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REPORT**

86-14**Migration of fission products and
actinides in compacted bentonite**

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**Migration of Fission Products and Actinides
in Compacted Bentonite**

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Summary

The migration in compacted bentonite, *i.e.*, the diffusivity, of the fission products strontium, technetium, iodine, and cesium and the actinides thorium, protactinium, uranium, neptunium, plutonium and americium have been studied in laboratory experiments.

The clay used in the experiments was a sodium bentonite, Wyoming Bentonite MX-80, compacted to a density of 2000 kg/m³. The aqueous phase was synthetic groundwater representative of Swedish deep granitic groundwaters, and was preequilibrated with the clay. The influence of complex-forming and redox controlling agents on the diffusion of fission products was studied by mixing the clay with small amounts of the chemical reagents PbO, KMnO₄ or powdered iron, or the minerals chalcopyrite/pyrite or cinnabar. Furthermore, the effect of mixing the clay with 1% Fe₃(PO₄)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 HCO₃⁻ and the diffusion of uranium after addition of 10 mg/l of humic acid to the aqueous phase was studied, as well.

The diffusivity of strontium was on the order of 10⁻¹¹ m²/s. For cesium and technetium (as pertechnetate) under oxidizing conditions the diffusivities are on the order of 10⁻¹² m²/s; for technetium under reducing conditions the diffusivity is about one order of magnitude lower. Iodine appears to diffuse with two mechanisms, resulting in two diffusion rates—one close to 10⁻¹² m²/s and the other one-tenth slower, 10⁻¹³ m²/s, contributing to the observed overall apparent diffusivity.

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 m²/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 m²/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 m²/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 hazardous fission products, *e.g.*, technetium and iodine, and the lighter actinides through americium in the environment. One important issue studied has been the mobility of radionuclides in clay [1-18].

This report presents the results of direct measurements of the transport, *i.e.*, the diffusion, of the fission products strontium, technetium, iodine, and cesium and the actinides thorium, protactinium, uranium, neptunium, plutonium and americium in a bentonite, compacted to a density of 2000 kg/m³ and saturated with a synthetic groundwater which was preequilibrated with the clay. The report is, with minor changes, identical to two papers published in *Radiochimica Acta* [19,20] which were based on previously published conference proceedings and a technical report [14-18,21], but with the diffusion coefficients reexamined.

2. Experimental

A complete list of the studied systems is given in Table I.

2.1. Radionuclides

2.1.1. Fission products

Among the fission products in spent nuclear fuel, nuclides of interest to study are strontium, technetium, iodine and cesium.

Technetium and iodine both have long-lived isotopes—technetium-99 (2.1×10^5 y) and iodine-129 (1.57×10^7 y)—and both are anionic under oxidizing condition; thus, they are expected to have only minor interactions with the solid phase and a mobility in the water-saturated clay close to the self-diffusion of ions in dilute water solutions. The isotopes used in the experiments were ⁹⁹Tc and ¹²⁵I with a total amount of approximately 10^{-6} and 10^{-13} moles added, respectively.

Strontium and cesium are the major contributors to the radiation hazards of spent nuclear fuel during the first 300 years after discharge from the reactor. They are also suitable model elements in studying the behavior of uncomplexed di- and monovalent cations. Approximately 10^{-12} moles of ⁸⁵Sr and ¹³⁴Cs were used in all experiments.

Table I. Studied systems (aqueous phase: artificial groundwater preequilibrated with the clay, *cf.*, Table II).

Diffusing species	Solid phase
^{85}Sr	Bentonite ^{a)}
^{99}Tc	Bentonite
^{99}Tc	Bentonite +0.5% Fe(s)
^{99}Tc	Bentonite/Bentonite +0.5% Fe(s) ^{b)}
^{125}I	Bentonite
^{125}I	Bentonite +0.5% Fe(s)
^{125}I	Bentonite +1% Fe(s)
^{125}I	Bentonite +1% KMnO ₄
^{125}I	Bentonite +0.5% Fe(s) +1% Chalcopyrite/pyrite
^{125}I	Bentonite +0.5% Fe(s) +1% Cinnabar
^{125}I	Bentonite +0.5% Fe(s) +1% PbO
^{125}I	Bentonite +1% Fe(s)/Bentonite +1% KMnO ₄ ^{b)}
^{125}I	Bentonite/Bentonite +1% KMnO ₄ ^{b)}
^{134}Cs	Bentonite
^{234}Th	Bentonite
^{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: $2 \times 10^3 \text{ kg/m}^3$; used in all experiments.

^{b)} One type in each half-cell.

2.1.2. Actinides

Thorium, as the short-lived ^{234}Th (half-life = 24.1 days), was recovered from ^{238}U by a sorption/extraction procedure [22] in which the separation is achieved by pH-adjustment. A total amount of 10^{-14} moles 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} moles.

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

2.2. Solids and the aqueous phase

Sodium bentonite (MX-80, Wyoming bentonite) compacted to a density of 2×10^3 kg/m³ and preequilibrated with simulated groundwater was used. The preequilibration was accomplished by first mixing the clay with water and then separating the two phases by high-speed centrifugation (~ 27000 g) after they had been in contact for more than one week. The clay was then dried in an oven (~ 105 °C), finely ground in an agate mortar, then used for the experiments.

The possibility of controlling the ion mobility in the clay was examined by mixing different additives, *i.e.*, *getters*, with the preequilibrated clay. Chemical interactors (complex-forming agents) were added in the form of finely ground minerals (chalcopyrite/pyrite, cinnabar) or chemical reagents (PbO), and in some experiments reducing conditions or oxidizing conditions were achieved by adding iron powder, iron phosphate or potassium permanganate, respectively.

The aqueous phase was originally an artificial groundwater representative of Swedish deep granitic groundwaters [23] but was preequilibrated with the clay (see above, this section). This caused the resulting pore water, consisting mainly of the cations sodium and potassium and the anions sulphate, chloride, and nitrate, to have a slightly higher ionic strength than the original artificial groundwater (*cf.*, Table II).

Table II. 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 was developed at the Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg, and is described in detail in reference [21]. The main principle of the experimental technique is that the studied species is introduced into a diffusion cell as a thin layer placed radially in the middle of a cylindrical clay sample (Figure 1). The entire diffusion cell is submerged in water and the species in the thin layer diffuses axially into the clay; thus, with time, a concentration profile moves slowly from the center out towards both ends. After a suitable diffusion time (*i.e.*, yielding measurable concentration profiles) the clay is sliced in thin sections and the radioactivity of the diffusing species analysed.

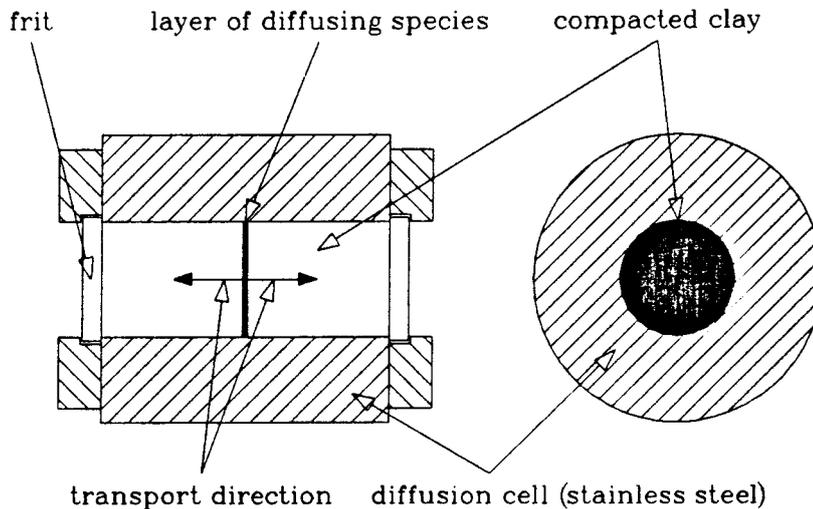


Figure 1. Schematic view of the diffusion cell (*cf.*, ref. 21).

Prior to the introduction of the diffusing species, the clay is wetted and homogenized with the preequilibrated water. The time allowed for the homogenization is about one month in order to minimize chemical concentration profiles in the pore water and density variations in the solid.

The radioactive species is introduced into the clay by first making a clay slurry, then taking drops of this slurry and drying them on a glass plate. When the drops are completely dry, the clay residue makes a thin (~ 0.2 – 0.5 mm) hard plate which is fairly easy to remove from the glass. On this plate the solution containing the radioactive species is dropped and evaporated to dryness under an IR-lamp. The radioactive sample is then placed on a wet, compacted, preequilibrated clay cylinder in the diffusion cell and another wet compacted clay cylinder is pressed over it (*cf.*, Figure 1).

After the necessary diffusion time, the diffusion cell is opened and the mantle surface of the sample removed to avoid measuring any surface diffusion along the cell wall. While the sample is still wet, it is sliced with a knife, and the concentration profile is analysed with an appropriate radioactive counter.

3. Diffusion theory

Flow of water through the clay is not possible; thus, the rate of transport of a species through the wet clay is dependent only on diffusion. Diffusion through a porous solid is dependent on molecular diffusion in the aqueous phase, on sorption phenomena and possibly surface transport on the solid, and also on the pore constrictivity and tortuosity. Therefore, the measured diffusivity is an apparent diffusivity, D_a , and not a pure molecular diffusivity, D . (When the diffusivity is mentioned in the text it is understood that the apparent diffusivity is meant and not the pure diffusivity unless otherwise noted.)

The apparent diffusivity for one-dimensional diffusion is given by the equation [24,25]:

$$\frac{dC}{dt} = \frac{\partial}{\partial x} \left(D_a \frac{dC}{dx} \right). \quad 1$$

For the one-dimensional diffusion of a plane source consisting of a limited amount of substance in a cylinder of infinite length and assuming diffusion independent of concentration, the solution of Eqn.(1) is:

$$\frac{C}{M} = \frac{0.5}{\sqrt{\pi D_a t}} \times e^{-\frac{x^2}{4D_a t}} \quad 2$$

where C = concentration (moles/m³), M = total amount of diffusing substance added per unit area (moles/m²), x = distance from source (m), D_a = apparent diffusivity (m²/s), and t = time (s).

If the sorption on the solid is reversible, with the sorption defined by the distribution coefficient, K_d (moles per kg solid/moles per m^3 liquid, m^3/kg), the relation between the apparent diffusivity (D_a) and the diffusivity not affected by sorption (D) is:

$$D = D_a (1 + K_d \rho (1 - \epsilon) / \epsilon) \quad 3$$

where ρ = density of the solid (kg/m^3) and ϵ = porosity of the solid (m^3 void fraction/ m^3 total volume).

If the sorption is concentration-dependent, both the distribution coefficient and the apparent diffusivity will vary with the concentration and Eqn.(2) will not be valid. In this case the sorption isotherm must be known and Eqn.(1) solved by numerical methods.

4. Results and discussion

With equation (2) rewritten as $\log C = \text{const.} - (1/(4D_a t))x^2$, 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 strontium, technetium, cesium, and iodine are shown in Figures 2-13 and the profiles for thorium, protactinium, uranium, neptunium, plutonium and americium are shown in Figures 14-25^a. Experimental parameters and calculated diffusivities are given in Tables III-VI.

Especially for the actinides, 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.*, Figure 15 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 [26]. Thus, it is reasonable to be able to distinguish between two and sometimes three diffusivities contributing to the overall diffusivity.

^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, and that the experimental range was $62.5 \times 10^{-5} m^2$ and not the $10 \times 10^{-5} m^2$ shown in the figures.

Using Equation (3), $D = D_a(1 + K_d\rho(1 - \epsilon)/\epsilon)$, 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 [19].

4.1. Strontium

The apparent diffusivity of strontium (as Sr^{2+}) was measured to be $2.0 \times 10^{-11} \text{ m}^2/\text{s}$ (Figure 2, Table III). Considering the high sorption of strontium (*cf.*, Table III), this indicates an unexpectedly high mobility in the clay. In fact, the diffusivity calculated from equation (3) is two orders of magnitude higher than self-diffusion in pure water which is, of course, not possible. Thus, either the measured batch- K_d is not applicable in the diffusion experiments or equation (3) is not valid for cation exchange sorption processes where the sorption/desorption rate is much faster than the diffusion process. The ionic strength of the pore water in the diffusion experiments is slightly higher than in the batch experiments, thus, giving a lower K_d . It is probably not possible, however, to use Eq. (3) for species sorbing by a cation exchange mechanism.

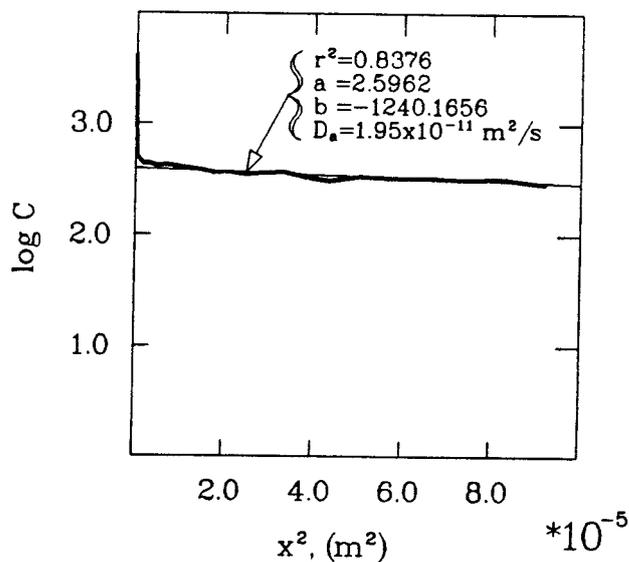


Figure 2. Diffusion of strontium in compacted bentonite. Diffusion time = 50 days.

Table III. Distribution coefficients [27-29] and measured diffusivities in bentonite (density of the clay = 2000 kg/m³)

Element	$\log C_i^{a)}$	Time (d)	$K_d^{b)}$ (m ³ /kg)	D_a (m ² /s)	$D^c)$ (m ² /s)
Sr	-12.3	50	2.9	2.0×10^{-11}	-
Tc	-5.8	69	0.0	1.2×10^{-12}	-
Tc ^{d)}	-5.8	70	0.05	1.5×10^{-13}	3.5×10^{-11}
Tc ^{e)}	-5.8	218	0.05	8.4×10^{-14} (Fe) 6.7×10^{-13} (no Fe)	2.0×10^{-11}
Cs	-11.4	53	1.4	2.4×10^{-12}	-

a) C_i = Number of moles initially added.

b) For a total nuclide concentration of 10^{-9} M.

c) Evaluated from Eq.(3).

d) 0.5% Fe(s) in the clay.

e) 0.5% Fe(s) in part of the clay.

4.2. Technetium

Technetium was measured under both oxidizing (Figure 3a) and reducing (Figure 3b) conditions and also when only part of the cell was filled with clay mixed with powdered iron (producing both reducing and oxidizing regions) (Figure 4). Under oxidizing conditions technetium is heptavalent and forms the anion pertechnetate, TcO_4^- , which is non-sorbing in bentonite. Without sorption, the apparent diffusivity (1.2×10^{-12} m²/s) is dependent only on the physical transport in the aqueous phase. Under reducing conditions, the apparent diffusivity was almost one order of magnitude lower (1.5×10^{-13} m²/s). An even lower apparent diffusivity (8.4×10^{-14} m²/s) was observed in the experiment with different conditions in the two half-cells. Obviously, the non-sorbing pertechnetate must be reduced by the iron to the tetravalent state, which forms sorbing species, the hydroxide ($Tc(OH)_4$) or the oxide (TcO_2) (*cf.*, Table III)[27]. The fact that the diffusivity is lower in the mixed half-cells is probably due to the much longer diffusion time, which provides sufficient time for the reduction (of greater amounts) of pertechnetate.

The sorption mechanism for technetium—physical adsorption of the oxide/hydroxide—is different from that of strontium. The diffusivity of technetium, evaluated from equation (3), is 2×10^{-11} m²/s which indicates that equation (3) is more feasible to use for technetium than for strontium. With a K_d of 0.01, a reasonable value considering the

ionic strength of the pore water, the diffusivity is $3.9 \times 10^{-12} \text{ m}^2/\text{s}$ which is close to the $1.2 \times 10^{-12} \text{ m}^2/\text{s}$ measured for the pertechnetate.

In Figure 4b it can be seen that a fraction of the technetium has diffused with the same rate as the pertechnetate. Because almost the same diffusivity is found for iodine and some of the actinides [20]; this value appears to be the diffusivity achieved for non-interactive transport through the clay.

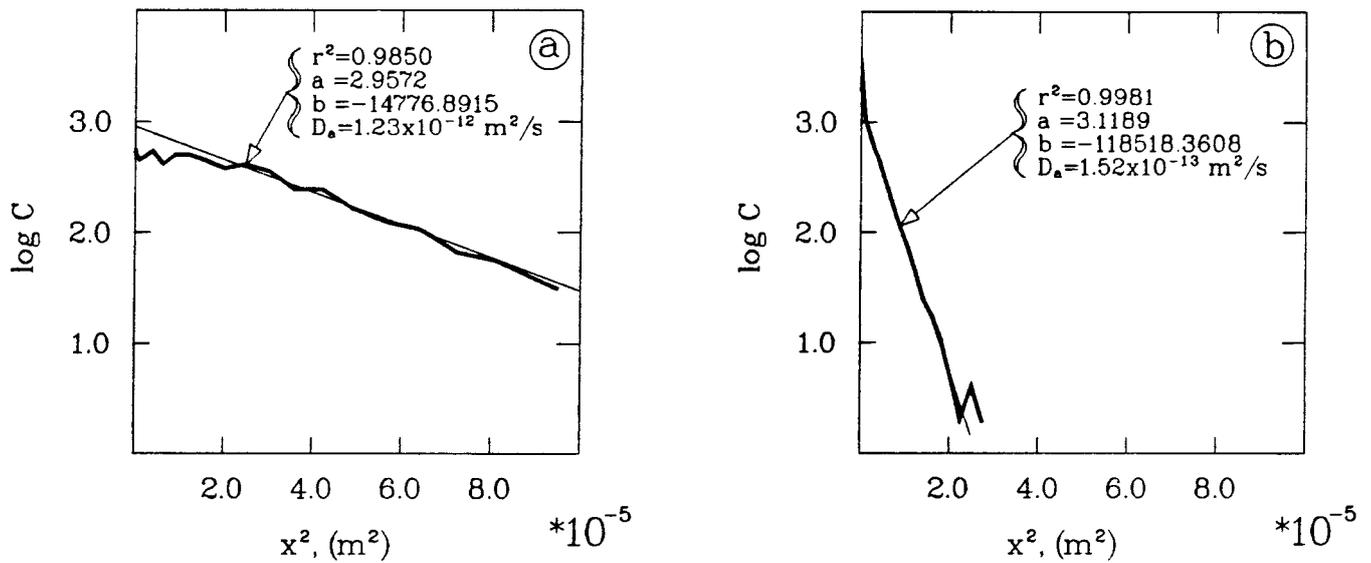


Figure 3. Diffusion of technetium in compacted bentonite. ^{a)} Ordinary bentonite, diffusion time = 69 days. ^{b)} Bentonite mixed with 0.5% iron powder, diffusion time = 70 days.

4.3. Cesium

Cesium, an uncomplexed monovalent cation, sorbs by cation exchange and has an apparent diffusivity of $2.4 \times 10^{-12} \text{ m}^2/\text{s}$ (Figure 5 and Table III). This is the same diffusivity as those of the non-sorbing elements. Thus, as for strontium, the high distribution coefficient does not seem to have any retarding influence on the transport rate; in fact, it seems to be almost the contrary, at least for strontium.

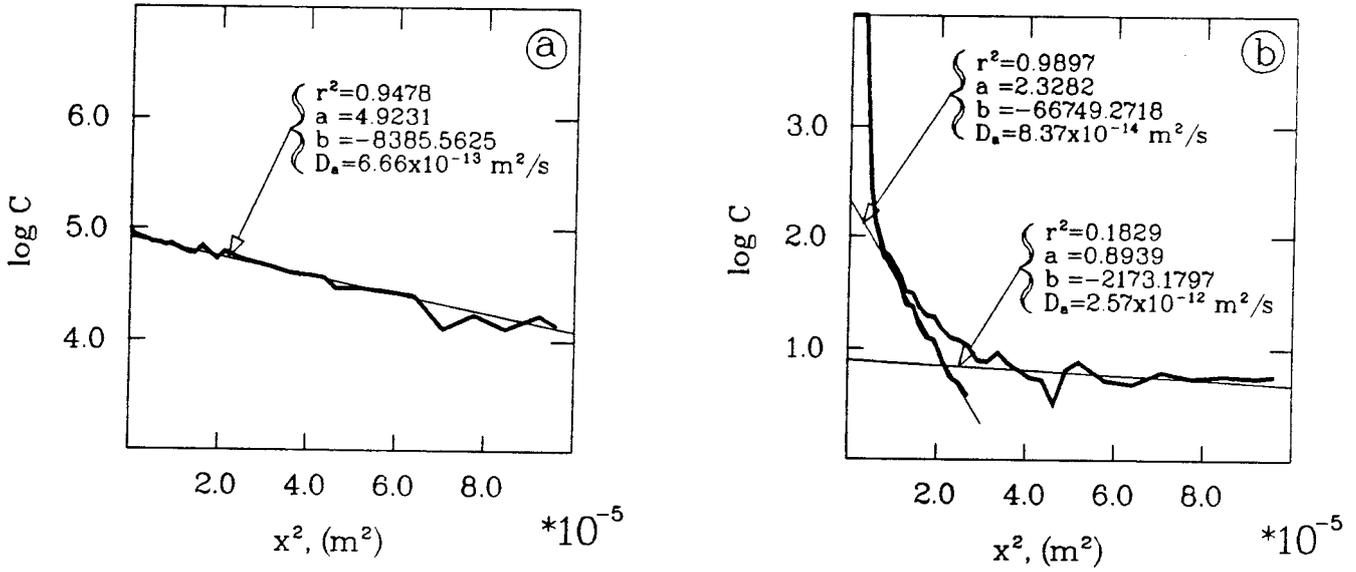


Figure 4. Diffusion of technetium in compacted bentonite with one half of the cell filled with ordinary clay ^{a)}, and the other half of the cell filled with clay mixed with 0.5% iron powder ^{b)}. Diffusion time = 218 days.

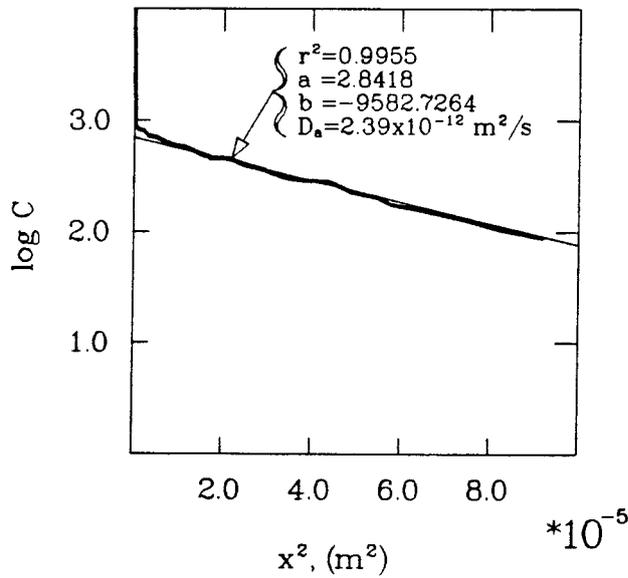


Figure 5. Diffusion of cesium in compacted bentonite. Diffusion time = 53 days.

Table IV. Distribution coefficients [30] and measured diffusivities for iodine in bentonite (init. amount of iodine = 1.8×10^{-13} moles; density of the clay = 2000 kg/m^3).

Additive	Time (d)	K_d^a (m^3/kg)	$(D_a)_{fast}$ (m^2/s)	$(D_a)_{slow}$ (m^2/s)	D^b (m^2/s)
-	157	0.001	2.6×10^{-12}	2.4×10^{-13}	1.4×10^{-12}
-	218	0.001	1.2×10^{-12}	1.1×10^{-13}	6.2×10^{-13}
0.5% Fe(s)	194	0.001	1.9×10^{-12}	1.7×10^{-13}	7.4×10^{-13}
1% Fe(s)	213	0.001	1.2×10^{-12}	7.2×10^{-14}	4.1×10^{-13}
1% KMnO4	210	0.001	1.3×10^{-12}	1.3×10^{-13}	7.4×10^{-13}
1% KMnO4 ^{c)}	213		1.1×10^{-12}	7.5×10^{-14} (KMnO4)	
			1.5×10^{-12}	1.5×10^{-13} (no KMnO4)	
1% KMnO4/1% Fe ^{d)}	225		1.4×10^{-12}	8.0×10^{-14} (KMnO4)	
			1.1×10^{-12}	5.3×10^{-14} (Fe(s))	
0.5% Fe + 1% Chalcopyrite	225	0.001	1.0×10^{-12}	9.6×10^{-14}	5.4×10^{-12}
0.5% Fe + 1% Cinnabar	226	0.8	1.4×10^{-12}	2.6×10^{-14}	1.5×10^{-12}
0.5% Fe + 1% PbO	224	0.6	1.3×10^{-12}	4.4×10^{-14}	2.5×10^{-12}

^{a)} For a total nuclide concentration of 10^{-9} M.

^{b)} Evaluated from Eq.(3) using $(D_a)_{slow}$.

^{c)} In half of the clay.

^{d)} Each in separate halves of the clay.

4.4. Iodine

The diffusion of iodine is dependent on two (or more) different mechanisms or on two diffusing species (*cf.*, Figure 6). Figure 6 shows that by subtracting the least square-fitted line of the “tail” of the curve from the measured curve, a new least square fit can be performed on the remaining curve. This indicates that the measured diffusion consists of two (or maybe more ^a) mechanisms, each satisfying equation (2) and each with a distinct diffusivity. The apparent diffusivities measured for iodine, as iodide (I^-), are 1.2 to $2.6 \times 10^{-12} \text{ m}^2/\text{s}$ and 1.1 to $2.4 \times 10^{-13} \text{ m}^2/\text{s}$. The two overlapping diffusivities are

^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 diffusing species 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 and are not “real” transport properties.

expected to be caused by either steric effects and dead end pores or by two different forms of iodine—iodide (I^-) and possibly hypoiodous acid (HIO , which is possibly stable under the chemical conditions in the clay [31]). The presence of two overlapping diffusivities is not an uncommon phenomenon. For the actinides especially, which can commonly exist in more than one chemical form simultaneously, two separate diffusivities contributing to the overall apparent diffusivity is often observed [20].

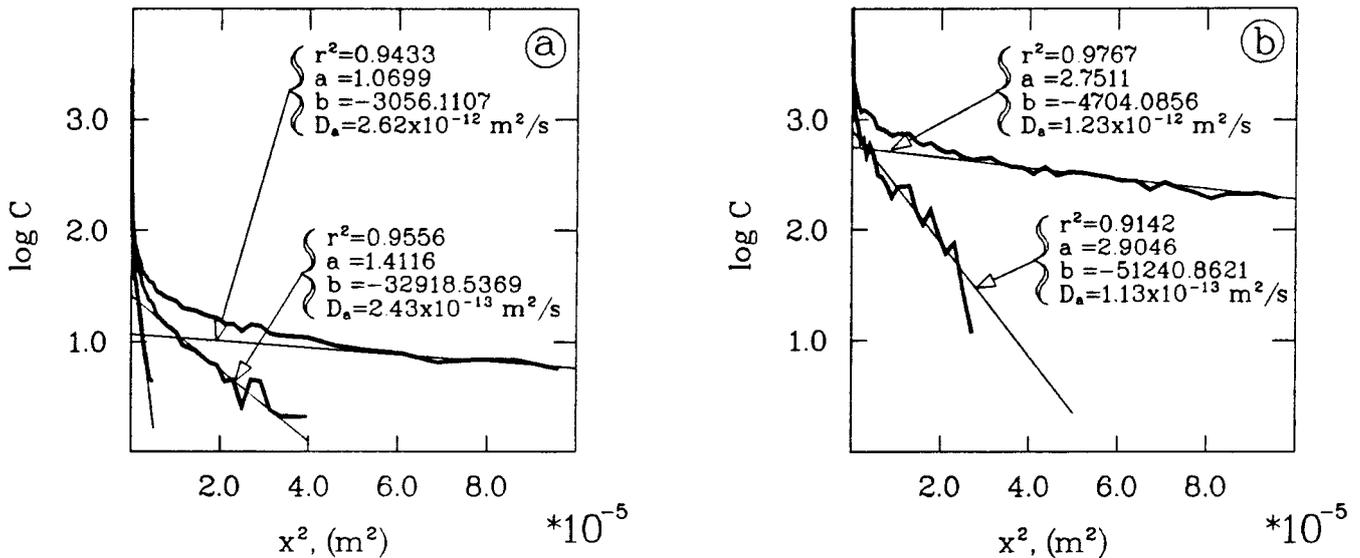


Figure 6. Diffusion of iodine in compacted bentonite. *a*) Diffusion time = 157 days. *b*) Diffusion time = 218 days.

By thinking of the clay as a two channel system—one large channel representing interconnected pores through which the main fraction of the iodide is transported and one small channel representing the dead-end pores and pores where the constrictivity severely hinders the diffusion—the idea that steric effects could lead to two observed diffusion mechanisms can be explained. This, too, would result in the slow transport of a more or less minor fraction of the iodine [32].

The experiments in which attempts were made to control and preserve the chemical speciation of the iodine (as I^- by adding metallic iron and as IO_3^- by adding $KMnO_4$) did not produce any significant differences in the diffusivities compared with the experiments in normal clay (Figures 7–10). The same phenomenon of two distinct mechanisms is observed, with virtually the same diffusivities as in normal clay (Table IV). Also, when the minerals containing iodide complex-forming agents and the iodide complex-forming chemical reagent were added to the clay, no significant change from the diffusion rate in the ordinary clay could be observed (Figure 11–13).

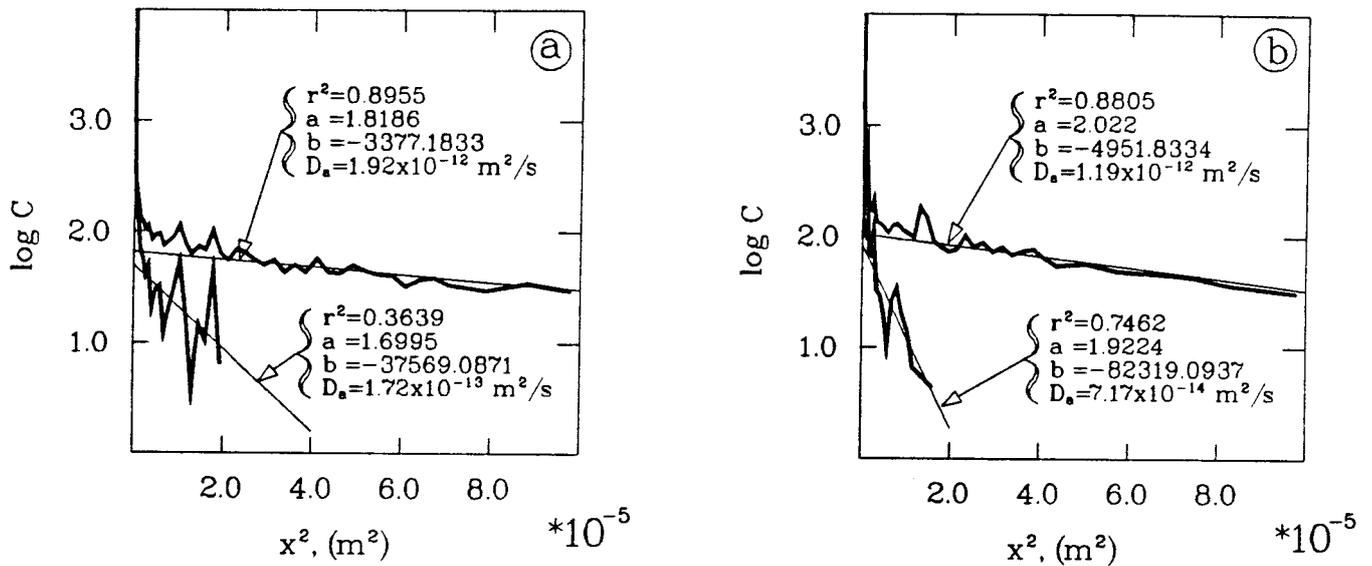


Figure 7. Diffusion of iodine in compacted bentonite. *a*) Bentonite mixed with 0.5% iron powder, diffusion time = 194 days. *b*) Bentonite mixed with 1% iron powder, diffusion time = 213 days.

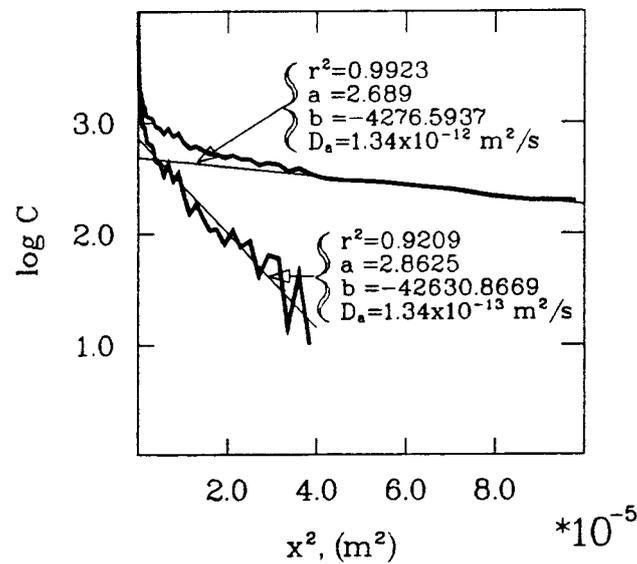


Figure 8. Diffusion of iodine in compacted bentonite mixed with 1% $KMnO_4$. Diffusion time = 210 days.

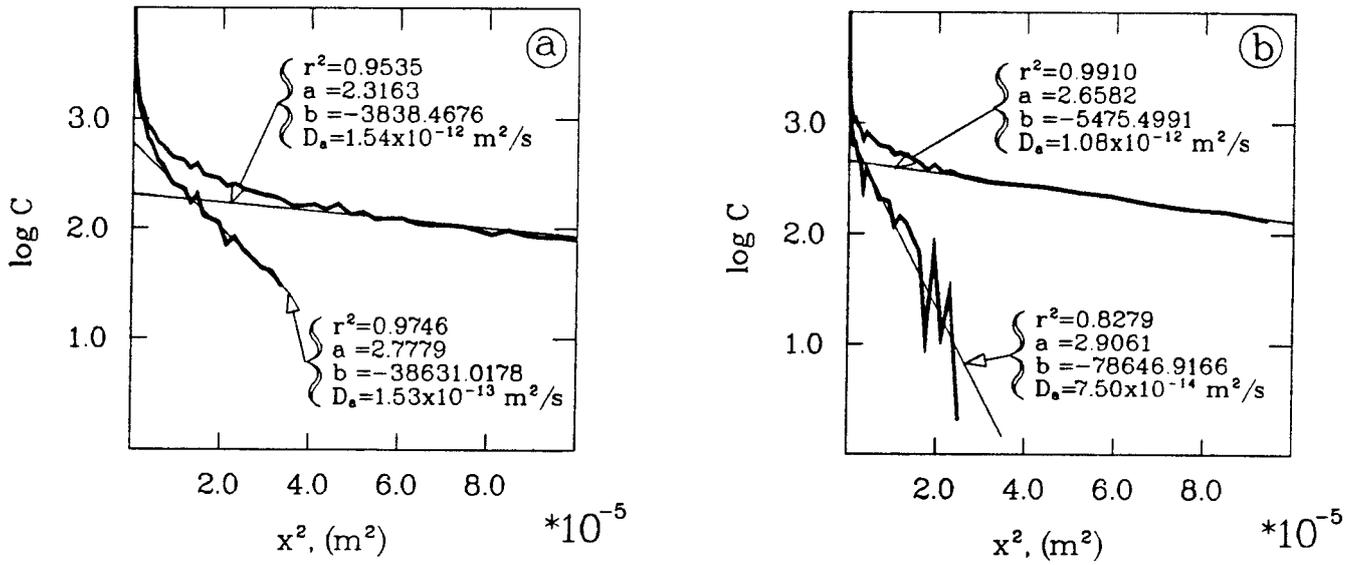


Figure 9. Diffusion of iodine in compacted bentonite with half of the cell filled with ordinary clay ^{a)}, and the other half of the cell filled with clay mixed with 1% KMnO4 ^{b)}. Diffusion time = 213 days.

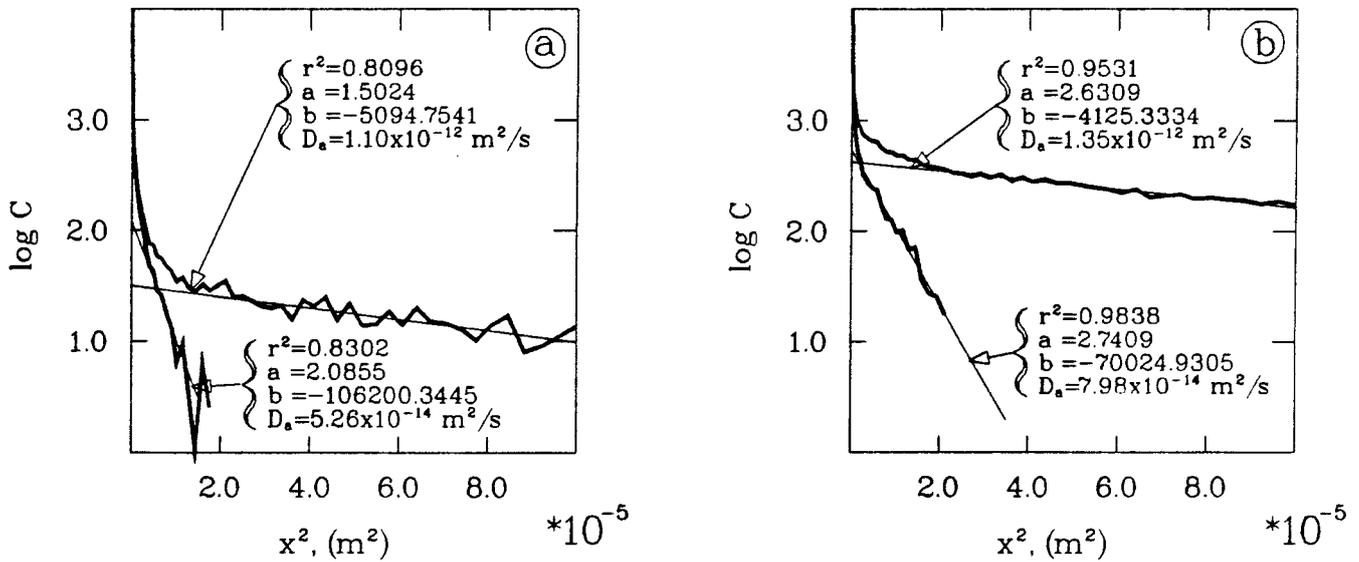


Figure 10. Diffusion of iodine in compacted bentonite with half of the cell filled with clay mixed with 1% iron powder ^{a)}, and the other half of the cell filled with clay mixed with 1% KMnO4 ^{b)}. Diffusion time = 225 days.

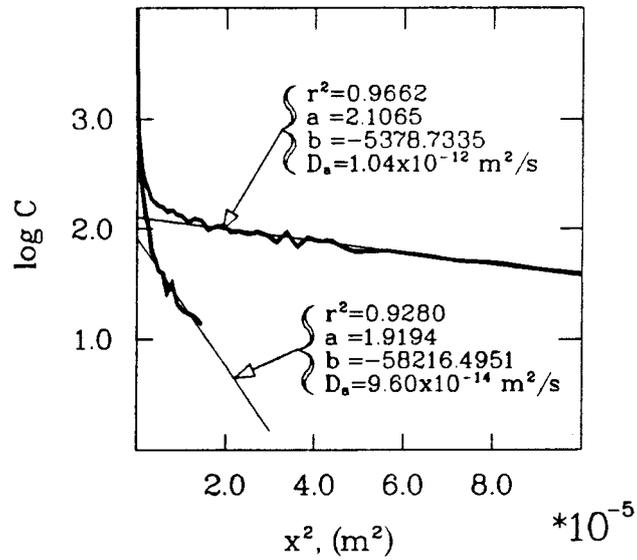


Figure 11. Diffusion of iodine in compacted bentonite mixed with 0.5% iron powder and 1% chalcopyrite/pyrite. Diffusion time = 225 days.

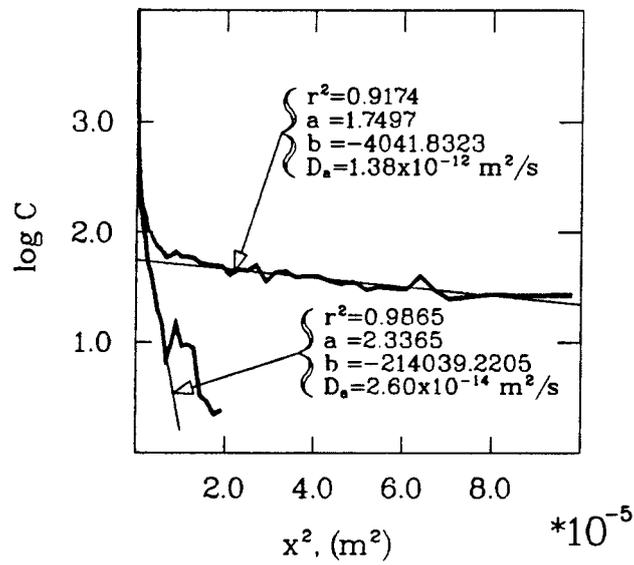


Figure 12. Diffusion of iodine in compacted bentonite mixed with 0.5% iron powder and 1% cinnabar. Diffusion time = 226 days.

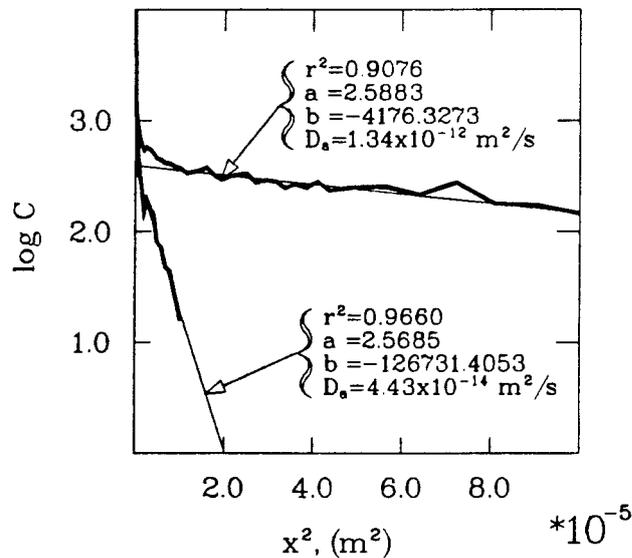


Figure 13. Diffusion of iodine in compacted bentonite mixed with 0.5% iron powder and 1% PbO. Diffusion time = 224 days.

4.5. 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 $\leq 7.7 \times 10^{-15} \text{ m}^2/\text{s}$, which is 2 to 3 orders of magnitude lower than is measured for the fission products strontium, technetium, iodine and cesium. 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.*, Figure 14), which is what is expected considering the fact that it has one prevailing oxidation state, does not form carbonate complexes, and is extensively hydrolyzed.

4.6. Protactinium

Protactinium is expected to be in the +5 oxidation state, as PaO_2^+ , but has a peculiar chemistry [33] and does not always behave as a typical pentavalent actinide. Its sorption on bentonite is strong ($K_d = 5 \text{ m}^3/\text{kg}$), which is in contrast with the poor sorption of neptunium(V) (*cf.*, Table V and VI). It exhibits one diffusion mechanism with a diffusivity, D_a , of $6.2 \times 10^{-13} \text{ m}^2/\text{s}$ (Figure 15). 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.

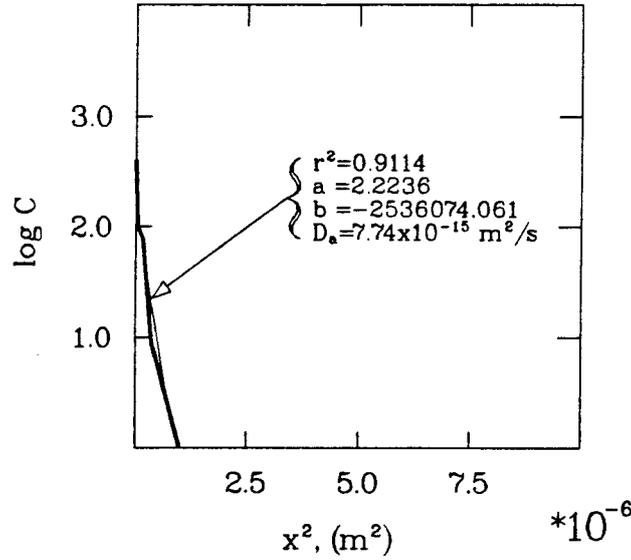


Figure 14. Diffusion of thorium in compacted bentonite. Diffusion time = 64 days.

4.7. Uranium

Under oxidizing conditions uranium is hexavalent, existing as the uranyl ion, UO_2^{2+} , which sorbs poorly on bentonite (*cf.*, Table V). Three diffusivities are observed (Figure 16a): $3.4 \times 10^{-12} \text{ m}^2/\text{s}$, $6.4 \times 10^{-13} \text{ m}^2/\text{s}$ and $2.7 \times 10^{-13} \text{ m}^2/\text{s}$ ^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. 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 $6.4 \times 10^{-13} \text{ m}^2/\text{s}$.

Even when metallic iron is added to the clay a small fraction of the uranium migrates quickly, *i.e.*, $3.3 \times 10^{-11} \text{ m}^2/\text{s}$. 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 $1.6 \times 10^{-13} \text{ m}^2/\text{s}$ (*cf.*, Figure 16b). The reduction of U(VI) to U(IV) by the metallic iron is expected to cause the decrease in the mobility.

^a *Cf.*, footnote in section 4.4.

Table V. Distribution coefficients [29] and measured diffusivities in bentonite for thorium, protactinium and uranium (density of the clay = 2×10^3 kg/m³).

Element	$\log C_i^{a)}$	Time [d]	K_d [m ³ /kg]	D_a [m ² /s]	$D^b)$ [m ² /s]
Th	-14.0	64	≥ 6	$\leq 7.7 \times 10^{-15}$	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_i = Number of moles initially added.

b) Evaluated from Eq.(3).

c) 0.5% Fe(s) added to the clay.

d) 1% Fe₃(PO₄)₂(s) added to the clay.

e) 600 mg/l NaHCO₃ added to the artificial groundwater.

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

The addition of 1% Fe₃(PO₄)₂(s) to the clay, or 600 mg/l NaHCO₃ or 10 mg/l humic acid to the aqueous phase, did not seem to have any significant influence on the uranium diffusion (Figures 17-19). The complex-formation constant for uranyl with HPO₄²⁻ is expected to be high ($\log K_1 = 8.4$ [26]), but, as shown in Figure 17, no significant effect on the transport is observed.

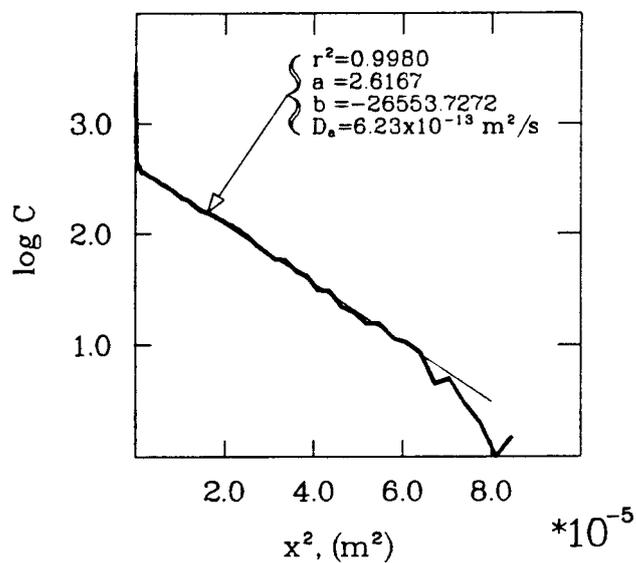


Figure 15. Diffusion of protactinium in compacted bentonite. Diffusion time = 76 days.

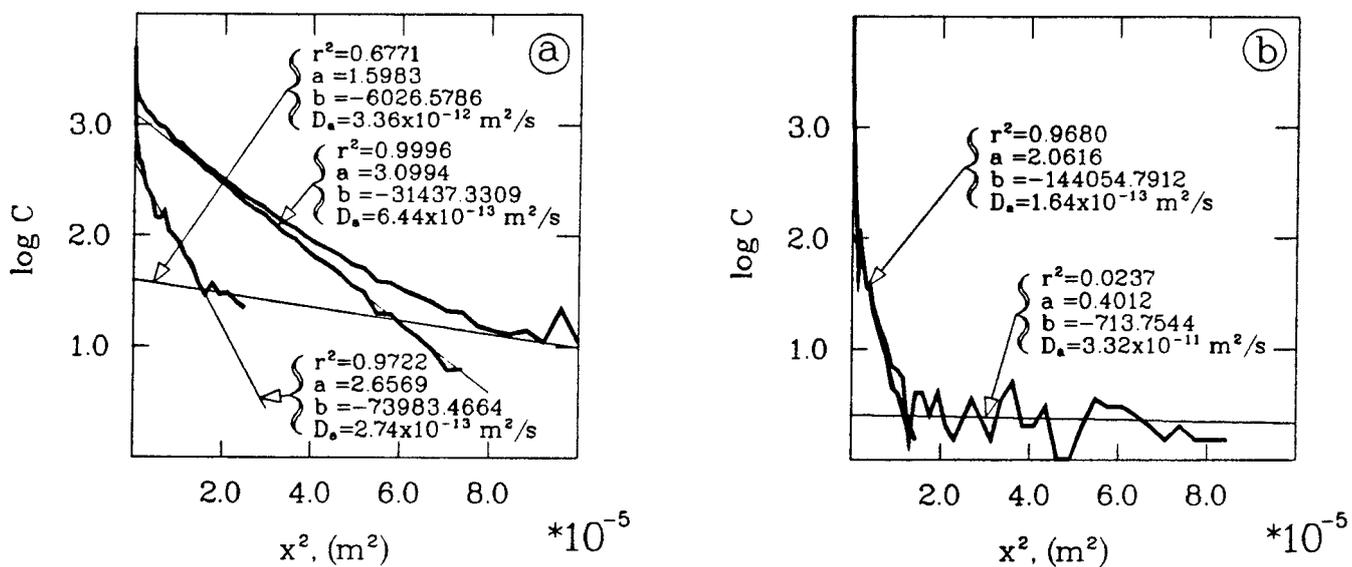


Figure 16. Diffusion of uranium in compacted bentonite. *a*) Ordinary bentonite, diffusion time = 62 days. *b*) Bentonite mixed with 0.5% iron powder. Diffusion time = 53 days.

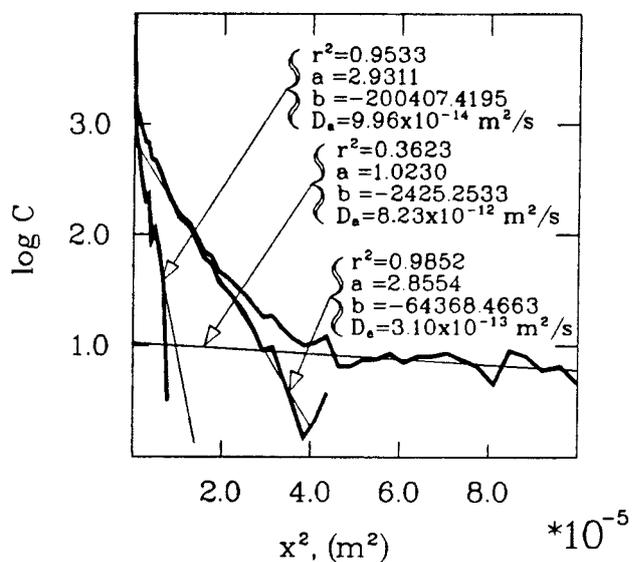


Figure 17. Diffusion of uranium in compacted bentonite, with the bentonite mixed with 1% $Fe_3(PO_4)_2$. Diffusion time = 63 days.

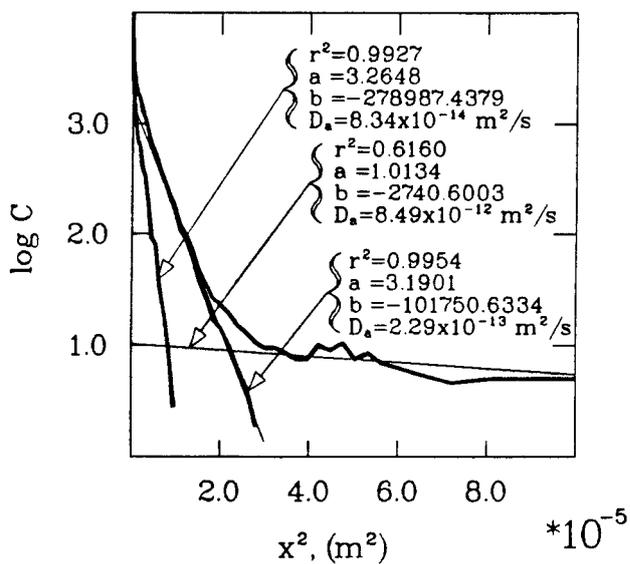


Figure 18. Diffusion of uranium in compacted bentonite with 600 mg/l $NaHCO_3$ added to the artificial groundwater. Diffusion time = 54 days.

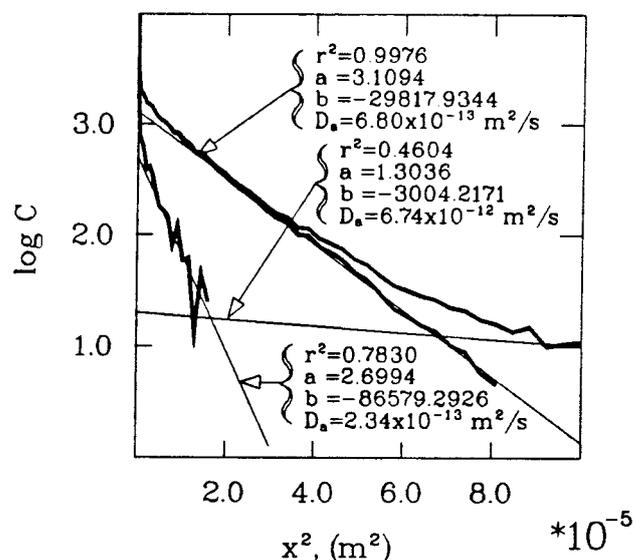


Figure 19. Diffusion of uranium in compacted bentonite with 10 mg/l humic acid added to the artificial groundwater. Diffusion time = 62 days.

4.8. Neptunium

Neptunium exists in the pentavalent oxidation state, as NpO_2^+ , under oxidizing conditions and, similar to uranium, apparently has three superimposed diffusivities: $1.2 \times 10^{-11} \text{ m}^2/\text{s}$, $3.7 \times 10^{-13} \text{ m}^2/\text{s}$, and $4.6 \times 10^{-14} \text{ m}^2/\text{s}$ (see Figure 20).

The main fraction of the neptunium is transported with a diffusivity very nearly the same as those of protactinium and the bulk of uranium (*i.e.*, $(4-6) \times 10^{-13} \text{ m}^2/\text{s}$). 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 $1.2 \times 10^{-11} \text{ m}^2/\text{s}$, 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 $4.2 \times 10^{-14} \text{ m}^2/\text{s}$ (*cf.*, Figure 21). 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 $3.5 \times 10^{-14} \text{ m}^2/\text{s}$. The diffusivity for the rest of the neptunium in the ordinary clay is $8.2 \times 10^{-13} \text{ m}^2/\text{s}$. 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.

Table VI. Distribution coefficients [29] and measured diffusivities in bentonite for neptunium, plutonium, and americium (density of the clay = 2×10^3 kg/m³).

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} $\leq 1.9 \times 10^{-15}$	$\leq 3.1 \times 10^{-11}$
Am	-8.4	524	6.6	$\leq 1.3 \times 10^{-14}$	$\leq 4.0 \times 10^{-10}$
Am ^{e)}	-8.4	350		$\leq 2.8 \times 10^{-16}$	

a) C_i = Number of moles initially added.

b) Evaluated from Eq.(3).

c) 0.5% Fe(s) in part of the clay.

d) 1% Fe₃(PO₄)₂(s) added to the clay.

e) 600 mg/l NaHCO₃ added to the artificial groundwater.

After mixing 1% Fe₃(PO₄)₂(s) with the clay (Figure 22), 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 NpO₂⁺ by Fe²⁺, however, is $K = 0.29$ at 25 °C, and, for the reduction of UO₂²⁺ by Fe²⁺ the equilibrium constant is $K = 10^{-15}$. Thus, neptunium could be reduced by Fe²⁺, forming an HPO₄²⁻ complex ($\log K_1 = 12.0-13.0$ [26]) or being hydrolyzed to Np(OH)₄ or NpO₂, while the uranium, if reduced, would be rapidly oxidized to the hexavalent state again [26,33,34]. 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.

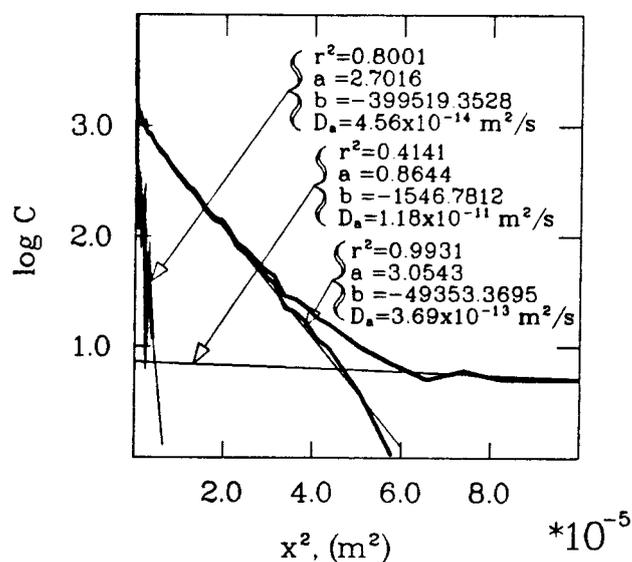


Figure 20. Diffusion of neptunium in compacted bentonite. Diffusion time = 69 days.

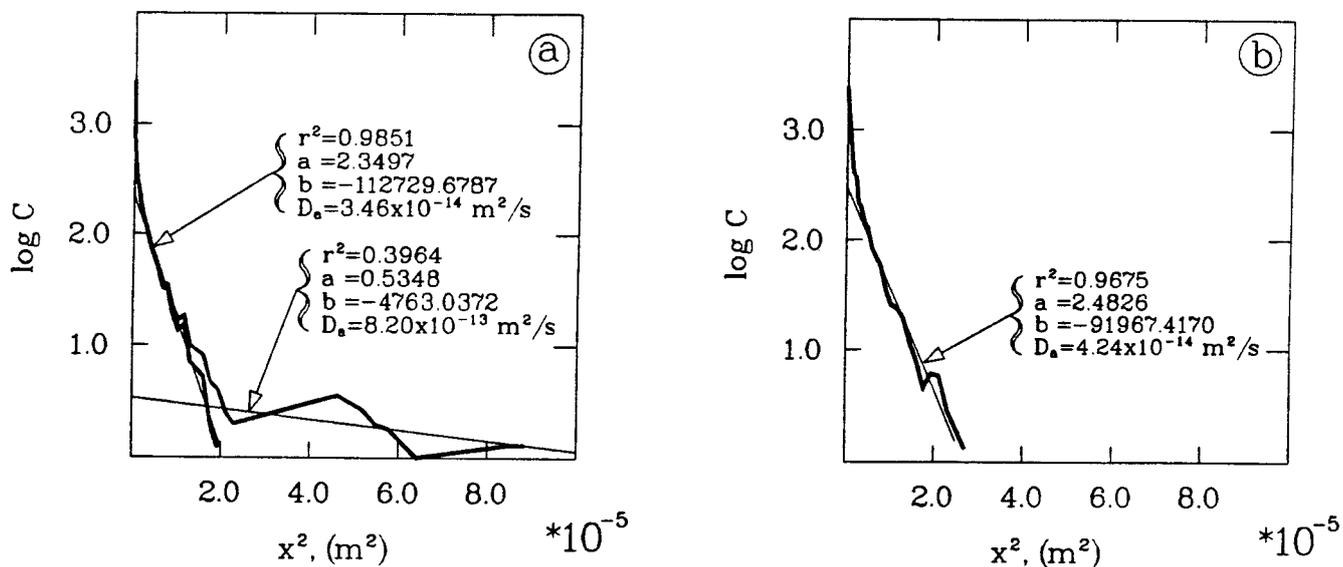


Figure 21. Diffusion of neptunium in compacted bentonite with one half of the cell ^{a)} in ordinary bentonite, and the other half of the cell ^{b)} with the bentonite mixed with 0.5% iron powder. Diffusion time = 322 days.

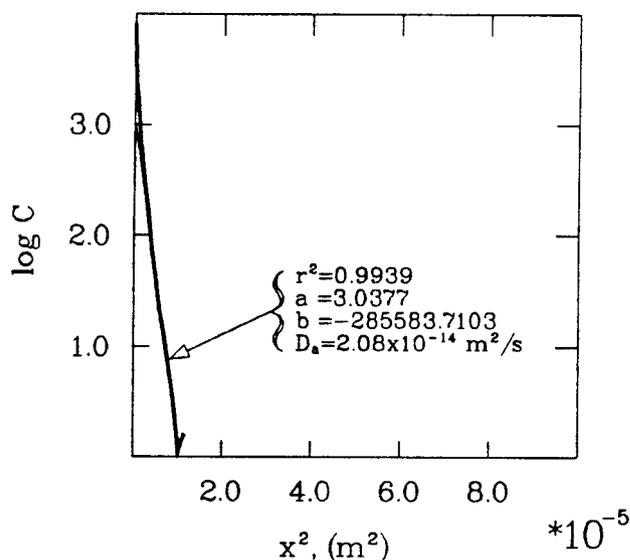


Figure 22. Diffusion of neptunium in compacted bentonite, with the bentonite mixed with 1% $\text{Fe}_3(\text{PO}_4)_2$. Diffusion time = 212 days.

4.9. Plutonium

The measured concentration profile for plutonium in compacted bentonite is shown in Figure 23. 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 4.4.). Thus, the diffusivity of the plutonium is expressed as $\leq 1.9 \times 10^{-15} \text{ m}^2/\text{s}$. One fraction of the plutonium moves rapidly through the clay ($D_a = 3.2 \times 10^{-12} \text{ m}^2/\text{s}$); again, this is the diffusivity expected for all species transported with the “water front.”

4.10. 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 $1.3 \times 10^{-14} \text{ m}^2/\text{s}$ (Figure 24). Americium appears to be transported by one mechanism only. No fast-moving fraction was observed.

In the experiment in which 600 mg/l HCO_3^- was added to the aqueous phase (Figure 25.), it is almost impossible to see any transport at all after 350 days diffusion time. The apparent diffusivity is $\leq 2.8 \times 10^{-16} \text{ m}^2/\text{s}$ (calculated from three points), indicating that the presence of HCO_3^- in the water would not, in any event, increase the mobility of americium.

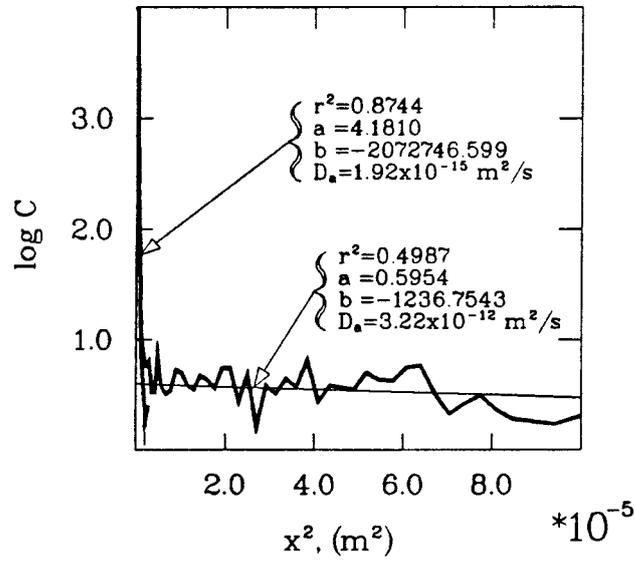


Figure 23. Diffusion of plutonium in compacted bentonite. Diffusion time = 316 days.

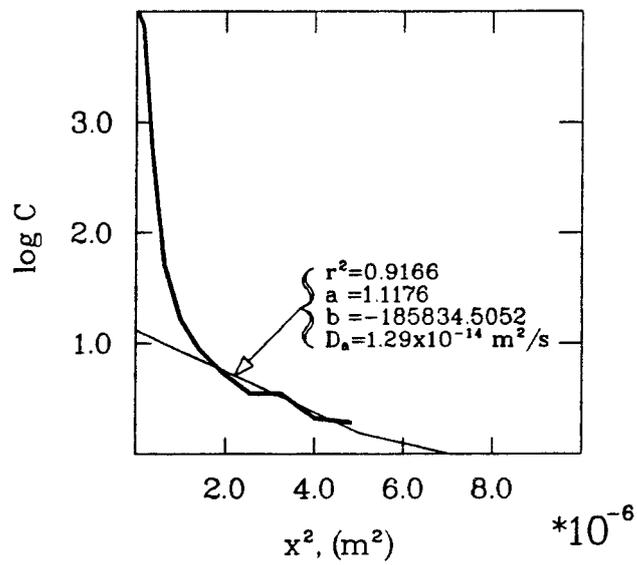


Figure 24. Diffusion of americium in compacted bentonite. Diffusion time = 524 days.

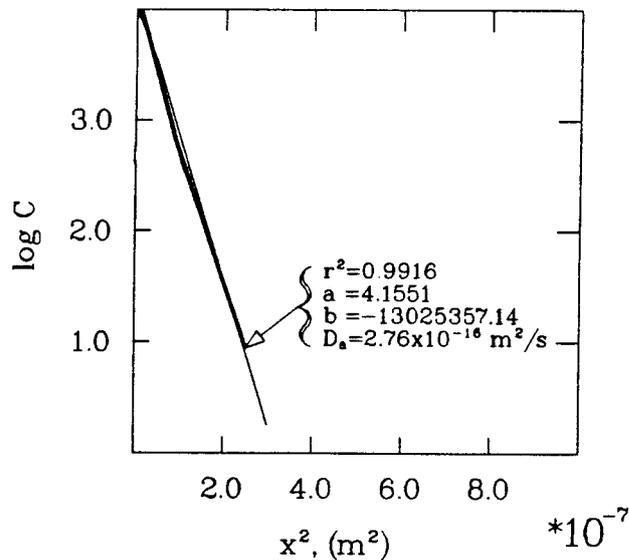


Figure 25. Diffusion of americium in compacted bentonite with 600 mg/l NaHCO_3 added to the artificial groundwater. Diffusion time = 350 days.

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.

Equation (3), $D = D_a(1 + K_d \rho (1 - \epsilon)/\epsilon)$, is not applicable for species sorbing by cation exchange processes when the diffusion is slow, but seems to be useful for species sorbing by chemisorption or physical adsorption.

The apparent diffusivity of strontium is $2.0 \times 10^{-11} \text{ m}^2/\text{s}$ and is $2.4 \times 10^{-12} \text{ m}^2/\text{s}$ for cesium. Both elements sorb by cation exchange; thus, it is not possible to calculate the diffusivity, D , from D_a and K_d according to equation (3). They exist in only one oxidation state, +2 for strontium and +1 for cesium, under the conditions expected in the clay, and have only one diffusion mechanism as evaluated from the figures.

Technetium, as pertechnetate, has an apparent diffusivity of $1.2 \times 10^{-12} \text{ m}^2/\text{s}$. Reduced to the tetravalent state, the apparent diffusivity of technetium is $1 \times 10^{-13} \text{ m}^2/\text{s}$, although a small fraction still exhibited the same mobility as the pertechnetate.

Iodine diffuses by two mechanisms, possibly due to different species of iodine in the form of I^- and HIO or IO_3^- , or perhaps due to pore-size effects in the clay. The two overlapping mechanisms observed result in apparent diffusivities an order of magnitude apart, $1.2 \times 10^{-12} \text{ m}^2/\text{s}$ and $1.1 \times 10^{-13} \text{ m}^2/\text{s}$ for long diffusion time (218 days). The same two diffusivities were observed in reducing media, oxidizing media, and when iodide complex-forming agents were added to the clay.

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 ($7.7 \times 10^{-15} \text{ m}^2/\text{s}$, $1.9 \times 10^{-15} \text{ m}^2/\text{s}$, and $1.3 \times 10^{-14} \text{ m}^2/\text{s}$, respectively) are maximum values.

For the actinides in the +5 and +6 oxidation states the apparent diffusivity was measured to be between 3 and $7 \times 10^{-13} \text{ m}^2/\text{s}$ ($6.2 \times 10^{-13} \text{ m}^2/\text{s}$ for protactinium, $6.4 \times 10^{-13} \text{ m}^2/\text{s}$ for uranium, and $3.7 \times 10^{-13} \text{ m}^2/\text{s}$ 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., $2.1 \times 10^{-14} \text{ m}^2/\text{s}$, when the clay was mixed with 1% $Fe_3(PO_4)_2$.

Using Equation (3), $D = D_a(1 + K_d\rho(1 - \epsilon)/\epsilon)$, the diffusivities for thorium, neptunium and uranium were calculated to be $(2-4) \times 10^{-10} \text{ m}^2/\text{s}$, and $3 \times 10^{-11} \text{ m}^2/\text{s}$ 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 the studied fission products. The diffusion coefficient, D_a , for this transport is determined to be somewhere between 10^{-11} and $10^{-12} \text{ m}^2/\text{s}$. 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.

A comparison of the diffusivities with diffusivities reported in the literature is given in Table VII. The values given for this study are the diffusivities evaluated from the curve considered to be the "bulk" of the diffusing radionuclide; that is, not the diffusivities evaluated for the fast moving fraction if present.

Table VII. Comparison of reported diffusivities of radionuclides in compacted bentonite from the literature.

Element	D_a , [m ² /s] ^a	Reference
Sr	$8-14 \times 10^{-12}$	1
	23×10^{-12}	2
	70×10^{-12}	7 ^b
	$10-12.5 \times 10^{-11}$	9
	$10-48.9 \times 10^{-12}$	10
	$7.8-9.5 \times 10^{-12}$	13
	2.0×10^{-11}	This report
Tc	3.2×10^{-10}	6 ^c
	1.1×10^{-14} (red. cond.)	6 ^c
	1.2×10^{-12}	This report
	8.4×10^{-14} (red. cond.)	This report
Cs	$1.5-3 \times 10^{-12}$	1
	7.5×10^{-12}	2
	40×10^{-12}	7 ^b
	$4.9-5.0 \times 10^{-12}$	8
	$1.1-10.2 \times 10^{-12}$	10
	$6.1-10 \times 10^{-13}$	13
	2.4×10^{-12}	This report
I	$4.01-22.4 \times 10^{-11}$	10
	$1.2-2.6 \times 10^{-12}$	This report

^a) D_a according to equation 3.

^b) In marine sediment.

^c) In brine solution.

Table VII. Comparison of reported diffusivities of radionuclides in compacted bentonite from the literature, *continued*.

Element	D_a , [m ² /s] ^a	Reference
Th	2.01–9.76 × 10 ⁻¹⁴ ≤ 7.7 × 10 ⁻¹⁵	10 This report
U	3.56 × 10 ⁻¹⁴ 6.4 × 10 ⁻¹³	10 This report
Np	1.5 × 10 ⁻¹² 3.7 × 10 ⁻¹³	6 ^c This report
Pu	1 × 10 ⁻¹⁴ ≤ 1.9 × 10 ⁻¹⁵	11 ^b This report

^a) D_a according to equation 3.

^b) In marine sediment.

^c) In brine solution.

6. Acknowledgements

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