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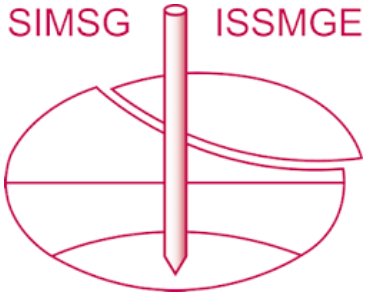

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Rowe Lecture
The role of diffusion in environmental geotechnics

Conférence Rowe
Le rôle de la diffusion en géotechnique environnementale

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ABSTRACT: Diffusion of contaminants can play a significant if not dominant role in many applications encountered within the field of environmental geotechnics. The objective of this paper is to provide an overview of the important role diffusion plays in such applications. The presentation proceeds from a historical perspective, beginning with the recognition in the late 1970s to early 1980s that diffusion may be an important process in assessing contaminant migration through low permeability barriers in waste containment applications. Data from the literature and simplified model simulations are used to illustrate under what conditions diffusion is important, and the significance of diffusion with respect to different barrier components and types of barriers in waste containment applications is illustrated. The barriers considered include natural clays, compacted clay liners, geomembrane liners, geosynthetic clay liners, composite liners, vertical cutoff walls, subaqueous caps for contaminated sediments, and highly compacted bentonite buffers for high level radioactive waste containment. The significance of semipermeable membrane behavior on liquid-phase diffusion through bentonite-based barriers also is highlighted. The potential importance of matrix diffusion as an attenuation mechanism for contaminant transport also is illustrated, and the roles of both liquid-phase and gas-phase diffusion under unsaturated conditions are discussed. Finally, the role of diffusion in terms of remediation applications is illustrated via an example analysis illustrating the impact of reverse matrix or back diffusion on the effectiveness of pump-and-treat remediation.

RÉSUMÉ: La diffusion de contaminants peut jouer un rôle significatif si ce n'est dominant dans le domaine de la géotechnique environnementale. L'objectif de cet article est de fournir une vue d'ensemble du rôle important de la diffusion dans de telles applications. La présentation suit une perspective historique : elle commence avec la reconnaissance vers la fin des années 70 au début des années 80, du fait que la diffusion peut être un processus important dans l'évaluation de la migration de contaminants à travers des barrières à perméabilité réduite dans des applications de confinement de déchets. Des données tirées de la littérature et des simulations avec des modèles simplifiés sont utilisées pour mettre en lumière sous quelles conditions la diffusion est importante. L'importance de la diffusion pour divers matériaux de barrières et types de barrières dans les applications de confinement des déchets est illustrée ; les barrières considérées comprennent les argiles naturelles, les liners d'argile compactée, les liners en géomembrane, les liners d'argile géosynthétique, les liners composites, les murs de confinement verticaux, les couvertures subaquatiques pour sédiments contaminés, et des zones tampons en bentonite fortement compactée pour le confinement des déchets radioactifs. L'importance du comportement des membranes semi-perméables sur la diffusion en phase liquide à travers des barrières à base de bentonite, telles que les liners en argile géosynthétique, est aussi présentée. L'importance potentielle de la diffusion en matrice en tant que mécanisme d'atténuation pour le transport de contaminants est aussi illustrée, et les rôles de la phase liquide comme de la phase gazeuse dans des conditions non saturées sont examinés. Finalement, le rôle de la diffusion en terme d'applications de dépollution est illustré via l'analyse d'un exemple qui décrit l'impact de la diffusion arrière sur l'efficacité de la dépollution « pump-and-treat » (pompage-écrémage-filtration).

KEYWORDS: Advection; Containment; Contaminant; Diffusion; Fick's laws; Membrane behavior; Remediation

1 INTRODUCTION

The advent of the formal sub-disciplinary field of geotechnical engineering known as environmental geotechnics can be traced to the early to mid 1970s, soon after the formation of environmental regulatory agencies, such as the United States Environmental Protection Agency (US EPA) formed in 1970, whose purpose was to enforce environmental regulations promulgated for the protection of human health and the environment (Shackelford 1999, 2000). One of the first orders of business for these regulatory agencies was to provide guidelines and regulations for the safe disposal of a variety of liquid and solid wastes, including hazardous solid waste (HSW) and municipal solid waste (MSW). For example, the Resource Conservation and Recovery Act (RCRA) promulgated in the US in 1976 provided detailed guidelines for the use of low permeability barriers of recompacted clay, since known as compacted clay liners (CCLs), to minimize the migration of liquids and contaminants emanating from HSW and MSW in the form of RCRA Subtitles C and D, respectively. Until this period of time, wastes had been disposed largely with relatively little or no regard for any potential environmental consequences, often in unlined pits and dumps or in facilities that relied primarily upon the inherent low permeability of any natural soil within the vicinity of the disposal location.

Because of the lack of concern for environmental consequences resulting from waste disposal prior to this period, contamination at numerous disposal sites (hundreds to thousands) had already occurred over the previous decades, such as the infamous Love Canal site located in Niagara Falls, New York, USA. Public awareness of the potential environmental health concerns from such existing contamination resulted in the realization of the need to clean up or remediate the existing contamination from sites that had already been polluted. An example of this

realization is the promulgation in the US in 1980 of the law known as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund, that authorized the US EPA to respond to releases, or threatened releases, of hazardous substances that may endanger public health, welfare, or the environment, and also enabled the US EPA to force parties responsible for environmental contamination to clean up such contamination and/or to reimburse the Superfund for response or remediation costs incurred by the government. Thus, the burgeoning field of environmental geotechnics began to address technical issues related not only to the prevention of contamination resulting from disposal of new waste, but also to the remediation or clean up of existing contamination resulting from improper disposal practices in the past.

Because of the experience of geotechnical engineers in using compacted clays for applications such as the low permeability cores of engineered earthen dams (e.g., Mitchell et al. 1965), geotechnical engineers immediately became involved and identified with the design and use of CCLs as engineered barriers for disposal of new wastes. However, the early emphasis in the use of CCLs as barriers for waste containment focused primarily on the physical and mechanical properties of the CCLs, such as minimizing the hydraulic conductivity, k_h, of the CCL in order to reduce the rate of seepage of contaminated liquids (e.g., leachates), v, through the CCLs resulting from the application of a hydraulic gradient, i_h, in accordance with Darcy's law (i.e., $v = k_h \cdot i_h$). The realization of the need to consider the chemical properties of the contaminants as well as the potential detrimental impacts resulting from the physico-chemical interactions between the liquids being contained and the soils used to contain the liquids was more gradual, and has developed over an extended time frame. In particular, beginning in the late 1970s to early 1980s, diffusion became recognized as a potentially important process in assessing contaminant migration through low permeability barriers in waste containment applications. This recognition led to a progressively greater understanding of the role diffusion plays in a wide variety of applications in environmental geotechnics, including applications in both waste containment and remediation. Thus, the objective of this paper is to provide an overview of the role diffusion plays in the field of environmental geotechnics.

2 WHAT IS DIFFUSION?

Diffusion is a fundamental, irreversible process whereby 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 (Quigley et al. 1987, Shackelford and Daniel 1991a, Shackelford and Moore 2013). Since chemical potential is directly related to chemical concentration, diffusion is more commonly 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 a porous medium 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 1991a, Shackelford and Rowe 1998):

$$J_d = nD^* i_c = n\left(\tau_a D_o\right) i_c \tag{1}$$

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 diffusion [$ML^{-2}T^{-1}$; M = units of mass, L = units of length, and T = units of time], n is the total porosity of the porous medium, D^* is the effective diffusion coefficient [L^2T^{-1}], τ_a (< 1) is the apparent tortuosity factor [-], D_o is the aqueous-phase or free solution (without porous medium) diffusion coefficient [L^2T^{-1}], and i_c is the concentration gradient in the direction of diffusion [-], which is positive when directed towards decreasing solute concentration. The apparent tortuosity factor, τ_a, represents the product of the actual matrix tortuosity factor representing the geometry of the interconnected pores, τ_m (< 1), and the restrictive tortuosity factor, τ_r, as follows (Malusis and Shackelford 2002a, Shackelford and Moore 2013):

$$\tau_a = \tau_m \tau_r \tag{2}$$

where τ_r represents the product of all other factors that may be effective in reducing the diffusive mass flux of a chemical species, such as ion exclusion. In essence, τ_r represents the ratio of the effective to total porosities, or (Shackelford and Moore 2013):

$$\tau_r = \frac{n_e}{n} \tag{3}$$

where $n_e \leq n$ such that $\tau_r \leq 1$.The recognition of an effective porosity takes into account the possibility that that there may be pores that are not interconnected or are inaccessible to specific solutes such that only a fraction of the pore space may be available for diffusion (Shackelford and Moore 2013).

Fick's second law governing transient one-dimensional diffusion of chemical species subject to first-order linear decay in porous media can be written as follows (e.g., Shackelford and Daniel 1991a, Shackelford and Rowe 1998, Shackelford and Moore 2013):

$$\frac{\partial C}{\partial t} = \frac{D^*}{R_d}\frac{\partial^2 C}{\partial x^2} - \lambda C = D_a \frac{\partial^2 C}{\partial x^2} - \lambda C \tag{4}$$

where C is solute concentration [ML^{-3}], R_d is the dimensionless retardation factor, D_a ($=D^*/R_d$) is the apparent diffusion coefficient [L^2T^{-1}], and λ is the decay constant [T^{-1}]. For chemical species subjected to first-order decay (e.g., radionuclides), λ is inversely related to the half life of the chemical species, $t_{1/2}$, such that λ decreases as $t_{1/2}$ increases. For this reason, the decay term in Eq. 4 can be (and often is) ignored without any significant loss in accuracy for chemical species with half lives that are considerably longer than the time frame being considered for diffusion (Shackelford and Moore 2013).

The retardation factor in Eq. 4 accounts for linear, reversible, and instantaneous sorption of a chemical species, and 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. For water saturated porous media, R_d may be expressed as follows:

$$R_d = 1 + \frac{\rho_d}{n} K_d \tag{5}$$

where 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 is the distribution coefficient [L^3M^{-1}], which relates the solid-phase concentration, C_s, expressed as the sorbed mass of the chemical species per unit mass of the solid phase [MM^{-1}], to the aqueous-phase concentration, C, of the chemical species (i.e., assuming linear, reversible, and instantaneous sorption), or $K_d = C_s/C$. 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. 4 represents a lumped effective diffusion coefficient that includes the effect of attenuation via R_d. For this reason, D_a also has been referred to as the effective diffusion coefficient of a reactive chemical species (Shackelford and Daniel 1991a). For water unsaturated porous media, the total porosity, n, in Eq. 5 is replaced by the volumetric water content, θ_w, where $\theta_w = nS_w$ and S_w is the degree of water saturation ($0 \le S_w \le 1$).

Since the notation for the various diffusion coefficients defined herein may not match the notation used by others (e.g., D^* as defined herein also is commonly designated as D_e), 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. Unless indicated otherwise, the default definition of the diffusion coefficient used herein is that corresponding to D^*. For liquid-phase diffusion of aqueous soluble chemical species in saturated porous media, values of D^* generally fall within range 10^{-9} $m^2/s > D^* > 10^{-11}$ m^2/s, with lower values of D^* being associated with finer textured and/or denser soils (Shackelford and Daniel 1991a, Shackelford 1991). Since $\tau_a < 1$, the upper limit on D^* of 10^{-9} m^2/s is dictated by the D_o values, which generally ranges from about 1 to 2 x 10^{-9} m^2/s for most aqueous soluble chemical species, except for those involving H^+ or OH^-, in which case D_o is approximately 2 to 4 times higher (Shackelford and Daniel 1991a). Values of $D^* < 10^{-11}$ m^2/s are possible in situations involving bentonite-based containment barriers, such as highly compacted bentonite buffers for high-level radioactive waste disposal, primarily as a result of ion exclusion resulting from the existence of semipermeable membrane behavior such that $\tau_r < 1$ (e.g., Malusis and Shackelford 2002a, Shackelford and Moore 2013). Liquid-phase values of D^* for unsaturated porous media generally decrease with decreasing θ_w or S_w and can be several orders of magnitude lower than the respective values at full water saturation (Shackelford 1991). Finally, values of D_a for reactive chemical species (e.g., heavy metal cations) typically range from one to several orders of magnitude lower than the corresponding D^* values due to attenuation mechanisms (e.g., sorption, ion exchange, precipitation, etc.), i.e., $R_d > 1$.

3 WHEN IS DIFFUSION SIGNIFICANT?

Following the approach of Shackelford (1988), the significance of diffusion on the migration of aqueous soluble chemical species, or solutes, through porous media can be illustrated with the aid of solute breakthrough curves, or BTCs, representing the temporal variation in the concentration of a given chemical species at the effluent end of a column of porous medium. As depicted schematically in Fig. 1a, BTCs can be measured in the laboratory for a column of a porous medium of length L by (a) establishing steady-state seepage conditions, (b) continuously introducing at the influent end of the column a chemical solution containing a known chemical species at a concentration C_o, and (c) monitoring the concentration of the same chemical species emanating from the column as a function of time, or $C(L,t)$ (Shackelford 1993, 1994, 1995, Shackelford and Redmond 1995). Because the source concentration, C_o, is constant, the BTCs typically are presented in the form of dimensionless relative concentration, $C(L,t)/C_o$, versus elapsed time. The time required for the solute to migrate from the influent end to the effluent end of the column is referred to as the "breakthrough time" or the "transit time."

For example, consider the three BTCs depicted in Fig. 1b for the case of a low permeability clay (k_h = 5 x 10^{-10} m/s) contained within a column of length 0.91 m and at a porosity of 0.5, and subjected to an applied hydraulic gradient, i_h, of 1.33. The chemical solution serving as the permeant liquid contains a nonreactive solute at a constant concentration of C_o and is assumed to be sufficiently dilute such that no adverse interactions between the clay and the solution result in any changes in k_h during the test.

The BTC in Fig. 1b labeled "pure advection" represents the case commonly referred to as "piston" or "plug" flow, whereby the breakthrough time is the time predicted in the absence of any dispersive spreading of the solute front using the seepage velocity, v_s, in accordance with Darcy's law (i.e., $t = L/v_s = nL/k_h i_h$). Under purely advective (hydraulic) transport conditions, 21.8 yr would be required for the solute to completely break through the effluent end of the column (i.e., $C(L,t)/C_o = 1$) in the absence of any dispersive spreading of the solute front, owing to the very low seepage rate.

The BTC in Fig. 1b labeled "advection plus mechanical dispersion" represents the spreading effect on the solute front primarily due to mechanical (advective) dispersion (i.e., diffusive dispersion is assumed negligible), which is the case commonly depicted in groundwater hydrology textbooks because the primary concern pertains to contaminant migration within aquifers, or coarse-grained, water-bearing strata subjected to relatively high seepage velocities. The BTC for this case, as well as that for the next case, was generated using a commonly applied analytical model to the advective-dispersive solute transport equation developed by Ogata and Banks (1961) for the stated conditions of the column test (e.g., Shackelford 1990). In this case, the dispersive spreading of the solute front is attributed to variations in the pore-scale velocity profiles at the column scale and heterogeneities in hydraulic conductivity at the field scale (e.g., Shackelford 1993). Due to this spreading effect of the solute front, there are an infinite number of possible breakthrough times depending on the value of $C(L,t)/C_o$ used to define the breakthrough time. However, the typical practice is to evaluate the breakthrough time at a relative concentration of 0.5, which is the time at which the BTCs for pure advection and advection plus mechanical dispersion intersect.

The BTC in Fig. 1b labeled "advection plus diffusion" is the true BTC for this column, as this BTC reflects the situation when the seepage velocity is sufficiently low such that the effect of diffusion is not masked by the effects of advection and mechanical dispersion. The spreading effect is still noticeable in this BTC, but this BTC is displaced to the left of the previous two BTCs, resulting in a breakthrough time at $C(L,t)/C_o$ of 0.5 of 14.8 yr, which is considerably less than the value of 21.8 yr for the two previous cases where diffusion is ignored. Thus, failure to include the diffusion as a transport process under the

conditions of this column test would result in not only an incorrect but also an unconservative (high) estimate of the breakthrough time.

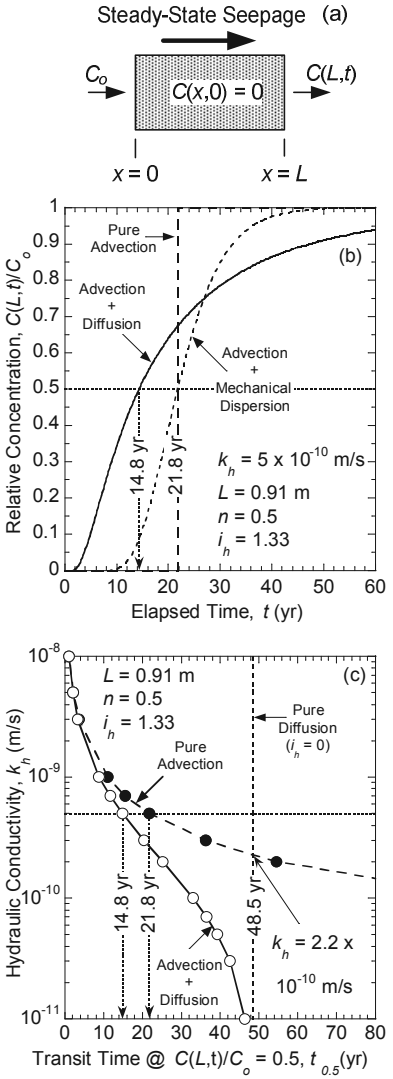

Figure 1. Effect of diffusion on solute transport through a column of soil of length L, porosity n, and hydraulic conductivity k_h, under a hydraulic gradient of i_h; (a) column containing porous medium; (b) breakthrough curves illustrating effect of diffusion at low k_h; (c) transit (breakthrough) times, $t_{0.5}$, as a function of k_h (modified after Shackelford 1988).

As previously implied, the decrease in the breakthrough time due to diffusion evident in the BTCs shown in Fig. 1b is a function of the magnitude of the seepage velocity. This dependence on v_s is illustrated in Fig. 1c, where the breakthrough times at $C(L,t)/C_o$ of 0.5, or $t_{0.5}$, are shown for the cases of pure advection and advection plus diffusion as a function of the k_h of the porous medium in the column, all other conditions being the same (i.e., L = 0.91 m, n = 0.5, i_h = 1.33). The limiting case of pure diffusion (i_h = 0) also is shown in Fig. 1c for comparison. The horizontal distance between the pure advection and advection plus diffusion curves represents the offset distance at $C(L,t)/C_o$ of 0.5, or $\Delta t_{0.5}$, in Fig. 1b for a given k_h. The independence of pure diffusion on k_h is represented by a vertical line corresponding to $t_{0.5}$ of 48.5 yr. Three observations are apparent from the curves shown in Fig. 1c (Shackelford 1988): (1) diffusion has an effect (i.e., $\Delta t_{0.5}$ > 0) even at a k_h of 10^{-9} m/s, which typically is the maximum regulated k_h value for many waste containment applications; (2) the sole use of Darcy's law (i.e., pure advection) to predict breakthrough times is extremely unconservative at k_h values less than about 2.2 x 10^{-10} m/s; and (3) diffusion starts to become the dominant transport process (i.e., as the curve for advection plus diffusion starts to approach asymptotically that for pure diffusion) at a k_h value of about 2 to 3 x 10^{-10} m/s. Of course, the solute mass flux also would be significantly reduced with decreasing k_h, but still may be environmentally significant (e.g., Johnson et al. 1989). Regardless, this simplified analysis illustrates the importance of diffusion in low permeability porous media.

In terms of concentration profiles, consider the scenario depicted in Fig. 2a corresponding to a ponded source of liquid containing a nonreactive chemical species at a constant concentration, C_o, underlain by an initially uncontaminated soil with an n of 0.5. The resulting concentration profiles beneath the source at an elapsed time of 5 yr assuming a D^* of 6 x 10^{-10} m^2/s are shown in Figs. 2b, 2c, and 2d for advective dominated (k_h = 10^{-8} m/s), diffusive significant (k_h = 10^{-9} m/s), and diffusive dominated (k_h = 10^{-10} m/s) cases, respectively. For the advective dominated case (Fig. 2b), the pure advective (seepage) front extends the furthest distance (> 4 m), there is little difference between mechanical dispersion and diffusion, and all concentration profiles intersect at $C(x,t)/C_o$ of 0.5. For the diffusive significant case (Fig. 2c), the pure advective front is much shallower (< 1 m), dispersion due to diffusion is much greater than that due to mechanical dispersion, and the concentration profile for advection plus diffusion intersects that for pure advection at $C(x,t)/C_o$ ~ 0.68. Finally, for the diffusive dominant case (Fig. 2d), the depth of penetration of the pure advective front is virtually imperceptible as is the concentration profile for advection plus mechanical dispersion, and almost the entire concentration profile for advection plus diffusion extends beyond that for the pure advection case. Thus, although the extent of contaminant migration is greatest when the k_h value of the subsurface soil is the greatest, the extent of migration predicted on the sole basis of advection (i.e., Darcy's law) becomes increasingly unconservative as the k_h of the subsurface soil decreases, such that diffusion becomes more prominent. As will be shown subsequently, associating the shapes of concentration profiles with the dominant transport processes played an important role in the recognition of diffusion as a potentially important transport process.

4 DIFFUSION IN CONTAINMENT APPLICATIONS

4.1 *Containment Scenarios*

In terms of waste containment scenarios, there are three general scenarios of interest, as illustrated in Fig. 3. The first case illustrated in Fig. 3a is the limiting case of pure diffusion. For waste containment scenarios involving horizontal barriers (liners), the likelihood that the pure diffusion case will be realized in practice is relatively remote, as there almost always will be a hydraulic gradient driving advective transport.

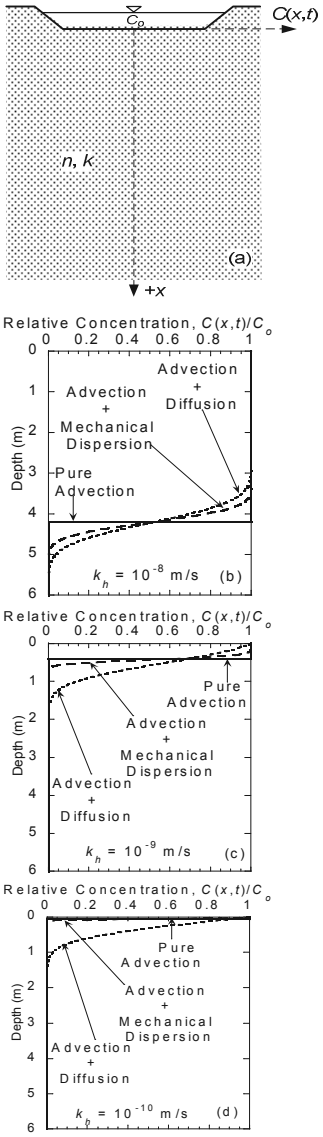

Figure 2. Representative concentration profiles beneath a ponded source of liquid after an elapsed time of 5 yr: (a) schematic of scenario (n = 0.5, D^* = 6 x 10^{-10} m^2/s, i_h = 1.33); (b) advective dominated case; (c) diffusive significant case; (d) diffusive dominated case.

The most common scenario is illustrated in Fig. 3b, where both hydraulic and concentration gradients act in the same direction to drive advective and diffusive chemical transport from the containment side of the barrier to the surrounding medium. This scenario also is the scenario depicted previously with respect to Figs. 1 and 2.

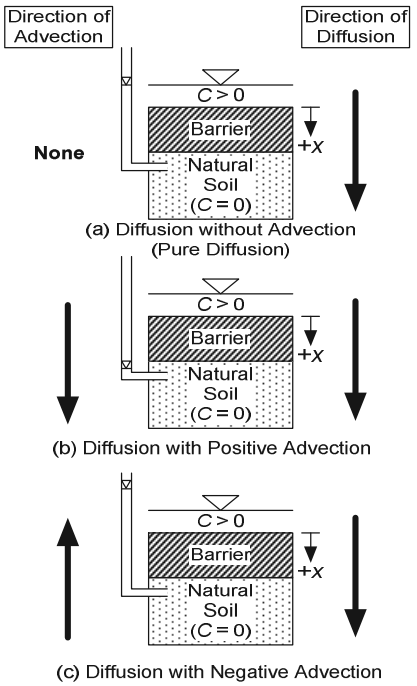

Figure 3. Transport scenarios across horizontal barriers for waste containment: (a) pure diffusion; (b) diffusion with positive (outward) advection; (c) diffusion with negative (inward) advection (modified after Shackelford 1989, 1993).

The third scenario (Fig. 3c) pertains to the case where the hydraulic and concentration gradients act in opposite directions, such that advective transport is directed inward towards the containment side of the barrier, whereas diffusive transport still is directed outward. As a result, the net outward advance of the chemicals is slowed or "retarded" by the opposing hydraulically driven transport. This situation would arise, for example, when the containment system is located at a site with a high groundwater table, such as a perched water table, such that the barrier is located below the water table. This scenario has been referred to as "zone of saturation" containment (e.g. Shackelford 1989, 1993). The scenario also has been referred to as a "hydraulic trap," because the inward directed hydraulic gradient enhances the containment function (e.g., Rowe et al. 2000, Badv and Abdolalizadeh 2004). However, because diffusion is still prevalent, the existence of an opposing hydraulic gradient does not necessarily mean that no contaminant will escape containment, as the net effect will depend on the magnitude of advective transport relative to that for diffusive transport. Also, the effectiveness of inward gradient landfills may not be as complete as expected in the case where the barrier possesses semipermeable membrane properties (Whitworth and Ghazifard 2009).

4.2 *Diffusion through Barriers or Barrier Components*

4.2.1 *Diffusion in Natural Clays*

The recognition that diffusion may play an important role in governing contaminant migration gained momentum in the late 1970s with the publication of a case study by Goodall and Quigley (1977) describing the field concentration profiles that existed beneath two landfill sites near Sarnia, Ontario, Canada, viz. the Confederation Road landfill and the Blackwell Road landfill. The pore water obtained from Shelby tube samples collected beneath a landfill sited directly on top of intact glacial till, and the

concentrations of the primary cations, i.e., K^+, Na^+, Ca^{2+} and Mg^{2+} were plotted as a function of depth beneath the interface of the waste and the till, as shown in Fig. 4. The k_h of the silty clay till in the vicinity of the landfills was measured using both laboratory and field methods over depths ranging from 1.5 to 27.4 m, and 14 of the 18 measured k_h values were lower than 10^{-10} m/s.

At the Confederation Road landfill site (Fig. 4a), the landfill was located directly upon unfissured, intact, gray clay below a desiccated crust, and piezometers indicated downward seepage gradients that enabled, together with measured values of k_h and n, calculating a maximum advective front of 0.04 m over the 6-yr life of the landfill. However, as shown in Fig. 4a, the measured disperse cation front extended to a much greater distance of about 0.3 m, well beyond the advective front. The authors recognized that advective migration in accordance with Darcy's law could not be the primary transport process, and that the cation concentration profiles resembled those that would be predicted on the basis of diffusive dominated conditions (e.g., compare Fig. 4a with Fig. 2d).

The same conclusions were drawn with respect to the cation concentration profiles beneath the Blackwell Road landfill, although the diffusive front had extended to an even greater depth (0.4-0.8 m), despite the existence of upward hydraulic gradients resulting from consolidation of the underlying till due to loading by the overlying MSW. In this case, the authors attributed the greater extent of cation migration to the existence of fissures in the clay, providing pathways for more rapid downward migration, followed by diffusion of the cations into the surrounding intact clay matrix resulting in the observed concentration profiles. This latter process is referred to as "matrix diffusion" and will be discussed in more detail later. A subsequent study reported by Crooks and Quigley (1984) involving additional field analyses and associated laboratory testing confirmed the earlier conclusions drawn by Goodall and Quigley (1984).

Another field study reported by Johnson et al. (1989) involved obtaining vertical core samples from an impervious, unweathered, water-saturated clay deposit beneath a 5-yr-old hazardous waste landfill site in southwestern Ontario, Canada. Sections of the cores were analyzed for chloride and volatile organic compounds (VOCs). Waste-derived chloride was detected in the clay to a maximum depth of ~ 0.83 m below the bottom of the landfill, whereas the most mobile VOCs were found to a depth of only ~ 0.15 m. The authors concluded that the downward transport of these chemical species was the result of simple Fickian diffusion and, more importantly, that the results of this study had important implications for clay-lined waste disposal sites. Specifically, they noted that for engineered clay liners of typical thickness of ~ 1 m, simple diffusion could cause breakthrough of mobile contaminants in approximately 5 yr, and that the diffusive flux emanating from such liners could be large, at least from the perspective of protection of human health and the environment.

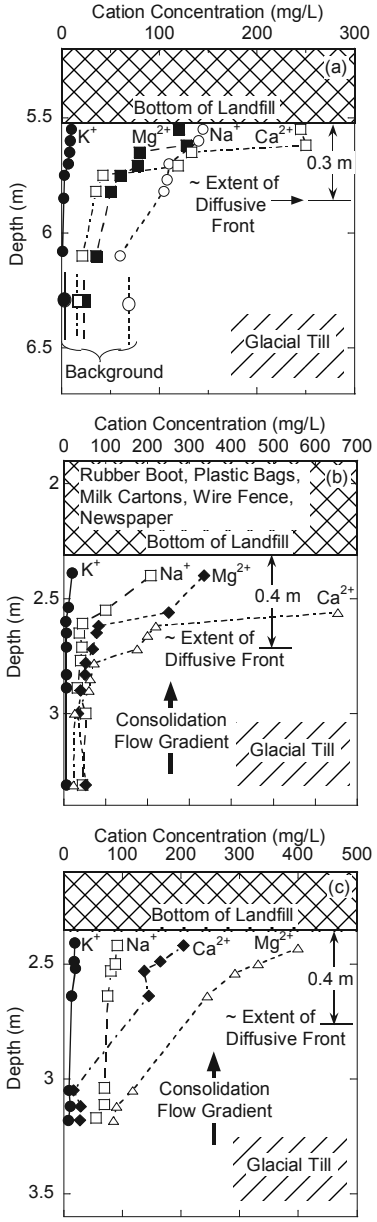

Figure 4. Cation concentration profiles beneath two landfills at Sarnia, Ontario, Canada: (a) Confederation Road landfill; (b) Blackwell Road landfill, borehole 1; (c) Blackwell Road landfill, borehole 3 (modified from Goodall & Quigley 1977).

As a result of these and other studies involving natural clays (e.g., Barone et al. 1989, Barone et al. 1992, Myrand et al. 1992, Sawatsky et al. 1997, Donahue et al. 1999, Itakura et al. 2003, Mieszkowski 2003, Appelo et al. 2008, Jakob et al. 2009), diffusion became recognized as an important transport process in low permeability porous media. This recognition led to studies focused on evaluating the role that diffusion played in terms of governing contaminant migration through engineered clay barriers, such as CCLs. The results of several of these studies are described in the following section.

4.2.2 *Diffusion through Engineered Clay Barriers*

Although several studies have focused directly on evaluating the role of diffusion in governing contaminant migration through engineered clay barriers, such as CCLs used for MSW, HSW, and low-level radioactive waste (LLRW) disposal as well as compacted bentonite buffers

used in high-level radioactive waste (HLRW) disposal, the vast majority of these studies have been laboratory scale studies (e.g., Crooks and Quigley 1984, Gillham et al. 1984, Shackelford et al. 1989, Shackelford and Daniel 1991b, Rowe and Badv 1996a,b, Cotten et al. 1998, Roehl and Czurda 1998, Foged and Baumann 1999, Headley et al. 2001, Rossanne et al. 2003, Çamur and Yazicigil 2005, Frempong and Yanful 2008, Hong et al. 2009, Korf et al. 2011, De Soto et al. 2012). By comparison, relatively few field-scale studies of diffusion in compacted clay barriers have been reported, primarily because the extent of contaminant migration under diffusion dominated conditions would not be sufficient within the operational time-frame of most barriers to allow for such evaluation without violating the integrity of the barrier via core sampling. However, two exceptions to this restriction are the Keele Valley Landfill (KVL) located north of Toronto in Maple, Canada, which was operational between 1984 and 2002 (Rowe 2005), and a field-scale CCL that was specifically constructed as a field research study on the campus of the University of Illinois to evaluate contaminant transport through CCLs and was operational for 13 yr (1988-2001) (Cartwright and Krapac 1990, Toupiol et al. 2002, Willingham et al. 2004).

Concentration profiles existing across the interface of sand overlying the clay liner at the KVL after 4.25 yr of operation are shown in Fig. 5. The profiles in Fig. 5a are for chloride, whereas those in Fig. 5b pertain to a group of VOCs known as the BTEX compounds (benzene, toluene, ethylbenezene, and xylene). The liner generally was 1.2 m in thickness, with a k_h that was regulated to be 10^{-10} m/s or less (King et al. 1993). The sand overlying the clay liner was meant primarily to be a protection layer for the underlying clay liner, and the upper portion of the sand layer became clogged within the first four years such that the sand layer did not contribute to the hydraulic performance of the leachate collection system (Rowe 2005). This clogging resulted in a lack of flow through the sand layer, such that the sand layer actually served as part of the low-permeability barrier system whereby diffusion was the dominant transport process. For example, Rowe (2005) reported that, in the case of the chloride concentration profile (Fig. 5a), the assumption of purely diffusive transport using a D^* value for chloride of 6 x 10^{-10} m^2/s resulted in a predicted profile that matched the measured profile well, and that the concentration profiles for the BTEX compounds, especially toluene, through both the sand and the clay resembled those for diffusion dominated conditions.

A detailed description of the construction and installation of monitoring for the prototype CCL constructed as a research project at the University of Illinois can be found in Cartwright and Krapac (1990). The compacted liner was approximately 0.9-m thick and was constructed using Batestown Till compacted wet of optimum water content. The dimensions of the liner facility were 10 m x 17 m x 1 m, which included an instrumented and ponded test area of 7.3 m x 14.6 m x 0.9 m (Willingham et al. 2004). The entire facility was enclosed within a heated shelter to minimize weather effects and prevent infiltration from rainfall. As part of the monitoring system, large-ring infiltrometers (LRI), 1.5 m in diameter were installed on the surface of the liner and subsequently filled to a depth of 0.295 m with water tagged with tracers (tritium, (HTO) and bromide (Br^-)). Approximately one year later, the water level was raised to 0.31 m and maintained at that level for about 8.5 yr, and then the water level was allowed to decrease due to evaporation and infiltration, but never reached the liner surface before the study was terminated (Willingham et al. 2004).

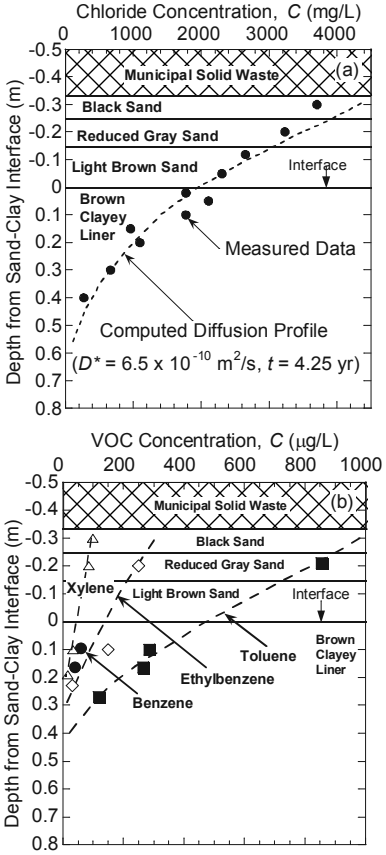

Figure 5. Concentration profiles within the engineered barrier system at the Keele Valley Landfill, Maple, Ontario, Canada: (a) chloride concentration profiles (modified after King et al. 1993); (b) concentration profiles for VOCs (modified after Rowe 2005).

A cross-sectional schematic for the LRI set-up is illustrated in Fig. 6a, and concentrations profiles of Br^- as a function of depth and radial distance, r, from the centerline of the LRI are shown in Figs. 6b,c. The profiles were fitted with an analytical three-dimensional transport model to the advective-dispersive-diffusive transport equation. As shown in Figs. 6b,c, reasonable fits to the measured data were obtained for D^* values varying from 3.0 x 10^{-10} m^2/s to 8.0 x 10^{-10} m^2/s. The authors concluded that: (a) Br^- transport through the field-scale liner was controlled by diffusion, (b) the vertical and horizontal diffusion coefficients were the same, and (c) CCLs can be constructed as diffusion controlled barriers that are capable of mitigating chemical transport from localized leaks or source zones.

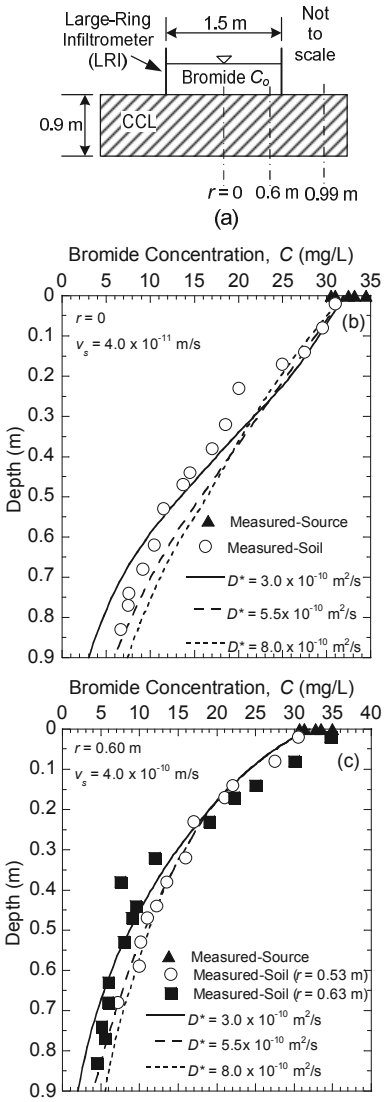

Figure 6. Bromide concentration profiles with a prototype compacted clay liner: (a) schematic cross section of large-ring infiltrometer; (b) and(c) concentration profiles at radii of 0 and 0.60 m, respectively, from the centerline of the LRI (modified after Willingham et al. 2004).

4.2.3 *Diffusion through Geomembrane Liners*

Geomembrane liners (GMLs) are thin (typically 0.76 mm to 3.05 mm) polymer-based materials that are commonly used as barriers or components of barrier systems for containment applications. In such applications, the only way for aqueous-phase inorganic contaminants to migrate through the polymer based GML is if the GML contains a defect, e.g., a puncture hole or crack, or is otherwise defective due to poor manufacturing or poor placement and protection procedures. In such cases, the GML will offer essentially no resistance to contaminant migration through the defect, such that contaminant migration will readily pass through the GML, i.e., unless the GML is founded upon a hydraulic resistant layer, such as natural, low-permeability clay, or the GML represents the upper component of a composite liner which includes an underlying low-permeability component, such as a CCL or geosynthetic clay liner (GCL).

In the case where the GML is entirely intact, the only way aqueous-phase contaminants can pass through the GML is via molecular diffusion, and the only contaminants that can diffuse substantially through the GML are those that can partition into the polymer comprising the GML, which generally limits the contaminants to organic compounds, such as VOCs. For example, Rowe (2005) reported the results of a long-term diffusion test involving a 2-mm-thick HDPE geomembrane subjected to a difference in NaCl concentration of 2.2 g/L, where the measured concentration of chloride on the downgradient side of the geomembrane after about 12 yr of exposure was only 0.02 % of the source concentration, which was within the range of the analytical uncertainty of the chemical analysis. Rowe (2005) also cites the results of an independent study that indicated negligible diffusion of heavy metals (Cd^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) from a 0.5 M acid solution (pH = 1-2) through an HDPE over a 4-yr period.

In this regard, there have been numerous studies evaluating diffusion of a wide variety of organic chemicals through a wide variety of different polymer-based GMLs (Rowe et al. 1995, Park and Nibras 1996, Park et al. 1996a,b, Xiao et al. 1996, Sangam and Rowe 2001a, Joo et al. 2004, 2005, McWatters and Rowe 2010, Jones et al. 2011, Saheli et al. 2011, Touze-Foltz et al. 2011). A primary outcome from most of these studies is that geomembranes formed from a single polymer, such as high density polyethylene (HDPE), linear low-density polyethylene (LLDPE), very low-density polyethylene (VLDPE), and polyvinyl chloride (PVC), typically provide little resistance to diffusion of VOCs (e.g., Edil 2003). In this regard, the general process for diffusion of such organic chemicals through GMLs in response to an aqueous-phase concentration difference, $-\Delta C = C_o - C_e > 0$, established across a GML is illustrated schematically in Fig. 7 (e.g., see Rowe 1998, Katsumi et al. 2001). First, the organic chemical partitions from the external aqueous solution into the geomembrane (adsorbs) at a concentration $K_g C_o$, where K_g is the chemical-geomembrane partitioning coefficient. Second, the chemical diffuses through the geomembrane in response to a concentration difference within the GML of $-\Delta C_g = K_g C_o - K_g C_e > 0$, where $K_g C_e$ has been established on the basis of the external aqueous-phase concentration, C_e. Finally, the chemical partitions from the geomembrane (desorbs) back into the lower bounding aqueous solution.

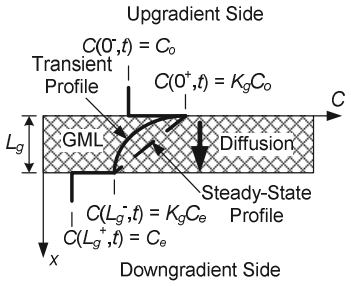

Figure 7. Schematic of concentration profile for organic chemical diffusion through an intact geomembrane liner (GML) (modified after Rowe 1998, Katsumi et al. 2001).

Since GMLs are relatively thin, steady-state diffusion through the GML can be established relatively quickly, such that the mass flux of the organic chemical can be expressed in accordance with Fick's first law as follows (Park et al. 1996a,b, Rowe 1998, Katsumi et al. 2001, Rowe 2005):

$$J_d = D_g K_g \frac{C_o - C_e}{L_g} \quad (6)$$

where D_g is the diffusion coefficient for the chemical in the GML. Conservative (high) estimates of J_d will occur when C_e is assumed to be zero.

Since geomembranes are not porous media, the nature of D_g is not the same as that of D^*. For example, based on an extensive summary of both K_g and D_g values from the literature reported by Rowe (1998), the upper limit on the vast majority of the D_g values is on the order of 1 x 10^{-11} m^2/s, with numerous values ranging from one to several orders of magnitude lower than this value. Thus, values of D_g generally are several orders of magnitude lower than values of D^*. However, despite such low magnitude D_g values, Park et al. (1996b) illustrate that molecular diffusion of organic chemicals through intact GMLs can be substantially greater than leakage through geomembrane defects. A major reason for this difference is that that cross-sectional area for diffusive mass flux through a GML is the entire surface of the GML, whereas mass flux due to leakage through a GML is associated with only a small percentage of the surface area (see Fig. 8).

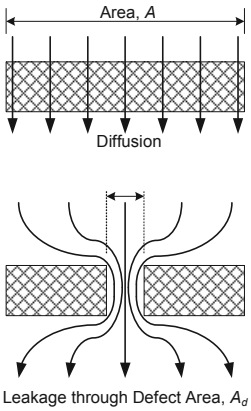

Figure 8. Cross-sectional areas for diffusion versus leakage through a GML.

Because diffusion of VOCs through single polymer GMLs has been an issue, recent research has focused on evaluating alternative GMLs for the ability to minimize VOC diffusion. For example, Sangam and Rowe (2005) evaluated the effect of fluorinating the surface of an HDPE on the diffusion of VOCs through the GML. In essence, the surface fluorination reduces the affinity of the GML to VOCs. Sangam and Rowe (2005) reported that the diffusion coefficient for the surface fluorinated HDPE was on the order of 1.5 to 4.5 times lower than that for the untreated HDPE, depending on the specific hydrocarbon evaluated. Similarly, McWatters and Rowe (2010) evaluated the ability of two coextruded GMLs to reduce the diffusive flux of VOCs. Coextrusion involves extruding two or more layers of dissimilar polymers into a single film. McWatters and Rowe (2010) reported improved resistance to BTEX diffusion for the two coextruded GMLs, a polyamide (nylon) GML and an ethylene vinyl-alcohol (EVOH) GML, relative to that for either an LLDPE or a PVC GML. The results of these and other studies indicate that alternatives to the single polymer GMLs may offer improved performance in terms of VOC diffusion.

4.2.4 *Diffusion through Geosynthetic Clay Liners*

Geosynthetic clay liners (GCLs) are relatively new barrier materials, having first been used in a landfill in 1986 (Bonaparte et al. 2002). Traditional or conventional GCLs are thin (~ 5 to 10 mm), prefabricated (factory manufactured) hydraulic barriers (liners) that consist primarily of a processed clay, typically sodium bentonite, or other low permeability material that is either encased or "sandwiched" between two geotextiles or attached to a single polymer membrane (i.e., geomembrane) and held together by needle-punching, stitching, and/or gluing with an adhesive. The hydraulic resistance of these conventional GCLs that do not include a geomembrane or polymer film is attributed to the bentonite component of the GCL, which swells in the presence of water to form a tight sealing layer. Although GCLs can be subjected to significant incompatibility upon permeation with chemical solutions or liquids, resulting in potentially significant increases in hydraulic conductivity, the values of k_h for GCLs permeated with dilute chemical solutions or water tend to be less than about 1 x 10^{-10} m/s (e.g., Shackelford et al. 2000). Such low k_h values and the relative thinness of GCLs imply that diffusion would be a significant, if not dominant, transport process through GCLs. Accordingly, several studies have evaluated the diffusion of chemicals through GCLs (Lake and Rowe 2000, 2005, Rowe et al. 2000, Malusis and Shackelford 2002a, Lange et al. 2009, Paumier et al. 2011, Malusis et al. 2013).

For example, consider the results of the study shown in Fig. 9 for diffusion of KCl through a GCL. In this study, diffusion of KCl was hypothesized to be affected by the ability of the bentonite in the GCL to exhibit semipermeable membrane behavior, whereby solutes are excluded from the smaller pores in the clays, thereby restricting the diffusion of the KCl (Malusis and Shackelford 2002b). Such solute restriction also results in chemico-osmosis, or the movement of liquid from lower solute concentration to higher solute concentration, or opposite to the direction of diffusion. Accordingly, the GCL was tested in an apparatus that was able to measure simultaneously both the membrane efficiency of the GCL and the D^* of the KCl.

The membrane efficiency refers to the relative degree or extent of solute restriction (also referred to as "ion exclusion"), and is quantified in terms of a membrane efficiency coefficient, ω (Shackelford et al. 2003). Although negative values of ω have been reported in some cases due to atypical circumstances resulting from processes such as "diffusion-osmosis" (Olsen et al. 1990), ω values typically range from zero for clays exhibiting no membrane behavior and, therefore, no solute restriction, to unity (100 %) for "perfect" or "ideal" membranes that restrict the passage of all solutes. Because soils generally exhibit a range of pore sizes, some of the pores in clays may be restrictive whereas others are not. As a result, most natural soils that exhibit membrane behavior do so as "imperfect" or "non-ideal" membranes, such that $0 < \omega < 1$ (Shackelford et al. 2003). In particular, bentonite has been shown to possess the potential for significant membrane behavior, such that the possible effect of membrane behavior on solute transport through any bentonite-based barrier should be considered (Shackelford 2011, 2012, 2013).

In terms of the results in Fig. 9, Fig. 9a shows the correlation between the measured value of ω for the GCL and the source concentration of KCl, C_o, used in the test. Due to physico-chemical interactions between the salts in the pore water of the bentonite and the bentonite particles,

higher salt concentrations result in compression of the adsorbed layers of cations associated with the bentonite particles and, therefore, larger pore openings between adjacent particles and lower ω. As shown in Fig. 9b, such larger pores due to higher salt concentrations also result in increasing values of D^* for KCl with increasing C_o. Note that the values of D^* shown in Fig. 9b are steady-state values in that the values correspond to after steady-state diffusion had been established with respect to both Cl^- and K^+. The combined effect of C_o on ω and D^* is shown in Fig. 9c, where D^* is shown to decrease with increasing ω such that, in the limit as $\omega \rightarrow 1$, $D^* \rightarrow 0$ as required on the basis of the definition of a perfect or ideal membrane. As indicated in Fig. 9b, this decrease in D^* with increasing ω was attributed to a decrease in the apparent tortuosity factor, τ_a (see Eq. 1).

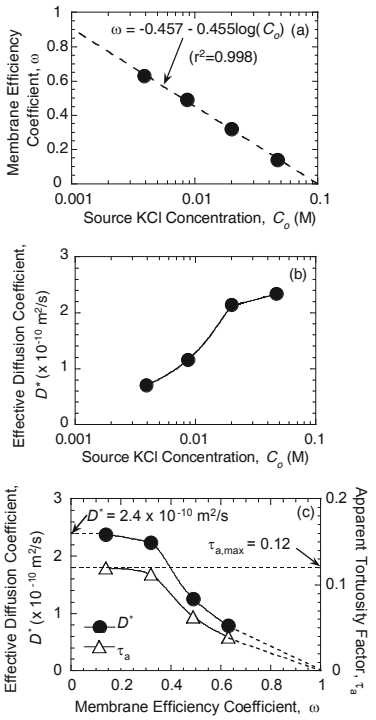

Figure 9. Results of a test to measure simultaneously the diffusion of KCl through a GCL and the membrane behavior of the GCL: (a) membrane efficiency of the GCL; (b) steady-state diffusion coefficient of KCl; (c) effect of membrane behavior on steady-state diffusion of KCl (modified after Malusis and Shackelford 2002a,b).

Malusis and Shackelford (2002a) compared their results with those reported by Lake and Rowe (2000) based on measurement of NaCl diffusion under constant volume conditions through granular sodium bentonite extracted from a GCL. The results of this comparison are shown in Fig.10 in the form of the D^* values for KCl and NaCl versus the source salt concentration, C_o. Overall, results in Fig. 10 indicate a similar trend of increasing D^* with increasing C_o. Although ω values were not measured by Lake and Rowe (2000), chemico-osmotic flow was reported to be sufficiently negligible such that the authors concluded that membrane behavior probably wasn't significant for the range of NaCl concentrations used (i.e., $C_o \geq 0.08$ M). The superimposed demarcation between membrane behavior ($\omega > 0$) and no membrane behavior ($\omega = 0$) based on the results shown in Fig. 9 tends to support this conclusion, although the relationship between ω and C_o for the granular bentonite used by Lake and Rowe (2000) may not be the same as that shown in Fig. 10 due, in part, to the different porosity of the specimens (n = 0.78 to 0.80 vs. n = 0.71), different salts used in the tests (KCl versus NaCl), and the potentially different properties of the granular bentonites in the two GCLs. Despite these differences, the results shown in Fig. 10 suggest that there is general agreement between the results reported in the two studies.

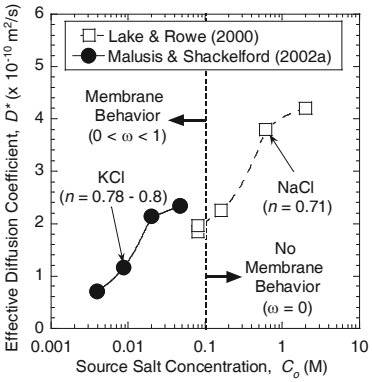

Figure 10. Comparison of the results for the diffusion of salts through GCLs from two different studies (modified after Malusis and Shackelford 2002a).

4.2.5 *Diffusion through Composite Liners*

Composite liners refer to engineered barriers that are comprised of more than one type of barrier in intimate contact with each other. Although there are a variety of possible composite liner systems, including those that contain more than two component types of barriers (e.g., Nguyen et al. 2011), the most common types of composite liners consist of a GML overlying and in intimate contact with either an underlying CCL or an underlying GCL, although other composite liner scenarios are possible. For these common composite liners, the effectiveness of the composite liner in restricting contaminant migration relies largely on the integrity of the overlying GML and on the intimacy of the contact between the overlying GML relative to the underlying CCL or GML (Rowe 1998, Foose et al. 2001, 2002). The fewer the number of defects in the GML and the more intimate (tighter) the contact between the two barriers, the more effective the barrier in restricting contaminant migration. However, failure to protect the GML could compromise the integrity of the composite liner.

For example, Rowe et al. (2003) evaluated the performance of a composite liner comprised of a 1.5-mm-thick HDPE GML overlying a 3-m-thick CCL after 14 years in operation as a leachate lagoon liner (also see Rowe 2005). The GML had been poorly protected, resulting in development of 528 defects (cracks, holes, patches) per hectare over the 14-yr operational life of the liner, which allowed leachate to seep between the GML and CCL. Data obtained upon decommissioning indicated that leachate leaking through the GML had spread quickly over the entire interface between the GML and CCL, essentially rendering the GML ineffective. However, there were questions as to when the GML became ineffective as a barrier component and to what extent contaminant had penetrated the underlying CCL. Based on these considerations, Rowe et al. (2003) evaluated the chloride concentration profile within the CCL based on samples recovered from five different locations. As illustrated in

Fig. 11, the resulting concentration profile was consistent with diffusion dominated transport, taking into consideration that reverse or back diffusion had occurred at the top of the profile due to the placement of water within the lagoon following removal of the leachate prior to decommissioning, resulting in a localized reversal in the concentration gradient. Additional calculations were performed to evaluate the duration of the effectiveness (i.e., lifespan) of the GML on the resulting concentration profiles, with the results indicating that the GML likely was effective only for an initial period ranging from 0 to 4 yr. Nonetheless, the overall conclusion was that diffusion was the dominant transport process, and the underlying groundwater was not impacted due to the 3-m thickness of the CCL.

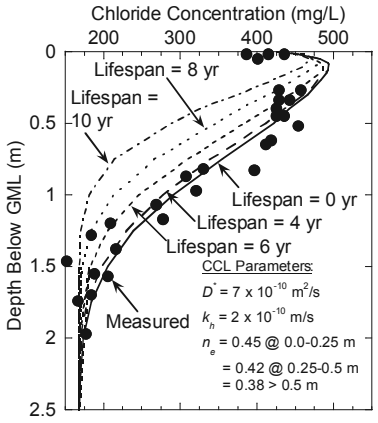

Figure 11. Measured and predicted chloride concentration profiles through the compacted clay portion of a composite liner system after 14 yr of operation (modified from Rowe et al. 2003, Rowe 2005).

Although there is substantial evidence indicating that composite liners are effective in terms of waste containment, i.e., when constructed properly (e.g., Sangam and Rowe 2001b, Bonaparte et al. 2002, Rowe 2005), there also is growing evidence the composite liners are not any more effective against minimizing VOC transport than are CCLs (e.g., Foose 2002, Foose et al. 2002, Shackelford 2005, Klett 2006). In this case, the VOC first must diffuse through the overlying GML similar to the situation for the single GMLs illustrated in Fig. 7. However, once the VOC has partitioned out from the downgradient side of the GML, the VOC then must diffuse through the underlying CCL or GCL, as illustrated in Fig. 12.

For example, Klett (2006) evaluated the measured concentrations of 11 VOCs existing in 94 lysimeters (e.g., Fig. 13) at 34 landfills in Wisconsin lined with either CCLs or composite liners (some landfills had multiple cells, each with a lysimeter). The lysimeter data set consisted of 2738 samples analyzed for VOCs. At least one VOC with a concentration above the limit of detection was detected in 1356 of these samples, and at least one VOC was detected during one sampling event in each of the 94 lysimeters evaluated. Toluene was detected most frequently (60% of the lysimeters) and ten VOCs (toluene, tetrahydrofuran, dichloromethane, benzene, acetone, chloromethane, xylene (total), ethylbenzene, trichloroethylene, and 1,1-dichloroethane) were detected in more than 25 % of the lysimeters. The most prevalent compounds were aromatic hydrocarbons (toluene and benzene), furans (tetrahydrofuran), and the alkanes (dichloromethane and 1,1- dichloroethane). Based on analysis of variance (ANOVA) of the measured concentrations, Klett (2006) concluded that the concentrations for 8 of the 11 VOCs were statistically no different between clay and composite lined landfills.

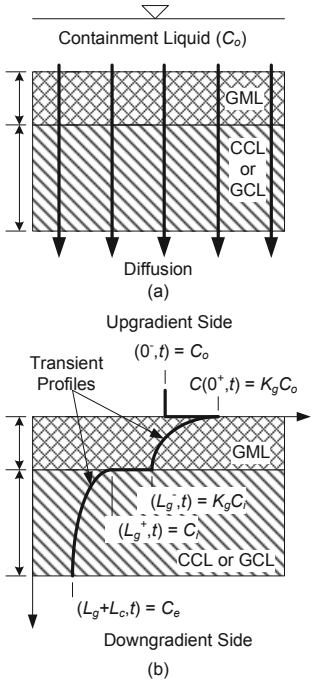

Figure 12. Schematics of diffusion of VOCs through intact composite liners: (a) conceptual transport; (b) concentration profiles (modified after Foose et al. 2001, Foose 2002)

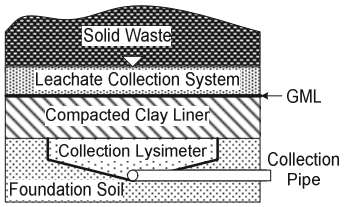

Figure 13. Schematic of typical collection lysimeter (underdrain) beneath a composite liner for a solid waste disposal facility (modified from Shackelford 2005).

An example of this comparison for dichloromethane (DCM) is presented in the form of box plots shown in Fig. 14. The center line in each box plot represents the median of the data, the outer edges of each box represent the interquartile range (i.e., 25th to 75th percentiles), and the outermost lines or "whiskers" represent the 5th and 95th percentiles. As shown in Fig. 14, the concentrations of DCM in collection lysimeters beneath composite lined cells were not any lower than those collected beneath cells lined only with compacted clay. This similarity in DCM concentrations is not necessarily surprising, given that aforementioned lack of resistance to VOC diffusion offered by most geomembranes. Thus, diffusion of VOCs through GML-based composite liners remains an issue that must be addressed when such contaminants are present.

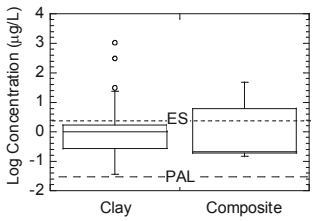

Figure 14. Box plot comparisons of dichloromethane (DCM) concentrations in collection lysimeters beneath composite lined and clay lined cells in landfills in Wisconsin; ES = enforcement standard; PAL = protective action limit (data from Klett 2006).

4.2.6 *Vertical Barriers*

A wide variety of vertical barriers have been used for *in situ* hydraulic and contaminant containment applications, including sheet-pile walls, grout curtains, concrete barriers, geomembrane barriers, gravel-filled trenches, and slurry based cutoff walls, such as soil-bentonite (SB), cement-bentonite (CB) and soil-cement-bentonite (SCB) walls (Mitchell et al. 2007). However, the slurry based vertical cutoff walls probably are the most commonly used vertical barriers for in situ containment of contaminants. Similar to the case of horizontal barriers (Fig. 3), contaminant transport through such vertical barriers can be categorized into three possible scenarios as illustrated in Fig. 15, *viz.*, pure diffusion (Fig. 15a), diffusion with positive (outward) advection (Fig. 15b), and diffusion with negative (inward) advection (Fig. 15c).

The pure diffusion scenario (Fig. 15a) exists when there is no applied hydraulic gradient across the barrier. This scenario would exist only in practice when there was little or no local groundwater flow in the vicinity of the barrier location prior to installation of the barrier, and no net accumulation or depletion of water on either side of the barrier during the operational life of the barrier. As a result, the only possible transport process is diffusion from the containment (inward) side of the barrier ($C > 0$) towards the outside of the barrier ($C = 0$). As the conditions for this scenario are not typically encountered in practice, this scenario may be considered as a limiting case.

The scenario for diffusion with positive (outward) advection (Fig. 15b) exists when the local groundwater level on the containment side of the barrier is allowed to rise, e.g., via infiltration of precipitation, such that a hydraulic gradient is established across the barrier in the same direction as the prevailing concentration gradient, i.e., from the containment (inward) side of the barrier ($C > 0$) towards the outside of the barrier ($C = 0$). Thus, both advection and diffusion occur in the same direction, i.e., outward.

The scenario for diffusion with negative (inward) advection (Fig. 15c) is analogous to the hydraulic trap scenario represented in Fig. 3c, and occurs when the groundwater level within the containment side is drawn down, e.g., by pumping or passive drainage (e.g., French drains), so as to generate an inwardly directed hydraulic gradient to drive advective transport that counteracts the outwardly directed diffusive transport, thereby minimizing the net outward contaminant flux. Transport analyses for this scenario have been reported by Shackelford (1989), Manassero and Shackelford (1994), Devlin and Parker (1996), and Neville and Andrews (2006).

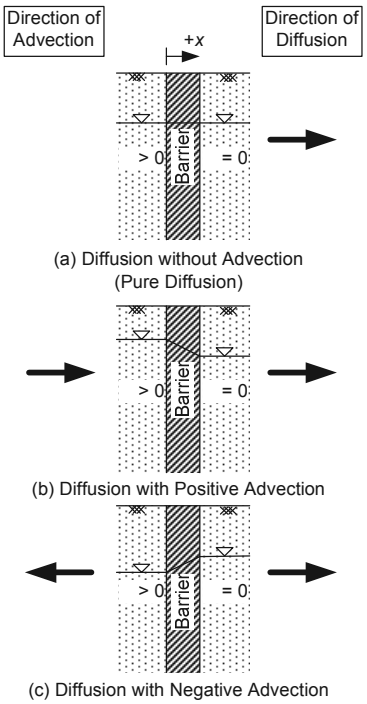

Figure 15. Contaminant transport scenarios across vertical barriers for in situ containment: (a) pure diffusion; (b) diffusion with positive (outward) advection; (c) diffusion with negative (inward) advection (modified after Gray and Weber 1984, Shackelford 1989, 1993, Manassero and Shackelford 1994, Devlin and Parker 1996, Neville and Andrews 2006, Sleep et al. 2006, Mitchell et al. 2007).

Although several studies have focused on evaluating contaminant transport through slurry based vertical cutoff walls (Gray and Weber 1984, Mott and Weber 1991a,b, Manassero et al. 1995, Devlin and Parker 1996, Khandelwal et al. 1998, Rabideau and Khandelwahl 1998, Krol and Rowe 2004, Britton et al. 2005, Neville and Andrews 2006, Malusis et al. 2010), only a few of these studies (e.g., Mott and Weber 1991a,b, Khandelwal et al. 1998, Krol and Rowe 2004) were extensively experimental studies focusing specifically on evaluating the diffusive properties of contaminants in traditional (unamended) SB backfills. In all of these studies, which were focused on diffusion and sorption of organic chemicals (e.g., 1,4-dichlorobenzne, 4-chlorophenol lindane, trichloroethylene, and aniline), the results indicated that the values of D^* typically were reduced by a factor of only about two to four relative to the corresponding values of D_o, and at most were no more than an order of magnitude lower than D_o, due, in part, to the relative high porosity values associated with most SB backfills. Also, sorption of the organic chemicals to the traditional (unamended) soil-bentonite backfills typically was negligible (i.e., $K_d \approx 0$) due to the typically low organic carbon contents of the unamended backfill materials (e.g., Malusis et al. 2010). These two factors (i.e., relatively high D^* and negligible K_d) combined with the typical inability to achieve backfill hydraulic conductivity values lower than about 10^{-10} m/s (e.g., D'Appolonia 1980, Evans 1991, 1993, 1994, Filz and Mitchell 1996, Shackelford and Jefferis 2000, Filz et al. 2003), suggest that the significance of diffusive transport across vertical cutoff walls is likely governed largely by the magnitude of the applied hydraulic gradient, i_h, across the barrier, with diffusive transport becoming more significant with decreasing magnitude in i_h (i.e., Fig. 15a).

Nonetheless, prudence dictates consideration of diffusive transport in terms of long-term performance assessments, as the results of several simplified transport analyses suggest that diffusion may be significant under some scenarios (e.g., Gray and Weber 1984, Shackelford 1989, Manassero and Shackelford 1994).

4.2.7 *Diffusion through Bentonite Buffers for High-Level Radioactive Waste (HLRW) Disposal*

Diffusion of radionuclides through highly compacted bentonites being considered as buffer barriers in HLRW disposal scenarios has been an area of substantial research over the past several decades, and in particular the past approximate decade. In fact, the number of referenced publications focused on evaluating diffusion of radionuclides through bentonite buffer barriers for HLRW disposal is too voluminous to cite here, but a representative listing can be found in Shackelford and Moore (2013). The high number of publications in this area results from the need for safe and secure, long-term disposal of HLRW (e.g., $\geq$ 10,000 yr) resulting from the significant past and present roles of nuclear energy in several countries (e.g., Belgium, Canada, France, Japan, Spain, Switzerland, United Kingdom, and the USA).

In particular, two issues related to radionuclide diffusion through highly compacted bentonite buffers have been identified, viz., the influence of surface and/or interlayer diffusion, and the existence of semipermeable membrane behavior as a result of ion exclusion (Shackelford and Moore 2013). Surface or interlayer diffusion refers to the diffusion of cations, typically metals, sorbed to clay particles 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 individual clay particle surfaces. This phenomenon is attributed 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, and is known as interlayer diffusion when referring to the excess of sorbed cations within the interlayer regions of smectitic based clays, such as bentonites (Glaus et al. 2007, Appelo et al. 2010). When prevalent, surface and/or interlayer diffusion can result in enhanced diffusion of cations, and diminished diffusion of anions, relative to the diffusion of neutral tracers such as tritium and deuterium (Appelo et al. 2010). However, Shackelford and Moore (2013) noted that conflicting results have been reported as to the significance of surface and/or interlayer diffusion, and that the phenomenon is likely to be significant only in high activity clays, such as bentonites, compacted at relatively high dry densities. Also, the significance of surface and/or interlayer diffusion will be a function of the chemical speciation of the diffusing radionuclide.

In terms of semipermeable membrane behavior, numerous studies have reported significant ion exclusionary properties of bentonite buffer barriers, but these properties historically have been taken into account qualitatively or indirectly by incorporating a correction (anion exclusion) factor within the form of Fick's first law (Shackelford and Moore 2013). However, recent advances in simultaneously testing for both solute diffusion and semipermeable membrane behavior as previously documented for GCLs have largely eliminated this restriction, such that quantification of the effect of semipermeable membrane behavior of radionuclide diffusion can now be assessed (e.g., see Fig. 9 and associated text). As a result of these advancements, and the continuing need to assess the performance of the containment structures used to isolate HLRW from the environment for extensive time frames, diffusion of radionuclides through bentonite buffer barriers is likely to remain an important research area for the foreseeable future.

4.3 *Diffusion as an Attenuation Mechanism (Matrix Diffusion)*

The process of matrix diffusion, whereby contaminants diffuse from interconnected pores or fractures into the surrounding intact clay or rock matrix, may be an important attenuation mechanism when the contaminant transport occurs through structured clay and/or rock formations (e.g., Foster 1975, Grisak and Pickens 1980, Neretnieks 1980, Feenstra et al. 1984, Lever et al. 1985, Rowe and Booker 1990, 1991, Boving and Grathwohl 2001, Polak et al. 2002, Lipson et al. 2005). In this regard, matrix diffusion has been considered in terms of the migration of radionuclides resulting from high-level radioactive waste disposal through fractured crystalline rocks (Neretnieks 1980, Sato 1999), the migration of pesticides resulting from agricultural practice through fractured clayey till (Jorgensen and Fredericia 1992, Jorgensen and Foged 1994), the migration of leachate resulting from solid waste landfills through underlying fractured clayey till (Rowe and Booker 1990, 1991), and the migration of dense-chlorinated solvents resulting from industrial spills and disposal practice through fractured geologic media (Parker and McWhorter 1994, Parker et al. 1994, 1996).

For example, consider the scenario depicted in Fig. 16 after Rowe and Booker (1990, 1991), whereby a clay-lined (CCL) waste containment facility is underlain by fractured till that serves as an "attenuation layer" (AL) that could attenuate the migration of any contaminants emanating from the containment facility to the underlying confined aquifer. In this scenario, the greater the ability of the fractured till to attenuate the migration contaminants, the more effective the overall or global containment system (i.e., CCL + AL). In this regard, the fractures may serve as conduits that facilitate the rate of downward migration of contaminants, but matrix diffusion of contaminants from the fractures into the surrounding intact clay matrix and any subsequent sorption of the contaminants to the individual clay particles within the matrix pores can provide for an effective retardation of advancing, downward contaminant migration.

Matrix diffusion also may be important in attenuating the migration of contaminants at the local or barrier scale. For example, Jo et al. (2006) proposed a three-compartment model that included rate-limited cation exchange controlled by matrix diffusion to explain the extensive tailing of eluted cations that often is observed during column tests conducted on aggregated soils with inorganic chemical solutions. As illustrated schematically in Fig. 17, the pore space in the saturated granular bentonite was assumed to consist of intergranular, interparticle, and interlayer (interlaminar) spaces. The pores between the granules constituted the intergranular pore space, whereas the interparticle pore spaces existed between the particles comprising the granules, but outside the interlayer space between the montmorillonite lamella. Water in the intergranular pore space was assumed to be hydraulically mobile. Water in the interparticle and

interlayer pores was assumed to be strongly bound by electrostatic forces and immobile. Ion exchange was assumed to occur as cations in the permeant solution passed through the intergranular pores (Fig. 17a) and gradually diffuse first into the interparticle pores (Fig. 17b) and subsequently into interlayer spaces (Fig. 17c). Cation exchange progressed until equilibrium was established between cations in the permeant solution and the montmorillonite surface.

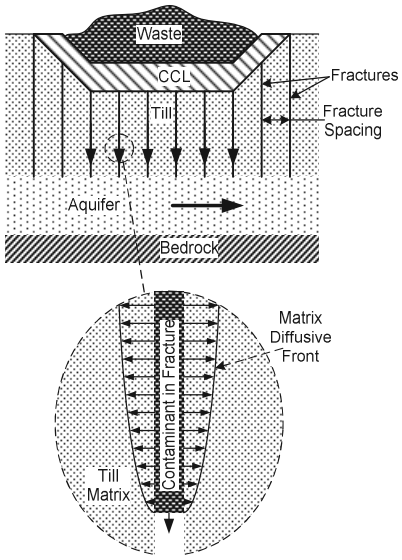

Figure 16. Idealized schematic cross section of lined waste containment system underline by fractured till and the concept of attenuation via lateral diffusion from fracture into the intact surrounding till matrix (modified after Rowe and Booker 1991).

Jo et al. (2006) compared measured breakthrough curves (BTCs) for calcium (Ca) transport through specimens of a GCL based on the results of six column tests versus predicted BTCs based on their theoretical model. The results of this comparison are shown in Fig. 18, where α_{gp} (s^{-1}) is the mass transfer coefficient for diffusion between the mobile intergranular and the immobile interparticle liquids, and α_{pl} (s^{-1}) is the mass transfer coefficient for diffusion between the immobile interparticle and interlayer liquids. The predictions obtained with the model for the base case generally were comparable to the data, even though the model input parameters were estimated independently (i.e., the parameters were not determined from calibration).

The model also predicted reasonably well the changes in the exchange complex, but the comparison between the predicted and measured eluted sodium (Na) concentrations was not quite as favorable (see Jo et al. 2006). Nonetheless, the results of the study by Jo et al. (2006) serve as an example of the role that diffusion can play as an attenuation mechanism during solute transport through barriers comprised of structured soils.

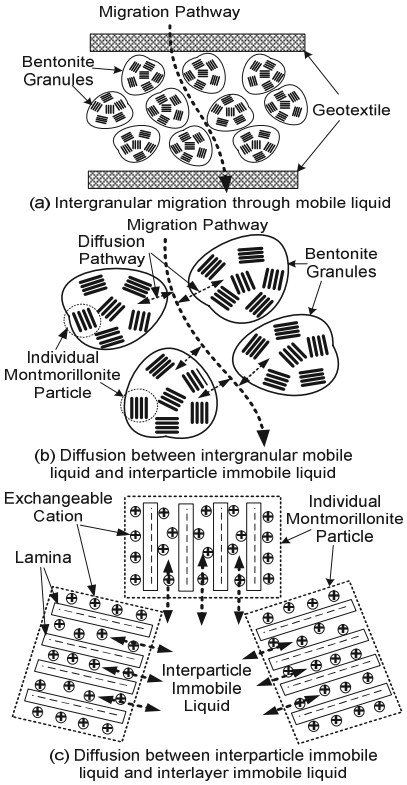

Figure 17. Effect of diffusion on solute migration through a GCL containing granular bentonite (modified after Jo et al. 2006 and Shackelford and Moore 2013).

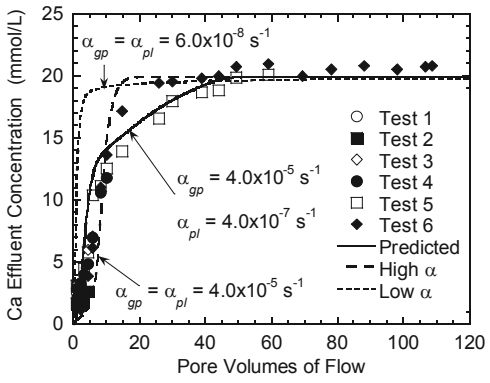

Figure 18. Measured and predicted breakthrough curves for calcium (Ca) transport through a GCL containing granular bentonite where matrix diffusion plays a significant role as an attenuation mechanism (modified after Jo et al. 2006).

4.4 *Liquid-Phase Diffusion in Unsaturated Media*

Although the vast majority of studies have focused on liquid-phase diffusion of chemicals through saturated porous media, there are a wide variety of applications in environmental geotechnics where liquid-phase diffusion through unsaturated porous media can be an important consideration. Some of the possible applications include diffusion of salts through unsaturated layers within an engineered cover system and the potential impact of such salts on the integrity of GCLs used as a component of the cover system (e.g., Benson and Meer 2009, Scalia and Benson 2011, Bradshaw et al. 2013), diffusion of radionuclides through unsaturated coarse-grained layers surrounding subsurface radioactive and hazardous waste

repositories (Conca and Wright 1990), and unsaturated diffusion of chemicals in the vadose zone (Charbeneau and Daniel 1993).

As an example of this last scenario, Rowe and Badv (1996b) evaluated the diffusion of chloride and sodium through a layered soil system consisting of an essentially saturated clayey silt overlying an unsaturated layer of either coarse sand or fine gravel. This two-layered soil system mimics the practical situation where a landfill may be sited in a hydrogeological setting where the predominant soil type below the proposed landfill base is granular (e.g., silt, sand, or gravel) and the water table is also at some depth. In this case, S_w of the soil below a liner may be expected to increase from about residual θ_w below the liner to almost full saturation (S_w = 1) at or near the water table. Based on the results of their study, Rowe and Badv (1996b) found that the value of D^* for chloride and sodium in the unsaturated soil, or D^*_{unsat}, relative to that in the saturated soil, D^*_{sat}, could be approximated reasonably well by a simple linear function of θ_w, or $D^*_{unsat}/D^*_{sat} = \theta_w/n$. Also, Rowe and Badv (1996b) concluded that, provided that the Darcy velocity can be kept low (e.g., by the construction of a good compacted clay or composite liner), the unsaturated fine gravel evaluated in their study may act as a diffusion barrier to the migration of the dissolved sodium and chloride ions.

4.5 *Gas-Phase Diffusion*

Gas-phase diffusion can be an important consideration in environmental geotechnics, including both waste containment applications (e.g., Yanful 1993, Aubertin et al. 2000, Mbonimpa et al. 2003, Aachib et al. 2004, Bouzza and Rahman 2004, 2007, Alonso et al. 2006, Demers et al. 2009) and remediation applications, such as in the use of the soil vapor extraction technology for removal of VOCs from the subsurface vadose zone (e.g., Johnson et al. 1990). The importance of gas-phase diffusion is accentuated because diffusion coefficients for chemicals in the gas-phase typically are four-to-five orders of magnitude greater than those for the same chemicals in the liquid phase (Cussler 1997). For this reason, the gas-phase diffusive mass flux of a chemical through soil can be reduced significantly by minimizing the continuity in the gas (air) phase of the medium, for example, by filling the voids with a sufficient amount of water such that the gas phase becomes discontinuous (e.g., Nicholson et al. 1989, Yanful 1993, Bouzza and Rahman 2004, 2007).

Two waste containment problems of interest involving gas-phase diffusion and the environmentally safe disposal of mine tailings are illustrated schematically in Fig. 19. The problem of acid drainage (Fig. 19a) occurs when sulphidic tailings (e.g., pyrite or FeS_2) are oxidized resulting in the production of a low pH solution (e.g., pH ≈ 2) that leaches potentially toxic heavy metals associated with the tailings during percolation through the tailings, resulting in the emanation of acid drainage form the tailings (e.g., Nicholson et al. 1989, Evangelou and Zhang 1995, Ribet et al. 1995). In the case of the disposal of uranium tailings (Fig. 19b), the tailings can serve as a localized source of radon gas that can be environmentally harmful if not controlled properly. In both of these cases, the objective in the cover design must include steps taken to minimize diffusive influx (O_2) or diffusive efflux (radon) of gas through the cover.

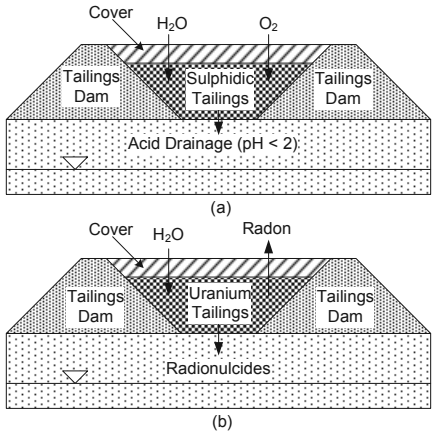

Figure 19. Tailings disposal scenarios where gas-phase diffusion plays an important role: (a) oxidation of sulphidic tailings and generation of acid drainage; (b) radon gas emission (modified after Shackelford and Nelson 1996, Shackelford 1997).

For example, Stormont et al. (1996) evaluated the effect of unsaturated flow through the three cover sections shown in Fig. 20a in terms of the effective air-phase diffusion coefficient for oxygen gas ($O_{2(g)}$), D_e, at a depth of 0.6 m (i.e., the interface between the cover and the underlying material). Their results are shown in Fig. 20b in the form of a normalized oxygen diffusion coefficient, D_N, defined as follows (e.g., see Charbeneau and Daniel 1993, Stormont et al. 1996):

$$D_N = \frac{D_e}{D_{e,max}} = \left(\frac{\theta_a}{n}\right)^{10/3} \tag{7}$$

where D_e is the effective air-phase diffusion coefficient (= $\theta_a \tau_a D_a$), θ_a is the volumetric air content, n is total soil porosity, τ_a is the apparent tortuosity factor for the air phase (= $\theta_a^{7/3}/n^2$), D_a is the pure air-phase diffusion coefficient (≈ 2.26 x 10^{-5} m^2/s), and $D_{e,max} = D_e$ at $\theta_a = n$. Thus, $0 \le D_N \le 1$, such that diffusion of $O_{2(g)}$ via the air phase will be minimized as θ_a approaches zero ($\theta_a \rightarrow 0$). However, as shown by Aachib et al. (2004), minimizing the diffusion of $O_{2(g)}$ via the air-phase does not necessarily mean that the liquid-phase diffusion of $O_{2(g)}$ also will be unimportant.

As shown in Fig. 20b, D_N for the monolithic and resistive covers remained relatively high because the water content at the 0.6-m depth tended to remain relatively constant at the field capacity of the soils. However, in the case of the capillary barrier, D_N was significantly lower and more variable than the other cover sections, because the water content immediately above the interface between the finer and coarser layers remained high due to the capillary barrier effect. Stormont et al. (1996) attributed the variability in D_N to the variability in water contents associated with wet and dry seasons.

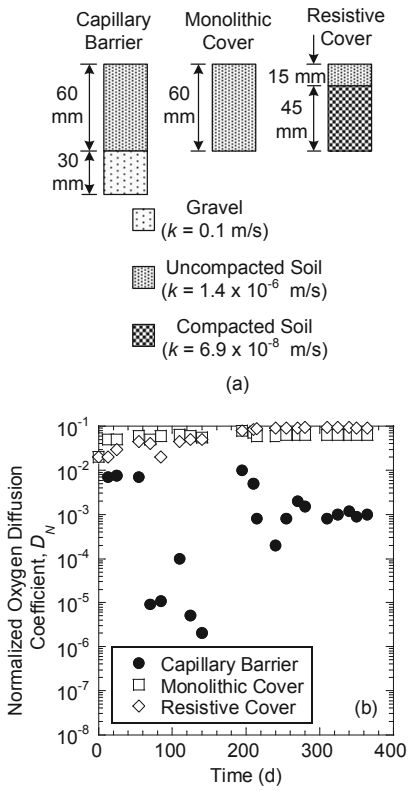

Figure 20. Gas-phase oxygen diffusion through three types of soil covers: (a) cross sections of cover types; (b) normalized oxygen diffusion coefficients at 0.6-m depths within the soil covers (data from Stormont et al. 1996; modified after Shackelford 1997).

5 DIFFUSION IN REMEDIATION APPLICATIONS

In terms of remediation, failure of the pump-and-treat technology to achieve clean-up goals has been attributed, in part, to the process of "reverse matrix" or "back" diffusion resulting in the slow and continuous release of contaminants from the intact clay and rock matrix into the surrounding, more permeable media, such as fractures or aquifer materials (e.g., Mackay and Cherry 1989, Mott 1992, Feenstra et al. 1996, Shackelford and Jefferis 2000, Chapman and Parker 2005, Seyedabbasi et al. 2012). Diffusion also has long been recognized as the transport process that controls the potential leaching of contaminants from stabilized or solidified hazardous waste, typically by the addition of pozzolanic materials such as cement, lime, and fly ash (e.g., Nathwani and Phillips 1980). Finally, diffusion may be a significant transport process with respect to controlling the rate of delivery of chemical oxidants (e.g., potassium permanganate, $KMnO_4$) injected into contaminated low-permeability media through hydraulic fractures for *in situ* treatment of chlorinated solvents (Siegrist et al. 1999, Struse et al. 2002).

5.1 *Reverse Matrix or Back Diffusion*

As an example of reverse matrix or back diffusion, consider the scenario illustrated conceptually in Fig. 21a, where initial contamination of the aquifer results in a difference in concentration between the contaminated aquifer and the clay lens resulting in diffusion of contaminants into the porous matrix of the clay lens. After pumping commences, the higher permeability portion of the heterogeneous aquifer is flushed of contamination relatively quickly, resulting in a reversal of the concentration gradient and an outward diffusive flux of the contaminant (Fig. 21b). This outward or reverse matrix (back) diffusion process results in a slow release of residual contamination back into the aquifer that can lead to failure of the pump-and-treat remediation technology to achieve regulatory levels within a short time frame, leading to extensive pumping and excessive costs (e.g., Feenstra et al. 1996).

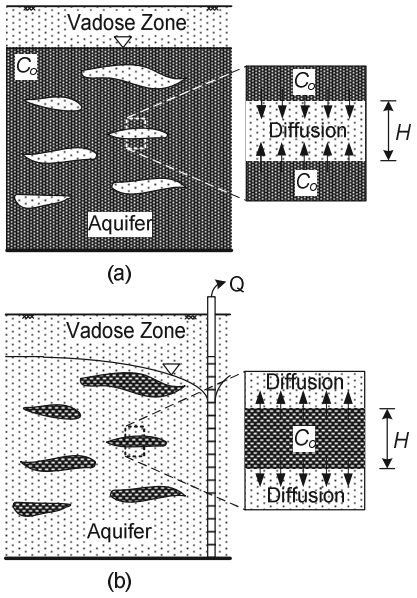

Figure 21. Matrix diffusion and reverse matrix diffusion: (a) diffusion into clay lens before pump-and-treat remediation; (b) reverse matrix or back diffusion out of contaminated clay lens during pump-and-treat. (modified after Shackelford and Lee 2005).

The effect of matrix diffusion on pump-and-treat remediation can be analyzed via superposition of an analytical solution based on the analogy between consolidation and diffusion and the principle of superposition (Shackelford and Lee 2005). For example, consider the case where the aquifer is initially contaminated with trichloroethylene (TCE) at a concentration, C_o, of 1000 ppm, such that TCE diffuses into a 1-m-thick (= H) clay lens for a period of time. However, before the clay lens becomes completely contaminated, pump-and-treat remediation is undertaken to clean up the aquifer. As a result, the initial TCE concentration profile within the 1-m-thick (= H) clay lens is sinusoidal as a result of incomplete matrix diffusion of TCE into the clay lens prior to pumping, with a maximum TCE concentration of 1000 ppm at the aquifer-clay interface and a minimum contaminant concentration of 300 ppm at the center of the clay lens. This initial distribution of contaminant within the clay lens is represented in Fig. 22a in terms of the relative concentration, $C(Z,T^*)/C_o$, of TCE as a function of the dimensionless depth, Z, corresponding to a value of the dimensionless diffusive time factor, T^*, of zero ($T^* = 0$), where (Shackelford and Lee 2005):

$$Z = \frac{z}{H_d} \quad ; \quad T^* = \frac{D^* t}{R_d {H_d}^2} = \frac{D_a t}{{H_d}^2} \tag{8}$$

and H_d is the maximum diffusive distance (= H/2 or 0.5 m in this example). The definition for the dimensionless

depth is identical to that for the case of consolidation, where H_d is the maximum drainage distance, whereas the definition for the diffusive time factor, T^*, is identical to that for the dimensional consolidation time factor, T, where D_a is replaced by the coefficient of consolidation, c_v (Shackelford and Lee 2005). On the basis that pumping results in "instantaneous" removal of contaminant from the surrounding aquifer at time $t = T^* = 0$, the resulting contaminant concentration profiles for $T^* > 0$ can be determined by means of superposition as shown in Fig. 22a. At times, T^*, less than about 0.1, both outward diffusion at the boundaries and inward diffusion near the center of the clay lens are occurring simultaneously, whereas after $T^* \cong 0.1$, the concentration profiles have dissipated to the extent that only outward diffusion of TCE occurs. The dissipation of residual contamination will proceed over time until all of the contaminant initially within the clay lens has diffused into the surrounding aquifer and been removed. However, this mass removal can take considerable time.

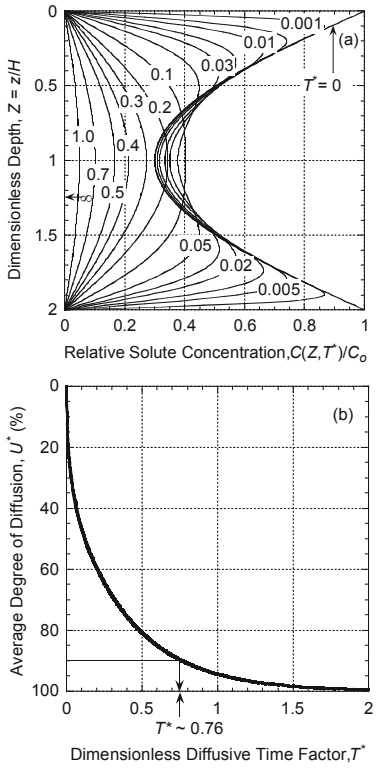

Figure 22. Results of example analysis for the reverse matrix diffusion from 1-m-thick clay lens contaminated with TCE resulting in an initial sinusoidal contaminant distribution: (a) time-dependency of relative TCE concentration versus dimensionless depth; (b) time dependency of the average degree of diffusion for contaminant removal (modified after Shackelford and Lee 2005).

For example, if we assume an R_d of 5.2 and D^* of 3.33 x 10^{-10} m^2/s for TCE and the clay based on Parker et al. (1996), then the degree of diffusion, U^*, which represents the relative degree of mass removal (Shackelford and Lee 2005), 10 yr after the beginning of pumping (i.e., $T^* \sim 0.081$) is approximately 0.43 or 43 %. Based on a porosity, n, of 0.60 for the clay lens and assuming complete reversibility of the sorbed TCE, the cumulative contaminant mass removed per unit area of the clay lens after 10 yr of pumping is approximately 749 g/m^2 (Shackelford and Lee 2005). More importantly, as indicated in Fig. 22b, 90 % contaminant mass removal (i.e., $U^* = 0.90$) corresponds to T^* of approximately 0.76, which is equivalent to 95 yr. Thus, this analysis indicates that approximately a century of pumping would be required to remove 90 % of the initial contaminant mass from a partially contaminated, 1-m-thick clay lens, which is consistent with the aforementioned observations attributing failure of some pump-and-treat systems to reverse matrix diffusion.

A similar analysis was presented by Feenstra et al (1996), but they assumed that the clay lens was initially completely (i.e., uniformly) contaminated. Such complete contamination of non-fissured clay lenses via matrix diffusion would be likely only in the case of relatively thin clay lenses and/or relatively long durations of aquifer contamination. Otherwise, the clay lenses likely would only be partially contaminated resulting in an initial concentration distribution within the clay lenses that is sinusoidal, thereby requiring the need for superposition in the resulting analysis (Shackelford and Lee 2005). Regardless of the level of contamination or the type of analysis required, this example supports the numerous observations that reverse matrix or back diffusion can play a significant role in affecting the remediation of contaminated aquifers.

5.2 *Diffusion through Subaqueous Caps for Contaminated Sediments*

Contaminated, subaqueous sediments represent a major environmental issue worldwide. One approach for dealing with this issue is to cap the sediments in situ. The caps should perform one or more of the following functions (Alshawabkeh et al. 2005): (a) physical isolation of the sediment; (b) sediment stabilization, in terms of preventing erosion and resuspension; and (c) reduction of dissolved contaminant flux. A conceptual schematic of the role of capping in situ sediments is illustrated in Fig. 23. Placement of the capping layer will reduce contaminant flux by (1) eliminating the bioturbation zone (i.e., mixing or dispersion caused by benthic organisms at the top several centimeters of the contaminated sediments), (2) increasing the length through which contaminants must migrate via advection and diffusion, (3) retarding contaminant migration via sorption to the capping materials, and (4) eliminating resuspension and direct desorption of contaminants to the overlying water column (Wang et al. 1991, Thoma et al. 1993). Capping materials do not necessarily have to be low permeability soils, as typically is the case with covers for above ground waste disposal, but the materials should possess some sorption capacity to minimize the rate of contaminant migration through the cap.

Initially, contaminant migration through the cap will occur both via advection and diffusion. The advective component of contaminant transport results from generation of excess pore-water pressures within the contaminated sediments due to placement of the capping material and the associated sediment consolidation. Some studies have indicated that consolidation induced contaminant mass flux can be several times greater than that due to diffusion during the initial, transient period when consolidation of the sediments is pronounced (e.g., Alshawabkeh et al. 2005). Nonetheless, diffusion still may play a significant role in terms of the contaminant mass flux through the cap during the initial transient transport stage of the process, and likely will be the dominant transport process under long-term, steady-state conditions

(Thoma et al. 1993). Although several studies have been undertaken towards the development of models that can handle the combined advective and diffusive mass transport of consolidating contaminated media (e.g., Smith 2000, Peters and Smith 2002, Alshawabkeh et al. 2005, Alshawabkeh and Rahbar 2006, Fox 2007a,b, Fox and Lee 2008, Lee and Fox 2009), comparatively fewer experimental studies for this scenario have been undertaken (e.g., Wang et al. 1991, Tang et al. 2005, Lee et al. 2009, Meric et al. 2010). Nonetheless, the issue of contaminant migration including diffusion from consolidating contaminated porous media remains an important area of research (e.g., Fox and Shackelford 2010).

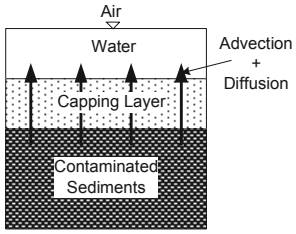

Figure 23. Schematic scenario of subaqueous cap for isolating contaminated sediments in situ.

6 CONCLUSIONS

The role of diffusion in environmental geotechnics was reviewed. Diffusion has been shown to be a significant contaminant transport process through low-permeability barrier materials, including natural and engineered clay barriers such as compacted clay liners (CCLs) and geosynthetic clay liners (GCLs), with values of hydraulic conductivity, k_h, lower than 10^{-9} m/s, and a dominant transport process for k_h values lower than about 2-5 x 10^{-10} m/s. The increasing significance of diffusion with decreasing k_h results in a situation whereby design of engineered clay barriers solely based on achieving low k_h is not only incorrect but also unconservative with respect to the duration of contaminant containment in such situations. As a result, achieving low k_h is a necessary, but not sufficient condition for assuring effective containment of contaminants with low- k_h barriers.

The existence of semipermeable membrane behavior is shown to affect the diffusion of simple salt solutions through bentonite based GCLs via ion exclusion. The greater the magnitude of the membrane behavior, the lower the effective diffusion coefficient. However, membrane behavior also is shown to diminish with increasing salt concentration, such that membrane behavior likely will play a minor, if any, role in affecting solute diffusion through traditional sodium bentonite based GCLs in many practical applications, such as landfills. Nonetheless, membrane behavior is likely to play a more significant role in terms of the diffusion of contaminants through other types of bentonite based barriers. For example, semipermeable membrane behavior is likely to be important in assessing diffusion of radionuclides through the highly compacted bentonite buffers being considered for containment of high-level radioactive waste, especially given the extremely long containment durations (e.g., 10,000 yr) associated with this application.

Diffusion is known to be the dominant liquid-phase transport process of VOCs through intact geomembrane liners (GMLs), either alone or as a component of a composite liner overlying and in intimate contact with an underlying CCL or GCL. In this regard, relatively recent data from clay-lined and composite-lined landfills in Wisconsin, USA, indicate that the GML component of composite liners offers virtually no added resistance to VOC diffusion relative to the CCLs. Diffusion also may be an important consideration for contaminant transport through slurry based vertical cutoff walls, but the significance of diffusion in this case likely is governed by the magnitude of the hydraulic gradient, i_h, across the wall, with the significance of diffusion increasing with decreasing i_h. Finally, diffusion through subaqueous caps used for in situ containment of contaminated dredged sediments has been an area of significant study, particularly in terms of long-term environmental impacts.

Matrix diffusion, whereby contaminants diffuse from interconnected pores or fractures into the surrounding intact clay or rock matrix, can be an important attenuation mechanism in assessing the potential environmental impact of migrating contaminants, both on a global scale such as beneath a landfill located over fissured or fractured clay or rock, and on a local scale such as through a GCL comprised of granular bentonite. However, the resulting contamination of the clay or rock matrix may result in ineffective and/or prolonged remediation of the sites due to the process of reverse matrix or back diffusion.

Finally, gas-phase diffusion also can play a significant role in environmental geotechnics, particularly since diffusion via the gas phase can be significantly faster than that via the liquid phase. Two examples where gas-phase diffusion is important include the diffusion of oxygen through covers resulting in oxidation of sulphidic bearing mine tailings and the subsequent generation of acid drainage, and the release of radon from uranium bearing tailings to the surrounding atmosphere.

7 ACKNOWLEDGMENTS

The author expresses his sincere gratitude to David Daniel, R. Kerry Rowe, Robert Quigley (deceased), John Cherry, Robert Gillham, and Donald Gray for their guidance and assistance during his PhD graduate studies on the topic of diffusion through clay barriers. The author also thanks Mario Manassero, Chair of ISSMGE Technical Committee TC215 on Environmental Geotechnics, for his support in receipt of the first *R. Kerry Rowe Honorary Lecture* which served as the basis for this paper. Finally, the author appreciates the assistance of his Ph.D. graduate student, Kristin Sample-Lord, in the preparation of this paper.

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