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DIFFUSION IN CLAY – EXPERIMENTAL TECHNIQUES AND THEORETICAL MODELS

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

A list of other reports published in this series during 1984 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28) and 1983 (TR 83-77) is available through SKBF/KBS.

Diffusion in clay - Experimental techniques and
theoretical models

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	CONTENTS	PAGE
	Summary	1
1	Introduction	2
2	Experimental techniques - limitations and merits	3
2.1	Method I	3
2.2	Method II	5
2.3	Method III	8
3	Transport models	12
3.1	The K_d -concept	12
3.2	K_d -measurements	14
4	Water uptake and water structure in bentonite	15
5	Ion mobility in clay	16
6	Diffusivities	16
6.1	Cations	17
6.2	Anions	17
6.3	H_2 , CH_4	18
6.4	Actinides	21
7	Conclusions	25
7.1	Experimental methods	25
7.2	Diffusion models	25

SUMMARY

A large number of experiments have been carried out by this and adjacent research groups to assess the diffusivity of a wide variety of dissolved species such as cations anions, macromolecules and gases in watersaturated clay at differing compaction. The results have been reported in a series of KBS-technical reports.

This report is a summary of the experiences gained by these experiments. Recommended experimental methods are described and a methodology to treat and interpret the experimental data is outlined. The mechanisms for diffusion in clay are also discussed in some detail - especially the influence of charge, molecular size and hydrolysis of the diffusing species.

1 INTRODUCTION

To be able to assess the long term storage of nuclear wastes in underground repositories, understanding of the migration mechanisms in groundwater systems is of great importance.

A clay backfill is generally recommended as a low permeability shield around the nuclear waste canisters. Diffusion will therefore be an important transport mechanism for radionuclides if the canisters fail. The radionuclide retardation, due to sorption, could be significant and diffusion in bentonite clay have therefore been the subject of several studies⁽¹⁻¹¹⁾.

Several experimental techniques have been used with somewhat varying results in measured diffusivities. Most of the work in the course of the KBS-supported studies have been concentrated on compacted sodium bentonite clay with densities up to $2.1 \text{ kg}\cdot\text{dm}^{-3}$.

Theoretical models have been developed to explain the experimental results and make possible predictions of radionuclide retentions. Torstenfelt et al^(5,9,11) as well as Neretnieks⁽¹²⁾ have treated the radionuclide diffusion according to a model based on the assumption that diffusion takes place exclusively in the pore water and the retardation is an equilibrium sorption process. The experimental data are not easily accommodated by this model, and Neretnieks⁽¹³⁾ has therefore suggested that surface migration is an important process⁽¹⁴⁾.

The purpose of this report is to summarize the experimental data from diffusion studies in compacted bentonite and to discuss the transport models used in interpreting the data.

2 EXPERIMENTAL TECHNIQUES - LIMITATIONS AND MERITS

These fundamentally different tracer methods, two instationary and one stationary have been used in the experiments conducted to date.

2.1 Method I

The tracer was added to synthetic ground water in contact with compacted watersaturated bentonite ($\rho = 2.1 \text{ kg} \cdot \text{dm}^{-3}$)⁽⁶⁾. The tracer solution was pumped through the oedometer (fig. 1) and the tracer concentration in the solution kept constant during the experiment. The bentonite was confined by a metallic filter forming an interface between the bentonite-gel* in the diffusion cell and the tracer solution. At the end of the experiment the bentonite was sliced into thin discs and the tracer concentration profile measured.

The diffusivity within the bentonite-gel is described by Fick's second law

$$\frac{\partial \bar{c}}{\partial t} = \bar{D} \cdot \frac{\partial^2 \bar{c}}{\partial x^2}$$

*) denotes watersaturated clay

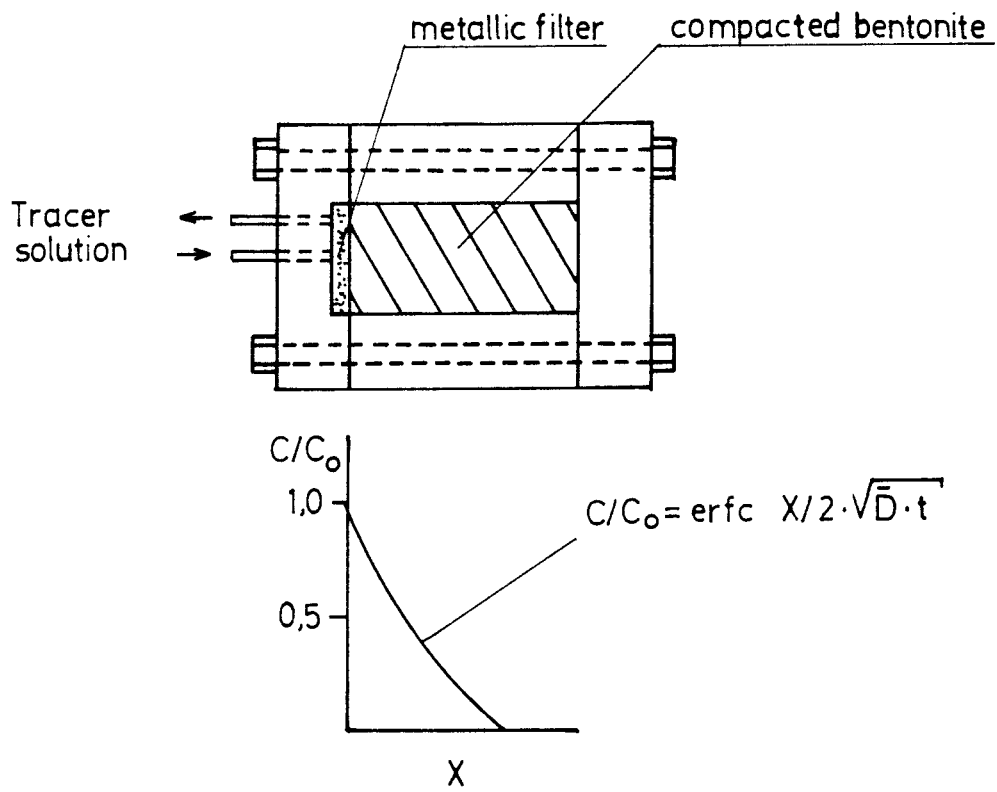


Fig. 1
Schematic drawing of diffusion cell,
theoretical concentration profile.(Method I)

where \bar{D} is the diffusion coefficient describing the total transport within the gel. The following initial and boundary conditions are assumed to describe the experimental constraints:

$$\bar{C}(x,0) = 0$$

$$\bar{C}(0,t) = \bar{C}_0$$

$$\bar{C}(d,t) = 0$$

where d is the distance from the solution/bentonite-gel interface to the other boundary of the diffusion cell and \bar{C} is the tracer concentration within the clay-gel. The concentration profile is given by ⁽¹⁵⁾ the solution.

$$\bar{C}/\bar{C}_0 = \text{erfc} \left[\frac{x}{2 \cdot (Dt)^{1/2}} \right]$$

The boundary condition $\bar{C}(0,t) = \bar{C}_0$ i.e. constant tracer concentration at the clay-gel surface is probably not satisfied for cationic diffusion as diffusion through the filter may be rate-determining during the first part of an experiment due to the high cationic exchange capacity of the bentonite.

Skewed concentration profiles were obtained for anions ⁽⁴⁾. The calculated anion diffusivities are therefore uncertain.

2.2 Method II

Compacted and water-saturated bentonite was either surface activated by exposure to a tracer solution for a few hours or equilibrated for several weeks with a tracer solution.

By pressing the tracer doped bentonite into contact with tracer free bentonite an impulse source or a planar source of limited extent was obtained (fig. 2a).

At the end of each experiment the concentration profile was measured as described for method I above. The initial and boundary conditions describing the physical constraints and the solutions describing the tracer distributions are as follows.

Impulse source:

A = interfacial area

M = total amount of tracer; remains constant throughout the experiment

$$\partial \bar{C} / \partial x (0, t) = 0$$

$$\bar{C}(\pm d, t) = 0$$

$$\bar{C}/M = \frac{1}{2 \cdot A (\pi D \cdot t)^{1/2}} \cdot e^{-x^2/4\bar{D} \cdot t} \quad (\text{fig. 2a})$$

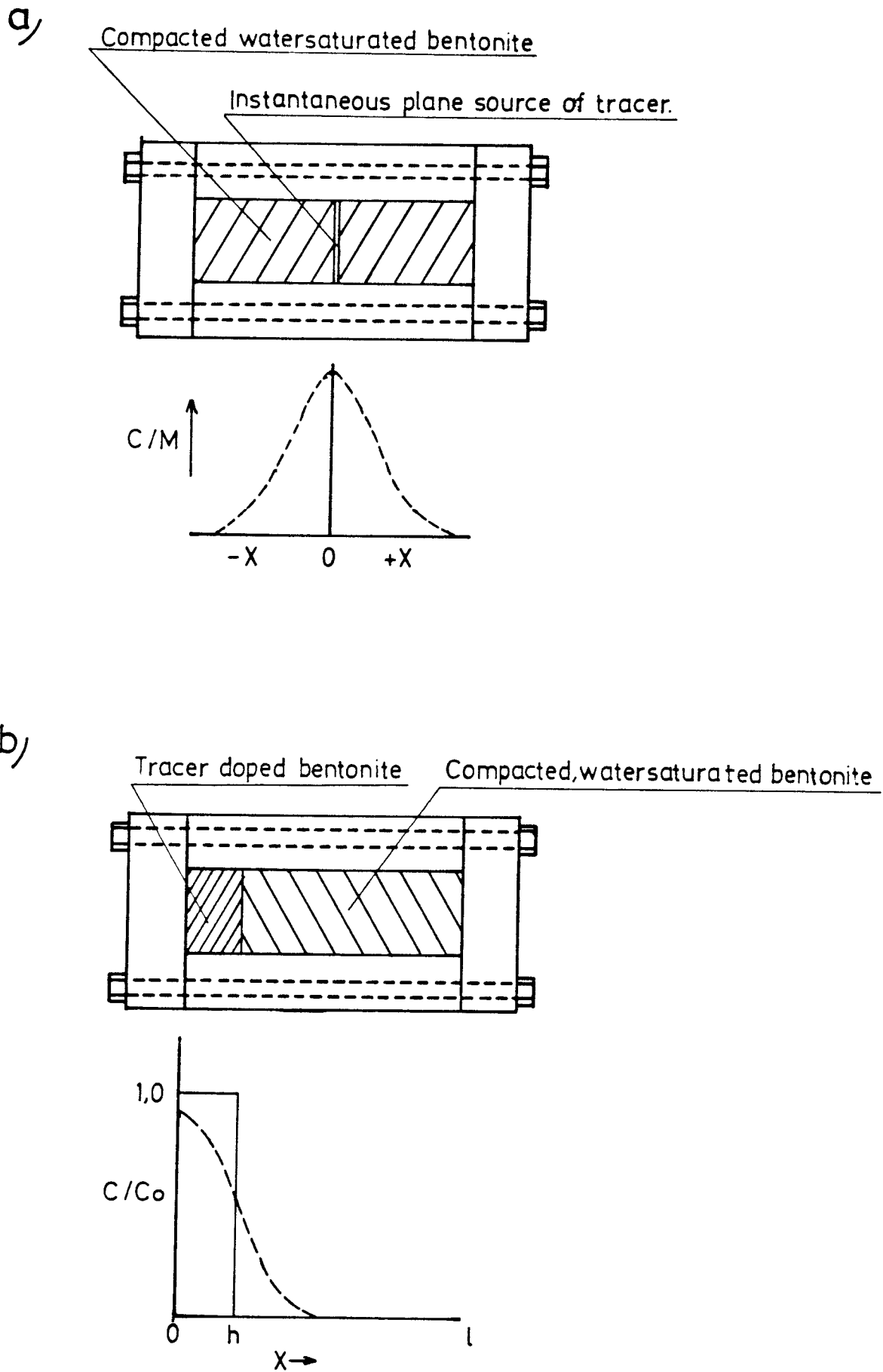
where x is the distance from tracer doped surface and 2d is total length of the diffusion cell.

Extended initial distribution:

$$\partial \bar{C} / \partial x (0, t) = 0$$

$$(x \leq h, 0) = \bar{C}_0$$

$$\bar{C}(x > h, 0) = 0$$



$$\bar{C}(d,t) = 0$$

$$\bar{C}/\bar{C}_0 = \frac{1}{2} \left[\operatorname{erf} \frac{1 - x/h}{2/h \cdot (\bar{D}t)^{1/2}} + \operatorname{erf} \frac{1 + x/h}{2/h \cdot (\bar{D}t)^{1/2}} \right] \quad (\text{fig. 2b})$$

where h = thickness of initially tracer equilibrated bentonite cylinder

d = total thickness of bentonite cylinder

In both cases the diffusion takes place within the clay-gel i.e. no solution/clay-gel interfacial transport is involved. The diffusivities (\bar{D}) obtained in these experiments describe the overall tracer transport within the gel. Some authors prefer to use the notation D_a (ie apparent diffusivity) but we are reluctant to use this notation as this usually is taken to mean D_p/R_a where D_p and R_a are the diffusivity in pore solution and R_a a retardation factor respectively.

2.3 Method III

A compacted water saturated bentonite disc of thickness d , confined by thin metallic filters, separated two volumes of ground water. The tracer was added to the solution on one side of the bentonite membrane and the temporal change in tracer concentration in the solution on the other side of the membrane measured.

The diffusion through the bentonite-membrane is given by Fick's second law

$$\frac{\partial \bar{C}}{\partial t} = \bar{D} \cdot \frac{\partial^2 \bar{C}}{\partial x^2}$$

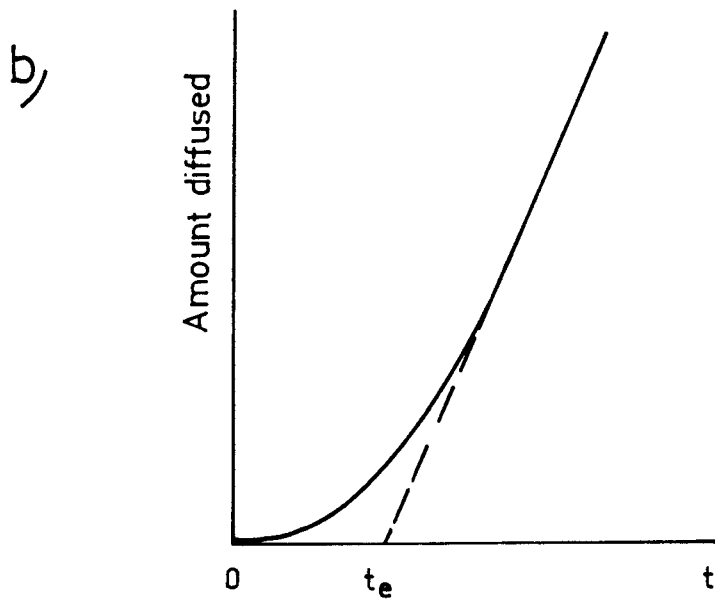
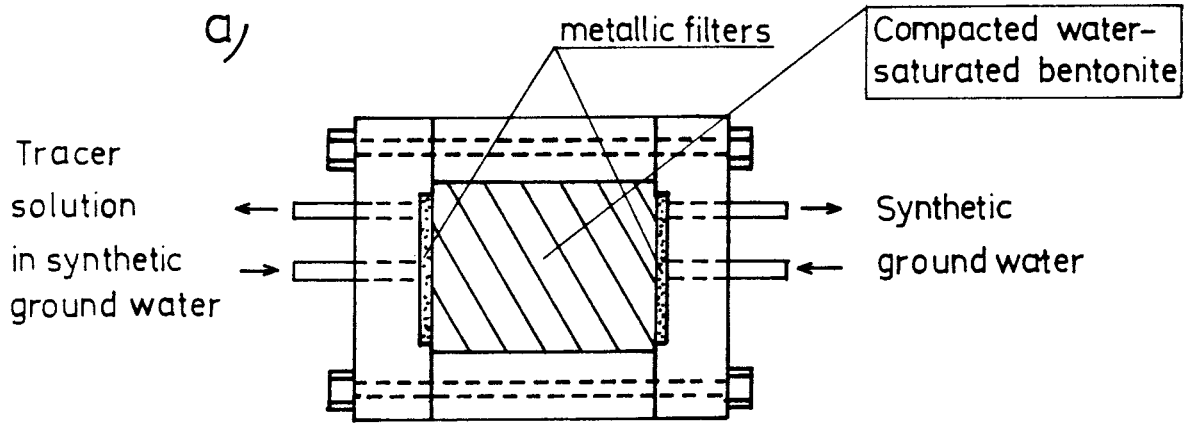


Fig.3

- a) Schematic drawing of diffusion cell.
- b) Idealized time dependence of tracer diffused through clay-membrane.(Method III)

and the initial and boundary conditions

$$\bar{C}(0 < x < d, 0) = 0$$

$$\bar{C}(0, t) = \bar{C}_0$$

$$\bar{C}(d, t) \ll \bar{C}_0$$

where \bar{C} = the tracer concentration within the clay-gel.

\bar{D} = diffusivity taking into account the overall tracer diffusion within the clay-gel.

The solution (describing the tracer concentration profile within the membrane) is (16).

$$\bar{C}(x, t) = \bar{C}_0(1-x/d) - \sum_{n=1}^{\infty} \frac{2\bar{C}_0}{n\pi} \exp(-\bar{D}t(\frac{n\pi}{d})^2) \sin \frac{n\pi x}{d}$$

The total amount of tracer accumulated in the solution at the far side of the membrane (Q) is obtained by integrating the flux at $x = d$ with time

$$\frac{Q}{A \cdot d \cdot \bar{C}_0} = \frac{\bar{D} \cdot t}{d^2} - \frac{1}{6} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left(\frac{\bar{D} \cdot (n\pi)^2 t}{d^2} \right)$$

as $t \rightarrow \infty$ the amount of tracer transported through the membrane is given by the asymptotic solution

$$Q/A = \frac{\bar{C}_0 \cdot \bar{D}}{d} \cdot t - \frac{\bar{C}_0 \cdot d}{6}$$

with the slope $\bar{C}_0 \cdot \bar{D}/d$ and the time lag, ie the intercept with the time axis

$$t_e = d^2/6 \cdot \bar{D}$$

It ought to be emphasized that in calculating the tracer diffusivity from the steady state transport one need to know the membrane interfacial concentration \bar{C}_0 . Normally the diffusivity calculations are based on the tracer concentration in the solution C_{sol} i.e. using the equation

$$\frac{dQ}{dt} = A \cdot \frac{C_{sol} \cdot D_{tr}}{d}$$

For anions and uncharged tracers it is generally assumed that the diffusion takes place in the pore solution only and that no sorption occurs. In this case $\bar{C}_0 = \epsilon_p \cdot C_{sol}$ where ϵ_p is the porosity and $D_{tr} = \bar{D} \cdot \epsilon_p$.

The assumption that the tracer concentration at the interface membrane/solution is the same in the pore water as in the external solution in contact with the clay-gel is however quite often not valid. For anions the tracer concentration in the pore solution is normally, as pointed out by Eriksen and Jacobsson⁽⁶⁾, much lower than the concentration in the external solution. The diffusivity D_{tr} as defined above is a measure of the transport capacity of the clay at the given experimental conditions. To calculate \bar{D} from D_{tr} the concentration \bar{C}_0 must be determined separately.

3 TRANSPORT MODELS

3.1 The K_d -concept

The modelling of radionuclide diffusion in porous media is usually based on the assumption of a two phase system, the solid framework and the interstitial pores. Diffusion is viewed as taking place in the pore solution only and the retardation as immobilization due to one of several physiochemical processes, eg sorption, ion exchange, precipitation (13,17-20). The tracer concentration is assumed to be the same in pore solution and external solution. In the simplest case a single valued retardation factor R_d is used, based on the assumption that the amount of radionuclide associated with the porous material is proportional to the concentration in the external solution i.e. $K_d = q/c$

where K_d = the distribution coefficient ($\text{dm}^3 \cdot \text{kg}^{-1}$)

q = concentration in solid $\text{mol} \cdot \text{kg}^{-1}$

c = concentration in solution $\text{mol} \cdot \text{dm}^{-3}$

Based on this assumption the measured diffusivity, often called the apparent diffusivity, D_a is related to the diffusivity in the pore solution D_p by the eqn $D_a = D_p / (1 + K_d \cdot \rho)$. In our notation $D_a = \bar{D}$.

When this relationship is used to calculate pore diffusivities for simple cations like Sr^{2+} , Na^+ , Cs^+ , D_p is found to be much higher than the diffusivity of these cations in aqueous solution, D_w , eg the diffusivity (\bar{D}) and K_d of Sr^{2+} is found to be $\sim 15 \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$ and $10^3 \text{ dm}^3 \cdot \text{kg}^{-1}$ respectively. Using the K_d concept this would give $D \sim 3 \cdot 10^{-8} \text{ m}^2 \cdot \text{sec}^{-1}$ whereas D_w is approximately $0.13 \cdot 10^{-8} \text{ m}^2 \cdot \text{sec}^{-1}$.

To explain these results Neretnieks ⁽¹³⁾ suggests that surface migration is an important transport mode.

A similar model was proposed as early as 1947 by GE Boyd et al ⁽²¹⁾ for diffusion in ion exchangers. These authors assume in essence that most of the counter ions in an ion exchanger are localized while only a few diffuse in macropores containing solution of about the same composition as the external solutions.

The relation $\bar{D}_i = D_i \delta / \lambda_i$, where λ_i is the molar distribution coefficient, was however found to drastically overemphasize one single effect. It was also suggested by Boyd ⁽²¹⁾ and others ^(22,23) that the counter ions may diffuse by surface migration along the chains of the ion exchanger matrix.

In later publications the overall cation transport in suspensions with low clay content ⁽²⁴⁻²⁵⁾ and on water saturated clay films ⁽²⁶⁾ have been explained by a model based on the assumption of diffusion taking place both in a solution phase and in an adsorbed phase.

In view of the models proposed it is of interest to discuss the K_d -measurements and the water uptake in bentonite.

3.2 The K_d -measurements

The sorption on bentonite has in most cases been studied by a batch technique. The radionuclide is added to a clay suspension and the solid and aqueous phases separated by filtration or centrifugation after a suitable contact time. The radionuclide concentration in the solid and aqueous phase is measured and the distribution coefficient calculated from

$$K_d = \frac{(C_0 - C)/m}{C/V}$$

where C_0 = initial radionuclide concentration in solution

C = radionuclide concentration in solution after a certain contact time

m = mass of sorbent

V = volume of solution

The K_d is thus a measure of the distribution between a clay-gel containing a certain amount of water and an external solution. The measurements give no information about the distribution, or the mobility of the radionuclide within the clay-gel. For radionuclides with low solubility precipitation may take place. In this case the measured K_d is of course not representing a clay-gel/solution phase distribution.

4 WATER UPTAKE AND WATERSTRUCTURE IN BENTONITE

The clay surface offer an unique environment for the study of water arrangement on an electrified interface and a great number of studies based on the use of different technique have been published.

The structure of water adsorbed on smectites has recently been reviewed (27,28). It seems clear that the first stage in water adsorption involves solvation of the exchangeable cations, the degree of solvation depending on the ability of the cation to solvate themselves. The solvation of cations is followed by water sorption on external surfaces and in micropores.

As the water content increases the behaviour of the hydrated cation becomes similar to that of a cation in aqueous solution. The situation within the clay can thus be described as a negatively charged surface (anion with a very large radius of curvature) enveloped by a solvent sheath and a cation cloud i.e. in correspondance with the double layer theory of electrified interfaces (29).

By regarding the clay-gel as a concentrated electrolytic system Marinsky has calculated (30) distribution coefficients for Sr^{2+} and Cs^{+} ions in good agreement with experimentally determined K_D -values. The low anionic exchange capacity and hence the low anion concentration in the pore solution caused by Donnan exclusion also explain the low concentrations of anionic tracers within the clay-gel (4,6,7).

5 IONIC MOBILITY IN CLAY

The cationic diffusion within the clay-gel is constrained by the immobility of the anionic surface and the requirement of electro-neutrality. The diffusion may also be slowed by sorption by non-coulombic processes on the clay-matrix.

The relative importance of the different sorption processes depends on the charge, ionic size, dipole moment, and polarizability of the diffusing species. For simple cations the ion-exchange process is dominating and there is, as also pointed out by Marinsky (30), no need to suppose that the counterions are immobilized. It ought to be emphasized that for the compacted bentonite used in the diffusion experiments discussed in this report the water content corresponds roughly to 2-4 water molecule layers (31). There is therefore really no "free water" and the measured diffusivity \bar{D} can be regarded as corresponding approximately to the diffusivity within the adsorbed phase as defined by Duffey and Landelout (24-25) as well as Ellis et al (26).

6 DIFFUSIVITIES IN COMPACTED BENTONITE

The diffusivities compiled in tables 1 and 2 are mostly taken from works by the authors (4,6-8) and B Allard's research group (9,11,12).

The tracers studied can be divided into four groups: cations, anions, actinides and gaseous molecules. Each group will be discussed separately below.

6.1 Cations

The simple cations Sr^{2+} and Cs^+ have been studied extensively by several groups (4,5, 6, 8,9). The "best values" of \bar{D} are probably $15 \cdot 10^{-12}$ and $2.5 \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$ for Sr^{2+} and Cs^+ respectively. In all studies Sr^{2+} was found to diffuse faster than Cs^+ . This might at first sight be surprising as $r_{\text{Sr}^{2+}(\text{solv})} > r_{\text{Cs}^+(\text{solv})}$. Cs^+ is, however, weakly hydrated and the low diffusivity is probably due to more site specific interaction (contact sorption⁽²⁹⁾) with the clay matrix.

Diffusivities of Cu^{2+} , Zn^{2+} and Mn^{2+} in the surface correlated cationic cloud on montmorillonite have been found by Ellis et al⁽²⁶⁾ to be nearly the same as the diffusivities of Sr^{2+} given in table 1.

6.2 Anions

As mentioned above, the anionic diffusivities measured by method I are rather uncertain, as skewed experimental distributions relative to the theoretically calculated distribution were obtained. The diffusivities calculated from steady state transport through a bentonite membrane, using the eqn $\bar{D} = d^2/6t_e$ are therefore used as "best values" in the following discussions.

The diffusivities of the spherical ions Cl^- , I^- , TcO_4^- are in the range $(90-35) \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$ and the diffusivity of $\text{HS}^- \sim 5 \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$.

The diffusivities \bar{D} of the large molecular weight anions AQS^- and LS^- are $(5-9) \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$.

In table 1 are also given the diffusivities D_{tr} , calculated from steady state transport data using the eqn $\frac{dQ}{dt} = A \cdot D_{\text{tr}} \cdot \frac{C_{\text{sol}}}{d}$ i.e. based on the geometrical area of the clay membrane and tracer concentration in the external solution.

If the tracer concentration in the pore water is the same as in the external solution the ratio $D_{\text{tr}}/\bar{D} \cdot \epsilon_p$ should be unity. The ratio is however, as shown in table 1, found to be much lower, clearly demonstrating the permselectivity of the clay-membrane due to the Donnan exclusion.

It is interesting to note that the ratio $D_{\text{tr}}/\bar{D} \cdot \epsilon_p$ is approximately the same for HS^- as for I^- and Cl^- . The most probable explanation to this is that the HS^- ion being a dipole interacts with the clay-matrix, possibly replacing OH^- . The lower $D_{\text{tr}}/\bar{D} \cdot \epsilon_p$ ratios for the large molecular weight anions AQS^- , LS^- indicate a constrictivity effect on the diffusion.

6.3 H_2 , CH_4

The diffusivities \bar{D} and D_{tr} calculated from diffusion through a bentonite membrane are $(16-41) \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$ and $(3.6-18) \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$ respectively.

Table 1. 1(2)

Experimentally measured diffusivities in compacted Na-bentonite ($\rho \sim 2.1 \text{ kg}\cdot\text{dm}^{-3}$).

Ref.	Diff. species	Exp. cond	$\bar{D} \cdot 10^{12}$ $\text{m}^2 \cdot \text{sec}^{-1}$	$(\bar{D} = d^2/6t) \cdot 10^{12}$ $\text{m}^2 \cdot \text{sec}^{-1e}$	$D_{tr} \cdot 10^{12}$ $\text{m}^2 \cdot \text{sec}^{-1}$	$D_{tr}/\bar{D} \cdot \epsilon_p$
4	Sr^{2+}	0x	23(I)*			
6			15±2(II)			
5,9			(1.8-12)II			
4	Cs^+	0x	7.5(I)			
6			2.5±0.5(II)			
5			0.9(II)			
9			1.4-2(II)			
10			5(II)			
5	Tc	Red	0.3(II)			
5	TcO_4^-	0x	14-53(II)			
4	I^-	0x	4	35	0.21	0.017
4	Cl^-	0x	6	92	0.31	0.01

(continued)

x) (I) and (II) refers to methods (I) and (II) described above.

Table 1. 2(2)

Experimentally measured diffusivities in compacted Na-bentonite ($\rho \sim 2.1 \text{ kg}\cdot\text{dm}^{-3}$).

Ref.	Diff. species	Exp. cond	$\bar{D} \cdot 10^{12}$ $\text{m}^2 \cdot \text{sec}^{-1}$	$(\bar{D} = d^2/6t_e) \cdot 10^{12}$ $\text{m}^2 \cdot \text{sec}^{-1}$	$D_{tr} \cdot 10^{12}$ $\text{m}^2 \cdot \text{sec}^{-1}$	$D_{tr}/\bar{D} \cdot \epsilon_p$
7	HS^-	N_2 atm	9(II)	4.8	0.018	0.006-0.011
7	AQS^- mol wt 240	N_2 atm		9	$2.1 \cdot 10^{-3}$	$6.7 \cdot 10^{-4}$
7	Eosin mol wt 548	N_2 atm			$>0.6 \cdot 10^{-3}$	
7	LS^- mol wt 30.000	N_2 atm		5.6	$0.75 \cdot 10^{-3}$	$3.8 \cdot 10^{-4}$
7	H_2			47	3.6	0.23
2	H_2			16	18	3.21
2	CH_4			14.5	39	7.7

*) (I) and (II) refers to methods (I) and (II) described above.

The corresponding diffusivities of CH_4 are $11.4 \cdot 10^{-12}$ and $39 \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$

Due to the uncertainties in the published values it is difficult to discuss the $D_{tr}/\bar{D} \cdot \epsilon_p$ values, but the diffusivities \bar{D} are of the same order of magnitude as for small anions.

6.4 Actinides

The diffusion of actinides in compacted bentonite have been studied extensively by Allard and coworkers and their data are compiled in table 2.

The actinides exhibit a broad range of oxidation states - from II- to VII - in aqueous solution ⁽³²⁾. To compare the diffusivities, one therefore needs to predict the speciation of each actinide at the experimental conditions.

The important complexing agents present in the synthetic groundwater used are OH^- and $\text{HCO}_3^-/\text{CO}_3^{2-}$. Whereas the OH^- concentration within the pore water most probably is higher (pH ~ 9.5) than in the external solution (pH ~ 8.2) the $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentration is expected to be somewhat lower.

The speciation of actinides in aerated aqueous solutions containing carbonate have been discussed by Allard et al ^(33,34).

Thorium exists only as Th(IV) and is assumed to be fully hydrolyzed i.e. the dominating species will be $\text{Th}(\text{OH})_4$ ⁽³⁴⁾.

Table 2.
Diffusivities of actinides^{*)}.

Actinide	Exp.cond.	$\bar{D} \cdot 10^{12} \text{ m}^2 \cdot \text{sec}^{-1}$
Th	0x	0.46-0.85 · 10 ⁻²
Pa	0x	≥ 0.57
U	0x	0.58-0.82
U	600 mg · dm ⁻³ HCO ₃ ⁻ in aq. phase	0.19-0.34
U	10 mg · dm ⁻³ humid acid in aq. phase	0.57-0.94
U	1% Fe(PO ₄) ₂ in the clay	0.2-0.38
U	0.5% Fe(s) in the clay	0.045-0.11
Np	0x	0.22-0.37
Np	0.5% Fe(s) in the clay	(0.45-1.6) · 10 ⁻²
Np	1% Fe(PO ₄) ₂ s in the clay	(0.86-3.4) · 10 ⁻²
Np	0.5% Fe(s) in part of the clay	(0.8-2.4) · 10 ⁻²
Pu	0x	(0.69-3) · 10 ⁻²
Am	0x	(0.4-1.4) · 10 ⁻²
Am	Added in 0.1 M acetate solution	(0.4-1.4) · 10 ⁻²
Am	Added as colloid pH 12	(0.4-1.4) · 10 ⁻²
Am	600 mg · dm ⁻³ HCO ₃ ⁻ in aq. phase	(0.28-0.95) · 10 ⁻²

^{*)} All data taken from Allard et al (ref 9 and personal communication).
(Profile analysis, method IIa)

Protactinium is in the Pa(V) oxidation state, although it is uncertain whether as PaO_2^+ or Pa(O)(OH)_2^+ (32). The dominating species is expected to be $\text{PaO}_2(\text{OH})_2^-$.

In aerated solutions uranium is in the U(VI) oxidation state and hydroxides and carbonate complexes $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{OH})_3^-$ are probably the dominating species. On addition of reducing agents to the clay the uncharged U(IV) hydroxide U(OH)_4 will be present in increasing concentration.

Under oxic condition Np(V) will dominate entirely and the most probably diffusing species are $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2(\text{OH})$ and possibly $\text{NpO}_2(\text{OH})_2^-$. On addition of reducing agents the uncharged Np(IV) hydroxide Np(OH)_4 is probably formed.

Under oxic conditions both Pu(V) and Pu(IV) could exist and probable diffusing species are Pu(OH)_4 and possibly $\text{PuO}_2(\text{CO}_3)_2^{3-}$ (depending on the carbonate concentration in the bentonite).

Americium is expected to be present only in the Am(III) oxidation state in aerated solution and the most abundant complexes formed in ground water and pH 8.2 are Am(OH)_2^+ , Am(OH)_3 , $\text{Am}(\text{CO}_3)^+$ and $\text{Am}(\text{CO}_3)_2^-$. If, as expected, the pH in the clay gel is higher (~9.5) and the CO_3^{2-} concentration lower than in the ground water Am(OH)_3 will be the dominating species.

Bearing this speciation in mind the experimental data given in table 2 can be divided into two groups:

- The diffusivities of the negatively charged hydroxide and carbonate complexes of Pa(V), U(VI), Np(V) are in the range $(0.2-0.9) \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$.
- The diffusivities of the neutral hydroxide complexes of Th(IV), U(IV) and Np(IV) are in the range $(0.4-1.4) \cdot 10^{-14} \text{ m}^2 \cdot \text{sec}^{-1}$.

The low diffusivity of Am(III) clearly indicates the formation of the $\text{Am}(\text{OH})_4$ complex.

These data clearly demonstrate the increasing interaction with the clay matrix, possibly by hydrogen bonding, caused by the OH-groups. This effect is also nicely demonstrated in the case of Tc diffusion. Under oxic conditions the dominating species is TcO_4^- ⁽³⁵⁾ having a high diffusivity whereason reduction of the heptavalent TcO_4^- the dominating soluble species will be $\text{TcO}(\text{OH})$. The diffusivity of $\text{TcO}(\text{OH})$ is found to be at least two orders of magnitude lower than the diffusivity of TcO_4^- .

7 CONCLUSIONS

7.1 Experimental methods

In choosing experimental methods great care must be taken in defining the experimental constraints. When measuring the diffusive transport through a clay membrane one must consider the effect of two clay/solution interfaces. If the clay is confined by metallic filters the diffusive resistance of these may quite often be the limiting factor.

7.2 Diffusion models

The following can be concluded regarding the mechanisms of diffusion of dissolved species in wet compacted bentonite clay.

- The diffusivity of cations and anions in compacted bentonite is found to be much lower than in aqueous solutions.
- There is no reason to assume that the ions are immobilized and the diffusivity within the clay gel can not be calculated using the K_d -concept.
- On calculating the diffusivity within a clay-membrane from the amount transported through the membrane, great care must be exercised in using a capacity factor given by the equation $\theta = \epsilon_p + \rho \cdot K_d$. This equation gives the lower capacity limit as ϵ_p , which is not the case for co-ions in high ion exchange capacity materials.
- The hydrolysis has a very great effect on the diffusivity. When unchanged hydroxides are formed, the sorption increases sharply leading to a sharp decrease in diffusivity. (This case corresponds more to K_d -koncept)

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REFERENCES

1. Neretnieks I, Skagius K:
Diffusionsmätningar i våt lera, Na-lignosulfonat,
 Sr^{2+} , Cs^+ . KBS-report 87.
2. Neretnieks I, Skagius K:
Diffusionsmätningar av metan och väte i våt lera.
KBS-report 86.
3. Allard B, Kipatsi H:
Mätning av diffusionshastigheten för silver i
lera-sandblandning. KBS-report 53.
4. Eriksen T E, Jacobsson A and Pusch R:
Ion diffusion through highly compacted bentonite.
KBS-report 81-06.
5. Torstenfelt B, Andersson K, Kipatsi H, Allard B
and Olofsson U:
Diffusion measurements in compacted bentonite.
Topp S (Ed), Scientific Basis for Nuclear Waste Management IV,
Elsevier 1982.
6. Eriksen T E, Jacobsson A:
Ion diffusion in compacted sodium and calcium bentonites.
KBS-report 81-12.
7. Eriksen T E, Jacobsson A:
Diffusion of hydrogen, hydrogensulfide and large molecular
weight anions in bentonite.
KBS-report 82-17.
8. Pusch R, Eriksen T E and Jacobsson A:
Ion/water migration phenomena in dense bentonites
in (Ed) Lutze W, Scientific Basis for Nuclear Waste
Management V, Elsevier 1982, p. 649.

9. Torstenfelt B, Kipatsi H, Andersson K, Allard B and Olofsson U:
Transport of actinides through a bentonite backfill.
ibid p. 659.
10. Murinen A, Rantanen R, Ovaskinen R and Heinonen O J:
Diffusion measurements in concrete and compacted bentonite in Brookins DG, (Ed) Scientific Basis for Nuclear Waste Management VI, Elsevier 1983, p.
11. Torstenfelt B, Allard B, Kipatsi H, Andersson K and Persson H:
Measurements of ion mobilities in clay in

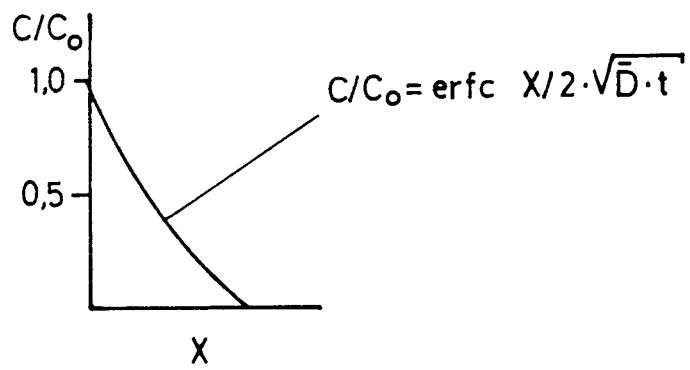
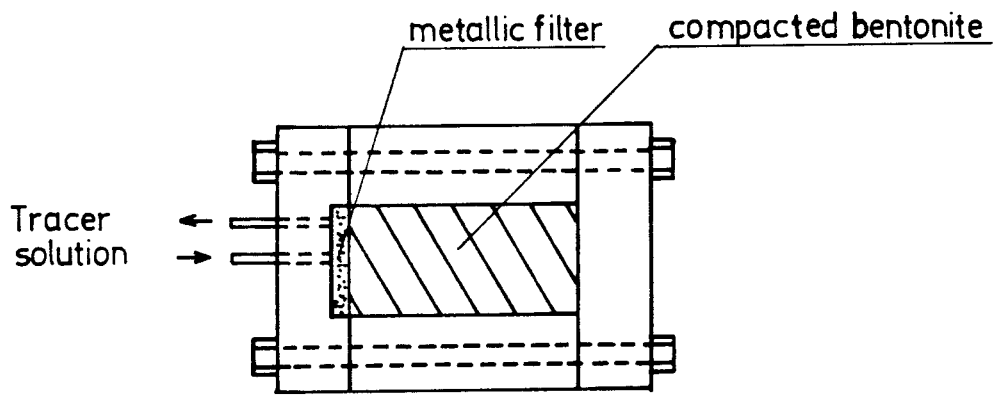
Kipatsi H:
Sorption behaviour of long-lived fission products and actinides in clay and rock. Dissertation, University of Gothenburg, 1983.
12. Torstenfelt B, Allard B, Andersson K, Kipatsi H, Eliasson L, Olofsson U and Persson H:
KBS report 83-34.
13. Nerethnieks I:
Diffusivities of some dissolved constituents in compacted wet bentonite clay-Mx 80 and the impact on radionuclide migration in the buffer. KBS-report 82-27.
14. Rasmuson A, Nerethnieks I:
Surface migration in sorption processes,
KBS-report 83-37
15. Crank J:
The mathematics of diffusion, Oxford 1957.
16. Helfferich F:
Ion exchange, Ch 8 p. 352, McGraw Hill, N.Y. 1962.

17. Andersson M, Pietz J, Smith D:
Solution to radionuclide migration with nonlinear retardation mechanisms in backfill material.
Interim Progress Report June - December 1982,
SAND-8 7089 and references therein.
18. Bradburg M H, Lever D and Kinsey:
Aqueous phase diffusion in crystalline rock,
Lutze W (Ed), Scientific Basis for Nuclear Waste
Management V, Elsevier 1982, p. 369.
19. Miller C W:
Toward a comprehensive model of chemical transport
in porous media. Mat. Res. Soc. Symp. Proc. Vol 15,
Elsevier 1983, p. 481.
20. Erickson K L:
Approximation for adapting porous media radionuclide
transport models to analysis of transport in jointed,
porous rock. Ibid p. 473.
21. Boyd G E, Adamson A W and Myers LS Jr:
The exchange adsorption of ions from aqueous solutions
by organic zeolites II, kinetics. J. Am. Chem. Soc.
1947, 69, 2836.
22. Jakubovic A O, Hills G J et Kitchener J A:
Coefficients D'autodiffusion des ions dans les résines
et les gels. J. Chim. Phys 1958, 55, 263.
23. Jakubovic A O, Hills G J and Kitchener J A:
Ion mobilities in ion exchange resins.
Trans Faraday Soc 1959, 55:2, 1570.

24. Duffey J E and Landelout H G:
Self-diffusion of anions in clay-gels.
J. Colloid. Interface Sci., 1975, 51, 278.
25. Duffey J E and Landelout H G:
Self-diffusion of sodium on clay surfaces as
influenced by two other alkali cations.
J. Colloid. Interface Sci., 1975, 52:2, 340.
26. Ellis J H, Bornhisel R I and Phillips R E:
The diffusion of copper, manganese and zinc as
affected by concentration, clay mineralogy
and associated anions.
Soil. Sci. Soc. Amer. Proc. 1970, 34, 866.
27. Fripiat J J and Stone W E E:
Water on the surface of clayminerals: orientation,
diffusion and proton exchange.
Rev. Chem. Liq 1978, Vol 7, p. 349-374, Gordon
and Breach Sci Publ.
28. Sposito G and Prost R:
Structure of water adsorbed on smectites
Chem Rev 1982, 86:6, 553.
29. Bockis J O M and Reddy A K N:
Modern electrochemistry. Vol 2, Chap. 7-8,
Plenum Press 1970.
30. Marinsky J A:
Analysis of KBS-report 81-06
(private communication)

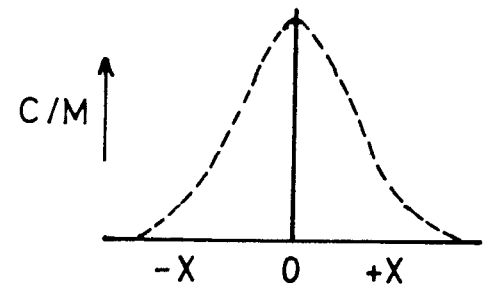
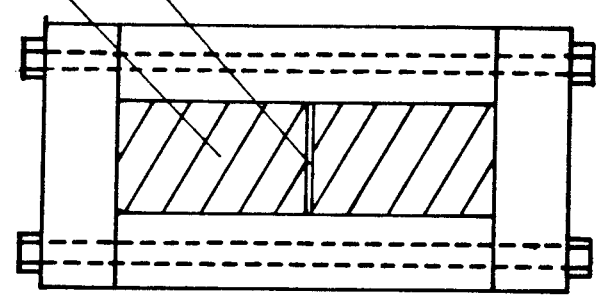
31. Jacobson A:
Clay-water interaction. Diss. Dept. of Geology,
University of Stockholm 1974.
32. Choppin G R:
Solution chemistry of the actinides. Radiochimica Acta
1983, 32, 45-53.
33. Allard B, Kipatsi H and Liljenzin J O:
Expected species of uranium, neptunium and plutonium in
neutral aqueous solutions. J. inorg. nucl. 1980, 42,
1015-1027.
34. Allard B, Olofsson V, Torstenfelt B and Kipatsi H:
Sorption behaviour of well-defined oxidation states.
KBS-report 83-61.
35. Allard B and Torstenfelt B:
On the solubility of technetium in geochemical systems.
KBS-report 83-60.

Fig 1



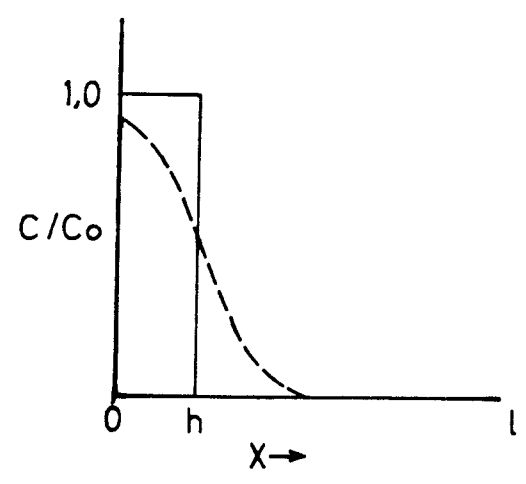
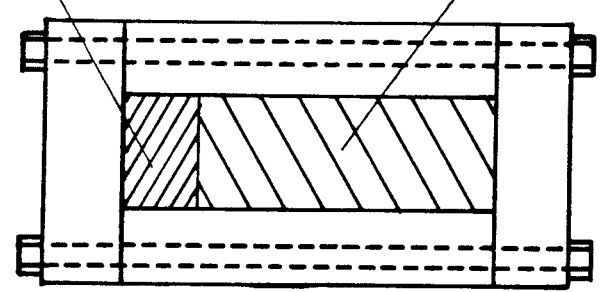
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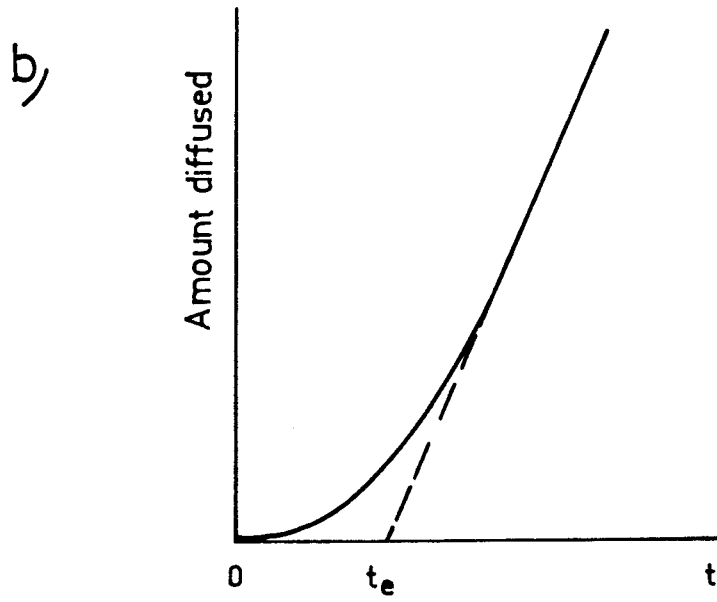
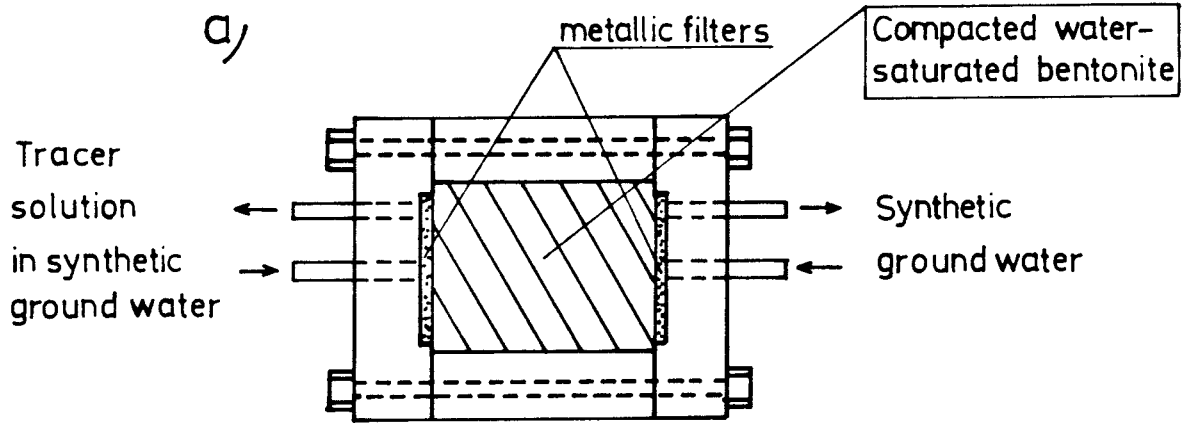
Compacted watersaturated bentonite
Instantaneous plane source of tracer.



b)

Tracer doped bentonite Compacted, watersaturated bentonite





List of KBS's Technical Reports

1977–78

TR 121

KBS Technical Reports 1 – 120.

Summaries. Stockholm, May 1979.

1979

TR 79–28

The KBS Annual Report 1979.

KBS Technical Reports 79-01 – 79-27.

Summaries. Stockholm, March 1980.

1980

TR 80–26

The KBS Annual Report 1980.

KBS Technical Reports 80-01 – 80-25.

Summaries. Stockholm, March 1981.

1981

TR 81–17

The KBS Annual Report 1981.

KBS Technical Reports 81-01 – 81-16.

Summaries. Stockholm, April 1982.

1982

TR 82–28

The KBS Annual Report 1982.

KBS Technical Reports 82-01 – 82-27.

1983

TR 83–77

The KBS Annual Report 1983.

KBS Technical Reports 83-01–83-76

Summaries. Stockholm, June 1984.

1984

TR 84–01

Radionuclide transport in a single fissure

A laboratory study of Am, Np and Tc

Trygve E Eriksen

Royal Institute of Technology

Stockholm, Sweden 1984-01-20

TR 84-02

Radiolysis of concrete

Hilbert Christensen

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Nyköping, Sweden

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Roskilde, Denmark 1984-03-16

TR 84-03

Effect of β -radiolysis on the products from

α -radiolysis of ground water

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Nyköping, Sweden

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1984-07-10

TR 84—04

Analysis of some laboratory tracer runs in natural fissures

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Stockholm, Sweden 1984-03-15