COMPARISON OF MEASURED AND CALCULATED DIFFUSION COEFFICIENTS FOR IODIDE IN COMPACTED CLAYS

D. W. OSCARSON

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

(Received 25 May 1993; revised 15 July 1993)

ABSTRACT: An understanding of the behaviour of contaminants in compacted clays is important in assessing the effectiveness of clay-based barrier materials used in many waste containment strategies. Here the diffusion and sorption behaviour of I⁻ with selected compacted clays is examined (¹²⁹I is a relatively long-lived radioisotope present in high-level nuclear fuel waste.) Diffusion coefficients, D, and distribution coefficients, Kd, were measured for I⁻ with four clays: bentonite, Lake Agassiz clay (a glacial lake clay composed mainly of smectite, illite, kaolinite, and quartz), interstratified illite-smectite, and kaolinite. For the diffusion experiments the clays were compacted to a dry bulk density, ρ, of ~1.2 Mg m⁻³. The mean measured D values, Dm, were as follows: bentonite, 310 μm² s⁻¹; Lake Agassiz clay, 0.62 μm² s⁻¹; illite-smectite, 190 μm² s⁻¹; and kaolinite, 74 μm² s⁻¹. The measured values were compared with those calculated, De, from the following model: 

$$D = \frac{D_0 n}{(n + \rho K_d)}$$

where D₀ is the diffusion coefficient in pure bulk water, n the apparent tortuosity factor, and the solution-filled porosity of the clay. Except for the Lake Agassiz clay, where Dm was about an order of magnitude lower than De, the Dm and De values agreed within a factor of about two. The Lake Agassiz clay has a markedly higher organic carbon content than the other three clays, and this could affect n, which may be overestimated in the model.

Compacted clay-based materials are important barriers in many waste disposal strategies. In Canada, for example, a disposal concept is being evaluated in which dense clay-based materials would be used to surround containers holding high-level nuclear fuel waste in a vault excavated 500–1000 m in granitic rock in the Canadian Shield (Hancox & Nuttall, 1991). These materials would also be used to backfill and seal large portions of the excavated vault after the waste containers were emplaced.

Because the permeability of dense clay-based materials is very low (Oscarson et al., 1990), the principal mechanism of mass transport through these materials is molecular diffusion. Diffusion coefficients are, therefore, critical parameters for predicting migration rates through these barriers.

In the long-term disposal of high-level nuclear fuel waste, the fission product ¹²⁹I is of concern, both because of its long half-life of 1.6 × 10⁷ yr and because it is poorly sorbed on most clay materials (Oscarson et al., 1984). Of all the radioisotopes present in nuclear fuel waste, ¹²⁹I has the greatest potential to reach the biosphere before decaying to insignificant levels.

This study had two objectives: to experimentally measure diffusion coefficients for I⁻ in compacted clays having a wide range of properties, and to compare the measured diffusion coefficients with those calculated from a model containing easily measured or readily available parameters. Since diffusion coefficients are relatively difficult and time-consuming to measure in compacted clays, it is desirable to have other means of estimating them; hence the need to compare measured and calculated diffusion coefficients.

MATERIALS AND METHODS

Clays

Four clays were used; their origin and composition are summarized below and some 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 ~80% smectite (montmorillonite), 10% illite, 5% quartz, and minor
TABLE 1. Selected properties of the clays.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Cation exchange capacity(^a) (cmol(\cdot)kg(^{-1}))</th>
<th>Specific surface area(^b) (10(^2) m(^2) kg(^{-1}))</th>
<th>Organic carbon(^c) (wt%)</th>
<th>pH(^d)</th>
<th>K(_d)^(^e) (m(^3) Mg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avonlea bentonite</td>
<td>60</td>
<td>480</td>
<td>0.31</td>
<td>7.3</td>
<td>0.25 ± 0.014</td>
</tr>
<tr>
<td>Lake Agassiz</td>
<td>50</td>
<td>303</td>
<td>1.2</td>
<td>7.1</td>
<td>12 ± 0.20</td>
</tr>
<tr>
<td>Illite-smectite</td>
<td>43</td>
<td>292</td>
<td>0.16</td>
<td>7.4</td>
<td>0.22 ± 0.009</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2.3</td>
<td>10</td>
<td>0.06</td>
<td>3.9</td>
<td>1.7 ± 0.18</td>
</tr>
</tbody>
</table>

\(^a\) Calcium and Mg\(^{2+}\) were the index and replacing cations, respectively (Jackson, 1975).
\(^b\) Ethylene glycol monethyl ether method (Carter et al., 1986).
\(^c\) Determined by igniting a sample at 900°C in an O\(_2\) stream; CO\(_2\) released was measured with an Astro 2001 organic C IR Analyser. Clays were pretreated with FeSO\(_4\) and H\(_2\)SO\(_4\) to remove inorganic C (Nelson & Sommers, 1982).
\(^d\) Synthetic groundwater solution-to-clay ratio of 2:1.
\(^e\) For I\(^-\) using eqn. 7.
\(^f\) Mean ± 1 standard deviation (n = 4).

amounts of gypsum, feldspar and carbonate (Oscarson & Dixon, 1989). The clay is a component of the reference buffer material in the disposal concept developed within the Canadian Nuclear Fuel Waste Management Program (CNFWMP). The buffer material is a 1:1 mix by dry mass of bentonite and sand compacted to a dry bulk density of 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 ~ 35% smectite, 20% illite, 15% quartz, 10% kaolinite, 10% calcite and minor amounts of feldspar and dolomite (Oscarson & Dixon, 1989). It is a component of the reference backfill material in the CNFWMP. The backfill material is a 1:1 mix by dry mass of Lake Agassiz clay and crushed granite aggregate, compacted to a dry bulk density of ~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-1. It is from the Mancos Shale, USA, and is described as a random interstratification of 60% illite and 40% smectite layers. This clay 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 thousands of years into an illite-smectite mixed-layered material (Oscarson & Hume, 1993). Hence, its diffusive properties are important for assessing the long-term performance of smectite-based barrier materials.

Kaolinite. This clay was also obtained from the Source Clays Repository and is designated KGa-1. It is a well-crystallized clay from Washington County, Georgia, USA.

Solution

The clays were saturated with a synthetic groundwater solution (SGW) with a pH of 7.2, effective ionic strength of 220 mol m\(^{-3}\), and the following composition (in mol m\(^{-3}\)): Na, 83; K, 0.36; Mg, 2.5; Ca, 53; HCO\(_3\), 0.28; Cl, 170; and SO\(_4\), 11. It was chosen to represent groundwater found deep in granitic rock in the Canadian Shield (Frape et al., 1984).

Diffusion experiments

The half-cell method used to measure diffusion coefficients in compacted clays is described in detail by Sawatsky & Oscarson (1991). A diagram of the diffusion cell is shown in Fig. 1. The technique involves the measurement of the amount of a diffusant that has diffused across the interface of a radioisotope-tagged clay plug and an untagged plug within a given time.
The clays were compacted to a target dry bulk density, $\rho$, of $\sim 1.2 \text{ Mg m}^{-3}$ (this is the approximate density of the clay component of both the reference buffer and the backfill material in the Canadian concept for the disposal of high-level nuclear fuel waste). Synthetic groundwater or SGW spiked with Na$^{125}$I was added to the loose clays (before compacting) in amounts such that the clays would be as close to saturated as possible when compacted to the target density.

Before the diffusion experiments, either two tagged or untagged clay plugs (~4 cm long and 2 cm in diameter) were placed in the diffusion cells for seven days to allow the moisture and $^{125}$I, in the case of the tagged plugs, to distribute uniformly throughout the plugs. After this equilibration period, and in preparation for the diffusion experiments, the clay plugs in the diffusion cells were switched so that tagged plugs were in contact with untagged plugs. A thin layer of a 1:1 mixture of the appropriate clay and SGW was added to one end of each untagged plug. This plug was then placed in contact with a tagged plug outside the diffusion cell; most of the clay paste oozed out and was immediately wiped off, leaving only a small amount of paste at the interface. It is felt that this procedure provided an excellent contact between the two plugs, and, at the same time, introduced only a slight error. The clay plugs were then placed in the diffusion cells and the cells immersed in a water bath at $23 \pm 0.1^\circ\text{C}$ for the diffusion period, which ranged from ~2–5 days. For each clay, experiments were conducted at least in triplicate.

After the diffusion period, the clay plugs were sectioned, starting at the end of the clay plug that was initially inactive, into slices 2–4 mm thick. The moisture content of a subsample of each slice was determined gravimetrically by heating at 105°C to constant mass; generally, the clays were >95% saturated during the tests, based on the calculated porosity of the compacted clay and its specific gravity. The activity of $^{125}$I in a second subsample of each slice was measured by gamma spectroscopy using an Ortec, high-purity germanium detector (EG & G Ortec, Oak Ridge, Tennessee). The activity of $^{125}$I in each slice from the initially untagged plug was summed to obtain the total activity of $^{125}$I in the plug after the diffusion period; this value was used to obtain the diffusion coefficient as described below.

The clay plugs were sectioned after the diffusion runs to obtain concentration profiles for $^{125}$I in the clay. The shape of these profiles can often provide useful information on the behaviour of diffusants in porous materials (Sawatsky & Oscarsson, 1991).

**Diffusion coefficients**

If coupled processes are neglected and transport is assumed to occur in only one direction, say the $x$-direction, the transient diffusional transport of a solute through an homogeneous and isotropic porous medium is given by Fick's second law:

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} \right),$$

where $c$ is the bulk concentration (based on the total volume—solution plus clay—of the system) of the diffusant, $t$ is time, and $D$ the diffusion coefficient (this $D$-value is often called the apparent diffusion coefficient). This $D$-value is related to the diffusion coefficient in pure bulk water under stationary conditions, $D_0$, by

$$D = D_0 \tau_a \mu (n + \rho K_d),$$

where $\tau_a$ is the apparent tortuosity factor (which includes not only the actual geometric tortuosity
but also all other factors that may be inherent in its measurement, such as the increased viscosity of water adjacent to surfaces of clay particles; \( n \) is the total solution-filled porosity of the clay; and \( K_d \) is the distribution coefficient, defined as the concentration of a species sorbed on the solid phase to the concentration of that species in solution at equilibrium.

In this study, \( I^- \) did not reach the ends of the clay plugs within the diffusion period, so the plugs can be considered to be infinite in extent. The appropriate solution to eqn. 1 is then (Crank, 1975),

\[
\frac{c}{c_o} = \frac{1}{2} \operatorname{erfc}\left[\frac{x}{2(Dt)^{1/2}}\right],
\]

subject to the following initial and boundary conditions:

\[
c(x,0) = 0 \text{ for } x > 0 \\
= c_o \text{ for } x \leq 0 \\
\]

and

\[
c(+\infty,t) = 0 \\
c(-\infty,t) = c_o,
\]

where \( c_o \) is the initial bulk concentration of the diffusant in the tagged clay plug.

For the half-cell method, the total quantity of \( ^{125}\text{I} \), \( Q_1 \), that has diffused from the tagged plug across the boundary at \( x = 0 \) (the interface of the two plugs) into the initially untagged plug in time \( t \) is most readily measured. To obtain this quantity, the integral of eqn. 3 is required; this is given by

\[
Q_1 = -DA \int_0^t \frac{\partial c(x,t)}{\partial x} \, dx = A c_o (D t/\pi)^{1/2},
\]

where \( A \) is the cross-sectional area of the clay plug. The total quantity of \( ^{125}\text{I} \), \( Q_t \), in the tagged clay plug at \( t = 0 \) is

\[
Q_t = Ah c_o,
\]

where \( h \) is the length of the clay plug (half-cell). Taking the ratio of \( Q_t/Q_1 = f \), one obtains

\[
f = (D t/\pi h^2)^{1/2}.
\]

Equation 6 is a simplified form of a manipulated solution to eqn. 1 (Crank, 1975). The simplified relation is close to the exact relation when \( f < 0.3 \) (Kemper, 1986), which is the case in this study. An explicit expression for \( D \) is then obtained by rearranging eqn. 6.

**Distribution coefficients**

Distribution coefficients, \( K_d \), for \( I^- \) with the four clays were determined as follows. Five grams of clay were suspended in 10 cm$^3$ of the SGW spiked with \( ^{125}\text{I} \) in 50 cm$^3$ polycarbonate centrifuge tubes. The initial \( ^{125}\text{I} \) concentration was 23 nmol m$^{-3}$—about the same concentration as used in the tagged plugs in the diffusion experiments described above. The tubes were capped, sealed in double polyethylene bags, and then placed in a water bath at 23 ± 0.1°C for 10 days. The tubes were shaken periodically. After the reaction period, the tubes were centrifuged at 5500 g for 10 min. The pH of the supernatant solution was measured with a glass electrode. A 1-cm$^3$ aliquot of the supernatant was withdrawn and added to 18 cm$^3$ of Instagel liquid scintillation cocktail. The activity of \( ^{125}\text{I} \) was measured by liquid scintillation counting (Beckman LS 5801, Beckman Instruments, Inc., Irvine, California). Control experiments, conducted identically but without the clay, showed that no detectable \( I^- \) was sorbed on the centrifuge tubes. Distribution coefficients were calculated from

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

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 (on a mass basis) and \( S_a \) the solution to clay ratio (or the gravimetric moisture content) of the air-dried clay, and \( \rho_w \) the density of the SGW.

**RESULTS**

In this study, \( I^- \) was the initial form of I. Iodide is stable across a wide range of pH and redox potential conditions, and from the data there is no indication that more than one form of I is present. Therefore, in this study \( I^- \) is assumed to be the only form of I.

Typical concentration profiles for \( I^- \) with each of the four clays are shown in Fig. 2; the shape of these profiles is consistent with molecular diffusion as given by Fick’s second law (Oscarson et al., 1992; Robin et al., 1987). All measured \( D \) values, \( D_m \), are given in Table 2. Avonlea bentonite and the illite-smectite clay have the highest \( D_m \) values, and the Lake Agassiz clay the lowest. Consistent with eqn. 2, the \( D_m \) values are inversely related to \( K_d \) (Tables 1 and 2). Diffusion coefficients calculated from eqn. 2, \( D_e \), are compared with \( D_m \) values in Table 2. (In eqn. 2,
**DISCUSSION**

With the exception of the Lake Agassiz clay, the agreement between $D_m$ and $D_c$ is generally good—within a factor of ~2. Good agreement between $D_m$ and $D_c$ values was also found by Robin *et al.* (1987) for Sr$^{2+}$ and by Sharma & Oscarson (1989) for Pu(IV) diffusion in compacted clay-based materials. Thus, the model as given in eqn. 2 is judged to be adequate for predicting $D$ for many diffusants in compacted clays having a broad range of properties.

The reason for the markedly lower $D_m$ value for I$^-$ compared with $D_c$ in the Lake Agassiz clay is not clear. This clay has by far the greatest organic carbon (OC) content (Table 1), and it is possible that I$^-$ diffuses into the OC matrix during the equilibration period. When the two plugs are joined to begin the diffusion process, I$^-$ would first have to diffuse through or out of this matrix and into the pore solution before it could move from the tagged to the untagged plug. If so, the $\tau_a$ value used in eqn. 2 is likely to be much lower than 0.1. This argument is supported by the fact that $D_m$ for I$^-$ in the Lake Agassiz clay as measured by the time-lag technique in a through-diffusion experiment is 28 $\mu$m$^2$ s$^{-1}$ at $\rho = 1.2$ Mg m$^{-3}$ (unpublished data); this value is close to
the $D_s$ value for this clay (Table 2). (See Cho et al. (1993b) for a discussion of the time-lag technique in through-diffusion experiments.) In the time-lag technique, $I^-$ is not in contact with the clay before the diffusion experiments as it is during the equilibration period in the half-cell method. Hence, $I^-$ would not diffuse into the organic matrix of the Lake Agassiz clay to the extent it does in the half-cell method.

For other clays that have been examined, there is generally good agreement between $D_m$ values obtained from the half-cell and time-lag techniques. For example, the $D_m$ value determined from the time-lag technique for $I^-$ is 130 $\mu$m$^2$ s$^{-1}$ in the Avonlea bentonite (Cho et al., 1993b) and 140 $\mu$m$^2$ s$^{-1}$ in the illite-smectite (unpublished data) at $\rho = 1.2$ Mg m$^{-3}$. These values are close to the $D_m$ values obtained from the half-cell method (Table 2).

It appears, then, that the half-cell method as used here is not reliable for obtaining $D_m$ values for $I^-$ in the Lake Agassiz clay. As suggested, this may be due to the comparatively high OC content of this clay. Further diffusion experiments with other clays having high OC contents are required to confirm this hypothesis.

In eqn. 2, the largest source of error is likely to be associated with $K_d$ and $n$. The measurement of $K_d$ values in clay suspensions and their use in mass transport equations have been discussed by many authors, including Robin et al. (1987) and Gillham & Cherry (1982).

In this study, $n$, the total porosity—calculated from the dry bulk density and specific gravity of the clay—was used in eqn. 2. (When the clay is saturated or nearly so, which is the case in this study, $n$ is equal to the volumetric moisture content.) Rather than $n$, an effective porosity, $n_e$, or the porosity available to the diffusant, should be used in eqn. 2. With the exception of the Avonlea bentonite (Oscarson et al., 1992), however, $n_e$ for these clays for $I^-$ diffusion is not known. As $n_e < n$, the use of $n$ rather than $n_e$ in eqn. 2 means $D_s$ is somewhat overestimated, but at most by less than a factor of 5 (Oscarson et al., 1992). Because of the properties of the clays, such as the specific surface area and particle size, the overestimation would probably be greatest for bentonite and lowest for kaolinite.

Another uncertainty associated with the $n$-value is that in the numerator of eqn. 2, $n$ is the transport porosity, whereas in the denominator it is the storage porosity; these porosities are not necessarily the same. The transport porosity is the porosity available for solute transport and occurs only in a fraction of the total pore volume. For example, Oscarson et al. (1992) found that for bentonite at $\rho = 1.3$ Mg m$^{-3}$, $n_e$ for the diffusion of $I^-$ was about 20% of $n$. The storage porosity, on the other hand, is a form of retardation or sorption and may, for example, involve dead-end pores and 'cul-de-sacs.' Most investigators assume that the transport and storage porosities are the same and, hence, eqn. 2 is often given as

$$D = D_s n/[1 + (\rho/n)K_d].$$

The term in the denominator is usually called the retardation factor. Obviously, much more work is required on the porosity of clays and soils and its relation to contaminant transport.

Organic matter is thought to be important in the sorption of $I^-$ by earthen materials (Sheppard & Thibault, 1991 and references therein). Except for kaolinite, there is a trend to increasing $K_d$ values with increasing OC content (Table 1).

The $K_d$ value for $I^-$ with kaolinite is relatively high and yet this clay has the lowest OC content of the clays examined (Table 1). De (1961) reported that kaolinite has a greater sorption capacity for $I^-$ than bentonite and vermiculite, which is consistent with the data reported here. De suggested that the structural hydroxyl groups on the surface of kaolinite particles may play an important role in sorbing $I^-$. Allard et al. (1980) found that the sorption of $I^-$ on clay minerals increases with decreasing pH, probably because of a greater positive surface-charge density on the clay at lower pH values. The lower pH of the kaolinite system could then, at least partially, explain the relatively high $K_d$ values. Couture & Seitz (1983), however, found very little sorption of $I^-$ on kaolinite in the pH range from 4–6.

With regard to containment barriers for wastes that contain $I^-$, the longest transport time would be provided by the Lake Agassiz clay: regardless of the method of measurement, $D$ is lower in this clay than in the other clays examined. This is encouraging as this clay is a component of the reference backfill material in the Canadian disposal concept.

The $D_m$ values for $I^-$ in the Avonlea bentonite and illite-smectite clay are virtually the same (Table 2). The $D_m$ values for Sr$^{2+}$, Ca$^{2+}$ and Na$^+$ are also similar in the two clays (unpublished.
data). This suggests that if a smectite-based barrier material is partially transformed to an illite-smectite mixed-layered material in a hydrothermal environment, such as that of a nuclear fuel waste disposal vault, there would be no adverse effect with respect to mass transport. It is recognized, however, that the fabric of an illite-smectite clay formed from the in situ transformation of smectite may be quite different from the fabric of the compacted clay powder used in this study, and this could affect D. On the other hand, the results of Cho et al. (1993b) suggest that at a given density, clay fabric is probably not an important factor in the diffusion of I\(^{-}\) and Cs\(^{+}\) in compacted bentonite.

ACKNOWLEDGMENTS

Mr H.B. Hume is thanked for his technical assistance. The Canadian Nuclear Fuel Waste Management Program is jointly funded by AECL Research and Ontario Hydro under the auspices of the CANDU Owners Group.

REFERENCES


