Clays and Clay Minerals, Vol. 42, No. 5, 534–543, 1994.

SURFACE DIFFUSION: IS IT AN IMPORTANT TRANSPORT MECHANISM IN COMPACTED CLAYS?

DENNIS W. OSCARSON

AECL Research, Whiteshell Laboratories, Pinawa
Manitoba R0E 1L0 Canada

Abstract—Surface diffusion, or migration within the electrical double layer next to mineral surfaces, is often invoked as a significant contributor to the overall diffusion coefficient in compacted clays, particularly where model predictions underestimate measured diffusion coefficients. The potential for surface diffusion of Sr^{2+}, Ca^{2+} and Na^{+} on three clays compacted to dry bulk densities of 1.25 and 1.60 Mg/m^3 was examined. The clays were a bentonite, an illite/smectite, and a glacial lake clay (composed mainly of smectite, illite, kaolinite and quartz). The clays were saturated with a Na-Ca-Cl-dominated synthetic groundwater solution with an effective ionic strength of 220 mol/m^3. Total intrinsic diffusion coefficients for the cations were determined from their steady-state flux through compacted clays, and apparent diffusion coefficients were obtained from the time-lag technique. Models of diffusive transport in compacted clays, based only on diffusion in the pore solution, adequately described the diffusion data for all clays and diffusants, and there was no need to invoke other transport mechanisms, like surface diffusion. The data indicate that surface diffusion is not a significant transport mechanism in compacted clays at least to a clay density of 1.60 Mg/m^3.

Key Words—Compacted clays, Surface diffusion, Transport mechanism.

INTRODUCTION

Compacted clay-based materials are important barriers in disposal strategies for nuclear fuel waste being developed in many countries. Clay minerals are considered important barrier materials because of their high sorptivity, low permeability and long-term structural stability. The low permeability of compacted clays means that diffusion will be the principal mechanism of mass transport through these materials.

It has been reported that some cations diffuse through aggregated materials such as bentonite or in fractured media like whole rock at greater rates than those predicted from aqueous phase diffusion alone (Kim *et al* 1993; Jahnke and Radke 1987; Bradbury *et al* 1986; Skagius and Neretnieks 1985; Rasmuson and Neretnieks 1983). Surface diffusion has been invoked to explain this phenomenon. If surface diffusion is significant in compacted clays and it is not accounted for in mass transport models, the performance of clay-based barriers will be overestimated.

Surface diffusion in earthen materials refers to migration within the electrical double layer next to mineral surfaces. There is a strong theoretical basis for the phenomenon (van Schaik *et al* 1966). The interaction of cationic diffusants with negatively charged surfaces of silicate minerals increases the concentration gradient perpendicular to the particle surface. The electrostatic potential of the mineral surface prevents the dissipation of the gradient. An increase in the gradient could cause a proportional increase in the flux along this surface.

Surface migration cannot occur unless there is appreciable sorption; yet if sorbed species are held so strongly as to be essentially immobile, surface diffusion will not be significant. Hence, the equilibrium relationship between the sorbed and solution species is essential for interpreting surface migration. The energies of bonds holding monovalent cations to exchange sites on clays created by isomorphic substitution are of the same order of magnitude as the energies holding cations in the network of water molecules and as the thermal energy, kT (Shainberg and Kemper 1966). This, along with the fact that the concentration of sorbed cations can be much greater than that in solution, means sorbed cations can play a potentially significant role in transport processes.

Some cations also sorb directly to the edges of clay minerals via coordinate covalent bonding. The energy of these bonds is often four or more times kT (Kemper 1986), and consequently the mobility of these cations when sorbed is much less than when they are in the pore solution. Hence, surface diffusion is potentially important only for cations sorbed principally via cation exchange, generally the alkali and alkaline earth cations.

There is conflicting experimental evidence for surface diffusion in clays and soils. From a review of the literature, Nye (1979) found little evidence of surface diffusion in soil for several ions. Nye postulated that the low surface mobility in soils might be due to surface pathway discontinuities. This could be caused by organic matter or Al- or Fe-oxyhydroxide materials on the edges of the aluminosilicate particles or in the interlayer. Cho *et al* (1993a) concluded that surface diffusion was not important in the transport of Cs^{+} in bentonite compacted to a dry density of 1.3 Mg/m^3. Others have also discounted surface diffusion as a sig-

Copyright © 1994, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

nificant transport mechanism in compacted or dense clays (Conca *et al* 1993). Moreover, if surface diffusion is important, diffusion coefficients should not decrease with decreasing volumetric moisture content of soil because the electrical double layer is not affected and only the pore water content decreases. However, diffusion coefficients in soils and clays generally decrease markedly with decreasing moisture content (Nye 1979; Olsen and Kemper 1968).

On the other hand, many investigators report rates of diffusion in soils and clays greater than predicted from aqueous phase diffusion alone that they attribute to surface diffusion. Berry and Bond (1992) reported that surface diffusion accounted for about 50% of the total diffusion of Sr^{2+} and 30% for Am in a London clay at a density of about 1.3 Mg/m^3. There was no evidence of surface diffusion of Cs^+, which agrees with the results of Cho *et al* (1993a). Jensen and Radke (1988) concluded that surface diffusion was the dominant mechanism of Cs^+ and Sr^{2+} transport in a Na-montmorillonite gel with a porosity of 0.93; they reported surface diffusion coefficients of about 200 $\mu m^2/s$ for both diffusants at 22°C and 800 $\mu m^2/s$ for Cs^+ at 90°C. In a bentonite compacted to a dry density of about 1.8 Mg/m^3, Muurinen *et al* (1985) obtained diffusion data for Cs^+ and Sr^{2+} that are consistent with surface diffusion, i.e., diffusion coefficients did not decrease as sorption increased. They reported surface diffusion coefficients of about 8 $\mu m^2/s$ for Cs^+ and 0.5 $\mu m^2/s$ for Sr^{2+}. The results of Staunton and Nye (1983) for a naturally aggregated clay soil suggest that Na^+ is mobile in the sorbed phase; the clay content of the soil was about 60% and was predominantly smectite. No correlation between surface phase mobility and moisture content or density was found. In a follow-up study, Staunton (1986) also found evidence for diffusion of Na^+ on the surfaces of a subsoil. And van Schaik *et al* (1966) reported that about 70% of exchangeable Na^+ and 25% of exchangeable Ca^{2+} were mobile in smectite/water systems. In this study, though, the clay flakes were oriented parallel to the direction of expected diffusive transport.

Clearly, there is much uncertainty regarding the relative importance of surface diffusion or, indeed, even its existence in clays and soils. In this investigation, the potential for enhanced transport (transport greater than predicted from aqueous phase diffusion alone) of Sr^{2+}, Ca^{2+} and Na^+ through three compacted clays under steady-state conditions is examined using a through diffusion technique. The clays are potential barrier materials in a disposal vault for nuclear fuel waste in Canada.

THEORETICAL BACKGROUND

In the absence of advective transport, and if surface diffusion is assumed to occur in porous media, the total mass flux, J_t, through homogeneous, isotropic and isothermal porous media can be given by,

$$J_t = J_p + J_s = -D_{iw}\frac{\partial c}{\partial x} - D_s\frac{\partial s}{\partial x}, \quad (1)$$

where

J_p = flux due to mass diffusion in the pore water,
J_s = flux due to surface diffusion,
D_{iw} = intrinsic diffusion coefficient in pore water, equal to $D_0\Psi$,
D_0 = diffusion coefficient in pure bulk water under stationary conditions,
Ψ = diffusibility of the porous medium, it is a lumped parameter that includes the porosity of the porous medium and geometry factors such as tortuosity and constrictivity; if no size factors influence diffusion, Ψ does not depend on the diffusant.
D_s = surface diffusion coefficient, it includes a surface tortuosity factor,
c = concentration of the diffusant in the pore water,
s = concentration of the diffusant sorbed on the solid phase in terms of volume of the solid.

Equation 1 may be expressed with c as the single independent variable as,

$$J_t = (D_{iw} + D_s s')\frac{\partial c}{\partial x}, \quad (2)$$

where s′ is ds/dc; for a linear sorption isotherm, $s' = \rho K_d$, where ρ is the dry bulk density of the solid phase and K_d the distribution coefficient. The coefficient in Eq. 2 ($D_{iw} + D_s s'$) is termed the total intrinsic diffusion coefficient, D_i; it is also called the effective diffusion coefficient by many investigators.

If sorption is linear, s′ does not vary with x, and D_{iw} and D_s are independent of concentration, another diffusion coefficient, the apparent diffusion coefficient, D_a, can be defined as,

$$D_a = \frac{D_i}{\alpha} = \frac{D_{iw} + D_s s'}{n_e + s'}, \quad (3)$$

with

$$\frac{\partial c'}{\partial t} = D_a\frac{\partial^2 c'}{\partial x^2}, \quad (4)$$

where α is the capacity factor (the capacity of the solution and solid per unit volume of bulk porous media to hold more of the diffusant as its concentration in the solution phase increases by one unit); n_e the effective porosity of the porous media or the porosity available to a diffusant, n_e is generally less than the total porosity because of factors such as small and occluded pores that the diffusant cannot enter; and c′ is the bulk concentration ($c' = c\alpha$).

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

Table 1. Selected properties of the clays.

Clay	Cation exchange capacity[1] ($cmol_c/kg$)	Specific surface area[2] (10^3 m^2/kg)	Organic carbon[3] (wt. %)
Avonlea	60	480	0.31
Illite/smectite	43	290	0.16
Lake Agassiz	50	300	1.2

[1] Calcium and Mg^{2+} were the index and replacing cations, respectively (Jackson 1975).
[2] Ethylene glycol monoethyl ether method (Carter *et al* 1986).
[3] Measured by igniting a sample at 900°C in an O_2 stream; CO_2 released was measured with an Astro 2001 organic C IR Analyzer. Clays were pretreated with $FeSO_4$ and H_2SO_4 to remove inorganic C (Nelson and Sommers 1982).

Table 2. Composition of the synthetic groundwater (SGW) solution and the pore solution of the clays after contact with the SGW.

	SGW (mol/m^3)	Pore solution (mol/m^3)		
		Avonlea	Illite/smectite	Lake Agassiz
Na	83	120	77	78
K	0.36	0.70	1.6	1.4
Mg	2.5	3.2	5.9	9.3
Ca	53	40	53	49
Cl	170	200	180	180
SO_4	11	14	12	12
HCO_3	0.28	0.20	0.21	0.21
pH	7.2	7.7	7.7	7.8

It is instructive to examine typical values of D_a. When there is little or no sorption ($s' \ll n_e$),

$$D_a = \frac{D_{iw}}{n_e} = D_p; \quad (5)$$

D_p is called the pore-water diffusion coefficient. When there is sorption, but little or no surface diffusion ($D_s \ll D_{iw}/s'$),

$$D_a = \frac{D_{iw}}{(n_e + s')}. \quad (6)$$

If s' is large, D_a will be much smaller than D_p, and so sorbed diffusants migrate slower than non-sorbed diffusants. However, if there is strong sorption and significant surface diffusion ($D_s s' \gg D_{iw}$),

$$D_a = D_s. \quad (7)$$

The D_s value should be less than D_p, so D_p and D_s give upper and lower bounds for D_a. If, however, D_s is only one or two orders of magnitude less than D_p, sorbed diffusants will migrate much faster than predicted by Equation 6. This emphasizes the importance of knowing whether surface diffusion is a significant transport mechanism.

MATERIALS AND METHODS

Clays

The origin and composition of the three clays are summarized below and selected properties are given in Table 1.

Avonlea bentonite. This clay is from the Bearpaw Formation of Upper Cretaceous age in southern Saskatchewan, Canada (Oscarson *et al* 1990). It contains about 80 wt. % smectite (montmorillonite), 10% illite, 5% quartz, and minor amounts of gypsum, feldspar, and carbonate (Oscarson and Dixon 1989). The clay is a component of the reference buffer material in the disposal concept for nuclear fuel waste being developed in Canada (Hancox and Nuttall 1991). The reference buffer material is a 1:1 mix by dry mass of bentonite and silica sand compacted to a dry bulk density of about 1.7 Mg/m^3.

Lake Agassiz clay. This clay originates from Pleistocene freshwater lake sediments of glacial Lake Agassiz in southern Manitoba, Canada. It contains about 35 wt. % smectite, 20% illite, 15% quartz, 10% kaolinite, 10% calcite and minor amounts of feldspar and dolomite (Oscarson and Dixon 1989). It is a component of the reference backfill material in the Canadian concept for the disposal of nuclear fuel waste. The reference backfill material is a 1:3 mix by dry mass of Lake Agassiz clay and crushed granite aggregate compacted to a dry bulk density of about 2.0 Mg/m^3.

Illite/smectite mixed-layered clay. This clay was obtained from the Source Clays Repository of the Clay Minerals Society, Columbia, Missouri; it is designated ISMt-2. It is from the Mancos Shale, U.S.A., and is described as a random interstratification of 60% illite and 40% smectite layers. It was included in the study because in a hydrothermal environment, such as that in a nuclear fuel waste disposal vault, there is a potential for the smectite component of the barrier materials to gradually transform over many thousands of years into an illite/smectite mixed-layered material (Oscarson and Hume 1993). Hence, an understanding of its diffusive properties is important for assessing the long-

Table 3. Selected properties of the radioisotopes.

Radioisotope	Half-life	Specific activity (PBq/mol)	c_0[1] ($\mu mol/m^3$)	D_0[2] ($\mu m^2/s$)
^{3}H	12.3 a	1.08	15	2450
^{85}Sr	64.8 d	74.6	0.36	757
^{45}Ca	164 d	29.5	0.56	760
^{22}Na	2.60 a	5.09	3.3	1270
^{125}I	60.2 d	80.3	0.14	1940

[1] Initial concentration in the source reservoir in through-diffusion experiments; for Sr and I stable isotope was added as a carrier so that c_0 was about 1 $mmol/m^3$.
[2] Diffusion coefficient in pure bulk water under stationary conditions.

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

term performance of smectite-based barrier materials. Besides illite/smectite, the clay contains minor amounts of kaolinite, feldspar, gypsum and quartz.

Solution

The clay was saturated with a synthetic groundwater (SGW) solution (Table 2). It represents groundwater found deep in granitic rock in the Canadian Shield (Frape *et al* 1984). The composition of the pore solutions after contacting SGW solution with compacted clays for at least four weeks is also given in Table 2. These data were obtained by flowing SGW solution through porous Ni discs sandwiched around compacted clay in through-diffusion cells. This is similar to the procedure used to saturate compacted clay before the diffusion experiments described below. The solutions were analyzed for Cl, NO_3 and SO_4 by ion chromatography; for Na and K by atomic absorption spectrometry; for Ca and Mg by inductively coupled plasma spectrometry; and for carbonate by acidimetric titration.

Diffusants

Some properties of the radioisotopes used as diffusants are given in Table 3. All radioisotopes were obtained from Amersham Canada Limited, Oakville, Ontario.

The D_0 value for ^3H (as HTO) at 23°C was taken to be 2450 $\mu m^2/s$ (McCall and Douglass 1965); and the values for the other diffusants were obtained from Li and Gregory (1974) and calculated for 23°C from,

$$(D_0\eta)_{T_1} = (D_0\eta)_{T_2}, \quad (8)$$

where η is the viscosity of water at the temperature of interest. The resulting D_0 values are given in Table 3.

The speciation distribution was estimated for Sr, Ca and Na in SGW solution and in the pore solutions of the clays using the CHEMVAL thermodynamic database (Chandratillake *et al* 1992). In SGW solution the approximate distribution is: Sr^{2+} (83% of total Sr in solution), $SrSO_4$ (10%), $SrCl^+$ (6%); Ca^{2+} (88%), $CaSO_4$ (10%), $CaCl^+$ (2%); and Na^+ (98%), NaCl (2%). In the pore solutions of the clays given in Table 2, the distribution of the various species differs by only a few percent, at most, from that in SGW solution. In the pore solutions of the clays during the diffusion experiments, therefore, the predominant diffusant for all three cations was the free, uncomplexed species. If other species that have a different size and charge predominate, the interpretation of the diffusion data could be affected. For example, the D_0 values would not be the same as those given in Table 3, which are for the free, uncomplexed species.

Diffusion experiments for each clay were conducted at ρ = 1.25 Mg/m^3 in the following sequence: HTO, ^{85}Sr, ^{22}Na, ^{125}I and ^{45}Ca. This sequence minimizes overlap of the energy spectra of these radioisotopes,

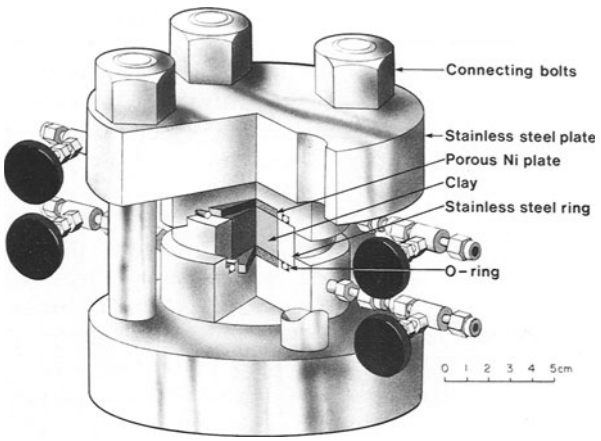


Figure 1. Diagram of the through-diffusion cell.

and hence facilitates their measurement by liquid scintillation counting. The anion, I^-, was included for comparison with the cations. At ρ = 1.60 Mg/m^3, experiments were performed with HTO and ^{85}Sr in Avonlea bentonite and Lake Agassiz clay. All experiments were conducted in triplicate for each clay.

To determine if the pore structure, as reflected in diffusion coefficients, of the clays changed during the course of these relatively long experiments, selected runs with HTO were repeated after the diffusion sequence given above. It is possible, for example, that the clays were not completely saturated before starting the diffusion experiments. If the clays reached saturation after the experiments started, the diffusion process could be altered. Diffusion coefficients for HTO were similar whether they were determined before or after the other diffusants, thus the properties of the clays did not change significantly during the experiments.

Diffusion experiments

Diffusion coefficients in the compacted clays were determined principally using a through-diffusion technique. Selected experiments were also performed using an in-diffusion method.

Through-diffusion. A diagram of the stainless steel diffusion cell is shown in Figure 1, and the cell is described in detail by Hume (1993). Clay was statically compacted (using a hydraulic press) in rings (inside diameter of 4.1 cm and 0.7 cm long) to a target dry density of 1.25 and 1.60 Mg/m^3. The lower density is the approximate effective clay density of clay-based barrier materials that would be used in a nuclear fuel waste disposal vault in Canada, and the higher density was used to examine the effect of increasing density on diffusive transport. (Effective clay density is the mass of clay divided by the combined volume of clay and voids.)

The rings with compacted clay were placed in the

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

diffusion cells and the clay allowed to saturate with the SGW solution (by flowing solution through porous discs next to the clay plugs) for at least three weeks—sufficient time to saturate the clay (Miyahara *et al* 1991).

After the clay was saturated, SGW solution spiked with a tracer diffusant (source reservoir) was passed over one end of the clay plug, and tracer-free SGW solution (collection reservoir) allowed to flow over the other end. The activity in the source reservoir was monitored by liquid scintillation counting (Beckman LS 5801, Beckman Instruments, Inc., Irvine, California). When it decreased to 90% of the starting activity, diffusant was added to bring its concentration up to that of the original solution. In this way, the diffusant concentration in the source reservoir was kept nearly constant throughout a run.

The solution in the collection reservoir was analyzed every few days by liquid scintillation counting. When the change in activity became constant with time, indicating a steady-state condition had been established, the experiment was stopped. A new solution with another diffusant was placed in the source reservoir and the experiment was repeated. The flow rate of the SGW solution over the outflow end of the clay plugs was such that when a diffusant passed through the plug, it was quickly "swept away." Thus, at the outflow end of the plug the diffusant concentration was always close to zero.

During the experiments, the temperature of the clay plugs was maintained at 23 ± 1°C by flowing water through a Tygon® tube (inside diameter = 3 mm) wrapped several times around the sample ring of the diffusion cell. The tube was connected to a peristaltic pump in a constant-temperature water bath.

After the diffusion experiments, the cells were disassembled and the clay plugs sliced into sections about 1 to 2 mm thick. The moisture content of each slice was determined gravimetrically by heating at 105°C to constant mass. The moisture content was uniform throughout the length of the clay plugs in all cases. The samples were assumed to be saturated and the actual density of the clays was calculated from the moisture content and specific gravity of the clays. In all cases, the calculated densities were within 5% of the target values.

From these experiments, D_i values were obtained from the diffusant flux and concentration gradient after steady-state was established from,

$$D_i = -\frac{(\Delta Q/A\Delta t)}{(\Delta c/L)}, \quad (9)$$

where ΔQ is the change in the total amount of a diffusant passing through a clay plug in an increment of time Δt, A the cross-sectional area and L the length of the clay plug, and Δc the difference in the concentration of a diffusant between the ends of the clay plug (since solutions were allowed to flow through porous discs next to the clay plug, the concentration of the diffusant was assumed to be equal to the concentration in the source reservoir, c_0, at one end of the plug and zero at the other end). Equation 9 was obtained by rearranging a form of Equation 2. The D_{iw} values for the diffusants were calculated from,

$$D_{iw} = D_0\Psi. \quad (10)$$

For each compacted clay, Ψ was obtained from HTO diffusion experiments as,

$$\Psi = \frac{D_i}{D_0}. \quad (11)$$

And D_ss′ values were obtained from the difference between measured D_i and calculated D_{iw} values.

Apparent diffusion coefficients [Eq. (3)] were determined from the time-lag technique in the through-diffusion experiments. The time lag, t_e, is obtained from the intercept on the time axis of a plot of cumulative flux versus time. For this experiment the appropriate solution to Fick's second law [Eq. (4)] is (Crank 1975),

$$\frac{Q}{ALc_0'} = \frac{D_a t}{L^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_1^\infty \frac{(-1)^n}{n^2}\exp\left(\frac{-D_a n^2\pi^2 t}{L^2}\right), \quad (12)$$

which, as $t \rightarrow \infty$, approaches the line,

$$\frac{Q}{A} = \frac{D_a c_0'}{L}\left(t - \frac{L^2}{6D_a}\right). \quad (13)$$

The intercept of the slope at the t-axis (Q/A = 0) gives t_e, which is related to D_a by,

$$D_a = \frac{L^2}{6t_e}. \quad (14)$$

Equation 12 is subject to the following initial and boundary conditions,

$$c'(0 < x \leq L, 0) = 0,$$

$$c'(0, t) = c_0',$$

and,

$$c'(L, t) \ll c_0',$$

where $c' = c\alpha$ and $c_0' = c_0\alpha$ and is the initial bulk concentration of the diffusant in the clay immediately adjacent to the source reservoir. The t_e values are obtained by extrapolating from the steady-state region of cumulative flux curves to the time axis (Figure 2).

The slope of the straight-line fit of cumulative flux curves used to obtain D_i values can be determined with some confidence. However, the t_e values determined from the intercept are less reliable, and so D_a values obtained from Eq. (14) are subject to greater uncertainty. For this reason, some D_a values were measured using the in-diffusion method for comparison with those obtained from the time-lag technique.

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

In-diffusion. The in-diffusion method (also called a half-cell or back-to-back technique) was used to determine D_a values for Sr^{2+} in Avonlea bentonite and Lake Agassiz clay at $\rho = 1.25$ Mg/m³. The diffusion cells are described in detail by Hume (1993), and the experimental procedure by Sawatsky and Oscarson (1991). The method involves the measurement of the amount of a diffusant that migrates from a tagged to an untagged clay plug within a given time (for Sr^{2+}, the diffusion time was 22 d). Clay plugs 4 cm long and 2.2 cm in diameter were used. After the diffusion period, the plugs were sectioned into slices about 1 mm thick and each slice was analyzed for ^{85}Sr by gamma spectroscopy using a high-purity germanium detector (EG & E Ortec, Oak Ridge, Tennessee). From these data, concentration profiles for Sr in the clay plugs were obtained.

In these experiments, Sr did not reach the ends of the diffusion cells within the allotted time so the clay plugs can be considered infinitely long. Under these conditions, the appropriate solution to Eq. (4) is (Crank 1975),

$$\frac{c'}{c'_0} = \frac{1}{2}\text{erfc}\left[\frac{x}{2(D_a t)^{1/2}}\right], \qquad (15)$$

subject to the following initial and boundary conditions,

$$c'(x, 0) = 0 \text{ for } x > 0,$$

$$c'(x, 0) = c'_0 \text{ for } x < 0,$$

and,

$$c'(+\infty, t) = 0,$$

$$c'(-\infty, t) = c'_0,$$

where c'_0 is the initial bulk concentration of the diffusant in the tagged plug. Values of D_a were obtained from a least squares fit of Eq. (15) to the measured concentration profiles.

Sorption experiments

The extent of sorption of Sr, Ca, Na and I on the three clays was determined as follows. Five grams of air-dried clay was suspended in 10 cm³ of the SGW solution spiked with a radioisotope in 50-cm³ polycarbonate centrifuge tubes. The initial radioisotope concentration was about the same as that used in the through-diffusion experiments. The solution-to-clay ratio of 2 m³/Mg is close to the lowest practical ratio that can be used with these clays and the SGW solution and still have sufficient solution for analysis after the reaction period. The tubes were capped, sealed in double polyethylene bags, and placed in a water bath at 23 ± 0.1°C for 60 d. The tubes were shaken periodically. After the reaction period, the tubes were centrifuged at 5500 g for 10 min. The activity of the radioisotopes remaining in solution was measured by liquid scintillation counting. Control experiments, conducted identically but without the clay, showed that no detectable amounts of any of the sorbates were sorbed on the centrifuge tubes. Distribution coefficients were calculated from,

$$K_d = \left[\frac{A_i}{A_e} - 1\right](S - S_a)/\rho_w, \qquad (16)$$

where A_i is the net count rate of the solution initially added to the clay, A_e the net count rate of the solution after the reaction period, S the solution-to-clay ratio (by mass) and S_a the solution-to-clay ratio, or gravimetric moisture content, of the air-dried clay, and ρ_w the density of the SGW solution.

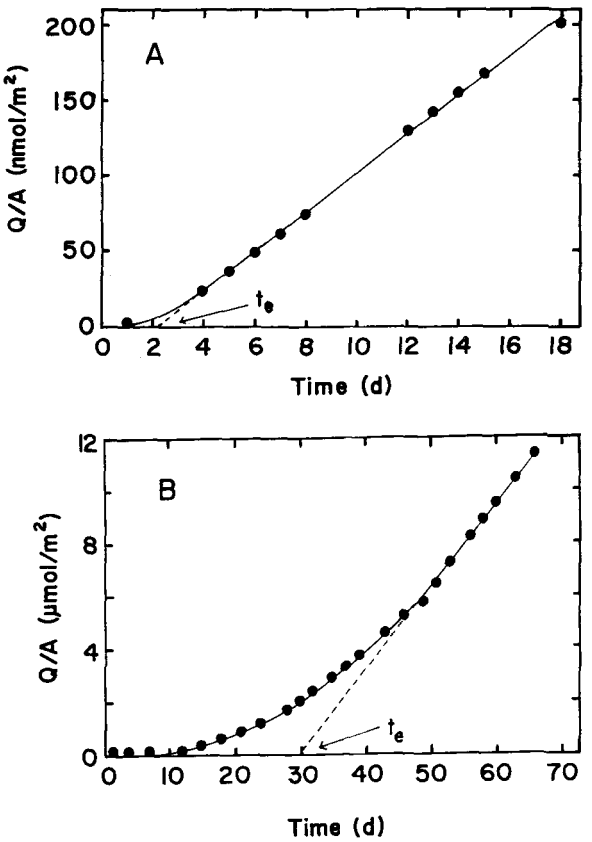


Figure 2. Cumulative flux from through-diffusion experiments for (A) HTO and (B) Sr^{2+} in Avonlea bentonite at $\rho = 1.25$ Mg/m³; also shown is t_e obtained by extrapolating from the steady-state region of the curve to the time axis.

RESULTS AND DISCUSSION

Typical cumulative flux curves for HTO and Sr^{2+} in Avonlea bentonite are shown in Figure 2; also shown is t_e, the point where the line extrapolated from the steady-state region of the curve intercepts the time axis. The mean D_i and D_a values, with indicated errors, are given in Table 4 for HTO and in Table 5 for the other

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

Table 4. Diffusion coefficients for HTO and diffusibility factors in compacted clays.

Clay	ρ[1] (Mg/m^3)	D_i (μm^2/s)	Ψ[1]	D_a (μm^2/s)
Avonlea	1.25	115 ± 15[2]	0.047	190 ± 82
	1.60	83.6 ± 4.6	0.034	210 ± 75
Illite/smectite	1.25	228 ± 17	0.093	150 ± 60
Lake Agassiz	1.25	191 ± 42	0.078	110 ± 24
	1.60	93.6 ± 4.8	0.038	130 ± 30

[1] ρ is the dry bulk density of the clays and Ψ the diffusibility factor for the clays.
[2] Mean ± one standard deviation, n = 3.

diffusants. On average, the standard deviation is about 20% of the mean for both D_i and D_a. The D_ss' values, calculated from the difference between D_i and D_{iw} values, are also given in Table 5.

As expected, D_i values for HTO decrease, and thus Ψ decreases, with an increase in clay density from 1.25 to 1.60 Mg/m^3 (Table 4). Berry and Bond (1992) reported an average Ψ value of 0.096 for London clay at $\rho \sim 1.3$ Mg/m^3—comparable to the values found here at $\rho = 1.25$ Mg/m^3.

Total intrinsic diffusion coefficients

For the cationic diffusants, $D_i > D_{iw}$ at $\rho = 1.25$ Mg/m^3. This suggests D_ss' contributes to D_i. For these diffusants D_ss' is about 30 to 60% of D_i. The D_ss'/D_i values for a given diffusant are, though, remarkably similar for all clays. For Sr, D_ss'/D_i is about 0.55 for all clays (Table 5). Moreover, Berry and Bond (1992) reported a similar value for Sr from diffusion experiments in London clay at $\rho \sim 1.3$ Mg/m^3. Given the large differences in the mineralogical composition of the clays, marked differences in D_ss'/D_i values would be expected among the three clays if surface diffusion was significant. The similarity in these values among the clays for a given diffusant suggests that factors other than surface diffusion are responsible for the enhanced diffusion of cations at $\rho = 1.25$ Mg/m^3. Furthermore, at $\rho = 1.60$ Mg/m^3, D_i and D_{iw} values are virtually the same for Sr in Avonlea bentonite and Lake Agassiz clay (Table 5). If surface diffusion is important, or even of the same magnitude as pore water diffusion, an increase in clay density would enhance surface diffusion by increasing the linkages between electrical double layers and decreasing the overall path length for surface migration. The fact that the D_i values for Sr decrease markedly with an increase in clay density, and that $D_i = D_{iw}$ at $\rho = 1.60$ Mg/m^3, indicates surface diffusion is not important even at higher clay densities.

It is not clear why $D_i > D_{iw}$ for all cations at $\rho = 1.25$ Mg/m^3, especially since $D_i = D_{iw}$ for Sr at 1.60 Mg/m^3. The agreement between D_i and D_{iw} at the higher density suggests the D_0 and Ψ values used to calculate D_{iw} (Eq. 10) are reasonable. If either D_0 or Ψ was underestimated, D_{iw} would be less than D_i at both densities. Perhaps the answer lies in the statement of Conca *et al* (1993): "Reasons why some tracer diffusion data do not fit model predictions must come from more advanced models, better retardation data, information on anion exclusion and pendular element surface film geometries, or re-evaluation of boundary conditions and assumptions."

Besides pore water diffusion and surface diffusion, Rasmuson and Neretnieks (1983) suggested surface flow could be a possible transport mechanism in porous media. This occurs through a difference in interfacial tension, caused by the concentration gradient. Surface flow and surface diffusion would be indistinguishable in this study, however. The surface diffusion term ap-

Table 5. Diffusion and distribution coefficients in compacted clays.

Clay	Diffusant	D_i (μm^2/s)	D_{iw} (μm^2/s)	D_ss' (μm^2/s)	D_ss'/D_i	D_a (μm^2/s)	Calc. D_a[1] (μm^2/s)	K_d[2] (m^3/mg)
Avonlea	Sr(L)[3]	79 ± 29[4]	36	43	0.54	11 ± 1.0	2.0	14 ± 2.1
	Sr(H)[3]	24 ± 12	26	—	—	16 ± 3.5	1.1	
	Ca	68 ± 41	36	32	0.47	26 ± 3.2	5.6	4.7 ± 0.20
	Na	99 ± 3.4	60	39	0.39	49 ± 24	34	1.0 ± 0.04
	I	12 ± 1.4	91	—	—	140 ± 17	45	0.25 ± 0.014
Illite/smectite	Sr	160 ± 17	70	90	0.56	16 ± 2.0	19	2.5 ± 0.24
	Ca	130 ± 23	71	59	0.45	27 ± 4.8	5.0	11 ± 3.9
	Na	180 ± 12	120	60	0.33	110 ± 50	140	0.25 ± 0.030
	I	57 ± 20	180	—	—	140 ± 3.0	220	0.22 ± 0.010
Lake Agassiz	Sr(L)	140 ± 26	59	81	0.58	23 ± 0.40	14	2.9 ± 0.07
	Sr(H)	23 ± 1.8	29	—	—	18 ± 3.8	5.6	
	Ca	91 ± 12	59	32	0.35	21 ± 2.0	15	2.8 ± 0.36
	Na	130 ± 7.5	99	31	0.24	66 ± 21	110	0.31 ± 0.010
	I	14 ± 1.5	150	—	—	28 ± 2.1	9.7	12 ± 0.20

[1] Calculated from Eq. 6.
[2] Measured in batch tests.
[3] Sr(L), $\rho = 1.25$ Mg/m^3; Sr(H), $\rho = 1.60$ Mg/m^3.
[4] Mean ± one standard deviation, n = 3.

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

plied here ($D_i - D_{iw}$) would include the combined effect of these two surface transport processes.

For I^-, $D_i < D_{iw}$ for all clays (Table 5). This may be due to anion exclusion, which means I^- cannot access the total porosity of the clays. If so, the Ψ values obtained from HTO experiments are overestimated for I^-. A lower Ψ value would give a proportionately lower D_{iw} value [Eq. (10)] for I^-, closer to the D_i value. Berry and Bond (1992) reported a significantly lower value of Ψ from I^- (0.012) than from HTO (0.096) experiments in London clay. In Avonlea bentonite at $\rho \sim 1.3$ Mg/m^3, both the geometry factor and effective porosity are about 0.1 (Oscarson *et al* 1992); since Ψ is the product of the geometry factor and porosity, Ψ would be about 0.01 in this clay, similar to the value reported by Berry and Bond (1992). If a Ψ value of 0.01 is used in Eq. (10) for I^- in all clays, rather than the values given in Table 4, D_{iw} would be 19 μm^2/s; a value within a factor of two or so of the measured D_i values for I^- in all clays (Table 5).

Apparent diffusion coefficients

A representative concentration profile for Sr in Avonlea bentonite is shown in Figure 3. The D_a value for Sr in Avonlea bentonite determined by the in-diffusion method is 23 ± 5.2 μm^2/s (mean $\pm$ one standard deviation, n = 4) and in Lake Agassiz clay, 45 ± 4.3 μm^2/s. These values compare favorably with those obtained from the time-lag method, 11 μm^2/s in Avonlea bentonite and 23 μm^2/s in Lake Agassiz clay (Table 5). The mean values obtained by the two methods differ by only a factor of about two, which is not uncommon for measured diffusion coefficients in compacted clays at a given density (Oscarson *et al* 1992; Robin *et al* 1987). Cho *et al* (1993b) also found good agreement between D_a values obtained by the time-lag and in-diffusion methods for both anions and cations in compacted bentonite. The D_a values measured by the time-lag method are, therefore, considered to be reasonably accurate.

Some data, however, reflect the limitations of the time lag method. For example, the D_a values for HTO in Avonlea bentonite and Lake Agassiz clay are higher at $\rho = 1.60$ than at 1.25 Mg/m^3 (Table 4), whereas the reverse should obviously be observed. The same trend is evident for the Sr/Avonlea bentonite system. Miyahara *et al* (1991), for example, using a more reliable method to measure D_a, reported a D_a value for HTO of 190 μm^2/s in bentonite at $\rho = 1.2$ Mg/m^3 and 94 μm^2/s at 1.6 Mg/m^3.

Values of D_a calculated from Eq. (6) are given in Table 5 for comparison with the measured D_a values. The K_d values used in the calculation are also shown in Table 5. In the application of Eq. (6), a linear sorption isotherm (i.e., $s' = \rho K_d$) is assumed. This is a reasonable assumption when the sorbate is present at low concentrations—<1 mmol/m^3 or so—which is the case here (Chang *et al* 1993; Meier *et al* 1987; Gillham and Cherry 1982). The total porosity, rather than the effective porosity, n_e, was used in Eq. (6) since the Ψ values used to calculate D_{iw} were obtained from HTO experiments, and HTO can access the total porosity of the clays. Considering the limitations in the D_a values determined by the time-lag technique and the measurement of K_d values in batch tests, the agreement between the measured and calculated D_a values is generally good. With a few exceptions, though, the measured D_a values are somewhat higher than the calculated ones, particularly in the Avonlea bentonite.

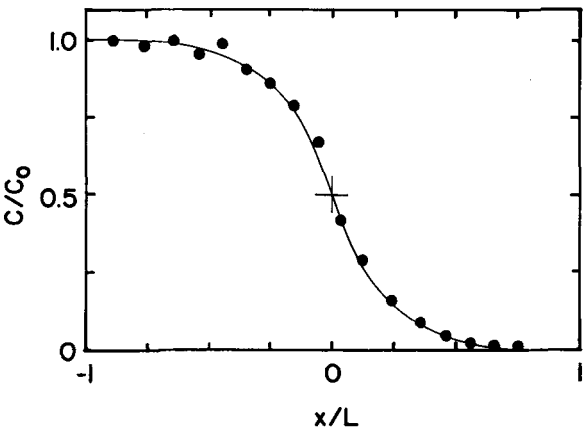


Figure 3. Concentration profile for Sr^{2+} in Avonlea bentonite at $\rho = 1.25$ Mg/m^3; solid circles are the experimental data and the line is the best fit curve from Eq. (15).

Rather than invoking surface diffusion to account for the difference between the measured and calculated D_a values, the discrepancy is largely attributed to an overestimation of the K_d values measured in batch tests. It is well documented that K_d values generally decrease with decreasing solution-to-clay ratio (Robin *et al* 1987; Meier *et al* 1987; Alberts *et al* 1986). Given that the solution-to-clay ratio of the saturated clays at $\rho = 1.25$ Mg/m^3, for example, is about 0.4 m^3/Mg, the K_d values for the compacted clays would be lower than those measured in the batch tests at a solution-to-clay ratio of 2 m^3/Mg. Moreover, at a given solution-to-clay ratio, K_d values for compacted clay are lower than those for the same clay when uncompacted or loose (Oscarson *et al* 1994). This is because the sorbate cannot enter small and occluded pores in compacted clay, and hence it cannot access the entire clay volume or all sorption sites. Oscarson *et al* (1994) proposed that a K_d value determined on loose clay be scaled down by a factor n_a/n (n_a is the porosity of compacted clay accessible to the sorbate and n the total porosity) to get an estimate of the K_d value for the same clay when compacted. For example, from the accessible porosity-density relationship for Avonlea bentonite given by Oscarson *et al* (1994), n_a/n is about 0.35 at $\rho = 1.25$ Mg/m^3. If this relationship applies to the diffusants

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

and other clays examined here, the K_d values in Table 5 should be reduced by about one-third. Lower K_d values would give greater calculated D_a values [Eq. (6)] and, in most cases, closer to the measured values.

In Avonlea bentonite and illite/smectite, the D_a values for I^- are greater than those of the cationic diffusants. This is largely due to a lower sorption (lower K_d) of I^- on these clays compared to the other diffusants. The D_a value for I^- in Lake Agassiz clay is relatively low, and the K_d value high, likely because of its high organic carbon content (Table 1)—organic matter effectively sorbs I^- (Oscarson 1994).

CONCLUSIONS

The pore diffusion model given by Eq. (6) adequately describes the transport of cationic diffusants in compacted clays, and there is no need to invoke other transport mechanisms, like surface diffusion. In such models, however, it is important that sorption parameters be determined under conditions as close as possible to those in the environment of interest. These conditions would include similar solution compositions and low solution-to-clay ratios; also an allowance should be made for the fact that less of a diffusant is sorbed on compacted clay per unit mass than the same loose clay commonly used in batch tests. Finally, if surface diffusion does occur in compacted clays, its effect is small and not likely to influence performance assessment modelling of clay-based barriers.

ACKNOWLEDGMENTS

I thank Mr. H. B. Hume for technical assistance, and Dr. J. McMurray for help with the speciation program. The Canadian Nuclear Fuel Waste Management Program is funded jointly by AECL Research and Ontario Hydro under the auspices of the CANDU Owners Group.

REFERENCES

Alberts, J. J., J. E. Pinder, E. Wurtz, and S. Lesnek. 1986. The effect of pH, solid phase, particle concentration and equilibrium time on the partition coefficients of curium on natural sediments. In *Application of Distribution Coefficients to Radiological Assessment Models.* T. H. Sibley and C. Myttenaere, eds. London: Elsevier Applied Science Publishers, 72–82.

Berry, J. A., and K. A. Bond. 1992. Studies of the extent of surface diffusion in the migration of radionuclides through geological materials. *Radiochim. Acta* **58/59**: 329–335.

Bradbury, M. H., A. Green, D. Lever, and I. G. Stephen. 1986. Diffusion and permeability based on sorption measurements in sandstone, anhydrite and upper magnesian limestone samples. UKAEA Report AERE-R 11995, United Kingdom Atomic Energy Agency, Oxfordshire, U.K.

Carter, D. L., M. M. Mortland, and W. D. Kemper. 1986. Specific surface. In *Methods of Soil Analysis, Part 1, 2nd Ed.* A. Klute, ed. Madison, Wisconsin: ASA and SSSA, 413–423.

Chandratillake, M., W. E. Falck, and D. Read. 1992. CHEMVAL Project: Guide to the CHEMVAL Thermodynamic Database. U.K. DOE Report No. DOE/HMIP/RR/92/094, 24 pp.

Chang, K.-P., C.-N. Hsu, and H. Tamaki. 1993. Basic study of ^{137}Cs sorption on soil. *J. Nucl. Sci. Technol.* **30**: 1243–1247.

Cho, W. J., D. W. Oscarson, M. N. Gray, and S. C. H. Cheung. 1993a. Influence of diffusant concentration on diffusion coefficients in clay. *Radiochim. Acta* **60**: 159–163.

Cho, W. J., D. W. Oscarson, and P. S. Hahn. 1993b. The measurement of apparent diffusion coefficients in compacted clays: An assessment of methods. *Appl. Clay Sci.* **8**: 283–294.

Conca, J. L., M. Apted, and R. Arthur. 1993. Aqueous diffusion in repository and backfill environments. *Mat. Res. Soc. Symp. Proc.* **Vol. 294**: 395–402.

Crank, J. 1975. *The Mathematics of Diffusion, 2nd Ed.* Oxford, England: Clarendon Press.

Frape, S. K., P. Fritz, and R. H. McNutt. 1984. Water-rock interaction and chemistry of groundwaters from the Canadian Shield. *Geochim. Cosmochim. Acta* **48**: 1617–1627.

Gillham, R. W., and J. A. Cherry. 1982. Contaminant migration in saturated unconsolidated geologic deposits. In *Recent Trends in Hydrology.* T. N. Narasimhan, ed. GSA Special Paper 189, Boulder, Colorado: Geological Society of America, 31–62.

Hancox, W. T., and K. Nuttall. 1991. The Canadian approach to safe, permanent disposal of nuclear fuel waste. *Nucl. Eng. Design* **129**: 109–117.

Hume, H. B. 1993. Apparatus and procedures for measuring diffusion and distribution coefficients in compacted clays. AECL Research Report, AECL-10981, COG-93-446. AECL Research, Chalk River, Ontario.

Li, Y.-H., and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* **38**: 703–714.

Jackson, M. L. 1975. *Soil Chemical Analysis-Advanced Course, 2nd Ed.* Madison, Wisconsin: Published by the Author, University of Wisconsin.

Jahnke, F. M., and C. J. Radke. 1987. Electrolyte diffusion in compacted montmorillonite engineered barriers. In *Coupled Processes Associated with Nuclear Waste Repositories.* C.-F. Tsang, ed. San Diego, California: Academic Press, 287–297.

Jensen, D. J., and C. J. Radke. 1988. Caesium and strontium diffusion through sodium montmorillonite at elevated temperature. *J. Soil Sci.* **39**: 53–64.

Kemper, W. D. 1986. Solute diffusivity. In *Methods of Soil Analysis, Part 1, 2nd Ed.* A. Klute, ed. Madison, Wisconsin: ASA and SSSA, 1007–1024.

Kim, H.-T., T.-W. Suk, S.-H. Park, and C.-S. Lee. 1993. Diffusivities for ions through compacted Na-bentonite with varying dry bulk density. *Waste Management* **13**: 303–308.

McCall, D. W., and D. C. Douglass. 1965. The effect of ions on the self-diffusion of water. I. Concentration dependence. *J. Phys. Chem.* **69**: 2001–2011.

Meier, H., E. Zimmerhackl, G. Zeitler, P. Menge, and W. Hecker. 1987. Influence of liquid/solid ratios in radionuclide migration studies. *J. Radioanal. Nucl. Chem.* **109**: 139–151.

Miyahara, K., T. Ashida, Y. Kohara, Y. Yusa, and N. Sasaki. 1991. Effect of bulk density on diffusion of cesium in compacted sodium bentonite. *Radiochim. Acta* **52/53**: 293–297.

Muurinen, A., J. Rantanen, and P. Penttilä-Hiltunen. 1985. Diffusion mechanisms of strontium, cesium and cobalt in compacted sodium bentonite. *Mat. Res. Soc. Symp. Proc.* **Vol. 50**: 617–624.

Nelson, D. W., and L. E. Sommers. 1982. Total carbon,

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press

organic carbon, and organic matter. In *Methods of Soil Analysis, Part 2*. A. L. Page, R. H. Miller, and D. R. Keeney, eds. Madison Wisconsin: ASA and SSSA, 539–579.

Nye, P. H. 1979. Diffusion of ions and uncharged solutes in soils and clays. *Adv. Agron.* **31**: 225–272.

Olsen, S. R., and W. D. Kemper. 1968. Movement of nutrients to plant roots. *Adv. Agron.* **20**: 91–151.

Oscarson, D. W. 1994. Comparison of measured and calculated diffusion coefficients for iodide in compacted clays. *Clay Miner.* **29**: 145–151.

Oscarson, D. W., and D. A. Dixon. 1989. Elemental, mineralogical, and pore-solution composition of selected Canadian clays. AECL Research Report, AECL-9891. AECL Research, Chalk River, Ontario, Canada.

Oscarson, D. W., D. A. Dixon, and M. N. Gray. 1990. Swelling capacity and permeability of an unprocessed and a processed bentonitic clay. *Eng. Geol.* **28**: 281–289.

Oscarson, D. W., and H. B. Hume. 1993. On the smectite to illite reaction. AECL Research Report, AECL-10842. AECL Research, Chalk River, Ontario, Canada.

Oscarson, D. W., H. B. Hume, and F. King. 1994. Sorption of cesium on compacted bentonite. *Clays & Clay Miner.* (in press).

Oscarson, D. W., H. B. Hume, N. G. Sawatsky, and S. C. H. Cheung. 1992. Diffusion of iodide in compacted bentonite. *Soil Sci. Soc. Am. J.* **56**: 1400–1406.

Rasmuson, A., and I. Neretnieks. 1983. Surface migration in sorption processes. SKB Technical Report 83-37, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden.

Robin, M. J. L., R. W. Gillham, and D. W. Oscarson. 1987. Diffusion of strontium and chloride in compacted clay-based materials. *Soil Sci. Soc. Am. J.* **51**: 1102–1108.

Sawatsky, N. G., and D. W. Oscarson. 1991. Diffusion of technetium in dense bentonite under oxidizing and reducing conditions. *Soil Sci. Soc. Am. J.* **55**: 1261–1267.

Shainberg, I., and W. D. Kemper. 1966. Conductance of alkali cations in aqueous and alcoholic bentonite pastes. *Soil Sci. Soc. Am. Proc.* **30**: 700–706.

Skagius, K., and I. Neretnieks. 1985. Diffusion measurements of caesium and strontium in biotite gniess. SKB Technical Report 85-15, Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden.

Staunton, S. 1986. The self-diffusion of sodium in soil: Factors affecting the surface mobility. *J. Soil Sci.* **37**: 373–377.

Staunton, S., and P. H. Nye. 1983. The self diffusion of sodium in a naturally aggregated soil. *J. Soil Sci.* **34**: 263–269.

van Schaik, J. C., W. D. Kemper, and S. R. Olsen. 1966. Contribution of adsorbed cations to diffusion in clay-water systems. *Soil Sci. Soc. Am. Proc.* **30**: 17–22.

(Received 8 April 1994; accepted 17 June 1994; Ms. 2490R)

https://doi.org/10.1346/CCMN.1994.0420504 Published online by Cambridge University Press