

## **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— $\text{Na}^+$  and  $\text{Ca}^{2+}$ —on the diffusion of  $\text{I}^-$  and  $^3\text{H}$  (as HTO) in compacted bentonite was examined using a through-diffusion method. Bentonite material used here was compacted to a density of  $1.3 \text{ Mg/m}^3$ , and Na-bentonite was saturated with a solution of  $100 \text{ mol NaCl/m}^3$  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- $\text{Na}^+$  and  $\text{Ca}^{2+}$ -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%  $\text{Na}^+$  and 20%

$\text{Ca}^{2+}$ , along with minor amounts of  $\text{Mg}^{2+}$  and  $\text{K}^{+}$ . However, as groundwater slowly moves through the buffer material in a disposal vault,  $\text{Ca}^{2+}$  will gradually become the predominant exchangeable cation. This is because the concentration of  $\text{Ca}^{2+}$  is generally greater than that of  $\text{Na}^{+}$  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  $\text{Ca}^{2+}$  than  $\text{Na}^{+}$  [5]. Besides  $\text{Ca}^{2+}$  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 triated water (as  $^3\text{H}$  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  $-1.59 \times 10^7 \text{ yr}$ —and because it is existing as negative form ( $\text{I}^{-}$ ) 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  $480 \times 10^3 \text{ m}^2/\text{kg}$ .

The buffer material is a 1:1 mix by dry mass of Avonlea bentonite and silica sand compacted to a dry density of about  $1.7 \text{ Mg/m}^3$ . 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  $\text{Na}^{+}$  or  $\text{Ca}^{2+}$ , 100g of bentonite were washed several times with  $500 \text{ cm}^3$  of a  $1000 \text{ mol/m}^3$  solution of NaCl or  $\text{CaCl}_2$ . 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,  $\rho$ , of  $1.3 \text{ Mg/m}^3$  in stainless-steel rings—4.1cm in diameter and 7cm long—using a hydraulic press. A clay density of  $3 \text{ Mg/m}^3$  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  $100 \text{ mol NaCl/m}^3$  and the Ca-clay with  $50 \text{ mol CaCl}_2/\text{m}^3$ .

### 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  $23 \pm 2^\circ \text{ C}$ , are described by Oscarson et al. [11]. Briefly, the experiment involves flowing a solution containing a radioactive diffusant ( $^{125}\text{I}$  or  $^3\text{H}$  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  $100 \text{ mol NaCl/m}^3$  or  $50 \text{ mol CaCl}_2/\text{m}^3$ . The flux of the diffusant through

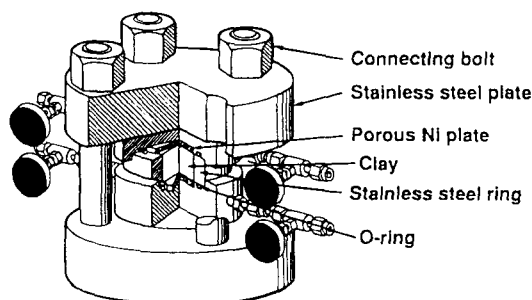


Fig. 1. Diagram of the Diffusion Cell Used in the Through-Diffusion Experiments.

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  $\Delta Q$  is the change in the total amount of diffusant passing through the clay plug in an increment of time  $\Delta t$ ,  $A$  the cross-sectional area and  $L$  the length of the clay plug, and  $\Delta c$  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  $\tau$  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  $\tau$ .

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  $\alpha$  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  $\Gamma$ , expressed as  $K_d$ , on Na- and Ca-bentonite was determined as follows. Five grams of clay were suspended in 30 cm<sup>3</sup> of 100 mol NaCl/m<sup>3</sup> or 50 mol CaCl<sub>2</sub>/m<sup>3</sup> solution spiked with <sup>125</sup>I in 50-cm<sup>3</sup> 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 <sup>125</sup>I 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  $\rho_w$  the density of the NaCl or CaCl<sub>2</sub> 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  $\Gamma^-$  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.

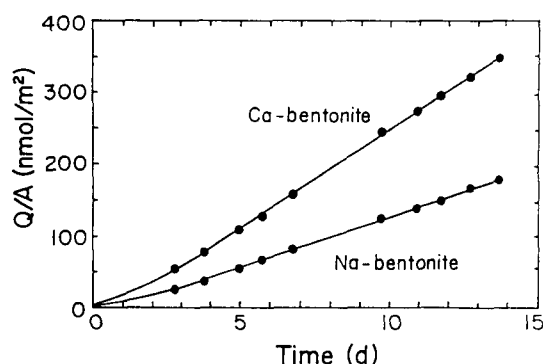


Fig. 2. Cumulative Flux Curves for  $H^3$  in Na- and Ca-bentonite.

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 <sup>+</sup>	7.0	47	3.5
		8.0	49	3.1
		—	—	3.5
		7.5 <sup>a</sup>	48	3.4
	Ca <sup>+2</sup>	40	23	6.9
		36	15	8.1
		12	8.8	7.2
		29	16	7.4
HTO	Na <sup>+</sup>	81	90	—
		42	57	
		110	93	
		78	80	
	Ca <sup>+2</sup>	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 Rhaïem 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/m<sup>3</sup>: Ca<sup>2+</sup>, 53.3; Na<sup>+</sup>, 82.6; Cl<sup>-</sup>, 171; and SO<sub>4</sub><sup>2-</sup>, 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  $\Gamma$  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  $\Gamma$  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  $\Gamma$  than HTO. Anion exclusion may also contribute to lower  $n_e$  values for  $\Gamma$  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 CaCl<sub>2</sub> solutions used here [17]. Therefore, the higher  $D_a$  value in Ca-bentonite is due to  $\tau$ . As the particles of Ca-bentonite are larger than those of Na-bentonite, the diffusion path is shorter in Ca-bentonite; this means  $\tau$ , 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,  $\tau$ , 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  $\tau$  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  $\Gamma$  is higher in Na-than Ca-bentonite. This is consistent with the greater sorption (higher  $K_d$  value) of  $\Gamma$

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

### 4. Conclusion

The effect of the exchangeable cation  $-\text{Na}^+$  and  $\text{Ca}^{2+}$  on the diffusive behaviour of  $\Gamma$  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.

### References

1. W.T. Hancox and K. Nuttall, The Canadian approach to safe, permanent disposal of nuclear fuel waste, *Nucl. Eng. Des.*, 129, 109~117 (1991)
2. I. Shainberg, N. Alperovitch and R. Keren, Effect of magnesium on the hydraulic conductivity of Na-smectite-sand mixtures, *Clays Clay Miner.*, 36, 432~438 (1988)
3. G.R. Dutt and P.F. Low, Relationship between the activation energies for deuterium oxide diffusion and exchangeable ion conductance in clay systems, *Soil Sci.*, 93, 195~203 (1962)
4. S.K. Frape, P. Fritz and R.H. McNutt, Water-rock interaction and chemistry of groundwaters from the Canadian Shield, *Geochim. Cosmochim. Acta*, 48, 1617~1627 (1984)
5. L.V. Benson, A tabulation and evaluation of ion

- exchange data on smectites, *Envir. Geol.*, 4, 23~29 (1982)
6. D.W. Oscarson, D.A. Dixon and M. Gray, Swelling capacity and permeability of an unprocessed and a processed bentonitic clay, *Eng. Geol.*, 28, 281~289 (1990)
  7. D.W. Oscarson and D.A. Dixon, Elemental, mineralogical, and poresolution compositions of selected Canadian clays. AECL Research Report, AECL-9891 (1989)
  8. R.W. Gillham, M.J. Robin, D.J. Dytynshyn and H.M. Johnston, Diffusion of nonreactive and reactive solutes through fine-grained barrier materials, *Can. Geotech. J.*, 21, 541~550 (1984)
  9. H.D. Sharma And D.W. Oscarson, Diffusion of plutonium(IV) in dense bentonite-based materials. p. 735~741. In Materials Research Society Symposium Proceedings 127, W. Lutze and R.C. Ewing (Eds.). Scientific Basis for Nuclear Waste Management XIII. Materials Research Society, Pittsburgh, PA (1989)
  10. H.B. Hume, Procedures and apparatus for measuring diffusion and distribution coefficients in compacted clays, AECL Research Report, AECL-10981 (1993)
  11. D.W. Oscarson, H.B. Hume, N.G. Sawatsky And S.C.H. Cheung, Diffusion of iodide in compacted bentonite. *Soil Sci. Soc. Am. J.*, 56, 1400~1406 (1992)
  12. W.D. Kemper, D.E.L. Maasland And L.K. Porter, Mobility of water adjacent to mineral surfaces, *Soil Sci. Soc. Am. Proc.*, 28, 164~167 (1964)
  13. W.J. Cho, D.W. Oscarson And P.S. Hahn, The measurement of apparent diffusion coefficients in compacted clays: an assessment of methods, *Appl. Clay Sci.*, 8, 283~294 (1993)
  14. G. Sposito, The Surface Chemistry of Soils, Oxford University Press, New York, NY, P. 234 (1984)
  15. H. Ben Rhaïem, C.H. Pons and D. Tessier, Factors affecting the microstructure of smectites: Role of cation and history of applied stresses, Proc. of Clay Conf., The Clay Minerals Society, Denver (1985)
  16. E.R. Nightingale, Phenomenological theory of ion solvation. Effective radii of hydrated ions, *J. Phys. Chem.*, 63, 1381~1387 (1959)
  17. D. McCall and D. Douglass, The effect of ions on the self-diffusion of water. I. Concentration dependence, *J. Phys. Chem.*, 69, 2001~2011 (1965)
  18. N.G. Sawatsky and D.W. Oscarson, Diffusion of technetium in dense bentonite under oxidizing and reducing conditions, *Soil Sci. Soc. Am. J.*, 55, 1261~1267 (1991)