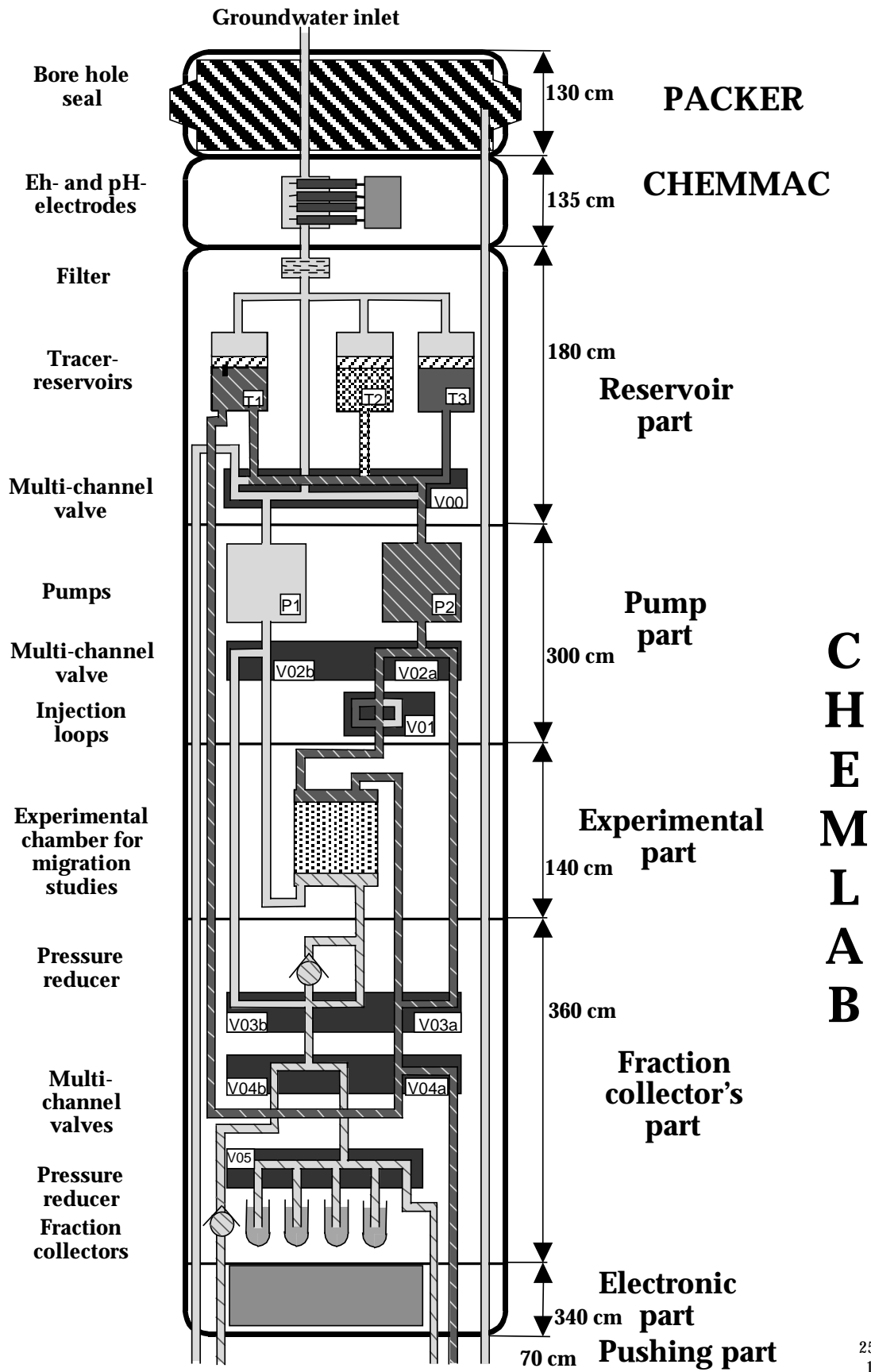
Figure 1-1. *One of six multi-channel valves in CHEMLAB.*

All components are constructed in the same compact but long manner. All together CHEMLAB measures 13.3 meters and has an outer diameter of 89 mm, including the 5 mm thick outer casing. A schematic overview of CHEMLAB can be seen in Figure 1-2.

The main components in CHEMLAB are:

- **Three reservoirs** for tracer solutions. The reservoirs are cylinders with caps at each end. One end of a reservoir is connected to the groundwater in the borehole and the other to the experimental system. A moveable piston is separating the groundwater from the radioactive solution. When solution is taken out of the reservoir the piston moves to compensate the volume loss and the opposite if solution is pumped into the reservoir. With this arrangement, the reservoir and groundwater pressure will remain the same during the experiment.

- **Two pumps**. The pumps are of HPLC type, modified to be able to operate aligned in any geometrical direction and to provide flow rates between 0.02 and 40 ml/h. In most of the outlined experiments there are two parallel flows of solution in CHEM-LAB, each controlled by a pump. One flow carries the radioactive solution, while the other is inactive and samples the radionuclides which has passed the experiment cell.

- **Experiment cell** designed specifically for the experiment to be performed. The cell is unique for each type of experiment. The experiment cell is the gist of CHEM-LAB, since the whole system is designed to supply the cell with the desired solution at a chosen flow rate.

- **A fraction collector** with 22 sampling tubes in which samples from the experiment can be collected

- **Six multi-channel valves** which direct the flow pattern in the probe. Each multi-channel valve has an a- and b-side. The solution on the a-side contains the radio-nuclide solution and the b-side the inactive solution.

- **PEEK tubes.** All tubing in CHEMLAB is made of PEEK (Poly-Ethene-Ethene-Ketone), which is a chemically inert, radiation resistant polymeric material.

Groundwater inlet

Bore hole seal

PACKER — 130 cm

Eh- and pH- electrodes

CHEMMAC — 135 cm

Filter

Tracer- reservoirs

180 cm

Reservoir part

T1 T2 T3

Multi-channel valve

V00

Pumps

Pump part

P1 P2

Multi-channel valve

V02b V02a

Injection loops

V01

300 cm

Experimental chamber for migration studies

Experimental part

140 cm

Pressure reducer

V03b V03a

360 cm

Fraction collector's part

Multi- channel valves

V04b V04a

V05

Pressure reducer
Fraction collectors

Electronic part — 340 cm

Pushing part — 70 cm

CHEMLAB

25 Jan. 1999

Figure 1-2. *Schematic drawing of the CHEMLAB system.*

2 Diffusion studies

Bentonite clay is proposed as buffer material in the Swedish concept for nuclear high level waste repository (KBS-3). One of the favourable properties of bentonite is that the main mineral montmorillonite swell when in contact with water. Since the space available is limited, the clay will become very compact, almost as dense as concrete and all transport to and from the copper canister will be by diffusion.

To obtain input data for a safety assessment of KBS-3, a large number of laboratory studies on diffusion in bentonite clay have been carried out with different ions, for reviews see /Muurinen, 1994; Yu and Neretnieks, 1997/. Even though the experiences from these studies are uniform, it is of great value to demonstrate that results of laboratory studies are valid *in situ*, where the natural contents of colloids, organic matter, bacteria, etc., are present in the experiments. Laboratory investigations have difficulties to simulate these conditions and are therefore dubious as validation exercises. The CHEMLAB borehole probe has been constructed and manufactured for validation experiments *in situ* in Äspö HRL at undisturbed natural conditions.

The composition of groundwater in Äspö HRL differs between sampling sites, but common for most groundwater samples taken at 500 meters depth is that they are significantly more saline than freshwater. At the site where the CHEMLAB experiments were performed, 320 meters underground, the ionic strength has varied from 0.17 to 0.12 moles per kg solvent. The variation is due to freshwater leakage from the surface into the tunnel. Furthermore, the water is also strictly anoxic, i.e. very reducing. Eh-values have been measured during the CHEMLAB experiments and are well below -200 mV vs. NHE.

Groundwater will, in the event of a canister failure, dissolve the fuel matrix and thereby release radionuclides. The rate of release and concentration of radionuclides are determined by their solubilities and the dissolution process. The effect of radiolytically generated oxidants is still not fully understood. Dissolved radionuclides will migrate by diffusion through the bentonite and then by flowing water in fractures in the host rock.

The migration of radionuclides will be retarded by a number of processes e.g. sorption on mineral surfaces in backfill material and host-rock. Slightly sorbing radionuclides will be much more mobile than more sorbing ones. For example, plutonium will probably not penetrate the backfill while iodine is almost certain to reach hundreds of meters.

In this work we have studied diffusion of the cations Cs^+, Sr^{2+} and Co^{2+} and the anions I^- and TcO_4^-.

The main sorbtion process for Cs^+ and Sr^{2+} is cation exchange. The sorption is dependent on the concentration of other cations ions present in the water phase, since there will be a competition for available sites.

The dominant mechanism for sorption of cobalt on bentonite is outer sphere complexation at acid to neutral pH and inner sphere complexation and/or surface precipitation at pH>7 /Papelis and Hayes, 1996/.

Technetium has very low solubility /Eriksen et al., 1992/ and mobility in its reduced tetravalent state as compared to the heptavalent pertechnetate ions. Deep groundwater is strictly oxygen free and the only oxidising components are sulphate ions (generally below 500 mg/l at depth) and traces of, for example, nitrate ions. Reducing components are only present at trace levels (a few mg/l to µg/l) at depth, for example Fe^{2+}, HS^-, Mn^{2+} and DOC. Reducing conditions are always found at repository depth at the experimental sites. However, redox pairs are not always in equilibrium with each other, as for instance for the redox pair TcO_4^-/Tc(IV) and it is therefore not obvious what will happen if Tc, for some reason (e.g. radiolysis), is released as pertechnetate ion. Cui and Eriksen /Cui and Eriksen, 1996(1)/ have presented convincing experimental evidence that stepwise one electron reduction of TcO_4^- to $TcO_2 \cdot nH_2O$ by Fe(II) (*aq*) is kinetically hindered and that sorption on surfaces of Fe(II) containing minerals or precipitates is a necessary precursor to the reduction.

2.1 Predictive simulations

Predictive simulations are carried out using the computer program ANADIFF /Eriksen and Jansson, 1996/ with due consideration taken to the effect of filter-plates. The ionic strength at the experimental site is taken to be 0.167 molal. The parameters used are discussed below and summarised in Table 2-1.

Table 2-1. Parameters used for predictions.

Ion	K_d-value (g cm^{-3})	α (= ϵ + K_d)	D_a (cm^2 s^{-1})
Cs^+	100 ± 40		$(2.2 \pm 0.6) \cdot 10^{-8}$
Sr^{2+}	40 ± 17		$(1 \pm 0.5) \cdot 10^{-7}$
Co^{2+}	700 ± 400		$(2 \pm 1) \cdot 10^{-9}$
I^-		0.08 ± 0.025	$(9.2 \pm 1.3) \cdot 10^{-7}$
TcO_4^-		0.08 ± 0.025	$(9.2 \pm 1.3) \cdot 10^{-7}$

2.1.1 Caesium

Cs^+ sorb to bentonite clay by cation exchange. From calculations based on laboratory experiments and the groundwater composition at the experimental site, the apparent diffusivity of Cs^+ is expected to be $(2.2\pm0.6)\cdot10^{-8}$ cm^{2}s^{-1} and the K_d-value 100 ± 40 cm^{3}g^{-1} /Eriksen and Jansson, 1996; Yu and Neretnieks, /1997/.

2.1.2 Strontium

The apparent diffusivity of Sr^{2+} in compacted bentonite is but slightly dependent on the ionic strength /Eriksen et al., 1999; Göltürk et al., 1995/ and is expected to be $(1\pm0.5)\cdot10^{-7}$ cm^2 s^{-1}. The K_d-value is expected to be about 40 ± 17 cm^3 g^{-1}. It should be stressed, though, that due to the high Sr^{2+} concentration in the groundwater, about 0.2 mM, the sorption process may display unlinearity and since the bentonite in diffusion cell is equilibrated with this water before experiment start, the observed tracer sorption is by isotope exchange, rather than cation exchange.

2.1.3 Cobalt

Co^{2+} is sorbed by surface complexion and at pH > 6.5 forms an inner-sphere complex with bentonite /Papelis and Hayes, 1996/. At pH > 6.5 the K_d-value is therefore strongly pH dependent. The pH-value of the Äspö groundwater at the experimental site is about 7.2, and the K_d-value is estimated to be 700 ± 400 cm^3 g^{-1} /Pusch et al., 1999/. The apparent diffusivity is expected to be $(2\pm1) \cdot 10^{-9}$ cm^2 s^{-1} /Eriksen and Jansson, 1996/.

2.1.4 Iodide

The transport capacity of iodide has been found to be increasing with increasing ionic strength of the groundwater used, due to anion exclusion. In earlier diffusion studies using saline synthetic groundwater (NASK, ionic strength=0.218 molal) the apparent and effective diffusivities obtained by analysis of break through curves were found to be $(9.2\pm1.3)\cdot10^{-7}$ and $(7.0\pm1.7)\cdot10^{-8}$ cm^2 s^{-1}, respectively /Eriksen and Jansson, 1996/.

2.1.5 Technetium

Technetium is a redox sensitive radionuclide. In an oxidising environment technetium occurs as pertechnetate ion (TcO_4^-), which has been found to be as mobile as the iodide ion. Under reducing conditions the thermodynamically favoured state is $TcO_2 \cdot nH_2O(s)$. However, it has been shown that the reduction of TcO_4^- by Fe(II) proceeds very slowly if at all in free solution, while when Fe(II) is sorbed to a surface or precipitated as $Fe(OH)_2(s)$ or $FeCO_3(s)$ the reduction rate is significantly faster /Cui and Eriksen, 1996 (1); Cui and Eriksen, 1996 (2)/.

3   Experimental

3.1   Selected diffusants

Cs^+, Sr^{2+} and Co^{2+} were chosen for the cation experiments. The choice of these cations were based on the following criteria:

- Diffusion behaviour at different chemical conditions should be well characterised.

- The dependence of sorption behaviour and sorption mechanisms on pH and composition of the water solution in contact with the bentonite should be well known.

- The dominating sorption mechanism should preferably be varied. (Cs^+ and Sr^{2+} are adsorbed by cation exchange while Co^{2+} is sorbed by inner-sphere complexation with the surface of the bentonite.)

I^- and Tc(VII), initially added as pertechnetate, TcO_4^-, were used in the anion experiment. The choice of anions were based on the following criteria:

- Diffusion behaviour at different chemical conditions should be well characterised.

- Two ions with different redox behaviour should be studied, one which is conservative and one which is redox sensitive.

A series of three experiments with different cocktails of the radionuclides, ^{57}Co, ^{134}Cs, and ^{85}Sr, ^{131}I and ^{99}Tc, respectively, were performed.

3.2   Experiment procedure

3.2.1   Materials

The bentonite used in this investigation was the American Colloid Co., type MX-80 (Wyoming Na-bentonite). The bentonite (MX-80) has a clay content ($< 2\mu m$) of approximately 85% and a montmorillonite content of 80–90 wt% of this fraction. The remaining silt fraction contains quartz, feldspar and some micas, sulphides and oxides /Pusch and Karnland, 1986/, see Table 3-1 for more specific data of the bentonite.

The solutions were prepared from analytical grade chemicals. The radionuclides used, ^{134}Cs, ^{57}Co, ^{99}Tc (Amersham) and ^{131}I, ^{85}Sr (DuPont Scandinavia) were obtained in aqueous solution. Tracer solutions were prepared by adding small aliquots of the stock solution to the solutions used in the experiments.

Table 3-1. Bentonite data.

Parameter	MX-80
Cation-exchange capacity, $(X)_T$	0.75 meq g^{-1}
Amphoteric edge sites, $(SOH)_T$	28.4 µmol g^{-1}
Edge surface area	3.0 m^2 g^{-1}
Exchangeable Na	80.8%
Exchangeable Ca	12.8%
Exchangeable Mg	5.5%
Exchangeable K	0.9%
Total carbonate (as $CaCO_3$)	1.5 wt%
Total quartz	~23 wt%
$CaSO_4$ impurity	0.58 wt%
$MgSO_4$ impurity	0.02 wt%
NaCl impurity	0.01 wt%
KCl impurity	0.01 wt%
Specific density	2 700 kg m^{-3}

3.2.2 Laboratory preparations

Before inserting the CHEMLAB probe in a borehole the experimental cell and tracer reservoir are prepared and mounted in sections 2 and 3, respectively, of CHEMLAB. This work is carried out in a radiochemical laboratory.

In the diffusion experiments the cell consists of a PEEK cylinder, in which bentonite clay compacted to a dry density of 1.8 g cm^{-3} is sandwiched between two filter plates.

A small volume (about 2 ml) of diffusant solution prepared from filtrated Äspö water and spiked with the radionuclide(s) used as tracer is transferred to the tracer reservoir. In the first experiment ^{57}Co, in the second ^{134}Cs and ^{85}Sr and in the third ^{131}I and ^{99}Tc were used as tracers. To reduce the oxygen content in the tubes of CHEMLAB, degassed water is pumped through the whole system.

3.2.3 Preparations at experiment Site

After laboratory preparations CHEMLAB is transported to the experiment site in the Äspö tunnel (borehole KA2512A) where the whole probe system (packer, CHEMMAC and the six CHEMLAB sections) is assembled and pushed into the borehole. The system is then pushed 18 meters to full depth of the borehole where a water carrying fracture is situated. The packer is expanded to seal off the test section in the borehole and all flow paths are flushed with groundwater before the experiment can start.

3.2.4 Experiment performance

The first step in the diffusion experiments was to dilute the radioactive solution in the tracer reservoir from 2 to 100 ml with groundwater. The next step was to saturate and equilibrate the bentonite clay with groundwater by pumping groundwater through the in- and outlet channels of the diffusion cell for two weeks. The diffusion was then started by pumping the radiotracer solution through a loop containing the inlet channel of the diffusion cell and the tracer reservoir. At intervals the solution in the outlet

channel was planned to be flushed to the fraction collectors to obtain a break-through curve.

In the cobalt diffusion experiment the gear of one of the multi-channel valves broke down after seven days of diffusion. The experiment was stopped and the concentration profile within the bentonite, but not the break-through curve, was obtained.

Since one of the parts of CHEMLAB was sent to Paris for reparation, the sampling in the fraction collectors was omitted in the diffusion experiment with caesium and strontium, therefore also in this experiment only the concentration profiles in the bentonite were measured. The length of the diffusion cell used in this experiment was increased from 5 to 10 mm so that the diffusants wouldn't reach the end of the cell causing reflection effects.

In the anion experiment the valve of the fraction collectors was contaminated during the experiment, hence the obtained concentration in the fraction collectors is dubious and only the concentration profile in the clay is evaluated.

The activity profiles were obtained by slicing the bentonite plugs into thin sections. All solid samples were weighed and analysed for activity. ^{57}Co, ^{134}Cs, ^{85}Sr and ^{131}I were analysed using a γ-spectrometer while ^{99}Tc was analysed by liquid scintillation.

4   Data evaluation

The cells used in the experiments are equipped with filter plates to avoid expansion of the bentonite clay on water saturation. The diffusive resistance of the filters has must be taken into account when evaluating the results, otherwise errors larger than 40% may arise /Put, 1991/. An analysis of the system, including filter plates, as represented schematically in Figure 4-1, is required.

The diffusive flux, J, through the inlet filter ($-F < x < 0$) is given by equation (4-1)

$$J = -A\varepsilon_f D_f \frac{\partial C_1}{\partial x} \tag{4-1}$$

and the boundary condition

$$C(-F,t)=C_0$$

where A is the cross-section area of the diffusion cell, ε_f is the filter porosity, D_f the apparent diffusivity of the filter, F the filter thickness, C_1 the concentration in the filter and C_0 the concentration in the inlet solution.

The diffusive transport through the compacted bentonite ($0 < x < L$) is given by equation (4-2)

$$J = -A\varepsilon D_a R \frac{\partial C_2}{\partial x} \tag{4-2}$$

where R is the capacity (retardation) factor, defined as $R = \dfrac{\varepsilon + \rho K_d}{\varepsilon}$ and C_2 the concentration in the pore solution.
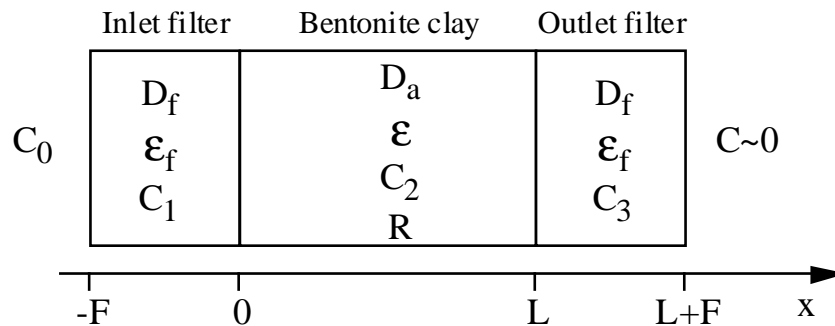

Figure 4-1. *Schematic representation of the diffusion cell. The bentonite clay is sandwiched between two filter plates.*

At the boundary between the inlet filter and the compacted bentonite the following conditions reign

$$C_1(0,t)=C_2(0,t)$$

meaning that the concentration in the liquid accessible by diffusion has to be equal and

$$A\varepsilon_f D_f \left(\frac{\partial C_1}{\partial x}\right)_{x=0} = A\varepsilon D_a R \left(\frac{\partial C_2}{\partial x}\right)_{x=0}$$

meaning that there is no storage in the boundary.

The corresponding transport equation and boundary conditions for the outlet filter are given by

$$J = -A\varepsilon_f D_f \frac{\partial C_3}{\partial x} \tag{4-3}$$

$$C_2(L,t)=C_3(L,t)$$

$$A\varepsilon DR\left(\frac{\partial C_2}{\partial x}\right)_{x=L} = A\varepsilon_f D_f \left(\frac{\partial C_3}{\partial x}\right)_{x=L}$$

$$C_3(L+F,t)=0$$

Normally in through diffusion experiments the accumulated flow of the diffusant passing through the boundary $x=L+F$ is monitored as a function of time. This quantity $Q(t)$ is given by equation (4-4).

$$Q(t) = A\varepsilon_f D_f \int_0^t \left(\frac{\partial C_3(x,t')}{\partial x}\right)_{x=L+F} dt' \tag{4-4}$$

An analytical solution to equation (4-4), defining the break-through curve, can be obtained by the Laplace transform method /Put, 1991/. However, to make use of all the experimental data, *i.e.* the break-through curve as well as the concentration profile in the bentonite clay, the computer code ANADIFF has been developed. The code is based on the finite difference method and calculates the break-through curve as well as the concentration profiles based on the input data D_a, K_a, A, ε, ε_f, D_f, C_0, F, L and ρ.

5 Results and discussion

Based on macroscopic observations the diffusion through compacted water saturated bentonite can be described by the apparent diffusivity (D_a) and a capacity factor α.

$$\alpha = \varepsilon + K_d\rho$$

where ρ is the dry density, ε the porosity of the compacted bentonite and K_d the distribution coefficient between solid phase and solution.

For nonsorbing neutral diffusants $\alpha = \varepsilon$, for cations (sorbing diffusants) $\alpha > \varepsilon$ and for anions, treating anion exclusion as negative sorption, $\alpha < \varepsilon$.

The concentration profiles in the clay for caesium and strontium can be seen in Figures 5-1 and 5-2.

The results of the downhole experiments with Sr^{2+} and Cs^+ are in good agreement with results from laboratory experiments with sodium bentonite compacted to 1.8 g cm^{-3} dry density and equilibrated with synthetic groundwater and electrolyte solutions of the same salinity as Äspö groundwater. It ought to be pointed out that the Sr^{2+} concentration in the Äspö groundwater is about 0.2 mM so the $^{85}Sr^{2+}$ sorption observed is really isotope exchange between sorbed Sr^{2+} and Sr^{2+} in the pore water in an equilibrated system.

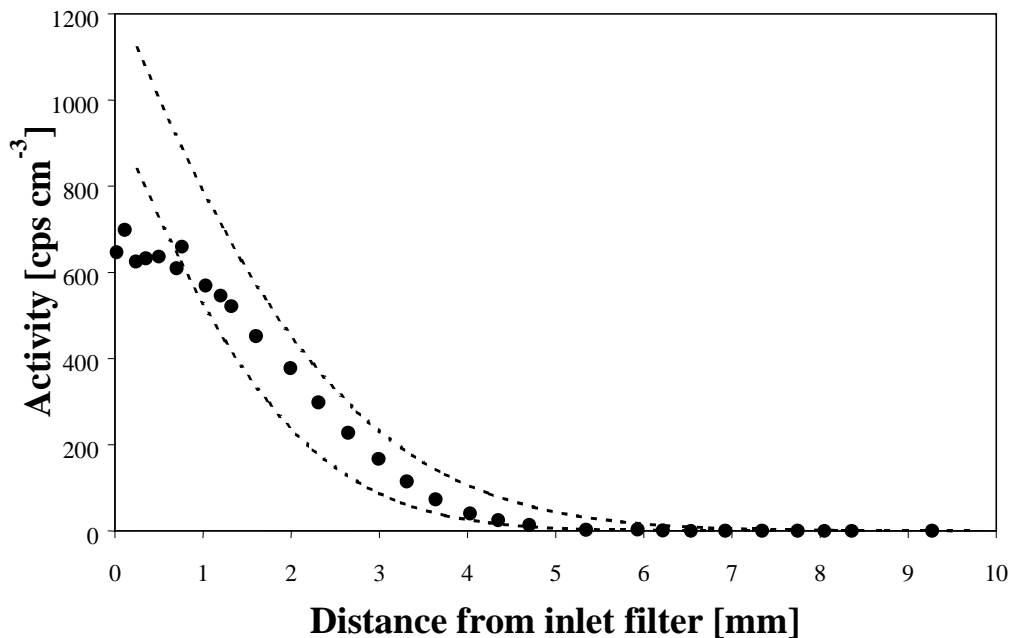The concentration profile for cobalt is shown in Figure 5-3.

Figure 5-1. *Predicted and experimental results for caesium. The dashed lines indicate the boundaries from simulations considering uncertainties in K_d and D_a.*
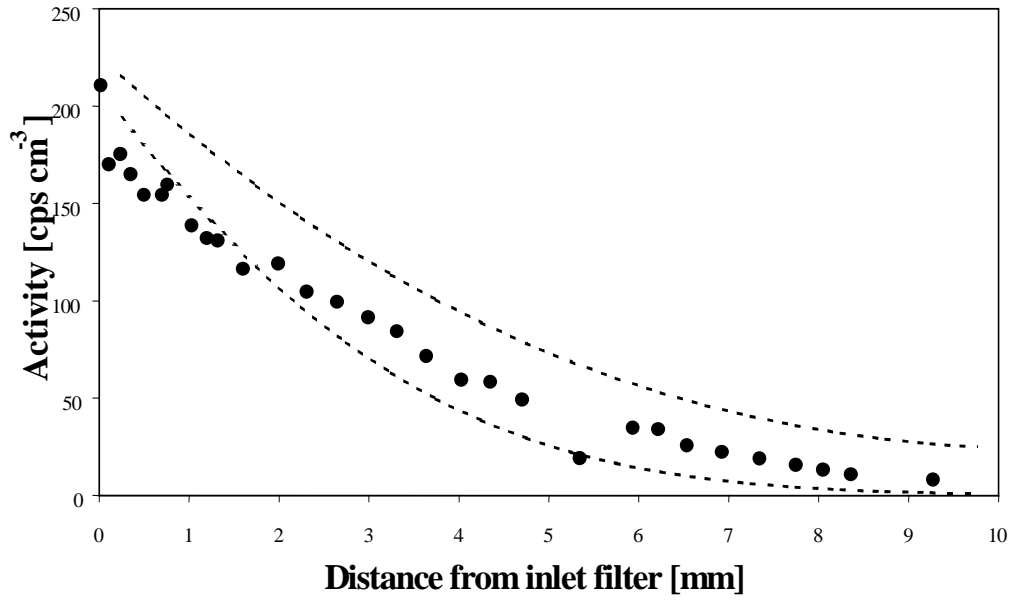
Figure 5-2. *Predicted and experimental results for strontium. The dashed lines indicate the boundaries from simulations considering uncertainties in K_d and D_a.*
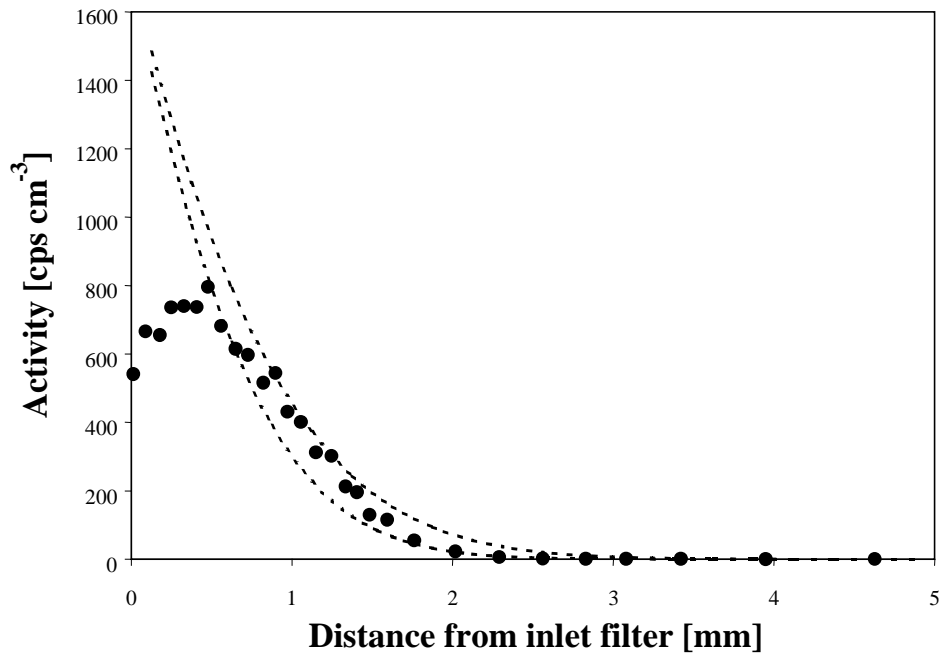

Figure 5-3. *Predicted and experimental results for cobalt. The dashed lines indicate the boundaries from simulations considering uncertainties in K_d and D_a.*
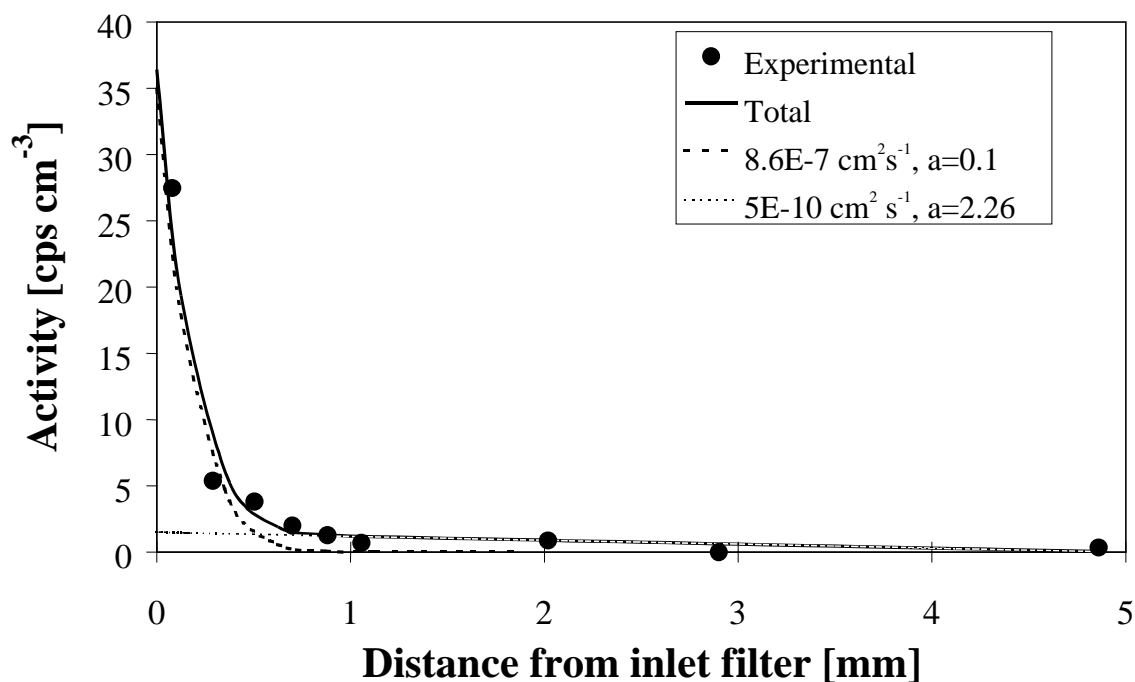
Figure 5-4. *Experimental and simulated results for iodide.*

The higher K_d values for Co^{2+} obtained in laboratory diffusion experiments with a synthetic Äspö groundwater is most probably caused by a slightly higher pH in the synthetic groundwater (pH ~7.5) used in the laboratory experiments than in the ground-water at the experimental site at Äspö (pH 7.2). Co^{2+} displays a sorption edge at pH ~6.5 with K_d increasing by two orders of magnitude between pH 6.5 and 8.5 /Eriksen et al., 1999/. Corresponding sorption edges on Na-montmorillonite for Ni, Zn and Ca have been modelled assuming the formation of surface complexes /Bradbury and Baeyens, 1995/.

At a first glance the measured activity profile for I^-, Figure 5-4, is quite different to the activity distribution expected from the analyses of break through curves obtained in laboratory experiments and can not easily be modelled assuming a single diffusion process.

The low activity distribution can be simulated using $D_a = 8.6 \cdot 10^{-7}$ cm^2 s^{-1} and $\alpha = 0.1$, in good agreement with data from laboratory break through curves.

High activity profiles at the inlet side of the bentonite plug has earlier been observed for I^- and Cl^- in laboratory experiments with MX-80 and Erbslöh bentonites /Eriksen and Jacobsson, 1981/.

The high-level activity profile can be modelled assuming a diffusion process with $D_a = 5 \cdot 10^{-10}$ cm^2 s^{-1} and $\alpha = 2.26$. The pore space accessible for this diffusive pathway is not known but the α-value indicates that the distribution coefficient K_d is in the range 1 to 1.2 cm^{3}g^{-1}.
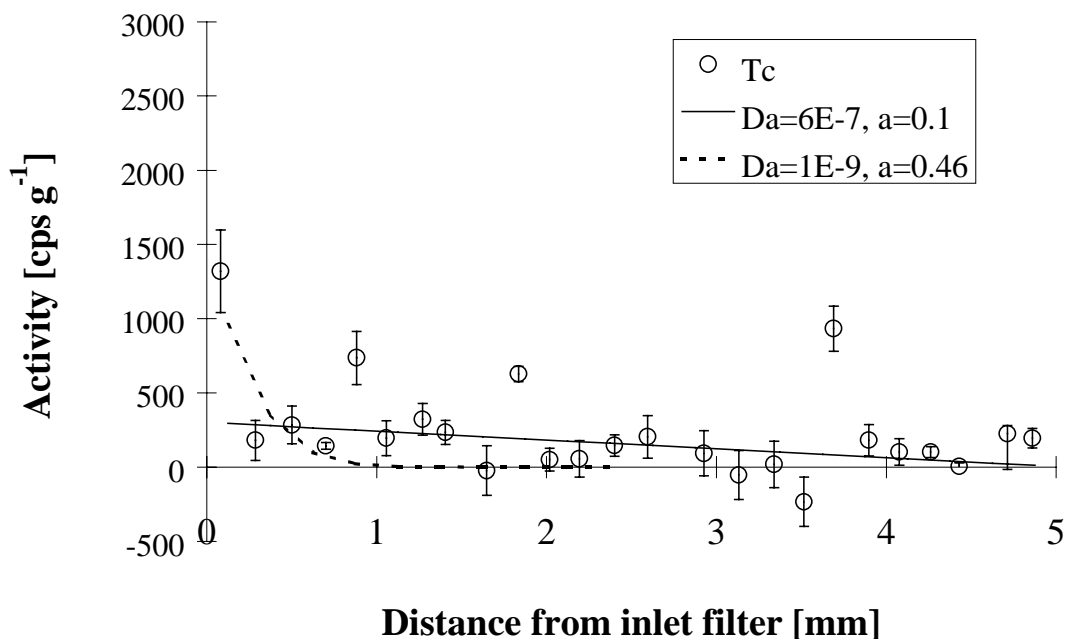
Figure 5-5. *Experimental and simulated results for technetium.*

Ionic strength and pH dependent adsorption of anions are reported in several studies /Swartzen-Allen and Matijevic, 1974/ and /Pusch et al., 1999/ reports K_d-values varying from 2 to 0.3 cm^3g^{-1} for bentonite equilibrated with groundwaters with ionic strength in the range 0.032 to 0.346.

The activity profile for Tc is plotted in Figure 5-5.

The profile can, as for I^-, be modelled by assuming two diffusive processes with $D_a = 6 \cdot 10^{-7}$ cm^2 s^{-1}, $\alpha = 0.1$ and $D_a = 1 \cdot 10^{-9}$ cm^2 s^{-1}, $\alpha = 0.46$, respectively.

The data clearly indicates that the diffusing species, in spite of the reducing conditions, is TcO_4^-. Technetium was added as a small volume of stock solution containing TcO_4^- and the stock solution diluted in situ with filtered groundwater. Surfaces in contact with the solution are, with the exception of the diffusion cell filters, chemically inert PEEK surfaces.

The reduction of Tc(VII) to Tc(IV) requires three electrons and the stepwise one electron reduction of TcO_4^- to $TcO_2 \cdot nH_2O$ by $Fe^{2+}(aq)$ is, although thermodynamically feasible, kinetically hindered /Cui and Eriksen, 1996/. Surface mediated reduction on Fe(II) bearing minerals and precipitates is therefore expected to be the dominating reaction path in natural systems and TcO_4^- is quite stable in the absence of such surfaces.

The data for I^- and TcO_4^- are in accordance with observations in laboratory experiments. The knowledge about the slow diffusive process is limited and the process is presently being studied in laboratory experiments.

6 Evaluation of CHEMLAB

The manufacturer of CHEMLAB, Métro Mesures S.V. in Paris, has previously manufactured four probes for borehole measurements for CEA Cadarache, but CHEMLAB is by far the most complex system. Since it is a novel technique, several teething problems have occurred during the experiments and tests. The borehole lock has broken, as well as valve gears. Clogging of valves, leading to water penetration of electrical connections, has caused corrosion. Sensitive components (valves and pumps) have been exposed to water due to leakage in the hydraulic system connections.

All in all CHEMLAB has proven to be a fragile system which has to be tended and cherished. The handling has to be very thorough, since the least leakage can cause severe damages. A lesson learned during the experiments is that since the Äspö groundwater has a relatively high iron concentration it is of great importance to minimise the oxygen content in CHEMLAB before the experiment starts to avoid oxidation of Fe(II) and precipitation of Fe(III) when meeting oxygen.

It should be stressed, though, that when CHEMLAB works correctly it is a very good tool for performing *in-situ* experiments.

7　References

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