

Effect of Exchangeable Cation on Radionuclide Diffusion In Compacted Bentonite

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Abstract

Diffusion coefficient is a critical parameter for predicting radiological source term (migration rate and flux of radionuclide) through given near field conditions in spent fuel or high level waste repository. The effect of exchangeable cation— Na^+ and Ca^{2+} —on the diffusion of Γ and ^3H (as HTO) in compacted bentonite was examined using a through-diffusion method. Bentonite material used here was compacted to a density of 1.3 Mg/m^3 , and Na-bentonite was saturated with a solution of 100 mol NaCl/m^3 and Ca-bentonite with $50 \text{ mol CaCl}_2/\text{m}^3$. The results show that effective diffusion coefficients are generally higher by a factor of two to five in Ca-than Na-clay. This is attributed to the larger particle size of Ca-compared to Na-bentonite; hence, Ca-bentonite has a greater proportion of relatively large pores, which make a greater contribution to mass transport than small pores. Although the nature of the exchangeable cation affects mass diffusion in compacted bentonite, the effect is small and not likely to influence performance assessment modeling of compacted bentonite-based barriers.

1. Introduction

Bentonite-based materials are being evaluated in several countries as potential barriers and seals in a disposal vault for nuclear fuel waste. In Canada, for example, a 1:1 mix by dry mass of bentonite and sand-the buffer material-would surround waste containers in a vault excavated 500 to 1000m deep in granitic rock of the Canadian Shield [1]. Because of the low permeability of compacted bentonite-based materials, diffusion is thought to be the principal mechanism of mass transport through these barriers and

diffusion coefficients for important radionuclides in reference clay material are being evaluated.

The nature of the cation on the exchange complex of bentonite greatly affects many of its properties, including its permeability and diffusivity [2, 3]. Here we examine the effect of the exchangeable cation- Na^+ and Ca^{2+} -on the diffusive properties of compacted Avonlea bentonite. This clay is a component of the reference buffer material in the disposal concept developed in Canada for nuclear fuel waste.

The cation exchange complex of untreated Avonlea bentonite contains about 60% Na^+ and 20%

Ca²⁺, along with minor amounts of Mg²⁺ and K⁺. However, as groundwater slowly moves through the buffer material in a disposal vault, Ca²⁺ will gradually become the predominant exchangeable cation. This is because the concentration of Ca²⁺ is generally greater than that of Na⁺ in deep groundwaters of the Canadian Shield where a disposal vault would be located [4], and clays, such as bentonite, have a greater selectivity coefficient for Ca²⁺ than Na⁺ [5]. Besides Ca²⁺ in groundwater, it may also be released from cement-based material that may be used in a repository system. Thus, it is important to evaluate the diffusive behaviour of both Na- and Ca-bentonite.

Iodide and tritiated water (as ³H or HTO) were used as diffusants. Iodine-129 is an important radioisotope in spent fuel or high level waste due to its long half-life - 1.59 × 10⁷ yr - and because it is existing as negative form (I⁻) across a wide range of environmental conditions and not strongly sorbed on earthen materials such as clays and rocks. And the migration behaviour of HTO, a comparatively small, non-sorbing species, can provide important information on the pore structure of compacted clay.

2. Materials and Experimentals

2.1. Clay

The Avonlea bentonite is from the Bearpaw Formation of Upper Cretaceous age in southern Saskatchewan, Canada [6]. The clay contains approximately 80% smectite (montmorillonite), 10% illite, 5% quartz, and minor amounts of gypsum, feldspar and carbonate [7]. It has a cation-exchange capacity of about 60 cmolc/kg and a specific surface area of 480 × 10³ m²/kg.

The buffer material is a 1 : 1 mix by dry mass of Avonlea bentonite and silica sand compacted to a dry density of about 1.7 Mg/m³. With respect to diffusive transport, however, clay is the active component of the buffer and sand is essentially inert filler [8, 9]. Hence, 100% clay was used in this study.

To saturate the clay's exchange complex with Na⁺ or Ca²⁺, 100g of bentonite were washed several times with 500cm³ of a 1000 mol/m³ solution of NaCl or CaCl₂. The Na- and Ca-clays were dialysed against deionized water for several days to remove excess salt from the clay, and then freeze-dried. The clays were compacted to a target dry density, ρ , of 1.3 Mg/m³ in stainless-steel rings - 4.1cm in diameter and 7cm long - using a hydraulic press. A clay density of 3 Mg/m³ is close to the effective clay density in a 1 : 1 mix of clay and sand. (Effective clay density is the mass of clay divided by the combined volume of clay and voids.) The rings were placed in through-diffusion cells and the Na-clay was saturated with a solution of 100 mol NaCl/m³ and the Ca-clay with 50 mol CaCl₂/m³.

2.2. Diffusion Experiments

A diagram of the diffusion cell is shown in Fig. 1, and it is described in detail by Hume [10]. The diffusion experiments, conducted in triplicate at 23 ± 2° C, are described by Oscarson et al. [11]. Briefly, the experiment involves flowing a solution containing a radioactive diffusant (¹²⁵I or ³H in these experiments) (source reservoir) over one end of the clay plugs and passing an unspiked solution (collection reservoir) over the other end. The solution in the source and collection reservoirs was either 100 mol NaCl/m³ or 50 mol CaCl₂/m³. The flux of the diffusant through

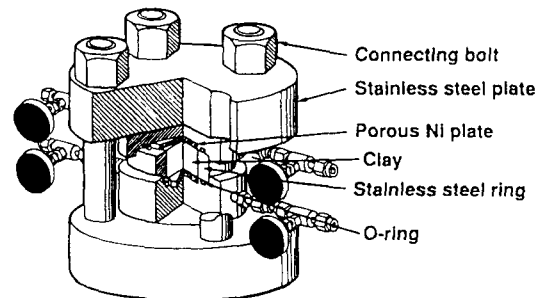


Fig. 1. Diagram of the Diffusion Cell Used in the Through-Diffusion Experiments.

the clay plugs was measured with time and when steady-state was established, effective diffusion coefficients, D_e , are calculated from Fick's first law as,

$$D_e = -(\Delta Q/A\Delta t)/(\Delta c/L) \quad (1)$$

where ΔQ is the change in the total amount of diffusant passing through the 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 diffusant concentration between the ends of the clay plug. In Eq. 1, the numerator is the steady-state flux and the denominator the concentration gradient of the diffusant. The D_e value is defined as,

$$D_e = D_o \tau n_e \quad (2)$$

where D_o is the diffusion coefficient in pure bulk water stationary conditions, n_e the effective porosity or the porosity that contributes to diffusive transport, and τ the tortuosity factor that accounts for a tortuous path around the clay particles; it is usually expressed as,

$$\tau = (d/d_e)^2 \quad (3)$$

where d is the straight-line distance between two points defining the diffusion path, and d_e the effective distance of diffusion through the clay between the same two points. In reality, may account for more than just the pore geometry of the clay. For example, the variation in the viscosity of the solution within the pores [12] would also be included in τ .

From these experiments, another diffusion coefficient, the apparent diffusion coefficient, D_a , can be determined from the time lag, t_e , as,

$$D_a = L^2/6t_e \quad (4)$$

The t_e value is obtained from the intercept on the time axis of a plot of cumulative flux versus time. The reader is referred to Cho et al. [13] for the assumptions involved in Eq. 4 and its mathematical formulation. The D_a value is defined as,

$$D_a = \frac{D_e}{\alpha} = \frac{D_o \tau n_e}{(n_e + \rho K_d)} \quad (5)$$

where α is the capacity factor and K_d the distribution coefficient; the use of K_d in Eq. 5 implies a linear sorption isotherm.

2.3. Sorption Experiments

The extent of sorption of Γ , expressed as K_d , on Na- and Ca-bentonite was determined as follows. Five grams of clay were suspended in 30 cm³ of 100 mol NaCl/m³ or 50 mol CaCl₂/m³ solution spiked with ¹²⁵I in 50-cm³ polycarbonate centrifuge tubes. The tubes were capped, sealed in polyethylene bags, and placed in a water bath at 23 ± 0.1°C for 14 days. The tubes were shaken periodically. After the reaction period, the tubes were centrifuged at 5500g for 40 min. The activity of ¹²⁵I in the supernatant solution was measured by liquid scintillation counting. Values of K_d were calculated from,

$$K_d = [(A_i/A_e) - 1] (S - S_o) / \rho_w \quad (6)$$

where A_i is the net activity of the solution initially added to the clay, A_e the net activity of the solution after the reaction period, S the solution-to-clay ratio (by mass) and S_o the solution-to-clay ratio, or gravimetric moisture content, of the air-dried clay, and ρ_w the density of the NaCl or CaCl₂ solutions.

3. Results and Discussions

Typical cumulative flux curves for HTO through Na- and Ca-bentonite are shown in Fig. 2. The flux through Ca-bentonite is greater than that through Na-bentonite. Since D_e is a proportionality constant relating the flux to the concentration gradient of a diffusant (Eq. 1), D_e is also greater in the Ca-clay; the concentration gradient was the same for both clays. The t_e values obtained by extrapolating from the

steady-state region of the curve to the time axis. A depiction of how these values are determined could be referred to Cho et al. [13]. Cumulative flux curves for Γ are similar to those for untreated Avonlea bentonite published elsewhere [11]. All D_e , D_a and K_d values are given in Table 1.

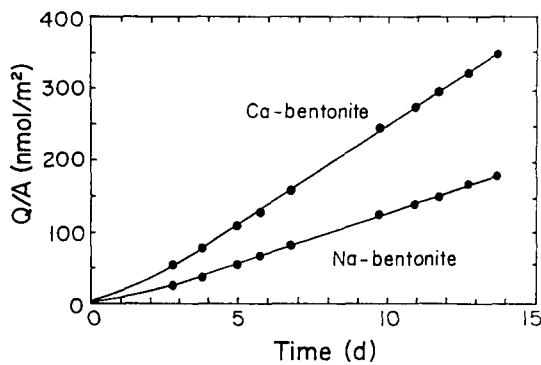


Fig. 2. Cumulative Flux Curves for H^3 in Na- and Ca-bentonite.

Table 1. Diffusion Coefficients in Compacted Bentonite

Radionuclide	Exchangeable Cation	D_e ($\mu m^2/s$)	D_a ($\mu m^2/s$)	K_d ($\mu m^2/s$)
Iodide	Na ⁺	7.0	47	3.5
		8.0	49	3.1
		7.5 ^a	48	3.4
	Ca ⁺²	40	23	6.9
		36	15	8.1
		12	8.8	7.2
HTO	Na ⁺	29	16	7.4
		81	90	—
		42	57	—
		110	93	—
	Ca ⁺²	78	80	—
		160	99	—
		150	110	—
		130	130	—
		150	110	—

Note a : Underlined values are means of the three replicates ; one of the diffusion cells for the I/Na-bentonite system failed, so there are only two replicates for this system.

3.1. Effective Diffusion Coefficients

For both diffusants, D_e values are higher in Ca- than Na-bentonite. At a given density, the total porosity of the two clays is the same and we, however, attribute this to a greater proportion of comparatively large pores in Ca-bentonite due to the larger quasicrystal or partial size compared to that of Na-bentonite. Quasicrystals are defined as several hydrated unit layers of montmorillonite stacked in roughly parallel alignment along the crystallographic c axis. This paraticle structure is stabilized by attractive interactions between the basal planes of unit layers mediated by adsorbed cations and water. In dilute aqueous suspension, Ca-bentonite forms quasicrystals with four to seven unit layers, while those of Na-bentonite are thought to average to 1.3 unit layers [14]. Ben Rhaiem et al [15]. reported that in a gel the number of unit layers per quasicrystal of Ca-montmorillonite ranged from 50 to 400, while that of Na-montmorillonite was 10 or less. From the results of other studies above, it could be analysed that compacted Ca-bentonite has a greater proportion of large pores, which are more effective in mass transport than small pores-this is reflected in the higher D_e values in Ca-bentonite. Oscarson et al. [11] reported a D_e value as measured in Ca-bentonite (Table 1). In their study, the clay was saturated with a synthetic groundwater solution with the following major-ion concentrations in mol/m³: Ca²⁺, 53.3; Na⁺, 82.6; Cl⁻, 171; and SO₄²⁻, 10.8. The similarity in the D_e values in the two systems suggests untreated Avonlea bentonite saturated with the synthetic groundwater solution has a fabric or pore structure similar to that of Ca-bentonite. A corollary is that the particles of untreated Avonlea bentonite in the synthetic groundwater solution are quasicrystals.

The mobility of the first molecular layer of sorbed water on Na- and Ca-bentonite is about 30% and 5%, respectively, of the mobility of water molecules in bulk water [12]. Therefore, other factors being equal, the D_e value for HTO would be expected to be high-

her in Na-bentonite. Since the opposite is observed (Table 1), the effect of the greater proportion of large pores in Ca-bentonite outweighs the comparatively low mobility of HTO in the water layer next to the particles of Ca-bentonite.

The D_e values in both clays are lower for Γ than HTO. Iodide is larger than HTO, and the larger the diffusant, the lower n_e because it cannot access as much of the pore space. (The effective hydrated radius of Γ is 0.33 nm and the radius of a water molecule, 0.14 nm [16]. Thus, n_e , and D_e (Eq. 2), is lower for Γ than HTO. Anion exclusion may also contribute to lower n_e values for Γ compared to HTO [11].

3.2. Apparent Diffusion Coefficients

The D_a value for HTO is also higher in Ca-than Na-bentonite. Since HTO is not sorbed, $K_d=0$, and Eq. 5 reduces to,

$$D_a = D_o \quad (7)$$

The D_o value for HTO is not significantly different in the NaCl and CaCl₂ solutions used here [17]. Therefore, the higher D_a value in Ca-bentonite is due to τ . As the particles of Ca-bentonite are larger than those of Na-bentonite, the diffusion path is shorter in Ca-bentonite; this means τ , and D_a values (Eq. 7), is greater. From the mean D_a values in Table 1 and a D_o value of $2450 \mu\text{m}^2/\text{s}$ for HTO, τ , calculated from Eq. 7, is 0.04 in Ca-bentonite and 0.03 in Na-bentonite. The D_a values determined from the time lag method (Eq. 4) are not particularly accurate [13], however, so these τ values should be viewed with some caution. They are, though, close to the value of 0.05 obtained for Avonlea bentonite at a similar density by Sawatsky and Oscarson [18] using a more accurate method to measure D_a .

Contrary to the results for HTO, the D_a value for Γ is higher in Na-than Ca-bentonite. This is consistent with the greater sorption (higher K_d value) of Γ

on Ca-bentonite (Table 1)-in theory, D_a is inversely proportional to K_d (Eq. 5). Finally, the lower D_a value for Γ compared to HTO in both clays is largely because Γ sorbs on the clays and HTO does not.

4. Conclusion

The effect of the exchangeable cation -Na⁺ and Ca²⁺ - on the diffusive behaviour of Γ and HTO in compacted bentonite is analysed. Generally, effective diffusion coefficients for both diffusants are higher by a factor of two to five in Ca-than Na-bentonite. We attribute this to the larger particle size of Ca-compared to Na-bentonite. Larger particles mean compacted Ca-clay has a greater proportion of relatively large pores, which are more effective in mass transport than small pores. Although mass diffusion in compacted bentonite depends on the nature of the exchangeable cation, the effect is small and not likely to influence performance assessment modelling of compacted bentonite-based barriers.

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