

Coupled multi-ion electrodiffusion analysis for clay soils

Christian Jungnickel, David Smith, and Stephen Fityus

Abstract: For a well-engineered compacted clay landfill liner, diffusive transport through the liner is the main mass transport mechanism from the landfill. Therefore, accurate estimates of diffusion coefficients for clay liners are essential for the engineering design of liner systems. A long-standing problem has been the effect of ion pairing on the estimation of diffusion coefficients for multicomponent ionic solutions migrating through clay liners. This paper considers the solution of a fully coupled set of transport equations describing the simultaneous diffusion of several ion species through a clayey soil. The analysis takes into account the diffusion coefficient for each ion species, ion pairing (as required by electroneutrality of the solution), and time-dependent first-order ion and (or) ligand exchange reactions with the clay particles. The behaviour of a double-reservoir diffusion cell, often employed for the estimation of diffusion coefficients in the laboratory, is analyzed using the coupled transport model. A detailed theoretical analysis is made of sodium fluoride transport through saturated kaolinitic clay.

Key words: multi-ion diffusion, finite element analysis, reactive transport, kaolinite, double-reservoir diffusion cell.

Résumé : Dans le cas d'une membrane d'étanchéité en argile ayant été soumise à un bon compactage mécanique pour un site d'enfouissement sanitaire, le transport par diffusion à travers la membrane est le principal mécanisme de transport de masse qui s'échappe du site d'enfouissement. En conséquence, des estimations précises des coefficients de diffusion pour les membranes d'argile sont essentielles pour la conception mécanique des systèmes de membranes. Un problème de longue date est l'effet de couplage d'ions sur l'estimation des coefficients de diffusion pour des solutions à multiples composantes migrant à travers les membranes d'argile. Cet article considère la solution d'un ensemble complètement couplé d'équations de transport décrivant la diffusion simultanée de plusieurs espèces d'ions à travers le sol argileux. L'analyse prend en compte le coefficient de diffusion pour chaque espèce d'ions, pour chaque couplage d'ions (tel que requis pour la neutralité électrolytique de la solution), et pour chaque ion de premier ordre dépendant du temps et (ou) liant les réactions d'échange avec les particules d'argile. Le comportement d'une cellule de diffusion à double réservoir, souvent utilisée pour l'estimation des coefficients de diffusion en laboratoire, est analysé au moyen du modèle de transport couplé. On fait une analyse théorique détaillée du transport de fluorure de sodium à travers l'argile de kaolin saturée.

Mots clés : diffusion de multi-ions, analyse en éléments finis, transport réactif, kaolin, cellule de diffusion à double réservoir.

[Traduit par la Rédaction]

Introduction

The engineering design of compacted clay liners for waste disposal facilities is now established, following intensive research by geoenvironmental engineers over the last 20 years (Day and Daniel 1985; Rowe et al. 1995; August et al. 1997; Shackelford and Rowe 1998). A key design aim is to minimize advective transport of solutes through the compacted clay liner by keeping the leachate mound height small and the permeability of the clay low. When this is successfully achieved, the main mechanism of mass transport from the landfill to the surrounding environment is diffusion of con-

taminants along their chemical potential gradient. For this reason, considerable effort has been devoted to estimating diffusion coefficients for solutes transported through compacted and natural clay soils (e.g., Shackelford and Daniel 1991; Cooke and Fong 1994; Lim et al. 1994; Rowe and Badv 1996; Kau et al. 1999; Rowe 2001).

When attempting to estimate the diffusion coefficients for ions in solution, a fundamental problem is associated with so-called "ion-pairing." Although each individual ion species has its own diffusion coefficient, each species does not diffuse at its own individual rate, as this would lead to significant charge separation. The movement of ions in solution is influenced by electric fields that tend to bring the ions back together so as to ensure local and overall electroneutrality of the solution at all times. The electrical forces tend to slow down the faster ion and speed up the slower ion, and the ion pair moves at some weighted average speed of the individual ions. Nevertheless, the ion with the larger diffusion coefficient tends (on average) to "lead" and the slower ion tends (on average) to "trail" in the ion pair, thereby creating ion-pair dipoles in the solution. It is the summed effect of the

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ion-pair dipoles in the solution that creates the macroscopic “diffusion potential” that may be measured in the solution (Bockris and Reddy 1998). Each individual ion in solution experiences a force due to the diffusion potential, and its transport is modulated accordingly.

Although the theory describing multicomponent ion transport is well established (Cussler 1997), the authors are unaware of this theory being used by researchers in geo-environmental engineering, probably because the theory is significantly more complex than the simple diffusion theory (requiring the solution of a set of coupled partial differential equations). It is common practice for geo-environmental engineers to estimate the diffusion coefficient for each ion in a clay soil using “standard diffusion theory” (that is, using Fick’s first law and ignoring the movement of ions in response to an electric field). This is not usually possible in a standard diffusion reservoir, however. For the diffusion reservoirs used commonly by geo-environmental engineers, diffusion coefficients can only be estimated for a particular ion pair. If the “partner” ion in the ion pair is changed (or if other ions are added to the solution), then a different diffusion coefficient will be estimated.

Often a linear, reversible, equilibrium-controlled reaction between the ions and the clay particles is included in the simplified landfill-liner analysis, using a so-called “partitioning coefficient” (Cussler 1997). A partitioning coefficient effectively introduces a single chemical reaction into the transport equation to model an ion or ligand exchange reaction with the clay particles. In this case, the original ion in an ion pair is substituted for another ion (i.e., the partner ion in the ion pair is changed at some location during its transport through the clay). If this occurs, the diffusion coefficient estimated from a diffusion test depends not only on the total ionic composition of the pore fluid, but also on the type of clay present (e.g., kaolinite or montmorillonite) and the kind of counter-ions maintaining electroneutrality of the clay particles (e.g., sodium, calcium, and magnesium are common counter-ions found in clay soils).

Further, if an external electric field develops across the clay barrier, this will also influence the estimated diffusion coefficient. Together, this means that the diffusion coefficients of the *individual ions* are not being estimated in standard diffusion tests; rather, the back-figured coefficients represent *mass transfer coefficients* for the particular system under investigation. This implies that estimating diffusion coefficients is something of a misnomer. In contrast to the “standard transport analysis” based on standard diffusion theory, which ignores electrical effects on charged solutes, the more rigorous theory to be employed here uses actual diffusion coefficients of the individual ions in the pore fluid and takes into account electrical effects on the charged solutes.

A standard diffusion analysis as employed by geo-environmental engineers to simplify the data analysis creates some uncertainty and a sense of unease about the interpretation of the experimental data for the reasons mentioned previously. Indeed, there are some cases where the standard diffusion analysis simply cannot explain the experimental data (Shackelford and Daniel 1991; Barone et al. 1992). No solution to the dilemma presented by these experimental results has been offered in the geo-environmental literature. Most

engineering researchers respond to the uncertainty in one of two ways. They either (i) state that the diffusion coefficient should be estimated using the particular clay and leachate likely to be encountered at a particular landfill (which is sound advice); or (ii) point to the fact that the estimated diffusion coefficients for different clays do not vary significantly, so even if there is some error introduced by the method of data interpretation, it is unlikely to cause a significant error.

Although it is true that diffusion coefficients for the most commonly encountered ions in saturated clay soils differ by less than two orders of magnitude (and usually less than one order of magnitude), it is clear that there is considerable opportunity for subtlety of behaviour in a complex system such as the one considered here. If possible, it seems prudent to see what insight might be afforded by using a more complete theory of diffusion. It is the primary purpose of this paper to examine the transport of a salt solution through a clay soil using a more rigorous theory of diffusion and to compare the theoretical results of this analysis with the predictions made using the standard diffusion analysis.

To do this, we first describe electrodiffusion theory for multiple ions moving through either a “free” solution or a saturated clay soil. The behaviour of a new finite element implementation of this electrodiffusion theory for a simple diffusion reservoir is verified by comparison with known analytic solutions and a semi-analytic solution using POL-LUTE (Rowe and Booker 1994). Further analysis then focuses on the double-reservoir diffusion cell, often employed for estimating diffusion coefficients in the geo-environmental laboratory (Rowe et al. 1995; Kau et al. 1995; Jungnickel et al. 2001). In particular, the diffusion of sodium fluoride (NaF) through kaolinitic clay is described and analyzed in detail. Account is also taken of a time-dependent first-order interaction of the fluoride with kaolinite, resulting in the release of hydroxyl ions into the pore fluid of the clay.

Although the sodium fluoride – kaolinite system considered here is a relatively simple system compared with the complex multispecies chemistry of a landfill leachate, it is useful in that it allows the subtleties of multi-ion diffusion to be explored without being confused by a multitude of effects. However, the approach described in this paper could readily be extended to consider extended systems where a large number of ionic species are present.

Background

The key equation describing ion transport in the presence of electrochemical forces is the Nernst–Planck equation, that is,

$$[1] \quad f_j^i = -D_j^i \left(c_{,j}^i + c^i z^i \frac{F}{RT} \psi_{,j} \right)$$

where $c_{,j}^i$ and f_j^i are the concentration gradient (mol/(m³·m)) and flux (mol/(m²·s)), respectively, of the *i*th ion in the *j*th direction (c^i is the concentration (mol/m³) of the *i*th ion); D_j^i is the diffusion coefficient (m²/s) of the *i*th ion in the *j*th direction; z^i is the valence of the *i*th ion; $\psi_{,j}$ is the voltage gradient (V/m) in the *j*th direction; F and R are the Faraday

and gas constants, respectively; and T is the absolute temperature (K).

The first term inside the parentheses results in transport of the i th ion species due to the chemical potential gradient (assuming an ideal solution). The second term inside the parentheses results in transport along the voltage gradient, the direction of the transport depending on the charge on the ion (z^i). The Nernst–Planck equation is a generalization of Fick’s law, taking into account electrical effects on charged solutes.

The voltage (ψ) is made up of two distinct parts (which may be simply added together). The first part of the voltage arises from any “external potential” applied to the system, and the second part arises from the potential generated by the different diffusion rates of the diffusing ions. This second potential is known as the diffusion potential.

Now let the superscript 1 refer to a univalent cation (e.g., sodium) and the superscript 2 to a univalent anion (e.g., fluoride) of a strong electrolyte (that is, one that completely dissociates in water). The ionic current (C/s) through the solution is then given by

$$[2] \quad f_j^1 - f_j^2 = I_j$$

where I_j is the ionic current in the j th direction. Substituting the fluxes (i.e., eq. [1]) in eq. [2] and collecting terms leads to

$$[3] \quad I_j = D_j^2 c_{j,j}^2 - D_j^1 c_{j,j}^1 - (D_j^1 c^1 + D_j^2 c^2) F \psi_{,j} / RT$$

Now substituting eq. [3] in eq. [1] (to eliminate the voltage gradient) reveals

$$[4] \quad f_j^i = - \left(\frac{2D_j^1 D_j^2}{D_j^1 + D_j^2} \right) c_{j,j}^i + \left(\frac{D_j^1}{D_j^1 + D_j^2} \right) I_j$$

If the ionic current is taken to be zero (i.e., $I_j = 0$, meaning there is no battery connected to the electrolytic system), eq. [4] indicates

$$[5] \quad f_j^1 = f_j^2 = D_j c_{j,j} = - \left(\frac{2D_j^1 D_j^2}{D_j^1 + D_j^2} \right) c_{j,j} = - \left(\frac{2}{1/D_j^1 + 1/D_j^2} \right) c_{j,j}$$

In other words, the diffusion coefficient for the ion pair is the harmonic mean (and not the average) of the diffusion coefficients of the individual ions. It can be shown that for an electrolytic solution formed from a completely soluble salt with arbitrary valence, the flux is given by (Cussler 1997)

$$[6] \quad f_j^T - D_j c_{j,j} = - \left(\frac{|z^1| + |z^2|}{|z^2| / D_j^1 + |z^1| / D_j^2} \right) c_{j,j}^T$$

where f^T and c^T are the net flux and concentration values of the electrolyte, respectively, given by

$$[7] \quad f^T = f^1 / |z^2| = f^2 / |z^1| \quad \text{and} \quad c^T = c^1 / |z^2| = c^2 / |z^1|$$

For example, if the diffusion coefficient of lanthanum ions (La^{3+}) is $0.62 \times 10^{-9} \text{ m}^2/\text{s}$ and the diffusion coefficient of chloride ions (Cl^-) is $2.03 \times 10^{-9} \text{ m}^2/\text{s}$, then eq. [6] shows the diffusion coefficient for the ionic salt is $1.29 \times 10^{-9} \text{ m}^2/\text{s}$. Alternatively, if the free diffusion coefficients for sodium ions (Na^+) and fluoride ions (F^-) in solution are $1.33 \times 10^{-9} \text{ m}^2/\text{s}$ and $1.47 \times 10^{-9} \text{ m}^2/\text{s}$, respectively, then eq. [5] shows the diffusion coefficient for the ionic salt is $1.395 \times 10^{-9} \text{ m}^2/\text{s}$. In this paper, the theoretical diffusion coefficient for sodium fluoride will be used to verify the new finite element solution for the complete set of equations governing coupled multi-ion reactive transport (CMIRT). These equations are developed in the next section.

Governing equations for coupled multi-ion transport

The key constitutive equation describing macroscale ion transport through an isotropic clay soil in the presence of electrochemical forces is very similar to the Nernst–Planck equation, viz.,

$$[8] \quad f_j^i = -nD^{ei} \left(c_{j,j}^i + \frac{F}{RT} c^i z^i \psi_{,j} \right)$$

where n is the porosity, and D^{ei} is the effective diffusivity of the i th ion in the clay. Two variables contributing to the effective diffusion coefficient in the clay are often identified, namely,

$$[9] \quad D^{ei} = \tau D^i$$

where D^i is the diffusion coefficient of the solute in a free solution², and τ is known as the tortuosity factor for the porous medium³ (Bear 1972; Shackelford and Daniel 1991; Cussler 1997). The tortuosity factor takes into account the indirect transport path of the solute created by a particular spatial arrangement of the particles in the porous medium and by any electrical charge on the particles. The tortuosity factor is clearly a function of the shape and size distribution of the particles, the density of the porous medium, and the charge on the particles.

The constitutive eq. [8] is supplemented by mass conservation equations. Mass conservation for a conservative ion species is expressed by

$$[10] \quad f_{j,j}^i = \frac{\partial c^i}{\partial t} + \frac{\partial s^i}{\partial t}$$

²Free diffusion coefficients are usually tabulated at infinite dilution under standard state conditions. If the conditions within the porous medium are different from the standard conditions (for example, a different temperature), then empirical or theoretical adjustments to the free diffusion coefficient can be made to account for this.

³In general, the tortuosity factor is a second-order tensor, but here it is considered a scalar describing an isotropic medium.

Table 1. Constants used for the CMIRT model and the standard-diffusion model.

Transport parameter	Values used in aqueous regions (free diffusion)	Values used in saturated kaolinite clay
Tortuosity, τ	1.0	0.4
Diffusion rate of fluoride ions, D_F (m ² /s)	1.47×10^{-9}	5.87×10^{-10}
Diffusion rate of sodium ions, D_{Na} (m ² /s)	1.33×10^{-9}	5.32×10^{-10}
Harmonic diffusion rate of NaF, D_{NaF} (m ² /s)	1.40×10^{-9}	5.58×10^{-10}
Diffusion rate of hydroxyl ions, D_{OH} (m ² /s)	5.27×10^{-9}	2.11×10^{-9}
Porosity, n	1.0	0.5
Partitioning coefficient, K_d (L/kg)		36
Ratio of forward to reverse rate constants, $k_f:k_r$ (eq. [14])		396:10
Dry density, ρ_d (g/cm ³)		1.1

where $f_{j,j}^i$ is the divergence of the flux of the i th ion, s^i is a source-sink term (mol/m³), and t is time. In the case of a first-order reversible chemical reaction,

$$[11] \quad \frac{\partial s^i}{\partial t} = k_f^i c^i - k_r^i s^i$$

where k_f^i is the i th forward rate constant (s⁻¹), and k_r^i is the i th reverse rate constant (s⁻¹). It can be shown that the partitioning coefficient K_d (m³/kg) is related to the forward and reverse rate constants by a proportionality constant (namely, the inverse of the dry density, ρ_d (kg/m³)). That is,

$$[12] \quad K_d = \frac{1}{\rho_d} \frac{k_f}{k_r}$$

Substitution of the flux equation in the mass conservation equation leads to the governing differential equation for mass transport. Gauss's electrostatic theorem exerts an important constraint on multi-ion system behaviour, however, by enforcing electroneutrality of the system at all times. Gauss's electrostatic theorem is expressed as

$$[13] \quad (\epsilon_0 \epsilon_w \psi_{,j})_{,j} = F \sum z^i c^i$$

where ϵ_0 is the permittivity of free space (C²/(N·m²)), and ϵ_w is the permittivity of water relative to the permittivity of free space. Of course, this system of simultaneous partial differential equations must be solved subject to appropriate initial and boundary conditions. The initial and boundary conditions are discussed as necessary for the problems analyzed in the next section.

Application of the CMIRT formulation to a real system

The multi-ion transport analysis is applied to a number of idealized (though realistic) examples involving the diffusion of sodium fluoride through both water and saturated kaolinite clay. Kaolinite is a layer silicate mineral, with one tetrahedral sheet linked through oxygens to one octahedral sheet of alumina (it has the chemical formula $Al_8Si_4O_{10}(OH)_8$). The surface of the octahedral sheet is exclusively hydroxyl groups (Velde 1992). The hydroxyl groups may undergo ligand exchange reactions with the fluoride according to



In the context of eq. [14], the forward reaction liberates hydroxyl ions at the expense of fluoride ions, and the reverse reaction would liberate fluoride ions at the expense of hydroxyl ions. This reaction is described for the sorption of fluoride onto alumina (Hao and Huang 1986; Schnoor 1996), and similar reactions are known to take place in kaolinite (Kau 1997), because of the gibbsite surface on kaolinite.

The transport parameters adopted in all examples that follow are shown in Table 1. Free diffusion coefficients for the different ionic species were obtained from Cussler (1997), and other parameters were chosen to be realistic estimates of values based on the available literature for sodium fluoride and kaolinite (e.g., Kau 1997; Kau et al. 1995; Jungnickel et al. 2001). The tortuosity value of 0.4 for sodium fluoride in kaolinite was chosen as a realistic estimate from the work of Kau (1997), where it was back-figured from experimental diffusion test results. The partitioning coefficient for fluoride onto kaolinite was also chosen as a realistic estimate from the results of batch testing by Kau. It is known that the rate of sorption of fluoride onto kaolinite (and alumina) is rapid (of the order of hours). Rate constants were chosen accordingly.

Validation of coupled multi-ion reactive transport solutions for multi-ion diffusion through water

A method for the simultaneous solution of the partial differential equations developed in the preceding section has been formulated using the finite element method. In the following, solutions found using this numerical approach are referred to as CMIRT solutions. As nearly all commercially available contaminant transport codes do not consider ion-pairing and electrical effects, their usefulness in validating the accuracy of the CMIRT solutions is limited. Limited validation of the solutions generated using the finite element method is possible, however.

This may be achieved by employing the diffusion coefficient for the ion pair (i.e., the harmonic mean of the individual diffusion coefficients found in eq. [5]) in a standard diffusion analysis, and comparing this solution to the finite

element solution (for the system of partial differential equations that takes into account electrical effects). This approach is adopted with the commercial contaminant transport code, POLLUTE, which employs a semi-analytic solution technique to model the transport of single ion species through saturated soils.

An assessment of the accuracy of the CMIRT solutions is achieved by considering an aqueous system comprising two connected regions, called region 1 and region 2, each of equal volume. The initial conditions are that region 1 contains a uniform concentration of sodium fluoride (5.30 mol/m^3), and region 2 contains pure water. The boundary conditions are that the system is closed and that the two aqueous regions become connected at time $t = 0$. This simple system is shown schematically in Fig. 1.

One set of solutions to this problem is obtained numerically using the CMIRT approach, in which there is simultaneous diffusion of an anion (i.e., fluoride) and a cation (i.e., sodium). As shown in Table 1, the diffusion coefficients for fluoride and sodium are different. A second set of solutions was obtained using the program POLLUTE, in which the harmonic mean of individual diffusion coefficients was employed in the analysis.

The two numerical solutions are compared in Figs. 2 and 3. Figure 2 presents the time-varying concentration of sodium fluoride at the extreme ends of the system, as indicated by the two “gray points” in Fig. 1. For selected times, Fig. 3 presents profiles of concentration throughout the system.

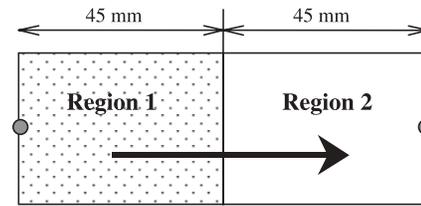
It is evident from the close agreement between solutions shown in both figures that the CMIRT numerical solution is able to accurately model the aqueous diffusion of a simple salt and successfully takes into account the electrical fields created by the anion and cation having different diffusion coefficients. This gives some confidence that the numerical formulation of the set of partial differential equations required for the CMIRT solution is correct. Further verification of the approach by comparison with experimental data is the subject of continuing research.

Application of the CMIRT model to a clay system

The CMIRT solution developed here has many applications in the study and practice of ionic transport processes, particularly if its scope is extended to include transport through porous substrates such as soils. One application, which will be studied here, is in the modelling and interpretation of saturated diffusion tests through clay soils. Such tests are often employed as a means of estimating transport parameters for use in the engineering design of clay barriers for waste disposal landfills.

A typical experimental setup used to estimate the diffusion coefficients of specific ions under saturated conditions is a so-called “double reservoir diffusion apparatus,” which comprises a “source reservoir” (or cell) and a “collector reservoir” (or cell), with a saturated clay plug between the two reservoirs, as shown in Fig. 4.

Fig. 1. Geometry of the two-layer multi-ion diffusion model.



The transport parameters for the system are back-figured by adjusting the parameters in a mathematical model until the theoretical results agree with the data obtained from periodic measurements of the concentrations of the ions in the source and collector reservoirs over time. In other words, the “inverse problem” is solved to estimate the material parameters for the system.

The experimental arrangement shown in Fig. 4 can be idealized as a “three-layer model,” as shown in Fig. 5⁴. Note that for this model, regions 1 and 3 correspond to regions 1 and 2 of Fig. 1, and region 2 now contains the saturated clay plug.

In the clay, the free diffusion coefficients will be modified by a tortuosity factor (eq. [9]) and by other soil-specific parameters including the porosity, dry density, and partitioning coefficient (if sorption occurs; eq. [12]). The parameters shown in Table 1 are used for the analyses that follow.

Figures 6 and 7 present the results of a CMIRT analysis of NaF diffusion through a 10 mm thick plug of saturated kaolinite. This analysis includes a ligand exchange reaction (i.e., the fluoride ion replaces the hydroxyl group as shown in eq. [14]). In other words, this analysis takes account of both the partitioning of fluoride onto the clay and the desorption of hydroxyl from the clay. Therefore, this analysis requires the simultaneous diffusion of three ion species, namely, sodium (Na^+), fluoride (F^-), and hydroxyl (OH^-) ions.

The initial condition has sodium fluoride at a concentration 5.30 mol/m^3 in region 1 (i.e., in the source reservoir) and no sodium fluoride in regions 2 and 3 (that is, the clay plug and the collector reservoir have zero concentration of sodium fluoride). The pH of the system is initially taken to be neutral. Because the concentration of hydroxyl ions is very small relative to other ion concentrations in the system (approximately four orders of magnitude less), the initial concentration of hydroxyl ions is approximated as zero. The boundary conditions simulate a closed system.

Figure 6 presents the time-dependent variation in the three ionic species in both the source and collector cells, as predicted by the CMIRT analysis. Most importantly, Fig. 6 facilitates a check on the validity of the CMIRT results. The results in Fig. 6 demonstrate the key feature of coupled ion diffusion, namely that at all times the net ionic charge in both the source and collector regions is balanced. In other words, the total concentration of cations (i.e., sodium ions) is equal to the total concentration of anions (i.e., the sum of the concentrations of the fluoride and hydroxyl ions) at all times and for all spatial locations. This is the necessary outcome of the electroneutrality condition in the governing dif-

⁴In fact, the arrangement shown in Fig. 4 is a one-dimensional problem and could be represented schematically as three lines, but a two-dimensional representation of the experimental apparatus is maintained for clarity.

Fig. 2. Comparison of boundary concentration variations using the CMIRT numeric solution and the semi-analytic POLLUTE solution for sodium fluoride diffusion in a simple aqueous system.

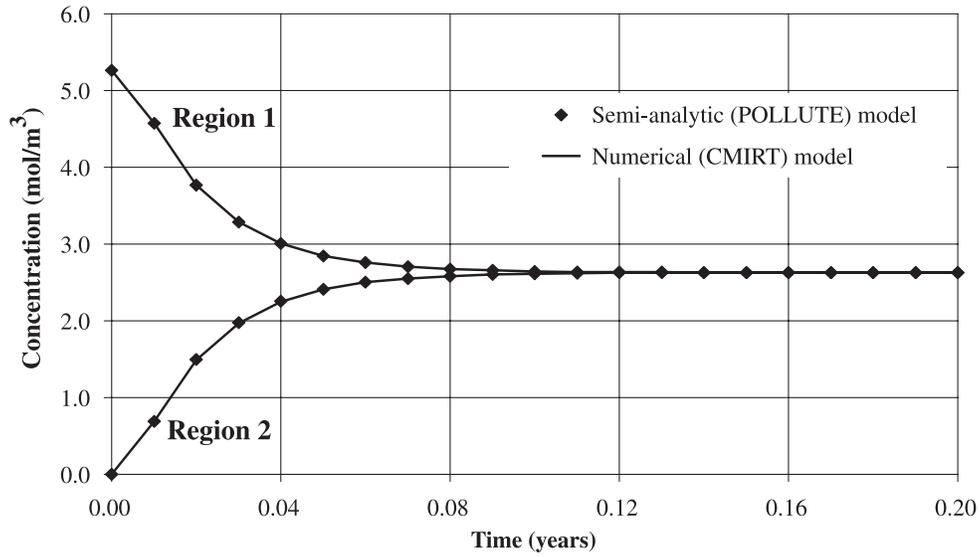


Fig. 3. Comparison of transient concentration profiles using the CMIRT numeric solution and the semi-analytic POLLUTE solution for sodium fluoride diffusion in a simple aqueous system. Time increments of 0.0, 0.01, 0.05, and 0.2 years are plotted.

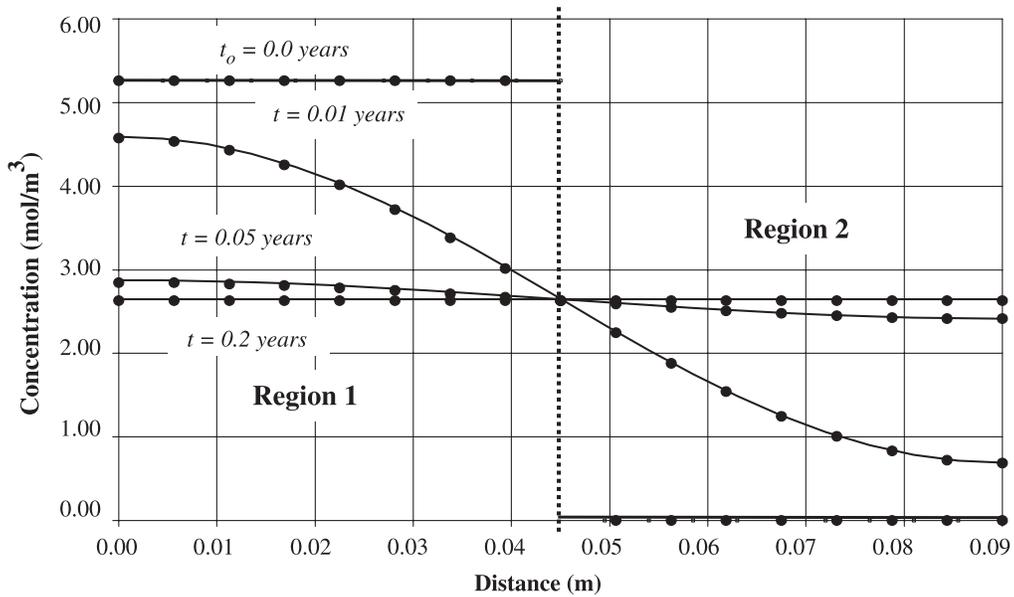


Fig. 4. Apparatus used in experimental determination of diffusion coefficients (Jungnickel et al. 2001).

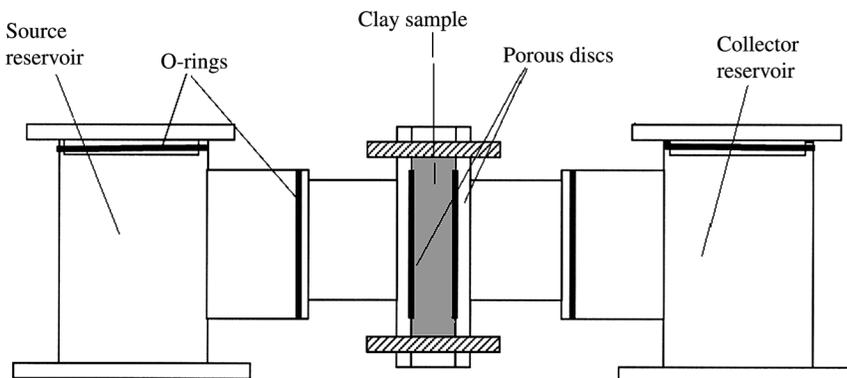
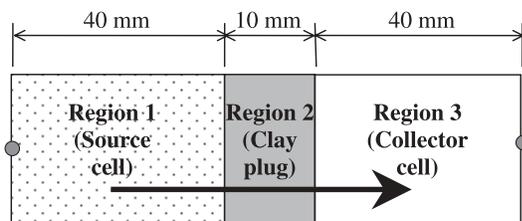


Fig. 5. Geometry of the three-layer multi-ion diffusion model. Region 1 has an initial concentration distributed evenly throughout the region. Regions 1 and 3 are aqueous reservoirs (cells). Region 2 consists of saturated clay. The extremities of the system are zero flux boundaries.



ferential equations which states that the net charge in each reservoir remains zero.

As expected, the sodium and fluoride ion concentrations in the source reservoir decrease over time, but it is seen that the fluoride concentration decreases much more rapidly than the sodium concentration. This behaviour is not consistent with a general expectation that sodium fluoride should migrate uniformly within the system and that both ions should redistribute within the system at similar rates. Further, this behaviour cannot successfully be predicted using simple diffusion models and is only possible if another ion appears in the system to maintain overall electroneutrality. Both sodium and fluoride ion concentrations in the collector reservoir increase over time, but the sodium ions appear first and rise to a much higher concentration than the fluoride ion concentration. These behaviours are observed because fluoride is permanently sorbed onto the kaolinite clay.

The results in Fig. 6 indicate that the hydroxyl ions, liberated through the reaction of fluoride with the clay, appear in both the source and collector reservoirs soon after the commencement of diffusion. The hydroxyl ions appear first in the source reservoir and soon after in the collector reservoir. The hydroxyl ions appear a little before the fluoride ions appear in the collector reservoir. The hydroxyl ions are generated at the site of the clay–fluoride interaction (they enter as a source term in the governing differential equation) and then diffuse along their electrochemical gradient in both directions.

Further insight into the behaviour of the coupled multi-ion reactive transport can be gained from the consideration of the spatial concentration profiles within the system at successive time intervals (Fig. 7). In Fig. 7a, with increasing time, the sodium ion concentration tends to a uniform value of 2.45 mol/m^3 , which is just less than half of the starting concentration of 5.30 mol/m^3 in region 1. This is consistent with the total moles of sodium in the system being conserved and by taking into account the porosity of the clay.

The profiles of fluoride ion concentration (Fig. 7b) show the fluoride concentration falling in region 1 at a much faster rate than it rises in region 2, as is expected for a system where fluoride is sorbing onto the clay. With increasing time, the concentration tends to a uniform value of 0.45 mol/m^3 , which is greatly reduced from the starting concentration of 5.30 mol/m^3 in region 1. Again, the total mass of fluoride is conserved when account is taken of both the sorbed mass and the solution mass.

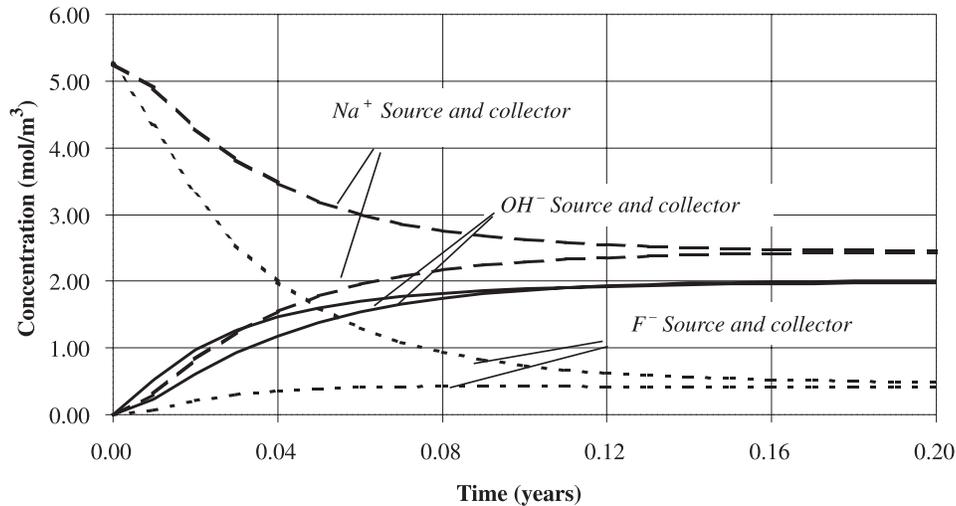
The profiles of hydroxyl ion concentration (Fig. 7c) show the hydroxyl concentration simultaneously increasing from zero in both region 1 and region 2, although slightly sooner in region 1. This is expected, since the first hydroxyl ions are liberated from the clay immediately adjacent to region 1. With increasing time, the concentration tends to a uniform value of 2.00 mol/m^3 . This is consistent with the mass of fluoride sorbed. It is noted that the concentration profiles of the hydroxyl ions are relatively “flat” compared to those of sodium and fluoride. The explanation for this is the relatively large diffusion coefficient for hydroxyl ions compared with those for the other species (the diffusion coefficient for hydroxyl ions is roughly four times greater than that for sodium), keeping the concentration gradients smaller. Again, it can be confirmed that at any spatial point in the diffusion cell and for any time interval, summing the concentrations of cations and anions shows that electroneutrality is satisfied.

The participation of the hydroxyl ions in the diffusion of sodium fluoride salt considerably complicates any consideration of the transport of the sodium and fluoride ions in the system. This is because there is diffusion of the hydroxyl ions along their electrochemical gradient from their site of production in the clay plug, back into region 1. This results in the migration of hydroxyl ions in a direction opposite (i.e., from region 2 back into region 1) to the direction of movement of the sodium and fluoride ions (i.e., from region 1 into region 2 and then into region 3). Since electroneutrality has to be preserved (i.e., ions move as ion pairs), the movement of hydroxyl ions into the source reservoir should be accompanied by a similar movement of sodium ions, and this suggests that the diffusion of sodium out of region 1 would be retarded.

The quantitative evaluation of this effect is made difficult, however, by the different diffusion rates of the hydroxyl and fluoride counter-ions. The effective diffusion coefficient of fluoride is $5.87 \times 10^{-10} \text{ m}^2/\text{s}$, whereas the effective diffusion coefficient of hydroxyl is considerably greater at $21.10 \times 10^{-10} \text{ m}^2/\text{s}$. The effective diffusion rate of sodium is similar to that of fluoride, and so when it moves as an ion pair with fluoride the harmonic mean diffusion rate is of a similar magnitude to the diffusion rate of each of the ions ($D_{\text{NaF}} = 5.07 \times 10^{-10} \text{ m}^2/\text{s}$). When the fluoride ion is exchanged for a hydroxyl ion, however, and the sodium and hydroxyl ions travel as an ion pair, their harmonic mean diffusion rate is considerably greater ($D_{\text{NaOH}} = 8.49 \times 10^{-10} \text{ m}^2/\text{s}$), and so sodium transport is hastened. Thus, the effects of the hydroxyl ions are both to slow the transport of sodium by forcing it to flow from the clay plug, back toward region 1, and at the same time to accelerate the transport of sodium by providing a more mobile ion pair partner for diffusion from the clay plug toward region 3. The net effect of these behaviours is apparent a priori but can be examined by considering the following three special situations:

- (1) An analysis of a system in which only *sodium and fluoride* ions are present, and in which there is no reaction between either of these ions with the clay (i.e., zero fluoride sorption) — This will allow the rate of sodium transport to be assessed for simple pairing with fluoride. This puts a “lower bound” on the likely system behaviour.

Fig. 6. Time-dependent reactive diffusion curves of NaF migration through kaolinite clay as predicted by the CMIRT model.



- (2) An analysis of a system in which only sodium and hydroxyl ions are present and in which there is no reaction between either of these ions and the clay — This will allow the increase in the rate of sodium transport to be assessed for simple pairing with hydroxyl, by avoiding any counter-flow effects from hydroxyl diffusing into region 1 from the clay. This puts an “upper bound” on the likely system behaviour.
- (3) The CMIRT results for sodium transport with fluoride sorption, as presented in Fig. 6 — This gives an accurate estimate of coupled transport, including the influence of ligand exchange. It would be expected that the results for this analysis lie somewhere between the upper and lower bounds for the first and second special cases.

The results of these analyses are shown in Fig. 8.

It is immediately clear that when the results of sodium transport in special situations 1 and 2 are compared, it is apparent that the sodium transport with the hydroxyl partner ion is considerably faster than that with the fluoride partner ion.

When the CMIRT results are considered, it is apparent that they are very similar, although different, to the results for simple nonreactive transport of sodium with fluoride. When reactive transport takes place (i.e., dotted lines in Fig. 8), the sodium disappears from region 1 slightly more slowly than special case 1 but appears in region 3 slightly more quickly (which is consistent with both of the effects due to the hydroxyl ions, as discussed previously).

The similarity between the reactive and nonreactive sodium fluoride diffusion cases suggests that the opposing effects of the hydroxyl ions (that is, acting both to retard and hasten sodium transport) are of similar magnitude and that they effectively “cancel each other out.” Further, it suggests that for this simple case the sodium transport in a reactive sodium fluoride – clay system could be successfully modelled using the single ion, semi-analytic approach of POLLUTE, using the harmonic mean for sodium and fluoride, without significant error. This would not be known a priori,

however (i.e., without having done the complete CMIRT analysis).

Comparison of CMIRT model to standard diffusion model

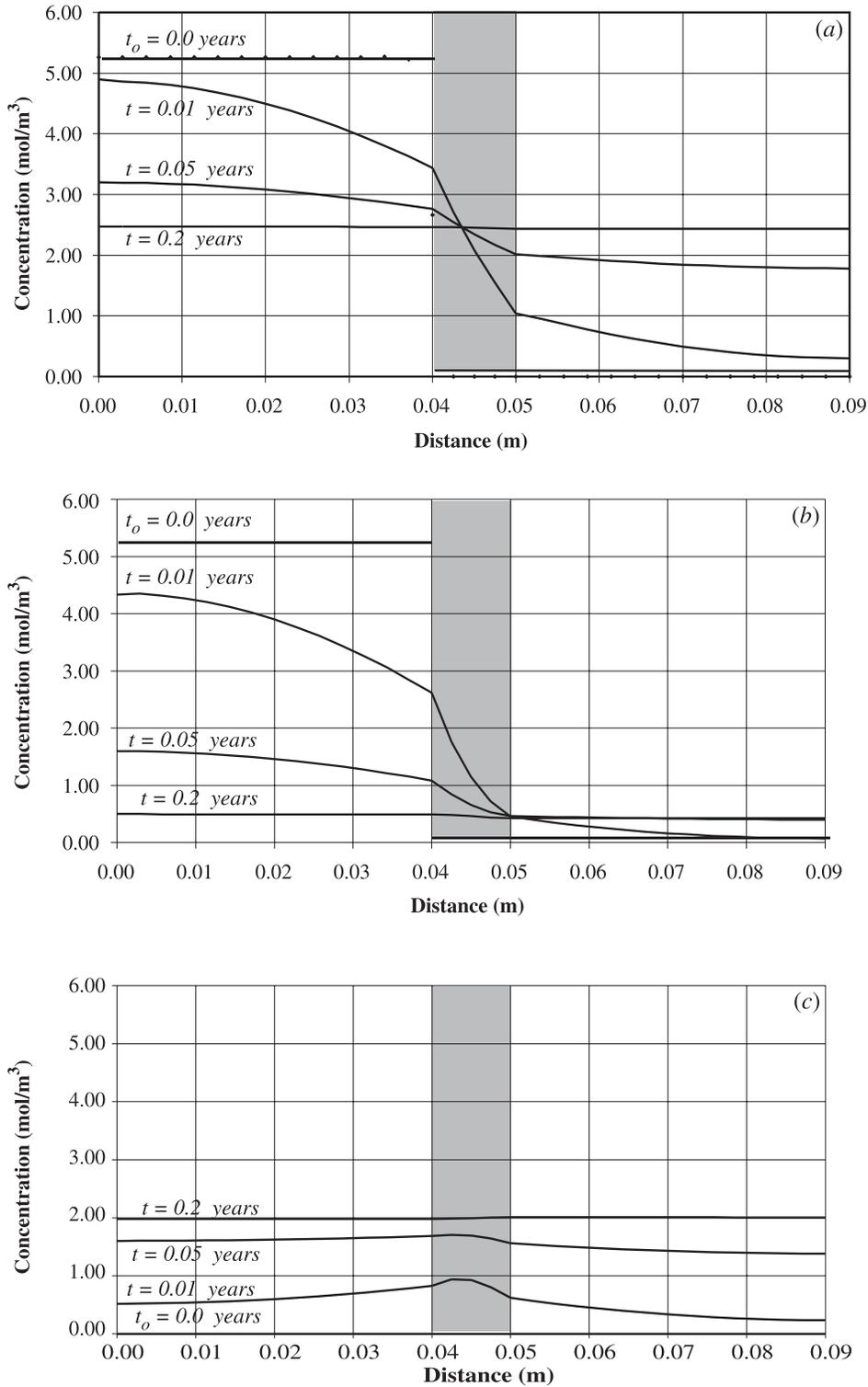
The results in the previous section suggest that a standard diffusion model such as POLLUTE might be employed to back-figure accurate mass transfer rates of particular ionic species from the experimental results of diffusion tests as illustrated in Fig. 4. The use of such a method to interpret experimental data on diffusion is commonplace, with each individual ionic species being considered separately (Rowe 2001).

In this section, the validity of the usual interpretation method is tested. The following approach is used:

- (1) A set of realistic, though approximate, reactive transport parameters for NaF are chosen from typical values in the literature. These are presented in the last column of Table 1.
- (2) The values from step 1 were employed in the CMIRT solution method to predict a realistic, though approximate, set of diffusion results for the experimental setup shown in Fig. 4. These numerical predictions (shown as points in Fig. 9) are now considered to represent a set of synthetic experimental readings.
- (3) The diffusive and reactive transport parameters are then back-figured from the simulated synthetic experimental results using POLLUTE (i.e., by using a trial and error selection of the transport parameters to generate POLLUTE transport curves, until the agreement between the two sets of results was optimized). The best-fit solutions that could be generated using POLLUTE are shown as continuous curves in Fig. 9.
- (4) The back-figured parameters are then compared with the actual parameters employed to generate the synthetic experimental results.

The parameter estimates using POLLUTE were optimized separately for sodium and fluoride. The CMIRT solutions,

Fig. 7. Concentration profiles for (a) sodium, (b) fluoride, and (c) hydroxyl ions.



and the best-fit POLLUTE approximation to them, are shown in Fig. 9. The parameters back-figured from POLLUTE are compared with those used to generate the CMIRT solutions in Table 2.

From a consideration of Fig. 9, the sodium concentration curves obtained from POLLUTE show a reasonably good agreement with the results of the CMIRT model (as might be

expected from the findings presented in the previous section). The estimated sodium diffusion coefficient ($5.07 \times 10^{-10} \text{ m}^2/\text{s}$) was only slightly smaller than the actual diffusion coefficient ($5.32 \times 10^{-10} \text{ m}^2/\text{s}$) employed in the CMIRT analysis.

The fluoride curves in Fig. 9 show a poorer agreement, with the fitted POLLUTE results lying below the synthetic

Fig. 8. Sodium diffusion results with varying counter-ion behaviour.

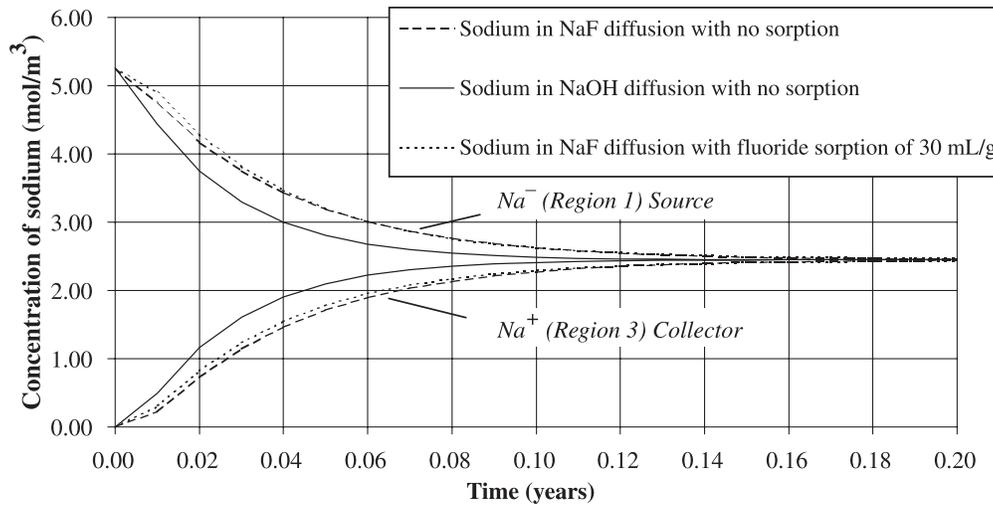


Fig. 9. Comparison of POLLUTE results using back-figured parameters to give an optimized agreement with predictions made using the CMIRT model.

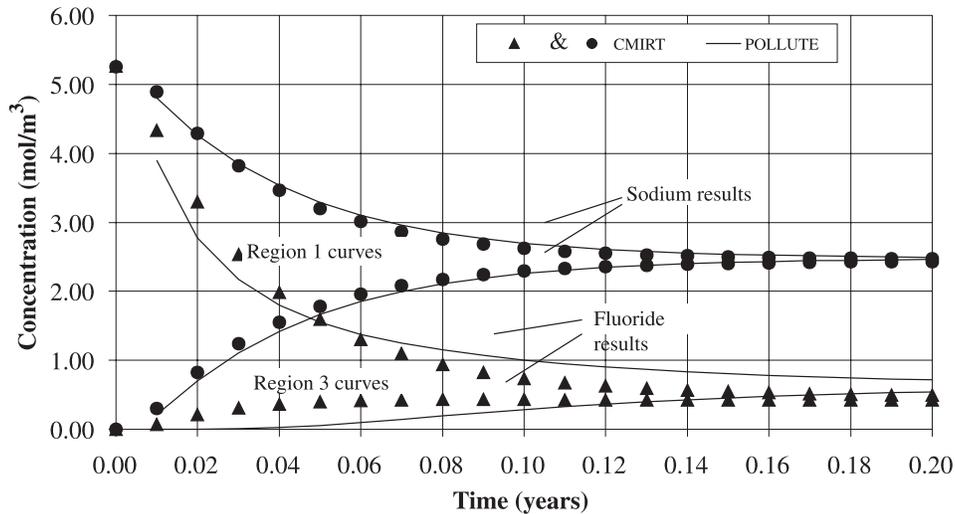


Table 2. Comparison of the parameters used to generate the CMIRT results and those back-figured from the CMIRT results using POLLUTE.

Constants used in numerical modelling	Values used in CMIRT clay region	Values used in POLLUTE clay region	Fitted values from POLLUTE clay region
Tortuosity, τ	0.4	0.4	
Diffusion rate of fluoride ions, D_F (m ² /s)	5.87×10^{-10}		3.81×10^{-10}
Diffusion rate of sodium ions, D_{Na} (m ² /s)	5.32×10^{-10}		5.07×10^{-10}
Porosity, n	0.5	0.5	
Partitioning coefficient, K_d (L/kg)	36		24
Ratio of forward to reverse rate constants, $k_f:k_r$	396:10	na	
Dry density, ρ_d (g/cm ³)	1.1	1.1	

Note: na, not applicable.

experimental results at early times and above at later times. Any attempt to adjust the transport parameters for fluoride in the POLLUTE analysis (that is, by adjusting the diffusion coefficient and the partitioning coefficient) will cause the

agreement to improve in some areas and become worse in others. In fact, the two sets of results have a fundamentally different curve shape, with the fluoride concentrations in POLLUTE decreasing more rapidly at early times and more

slowly at later times. There is no combination of diffusion rate and partitioning coefficient that will allow the POLLUTE results for fluoride to accurately emulate the curve shape of the synthetic experimental results (i.e., the CMIRT solution for fluoride).

The best-fit curve for fluoride resulted in an estimated diffusion coefficient of 3.81×10^{-10} m²/s, which is only two thirds that of the actual diffusion coefficient (5.87×10^{-10} m²/s). Further, the best-fit curve for fluoride resulted in an estimated partitioning coefficient of 24 L/kg, again only two-thirds of the actual partitioning coefficient (36 L/kg).

The findings of this theoretical analysis for a realistic problem suggest that in a multi-ion reactive transport system, parameter estimates based on the standard diffusion equation for a single ion can give inaccurate estimates of actual transport parameters. The estimated transport parameters are system specific and need to be treated with caution when employed to estimate the behaviour of another system.

Implicit in any conclusions drawn from these results is the assumption that the CMIRT predictions are more accurate than the POLLUTE predictions. Although as yet no experimental comparison has been achieved to test this assumption, the importance of electrochemical phenomena in reactive diffusion processes of charged species is well recognized in the literature (e.g., Newman 1991; Cussler 1997), and so is a logical progression in model accuracy and sophistication.

Conclusions

The movement of ions through clay soils is controlled by their electrochemical gradient (i.e., controlled by both concentration gradients and by any electric field present). It is common in geoenvironmental engineering practice to model diffusion processes in multi-ion systems in clay soil by modelling the transport for each ion separately and employing a model based on simple diffusion theory to do this (that is, ignoring the movement of ions in response to an electric field by assuming that Fick's first law is an adequate constitutive relation). By employing a finite element solution for the complete set of equations governing coupled multi-ion reactive transport, the examples presented here demonstrate that not accounting for charge effects can lead to inaccurate estimates of system parameters. The fundamental reason leading to inaccurate estimates is that account is not taken of electrical forces on the ions in a standard diffusion analysis.

Inaccurate parameter estimates are particularly likely to occur for reactive transport problems where one or more ions are partitioned onto the clay soil particles by an ion and (or) ligand exchange reaction. In this case, the original ion in an ion pair is substituted for another ion (i.e., the partner ion in the ion pair is changed at some location during the transport through the clay). In this case, the diffusion coefficient estimated from a standard diffusion test depends not only on the total ionic composition of the pore fluid, but also on transport reaction.

An important consequence of this is demonstrated by the example problem for the synthetic experimental tests results generated by the CMIRT analysis. In the case of nonreactive transport (in the absence of external electric fields), diffusion coefficients could be accurately estimated. In the case

of reactive transport, a very different diffusion coefficient was estimated when compared with the actual diffusion coefficient employed in the CMIRT analysis. In summary, this means that the diffusion coefficients back-figured from a standard diffusion analysis are not the actual diffusion coefficients of the individual ions, rather the back-figured coefficients represent system-specific mass transfer coefficients and should only be extrapolated to new systems with caution.

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