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SUMMARY

Transport rates of the fission products strontium, technetium, iodide and cesium as well as the actinides thorium, protactinium, uranium, neptunium, plutonium and americium in compacted bentonite have been studied.

A sodium bentonite, Wyoming Bentonite MX-80, was used in all experiments, in a few cases mixed with 1% $Fe_3(PO_4)_2$, 1% PbO or 0.5% Fe(s), or 1% of one of the minerals apatite, pyrite, chalcopyrite/pyrite, cinnabar or olivine. The aqueous phase was a synthetic groundwater representative of Swedish deep granitic groundwaters, preequilibrated with the clay. Uranium and americium migration was also studied with high carbonate content and 10 mg/l humic acid, respectively, added to the water.

The diffusivity was measured in compacted clay (density $2x10^3$ kg/m^3) and calculated from concentration profiles.

The diffusivities for the fission products where of the order of 10^{-12} m^2/s under oxidizing conditions and about one order of magnitude lower for technetium under reducing conditions (Fe(s) in the clay).

Penta- and hexavalent actinides had diffusivities around 10^{-13} m^2/s and tri- and tetravalent actinides around 10^{-15} m^2/s. The influence of the additives to the clay or the water was minor in the uranium systems except when Fe(s) was added to the clay, which decreased the transport rate by a factor of 10.

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1. INTRODUCTION

Compacted bentonite has been proposed as a suitable backfill material in the Swedish concept for underground storage of high-level waste and spent nuclear fuel[1]. The backfill material will serve as a physical barrier, preventing convective water flow in the vicinity of the waste containers and thus allowing radionuclide penetration only by diffusion. It will also act as a chemical barrier capable of interacting with the radionuclides in sorption processes.

In this study the diffusivity of some fission products and actinides has been determined. The radionuclide was introduced in the middle of a compacted clay sample as a planar source, and the transport by diffusion from this source was evaluated from the concentration profile in the clay. Measurements of strontium and cesium diffusion have recently been reported, using a similar technique, but a different diffusion cell[2,3]. This report is largely based on previously published results, where a detailed description of the technique is given[4-7].

2. RADIONUCLIDES AND CLAY/WATER SYSTEMS

The various systems that were studied are listed in Table 1. The short-lived nuclides ^{234}Th and ^{233}Pa were recovered from ^{238}U and ^{237}Np, respectively.

A sodium bentonite, Wyoming Bentonite MX-80, was used in all experiments[8]. The possibility of reducing the transport rate of the radionuclides by complex formation or by reduction of redox sensitive elements to their lower oxidation states was studied by adding 0.5-1% of apatite, pyrite, chalcopyrite, cinnabar, or PbO, or by Fe, $Fe_3(PO_4)_2$ or olivine, respectively, to the clay. The aqueous phase was a synthetic groundwater[9] with a total salt concentration of 306 mg/l, a total carbonate concentration of 123 mg/l and pH around 8.2. In some experiments 477 mg/l HCO_3^- (giving a total of 600 mg/l HCO_3^-) or 10 mg/l humic acid was added to the aqueous phase.

Table 1. System characterization

Radionuclide	Solid phase	Aqueous phase
^{85}Sr	Bentonite[a]	G.W.[b]
^{134}Cs	Bentonite	G.W.
^{85}Sr+^{134}Cs	Bentonite[c]	
^{85}Sr+^{134}Cs+^{241}Am	Bentonite	G.W.
^{99}Tc	Bentonite	G.W.
^{99}Tc	Bentonite+1% pyrite	G.W.
^{99}Tc	Bentonite+1% olivine	G.W.
^{99}Tc	Bentonite+1% $Fe_3(PO_4)_2$	G.W.
^{99}Tc	Bentonite+0.5% Fe(s)	G.W.
^{99}Tc	Bentonite+0.5% Fe(s)[f]	G.W.
^{125}I	Bentonite	G.W.
^{125}I	Bentonite+1% chalcopyrite/ pyrite	G.W.
^{125}I	Bentonite+1% cinnabar	G.W
^{125}I	Bentonite+1% PbO	G.W
^{234}Th	Bentonite	G.W.
^{233}Pa	Bentonite	G.W.
^{233}U	Bentonite	G.W.
^{233}U	Bentonite	G.W. with 600 mg/l HCO_3^-
^{233}U	Bentonite	G.W. with 10 mg/l humic acid
^{233}U	Bentonite+1% $Fe_3(PO_4)_2$	G.W.
^{233}U	Bentonite+0.5% Fe(s)	G.W.
^{233}U	Bentonite+0.5% Fe(s)[f]	G.W.
^{237}Np	Bentonite	G.W.
^{237}Np	Bentonite+1% $Fe_3(PO_4)_2$	G.W.
^{237}Np	Bentonite+0.5% Fe(s)	G.W.
^{237}Np	Bentonite+0.5% Fe(s)[f]	G.W.
^{239}Pu	Bentonite	G.W.
^{241}Am	Bentonite	G.W.
^{241}Am	Bentonite+1% apatite	G.W.
^{241}Am[d]	Bentonite	G.W.
^{241}Am[e]	Bentonite	G.W.
^{241}Am	Bentonite	G.W. with 600 mg/l HCO_3^-

[a] Compacted to a density of ca. 2×10^3 kg/m^3 in all experiments

[b] Synthetic groundwater

[c] Dry clay not in contact with water (contains ca 10% water)

[d] Am in 0.1 M acetate solution

[e] Am added as a colloid (at pH 12)[10]

[f] 0.5% Fe in part of the clay

3. DIFFUSION MEASUREMENTS

Water and clay were mixed and left several weeks for preequilibration and then separated by centrifugation. The clay was dried at 105°C, crushed and sieved, and compacted in a holder, Fig. 1, to a density of $(1.9\text{-}2.3)\times10^3$ kg/m^3 using a KBr-pellet press. The water from the prequilibration was used as the mobile aqueous phase in the subsequent diffusion experiments. Thus, both the clay and the aqueous phase were in equilibrium with each other prior to the introduction of the radionuclide.

The holder with the compacted clay was submerged in the aqueous phase for about 1 week without activity addition, thus allowing the clay to be water saturated and homogenized prior to the start of the measurements. After this homogenization and wetting period half of the cylindrical clay sample was pressed into an empty holder. A thin clay slice containing the active radionuclide was placed on the clay, and the other half of the homogenized clay sample was pressed on the radionuclide-containing active layer. After this procedure the active layer was located in the middle of a homogenous compacted clay cylinder, thus acting as a planar radionuclide source. The whole diffusion cell, Fig. 2, was submerged in the aqueous phase for a period of 2 to 15 months, depending on the choice of radionuclide.

After adequate contact time with the water the clay sample was pressed out of the diffusion cell through a punching tool, Fig. 3, which removed about 1 mm of the mantle surface of the clay cylinder. By this procedure any activity that had been transported along the walls of the metal holder was removed from the sample. Successive 0.1 mm thick slices were cut from the clay cylinder, Fig. 4, and their content of the radionuclide in question was determined from measurements of the total activity.

The design of the diffusion equipment and details on the experimental procedure are further described in ref. 6.

4. DIFFUSION THEORY

The apparent diffusivity (D_a) is given by the equation

$$\frac{dc}{dt} = \frac{d}{dx}\left(D_a \frac{dc}{dx}\right) \tag{1}$$

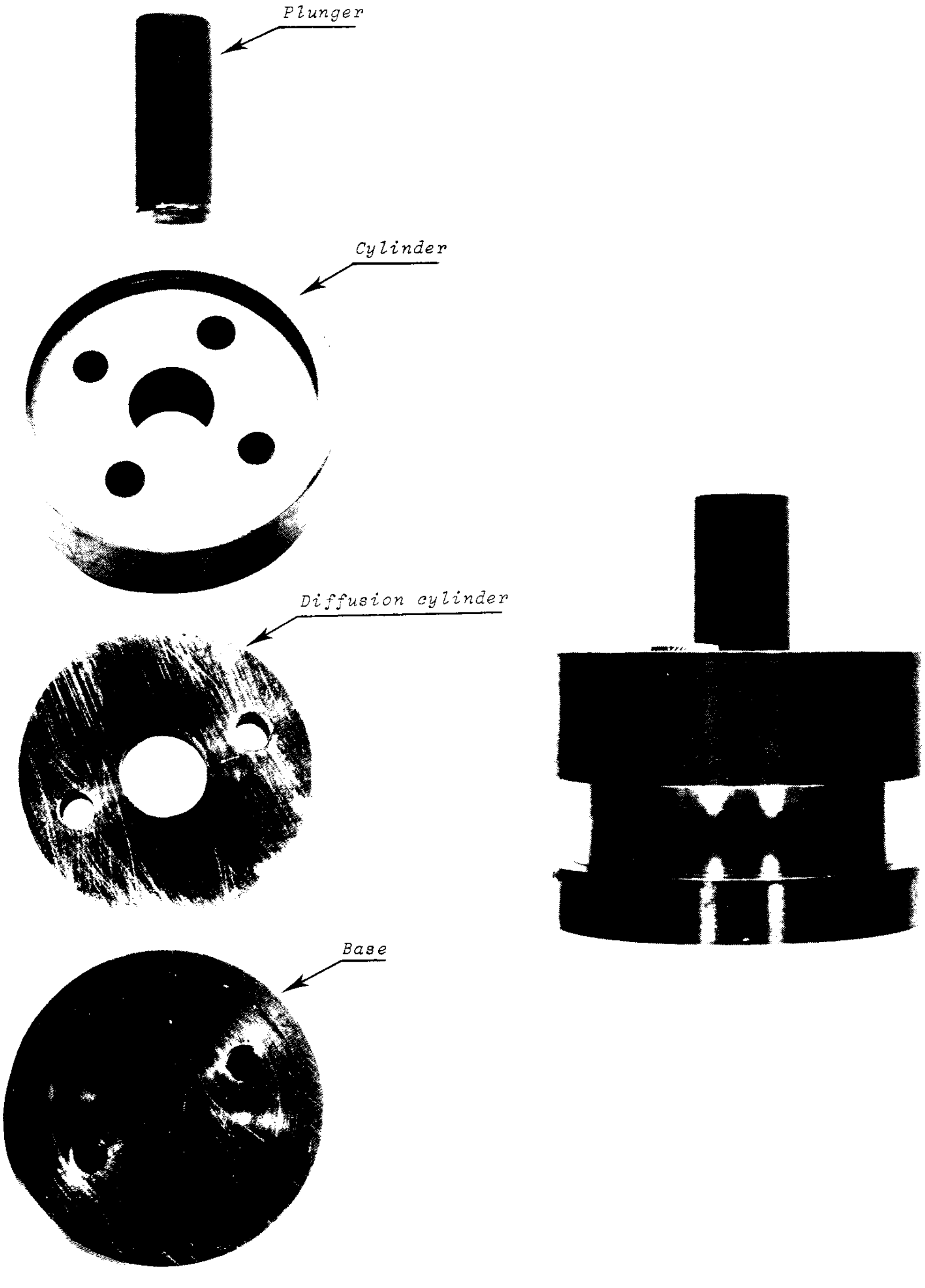

Figure 1. Sample holder and pressing device.

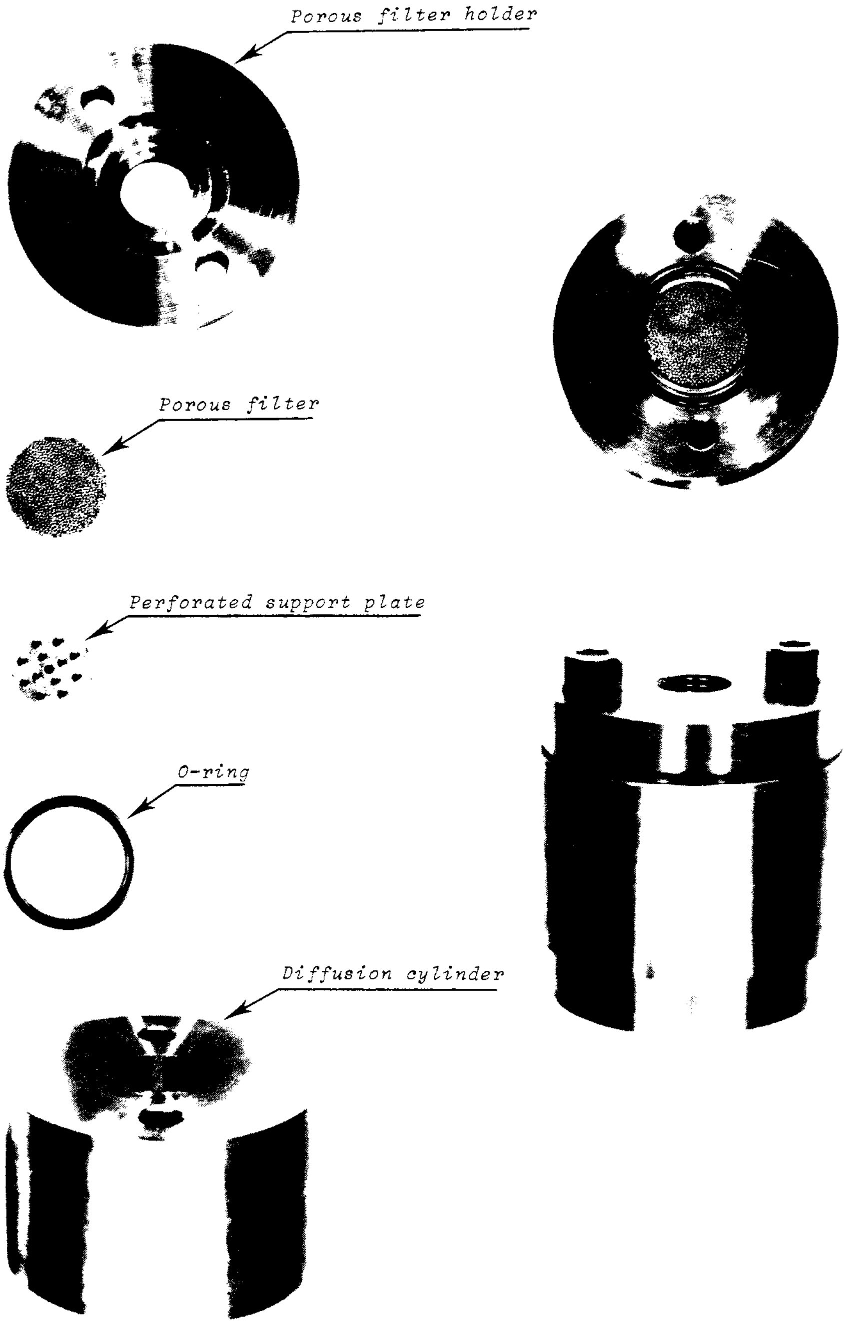

Figure 2. Diffusion cell.

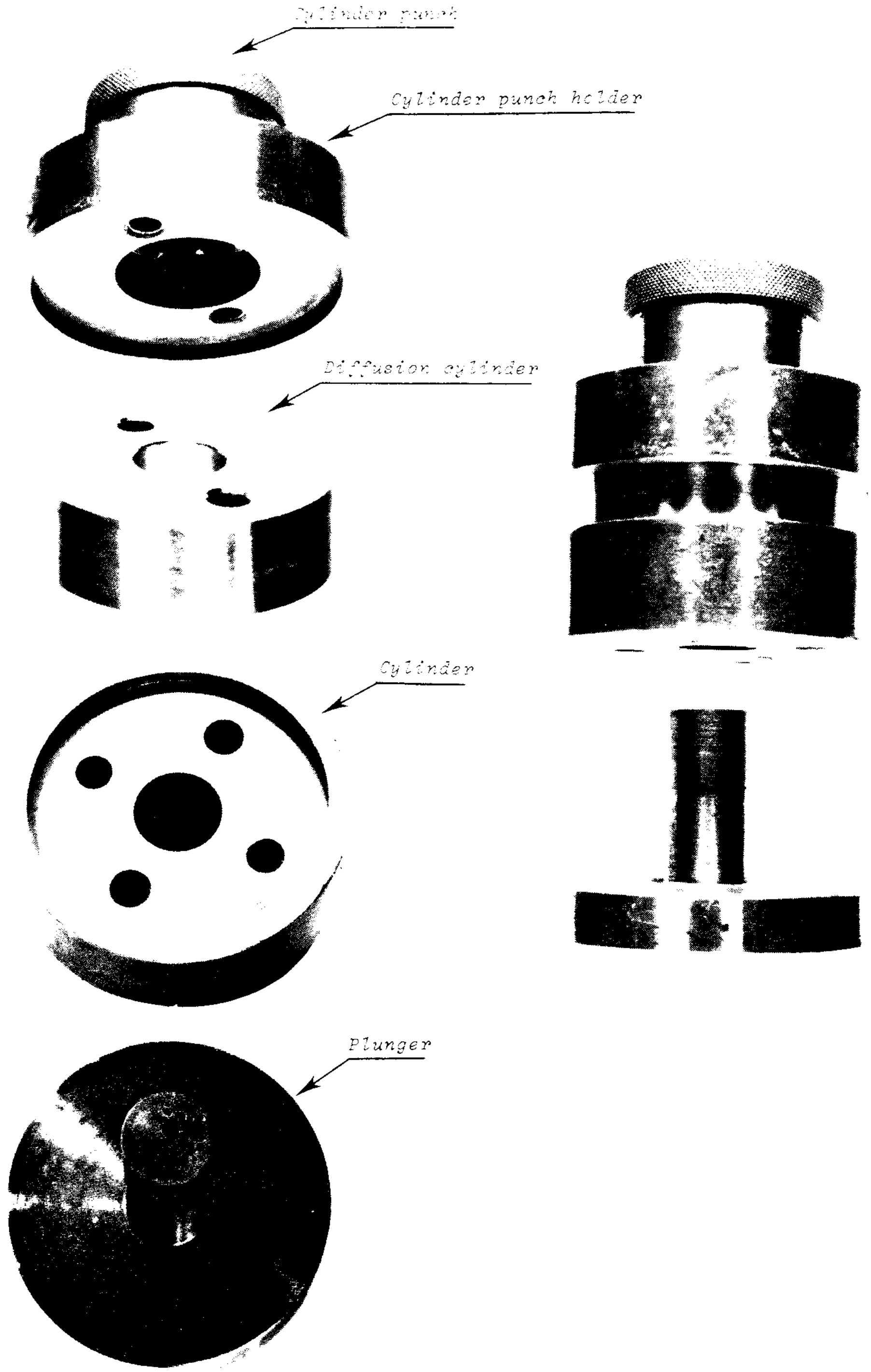

Figure 3. Punching tool.

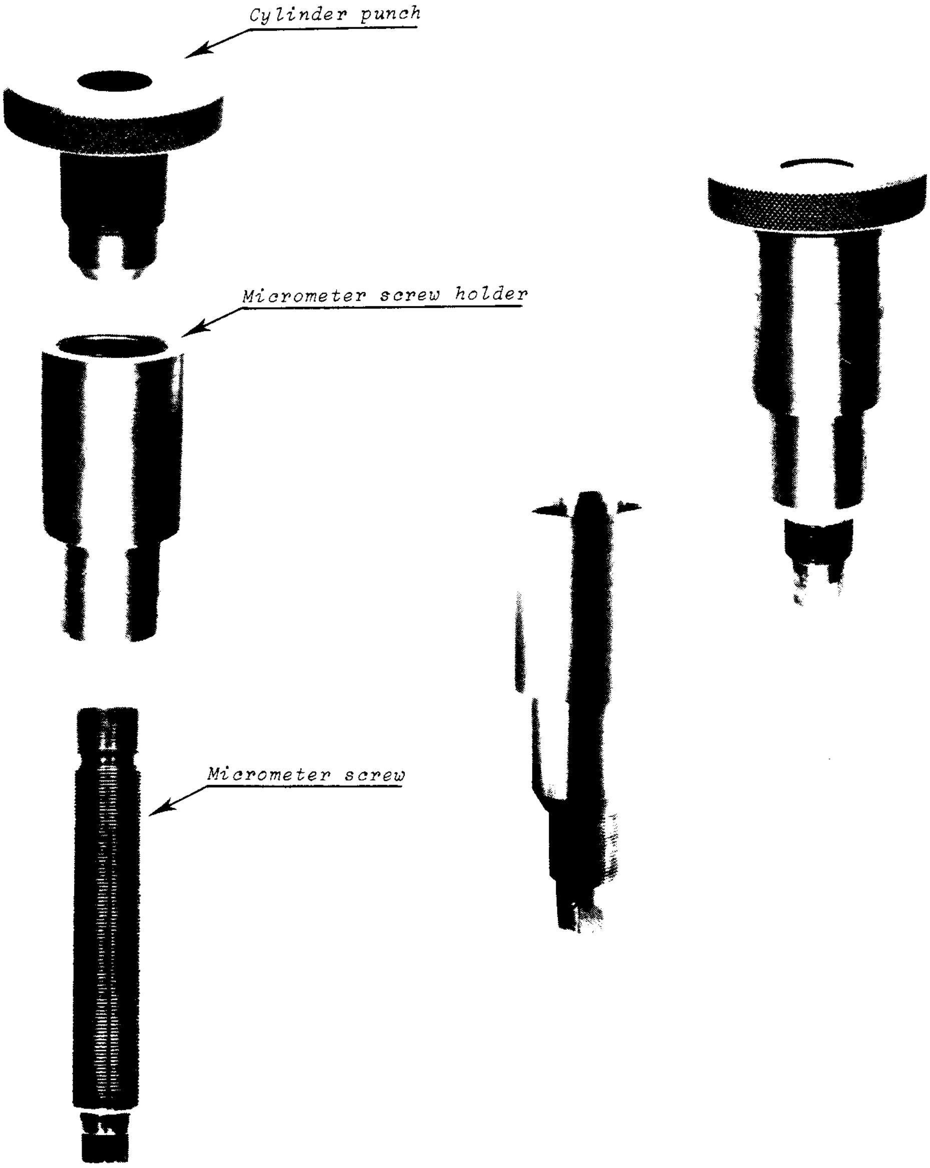

Figure 4. Slicing in thin sections.

(valid for one-dimensional diffusion), which has to be solved by applying appropriate initial and boundary conditions[11]. In the present case with a plane source containing a limited amount of substance which is diffusing in a cylinder of infinite length and assuming a concentration independent diffusion, the solution to Eqn (1) is given by

$$\frac{c}{M} = \frac{1}{2(\pi D_a t)^{1/2}} e^{-x^2/4D_a t} \tag{2}$$

where c = concentration (mol/m^3), M = total amount of the diffusing species added per unit area (mol/m^2), x = distance from source (m), D_a = apparent diffusivity (m^2/s), and t = time (s).

The effect of sorption on the solid is included in D_a. In case of a reversible sorption on the clay, defined by a concentration independent distribution coefficient (K_d, m^3/kg), the relation between the apparent diffusivity (D_a) and the diffusivity not affected by sorption (D) is

$$D = D_a(1+K_d\rho(1-\varepsilon)/\varepsilon) \tag{3}$$

where ρ = density of the solid (kg/m^3) and ε = porosity of the solid (m^3/m^3). If K_d is concentration dependent, also the apparent diffusivity will vary with the concentration, and Eqn (2) will not be valid. In this case Eqn (1) must be solved by numerical methods, taking the sorption isotherm into account.

5. RESULTS AND DISCUSSION

The concentration profiles measured for the fission products Sr, Tc, I and Cs, and the actinides Th, U, Np, Pu and Am, respectively, are shown in Fig. 5-22, and some experimental parameters and calculated diffusivities are given in Table 2.

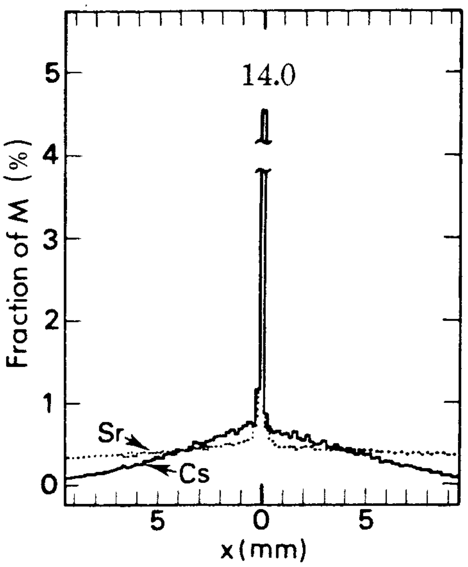

Figure 5. Concentration profiles for Sr and Cs

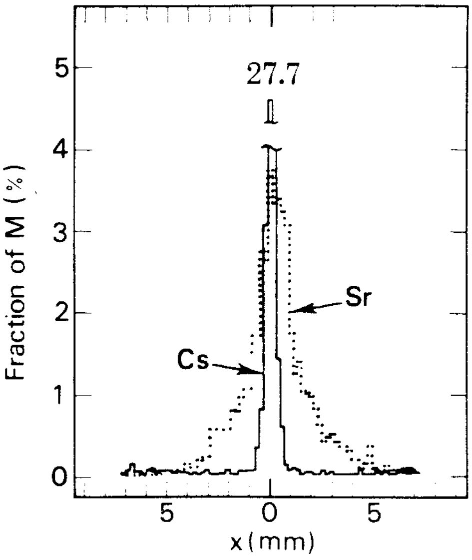

Figure 6. Concentration profiles for Sr and Cs in dry clay (water content 10%)

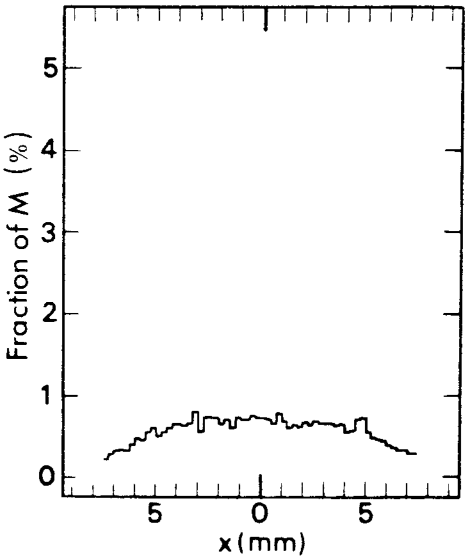

Figure 7. Concentration profile for Tc

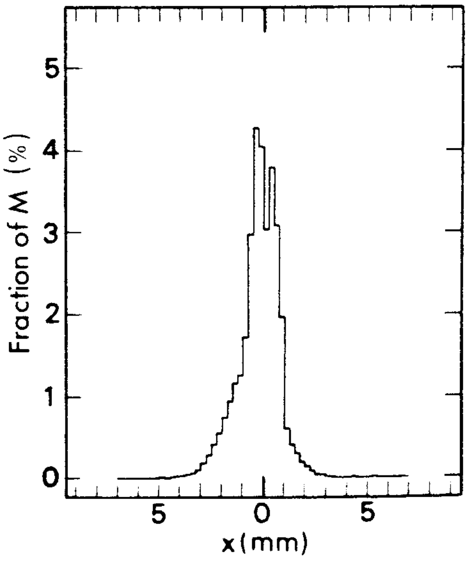

Figure 8. Concentration profile for Tc with 0.5% Fe(s) in the clay

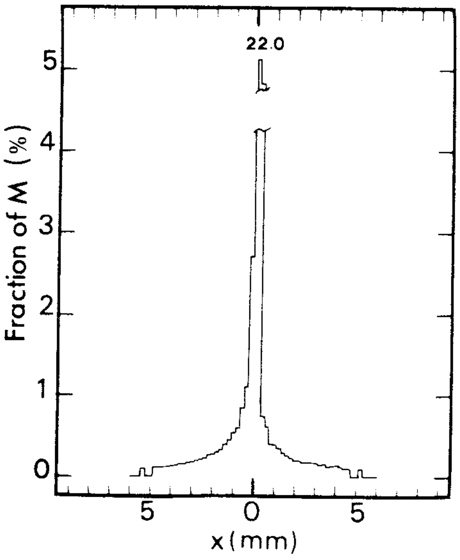

Figure 9. Concentration profile for I

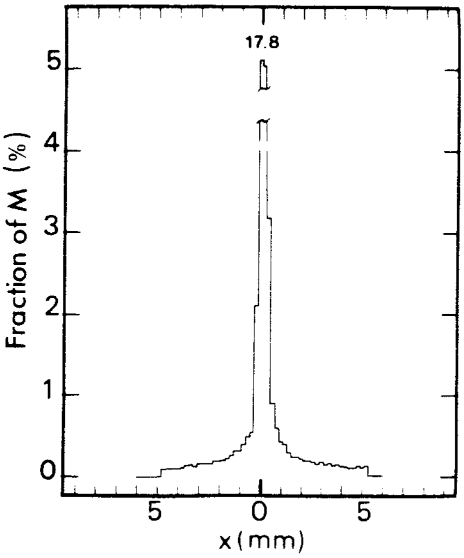

Figure 10. Concentration profile for I with 1% cinnabar in the clay

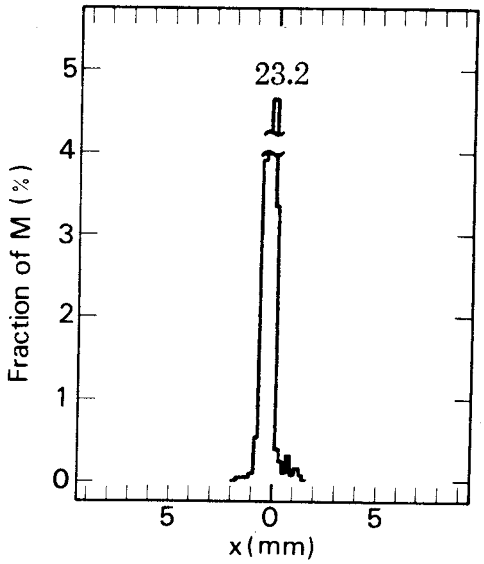

Figure 11. Concentration profile for Th

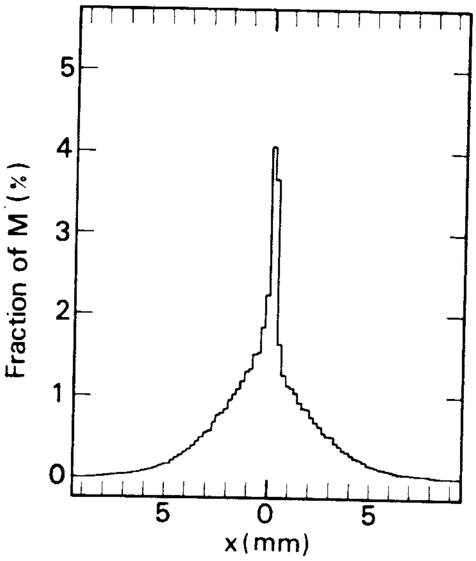

Figure 12. Concentration profile for U

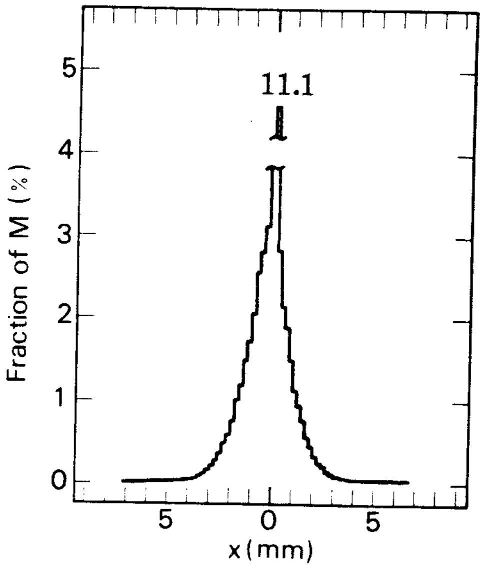

Figure 13. Concentration profile for U with 600 mg/l HCO_3^- in the aqueous phase

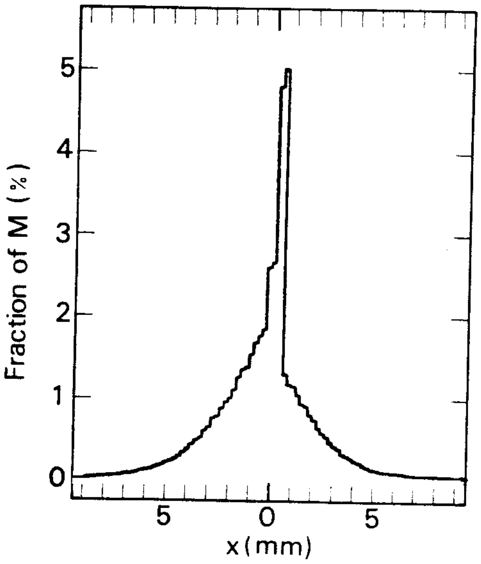

Figure 14. Concentration profile for U with 10 mg/l humic acid in the aqueous phase

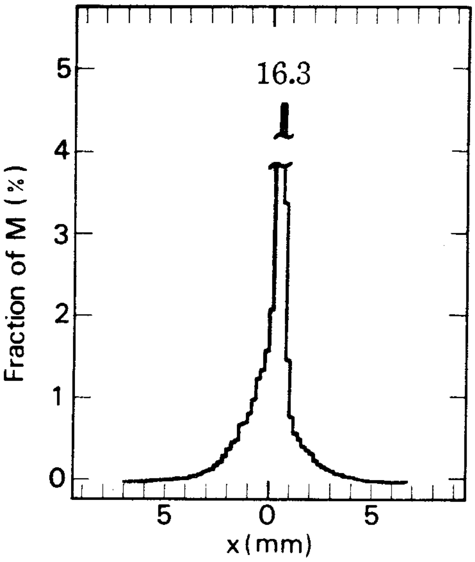

Figure 15. Concentration profile for U with 1% $Fe_3(PO_4)_2(s)$ in the clay

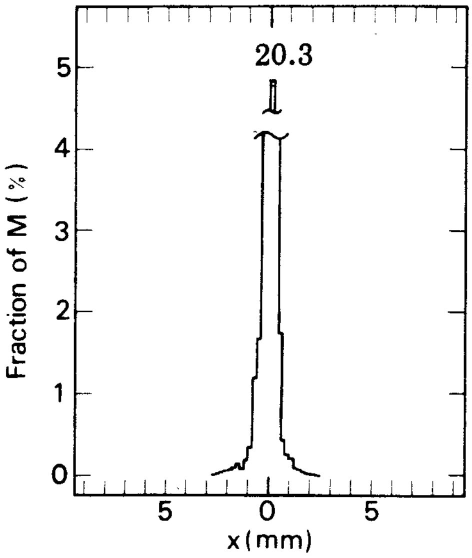

Figure 16. Concentration profile for U with 0.5% Fe(s) in the clay

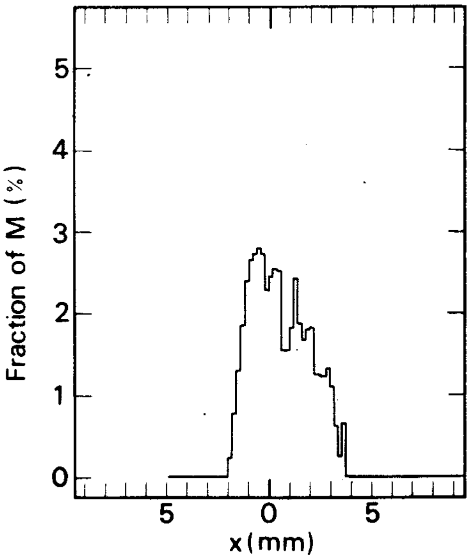

Figure 17. Concentration profile for U with 0.5% Fe(s) in part of the clay

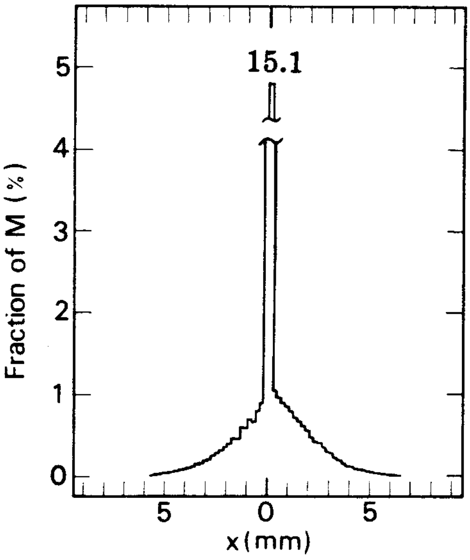

Figure 18. Concentration profile for Np

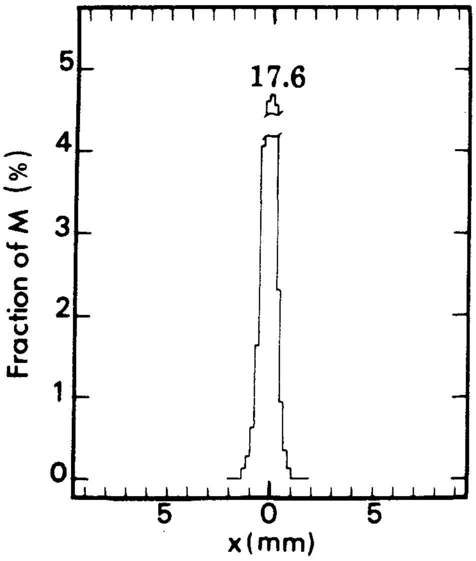

Figure 19. Concentration profile for Np with 0.5% Fe(s) in the clay

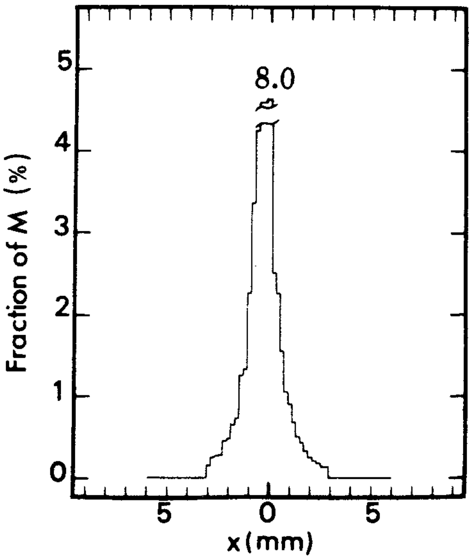

Figure 20. Concentration profile for Np with 0.5% Fe(s) in part of the clay

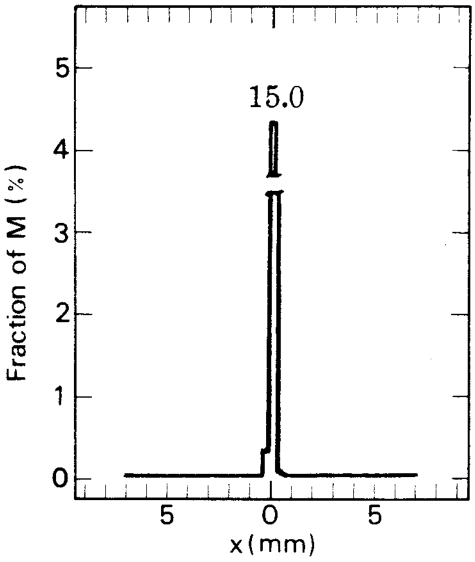

Figure 21. Concentration profile for Pu

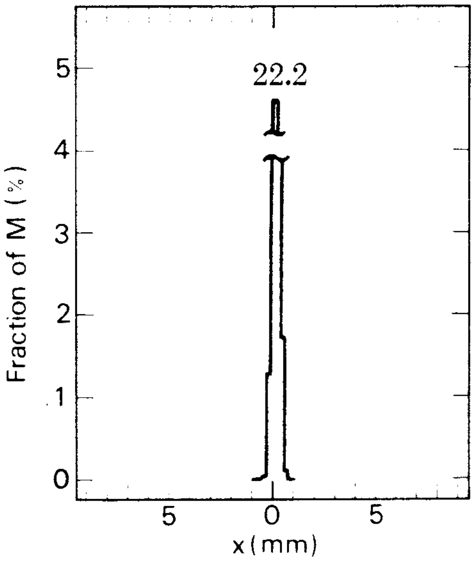

Figure 22. Concentration profile for Am

Table 2. Measured diffusivities and distribution coefficients

Element	log C_i[a]	Time (d)	$(D_a)_{av} \times 10^{14}$ (m^2/s)	$(D_a)_{max} \times 10^{14}$ (m^2/s)	K_d[b] (m^3/kg)	$D_{av} \times 10^{10}$ (m^2/s)	$D_{max} \times 10^{10}$ (m^2/s)
Sr	-11	50	180	1200	2.9	100	670
Tc	-10	69	140	530	0.0	0.014	0.053
Tc[c]	-10	70	140		0.002	0.070	
Tc[d]	-10	70	140		0.002	0.070	
Tc[e]	-10	225	6.6	23	0.002	0.0033	0.011
Tc[f]	-10	70	30		0.05	0.30	
Tc[g]	-10	218	17	48			
I	-11	157	3.2	12	0.001	0.0010	0.0035
I[h]	-11	213	2.0	6.4			
I[i]	-11	213	2.6	9.2	0.8	0.42	1.5
I[j]	-11	213	3.02	14	0.6	0.36	1.7
Cs	-10	53	140	200	1.4	39	57
Th	-14	64	0.46	0.85	-6	-0.55	-1.0
Pa	-13	76	-57[o]	-60[o]	5.0	-55	-60
U	-8	62	58	82	0.093	1.1	1.5
U[k]	-8	54	19	34	0.093	0.36	0.64
U[l]	-8	62	57	94	0.093	1.1	1.8
U[e]	-8	63	20	38	0.093	0.37	0.71
U[f]	-8	53	4.5	11	5.0	4.5	11
U[l]	-8	225		22			
Np	-9	69	22	37	0.12	0.52	0.88
Np[e]	-9	212	0.86	3.4	0.12	0.021	0.082
Np[f]	-9	322	0.45	1.6	5.0	0.45	1.6
Np[g]	-9	322	0.80	2.4			
Pu	-9	316	0.32	0.86	3.5	0.22	0.60
Am	-9	524	0.20	0.73	6.6	0.26	0.96
Am[m]	-9	68	0.40	1.4			
Am[n]	-9	68	0.40	1.4			
Am[k]	-9	350	0.28	0.95			

[a] Number of moles initially added

[b] For total nuclide concentration of -10^{-9} M

[c] 1% pyrite in the clay

[d] 1% olivine in the clay

[e] 1% $Fe_3(PO_4)_2(s)$ in the clay

[f] 0.5% Fe(s) in the clay

[g] 0.5% Fe in part of clay

[h] 1% chalcopyrite/pyrite

[i] 1% cinnabar

[j] 1% PbO

[k] 600 mg/l HCO_3^- in the aqueous phase

[l] 10 mg/l humic acid in the aqueous phase

[m] Added in 0.1 M acetate solution

[n] Added as a colloid (at pH 12)

[o] Preliminary values

5.1 Fission products

The fission products strontium and cesium are both non-hydrolyzed positively charged cations in aqueous solution and exhibits high transport rates and apparent diffusivities. With the effect of sorption removed the diffusivity (D) for both of the elements was about 10^{-8} - 10^{-9} m^2/s which is of the same order of magnitude as the diffusivity in water (10^{-9} m^2/s)[12].

Also the diffusivity of technetium was high (as TcO_4^- in the absence of reducing agents).

In one measurement strontium and cesium were placed in a cell with compacted bentonite, but with no water present. The dry clay contains 10% water, and as shown in Fig. 6 there was a significant transport of both elements with only the pore water present.

The observed transport rate for technetium was of the same order of magnitude or faster than for strontium and cesium despite the fact that the sorption of technetium on the clay is almost negligible, while both strontium and cesium are strongly sorbed (cf. Table 2). A similar fast transport of cesium in granitic rock confined to veins containing minerals with high cation exchange capacities (and consequently high distribution coefficients) was previously observed[13]. This indicates a different transport mechanism for anions and cations, and also that the use of Eqn (3) might not be appropriate.

An addition of metallic iron to the clay decreased the transport rate of technetium by one order of magnitude (Fig. 8), most certainly due to a reduction of heptavalent technetium (TcO_4^-) to the tetravalent state ($Tc(OH)_4$ or TcO_2). The minerals pyrite and olivine, both iron containing minerals, mixed with the clay had no significant effect on the transport rate during the short contact time (ca 2 months).

The transport rate for iodide was found to be more than one order of magnitude slower than for technetium, although the negatively charged iodide ion would be expected to have a diffusivity similar to that of pertechnetate since none of these ions interact significantly with the bentonite (cf. Table 2 and Fig. 9). The transport rate for both iodide and pertechnetate in the clay would be decreased by the negatively charged surface of the solid, which reduces the effective water volume accessible for diffusion. A similar diffusion resistance for negatively charged ions in clay has been reported by others[2]. A partial oxidation to iodate, IO_3^-, which would form a sparingly soluble calcium complex, could explain the reduced iodide mobility in comparison with the mobility of pertechnetate.

An addition of 1% cinnabar (Fig. 10) or 1% chalcopyrite/pyrite to the clay gave a slightly decreased diffusivity. Both minerals contain iodide complex-forming agents (Table 3). An addition of lead oxide had no observable effect during the short contact time of the experiment.

5.2. Actinides

The high distribution coefficients (cf. Table 2) and corresponding low apparent diffusivities for thorium and americium seem to be representative of the behaviour of actinides in their lower oxidation states (highly hydrolyzed species with low mobility)[14,15]. There were no observable differences in the americium mobilities when the element was added in acetate stock solution, as a colloid or when the clay was mixed with 1% apatite or the water contained 600 mg/l HCO_3^-.

According to the shape of the diffusion curve in Fig. 19 plutonium exists predominantly in one of the lower oxidation states, most likely in the tetravalent state[15]. A small fraction of the plutonium seemed to migrate fast, possibly as Pu(V).

Indications of a reduction of U(VI) to U(IV) in the presence of Fe(s) are evident (Fig. 16-17). The presence of 600 mg/l HCO_3^- (Fig. 13) in the water or $Fe_3(PO_4)_2(s)$ (Fig. 15) in the clay had a minor but possibly decreasing effect on the transport rate. The complexing agent CO_3^{2-} would probably form negatively charged complexes with uranium which normally would enhance the mobility in geologic environments. However, in the case of a compacted clay there could be a steric effect. The negatively charged complexes could be big enough to affect the mobility in the clay. An addition of humic acid to the water did not affect the uranium mobility significantly.

Table 3. Complex formation constants (log K_1) and solubility products (log K_s) for metal iodides at zero ionic strength (Extrapolated or estimated values in parenthesis).

Metal	log K_1	log K_s	Metal	log K_1	log K_s
Cu^+	(6)	-12.0	Hg^{2+}	(12)	(-29)
Ag^+	(6.8)	-16.08	Pb^{2+}	1.92	-8.10
Cd^{2+}	2.28	(-8)			
Hg_2^{2+}	(12)	-28.33	Bi^{3+}	(2.4)	(-21)

The measured concentration profiles agree very poorly with theoretical curves obtained from Eqn (2). The calculated apparent diffusivities are significantly lower close to the radionuclide source, than at some distance from it. Non-linear sorption isotherms could lead to such results[11], but both for strontium[9] and the actinides in their lower oxidation state[14] the observed sorption isotherms are almost linear in the concentration range 10^{-4} - 10^{-8} M (for Sr) and 10^{-7} - 10^{-9} M (for the actinides). However, for the actinides in the tri- and tetravalent state (Th, Pu and Am in the experiments) it is likely that the solubility products for the trivalent carbonate and tetravalent oxide/hydroxide have been exceeded (cf. Fig. 11, 19 and 20). Under the present conditions the maximum solubilities of trivalent and tetravalent actinides would be of the order of $10^{-6.5}$ M and $10^{-3.5}$ M, respectively[15]. This would correspond to $C/C_o = 1.9\times10^{-3}$ and 2×10^{-5}, respectively, considering the amount of radionuclide added and the available pore water in the clay. Thus, only the maximum diffusivities, representative of species that have travelled far from the source, would correspond to the migration of truly soluble species. For the penta- and hexavalent states (Pa, Np and U, except possibly for the U-Fe-system) the solubility limit would not be exceeded. Theoretical curves for two of the measured concentration profiles are given in Fig. 23 and 24.

6. RETENTION IN A REPOSITORY

For a diffusion process, the retention time t would be given by:

$$t = 0.1\ z^2/D_a \qquad (4)$$

where z = barrier thickness (m)[17]. Breakthrough is here assumed to occur when the concentration outside the clay barrier reaches 5% of the concentration at the source.

The retention time t according to Eqn (4) and the remaining fraction of some long-lived fission products and actinides in spent fuel after this time are given in Table 4. A barrier thickness z of 0.5 and 1 m and the measured apparent diffusivities given in Table 2 are used in the calculations. Of these nuclides ^{99}Tc, ^{129}I and ^{237}Np are not significantly retarded after t or 4t. Even after a reduction of both technetium and neptunium to the tetravalent state and assuming a barrier thickness of 1 m about 97% and 89%, respectively, of the nuclides would remain after breakthrough. In order to reduce ^{237}Np to less than 10^{-3} a barrier thickness of ca 4.5 m or more has to be introduced, assuming reducing conditions.

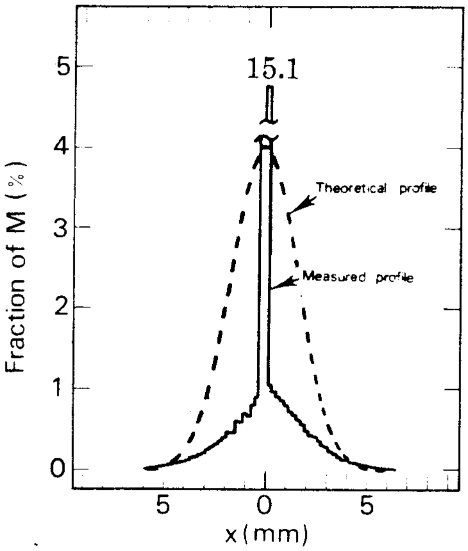

Figure 23. Theoretical concentration profile for Np according to eqn. (2), $D_{Np}=2.2\times10^{-13}$ m^2/s

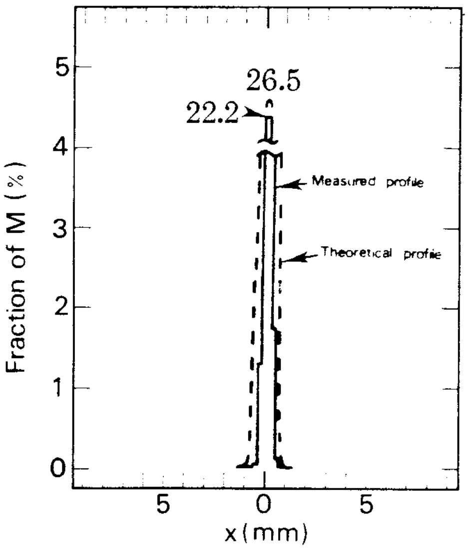

Figure 24. Theoretical concentration profile for Am according to eqn. (2), $D_{Am}=0.40\times10^{-14}$ m^2/s

Table 4. Retention of long-lived radionuclides in compacted bentonite.

Nuclide	t (y)	$t/t_{1/2}$ [a]	Remaining fraction after t	Remaining fraction after 4t [b]
^{90}Sr	68	2.4	1.9×10^{-1}	1.3×10^{-3}
^{99}Tc	15	7.1×10^{-5}	1.0	1.0
^{99}Tc [c]	2.6×10^{3}	1.3×10^{-2}	9.9×10^{-1}	9.7×10^{-1}
^{129}I	2.9×10^{4}	1.8×10^{-3}	1.0	1.0
^{137}Cs	3.9×10^{2}	13	1.2×10^{-4}	< [e]
^{229}Th	9.3×10^{4}	13	1.5×10^{-4}	< [e]
^{237}Np	2.2×10^{3}	1.0×10^{-3}	1.0	1.0
^{237}Np [d]	9.3×10^{4}	4.4×10^{-2}	1.0	8.9×10^{-1}
^{239}Pu	2.6×10^{4}	1.1	4.7×10^{-1}	5.2×10^{-2}
^{240}Pu	2.6×10^{4}	4.0	6.3×10^{-2}	1.6×10^{-5}
^{241}Am	5.8×10^{4}	13.5	< [e]	< [e]
^{243}Am	5.8×10^{4}	7.9	4.2×10^{-3}	< [e]

---

[a] $t_{1/2}$ = half-life, y; t according to eqn (4) for z = 0.5.

[b] For z = 1

[c] Reducing conditions; Tc in tetravalent state.

[d] Assuming reduction to Np(IV); values for Th(IV) used.

[e] $<10^{-9}$.

7. CONCLUSIONS

Strontium and cesium migrated faster than could be expected considering sorption data.

The apparent diffusivity of technetium was comparable to those obtained for strontium and cesium which indicates different transport mechanisms, considering the differences in sorption properties between technetium (almost non-sorbed) and strontium/cesium (high sorption in terms of the distribution coefficients due to ion exchange processes).

Addition of Fe(s) to the clay, giving reducing conditions, decreased the diffusivity of technetium, which indicates a reduction from TcO_4^- to Tc(IV).

The iodide diffusivity was more than one order of magnitude lower than for pertechnetate. This low diffusivity, in comparison with the values for TcO_4^-, could indicate a partial oxidation to iodate, IO_3^-, which would form sparingly soluble calcium complexes.

The actinides uranium and neptunium in their higher oxidation states (V, VI) had transport rates slightly lower than what was observed for cesium, as defined by the apparent diffusivities. The other actinides (Th, Pu and Am), all in their lower oxidation states (III, IV), had apparent diffusivities 1-3 orders of magnitude lower.

The dominating oxidation state for plutonium was probably IV, and U(VI) seems to be reduced to U(IV) when iron-powder is mixed with the clay.

The presence of a high carbonate concentration or humic acid in the water or iron phosphate in the clay had a only minor (and possibly not significant) effects on the U(VI)-diffusivity under the present conditions.

Americium exhibited similar diffusivities regardless of its initial chemical state (acetate complex, hydroxide colloid, humic acid complex) under the present conditions.

The nuclides ^{137}Cs, ^{229}Th, ^{241}Am and ^{243}Am would all decay to insignificant concentrations before breakthrough, considering a 1 m thick clay barrier of compacted bentonite. The concentration of ^{90}Sr, ^{239}Pu and ^{240}Pu would be significantly reduced, while the concentration of ^{99}Tc and ^{237}Np, however, would be very little reduced.

8. ACKNOWLEDGEMENT

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APPENDIX

The transport rate of ions through a solid is related to the physical properties of the solid but also to the physical and chemical interactions (the sorption) of the solute with the solid. By measuring the apparent diffusivity (D_a) of radionuclides in compacted clay and using the equation

$$D = D_a(1 + K_d\rho(1 - \varepsilon)/\varepsilon) \qquad \text{(A1)}$$

where D = diffusivity without interactions (m^2/s) , K_d = distribution coefficient (m^3/kg), ρ = density of the solid (kg/m^3) and ε = porosity of the solid (m^3/m^3), it is possible to calculate the distribution coefficient if the porosity is known and the diffusivity without sorption is assumed to be equal to the diffusivity in water, i.e. ca 10^{-9} m^2/s.

Measured diffusivities and distribution coefficients and calculated distribution coefficients according to Eqn (A1) for some actinides and fisson products are given in Table A1.

It is obvious from the calculated distribution coefficients that there are different transport processes involved; the non-complexed cations, strontium and cesium, have significantly lower calculated K_d-values than measured, while all the others are either equal or larger than measured values, in some cases orders of magnitude larger. For strontium and cesium a transport not only in the water phase but also in and/or on the solid phase can not be excluded (a similar behaviour is found in granite where calculated distribution coefficients for technetium, cesium and americium were 0.0004, 0.003 and 6.3 m^3/kg, respectively, which for cesium is much lower than measured). A colloid formation leading to higher transport rate and lower distribution coefficients is not likely, according to previous experiments.

For hydrolyzed species, neutral or charged, the calculated sorption is equal to or larger than the measured sorption, and for iodine much larger ($K_{d,calc}$ = 8.4 and $K_{d,m}$ = 0.001). Steric hindrances or a charge repulsion leading to the slow transport rate observed in the clay could possibly lead to the results for iodine.

A conclusion is, that Eqn (A1) is hardly suitable for describing the transport av various radionuclides by diffusion in a high-capacity matrix like bentonite because of the fundamentally different interaction mechanisms that would influence the transport.

Table A1. Measured apparent diffusivities (D_a) and distribution coefficients ($K_{d,m}$) and calculated distribution coefficients ($K_{d,calc}$) according to Eqn (A1)($\rho = 2x10^3$ kg/m^3, $\varepsilon = 0.35$ and $D = 1x10^{-9}$ m^2/s)

Element	$\log C_i$	Time (d)	$(D_a)_{av}x10^{14}$ (m^2/s)	$(D_a)_{max}x10^{14}$ (m^2/s)	$K_{d,m}$ (m^3/kg)	$K_{d,calc}$ a) (m^3/kg)	$K_{d,calc}$ [b] (m^3/kg)
Sr	-11	50	180	1200	2.9	0.15	0.022
Tc	-10	69	87	160	0	0.31	0.17
Tc c)	-10	70	8.0	13.5	0.05	3.4	2.0
I	-11	157	3.2	6.7	0.001	8.4	4.0
Cs	-10	53	140	200	1.4	0.19	0.13
Th	-14	64	0.46	0.85	$\geq$6	59	32
Pa	-13	76	$\geq$57	$\geq$60	5.0	0.47	0.45
U	-8	62	58	82	0.093	0.46	0.33
U d)	-8	54	19	34	(0.093)	1.4	0.79
U e)	-8	62	57	94	(0.093)	0.47	0.29
U f)	-8	63	20	38	(0.093)	1.3	0.71
U c)	-8	53	4.5	11	5	6.0	2.4
Np	-9	69	22	37	0.12	1.2	0.73
Np c)	-9	322	0.45	0.97	5 [g]	60	28
Pu	-9	317	0.32	0.65	3.5	84	41
Am	-9	350	0.29	0.62	6.6	93	43

a) For $(D_a)_{av}$

b) For $(D_a)_{max}$

c) 0.5% Fe added to the clay

d) 600 mg/l HCO_3^- added to the aqueous phase

e) 10 mg/l humic acid added to the aqueous phase

f) 1% $Fe_3(PO_4)_2$ added to the clay

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