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Migration of the Actinides Thorium, Protactinium, Uranium, Neptunium, Plutonium and Americium in Clay

By BÖRJE TORSTENFELT, Department of Nuclear Chemistry, Chalmers University of Technology, S-41296 Göteborg, Sweden

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Actinides/Bentonite clay/Diffusion mechanisms/Laboratory measurements/Migration

Abstract

The migration, i. e., the diffusivity, in compacted bentonite of the actinides thorium, protactinium, uranium, neptunium, plutonium and americium have been studied in laboratory experiments.

A sodium bentonite, Wyoming bentonite MX-80, compacted to a density of 2×10^3 kg/m^3, was used in all experiments. The effect of mixing the clay with 1% $Fe_3(PO_4)_2$ or 0.5% iron powder on the diffusion of uranium and neptunium was examined. The diffusion of uranium and americium after addition of 600 mg/l of HCO_3^- and the diffusion of uranium after addition of 10 mg/l of humic acid to the aqueous phase was studied, as well.

The aqueous phase was a synthetic groundwater representative of Swedish deep granitic groundwaters, and was preequilibrated with the clay.

The apparent diffusivities measured for the penta- and hexavalent actinides – protactinium: Pa(V); neptunium: Np(V); uranium: U(VI) – were between 3.7 and 6.5×10^{-13} m^2/s. For the tri- and tetravalent actinides – americium: Am(III); thorium: Th(IV), plutonium: Pu(IV) – the apparent diffusivities were between 1.9 and 12.9×10^{-15} m^2/s. The metallic iron added to the clay lowered the diffusivity of the uranium and the neptunium. Iron phosphate lowered the neptunium diffusivity but had no effect on the uranium diffusivity. While adding bicarbonate to the aqueous phase may have had the effect of decreasing the americium mobility, the addition of bicarbonate or humic acid had no significant effect on the mobility of uranium.

A small fraction of the uranium, neptunium, and plutonium had diffusivities on the order of 10^{-12} m^2/s, which is that expected for a non-sorbing species transported through the clay. Uranium and neptunium seem to diffuse by more than one mechanism or species – one fraction with a mobility similar to what was measured for the penta- and hexavalent actinides and the other fraction with a mobility similar to what was observed for the tetravalent actinides.

1. Introduction

As a consequence of the introduction of nuclear power, there has been a profound interest in the behaviour of the lighter actinides through americium in the environment.

This paper presents the results of direct measurements of the transport, i. e., the diffusion, of the actinides thorium, protactinium, uranium, neptunium, plutonium and americium in compacted bentonite. The paper is based on previously published conference proceedings and a technical report [1–3], but the diffusion coefficients have been reexamined.

2. Experimental

The studied systems are given in Table 1.

Table 1. Studied systems (aqueous phase: artificial groundwater preequilibrated with the clay, cf., Table 2).

Diffusing species	Solid phase
^{234}Th	Bentonite [a]
^{233}Pa	Bentonite
^{233}U	Bentonite
^{233}U	Bentonite + 0.5% Fe(s)
^{233}U	Bentonite + 1% $Fe_3(PO_4)_2$(s)
^{233}U	Bentonite; 600 mg/l $NaHCO_3$ added to the artificial groundwater
^{233}U	Bentonite; 10 mg/l humic acid in the aqueous phase
^{237}Np	Bentonite
^{237}Np	Bentonite/Bentonite + 0.5% Fe(s) [b]
^{237}Np	Bentonite + 1% $Fe_3(PO_4)_2$(s)
^{239}Pu	Bentonite
^{241}Am	Bentonite
^{241}Am	Bentonite; 600 mg/l $NaHCO_3$ added to the artificial groundwater

[a] Wyoming bentonite, MX-80; density: 2×10^3 kg/m^3; used in all experiments.
[b] One type in each half-cell.

2.1. Radionuclides

Thorium, as the short-lived ^{234}Th (half-life = 24.1 days), was recovered from ^{238}U by a sorption/extraction procedure [4] in which the separation is achieved by pH-adjustment. A total amount of 10^{-14} mol was added to the clay.

Protactinium, as ^{233}Pa (half-life = 27 days), was recovered from ^{237}Np using the same technique. The total amount of protactinium added was 10^{-13} mol.

The amounts of uranium, neptunium, plutonium, and americium used in all experiments were, respectively, 3×10^{-7} mol of ^{233}U, 5×10^{-6} mol of ^{237}Np, 3×10^{-8} mol of ^{239}Pu and 4×10^{-9} mol of ^{241}Am.

2.2. Solids and the aqueous phase

Information on the clay used and on the preparation of

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the clay and the aqueous phase is in the preceding paper, "The migration of the fission products strontium, technetium, iodine, and cesium in clay". *

For the redox-sensitive actinides uranium and neptunium, the diffusion under reducing conditions was studied by mixing the clay with 0.5% metallic iron (iron powder) or with 1% $Fe_3(PO_4)_2$. In addition, the phosphate is also a strong complex-forming agent.

Table 2. Composition of the aqueous phase (pH 8.8 – 9.0)

Cation	ppm	Anion	ppm
K^+	11	Cl^-	132
Na^+	670	NO_3^-	6.8
Ca^{2+}	6.6	SO_4^{2-}	870
Mg^{2+}	1.7		

2.3. Diffusion measurements

The technique used for studying the diffusion is described in the preceding paper, and in detail in reference [5].

3. Diffusion theory

The diffusion theory is given in the preceding paper.

4. Results and discussion

From the diffusion equation, $\log C = \text{const.} - (1/(4D_a t))x^2$, the apparent diffusivity is given from the slope of $\log C$ versus the square of the transport distance, x. The measured concentration profiles, given as $\log C$ versus x^2, for thorium, protactinium, uranium, neptunium, plutonium and americium are shown in Figures 1 – 12[a]. Experimental parameters and calculated diffusivities are given in Tables 3 and 4.

Often only the far end of the curve (corresponding to the highest values of x^2) is a straight line while the curve increases rapidly for low values of x^2 (cf., Fig. 3 etc.). This nonlinear behaviour could be explained by concentration-dependent sorption isotherms, the superposition of more than one diffusion mechanism, etc. If doing a least square fit on the linear part of the curve and subtracting this from the entire curve yields a new linear curve, however, then the diffusion could be expected to consist of superimposed mechanisms. Thus, if this is the case, two (or more) independent apparent diffusivities can be calculated by doing consecutive least square fits on the measured concentration profile. These diffusivities together result in the observed transport through the clay.

The actinides have a complicated redox chemistry with possible oxidation states ranging from +3 to +6 in a natural aqueous environment [6]. Thus, it is reasonable to be able to distinguish between two and sometimes three diffusivities contributing to the overall diffusivity.

Using the equation, $D = D_a(1 + K_d\rho(1-\epsilon)/\epsilon)$, the diffusivity through the pores can be calculated. This equation appears to be valid for species sorbing by chemisorption or physical adsorption, but is not applicable to diffusion measurements when the species is sorbed by a cation exchange reaction [7]. The diffusivity, D, for thorium, uranium, neptunium and americium is calculated to be $(2-4) \times 10^{-10}$ m^2/s; for plutonium it is 3×10^{-11} m^2/s. For protactinium, however, the diffusivity is 1.4×10^{-8} m^2/s which implies it has a greater mobility than that of ions self-diffusing in dilute water solutions. Therefore, if the K_d-value is correct, the equation is not applicable to the diffusion of protactinium (see Section 4.2.).

4.1. Thorium

Thorium is tetravalent, Th(IV), under the conditions expected in natural waters. It is highly hydrolyzed and sorbs strongly on solids. The measured diffusivity for thorium is $\leq 7.7 \times 10^{-15}$ m^2/s, which is 2 to 3 orders of magnitude lower than is measured for the fission products strontium, technetium, iodine and cesium [7]. The mobility is so slow, in fact, that it is difficult to separate the actual transport from the possible errors in determining the starting point of the diffusion; thus, the diffusivity must be expressed as "less than or equal to" the calculated value. Thorium appears to diffuse by only one mechanism (cf., Fig. 1), which is what is expected considering the fact that it has one prevailing oxidation state, does not form carbonate complexes, and is extensively hydrolyzed.

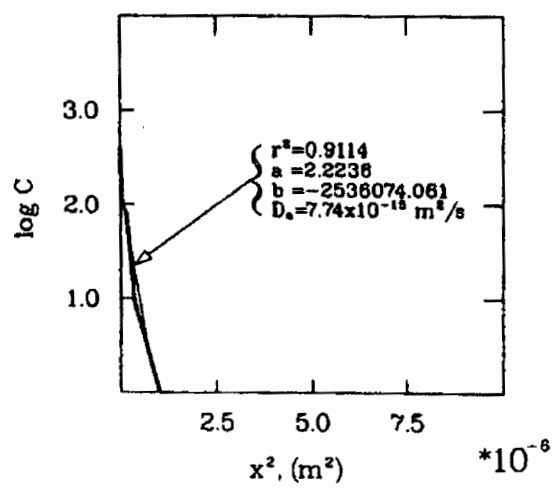

Fig. 1. Diffusion of thorium in compacted bentonite. Diffusion time = 64 days.

* TORSTENFELT, B.: Radiochim. Acta 39, 97–104 (1986).

[a] The values for r^2, a and b from the least square fit of $\log C = a + b \times x^2$ and the apparent diffusivity calculated from the b-value are given. Note that the scale on the x-axis is varied for the different actinides.

Table 3. Distribution coefficients [8] and measured diffusivities in bentonite for thorium, protactinium and uranium (density of the clay = 2×10^3 kg/m^3)

Element	$\log C_l^a$	Time [d]	K_d [m^3/kg]	D_a [m^2/s]	D^b [m^2/s]
Th	−14.0	64	>6	$<7.7 \times 10^{-15}$	2.2×10^{-10}
Pa	−13.7	76	5.0	6.2×10^{-13}	1.4×10^{-8}
U	− 6.5	62	0.093	3.4×10^{-12} 6.4×10^{-13} 2.7×10^{-13}	2.78×10^{-10}
U[c]	− 6.5	53		3.3×10^{-11} 1.6×10^{-13}	
U[d]	− 6.5	63		8.2×10^{-12} 3.1×10^{-13} 1.0×10^{-13}	
U[e]	− 6.5	54		8.5×10^{-12} 2.3×10^{-13} 8.3×10^{-14}	
U[f]	− 6.5	62		6.7×10^{-12} 6.8×10^{-13} 2.3×10^{-13}	

a C_l = Number of moles initially added.
b Evaluated from Eq. (3), preceding paper.
c 0.5% Fe(s) added to the clay.
d 1% $Fe_3(PO_4)_2$(s) added to the clay.
e 600 mg/l $NaHCO_3$ added to the artificial groundwater.
f 10 mg/l humic acid added to the aqueous phase.

4.2. Protactinium

Protactinium is expected to be in the +5 oxidation state, as PaO_2^+, but has a peculiar chemistry [9] and does not always behave as a typical pentavalent actinide. Its sorption on bentonite is strong (K_d = 5 m^3/kg), which is in contrast with the poor sorption of neptunium(V) (cf., Table 4). It exhibits one diffusion mechanism with a diffusivity, D_a, of 6.2×10^{-13} m^2/s (Fig. 2). This is also in contrast with what is observed for the pentavalent neptunium and the hexavalent uranium, both of which seem to have three superimposed diffusivities.

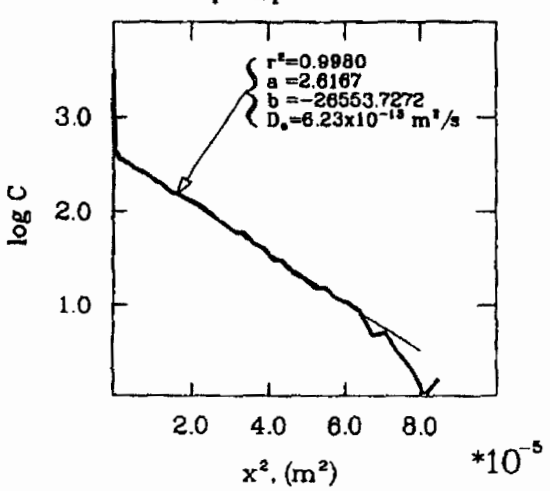

Fig. 2. Diffusion of protactinium in compacted bentonite. Diffusion time = 76 days.

4.3. Uranium

Under oxidizing conditions uranium is hexavalent, existing as the uranyl ion, UO_2^{2+}, which sorbs poorly on bentonite (cf., Table 3). Three diffusivities are observed (Fig. 3a): 3.4×10^{-12} m^2/s, 6.4×10^{-13} m^2/s and 2.7×10^{-13} m^2/s[a]. The fastest migrating fraction has a mobility expected to be equal to the mobility of the "water front"; this mobility is observed independent of the identity of the element for the actinides uranium, neptunium, and plutonium, and for the fission products strontium, technetium, iodine, and cesium [7]. The second and the third fraction are probably two different complexes of hexavalent uranium, with the bulk of the uranium migrating with an apparent diffusivity of 6.4×10^{-13} m^2/s.

Even when metallic iron is added to the clay a small fraction of the uranium migrates quickly, i.e., 3.3×10^{-11} m^2/s. The migration of the major part of the uranium, however, is decreased by a factor of 3 or 4 and has an apparent diffusivity of 1.6×10^{-13} m^2/s (cf., Fig. 3b). The reduction of U(VI) to U(IV) by the metallic iron is expected to cause the decrease in the mobility.

a Sometimes it is possible to fit a final linear curve close to the starting point. This is probably not a "true" diffusivity but, rather, is dependent either on precipitation of the actinide at the starting point or the movement or reorientation of the layer of the diffusing species after closure of the cell. Both effects are artifacts of the experimental technique

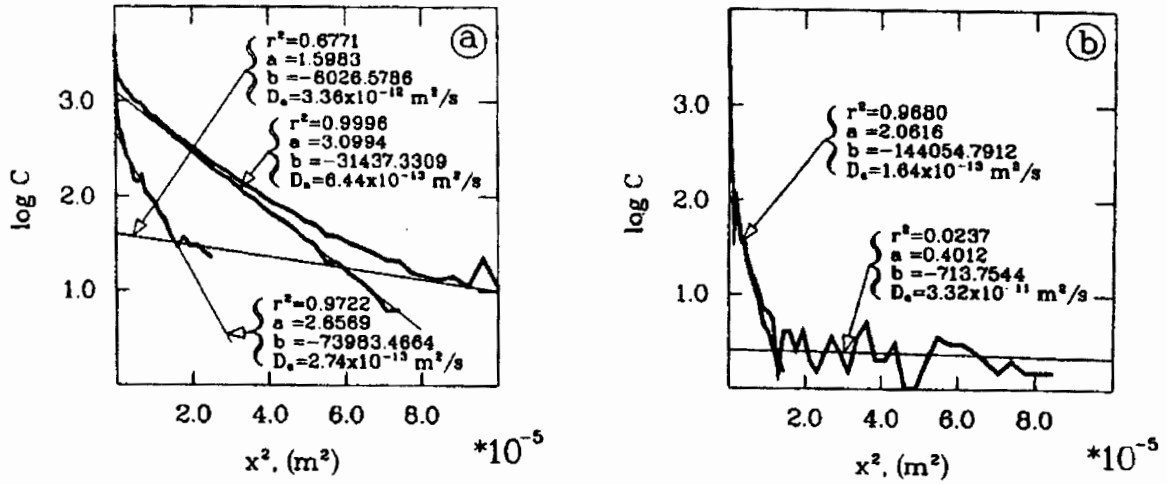

Fig. 3. Diffusion of uranium in compacted bentonite. a) Ordinary bentonite, diffusion time = 62 days. b) Bentonite mixed with 0.5 % iron powder. Diffusion time = 53 days.

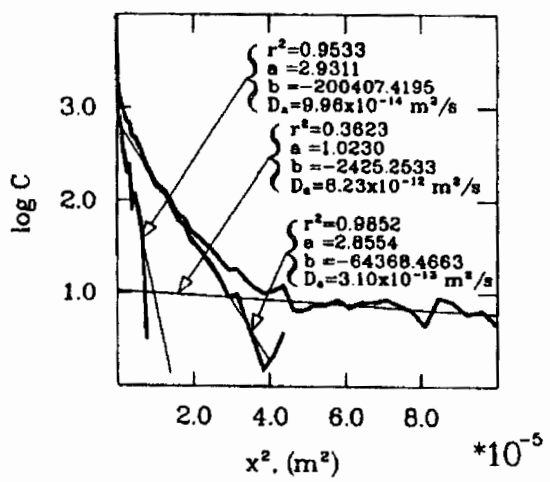

Fig. 4. Diffusion of uranium in compacted bentonite, with the bentonite mixed with 1 % $Fe_3(PO_4)_2$. Diffusion time = 63 days.

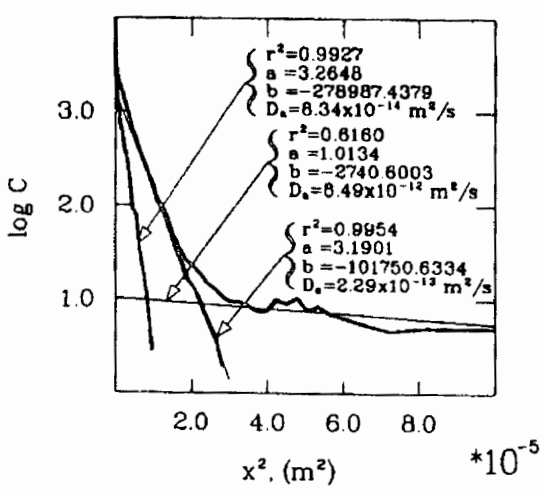

Fig. 5. Diffusion of uranium in compacted bentonite with 600 mg/l $NaHCO_3$ added to the artificial groundwater. Diffusion time = 54 days.

The addition of 1% $Fe_3(PO_4)_2$ (s) to the clay, or 600 mg/l $NaHCO_3$ or 10 mg/l humic acid to the aqueous phase, did not seem to have any significant influence on the uranium diffusion (Figs. 4–6). The complex-formation constant for uranyl with HPO_4^{2-} is expected to be high ($\log K_1$ = 8.4 [6], but, as shown in Figure 4, no significant effect on the transport is observed.

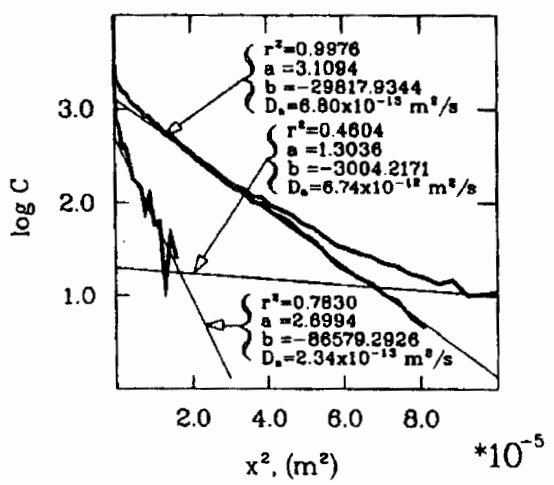

Fig. 6. Diffusion of uranium in compacted bentonite with 10 mg/l humic acid added to the artificial groundwater. Diffusion time = 62 days.

4.4. Neptunium

Neptunium exists in the pentavalent oxidation state, as NpO_2^+, under oxidizing conditions and, similar to uranium, apparently has three superimposed diffusivities: 1.2×10^{-11} m^2/s, 3.7×10^{-13} m^2/s, and 4.6×10^{-14} m^2/s (see Fig. 7).

The main fraction of the neptunium is transported with a diffusivity very nearly the same as those of pro-

Table 4. Distribution coefficients [8] and measured diffusivities in bentonite for neptunium, plutonium, and americium (density of the clay = 2×10^3 kg/m^3)

Element	$\log C_i$ [a]	Time [d]	K_d [m^3/kg]	D_a [m^2/s]	D [b] [m^2/s]
Np	−5.3	69	0.12	1.2×10^{-11} 3.7×10^{-13} 4.6×10^{-14}	2.1×10^{-10}
Np [c]	−5.3	322		8.2×10^{-13} (no Fe(s)) 3.5×10^{-14} (no Fe(s)) 4.2×10^{-14} (Fe(s))	
Np [d]	−5.3	212		2.1×10^{-14}	
Pu	−7.6	316	3.5	3.2×10^{-12} $<1.9 \times 10^{-15}$	$<3.1 \times 10^{-11}$
Am	−8.4	524	6.6	$<1.3 \times 10^{-14}$	$<4.0 \times 10^{-10}$
Am [e]	−8.4	350		$<2.8 \times 10^{-16}$	

a C_i = Number of moles initially added.
b Evaluated from Eq. (3) in preceding paper
c 0.5% Fe(s) in part of the clay.
d 1% $Fe_3(PO_4)_2$ (s) added to the clay.
e 600 mg/l $NaHCO_3$ added to the artificial groundwater.

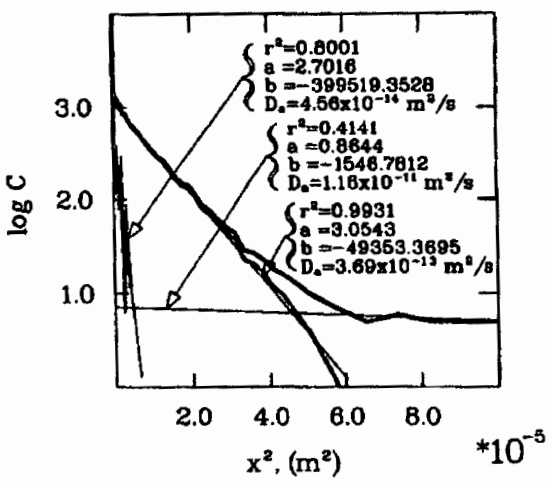

Fig. 7. Diffusion of neptunium in compacted bentonite. Diffusion time = 69 days.

tactinium and the bulk of uranium (i.e., $(4-6) \times 10^{-13}$ m^2/s). This value seems to be the diffusivity for the "-yl" ions (AnO_2^+ and AnO_2^{2+}) in the compacted bentonite. Neptunium also has a fraction migrating with a diffusivity of 1.2×10^{-11} m^2/s, a value which appears to be independent of the identity of the element. The fraction with the lowest diffusivity is either a neptunyl complex or tetravalent neptunium, which, as thorium, should exhibit a low mobility in the clay.

When metallic iron is added to the clay, the neptunium is reduced to the tetravalent state with a diffusivity of 4.2×10^{-14} m^2/s (cf., Fig. 8). Close to the starting point (i.e., the interface between the ordinary clay and the clay containing metallic iron) neptunium is reduced throughout, even in the ordinary clay, resulting in a diffusivity of 3.5×10^{-14} m^2/s. The diffusivity for the rest

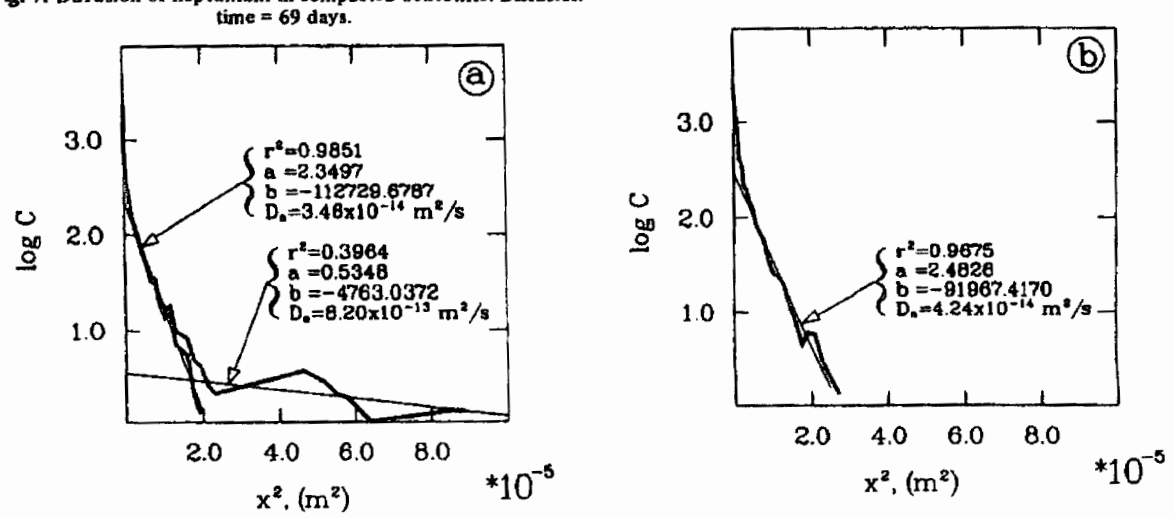

Fig. 8. Diffusion of neptunium in compacted bentonite with one half of the cell a) in ordinary bentonite, and the other half of the cell b) with the bentonite mixed with 0.5% iron powder. Diffusion time = 322 days.

of the neptunium in the ordinary clay is 8.2×10^{-13} m^2/s. No fast-moving fraction is observed in the chemically reducing part of the clay. In the chemically oxidizing part of the clay a fast-moving fraction is not distinguishable; only the diffusion of the neptunyl ion is observed due to the long experimental time.

After mixing 1% $Fe_3(PO_4)_2(s)$ with the clay (Fig. 9), the mobility of neptunium is decreased to a diffusivity one order of magnitude lower than that observed in normal bentonite. This is in contrast to what was found in the uranium experiment in which the addition of iron(II) phosphate had no significant effect on the diffusion. The equilibrium constant for the reduction of NpO_2^+ by Fe^{2+}, however, is $K = 0.29$ at 25°C, and, for the reduction of UO_2^{2+} by Fe^{2+} the equilibrium constant is $K = 10^{-15}$. Thus, neptunium could be reduced by Fe^{2+}, forming an HPO_4^{2-} complex ($\log K_1 = 12.0-13.0$ [6]) or being hydrolyzed to $Np(OH)_4$ or NpO_2, while the uranium, if reduced, would be rapidly oxidized to the hexavalent state again [6,9,10]. Therefore, the difference in uranium and neptunium mobility in these experiments is most likely in agreement, although the phosphate would still be expected to form a complex with the uranium. No fast-moving fraction was observed in this experiment.

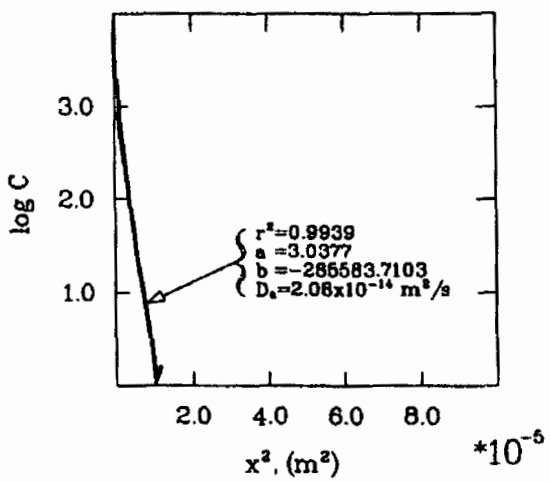

Fig. 9. Diffusion of neptunium in compacted bentonite, with the bentonite mixed with 1% $Fe_3(PO_4)_2$. Diffusion time = 212 days.

4.5. Plutonium

The measured concentration profile for plutonium in compacted bentonite is shown in Figure 10. As with thorium, the transport is very slow, and even after almost 1 year it is difficult to separate the concentration profile from the starting point of the experiment (cf., the footnote in section 4.3.). Thus, the diffusivity of the plutonium is expressed as $\leq 1.9 \times 10^{-15}$ m^2/s. One fraction of the plutonium moves rapidly through the clay ($D_a = 3.2 \times 10^{-12}$ m^2/s); again, this is the diffusivity expected for all species transported with the "water front."

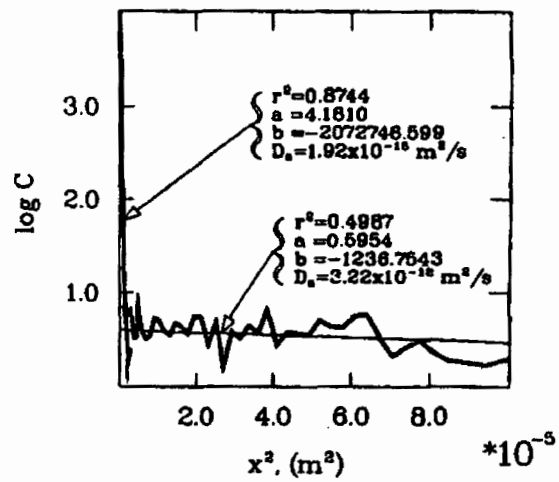

Fig. 10. Diffusion of plutonium in compacted bentonite. Diffusion time = 316 days.

4.6. Americium

Similar to thorium and the main part of the plutonium, americium is virtually immobile during the extent of the experiment. After 524 days the apparent diffusivity was determined to be less than or equal to 1.3×10^{-14} m^2/s (Fig. 11). Americium appears to be transported by one mechanism only. No fast-moving fraction was observed.

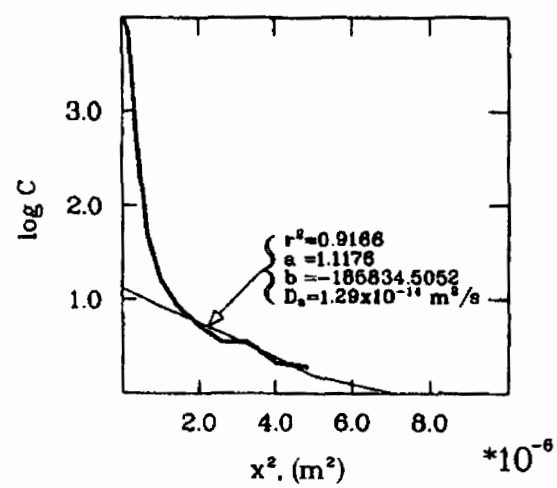

Fig. 11. Diffusion of americium in compacted bentonite. Diffusion time = 524 days.

In the experiment in which 600 mg/l HCO_3^- was added to the aqueous phase (Fig. 12), it is almost impossible to see any transport at all after 350 days diffusion time. The apparent diffusivity is $\leq 2.8 \times 10^{-16}$ m^2/s (calculated from three points), indicating that the presence of HCO_3^- in the water would not, in any event, increase the mobility of americium.

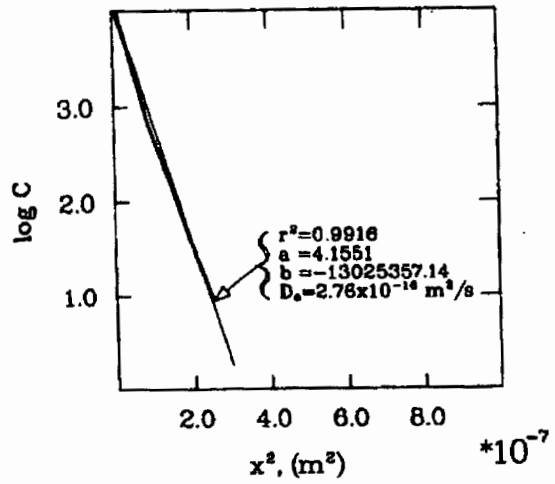

Fig. 12. Diffusion of americium in compacted bentonite with 600 mg/l $NaHCO_3$ added to the artificial groundwater. Diffusion time = 350 days.

5. Conclusions

With the diffusion equation written as $\log C = \text{const.} - (1/(4D_a t))x^2$, a plot of $\log C$ versus x^2 makes it possible to evaluate whether the diffusion of a species consists of one linear diffusion mechanism, two or more superimposed linear mechanisms, or a nonlinear diffusion mechanism. In the case of superimposed linear mechanisms, consecutive least square fits of the $\log C$ versus x^2 curve give the apparent diffusivities of the diffusion mechanisms contributing to the overall transport observed.

The mobility of actinides in the +3 and +4 oxidation states is very low. Even after diffusion times greater than one year it is difficult to distinguish between actual transport and errors in determining the exact starting point. Thus, the diffusivities evaluated for thorium, plutonium and americium (7.7×10^{-15} m²/s, 1.9×10^{-15} m²/s, and 1.3×10^{-14} m²/s, respectively) are maximum values.

For the actinides in the +5 and +6 oxidation states the apparent diffusivity was measured to be between 3 and 7×10^{-13} m²/s (6.2×10^{-13} m²/s for protactinium, 6.4×10^{-13} m²/s for uranium, and 3.7×10^{-13} m²/s for neptunium).

The addition of metallic iron to the clay decreased the mobility of both uranium (VI) and neptunium (V), a factor of 3 to 4 for uranium and one order of magnitude for neptunium. Reduction to the tetravalent states is expected to cause the lower mobility. The fact that neptunium has a lower mobility than uranium is thought to be due to a more complete reduction of Np (V) relative to that of U (VI).

The addition of 1% $Fe_3(PO_4)_2$ to the clay, or of 600 mg/l $NaHCO_3$ or 10 mg/l humic acid to the aqueous phase, did not significantly influence the diffusion of uranium.

Neptunium had a diffusivity one order of magnitude lower than that observed for diffusion in normal compacted bentonite, i. e., 2.1×10^{-14} m²/s, when the clay was mixed with 1% $Fe_3(PO_4)_2$.

Using the equation, $D = D_a(1 + K_d\rho(1-\epsilon)/\epsilon)$, the diffusivities for thorium, neptunium and uranium were calculated to be $(2-4) \times 10^{-10}$ m²/s, and 3×10^{-11} m²/s for plutonium. The equation is not applicable to the protactinium system.

Two or three diffusion mechanisms were observed for uranium, neptunium and plutonium. In each of the runs using these elements, there seems to be a small fraction exhibiting the transport rate that is expected for a non-interacting species; it is the same as that observed for some fission products. The diffusion coefficient, D_a, for this transport is determined to be somewhere between 10^{-11} and 10^{-12} m²/s. Also, small fractions of the uranium and neptunium have a lower mobility than the remaining fractions, which is close to what is measured for the tri- and tetravalent actinides. This low-mobility fraction could be attributed to the existence of a portion of the actinides in the tetravalent state or to complex-formation of the penta- and hexavalent actinide.

6. Acknowledgements

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