

Fickian diffusion of radionuclides for engineered containment barriers: Diffusion coefficients, porosities, and complicating issues

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ABSTRACT

A review of the literature was undertaken primarily with the goal of discerning the types of diffusion coefficients that have been reported with respect to diffusion of radionuclides through engineered containment barriers. Although the nomenclature and form for diffusion coefficients in porous media vary widely, the review identified four definitions of diffusion coefficients, viz., D^* , D_e , D_p , and D_a , which differ on the basis of the forms of Fick's first and second laws for governing macroscopic diffusion through porous media. All forms of Fick's first law for diffusive mass flux include an effective porosity, ε_{eff} , whether this term is shown explicitly in Fick's first law or is buried within the definition of the diffusion coefficient. The relative magnitudes of the different diffusion coefficients are shown to vary depending on whether the diffusing radionuclide is nonadsorbing (tracer) or adsorbing, and for adsorbing radionuclides, vary as a function of the relative magnitude between the total porosity, ε , and the inverse of the retardation factor, R_d^{-1} . In addition to ε_{eff} and ε , a diffusion accessible porosity, ε_{diff} , that takes into account the possibility of diffusion into dead-end pores also has been identified. The three porosity terms vary as $\varepsilon_{eff} \leq \varepsilon_{diff} \leq \varepsilon$, although there can be more than one value of ε_{diff} depending on the species of radionuclide. The value of ε_{diff} for a non-charged tracer, such as tritium (HTO), generally is found to be the same as ε , whereas the values of ε_{diff} for anionic radionuclides (e.g., $^{36}\text{Cl}^-$) generally are lower than ε due to anionic repulsion and/or steric hindrance. The common assumption that ε_{diff} for a given chemical species is the same as ε_{eff} is shown conceptually to not necessarily always be valid. Finally, three potentially significant complicating issues were identified, viz., the geochemistry of the barrier system, the influence of surface and/or interlayer diffusion, and the existence of semipermeable membrane behavior as a result of anion exclusion. Each of these issues is described in detail. Overall, the review provides a basis for identifying the factors that need to be addressed in terms of studies that focus on the diffusion of radionuclides through engineered barriers used for radioactive waste containment.

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1. Introduction

Diffusion of chemical species is known to be a significant, if not dominant, transport process in porous media where hydraulically driven transport (advection) is relatively minor. Since a primary goal in using engineered barriers in waste containment applications (e.g., high and low level radioactive waste disposal) is to prevent or otherwise minimize advective transport of potentially harmful chemical species (i.e., contaminants), diffusion can be expected to be a principal transport process through such barriers (e.g., Goodall and Quigley, 1977; Crooks and Quigley, 1984; Shackelford, 1988a; Johnson et al., 1989; Shackelford, 1989). As a result, there is a need to establish a basis for the factors affecting diffusive migration of contaminants through engineered containment barriers.

In this regard, there is an overwhelming abundance of published studies on diffusion of radionuclides through highly compacted bentonites being considered as buffer barriers in high-level radioactive waste (HLRW) disposal scenarios. In fact, there has been a virtual explosion of publications on this topic over the past approximate decade (e.g., García-Gutiérrez et al., 2001; Kozai et al., 2001; Kozaki et al., 2001; Tachi et al., 2001; Tsai et al., 2001; Jansson, 2002; Molera and Eriksen, 2002; Szántó et al., 2002; Cormenzana et al., 2003; Molera et al., 2003; Sato and Suzuki, 2003; Wersin, 2003; Fernandez et al., 2004; García-Gutiérrez et al., 2004a,b; Melkior et al., 2004; Sato and Miyamoto, 2004; Wang and Liu, 2004; Wang et al., 2004; Montes-H et al., 2005; Wang et al., 2005a,b; Xia et al., 2005; García-Gutiérrez et al., 2006; Ochs et al., 2006; Vopalka et al., 2006; Glaus et al., 2007; Van Loon et al., 2007; Wersin et al., 2007; Yamaguchi et al., 2007; González Sánchez et al., 2008; Higashihara et al., 2008; Kozaki et al., 2008; Sato, 2008; Alonso et al., 2009; Birgersson and Karnland, 2009; Melkior et al., 2009; Fernandez et al., 2010; Glaus et al., 2010, 2011). The high number of publications in this area reflects the continuing emphasis placed on need for safe and secure long-term disposal of HLRW resulting from the significant role of nuclear energy in several countries (e.g., Belgium, Canada, France, Japan, Spain, Switzerland, the United Kingdom, and the United States). In contrast, the number of studies related to radionuclide diffusion through other types of engineered containment barriers, such as compacted clay liners (CCLs), geosynthetic clay liners (GCLs), and in situ soil–bentonite (SB) and cement–bentonite (CB) vertical cutoff walls commonly used in the disposal of low level radioactive waste (LLRW) pales in comparison. As a result, the U.S. Department of Energy has undertaken an initiative to evaluate the state of the art with respect to containment barrier technologies that are suitable for containment of LLRW, with a goal of identifying future research efforts with respect to such containment barriers.

This particular review is the first in a series devoted towards providing the background necessary to pursue advances in research aimed at characterizing the diffusion of radionuclides through engineered containment barriers commonly used in LLRW disposal. The primary focus of this review was on establishing a basis for Fickian diffusion through engineered containment barriers and identifying potentially complicating issues that may confound interpretation of such diffusion. The influence of the type of porosity of the porous medium was identified as a significant factor potentially affecting both the diffusive mass flux and the rate of migration of radionuclides, and three complicating issues were identified as being potentially significant, viz., the effects of geochemistry on the diffusion of radionuclides, the potential for surface and/or interlayer diffusion of cations being more dominant than

pore-water diffusion of anions, and the potential existence of semipermeable membrane behavior in bentonite based barriers. Subsequent reviews will elucidate the various methods for measuring diffusion coefficients of radionuclides, and will provide a comprehensive comparison of the diffusion coefficients of a wide variety of radionuclides with respect to a range of containment barrier materials, including concrete (e.g., Albinsson et al., 1996).

2. Fickian diffusion

2.1. Fickian diffusion in aqueous solution

Diffusion is a fundamental, irreversible process whereby matter is transported spontaneously from one part of a system to another part as the result of random molecular motions (Robinson and Stokes, 1959; Crank, 1975). These random molecular motions result in the net transport of a chemical species (e.g., ion, molecule, compound, radionuclide, etc.) from a region of higher chemical potential to a region of lower chemical potential. Since chemical potential is directly related to chemical concentration, diffusion is more conveniently described as the net transport of a chemical species due to a gradient in the concentration of the chemical species.

The mass flux of a chemical species in aqueous solution due to diffusion can be described by Fick's first law, which for one-dimensional diffusion may be written as follows (e.g. Shackelford and Daniel, 1991):

$$J_d = -D_o \frac{\partial C}{\partial x} \quad (1)$$

where J_d is the diffusive mass flux, or the rate of change in mass of the chemical species per unit cross-sectional area perpendicular to the direction of transport [$\text{ML}^{-2}\text{T}^{-1}$; M = units of mass, L = units of length, and T = units of time], C is the aqueous-phase concentration of the chemical species [ML^{-3}], x is the direction of transport [L], and D_o (sometimes designated as D_w , where the subscript refers to "water") is the coefficient of diffusion for the chemical species in aqueous solution [L^2T^{-1}], also commonly known as the *aqueous-phase* or *free-solution diffusion coefficient*, where the latter terminology refers to the absence of a porous medium. The negative sign in Eq. (1) is required because diffusion occurs in the direction of decreasing concentration, such that the diffusive mass flux will be a positive quantity when the direction of diffusion assumed is correct and strict mathematical sign convention is followed. The free-solution diffusion coefficient represents the primary parameter governing diffusion of a chemical species in aqueous solution (solutes), and is affected fundamentally by a number of factors, including the temperature, viscosity, and dielectric constant of the solution, the radius and valence of the solute, the requirement for electrical neutrality among all chemical species in solution, the degree of association or dissociation of the solute, and the concentration of the solute (Quigley et al., 1987; Shackelford, 1988b; Shackelford and Daniel, 1991). A detailed evaluation of each of these factors is beyond the scope of this presentation, but can be found elsewhere (e.g., Li and Gregory, 1974; Shackelford, 1988b; Shackelford and Daniel, 1991).

Fick's second law, which describes the temporal concentration distribution due to diffusion, results when Fick's first law is combined

with the conservation of mass. For diffusion in one direction (e.g., the x direction), Fick's second law for diffusion in aqueous solution may be written as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_o \frac{\partial C}{\partial x} \right). \quad (2)$$

If D_o is further assumed to be independent of the position of transport, then Eq. (2) can be reduced further as follows:

$$\frac{\partial C}{\partial t} = D_o \frac{\partial^2 C}{\partial x^2}. \quad (3)$$

Eq. (3) is the most common form of Fick's second law governing one-dimensional transient diffusion of chemical species in aqueous solution.

If the chemical species is radioactive and undergoes first-order decay, then Eq. (3) must be modified to take into account the effect of this decay on the temporal distribution of the chemical species, as follows:

$$\frac{\partial C}{\partial t} = D_o \frac{\partial^2 C}{\partial x^2} - \lambda C \quad (4)$$

where λ [T^{-1}] is the decay constant for the specific radionuclide, which is related to the radionuclide half-life, $t_{0.5}$ [T], through the relationship $\lambda = 0.693/t_{0.5}$ (e.g., Shackelford, 1993).

2.2. Fickian diffusion in porous media

The inclusion of a porous medium affects the forms of Fick's first and second laws for diffusion of chemical species in aqueous solution in two general ways (Shackelford and Daniel, 1991). First, the existence of the solid particles comprising the porous medium results in diffusion pathways that are more tortuous (i.e., meandering) than those that exist in absence of the porous medium. This increased tortuosity reduces the macroscopic concentration gradient (i.e., increases the distance over which the concentration difference is applied) and, therefore, reduces the diffusive mass flux relative to that which would exist in the absence of the porous medium. Also, since chemical species cannot migrate through the solid (crystalline) particles, the cross-sectional area through which diffusive mass flux can occur is reduced relative to the macroscopic, total cross-sectional area. Therefore, the diffusive mass flux in the presence of a porous medium also is reduced relative to that existing in the absence of the porous medium. Second, there may be interactions between the diffusing chemical species and the solid porous media that either directly affect the mass of diffusing species in aqueous solution (e.g., sorption) and/or result in physico-chemico interactions that affect the tortuosity (e.g., semipermeable membrane behavior; see Malusis and Shackelford, 2002a).

2.3. Fick's first law for diffusion in porous media

The previously described differences between diffusion in free or aqueous solution (i.e., in the absence of a porous medium) versus diffusion in porous media can be taken into account by modifying Eq. (1) as follows (Shackelford and Daniel, 1991):

$$J_d = -\theta \tau_m D_o \frac{\partial C}{\partial x} \quad (5)$$

where θ is the *volumetric moisture (water) content*, or volume of water per unit total volume of porous medium, and τ_m is the *geometric or matrix tortuosity factor* defined as follows:

$$\tau_m = \Lambda^2 \quad (6)$$

where Λ is the *tortuosity* defined as follows:

$$\Lambda = \frac{L}{L_e}, \quad (7)$$

L is the straight-line, macroscopic distance between two points within a porous medium, and L_e is the effective or actual, microscopic distance between the same two points. Thus, since $0 < L \leq L_e$, $\tau_m \leq 1$. As noted, the tortuosity factor given by Eq. (6) represents the square of the tortuosity given by Eq. (7) to account for the reduction in the macroscopic concentration gradient and to correct for the non-parallel direction of the actual pathways through which the chemical species must diffuse (e.g., Porter et al., 1960).

The definitions of the tortuosity factor and tortuosity given by Eqs. (6) and (7), respectively, are those typically adopted in the soil science literature (e.g., Porter et al., 1960; Nielsen et al., 1972). In the geological sciences, the tortuosity commonly has been defined as the inverse of Eq. (7) (e.g., Wyllie and Spangler, 1952; Li and Gregory, 1974), such that the tortuosity factor, T_m , is defined as follows (Shackelford and Daniel, 1991):

$$T_m = \left(\frac{1}{\Lambda} \right)^2 = \left(\frac{L_e}{L} \right)^2. \quad (8)$$

When the tortuosity factor is defined by Eq. (8), Fick's first law for one-dimensional diffusion in a porous medium must be written as follows:

$$J_d = -\frac{\theta D_o}{T_m} \frac{\partial C}{\partial x} \quad (9)$$

which results in the same diffusive mass flux as given by Eq. (5). However, since $0 < L \leq L_e$, $T_m \geq 1$. Thus, although the upper limit on τ_m is constrained at unity (i.e., $0 \leq \tau_m \leq 1$), the upper limit on T_m is unconstrained ($1 \leq T_m \leq \infty$).

In general, the volumetric water content is related to the degree of water saturation, S , as follows:

$$\theta = \varepsilon S \quad (10)$$

where ε is the porosity of the porous medium (typically designated by n in the geotechnical engineering literature and by ϕ in the groundwater literature), defined as the volume of voids per unit total volume of porous medium, and S is defined as the volume of water per unit volume of voids ($0 \leq S \leq 1$). Thus, Eqs. (5) and (9) may be written as follows:

$$J_d = -\varepsilon S \tau_m D_o \frac{\partial C}{\partial x} = -\frac{\varepsilon S D_o}{T_m} \frac{\partial C}{\partial x}. \quad (11)$$

In the case where the porous medium is saturated (i.e., $S = 100\% = 1$), Eq. (11) is written more succinctly as follows:

$$J_d = -\varepsilon \tau_m D_o \frac{\partial C}{\partial x} = -\frac{\varepsilon D_o}{T_m} \frac{\partial C}{\partial x}. \quad (12)$$

In addition to the matrix tortuosity effect, Shackelford and Daniel (1991) noted that additional effects that reduce the rate of diffusive transport in porous media relative to that in aqueous solution often are taken into account by incorporating additional reduction factors into Eq. (12). These factors include such effects as an increased viscosity of the water adjacent to solid particles (μ) and anion exclusion (γ). When these additional effects are considered to be relevant, Eq. (12) is written as follows (Shackelford and Daniel, 1991):

$$J_d = -\varepsilon \mu \gamma \tau_m D_o \frac{\partial C}{\partial x} = -\frac{\varepsilon \mu \gamma D_o}{T_m} \frac{\partial C}{\partial x} \quad (13)$$

where both μ and γ are <1 . Van Brackel and Heertjes (1974) introduced a *constrictivity factor*, δ , into Eq. (13) that essentially represents the product $\mu\gamma$ ($=\delta$). However, Van Brackel and Heertjes (1974) defined the constrictivity factor more generally to account for variation in the cross-sectional area of the pores over the length of the porous medium without regard for the mechanisms causing such variations. In some cases (e.g., Vopalka et al., 2006), the product $\mu\gamma\tau_m$ ($=\mu\gamma/T_m = \delta/T_m$) in Eq. (13) has been referred to as the *geometric factor*, G , whereas in other cases (e.g., González Sánchez et al., 2008; Appelo et al., 2010), the geometric factor has been defined as the inverse of this product (i.e., $G = 1/\mu\gamma\tau_m = T_m/\mu\gamma = T_m/\delta$). Due to these different definitions, caution should be exercised in terms of understanding the basis for the definitions of terms before making comparisons among the various published studies.

Similar to τ_m (or T_m), independent measurement of the reduction factors μ and γ , (or δ) is difficult if not impossible (Shackelford and Daniel, 1991). As a result, all of these factors commonly are lumped together into a single reduction factor. For example, Olsen et al. (1965) wrote Eq. (13) as follows:

$$J_d = -t_r D_o \frac{\partial C}{\partial x} \quad (14)$$

where t_r ($=\theta\mu\gamma\tau_m = \theta\mu\gamma/T_m$) was referred to as the *transmission factor* (for unsaturated soils such that ε was replaced by θ as per Eq. (13)), whereas Nye (1979) wrote Eq. (13) as follows:

$$J_d = -\varepsilon f_i D_o \frac{\partial C}{\partial x} \quad (15)$$

where f_i ($=\mu\gamma\tau_m = \mu\gamma/T_m$) was referred to as the *impedance factor*. Shackelford and Daniel (1991) noted that, because of the inherent difficulty associated with measuring the various reduction factors independently, values of the matrix tortuosity factor, τ_m (or T_m), commonly are reported when in reality they may be transmission factors or impedance factors. Thus, Shackelford and Daniel (1991) proposed a more general form of Eq. (13) as follows:

$$J_d = -\varepsilon\tau_a D_o \frac{\partial C}{\partial x} \quad (16)$$

where τ_a is an *apparent tortuosity factor* ($=1/T_a$) that represents the product of the actual matrix tortuosity factor and all other inherent reduction factors, as follows (e.g., see Malusis and Shackelford, 2002a):

$$\tau_a = \tau_m \tau_r = \tau_m \prod_{i=1}^N \tau_i = \tau_m (\tau_1 \tau_2 \dots \tau_N) \quad (17)$$

or

$$\frac{1}{T_a} = \frac{1}{T_m T_r} = \frac{1}{T_m} \prod_{i=1}^N \frac{1}{T_i} = \frac{1}{T_m} \left(\frac{1}{T_1 T_2 \dots T_N} \right) \quad (18)$$

where τ_r ($=1/T_r$) is a *restrictive tortuosity factor* that represents the product of N other factors ($\tau_i = 1/T_i$) that contribute to the apparent tortuosity factor by acting to reduce or restrict the diffusive solute flux through the porous medium.

Although attempts have been made to determine values of the matrix tortuosity factor (T_m or τ_m) indirectly, e.g., through the use of electrical resistivity measurements (e.g., Wyllie and Spangler, 1952; Manheim, 1970), the success of these attempts for charged porous media such as clays has varied such that independent determination of the matrix tortuosity factor in these media generally is considered to be unreliable. Similarly, independent determination of the restrictive tortuosity factor also is usually problematic. Thus,

Fick's first law for one-dimensional diffusion in porous media given by Eq. (16) commonly is rewritten as follows:

$$J_d = -\varepsilon D^* \frac{\partial C}{\partial x} \quad (19)$$

where D^* ($=\tau_a D_o = D_o/T_a$) is known as the *effective diffusion coefficient* [L^2T^{-1}] (Shackelford and Daniel, 1991). In the geological sciences literature, the effective diffusion coefficient typically is defined to include the porosity and is designated as D_e ($=\varepsilon\tau_a D_o = \varepsilon D_o/T_a$), such that Eq. (16) is written as follows (e.g., De Soto et al., 2012):

$$J_d = -D_e \frac{\partial C}{\partial x} \quad (20)$$

where D_e also is known as the *effective diffusion coefficient* [L^2T^{-1}].

An argument in favor of Eq. (19) is that the porosity generally can be determined independently, such that there is no reason to lump ε into the definition of the effective diffusion coefficient. An argument in favor of Eq. (20) is that the resulting form of Fick's first law for diffusion in porous media is the same as that for diffusion in aqueous solution given by Eq. (1).

An alternative form of Fick's first law for one dimensional diffusion in saturated porous media represented by Eq. (13) is as follows (e.g., Skagius and Neretnieks, 1986; Pearson, 1999):

$$J_d = -\varepsilon_{eff} \tau_m D_o \frac{\partial C}{\partial x} = -\frac{\varepsilon_{eff} D_o}{T_m} \frac{\partial C}{\partial x} = -\varepsilon_{eff} D_p \frac{\partial C}{\partial x} \quad (21)$$

where ε_{eff} is an *effective or through-diffusion porosity* defined such that $\varepsilon_{eff} \leq \varepsilon$, and D_p [L^2T^{-1}] is referred to as the *pore diffusion coefficient*. The use of an effective porosity in lieu of a total porosity in Eq. (21) takes into account the possibility that there may be pores that are not interconnected and, therefore, represent dead ends (i.e., dead-end pores), such that only a fraction of the pore space may be available for mass transport.

A comparison of Eq. (21) with Eqs. (16) and (17) or (18) reveals that the effective porosity in Eq. (21) may be taken as the product of the total porosity and a restrictive tortuosity factor, or:

$$\varepsilon_{eff} = \varepsilon \tau_r. \quad (22)$$

In addition, this comparison reveals that the definition of D_p ($=\tau_m D_o = D_o/T_m$) is not the same as that of D^* ($=\tau_a D_o = D_o/T_a$), in that $D^* = \tau_r D_p$ ($=D_p/T_r$). In general, since τ_r ($=1/T_r$) ≤ 1 , $D^* \leq D_p$. Thus, the effect of an interconnected pore space being less than the total pore space within a porous medium may be taken into account either through an apparent tortuosity factor via Eq. (16) or through an effective porosity effect via Eq. (21). However, the advantage of the use of D^* via Eq. (19) versus D_p via Eq. (21) is that the only a priori unknown parameter in Eq. (19) is D^* , whereas both ε_{eff} and D_p in Eq. (21) generally are unknown a priori. Of course, in the limit as ε_{eff} approaches ε , τ_r approaches unity via Eq. (22), such that D^* approaches D_p (i.e., as $\varepsilon_{eff} \rightarrow \varepsilon$, $\tau_r \rightarrow 1$ and $D^* \rightarrow D_p$). Thus, assuming that ε_{eff} is equivalent to ε is the same as assuming that D^* is equivalent to D_p , which, as will be shown subsequently, is not necessarily always the case.

2.4. Fick's second law for diffusion in porous media

Fick's second law governing transient diffusion of a non-decaying chemical species in porous media can be written as follows (e.g., Skagius and Neretnieks, 1986; Shackelford and Daniel, 1991; Van Loon et al., 2003):

$$\frac{\partial C}{\partial t} = \frac{D^*}{R_d} \frac{\partial^2 C}{\partial x^2} = \frac{D_e}{\alpha} \frac{\partial^2 C}{\partial x^2} = D_a \frac{\partial^2 C}{\partial x^2} \quad (23)$$

where R_d is the dimensionless *retardation factor*, α is the dimensionless *rock capacity factor* and $D_a (=D^*/R_d=D_e/\alpha)$ is the *apparent diffusion coefficient* [L^2T^{-1}]. The retardation factor as used in Eq. (23) takes into account linear, reversible, and instantaneous sorption of a chemical species. Based on mass balance for a water saturated porous medium, R_d represents the ratio of the total mass of chemical species per unit total volume of porous medium relative to the aqueous-phase mass of chemical species per unit total volume of porous medium, or

$$R_d = \frac{\varepsilon C + \rho_d C_s}{\varepsilon C} = 1 + \frac{\rho_d C_s}{\varepsilon C} = 1 + \frac{\rho_d}{\varepsilon} K_d \quad (24)$$

where C_s is the solid-phase concentration expressed as the sorbed mass of the chemical species per unit mass of the solid phase [MM^{-1}], ρ_d is the *dry density* of the solid phase, or mass of solids per unit total volume of solids [ML^{-3}], and $K_d (=C_s/C)$ is the *distribution coefficient* [L^3M^{-1}], which relates the solid-phase concentration to the aqueous-phase concentration of the chemical species (i.e., assuming linear, reversible, and instantaneous sorption). As a result, for sorbing chemical species, $K_d > 0$ such that $R_d > 1$, whereas for nonsorbing chemical species, $K_d = 0$ (i.e., $C_s = 0$) such that $R_d = 1$. Thus, D_a as given by Eq. (23) represents a lumped effective diffusion coefficient that includes the effect of attenuation via either R_d or α . For this reason, D_a also has been referred to as the *effective diffusion coefficient of a reactive chemical species* (Shackelford and Daniel, 1991).

The dry density of the porous medium also is commonly referred to as the *bulk* or *dry-bulk density* of the solid phase and is designated as ρ_b . The dry density of the solid phase is related to the particle density of the solid phase, ρ_s , and the density of water, ρ_w , as follows:

$$\rho_d = (1-\varepsilon)\rho_s = (1-\varepsilon)G_s\rho_w \quad (25)$$

where G_s is the specific gravity of solids (i.e., $G_s = \rho_s/\rho_w$). Thus, Eq. (24) may be rewritten as follows:

$$R_d = 1 + \frac{(1-\varepsilon)\rho_s}{\varepsilon} K_d = 1 + \frac{(1-\varepsilon)G_s\rho_w}{\varepsilon} K_d \quad (26)$$

In the case of an unsaturated porous medium involving a non-volatile chemical species, the ε in the denominator of Eq. (26) should be replaced by θ , whereas ε remains in the numerator in Eq. (26). In this case, Eqs. (24) and (26) are written as follows:

$$R_d = 1 + \frac{\rho_d}{\theta} K_d = 1 + \frac{(1-\varepsilon)\rho_s}{\theta} K_d = 1 + \frac{(1-\varepsilon)G_s\rho_w}{\theta} K_d \quad (27)$$

The rock capacity factor, α , in Eq. (23) is related to the retardation factor as follows:

$$\alpha = \frac{\varepsilon C + \rho_d C_s}{C} = \varepsilon + \rho_d \frac{C_s}{C} = \varepsilon + \rho_d K_d = \varepsilon R_d \quad (28)$$

Whereas the retardation factor represents the ratio of the total mass of chemical species (aqueous- plus solid-phase masses) per unit void volume of porous medium relative to the pore-water concentration, the rock capacity factor represents the ratio of the total mass of chemical species per unit total volume of porous medium relative to the pore-water concentration. The rock capacity factor also has been referred to as the *volumetric capacity of the porous medium for the chemical species* (Pearson, 1999).

For a radionuclide subject to first-order linear decay, Eq. (23) is written as follows:

$$\frac{\partial C}{\partial t} = \frac{D^*}{R_d} \frac{\partial^2 C}{\partial x^2} - \lambda C = \frac{D_e}{\alpha} \frac{\partial^2 C}{\partial x^2} - \lambda C = D_a \frac{\partial^2 C}{\partial x^2} - \lambda C \quad (29)$$

For radionuclides with half-lives, $t_{0.5}$, that are considerably longer than the time frame being considered for diffusion, the decay term in

Eq. (29) can be (and often is) ignored without any significant loss in accuracy.

A summary of the four definitions for diffusion coefficients in porous media as defined herein is provided in Table 1. Since the notation for the various diffusion coefficients shown in Table 1 may not match the notation used by others, or the notation may in fact be switched (e.g., D^* as defined herein is represented as D_e , or D_e as defined herein is represented by D_p), caution should be exercised in terms of understanding the basis for the definition of the various diffusion coefficients when interpreting values extracted from the published literature.

2.5. Relative magnitudes of diffusion coefficients

A comparison of Eqs. (19), (20), (21), and (23) reveals the following relationships among the different definitions for the diffusion coefficients in porous media:

$$\varepsilon D^* = D_e = \varepsilon_{eff} D_p = \alpha D_a = \varepsilon R_d D_a \quad (30)$$

or

$$D^* = \frac{D_e}{\varepsilon} = \left(\frac{\varepsilon_{eff}}{\varepsilon} \right) D_p = \left(\frac{\alpha}{\varepsilon} \right) D_a = R_d D_a \quad (31)$$

Also, $\varepsilon < 1$ and $\varepsilon_{eff} \leq \varepsilon$. Thus, in the case of nonsorbing chemical species, i.e., $K_d = 0$, $R_d = 1$ and $\alpha = \varepsilon$, the relative order in the magnitudes of the four different diffusion coefficients should be as follows: $D_p \geq D^* = D_a > D_e$. In the case of sorbing chemical species, i.e., $K_d > 0$, $R_d > 1$ and $\alpha > \varepsilon$, the relative magnitudes for the four different diffusion coefficients will depend on the relative magnitudes between R_d^{-1} and ε . If $R_d^{-1} \leq \varepsilon$, then $D_p \geq D^* > D_e \geq D_a$, whereas if $R_d^{-1} \geq \varepsilon$, then $D_p \geq D^* > D_a \geq D_e$. This latter relationship is likely to govern in the case of diffusion through intact (unfractured) rock where sorption to the solid matrix is minimal and the matrix porosity is low (e.g., see Parker et al., 1994). A summary of these relative magnitude relationships is provided in Table 2.

3. Definitions of porosity

Thus far, two different porosity terms have been identified, viz., the total porosity, ε , and the effective porosity, ε_{eff} . With respect to Fick's first law for diffusive mass flux through a porous medium, the correct porosity to use is the effective porosity, whether this porosity is taken into account explicitly in the form of Fick's first law (e.g., Eq. (21) and Table 1), or implicitly via a restrictive tortuosity factor, τ_r , buried within the definition of the effective diffusion coefficient (e.g., Eqs. (19) or (20) and Table 1). A third porosity term, referred to as the *diffusion accessible*

Table 1
Summary of definitions for diffusion coefficients in porous media.^{1,2}

Governing equation	Form of diffusion coefficient [L^2T^{-1}]	Common terminology for diffusion coefficient
$J_d = -\varepsilon D^* \partial C / \partial x$	$D^* = D_o \tau_a = D_o \tau_m \tau_r$	Effective diffusion coefficient
$J_d = -D_e \partial C / \partial x$	$D_e = \varepsilon D_o \tau_a = \varepsilon D_o \tau_m \tau_r$	Effective diffusion coefficient
$J_d = -\varepsilon_{eff} D_p \partial C / \partial x$ (where $\varepsilon_{eff} = \varepsilon \tau_r$)	$D_p = D_o \tau_m$	Pore diffusion coefficient
$\partial C / \partial t = D_a \partial^2 C / \partial x^2$	$D_a = D^* / R_d = D_e / \alpha$	Apparent diffusion coefficient

¹M = units of mass; L = units of length; T = units of time.

² J_d = diffusive mass flux [$ML^{-2}T^{-1}$];

C = aqueous-phase concentration of diffusing chemical species [ML^{-3}];

x = direction of transport [L];

ε = total porosity [–];

ε_{eff} = effective porosity [–];

D_o = aqueous-phase or free-solution diffusion coefficient of chemical species [L^2T^{-1}];

τ_a, τ_m, τ_r = apparent, matrix, and restrictive tortuosity factors, respectively [–], where $0 \leq \tau_a, \tau_m, \tau_r \leq 1$;

R_d = retardation factor [–], where $R_d \geq 1$;

α = rock capacity factor [–], where $\alpha \geq \varepsilon$.

porosity, ε_{diff} , also has been identified as the volume of liquid into which diffusion occurs relative to the total volume of the medium (Pearson, 1999). Thus, the diffusion accessible porosity can include dead-end pores into which diffusion of a chemical species can occur during migration through a porous medium, such that ε_{diff} may be greater than the effective porosity, ε_{eff} , but still less than the total porosity, ε (i.e., $\varepsilon_{eff} \leq \varepsilon_{diff} \leq \varepsilon$), e.g., when the total porosity includes occluded pores that are not accessible to diffusion. Inaccessibility to dead-end pores generally is attributed to charge repulsion (e.g., anions being repulsed by negative surface charges on individual soil particles) and/or steric hindrance (geometric restriction resulting from the size of migrating chemical species being larger than the size of the pore opening). Thus, only a portion of the total pore space may be accessible in the case of anions, whereas all of the pore space (i.e., except for any isolated or occluded pores) generally is assumed to be available to cations and neutral species (García-Gutiérrez et al., 2004a), although this may in reality not always be the case (e.g., see Appelo et al., 2010). As a result, the magnitude of any diffusion accessible porosity will be a function of the chemical species.

For example, as described by Pearson (1999) based on results reported by Bourke et al. (1993) for London clay, the “through-diffusion porosities” based on diffusion of tritium (HTO) and deuterium (HDO) were 0.6, which was approximately the same values as the total porosity of the clay. However, the through-diffusion porosity of iodide, I^- , was only 0.2. This difference in through-diffusion porosities for the different chemical species was attributed to I^- being excluded from the smaller pores and negatively charged mineral sites due to the larger size and negative charge of I^- , respectively.

To further elucidate the differences among the possible definitions of porosity, consider the schematic illustration shown in Fig. 1 of a representative segment of a water-saturated porous medium through which two tracers, viz. neutral HTO and anionic chloride, $^{36}Cl^-$ ($Cl-36$), are diffusing. As illustrated, a porous medium may contain interconnected voids (V_{v1}), accessible but non-interconnected (dead-end) voids (V_{v2} and V_{v3}), and inaccessible or occluded voids (V_{v4}). For this scenario, the total porosity, ε , would be the porosity determined on the basis of oven drying the soil sample, and would be defined as follows:

$$\varepsilon = \frac{V_{v1} + V_{v2} + V_{v3} + V_{v4}}{V_T} \quad (32)$$

whereas the effective porosity, ε_{eff} , would be the porosity associated only with the interconnected pore space through which both HTO and $^{36}Cl^-$ diffuse through the porous medium, or:

$$\varepsilon_{eff} = \frac{V_{v1}}{V_T} \quad (33)$$

Thus, in the case depicted in Fig. 1, $\varepsilon_{eff} < \varepsilon$. However, as HTO and $^{36}Cl^-$ are diffusing through the porous medium, dead-end pores represented by V_{v2} and V_{v3} are encountered. As illustrated, HTO may be accessible to all of the dead-end pore space (V_{v2} and V_{v3}), whereas $^{36}Cl^-$ may be

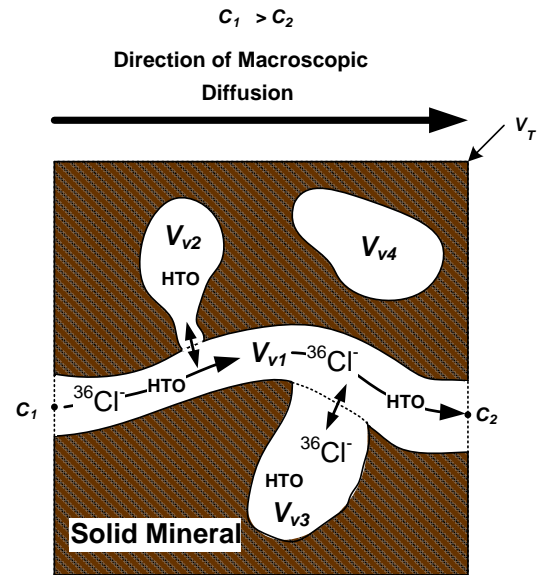


Fig. 1. Schematic illustration of the diffusion of tritium (HTO) and chloride ($^{36}Cl^-$) through a representative elementary volume (V_T) of a water saturated porous medium with different components of void volume (V_v) [C = solute concentration].

accessible to only a portion of the dead-end pore space (V_{v3}), i.e., due to charge repulsion and/or steric hindrance. Thus, with respect to Fig. 1, the diffusion accessible porosities for HTO and $^{36}Cl^-$ would be defined as follows:

$$\varepsilon_{diff,HTO} = \frac{V_{v1} + V_{v2} + V_{v3}}{V_T}; \quad \varepsilon_{diff,Cl-36} = \frac{V_{v1} + V_{v3}}{V_T} \quad (34)$$

Based on the above considerations, the relative relationship among the various definitions of porosity with respect to Fig. 1 is as follows: $\varepsilon_{eff} < \varepsilon_{diff,Cl-36} < \varepsilon_{diff,HTO} < \varepsilon$. Of course, in the absence of an inaccessible or occluded void space (i.e., $V_{v4} = 0$ in Figure 1), the diffusion accessible porosity with respect to HTO would be the same as the total porosity, i.e., $\varepsilon_{diff,HTO} = \varepsilon$ (e.g., Berry and Bond, 1992).

For example, consider the data extracted from García-Gutiérrez et al. (2004a) and shown in Fig. 2, where values of ε_{diff} based on diffusion of $^{36}Cl^-$ in compacted FEBEX bentonite ranged from 5.7% to 28.6% of ε as the dry density, ρ_d , ranged from 1.65 Mg/m³ ($\varepsilon = 0.389$) to 1.0 Mg/m³ ($\varepsilon = 0.630$), respectively. In contrast, the diffusion accessible porosity based on HTO diffusion was approximately equal to, albeit slightly greater than, the total porosity ($\varepsilon_{diff} \approx \varepsilon$) over the entire range of ρ_d . García-Gutiérrez et al. (2004a) attributed the rapid decrease in ε_{diff} for $^{36}Cl^-$ with increasing ρ_d to a greater extent of anion exclusion from the smaller pores, due to the closer proximity of negatively charged bentonite particles with increasing ρ_d . Overall, the results in Fig. 2 illustrate that the accessibility of pores in a given porous medium can be a function of not only the porous medium but also the chemical species.

As a result of the distinction between ε_{eff} and ε_{diff} , the relationship for the apparent diffusion coefficient given by Eq. (23), i.e., $D_a = D^*/R_d$, is strictly valid only when $\varepsilon_{eff} = \varepsilon_{diff}$ (Pearson, 1999). This criterion generally is not satisfied in the case of fractured rock that includes a through-transport porosity (i.e., ε_{eff}) and a significant volume of dead-end pores, but generally is satisfied in the case in mudrock and other similar porous media when the quantity of dead-end pores is likely to be minimal (Pearson, 1999).

In bentonites, dead-end pores may be represented by the space between individual particles of the bentonite and/or by the interlayer space within the montmorillonite mineral comprising the solid phase of the bentonite particles (Ichikawa et al., 2004; Jo et al., 2006; Holmboe et al., 2012). For example, consider the case of factory manufactured

Table 2
Relative magnitudes of diffusion coefficients in porous media.

Type of chemical species ¹	Criteria	Relative magnitudes ²
Nonsorbing ($K_d = 0, R_d = 1, \alpha = \varepsilon$)	–	$D_p \geq D^* = D_a > D_e$
Sorbing ($K_d > 0, R_d > 1, \alpha > \varepsilon$)	$R_d^{-1} \leq \varepsilon$	$D_p \geq D^* > D_e \geq D_a$
Sorbing ($K_d > 0, R_d > 1, \alpha > \varepsilon$)	$R_d^{-1} \geq \varepsilon$	$D_p \geq D^* > D_a \geq D_e$

¹ K_d = distribution coefficient [L^3M^{-1} , where L = units of length and M = units of mass]; R_d = retardation factor [–], where $R_d \geq 1$; ε = total porosity [–], where $\varepsilon < 1$; and α = rock capacity factor [–], where $\alpha \geq \varepsilon$.

² Refer to Table 1 for definitions of diffusion coefficients.

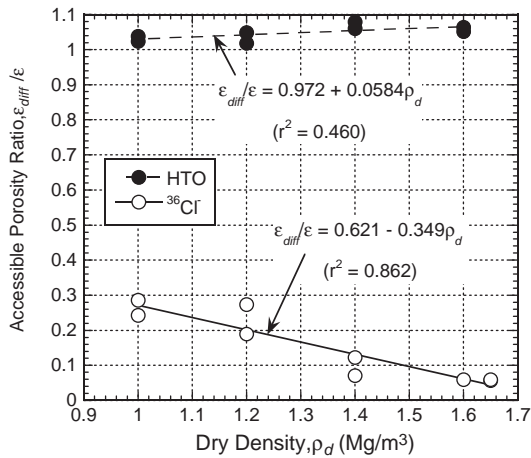


Fig. 2. Ratio of diffusion accessible porosity to total porosity for diffusion of tritium (HTO) and chloride-36 (³⁶Cl⁻) as a function of the dry density of compacted FEBEX bentonite.

Data extracted from García-Gutiérrez et al. (2004a).

bentonite-based barriers known as geosynthetic clay liners, or GCLs, composed of agglomerations of bentonite particles referred to as granules (see Figure 3). In this case, the liquid phase within the GCL can be separated into mobile and immobile fractions, with the mobile liquid fraction being associated with the intergranular pore space (Figure 3a) and the immobile liquid fraction being composed of the combination of interparticle pore space within each granule (Figure 3b) and the interlayer pore space within each particle (Figure 3c). For this scenario, the mobile liquid fraction represents the effective pore space, whereas the immobile liquid fraction represents the dead-end pore space, such that $\epsilon_{eff} < \epsilon_{diff}$. Of course, the accessibility of the dead-end pore spaces also would be a function of the chemical species, such that ϵ_{diff} would not necessarily be the same for all chemical species diffusing through the GCL. Similar descriptions also have been offered for describing radionuclide diffusion through smectitic based geologic formations and highly compacted bentonite buffers, where the immobile liquid commonly is referred to as “bound water” that includes both interlayer water and diffuse double layer water (e.g., Nakashima, 2002; Bourg et al., 2003, 2006, 2007, 2008; Appelo and Wersin, 2007; Appelo et al., 2010).

The overall point is that ϵ_{eff} and ϵ_{diff} are often taken to be equivalent (e.g., Van Loon et al., 2007), although this equivalency may not necessarily always be the case, e.g., as depicted conceptually in Fig. 1 where $\epsilon_{eff} < \epsilon_{diff, Cl-36}$. This difference between ϵ_{eff} and ϵ_{diff} may be particularly important when the barrier consists of granules of bentonites and/or the interlayer spaces within individual particles of bentonites are accessible to diffusing chemical species, such as in the case of GCLs. Thus, unless there is independent evidence that none of the dead-end pore space is accessible to a given chemical species, prudence dictates that ϵ_{eff} should not be assumed to be the same as ϵ_{diff} for a given chemical species.

3.1. Determination of component porosities

Of the three porosity terms, viz., ϵ , ϵ_{eff} , and ϵ_{diff} , the total porosity, ϵ , is the easiest term to determine. Generally, ϵ is determined by oven drying a sample of soil to determine the moisture content, and together with knowledge of the total volume of the sample, V_T , and the G_s for the soil, ϵ can be calculated from the following simple phase-relationship expression:

$$\epsilon = 1 - \frac{m_s}{G_s \rho_w V_T} \quad (35)$$

where m_s is the dry mass of the soil after oven drying. This method for determining ϵ for soils should result in inclusion of any occluded void space (e.g., V_{v4} in Figure 1). In contrast, determination of ϵ_{eff} and ϵ_{diff} is more complicated.

As previously described, ϵ_{eff} cannot necessarily be assumed to be the same as ϵ_{diff} . Thus, ϵ_{eff} generally is determined in laboratory studies by performing a column test whereby tracer effluent breakthrough curves are monitored over time under advective-dominant conditions, i.e., diffusion is negligible (e.g., Shackelford, 1993, 1994, 1995; Stephens et al., 1998). The basis of this approach is that there is no hydraulic gradient for flow of the tracer into any dead-end pore space (e.g., V_{v2} and V_{v3} in Figure 1), and that any mass loss of tracer due to diffusion into dead-end pores is nil as a result of the dominance of advection in the test. As a result, the tracer should break through the end of the column prior to the time based on the assumption that all of the pore space is effective for solute migration, such that the ratio of the two breakthrough times (the actual measured breakthrough time versus the breakthrough time predicted on the basis that all the pore space is interconnected) provides an indication of the percentage of pore space that is actually effective.

Tracers (nonadsorbing solutes such as HTO, HDO, ³⁶Cl⁻, etc.) also are used to determine ϵ_{diff} , since in the case of tracers, $C_s = 0$ such that $K_d = 0$ and $R_d = 1$ in Eq. (24), and by Eq. (28), $\alpha = \epsilon = \epsilon_{diff}$. Thus, via Eq. (29), the following relationship is given:

$$\frac{D_e}{\alpha} = \frac{D_e}{\epsilon_{diff}} = D_a. \quad (36)$$

Based on Eq. (36), ϵ_{diff} is represented by the ratio of D_e to D_a (i.e., $\epsilon_{diff} = D_e/D_a$), such that ϵ_{diff} can be determined by measuring both D_e and D_a for a given tracer, and then using the measured values of D_e and D_a to calculate ϵ_{diff} via Eq. (36). A potential problem with this approach is that there are several methods that can be used to measure D_e and/or D_a , and the measured values for D_e and/or D_a may depend on the method used in the measurement (e.g., García-Gutiérrez et al., 2004a).

In general, D_e and D_a may be determined from a single diffusion test consisting of one test specimen or from different diffusion tests consisting of two, presumably identical test specimens. Detailed descriptions of these different diffusion testing methods are beyond the scope of this study, but may be found elsewhere (e.g., Lever, 1986; Shackelford, 1991; Cho et al., 1993a; García-Gutiérrez et al., 2006). However, to illustrate the methodology for determining ϵ_{diff} , a description of the test method whereby both D_e and D_a are measured from a single specimen is provided herein. This method has historically been referred to as the *time-lag method* (e.g., Shackelford, 1991; Bourke et al., 1993), but is more commonly known as the *through-diffusion method* (e.g., Berry and Bond, 1992).

In the time-lag or through-diffusion method, a test specimen of total cross-sectional area, A , and thickness, L , is placed between two reservoirs containing different concentrations of a given chemical species, say C_2 and C_1 where $C_2 > C_1$, such that a concentration difference across the specimen, $-\Delta C (= C_2 - C_1)$, is established. In this case, diffusion of the chemical species occurs from the boundary of the specimen adjacent to the reservoir containing C_2 to the boundary of the specimen adjacent to the reservoir containing C_1 . If the boundary concentrations are maintained essentially constant (e.g., by periodically or continuously replacing the source reservoir (i.e., C_2) and removing the collection reservoir (i.e., C_1)), there will be an initial transient stage of the test where the mass of the chemical species being monitored in the collection reservoir is continuously increasing, followed by a steady-state stage whereby the change in mass with respect to time is constant. Liquid samples are recovered incrementally from the collection reservoir over a time period, Δt_i , and the concentration in each sample, C_i , is determined by a suitable means (e.g., scintillation counting for radionuclides, ion chromatography

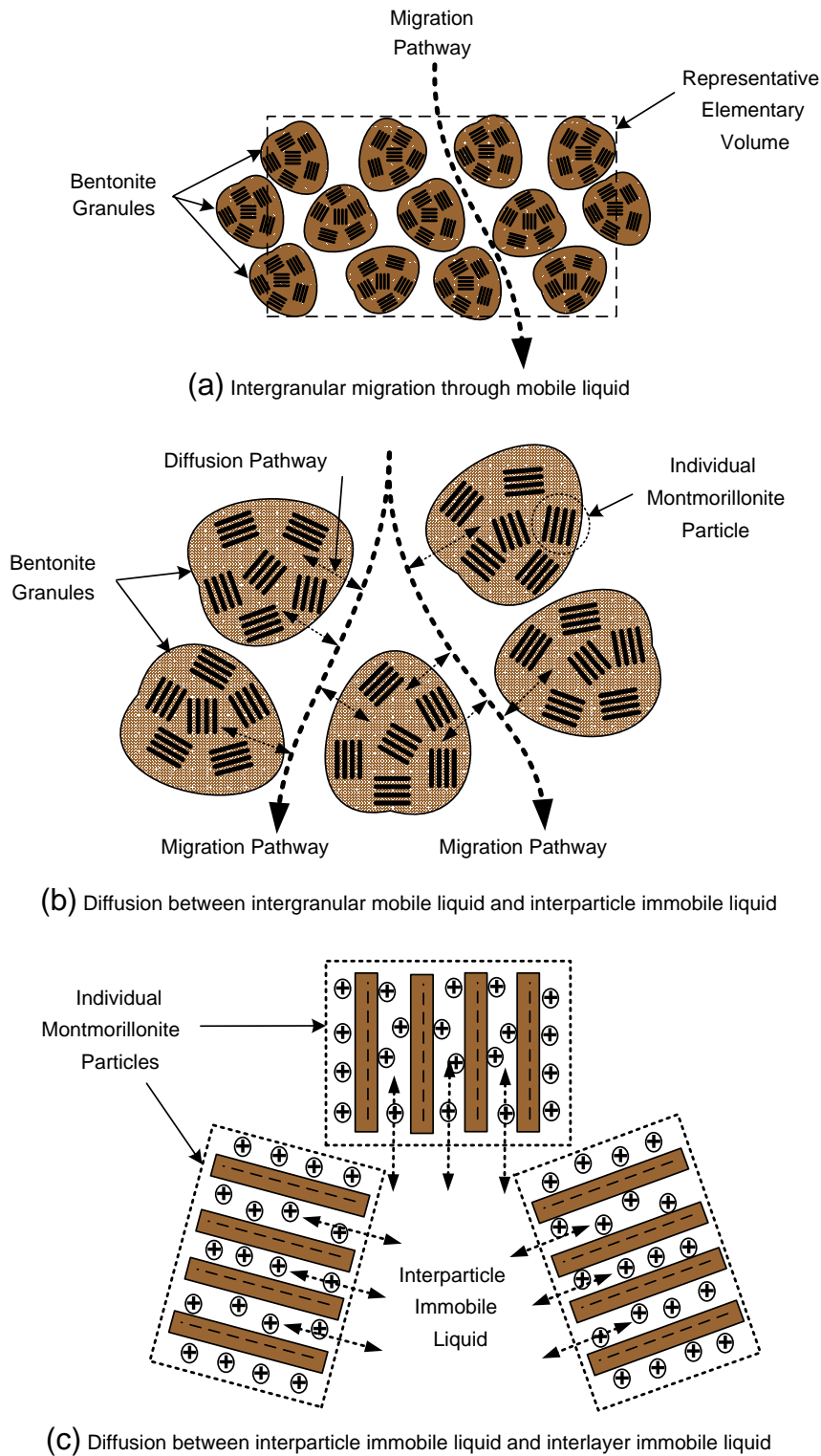


Fig. 3. Schematic illustration of the mobile and immobile fractions within a cross-section of a geosynthetic clay liner composed of granules of bentonite. Redrawn after Jo et al. (2006).

(IC) for anions, inductively coupled plasma (ICP) for cations). The incremental mass of the chemical species collected in each liquid sample, Δm_i , then is determined by multiplying the volume of the collected sample, ΔV_i , by C_i , (i.e., $\Delta m_i = C_i \cdot \Delta V_i$). The resulting data generally are plotted as the cumulative diffusive mass normalized with respect to the area of the specimen, $Q_t (= \sum(\Delta m_i)/A)$, versus

the elapsed time for diffusion, $t (= \sum(\Delta t_i))$, as illustrated schematically in Fig. 4. The value of D_e then can be determined from the steady-state slope of the data as follows:

$$D_e = \left(\frac{L}{-\Delta C} \right) \left(\frac{Q_t}{t} \Big|_{steady-state} \right). \tag{37}$$

Once D_e is known, the value for ε_{diff} can be determined from the time-lag, t_L , representing the x-axis intercept of the steady-state portion of the data shown in Fig. 4, as follows (e.g., Berry and Bond, 1992):

$$\alpha = \varepsilon_{diff} = \frac{6D_e t_L}{L^2}. \quad (38)$$

Note that the ratio of D_e/α in the definition of the time-lag in Fig. 4 is the apparent diffusion coefficient, D_a . The reader is referred to García-Gutiérrez et al. (2004a) for examples of other approaches for determining ε_{diff} .

4. Complicating issues

Several issues can complicate or otherwise influence the interpretation of radionuclide diffusion through engineered containment barriers. Among the issues identified in this review, three were considered to be potentially significant for LLRW disposal, viz., the geochemistry of the barrier system, the potential role of surface and/or interlayer diffusion, and the contribution of anion exclusion to semipermeable membrane behavior. The potential importance of these three issues is expounded upon in the following sections.

4.1. Geochemistry

Geochemistry can play a major role in determining the rate of diffusion of radionuclides in engineered containment barriers. In general, diffusion of radionuclides through engineered containment barriers is affected both by the nature and the magnitude of the surface charge on the solids comprising the barrier, and by the speciation of the chemicals within the aqueous phase or pore water of the barrier material.

In the case of clay containment barriers, the solid phase will be dominated by clay particles composed of clay minerals. For clays such as sodium bentonites (Na-bentonites) that consist primarily of sodium montmorillonite or other high activity smectitic clay minerals, the dominant surface charge will be negative due to isomorphous substitution, such that cationic species will be adsorbed to both internal (interlayer) and external surfaces of individual clay particles (e.g., Mitchell and Soga, 2005). In kaolinite based clays (e.g., kaolin), the surface charge will be a function of the pH of the pore water, such that at relatively low pH, the predominant surface charge will be positive, whereas at relatively high pH, the predominant surface charge will be negative (e.g., Bohn et al., 1985). Thus, in kaolinite based clays, anionic chemical species may be adsorbed at relatively low pH, whereas cationic chemical species would be adsorbed at relatively high pH.

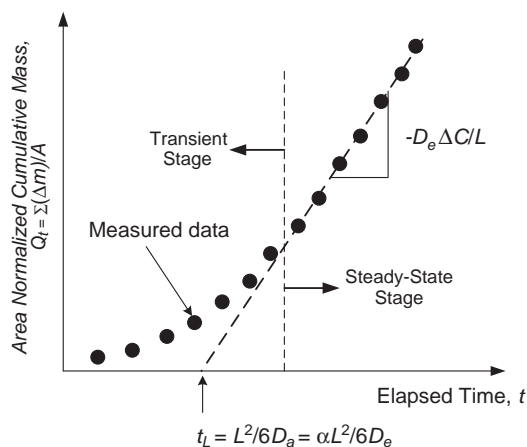


Fig. 4. Schematic representation of measured data from a time-lag or through-diffusion test.

Given the aforementioned relation between surface charge and ionic sorption, the sign and magnitude of the charge associated with the radionuclides within the pore water also will affect whether the radionuclides are attracted or repelled by the surface charges of solid particles. In this regard, the effect of the chemical speciation of the radionuclide on the rate of diffusion through an engineered earth-en barrier can be important.

For example, Sawatsky and Oscarson (1991) evaluated the diffusion of technetium (^{99}Tc), with a half life of 2.1×10^5 yr, in compacted Avonlea bentonite ($G_s = 2.75$) under both oxidizing and reducing conditions (the authors actually used $^{95\text{m}}\text{Tc}$, a gamma emitter, to permit activity analysis without having to separate the Tc from the clay). The tests were conducted at temperatures of 25 and/or 80 °C for durations of either 2 or 30 d. The results in the form of D^* values are shown in Fig. 5 as a function of ρ_d and ε (via Eq. (25)).

As shown in Fig. 5, the D^* values generally decreased with increasing ρ_d (decreasing ε), except for the D^* values measured under reducing conditions with contact times of 30 d, which were determined on specimens at the same porosity ($\varepsilon = 0.53$). In this case, the differences in the D^* values ($2.7 \times 10^{-12} \leq D^* \leq 8.2 \times 10^{-12}$ m²/s) represented the variability in the measurements. Sawatsky and Oscarson (1991) attributed this decrease in D^* with increasing ρ_d (decreasing ε) to a decrease in the pore space due to a decrease in dry density (i.e., τ_m effect) and an increase in anion exclusion (i.e., τ_r effect). Also, the D^* values under oxidizing conditions measured at 80 °C were greater than those measured at 25 °C. This effect of temperature on D^* was attributed to a decrease in the viscosity of the saturating solution with increasing temperature in accordance with the Stokes–Einstein equation.

In terms of geochemistry, the D^* values under reducing conditions were one to two orders of magnitude lower than those under oxidizing conditions. Precipitation was ruled out as a cause of this difference because the concentration of Tc-95m used in the tests was much lower than the solubility of Tc-95m, and sorption was excluded as a possible reason because no sorption was observed in separate sorption experiments, probably because only anionic species of Tc were considered likely under both oxidizing and reducing conditions. Sawatsky and Oscarson (1991) hypothesized that the lower D^* values in the reducing relative to oxidizing environment were attributed to reduction of Tc(VII) to Tc(IV) and the subsequent formation of Tc(IV)-carbonate species such as $\text{Tc}(\text{OH})(\text{CO}_3)_2^-$. This complex is larger and has a different stereochemistry than the TcO_4^- species present in an oxidizing

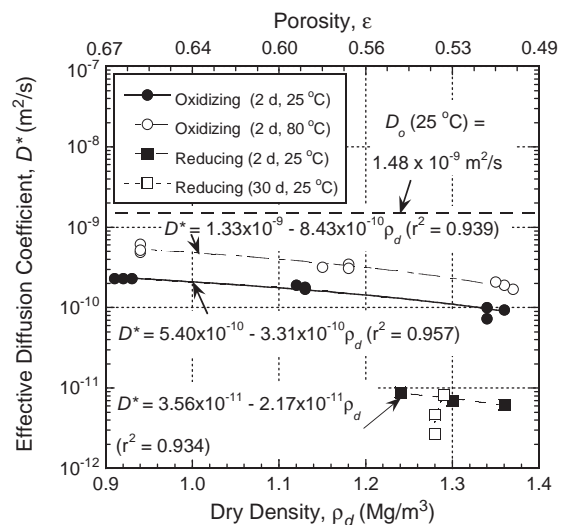


Fig. 5. Effects of redox conditions on the effective diffusion coefficient of technetium ($^{95\text{m}}\text{Tc}$) in compacted Avonlea bentonite. Data extracted from Sawatsky and Oscarson (1991).

environment, which causes the mobility of $\text{Tc}(\text{OH})(\text{CO}_3)_2^-$ to be significantly lower than that of TcO_4^- due to ion size and/or steric effects.

The study by Sawatsky and Oscarson (1991) illustrates the potentially significant roles of geochemical reactions, such as oxidation/reduction, precipitation/dissolution, and complexation on radionuclide diffusion through engineered containment barriers. Other examples of the importance of geochemistry on the diffusion of radionuclides can be found in Christiansen and Torstenfelt (1988), Mukai and Kataoka (1998), Eriksen et al. (1999), Cole et al. (2000), Kozaki et al. (2001), Tachi et al. (2001), Wersin (2003), Fernandez et al. (2004), Wang et al. (2004), Wang and Liu (2004), Xia et al. (2005), Wersin et al. (2007), Yamaguchi et al. (2007), Descostes et al. (2008), González Sánchez et al. (2008), Higashihara et al. (2008), Kozaki et al. (2008), Jakob et al. (2009), Melkior et al. (2009), and Fernandez et al. (2010).

Finally, in contrast to controlled laboratory experiments where the numbers and types of radionuclide species are limited and/or controlled, actual waste disposal scenarios often involve multiple species of a given radionuclide and/or different radionuclides. Under such conditions, consideration of the influence of the interaction of these species during diffusion via multispecies modeling will be required (e.g., Appelo and Wersin, 2007; Appelo et al., 2010).

4.2. Surface and/or interlayer diffusion

In some studies, diffusion of cations sorbed to clay particles has been evaluated in addition to diffusion of cations within the mobile pore water between particles, i.e., outside the extent of influence of the negative electrical potentials associated with the clay particle surfaces (e.g., van Schaik et al., 1966; Muurinen et al., 1987; Cheung, 1990; Berry and Bond, 1992; Conca et al., 1993; Kim et al., 1993; Eriksen et al., 1999; Cole et al., 2000; Molera and Eriksen, 2002; Bourg et al., 2003; Cormenzana et al., 2003; Appelo and Wersin, 2007; Glaus et al., 2007; Melkior et al., 2009; Appelo et al., 2010). This surface diffusion also has been referred to as the *excess mobility of the cation* (e.g., Molera and Eriksen, 2002) due to the excess of sorbed cations in the diffuse double layers surrounding negatively charged clay surfaces relative to the concentration of cations that exists in the mobile pore water. When referring to the excess of sorbed cations within the interlayer regions of smectitic based clays, such as bentonites, this phenomenon has been referred to more specifically as interlayer diffusion (Glaus et al., 2007; Appelo et al., 2010). When prevalent, surface and/or interlayer diffusion results in enhanced diffusion of cations, and diminished diffusion of anions, relative to the diffusion of neutral tracers such as HTO and HDO (Appelo et al., 2010).

Various studies have arrived at different conclusions regarding the significance of surface and/or interlayer diffusion, ranging from conclusions that surface diffusion was significant if not dominant (e.g., van Schaik et al., 1966; Muurinen et al., 1987; Cheung, 1990; Kim et al., 1993; Glaus et al., 2007) to conclusions that surface and/or interlayer diffusion was either nil or insignificant (e.g., Cho et al., 1993b; Conca et al., 1993; Oscarson, 1994; Cormenzana et al., 2003). In addition, the results of some studies indicate that the significance of surface diffusion is dependent on the chemical species. For example, Berry and Bond (1992) reported that surface diffusion of strontium (^{90}Sr) and americium (^{241}Am) accounted for 50 to 80% and 5 to 60% of the total diffusion, respectively, for diffusion through London clay and Darley Dale sandstone, but was nil for cesium (^{137}Cs). In contrast, Appelo et al. (2010) concluded that surface and/or interlayer diffusion contributed significantly to the diffusive mass flux of $^{134}\text{Cs}^+$ through Opalinus Clay, but that surface and/or interlayer diffusion of $^{22}\text{Na}^+$ and $^{85}\text{Sr}^{2+}$ was insignificant.

In terms of bentonites, Kim et al. (1993) concluded that diffusion of both $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ in a compacted bentonite was dominated by surface diffusion, whereas Cho et al. (1993b) reported that surface

diffusion of $^{137}\text{Cs}^+$ in compacted specimens of Avonlea bentonite and Lake Aggassiz clay was not important. Molera and Eriksen (2002) found that adsorbed $^{22}\text{Na}^+$, $^{85}\text{Sr}^{2+}$, and $^{134}\text{Cs}^+$ were all mobile to varying degrees in compacted bentonites, but that adsorbed cobalt ($^{57}\text{Co}^{2+}$) was completely immobilized upon adsorption as the result of formation of inner sphere complexes. Complete immobilization of Co^{2+} upon sorption to compacted MX-80 bentonite also was found by Eriksen et al. (1999), who noted that Co^{2+} formed outer sphere complexes with the permanent layer sites and, with increasing cobalt concentration and pH, formed surface complexes/precipitates with surface hydroxyl groups.

The significance of surface and/or interlayer diffusion also is likely to increase with increasing density of the clay (Conca et al., 1993). For example, Oscarson (1994) found that surface diffusion of three cations, $^{85}\text{Sr}^{2+}$, $^{45}\text{Ca}^{2+}$, and $^{22}\text{Na}^+$, in three different clays, viz. Avonlea bentonite, an illite/smectite, and a glacial lake clay composed primarily of smectite, illite, kaolinite, and quartz, was not significant up to compacted dry densities of 1.60 Mg/m^3 . In contrast, Kozaki et al. (2001) concluded that surface diffusion also may be important for anions, such as chloride (Cl^-), in sodium montmorillonite compacted at dry densities $\geq 1.8 \text{ Mg/m}^3$, when the pore spacings become almost identical to the interlayer spacings. Kozaki et al. (2001) postulated that the observed significance of surface diffusion for Cl^- was due to a requirement for charge compensation between Na^+ and Cl^- .

One of the criticisms of studies claiming significant, if not dominant, surface and/or interlayer diffusion has been the need to know the precise distributions of cations near the particle surfaces (e.g., Lever, 1986; Conca et al., 1993). For example, in the case where surface diffusion is being considered, the effective diffusion coefficient, D^* , can be related to the apparent diffusion coefficient, D_a , based on the following expression presented by Molera and Eriksen (2002)

$$D^* = D_a \frac{(\varepsilon + \rho_d K_d)}{(\varepsilon + f \rho_d K_d)} \quad (39)$$

where f is referred to as the mobile fraction, which represents the ratio of the surface related diffusion coefficient, D_s , to D^* , or

$$f = \frac{D_s}{D^*}. \quad (40)$$

Molera and Eriksen (2002) presented Eqs. (39) and (40) without derivation, so the derivation is presented as Appendix A for completeness. As indicated by Eq. (39), K_d representing the distribution between the sorbed concentration versus the concentration in the pore water is required to assess the relative contribution of surface diffusion (e.g., Cho et al., 1993b; Eriksen et al., 1999; Cole et al., 2000). Thus, the primary basis for the criticism of studies evaluating the significance of surface and/or interlayer diffusion appears to be related to the limitations associated with determining K_d , which is commonly obtained via batch equilibrium sorption tests where the conditions have long been known to be unrepresentative of those existing in compacted clays (e.g., Cherry et al., 1984; Tsai et al., 2001).

The overall conclusion resulting from the review of surface and/or interlayer diffusion of radionuclides is that the phenomenon is likely to be significant only in high activity clays, such as bentonites, compacted at relatively high dry densities, and that the significance will be a function of chemical speciation. Although the dry densities of compacted bentonites used in HLRW disposal generally are high and may be greater than those considered for use in LLRW disposal, some consideration of the potential significance of surface and/or interlayer diffusion of radionuclides in engineered containment barriers for LLRW disposal is warranted (e.g., Cho et al., 1993b).

4.3. Anion exclusion and semipermeable membrane behavior

Traditionally, solute restriction has been referred to as anion exclusion (e.g., Porter et al., 1960; van Schaik and Kemper, 1966; Shackelford and Daniel, 1991; Berry and Bond, 1992; Van Loon et al., 2007; Descostes et al., 2008), primarily because the phenomenon generally has been associated with clays such as bentonites that are dominated by high activity smectitic clay minerals (e.g., Na-montmorillonite), with predominantly negative surface charges. In this case, when the clay is compressed to a sufficiently high density such that the pore spaces between adjacent clay particles are minimized to the extent that the electrostatic (diffuse double) layers surrounding the particles overlap, the overlapping negative potentials repel invading anions such that the pore becomes excluded to the anion. Cations also may be excluded to the extent that electrical neutrality in solution is required (e.g., Robinson and Stokes, 1959).

This phenomenon of anion exclusion also is responsible for the existence of semipermeable membrane behavior, which refers to the ability of a porous medium to restrict the migration of solutes, while allowing passage of the solvent (e.g., Shackelford, 2012). The existence of semipermeable membrane behavior leads to chemico-osmosis (e.g., Heister et al., 2006; Garavito et al., 2007), or liquid flow from a region of lower solute concentration (higher water chemical potential) to a region of higher solute concentration (lower water chemical potential). Also, in clays where there is a distribution in pore sizes, some of the pores may be restrictive whereas others are not. In this case, diffusion of solutes also can occur simultaneously from a region of higher solute concentration to a region of lower solute concentration, although the rate of this diffusion would be slowed relative to that which would exist in the case where all the pores were accessible (e.g., Descostes et al., 2008).

For example, Moore and Shackelford (2011) reported values of the apparent tortuosity factor, τ_a , calculated on the basis of D_e and ε values reported in Muurinen (1990) for diffusion of uranium in compacted bentonites, assuming a D_o value for hexavalent uranium (U^{6+}) of $3.9\text{--}4.9 \times 10^{-10}$ m²/s. Hexavalent uranium was assumed as the governing species, because only the U^{4+} and U^{6+} species are stable in aqueous solution, and U^{4+} is relatively insoluble compared with U^{6+} and also typically is oxidized to U^{6+} in the form of the aqueous soluble uranyl cation, UO_2^{2+} (Moore and Shackelford, 2011). The resulting values of τ_a are shown in Fig. 6 as a function of ε , and compared with those predicted on the basis of the following commonly applied empirical correlation (Parker et al., 1994):

$$\tau_a = a\varepsilon^b \quad (41)$$

where $a = 1$ and b typically ranges from 1.3 to 5.4, depending on the porous medium. However, as shown in Fig. 6, reasonable estimates of τ_a for the results based on Muurinen (1990) are obtained using Eq. (41) with values of a ranging from 0.150 to 0.188 and a value for b of 8.18. These values for a and b result in significantly lower values of τ_a than predicted by Eq. (41), i.e., for the range of ε considered, reflecting the significantly increased apparent tortuosity (decreased apparent tortuosity factor) afforded by highly compacted bentonites relative to other porous media. Moore and Shackelford (2011) concluded that such low τ_a values are likely due, in part, to the existence of semipermeable membrane behavior (ion exclusion) in bentonites, which can significantly reduce the magnitude of D_e or D^* in bentonites depending on the porosity of the bentonite and the concentration of the chemical species (Shackelford, 2012).

Substantial evidence based on research conducted in the past approximate decade indicates that semipermeable membrane behavior is a potentially significant factor governing the migration of solutes through bentonite-based engineered containment barriers (e.g., Malusis et al., 2001; Malusis and Shackelford, 2002a,b; Yeo et al., 2005; Henning et al., 2006; Kang and Shackelford, 2009, 2010, 2011; Mazzieri et al., 2010). For example, consider the results from

Shackelford (2012) shown in Fig. 7, where the membrane efficiency coefficient is plotted as a function of the bentonite content of the barriers, which include a GCL, an unamended compacted clay liner (CCL) and a bentonite amended CCL (5% bentonite content by dry weight), and two backfills representative of those used in SB vertical cutoff walls. The membrane efficiency coefficient, ω , ranges from zero in the case of no membrane behavior (e.g., a sand) to unity in the case of an ideal or perfect membrane behavior in which all solutes are restricted from migration.

As shown in Fig. 7, except for the bentonite amended CCL, there is a general trend of increasing ω with increasing bentonite content, with values of ω increasing from 0.013 for the unamended CCL to $0.48 \leq \omega \leq 0.68$ for the GCL containing 100% sodium bentonite. Except for the case of the bentonite amended CCL, Shackelford (2012) attributed the variability in ω at a given bentonite content to slight variability in the porosity of the test specimens (GCL and SB backfills) or variability inherent in the measurements. The lack of data for bentonite contents between 7.2% and 100% was attributed primarily to the fact that bentonite amendments to natural soils used as engineered containment barriers greater than about 10% generally are considered prohibitive from a cost standpoint, such that alternative, more cost efficient barrier materials (e.g., GCLs or geomembranes) generally are preferred. The greatly enhanced membrane behavior of the bentonite amended CCL (i.e., $0.73 \leq \omega \leq 0.76$) relative to the unamended CCL ($\omega = 0.013$) has been attributed to the contribution of the high fines content (89%) of the base natural clay in constricting the sizes of the pores upon addition of the small amount (5%) of bentonite (Kang and Shackelford, 2010).

The effects of anion exclusion on diffusion have historically been taken into account qualitatively or indirectly by incorporating a correction or anion exclusion factor within the form of Fick's first law (e.g., γ in Eq. (13)). This approach resulted because there was no direct method to determine the effects of anion exclusion exclusive from diffusion. However, Malusis et al. (2001) developed a laboratory testing apparatus that allows simultaneous measurement of both ω and D^* of salts for clays. By using this apparatus, Malusis and Shackelford (2002a) measured both the steady-state values of D^* for a simple salt, KCl, at relatively dilute concentrations (≤ 47 mM) diffusing through a GCL and the corresponding values of ω . The results of their measurements based on chloride (Cl^-) are shown in Fig. 8a. Although the D^* values measured by Malusis and Shackelford (2002a) were reported as coupled diffusion coefficients, D_{ω}^* , a recent re-evaluation of the theory upon which their analysis was based by Malusis et al. (2012) has indicated that the D_{ω}^* values reported by Malusis and Shackelford (2002a) are actually the true, uncoupled D^*

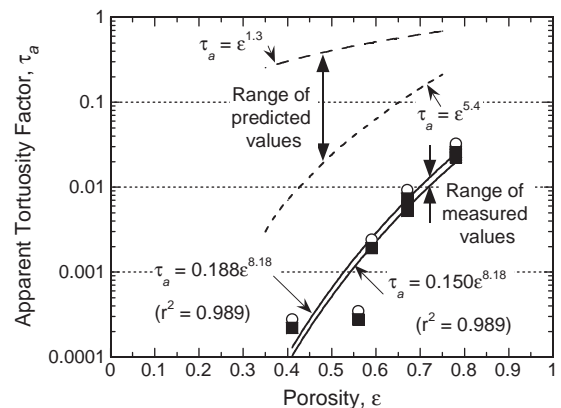


Fig. 6. Predicted and measured apparent tortuosity factor versus total porosity based on uranium (U^{6+}) diffusion in compacted bentonite. Replotted after Moore and Shackelford (2011).

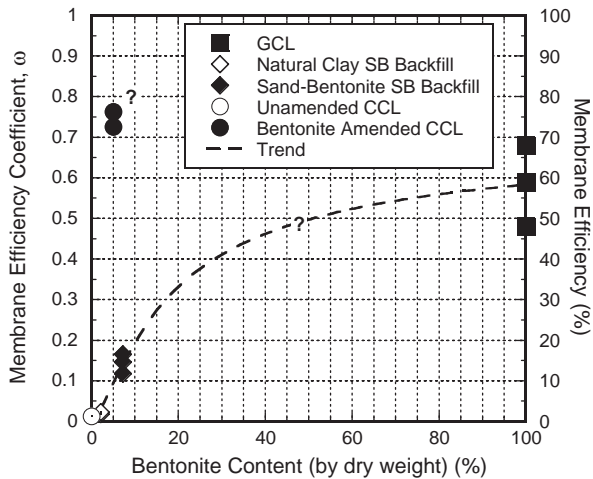


Fig. 7. Correlation between membrane efficiency coefficient and bentonites content of engineered containment barriers. Replotted after Shackelford (2012).

values for the case of mutual or salt diffusion, which is the case more relevant to waste disposal applications. As a result, the diffusion coefficients in Fig. 8a are shown as D^* values.

As shown in Fig. 8a, the trend in D^* versus ω is towards $D^* = 0$ at $\omega = 1$, which is required based on the principle that no solutes can pass through an ideal or perfect membrane. Thus, as expected, the data in Fig. 8 reflect a direct correlation between semipermeable membrane behavior and diffusion of inorganic chemical species.

Values for the apparent tortuosity factor, τ_a , also are shown in Fig. 8a. These τ_a values were calculated as the ratio of D^*/D_0 based on Eqs. (16) and (19), where D_0 was taken as $19.93 \times 10^{-10} \text{ m}^2/\text{s}$ for KCl at 25 °C, i.e., since the measured values for D^* represented those at steady-state diffusion of KCl (Malusis and Shackelford, 2002a). As indicated in Fig. 8a, the trend in τ_a versus ω mimics the trend in D^* versus ω . Also, by extrapolation, the limiting, maximum value of τ_a at $\omega = 0$, or $\tau_{a,max}$ is approximately 0.12. Since $\omega = 0$ corresponds to the case of no solute restriction, $\tau_{a,max}$ also represents an estimate of the matrix tortuosity factor, τ_m (Malusis and Shackelford, 2002a). Thus, based on $\tau_m = 0.12$, values of $\tau_r (= \tau_a/\tau_m)$ can be calculated as a function of ω , as shown in Fig. 8b.

The resulting trend in τ_r versus ω in Fig. 8b again reflects a tendency towards $\tau_r = 0$ at $\omega = 1.0$, as required. In fact, based largely on the data shown in Fig. 8b, Manassero and Dominijanni (2003) proposed a simple expression for the relationship between τ_r and ω , viz., $\tau_r = 1 - \omega$ (see Figure 8b). A theoretical basis for this simple expression also has been provided (e.g., see Dominijanni and Manassero, 2012a,b).

Thus, the data in Fig. 8 illustrate a direct correlation between semipermeable membrane behavior and the diffusion of inorganic chemical species through clays. Although membrane behavior of bentonite-based barriers has been shown to decrease with increasing salt concentration as well as increasing charge of salt cation (e.g., Malusis and Shackelford, 2002b; Shackelford, 2012), such that diffusion of invading multivalent cations into imperfect membranes may ultimately destroy any membrane behavior (e.g., Shackelford and Lee, 2003), the potential impact of semipermeable membrane behavior on radionuclide diffusion through engineered containment barriers may be significant. As a result, prudence dictates that the potential for semipermeable membrane behavior be considered when undertaking studies focused on radionuclide diffusion through bentonite-based engineered containment barriers or other clays composed of significant amounts of high activity clay minerals, especially if these barriers are to be compacted at relatively high dry densities.

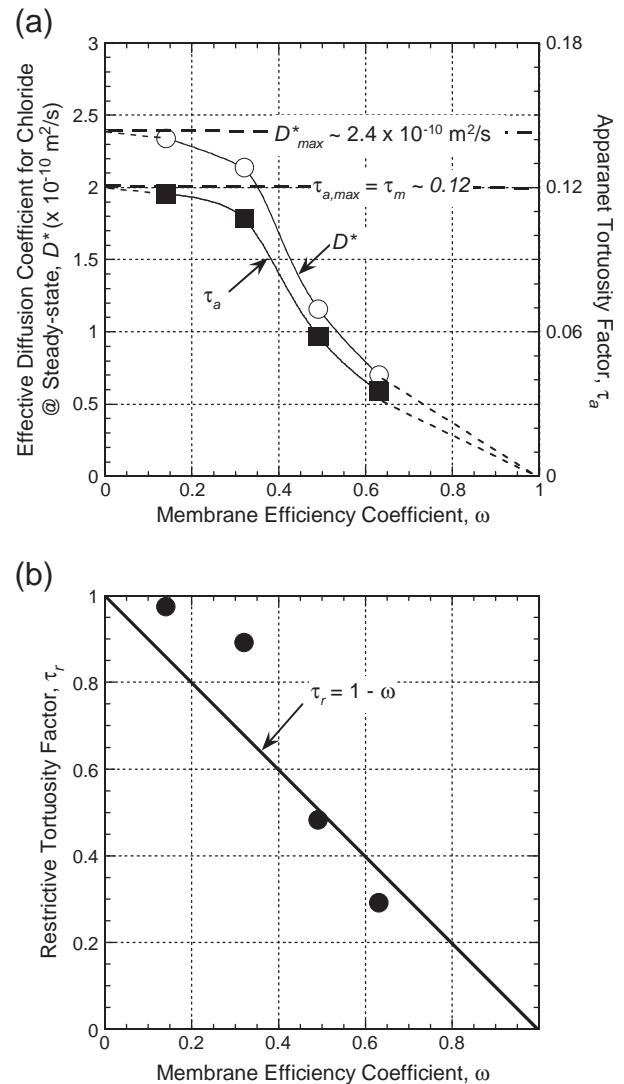


Fig. 8. Effect of semipermeable membrane behavior on (a) the effective diffusion coefficient of chloride (Cl^-) and apparent tortuosity factor, and (b) the restrictive tortuosity factor of a geosynthetic clay liner. Data from Malusis and Shackelford (2002a).

5. Conclusions

The results of a literature review focused on Fickian diffusion of radionuclides for engineered containment barriers were presented. Four different definitions of the diffusion coefficient were identified as represented by D^* , D_e , D_p , and D_a . The differences in the definitions of these diffusion coefficients result from the different forms of Fick's first and second laws governing macroscopic diffusion through porous media. All forms of Fick's first law for diffusive mass flux include an effective porosity, ε_{eff} , whether this term is shown explicitly in Fick's first law or is buried within the definition of the diffusion coefficient. The relative magnitudes of the four different diffusion coefficients are shown to vary depending on whether the diffusing radionuclide is nonsorbing (tracer) or sorbing, and for sorbing radionuclides, vary as a function of the relative magnitude between the total porosity, ε , and the inverse of the retardation factor, R_d^{-1} . For nonsorbing radionuclides, the magnitudes of the diffusion coefficients should vary in the order: $D_p \geq D^* = D_a > D_e$. In the case of sorbing radionuclides when $R_d^{-1} \leq \varepsilon$, then $D_p \geq D^* > D_e \geq D_a$, whereas if $R_d^{-1} \geq \varepsilon$, then $D_p \geq D^* > D_a \geq D_e$.

In addition to ε_{eff} and ε , a diffusion accessible porosity, ε_{diff} , that takes into account the possibility of diffusion into dead-end pores

also has been identified. The three porosity terms generally vary as $\varepsilon_{eff} \leq \varepsilon_{diff} \leq \varepsilon$, but there can be more than one value of ε_{diff} depending on the species of radionuclide. The value of ε_{diff} for a non-charged tracer, such as tritium (HTO), generally is found to be the same as ε , whereas the values of ε_{diff} for anionic radionuclides (e.g., $^{36}\text{Cl}^-$) generally are lower than ε due to anionic repulsion and/or steric hindrance. The common assumption that ε_{diff} for a given chemical species is the same as ε_{eff} is shown, at least conceptually, to not necessarily be valid.

Finally, three potentially significant complicating issues were identified, viz., the geochemistry of the barrier system, the potential influence of surface and/or interlayer diffusion, and the potential existence of semipermeable membrane behavior as a result of anion exclusion. Both the surface charge of the solid phase of the barrier and the chemistry of the aqueous phase can radically affect the rate and magnitude of diffusion of radionuclides through engineered containment barriers. The results of a study evaluating the influence of redox conditions, temperature, and test duration on the diffusion of technetium (^{99}Tc) through a compacted bentonite illustrated the significance of redox conditions, precipitation, and sorption of different chemical species of ^{99}Tc on the overall diffusive transport of the radionuclide. In cases where multiple species of a given radionuclide and/or different radionuclides exist, consideration of the potential need for multispecies modeling is required.

When prevalent, surface and/or interlayer diffusion results in enhanced diffusion of cations, and diminished diffusion of anions, relative to the diffusion of neutral tracers such as HTO and HDO. However, surface and/or interlayer diffusion of radionuclides is likely to be significant only in high activity clays, such as bentonites, compacted at relatively high dry densities, and the significance will be a function of chemical speciation. Although these conditions may not exist for engineered barriers used for LLRW containment, prudence dictates consideration of the potential significance of surface and/or interlayer diffusion of radionuclides.

Semipermeable membrane behavior resulting from anion exclusion has been shown to exist in bentonite based barriers for waste containment. Relatively recent advances in testing equipment have allowed for simultaneous quantification of both the membrane behavior resulting from anion exclusion and the diffusion properties of the barrier material. The use of this equipment to assess the diffusion of a simple salt (KCl) solution has indicated a direct correlation between decreasing diffusion with increasing membrane behavior. Thus, although the existence and magnitude of membrane behavior have been shown to be significant only for relative dilute concentrations of simple salt solutions, consideration of the potential significance of the effect of membrane behavior on radionuclide diffusion through engineered containment barriers is recommended.

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Appendix A. Effect of surface diffusion of cations

The negative surface charge that exists in clays due to isomorphic substitution results in an excess of cations adsorbed to the particle surfaces relative to the distribution of anions in order to satisfy the requirement for electroneutrality of the solid phase due to the negative surface charge of the particles. This electrostatically held layer of excess cations often is referred to as the *diffuse double layer* (DDL), the *Gouy–Chapman layer*, or simply the *adsorbed layer of cations*. Some

studies have assumed that this excess distribution of cations immediately adjacent to the clay particle surface can contribute to the overall diffusion of the cations within the free pore water between adjacent clay particles (e.g., Molera and Eriksen, 2002). In this case, the overall apparent diffusion coefficient, D_a , is presupposed to represent a mass based weighted average of the diffusion of the cation within the free pore water as represented by D^* and a surface diffusion coefficient, D_s , as follows:

$$D_a = \frac{M}{M_T} D^* + \frac{M_s}{M_T} D_s \quad (\text{A.1})$$

where M is the mass of the mobile chemical species (cation) in the free pore water, M_s is the mass of the same chemical species sorbed to the particle surface, and M_T is the total mass of the cation, or $M_T = M + M_s$. The relationship between M_s and M is given as follows:

$$M_s = \frac{\rho_d K_d}{\varepsilon} M \quad (\text{A.2})$$

where ρ_d and ε are the dry density and porosity of the clay, respectively, and K_d is the *distribution coefficient* representing the ratio of the concentration of the chemical species sorbed to the solid phase of the porous medium, C_s , relative to the concentration of the same chemical species in the free pore water, C , or:

$$K_d = \frac{C_s}{C} \quad (\text{A.3})$$

where C_s is defined as M_s per unit mass of dry solids, m_s , and C is expressed as M per volume of voids, V_v (i.e., assuming saturated pores). Thus, Eq. (A.3) may be represented as follows:

$$K_d = \frac{M_s V_v}{m_s M} \quad (\text{A.4})$$

and the total mass of the chemical species is related to the mass of the chemical species in the free pore water as follows:

$$M_T = M + M_s = M + \frac{\rho_d K_d}{\varepsilon} M = \left(\frac{\varepsilon + \rho_d K_d}{\varepsilon} \right) M \quad (\text{A.5})$$

Therefore,

$$\frac{M}{M_T} = \frac{\varepsilon}{\varepsilon + \rho_d K_d} \quad (\text{A.6})$$

and

$$\frac{M_s}{M_T} = \frac{\frac{\rho_d K_d}{\varepsilon} M}{\left(\frac{\varepsilon + \rho_d K_d}{\varepsilon} \right) M} = \frac{\rho_d K_d}{\varepsilon + \rho_d K_d} \quad (\text{A.7})$$

Substituting Eqs. (A.6) and (A.7) into Eq. (A.1) gives the following general expression for D_a in terms of D^* and D_s :

$$D_a = \left(\frac{\varepsilon}{\varepsilon + \rho_d K_d} \right) D^* + \left(\frac{\rho_d K_d}{\varepsilon + \rho_d K_d} \right) D_s \quad (\text{A.8})$$

or

$$D_a = D^* \left(\frac{\varepsilon + f \rho_d K_d}{\varepsilon + \rho_d K_d} \right) \quad (\text{A.9})$$

where f is given as follows:

$$f = \frac{D_s}{D^*} \quad (\text{A.10})$$

Eq. (A.10) can be rearranged to give D^* as a function of D_a as follows:

$$D^* = D_a \left(\frac{\varepsilon + \rho_d K_d}{\varepsilon + f \rho_d K_d} \right) \quad (\text{A.11})$$

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