Fundamental considerations for column testing of engineered, clay-based barriers

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ABSTRACT

The purpose of column testing is to determine the transport and fate properties, typically the hydrodynamic dispersion coefficient ($D_h$) and retardation factor ($R_d$), of aqueous miscible chemical species (solutes) with respect to a given porous medium. This paper presents fundamental considerations required for column testing of engineered, low-permeability, clay-based barriers, such as compacted clay liners, geosynthetic clay liners, and soil-bentonite vertical cutoff walls, used to contain chemicals in a variety of solid and liquid waste containment and remediation applications. The presentation is limited to column tests conducted with a constant solute source concentration, and includes descriptions of the general procedures for conducting column tests as well as the expected behavior of the solute (effluent) breakthrough curve (BTC) based on several considerations. Significant information can be gained simply from the shape of the solute BTC. For example, a sigmoidal symmetric BTC implies advective-dominated solute transport with linear, instantaneous, and reversible sorption, whereas a sigmoidal asymmetric BTC can result from diffusion-dominated transport, nonlinear sorption, and/or nonequilibrium (kinetic) sorption. Also, because clay-based barriers are susceptible to hydraulic incompatibility when permeated with chemical solutions, significant hydraulic incompatibility can lead to a significant change in the seepage velocity ($v_s$) under the constant hydraulic head (gradient) condition, which invalidates the use of analytical transport models to determine $D_h$ and $R_d$ via fitting of the measured solute BTCs, as well as the use of dimensionless time or pore volumes of flow. For this reason, constant flow hydraulic control is recommended for conducting column tests with engineered, low-permeability, clay-based barriers, because significant changes in hydraulic conductivity do not significantly affect $v_s$. Finally, the potential significance of diffusion on solute transport through clay-based barriers can complicate interpretation of the existence of an effective porosity and determination of the correct, mass-based definition of $R_d$ from the BTCs emanating from traditional concentration-based column tests. However, these issues are readily discerned when cumulative mass column testing is performed. Example results from both traditional, concentration-based column testing and alternative, cumulative mass column testing of clay-based barriers are provided to illustrate application of the concepts presented.

Keywords: breakthrough curve, chemical containment, clay barriers, column testing, compatibility, cumulative mass, diffusion, dispersion, effective porosity, hydraulic conductivity, membrane behavior, retardation, solute transport

1 INTRODUCTION

Engineered, low-permeability, clay-based barriers, such as compacted clay liners (CCLs), geosynthetic clay liners (GCLs), and soil-bentonite (SB) vertical cutoff walls, typically are required for chemical containment applications, including solid and liquid waste containment facilities (e.g., municipal, hazardous, and radioactive waste landfills, tailings impoundments, wastewater treatment lagoons, etc.) and in situ containment of contaminated groundwater. The primary consideration for these barriers for chemical containment is the ability to achieve a suitably low hydraulic conductivity (e.g., $k \leq 1.0 \times 10^{-9}$ m/s) with respect to the contained liquid (e.g., waste leachate, contaminated groundwater), in order to minimize advective (hydraulically driven) transport of chemical contaminants through the barrier. A secondary consideration is the evaluation of the barrier performance with respect to the fate and transport (migration) of aqueous miscible chemicals (solutes) through the barrier (e.g., Shackelford, 1990). The term “fate” refers to the various physical, chemical, and biological processes that may govern the migration of solutes through a porous medium (e.g., Shackelford and Rowe, 1998).

Column testing has been used extensively for assessing the fate and transport of chemicals through CCLs (e.g., Crooks and Quigley, 1984; Acar and Haider, 1990; Shackelford and Redmond, 1995; Kim et al., 1997, 2001; Valderrama et al., 2011; Javadi et al., 2017), GCLs (e.g., Malusis and Shackelford, 2004; Jo et al., 2006; Mazzieri, 2012; Mazzieri et al., 2013; Mazzieri and Pasqualini, 2016), and SB cutoff walls (e.g., Bierck and Chang, 1994; Park et al., 1997; Hong and Shackelford, 2017a,b, 2019; Shackelford and Hong, 2020). However, because column tests have been performed more traditionally in disciplines other than those related to the
design of engineered, clay-based containment barriers, the fundamental considerations required to properly conduct column tests and interpret the results typically are unfamiliar to those who are responsible for such design.

The purpose of this paper is to describe and illustrate the fundamental considerations required for column testing of engineered, low-permeability, clay-based chemical containment barriers. First, the theoretical background governing solute transport through porous media is presented. Second, the procedures required for conducting traditional concentration-based column tests are described. Third, the procedures for conducting alternative, cumulative mass column tests are presented. Finally, conclusions are drawn with respect to column testing of engineered, low-permeability, clay-based chemical containment barriers.

2 THEORETICAL BACKGROUND

2.1 Fate and transport processes

The physical processes governing solute transport in porous media include advection, diffusion, and mechanical dispersion. Diffusion refers to chemical mass spreading or dispersion resulting from a concentration gradient as described by Fick’s first and second laws (Shackelford, 2014). Mechanical dispersion refers to advective-dominated dispersion that occurs as a result of variations in the flow field and is described theoretically in terms of an equation that is analogous to Fick’s first law for diffusion, but is a function of the seepage velocity. Advection and mechanical dispersion tend to be dominant for high flow-rate media (e.g., coarse-grained soils) and/or under high imposed hydraulic gradients, whereas diffusion tends to be dominant for low flow-rate media (e.g., fine-grained soils) and/or low imposed hydraulic gradients.

The fate of chemicals refers to the various chemical and biological processes that can affect the mobility and/or attenuation of chemicals during migration through porous media. Attenuation refers to processes that immobilize, retard, or otherwise degrade chemicals (Shackelford, 1999). Chemical processes include sorption, radioactive decay, dissolution/precipitation, acid/base, complexation, hydrolysis/substitution, and oxidation/reduction (redox) reactions (Shackelford and Rowe, 1998). Sorption refers to partitioning of chemicals between the liquid phase (pore water) and the solid phase (soil particles) and can result, for example, from cation exchange in the case of metals (e.g., Cd, Pb, Zn) or hydrophobic partitioning in the case of hydrophobic organic compounds. Radioactive decay refers to the degradation in the activity of radionuclides. All of the other aforementioned chemical processes affect the chemical speciation (e.g., Cr$^{3+}$ vs. Cr$^{6+}$) and/or the phase of the chemical (e.g., gas, liquid, or solid) which, in turn, affects the mobility/attenuation of the chemical during migration.

Biological processes are those that are controlled or mediated by microorganisms. For inorganic chemicals (e.g., metals), biological processes tend to affect chemical speciation which, in turn, affects mobility/attenuation. For organic compounds, biological processes can result in biodegradation or decay of the compound which contributes to the attenuation of the compound.

2.2 Solute transport theory

The governing equation for one-dimensional solute transport through saturated soil is the continuity equation describing solute transport through a representative elementary volume of a porous medium, more commonly known as the advection-dispersion-reaction equation (ADRE). The ADRE may be written as follows (van Genuchten and Alves 1982):

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D_h \frac{\partial C}{\partial x} \right) - \frac{\partial}{\partial x} (v_x C) - \lambda C + \Gamma \]

where \( C \) = aqueous-phase (pore-water) solute concentration [ML$^{-3}$, M = mass units, L = length units], \( x \) = direction of solute transport [L], \( t \) = elapsed time [T], \( R_D \) = the retardation factor [-], \( D_h \) = the hydrodynamic dispersion coefficient [L$^2$T$^{-1}$], \( v_x \) = the seepage velocity [LT$^{-1}$], which is also known as the pore-water, average linear, or interstitial velocity, \( \lambda \) = decay constant for linear, first-order decay [T$^{-1}$], and \( \Gamma \) = the rate coefficient for zero-order production [ML$^{-3}$T$^{-1}$]. Note that both \( \lambda \) and \( \Gamma \) are lumped parameters that include the respective processes in both the liquid (aqueous) and solid phases (van Genuchten and Alves, 1982).

The seepage velocity is based on Darcy’s law, or

\[ v_x = \frac{q}{nA} = \frac{v_i k_i}{n} \]

where \( q \) = the volumetric flow rate [L$^3$T$^{-1}$], \( n \) = the total porosity of the soil [-], \( A \) = total cross-sectional area of the soil perpendicular to the direction of flow [L$^2$], \( v \) = the Darcy velocity or liquid flux [LT$^{-1}$], \( k \) = the hydraulic conductivity [LT$^{-1}$], and \( i \) = the hydraulic gradient [-]. Note that \( v_x \) as defined by Eq. 2 is based on the explicit assumption that all of the pore space within the soil is available for liquid flow and solute transport. In some soils, only a fraction of the pore space may be available for liquid flow and solute transport due, for example, to the existence of dead-end pores or semipermeable membrane behavior. In this case, \( n \) in Eq. 2 typically is replaced by an effective porosity, \( n_e \) (< \( n \)), where \( n_e \) is defined as the volume of voids available for liquid (water) flow and solute transport relative to the total volume of voids. However, Dominijanni et al. (2020) note that the effective pore space available for solute transport may be lower than that available for water flow due to solute restriction via semipermeable membrane
behavior resulting from charge repulsion in clays (e.g.,
anion exclusion). As a result, Dominijanni et al. (2020) distinguish between water effective porosity, \( n_{ew} \), and solute effective porosity, \( n_{es} \), such that \( n_{es} \leq n_{ew} \), and define the seepage velocity given by Eq. 2 with respect to \( n_{ew} \), i.e., \( v_s = \frac{ki}{n_{ew}} \).

The hydrodynamic dispersion coefficient in Eq. 1, \( D_h \), represents dispersion due to both advection, commonly referred to as mechanical dispersion, and diffusion, and may be written as follows:

\[
D_h = D_m + D^* = \alpha_L V_s + \tau_m D_o
\]

where \( D_m \) is the mechanical dispersion coefficient \([L^2 T^{-1}]\), \( D^* \) is the effective diffusion coefficient \([L^2 T^{-1}]\), \( \alpha_L \) is the longitudinal dispersivity \([L]\), \( \tau_m \) is the matrix or geometric tortuosity factor \([-]\), and \( D_o \) is the aqueous-phase diffusion coefficient of the solute in the absence of a porous medium \([L^2 T^{-1}]\). Note that \( \tau_m \) is defined as the ratio of the ratio of the macroscopic or straight-line distance of diffusion, \( L \), relative to the effective or pore-scale distance of diffusion, \( L_s \), i.e., \( \tau_m = (L/L_s)^2 \), such that \( \tau_m < 1 \) (e.g., Shackelford, 1989; Shackelford and Daniel, 1991). Based on Eq. 3, when \( v_s \) is relatively high such as with high-permeability media (e.g., sands and gravels), \( D_m \gg D^* \) such that \( D_h = D_m \), whereas when \( v_s \) is relatively low such as with low-permeability media (e.g., silts and clays), \( D^* \gg D_m \) such that \( D_h \approx D^* \). Also, the limiting case of “pure advection,” also referred to as piston displacement or plug flow, represents the situation when there is no dispersion, i.e., \( D_h = 0 \), whereas the limiting case of “pure diffusion” represents the situation when there is no advection, i.e., \( v_s = 0 \), such that \( D_h = D^* \).

In this latter case, Eq. 1 reduces to:

\[
R_d \frac{\partial C}{\partial t} = D^* \frac{\partial^2 C}{\partial x^2} - \lambda C + \Gamma
\]

which is a form of Fick’s second law for diffusion in porous media.

The retardation factor accounts for sorption of solutes to the solid phase of the soil (e.g., adsorption), and can be represented as follows (Freeze and Cherry, 1979):

\[
R_d = 1 + \frac{\rho_d}{n} K_d
\]

where \( \rho_d \) is the dry (bulk) density of the soil \([ML^{-3}]\), and \( K_d \) is the distribution coefficient \([LM^{-1}]\) representing linear, reversible, and instantaneous sorption of the solutes from the liquid phase (pore water) to the solid phase (solid soil particles). The distribution coefficient may be defined further as follows:

\[
K_d = \frac{C_s}{C}
\]

where \( C_s \) is the solid-phase concentration of the solute defined as the mass of solute adsorbed to the solid phase relative to the mass of solute in the liquid phase \([MM^{-1}]\).

The definition of \( K_d \) given by Eq. 6 implicitly assumes that the relationship between \( C \) and \( C_s \) is linear and passes through the origin, i.e., \( C = 0 \) when \( C_s = 0 \).

The decay constant, \( \lambda \), is related to the half-life of a chemical species, \( \tau_b \), i.e., \( \lambda = 0.693/\tau_b \), where \( \tau_b \) is the time required for half of the concentration of a given chemical species to decay, and generally is used to describe radionuclide decay during migration through porous media (Shackelford, 1993; Shackelford and Rowe, 1998). However, since \( \lambda \) decreases as \( \tau_b \) increases, if \( \tau_b \) is significantly longer than the duration of migration, \( \lambda \) in Eq. 1 can be ignored without significant loss in accuracy (i.e., \( \lambda = 0 \)).

Zero-order reactions (i.e., \( \Gamma \) in Eq. 1) are reactions governed by a constant rate that is independent of solute concentration. This term also is not likely to be relevant for most column tests conducted with engineered, clay-based barriers (i.e., \( \Gamma = 0 \)).

Note that the form of the ADRE given by Eq. 1 is based explicitly on the assumption that \( v_s \) is constant (Freeze and Cherry, 1979). Therefore, the application of any mathematical solution based on Eq. 1, i.e., solute transport model, also requires that \( v_s \) must be constant (Shackelford and Rowe, 1998). This requirement is an important consideration with respect to the hydraulic control condition that is imposed when conducting a column test as well as the correct interpretation of the test results, as will be discussed subsequently.

### 3 CONCENTRATION-BASED COLUMN TESTING

Traditional column testing involves permeating a column of soil of length, \( L_s \), with a chemical solution (influent) containing one or more solutes of interest at initial concentrations, \( C_o \), and measuring the concentrations of the same solutes within the pore water of the soil as a function of location and time, \( C(x,t) \), also referred to as “resident concentrations, \( C_r \),” and/or in the effluent as a function of time, \( C(L,t) = C_e \), also referred to as “flux-averaged concentrations, \( C_f \)” (see van Genuchten and Parker, 1984; Shackelford, 1994a).

Column tests in which the influent is permeated continuously throughout the duration of the test are referred to as constant-source, infinite-source, or step column tests, whereas those in which only a finite volume of influent is permeated through the soil are referred to as finite-source or pulse column tests. In general, measurement of pore-water concentrations is practically more difficult than measurement of effluent concentrations. For this reason, emphasis herein is placed on column tests involving measurement of effluent concentrations. Also, because typical applications for the results of column tests (e.g., waste containment) are based on the assumption that the concentrations of chemical species in the influent are constant (e.g., chemical species in waste leachate), only
constant-source (step) column tests will be considered. Detailed descriptions of the differences between resident versus fluxed-averaged concentrations and pulse versus step column tests are provided by Shackelford (1994a).

3.1 Typical procedure and results

The typical procedure for performing a traditional, constant-source column test comprises four stages as illustrated schematically in Fig. 1 (e.g., Shackelford 1994a,c; Mazzieri et al., 2015). The first stage is the preliminary stage (Stage 0), whereby the solvent, usually water, is permeated through a column of soil of length $L$ until steady-state flow (seepage) is established ($i.e., q_{in} = q_{out} = q$). Second, while maintaining steady-state flow, the permeant liquid is “instantaneously” changed from the solvent to the desired chemical solution (influent) containing one or more solutes, each at an initial, constant source concentration $C_o$, that may or may not be the same. This stage (Stage 1) represents the start of the column test corresponding to an elapsed time, $t_0$, of zero ($i.e., t_0 = 0$). Third, the effluent is sampled periodically and the effluent concentrations, $C_e$, of the desired solutes in each sample are measured to develop a temporal profile of effluent concentration ($i.e., C_e$ vs. $t$) referred to as an effluent or solute breakthrough curve (BTC). Fourth, complete breakthrough of the solute has occurred such the $C_e = C_o$, representing steady-state solute transport. Note the distinction between steady-state flow, which is established in Stage 0 and maintained thereafter, and steady-state transport, which is established in Stage 3 and maintained thereafter. Also, note that column tests may be terminated prior to the establishment of steady-state transport, i.e., during Stage 2.

As indicated in Fig. 2b, $t_1$ is the initial time corresponding to when the solute first appears in the effluent, $t_{1st}$ is the time corresponding to the beginning of steady-state solute transport, and $t_1$ is the characteristic breakthrough time corresponding to when $C_e$ is equal to half of the source concentration, i.e., $C_e = 0.5C_o$. For this reason, $t_1$ is also designated as $t_{b,50}$. Note that all of the concentration profiles shown in Fig. 2 correspond to the case where the flow rate is relatively high ($i.e., \nu_f$), such that diffusion is negligible, i.e., $D_m \gg D'$ and $D_h \approx D_m$. Differences in these profiles for the case where diffusion is significant or dominant, corresponding to low flow rates ($i.e., \nu_f$), i.e., $D' \gg D_m$ and $D_h \approx D'$, will be illustrated subsequently.

The case of pure advection is analogous to the solute migrating as an abrupt front through the column of soil, such that the concentration everywhere behind the solute front is $C_o$ and the concentration immediately ahead of the solute front is zero (see Fig. 2a). The added effect of

![Fig. 1. Schematic illustration of the four stages of a traditional, concentration-based column test with a constant-source concentration, $C_o$ ($q =$ volumetric flow rate, $C =$ concentration).](image-url)
dispersion is to spread out the migrating front, such that concentrations immediately behind the migrating front are lower than \( C_o \), whereas those immediately ahead of the migrating front are greater than zero. For the limiting case of advective-dominated solute transport, the conceptual concentration profiles based on advection plus dispersion intersect the pure advection profiles at half the source concentration, i.e., \( C(x,t) = C_e = 0.5C_o \).

The shape of the BTC shown in Fig. 2b is referred to as sigmoidal symmetric. The difference between sigmoidal symmetric and sigmoidal asymmetric BTCs is illustrated conceptually in Fig. 3. Sigmoidal symmetric BTCs are expected only when solute transport is advective dominated and adsorption is linear, instantaneous, and reversible. Sigmoidal asymmetric BTCs can result from several effects, such as diffusion-dominated solute transport, nonlinear adsorption, and/or nonequilibrium (kinetic) adsorption. Since advective-dominated solute transport is likely only for high-permeability, coarse-grained porous media, the shape of BTCs for low-permeability, clay-based barriers used for chemical containment typically are sigmoidal asymmetric, reflecting the significance of diffusion on solute transport. Examples of measured BTCs that are sigmoidal symmetric versus sigmoidal asymmetric are shown in Cao et al. (2019) for cesium (Cs) and strontium (Sr), respectively, based on the results of a column test conducted with a poorly graded silty sand.

\[
\begin{align*}
&\text{Stage 1: Pure Advection (Piston Displacement or Plug Flow)} \\
&\text{Stage 2: Advection + Dispersion} \\
&\text{Stage 3: Diffusion Dominant} \\
&\text{Stage 4: Advection + Dispersion + Decay} \\
&\text{Stage 5: Pure Advection + Sorption} \\
&\text{Stage 6: Advection + Dispersion + Sorption} \\
&\text{Stage 7: Advection + Dispersion + Sorption + Decay}
\end{align*}
\]

Fig. 4. Effect of physical, chemical, and biological processes on the shapes of solute breakthrough curves in terms of effluent concentration, \( C_e \), versus elapsed time, \( t \), for a constant-source concentration column test (modified after Shackelford, 1994c).

### 3.3 Non-zero initial concentration

In some cases, the pore water of the soil may not be devoid of one or more of the solutes of interest in the influent. In this case, the \( C_i \) in Stage 0 (Fig. 1) will not be zero, but rather will equal the initial concentration of the solute in the soil pore water, \( C_i \), i.e., \( C_e = C_i \). For this situation, there are two possibilities to consider.

First, the soil may be permeated continuously with the solvent (e.g., water) during Stage 0 until \( C_i \approx 0 \) (e.g., Shackelford and Redmond, 1995). In this case, the BTC will resemble that shown in Fig. 2. Second, if the initial solute concentration within the soil is considered to be constant, then the corresponding solute BTC is considered to be relative to \( C_i \), as illustrated schematically in Fig. 5 for the case of advective-dominated solute transport (e.g., see the BTC for Sr in Cao et al., 2019). In either case, consideration needs to be given to the possibility that one or more of the solutes of interest in the influent also may be present initially in the pore water of the soil, and to what implications the presence of \( C_i > 0 \) may have on the results.

\[
\begin{align*}
&\text{Stage 1: Pure Advection (Piston Displacement or Plug Flow)} \\
&\text{Stage 2: Advection + Dispersion} \\
&\text{Stage 3: Diffusion Dominant} \\
&\text{Stage 4: Advection + Dispersion + Decay} \\
&\text{Stage 5: Pure Advection + Sorption} \\
&\text{Stage 6: Advection + Dispersion + Sorption} \\
&\text{Stage 7: Advection + Dispersion + Sorption + Decay}
\end{align*}
\]

Fig. 5. Solute breakthrough curve (BTC) in terms of effluent concentration, \( C_e \), versus elapsed time, \( t \), for a constant-source concentration column test (modified after Shackelford, 1994c).
3.4 Dimensionless parameters

Instead of absolute concentration and real time, BTCs often are presented in terms of relative concentration, \( RC \), and dimensionless time, \( T \), where \( RC \) is defined as follows:

\[
RC = \frac{C_e - C_l}{C_0 - C_l}
\]  

and \( T \) is defined as follows:

\[
T = \frac{v_s t}{L} \tag{8}
\]

Note that, for a constant-source column test, \( 0 \leq RC \leq 1 \). Also, \( T \) as defined by Eq. 8 is strictly valid only if \( v_s \) is constant, in which case \( T \) is equivalent to the dimensionless pore volumes of flow, \( PVF \), defined as the cumulative volume of flow, \( qt \) [L³], relative to the void volume of the soil, \( V_v \) [L³], or:

\[
PVF = \frac{qt}{V_v} = \frac{kiAt}{nAL} = \frac{ki t}{n L} = \frac{v_s t}{L} = T \tag{9}
\]

Thus, in accordance with Eq. 9, if \( v_s \) is not constant, then \( PVF \neq T \).

The BTC in Fig. 5 is shown in Fig. 6 in terms of dimensionless parameters, where the dimensionless times \( T_i \), \( T_{0.5} \), and \( T_{ss} \), shown in Fig. 6 correspond to the respective elapsed times \( t_i \), \( t_{0.5} \) (= \( t_{0.5} \), and \( t_{ss} \) shown in Fig. 5.

\[
RC = \begin{cases} 
1 & \text{Stage 1} \\
0.5 & \text{Stage 2} \\
0 & \text{Stage 3}
\end{cases}
\]

Fig 6. Solute breakthrough curve (BTC) in terms of relative concentration, \( RC \), versus dimensionless time, \( T \), or pore volumes of flow, \( PVF \), for a constant seepage velocity.

3.5 Measurement of effluent concentrations

The BTCs illustrated thus far are described by continuous, temporal distributions in effluent concentrations. However, instantaneous concentrations cannot be measured. Therefore, the approach to measuring concentration-based BTCs is to collect discrete but small samples of effluent periodically for measurement of the concentrations of the solutes being monitored. The concentrations so measured actually represent average concentrations over the interval of time corresponding to the effluent sample volume upon which the measured concentration is based.

For example, consider the schematic BTC shown in Fig. 7a, where discrete effluent concentrations are measured over periodic time intervals, \( \Delta t \). Based on a constant flow rate, \( q \), the incremental volume of effluent, \( \Delta V_e \), collected during this time interval is given as \( \Delta V_e = q \Delta t \). Within this incremental sample volume, there will be a corresponding increment of solute mass, \( \Delta m \), such that the measured effluent concentration is an average concentration, \( C_{e,avg} \), equivalent to \( \Delta m/\Delta V_e = \Delta m/q \Delta t \). The concept then is to minimize \( \Delta t \) and, therefore, \( \Delta V_e \), so that the measured \( C_{e,avg} \) will represent a reasonable estimate of an “instantaneous” concentration, i.e.,

\[
\lim_{\Delta t, \Delta V_e \to 0} C_{e,avg} \to C_e \tag{10}
\]

Note that a sufficient number of measured, discrete (average) effluent concentrations is required to adequately define the BTC.

\[
\Delta T \approx t_f - t_i
\]

Fig. 7. Measured solute breakthrough curve (BTC) in terms of effluent concentration, \( C_e \), versus elapsed time, \( t \): (a) discrete effluent concentrations over a time intervals, \( \Delta t \); (b) effect on the BTC of locating the measured (average) concentration, \( C_{e,avg} \), at the time corresponding to the middle of the sample interval, \( t_m \), versus the time corresponding to the mass centroid of the sampling interval, \( t_c \).

The other consideration is the time to which the measured \( C_{e,avg} \) should be assigned (see Fig. 7b). Primarily for convenience, the measured \( C_{e,avg} \) typically is plotted at the time corresponding to the middle of the sampling interval, \( t_m \), where \( t_m = (t_i + t_f)/2 \). In reality, the measured \( C_{e,avg} \) conceptually should be plotted at the time corresponding to the solute mass centroid of the area under the BTC for the interval \( \Delta t \), or \( t_c \). As illustrated in Fig. 7b, the shape of the BTC over the interval \( \Delta t \) approximately resembles that of a trapezoid, such that \( t_c \) should be slightly greater than \( t_m \). Thus, plotting the measured \( C_{e,avg} \) at \( t_c \) would result in a slight shift in the BTC, such that plotting the measured \( C_{e,avg} \) at \( t_m \) actually results in some error. However, given that the location of the BTC is not known \textit{a priori}, determining \( t_c \) is not practical, and as long as the magnitude of \( \Delta t \) is small (\( \lim \Delta t \to 0 \)) and/or the slope of the BTC is...
relatively flat (lim dC_e/dt → 0), the difference between τ_c and τ_m likely is minor, such that the magnitude in any error resulting from using τ_m should be minimal (Shackelford, 1994a).

Another factor to consider in terms of the elapsed time corresponding to the measured effluent concentration is the potential for a dilution effect as described by Mazzieri et al. (2015). This effect results from the storage of the permeant liquid in (i) the porous disk (stone) on the outflow (effluent) side of the column specimen, (ii) the effluent line connecting the specimen to a collection reservoir, and (iii) the collected effluent when a bladder accumulator is used to isolate the effluent (e.g., see Daniel, 1994). In this case, the stored liquid dilutes the measured effluent concentration, which ultimately can result in inaccurate estimates in the determined values of both D_h and R_d with the tendency being to underestimate D_h and overestimate R_d (Mazzieri et al., 2015). Thus, when performing column tests using porous disks, lengthy effluent lines, and/or bladder accumulators as part of the apparatus, care should be taken to account for any effect of dilution on the measured effluent concentrations to ensure accurate determination of the solute transport parameters.

### 3.6 Determination of transport parameters

In the absence of first-order decay and zero-order production processes, the two primary solute transport properties of interest are D_h and R_d. Both of these parameters can be determined by fitting the measured BTC with an appropriate model based on Eq. 3, i.e., for a known value of v_c and assuming λ = Γ = 0. Based on the study by van Genuchten and Parker (1984), the most appropriate analytical model for evaluating flux-averaged, effluent concentrations (i.e., C_e = C_o) from laboratory column tests is as follows (see also van Genuchten and Alves, 1982; Parker, 1984; Shackelford, 1994a):

\[
RC = 0.5 \left[ \text{erfc} \left( \beta_1 \right) + \exp \left( \beta_2 \right) \text{erfc} \left( \beta_3 \right) \right] \tag{11}
\]

where \( \text{erfc} \) is the complementary error function, \( \exp \) is the exponential function, and \( \beta_1, \beta_2, \) and \( \beta_3 \) are dimensionless arguments defined as follows:

\[
\beta_1 = \frac{1 - T_B}{2\sqrt{T_R/\ell_L}}, \quad \beta_2 = \frac{v_c L}{D_h}, \quad \beta_3 = \frac{1 + T_B}{2\sqrt{T_R/\ell_L}} \tag{12}
\]

and

\[
T_R = \frac{v_c t}{R_d L}, \quad R_d = \frac{R_d}{R_d} \tag{13}
\]

The dimensionless parameter \( P_L \) in Eq. 12 is known as the column Peclèt number. The procedure is to perform a nonlinear fitting of the measured BTC using Eq. 11 to find the values of \( P_L \) and \( R_d \) that provide the best fit (e.g., minimum error or highest coefficient of determination, \( r^2 \)), and then determine \( D_h \) via the definition of \( P_L \) given by \( \beta_2 \) in Eq. 12, i.e., with the known values for \( v_c \) and \( L \) (e.g., see Mo et al., 2020).

The previously noted limiting case of advective-dominated solute transport with mechanical dispersion is described theoretically by a truncated form of Eq. 11, whereby the second term in Eq. 11 is assumed to be zero (e.g., Shackelford, 1994a), or:

\[
RC = 0.5 \text{erfc} \left( \beta_1 \right) \tag{14}
\]

Based on Eq. 14, as \( P_L \) increases in magnitude, the shapes of the BTCs become increasingly closer to sigmoidal symmetric about \( RC = 0.5 \), which corresponds to \( C_e = 0.5C_o \) when \( C_i = 0 \) or \( C_e = 0.5(C_o + C_i) \) when \( C_i > 0 \). In this case, the value for \( R_d \) can be determined independently as follows (Shackelford, 1993; Cao et al., 2019):

\[
R_d = \frac{v_c L}{\tau_p} = \frac{L}{\tau_p} = \frac{L}{v_c L} = \frac{L}{v_c L} \tag{15}
\]

where \( v_c \) = the velocity of the reactive (adsorbing) solute [LT^-1], and \( \tau_p \) and \( \tau_t \) = the characteristic breakthrough times [T], i.e., the times corresponding to piston displacement or plug flow, for the nonadsorbing solute (tracer) and the adsorbing solute, respectively, as illustrated schematically in Fig. 4.

Also, as previously noted, when advection dominates solute transport, \( t_{0.5} \) for the BTC is the same as \( t \) corresponding to piston displacement or plug flow, \( t_p \), where \( t_p \) is given by:

\[
t_{0.5} = t_p = \frac{L}{v_c L} = \frac{LR_d}{v_c L} \tag{16}
\]

or, in terms of dimensionless time,

\[
T_{0.5} = T_p = \frac{v_c t_p}{L} = \frac{LR_d}{L} = R_d \tag{17}
\]

which indicates that \( R_d \) is exactly equivalent to \( T_{0.5} \) or the PVF corresponding to \( RC = 0.5 \).

Note again that the aforementioned definitions for \( R_d \) (Eqs. 15 and 17) are applicable only when \( v_c \) is constant and all of the pores in the soil are effective in conducting liquid flow and solute transport. Also, as previously noted, solute transport must be dominated by advection (i.e., diffusion is negligible) in order for \( R_d \) to be given by Eqs. 15 or 17. The reason for this latter condition is that the true definition for \( R_d \) is based on the solute mass that is contained within the soil upon achieving steady-state solute transport, i.e., when \( RC = 1.0 \) (van Genuchten and Parker, 1984; Shackelford, 1994a).

For example, when \( RC = 1.0 \), the solute concentration in the pore water of the soil is equivalent to the source concentration, i.e., \( C(0 ≤ x ≤ L, t_o) = C_o \). Under this condition, the total adsorbed concentration of the solute is given by Eq. 6 with \( C = C_o \), or \( C_e = K_d C_o \). Thus, based on the definition for \( R_d \) given by Eq. 5 with \( K_d = C_o/C_o \),...
$R_d$ is defined as follows (Hong and Shackelford, 2019):

$$R_d = 1 + \frac{\rho_d}{n} \frac{C_s}{C_o} = \frac{nC_o + \rho_dC_s}{nC_o} = \frac{m_{pw}}{m_{pw} + m_s} = RH \quad (18)$$

where $m_{pw}$ is the mass of the solute in the pore water of the soil at steady-state transport [M], $m_s$ is the solid-phase or adsorbed solute mass in the soil at steady-state transport [M], and $RH = \text{the relative holdup}$ (van Genuchten and Parker, 1984; Shackelford, 1994a). As illustrated in Fig. 8, $RH$ represents the area behind the solute BTC at steady-state transport. In the limiting case where advection dominates solute transport, the solute BTC is sigmoidal symmetric such that the deficit in solute mass relative to plug flow is exactly matched by the excess in solute mass relative to plug flow. Thus, $RH$ given by plug flow is exactly the same as the $RH$ for the actual solute BTC. As a result, $T_{0.5} (= T_p)$ is representative of the $RH$, i.e., $T_{0.5} = T_p = R_d = RH$ (Fig. 8a). In the case where the solute is nonadsorbing, $m_s = 0$ in Eq. 18 such that $R_d = RH = T_{0.5} = 1.0$. This result means that breakthrough of a nonadsorbing solute or tracer based on $T_{0.5}$ will occur exactly at one pore volume of flow ($PVF = 1.0$), i.e., assuming that all pores are effective in conducting liquid flow and solute transport (e.g., see BTCs for KCl with humic acid coated sands in Joo et al., 2021).

![Fig. 8. Breakthrough curve (BTC) in terms of relative concentration, $RC$, versus dimensionless time, $T$, or pore volumes of flow, $PVF$, for an adsorbing solute illustrating the relative holdup, $RH$: (a) sigmoidal symmetric BTC; (b) sigmoidal asymmetric BTC.](image)

However, when the solute BTC is sigmoidal asymmetric (Fig. 8b), the deficit and excess of solute mass relative to plug flow do not balance, such that $T_{0.5}$ does not represent the $RH$ and $R_d \neq T_{0.5}$. In this case, the value for $T_{0.5}$ generally is less than the $RH$, such that $R_d$ based on $T_{0.5}$ is underestimated (e.g., see Fig. 7 in Shackelford, 1994a). Thus, when the solute BTC is sigmoidal asymmetric, Eqs. 15 or 17 should not be used to determine $R_d$.

### 3.7 Hydraulic control

Stage 0 of a column test as illustrated in Fig. 1 represents a hydraulic conductivity test based on permeation with water (i.e., solvent), and Stages 1 through 3 represent a hydraulic conductivity test based on permeation with the chemical solution, commonly referred to as a hydraulic compatibility test (e.g., ASTM D7100-11, 2011). Thus, in addition to determining the transport properties of solutes with respect to the barrier material, the $k$ of the barrier material with respect to both water and the chemical solution can and should be measured during column testing (e.g., see Figs. 5 and 6 in Ishimori et al., 2020).

In principle, any set of hydraulic boundary conditions could be used for hydraulic control and measurement of $k$ during column testing. Typical hydraulic control conditions include constant head (CH) or constant gradient (CG), falling headwater (FH), falling headwater-rising tailwater (FH-RT), and constant flow (CF) (Daniel, 1994; ASTM D5084-10, 2010; ASTM D7100-11, 2011). Cao et al. (2019) argue that the CH (or CG) condition is preferred on the basis that this condition is the most appropriate relative to field applications. Redmond and Shackelford (1994) recommend the use of the CF condition on the basis that the CF condition will better maintain a constant $v_s$, which is a requirement for the use of Eqs. 1, 8, 9, and 11, even when there is significant incompatibility in the $k$ of the soil, i.e., $k_c/k_w >> 1$ or $\Delta k (= k_c - k_w) >> 0$, where $k_w$ is $k$ based on permeation with water from Stage 0, and $k_c$ is $k$ based on permeation with the chemical solution from Stages 1 through 3.

For example, based on Eq. 2, $v_s$ is given by $q/nA$ and by $ki/n$. For the CH (or CG) condition, $i$ is maintained constant (i.e., assuming $L$ is constant), whereas for CF condition, $q$ is maintained constant. Changes in porosity during permeation, $\Delta n$, are likely to be minimal, especially since the range in $n$ is narrow, i.e., $0 < n < 1$. Also, since $n$ appears in the denominator of both definitions of $v_s$, i.e., $ki/n$ and $q/nA$, any effect of $\Delta n \neq 0$ on $v_s$ during permeation with a chemical solution will be the same. Similarly, a change in $A$ during permeation with a chemical solution, i.e., $\Delta A \neq 0$, will affect the definition of $v_s$ based on $q/nA$, but again, $\Delta A$ generally is minimal (i.e., $\Delta A \approx 0$). Therefore, the magnitude of $\Delta v_s$ will be dictated largely by $\Delta k$ or $\Delta q$. Thus, if $i$ is maintained constant under the CH or CG condition, then $k_c/k_w >> 1$ (or $\Delta k >> 0$) results in $\Delta v_s >> 0$. In contrast, if $q$ is maintained constant in accordance with the CF condition, then $k_c/k_w >> 1$ (or $\Delta k >> 0$) will have virtually no effect on $v_s$, i.e., if $\Delta q = 0$, then $\Delta v_s = 0$ even if $k_c/k_w >> 1$ (or $\Delta k >> 0$), assuming $\Delta n$ and $\Delta A$ are negligible (e.g., Shackelford and Hong, 2020).
effect of incompatibility of $k$ on $v_s$ is an important consideration for column testing of engineered, low-permeability, clay-based chemical containment barriers, because such incompatibility is likely to increase with increasing content of clay, particularly high swelling clay (e.g., sodium bentonite), in the barrier and/or increase in the chemical strength (e.g., ionic strength, $I$) of the chemical solution (e.g., Shackelford, 1994b; Shackelford et al., 2000; Kolstad et al., 2004; Jo et al., 2005; Lee and Shackelford, 2004, 2005b; Shackelford and Sample-Lord, 2014).

For example, Lee and Shackelford (2005b) and Shackelford et al. (2010) report values of $k_c/k_w$ up to several orders of magnitude (i.e., $3 < \log (k_c/k_w) < 5$) for bentonite-based GCLs permeated with high ionic strength CaCl$_2$ solutions (i.e., $0 \leq I \leq 1.5$ M). Of course, such large increases in $k$ of the barrier may render consideration of solute transport unimportant. Nonetheless, the potential effect of incompatibility of $k$ on the ability to maintain a constant $v_s$ should be considered when choosing the most appropriate hydraulic control condition to impose for column testing of engineered, low-permeability, clay-based chemical containment barriers.

3.8 Type of column cell

The two general categories of cells, also commonly referred to as permeameters, that can be used for column testing are rigid-wall (fixed-wall) cells and flexible-wall cells (Daniel et al., 1984, 1985; Daniel, 1994; Shackelford, 1994b). The advantages and disadvantages of each type of cell for the purpose of measuring $k_w$ and $k_c$ are detailed in Daniel et al. (1985), Daniel (1994), Shackelford (1994), and Petrov et al. (1997).

The primary issue related to the use of rigid-wall cells when permeating fine-grained soils with chemical solutions is that incompatibility can lead to shrinkage of the soil, resulting in a gap between the inner side-wall of the cell and the outer boundary of the soil specimen, such that the permeant liquid passes around rather than through the soil. This effect, commonly referred to as “sidewall leakage,” can result in a significant increase in measured $k$, i.e., $k_c/k_w >> 1$, and solute that bypasses the soil in the column, commonly referred to as “short circuiting.” For this reason, the use of a flexible-wall cell, whereby the application of a confining or cell pressure maintains intimate contact between the flexible (polymer) membrane and the test specimen, has been recommended for column testing (e.g., Redmond and Shackelford, 1994; Shackelford and Redmond, 1995; Hong and Shackelford, 2017a; Cao et al., 2019). In addition, flexible-wall cells have the advantage of being able to ensure saturation of the test specimens via back-pressure saturation, e.g., see ASTM D5084-10 (2010) and ASTM D7100-11 (2011), and complete control of the stress conditions to which the test specimen is subjected.

Two potential issues that require consideration when flexible-wall cells are used are the potential incompatibility between the permeant liquid (chemical solution) and the flexible (polymer) membrane, and the potential for application of unrepresentative, high stresses during permeation. The flexible membrane incompatibility issue can occur when the permeant liquid contains aqueous miscible organic compounds or corrosive properties such as extreme pH (e.g., $\text{pH} \leq 2$) that can penetrate and/or deteriorate the integrity of the membrane (Daniel et al., 1984, 1985; Dunn and Mitchell, 1985). In this case, wrapping the membrane with Teflon tape has been recommended (Daniel et al., 1984).

In terms of stresses, the application of high hydraulic gradients to reduce the testing durations of clays with low $k$ also can result in unrealistically high, seepage induced effective stresses (e.g., Shackelford et al., 2000; Hong and Shackelford, 2017a). For this reason, careful consideration of the effect of either the applied or induced hydraulic gradient in the case of CH (CG) or CF hydraulic control, respectively, on the resulting effective stresses in the test specimen is required to ensure proper interpretation of the test results relative to the intended field application.

3.9 Effect of diffusion

In low-permeability clay barriers, diffusion is likely to be a significant if not dominant process of solute transport (e.g., Shackelford, 1988; Shackelford and Daniel, 1991a,b; Shackelford, 2014). In terms of column testing of these barriers, the ability to recognize when diffusion plays a significant role in solute transport is an important consideration.

As previously illustrated in Figs. 3 and 4, when diffusion becomes significant, the shape of the BTC is sigmoidal asymmetric, and the arrival time of the solute at the end of the column of soil will be delayed relative to that when advection dominates solute transport (e.g., BTC 3 in Fig. 4). However, diffusion only becomes significant or dominant at low $v_s$ (Shackelford, 1988, 1989, 2014). In this case, not only is the BTC sigmoidal asymmetric, but also the value of $t_{0.5}$ or $T_{0.5}$ occurs sooner than that predicted on the basis of advective-dominated solute transport (see Fig. 9), where $t_p$ and $T_p$ are given by Eqs. 16 and 17, respectively (also, compare $t$ at $C_r = 0.5C_d$ for BTC 3 versus $t_c$ in Fig. 4). In general, the difference between the time to breakthrough based on piston displacement or plug flow and $t_{0.5}$ or $T_{0.5}$ for the actual BTC, i.e., $\Delta t_{0.5}$ or $\Delta T_{0.5}$, increases with decrease in $v_s$ (Shackelford, 1988, 1989, 2014).

For example, consider the scenario shown conceptually in Fig. 10, where the pore network includes both mobile pores through which both liquid flow and solute transport occur, and dead-end pores that are immobile to liquid flow and solute transport through the soil. In this case, the soil commonly is referred to as a dual porosity medium, comprising a mobile porosity, $n_m$, defined as the sum of the mobile pore space relative to
the total volume, or \( n_m = \Sigma V_m/V \), and an immobile porosity, \( n_{im} \), defined as the sum of the immobile pore space relative to the total volume, or \( n_{im} = \Sigma V_{im}/V \), such that \( n = n_m + n_{im} \) (e.g., see McCarter et al., 2019). Also, for this situation, the effective porosity, \( n_e \), is the same as the mobile porosity, i.e., \( n_e = n_m \), although in the aforementioned study by Dominijanni et al. (2020), the mobile porosity is considered to be the water-effective porosity, \( n_m = n_{ew} \), i.e., the porosity related to water movement.

For example, for the column test results shown in Fig. 11, \( n_e/n = 0.8 \). The reason for this outcome is that the value of \( T \) used to plot the BTC is based on \( n \), not \( n_e \), because \( n_e \) was not known a priori. If \( n_e \) was known a priori, an effective dimensionless time, \( T_e = (n_e/n)T \), could be used in place of \( T \) in Fig. 11, in which case the breakthrough time for the tracer would occur at \( PVF = 1.0 \) (see Shackelford, 1993).

As previously noted, diffusion-dominated transport of a nonadsorbing, nonreactive tracer also results in early breakthrough of the solute (Fig. 9). Thus, when the solute BTC is sigmoidal asymmetric due to diffusion-dominated transport, distinguishing between the individual roles of diffusion and effective porosity in causing the early breakthrough of the solute from a single column test is not possible (e.g., Shackelford, 1995a). In this case, two column tests will be required, i.e., one column test conducted at an elevated flow rate such that advection dominates solute transport to determine \( n_e \) and another column test conducted at a more realistic (lower) flow rate to determine the separate effect of diffusion, i.e., after knowing the value for \( n_e \). However, proper consideration should be given to the effects of the different flow rates on the differences in the stress conditions between the two column specimens.

There are two other considerations inherent in the determination of \( n_e \) based on the analysis in Fig. 11. First, even though the tracer is nonadsorbing, mass transfer of the tracer from the mobile to the immobile (dead-end) pores results in some mass storage capacity for the tracer within these pores, i.e., \( \Sigma V_{im}C_{im} \), where \( C_{im} \) = the tracer concentration in the immobile pores (e.g., van Genuchten and Wirenga, 1976). Thus, even though the tracer is nonadsorbing, this mass storage results in a retardation effect for the tracer, such that the \( n_e \) based on the measured BTC likely will be underestimated, i.e., the actual \( n_e \) will be lower than that indicated in Fig. 11. The error in underestimation of \( n_e \) will be dependent on the...
stored tracer mass, i.e., the greater $\Sigma V_{im}C_{im}$, the greater the underestimation.

Second, the tracer BTC in Fig. 11 implies an instantaneous solute mass transfer rate between the mobile and immobile pores. When the mass transfer rate is slower, the BTC is more likely to be sigmoidal asymmetric. In this case, the shape of the resulting BTC can be used to discern the actual mechanisms involved in the asymmetry (e.g., see Figs. 2-5 in Coats and Smith, 1964). Of course, the effect of the mass transfer rate is relative to the flow rate through the mobile pores, i.e., instantaneous mass transfer is more likely to be prevalent the lower the flow rate, and vice versa (Shackelford, 1999; Shackelford and Jefferis, 2000).

For example, Jo et al. (2006) evaluated calcium (Ca$^{2+}$) transport through a GCL comprising granular bentonite, whereby the granules of bentonite were considered as aggregates or clods of multiple bentonite particles. In this case, the mobile pores were considered to be those existing between the aggregates or granules of bentonite particles, referred to as intergranular pores, and the dead-end or immobile pores included both the interparticle pores (i.e., pores between the particles comprising the granules) and the interlayer pores (i.e., pores between the aluminosilicate layers comprising individual clay particles). The rates of mass transfer between the mobile and immobile pores were considered to be governed by diffusion, and included mass transfer (rate) coefficients governing diffusion between the mobile intergranular and immobile interparticle pores, $\alpha_{gp}$ [T$^{-1}$], and the immobile interparticle and interlayer pores, $\alpha_{pl}$ [T$^{-1}$]. Their model also included sorption of Ca$^{2+}$ via cation exchange between both the interparticle liquid and solid surfaces of the particles, and between the interlayer liquids and solid surfaces of the aluminosilicate layers. They conducted six separate constant-source column tests with a $C_{0}$ of 20 mM CaCl$_2$ solution (i.e., 20 mM Ca$^{2+}$ and 40 mM Cl$^{-}$). Their results for Ca$^{2+}$ comparing the measured BTCs versus the theoretical BTC predicted on the basis of their multiple porosity model are shown in Fig. 12. Based on these results, Jo et al. (2006) concluded that the most important variables affecting the rate of cation exchange are advection in the intergranular pores, the interlayer mass transfer coefficient ($\alpha_{pl}$), and the number of sorption sites on the mineral surface.

One method to determine the existence of dual porosity a priori is to measure the soil-water characteristic curve (SWCC) of the soil under unsaturated conditions (Burger and Shackelford, 2001a,b). In this case, the existence of a bimodal SWCC is indicative of two networks of pores, viz., interconnected or mobile pores and nonconductive or immobile pores.

For example, Burger and Shackelford (2001b) measured the SWCC of mixtures of sand and granular diatomaceous earth (DE), with the particle sizes of the sand and DE being approximately the same. Based on microphotographs, the particles of DE were known to contain immobile or dead-end pores (Burger and Shackelford, 2001a). From analysis of the resulting measured SWCCs using bimodal SWCC functions, the distributions between the mobile or effective porosity and the immobile porosity could be discerned as a function of the DE content in the mixtures (e.g., see Fig. 13). Thus, measuring the SWCC of a given soil may provide evidence of an effective porosity, e.g., bimodal SWCC, and also an indication of the resulting magnitude of $n_e$.

![Fig. 12. Measured and predicted solute breakthrough curves for calcium migration through a GCL containing granular bentonite (modified after Jo et al., 2006).](image)

![Fig. 13. Distributions in mobile and immobile porosities in mixtures of sand and diatomaceous earth based on measured, bimodal soil water characteristic curves (modified after Burger and Shackelford, 2001b).](image)

3.10 Semipermeable membrane behavior

Soils that exhibit an ability to restrict solute migration are referred to as semipermeable membranes. In terms of engineered clay barriers, those barriers that contain bentonite, such as GCLs, compacted sand-bentonite mixtures, and SB cutoff walls, have the ability to behave as semipermeable membranes, with the magnitude of solute restriction generally increasing with increasing bentonite content (Shackelford, 2011, 2012, 2013; Shackelford and Scalia, 2016). The resulting
membrane behavior of these clay barriers is a function of several factors (Shackelford and Scalia, 2016, 2020), and can range from substantial for GCLs comprising virtually 100 % sodium bentonite to essentially nil for SB backfills with less than 10 % bentonite content (Malusis and Shackelford, 2002; Evans et al., 2008). Since solute restriction can enhance the performance of engineered, clay-based barriers with respect to chemical containment, semipermeable membrane behavior is a desirable characteristic for these chemical containment barriers. Therefore, determining the existence and magnitude of membrane behavior for engineered, clay-based barriers can be an important consideration for design and/or evaluating performance.

The key parameter of interest with respect to semipermeable membrane behavior is the membrane efficiency or reflection coefficient, \( \omega \), which typically ranges from zero for no solute restriction to unity for complete solute restriction \((0 \leq \omega \leq 1.0)\), although slightly negative values of \( \omega \) are also possible. Column tests that are conducted to measure \( \omega \) are commonly referred to as hyperfiltration or ultrafiltration tests (e.g., Fritz, 1986; Hart, 2013). In these tests, the source solution is forced through the soil under an applied hydraulic head, and if the soil behaves as a semipermeable membrane, the solute is filtered out such that only a fraction of the source concentration appears in the effluent (see Fig. 14). The filtered solute accumulates on the influent side of the specimen in a zone referred to as the concentration polarization layer (CPL). The value of \( \omega \) is defined as the ratio of the solute effluent concentration, \( C_e \), relative to the influent solute concentration at the interface between the influent and the soil specimen, \( C_{oi} \), i.e., \( \omega = C_e/C_{oi} \), where \( C_{oi} \) is greater than \( C_{e} \) due to the aforementioned solute filtration effect (Odour and Whitworth, 2005).

Fig. 14. Conceptual effect of hyperfiltration on the solute breakthrough curve (BTC) as a function of the membrane efficiency coefficient, \( \omega \) (modified after Shackelford, 2013).

The mechanism for solute restriction in clays is an effective porosity effect due to anion exclusion (Shackelford and Scalia, 2020). For example, Manassero and Dominijanni (2003) proposed the following correlation between \( \omega \) and the effective porosity:

\[
\omega = (1 - \frac{n_e}{n})
\]

(19)

Thus, as \( \omega \to 1 \), \( n_e \to 0 \). Note that, based on the aforementioned study by Dominijanni et al. (2020), \( n_e \) in Eq. 16 represents the effective porosity with respect to solute transport, \( n_{es} \), which can be less than the effective porosity due to water flow, \( n_{ew} \) in clays due to anion exclusion (membrane behavior), i.e., \( n_{es} \leq n_{ew} \leq n \). Although Eq. 19 is based on theoretical considerations, the results of several experimental studies suggest that Eq. 19 provides a reasonably representative estimate of effective porosity resulting from semipermeable membrane behavior (e.g., Dominijanni and Manassero, 2012; Dominijanni et al., 2013; Malusis et al., 2015; Malusis and Daniyarov, 2016; Musso et al., 2017).

3.11 Example results

The following results from Shackelford and Redmond (1995) help to illustrate the application of the fundamental considerations for traditional constant source column testing of engineered, clay-based barriers. The results pertain to two column tests that were conducted on compacted specimens of kaolin (~96% kaolinite) contained within flexible-wall cells and subjected to constant-flow conditions using a flow-pump system as described by Redmond and Shackelford (1994). The two column tests were performed at different, constant flow rates of 2.3 x 10^-4 m^3/d and 2.3 x 10^-6 m^3/d to evaluate the effect of flow rate on the resulting BTCs and solute transport parameters. Note that, even though one flow rate is lower than the other, both flow rates likely would be considered as “low” from an absolute perspective. After back-pressure saturation, the specimens initially were permeated with deaired, distilled water (DDW) for approximately two weeks (13.7 and 14.1 d) to flush soluble salts initially in the pore water of the specimens (i.e., \( C_i > 0 \)), followed by permeation with a 10 mM NaCl solution for approximately 37 d for the test with the higher flow rate and 109 d for the test at the lower flow rate. The \( k \) with respect to DDW \( (k_{oi}) \) and the NaCl solution \( (k_{e}) \) for both specimens were \( < 1.0 \times 10^{-9} \) m/s, indicating compliance with the typical regulated maximum hydraulic conductivity for engineered CCLs, and \( k_e/k_{oi} \) for both specimens was \( < 1.0 \), indicating no chemical incompatibility due primarily to the low \( I \) of the salt solution and the relatively low activity \( (A) \) of 0.28 for the kaolin. The measured BTCs for both Cl^- and Na^+ were fitted using Eq. 11, and the results are shown in Fig. 15. Note that some of the Cl^- concentrations for the measured BTCs are not shown in Fig. 15, because Shackelford and Redmond (1995) did not include measured Cl^- concentrations that were considered to be inconsistent in their fitting analyses.

The results for both tests shown in Fig. 15 are consistent in that: (1) all of the BTCs are sigmoidal.
asymmetric, suggesting that diffusion was a significant if not dominant transport process at the low imposed flow rates; (2) chloride (Cl\textsuperscript{-}) broke through earlier than sodium (Na\textsuperscript{+}), which is consistent with greater retardation for Na\textsuperscript{+} relative to Cl\textsuperscript{-}; and (3) the fitted values of $R_d$ for Cl\textsuperscript{-} and Na\textsuperscript{+} are higher than the values based on $T_{0.5}$, which is consistent with the sigmoidal asymmetric BTCs and the significant role of diffusion on the solute transport. The dominance of diffusion also was supported by the fitted values of $D_h$ for both Cl\textsuperscript{-} and Na\textsuperscript{+} (i.e., based on the fitted values of $P_L$ and known values of $L$ and $v_s$ in accordance with Eq. 12), which ranged from $2.84 \times 10^{-10} \text{ m}^2/\text{s}$ to $8.75 \times 10^{-10} \text{ m}^2/\text{s}$. Since this range in $D_h$ is within the range of $D^*$ reported in the literature for both Cl\textsuperscript{-} and Na\textsuperscript{+}, Shackelford and Redmond (1995) concluded that $D_h \approx D^*$ and $D_m \approx 0$.

One apparent inconsistency in the results shown in Fig. 15 is that Cl\textsuperscript{-} did not behave as a nonadsorbing tracer, since the fitted $R_d$ for Cl\textsuperscript{-} for both tests were $> 1$, and considerably greater for the lower flow rate test (i.e., $R_d = 9.53$), indicating that Cl\textsuperscript{-} was adsorbed during transport. However, Shackelford and Redmond (1995) noted that the surface charge for kaolinite is pH-dependent that results in anion exchange at low pH and cation exchange at high pH. Based on the measured effluent pH, which decreased upon permeation with the NaCl solution due to Na\textsuperscript{+}-for-H\textsuperscript{+} exchange, and the results of separate batch equilibrium adsorption tests that indicated linear adsorption of both Cl\textsuperscript{-} and Na\textsuperscript{+} over the range of concentrations of interest with $5.4 \leq \text{pH} \leq 5.9$, Shackelford and Redmond (1995) concluded that simultaneous anion and cation sorption were possible during the column tests. As noted subsequently by Mazzieri et al. (2015), values of $R_d > 1$ for Cl\textsuperscript{-} also could be attributed, in part, to a dilution effect that was not taken into account by Shackelford and Redmond (1995). Nonetheless, when conducting column tests using porous media with a pH-dependent surface charge, such as kaolin and residual soils with significant kaolinite and/or metal oxide content, anionic chemical species such as Cl\textsuperscript{-} may not behave as nonadsorbing tracers such that $R_d > 1.0$.

There also are some differences between the results of the two tests based on the two different imposed flow rates. First, the number of PVF for the test with the slower flow rate ($\sim$2) is significantly lower than that for the test with higher flow rate ($\sim$7), despite a test duration for the former that was almost 3X longer than that for the latter. Second, the extent of breakthrough for both Cl\textsuperscript{-} and Na\textsuperscript{+} is clearly less for the slower flow rate test. Third, the values of $R_d$ based on fitting for both Cl\textsuperscript{-} and Na\textsuperscript{+} are significantly greater for the slower flow rate test. Finally, the difference in $R_d$ based on fitting with Eq. 11 versus $R_d$ based on $T_{0.5}$ is clearly greater in the case of the slower flow rate test, simply because diffusion was more prominent in that test.

![Fig. 15. Measured and fitted solute breakthrough curves for compacted specimens of kaolin at two different flow rates: (a) higher flow rate test (2.3 x 10$^{-5}$ m$^3$/d); (b) lower flow rate test (2.3 x 10$^{-6}$ m$^3$/d) (data from Shackelford and Redmond, 1995).](image-url)

4 CUMULATIVE MASS COLUMN TESTING

4.1 Procedure and BTCs

Shackelford (1994a) proposed an alternative column testing method that is based on the cumulative mass of a solute in the effluent rather than the effluent solute concentration. The procedure for conducting cumulative mass column tests is the same as that depicted in Fig. 1, except all of the effluent is continuously collected for chemical analysis versus collecting only isolated, discrete samples of effluent for chemical analysis as previously illustrated in Fig. 7.

The concept of collecting all the effluent is illustrated schematically in Fig. 16. In this case, the sampling intervals, $\Delta t$, and the corresponding incremental volumes of effluent, $\Delta V_e = q \Delta t$, are adjacent and continuous, such that the $\Sigma \Delta V_e$ represents all of the collected effluent. The resulting increment of solute mass contained within each $\Delta V_e$, or $\Delta m$, is the product of the measured average solute concentration, $C_{\text{avg}}$, and $\Delta V_e$, or $\Delta m = C_{\text{avg}} \Delta V_e = C_{\text{avg}} q \Delta t$, and the cumulative solute mass is equal to the sum of all the incremental solute masses, or $\Sigma m = \Sigma C_{\text{avg}} \Delta V_e = C_{\text{avg}} q \Delta t$, up to the cumulative time...
corresponding to the respective sample, i.e., \( t = \Sigma \Delta t \).

\[
C(L, t) = C_e \text{ Measured (average) concentrations}
\]

Fig. 16. Concept of the cumulative mass basis for conducting column tests whereby all of the effluent is continuously collected and sampled for chemical analysis.

As illustrated schematically in Fig. 17a, the resulting values of \( \Sigma \Delta m \) plotted versus the cumulative elapsed time, or \( t = \Sigma \Delta t \), represent the cumulative mass BTC, and Stages 1, 2, and 3, and \( t_i \) and \( t_{ss} \) represent the same as those depicted with respect to Fig. 2 for the concentration-based BTC, i.e., Stage 1 represents the period of the test before time, \( t_i \), corresponding to when the solute initially appears in the effluent, Stage 2 represents the transient period from \( t_i \) to the time corresponding to the onset of steady-state transport, \( t_{ss} \), during which the solute concentration in the effluent increases nonlinearly from zero to the source concentration, i.e., \( 0 \leq C_e \leq C_o \), and Stage 3 represents the period after \( t_{ss} \), during which steady-state solute transport through the column has been established such that \( C_e = C_o \). Note that the slope of the cumulative mass BTC after \( t_{ss} \) is linear because the solute mass flux exiting the soil column is constant, given that \( q \) and \( C_o \) are constants, i.e., \( dm/dt = qC_o = \text{constant} \).

### 4.2 Analytical transport model

Similar to the case of the concentration-based approach to column testing, where there are a number of analytical solute transport models based on Eq. 4 and different boundary conditions that can be used to fit the measured BTC data, there also are a number of analytical solute transport models to Eq. 4 that can be used to describe the results of cumulative mass BTCs as a function of \( R_d \), \( P_L \), and \( T \) for the same boundary conditions and the case where \( \lambda = \Gamma = 0 \) (Shackelford, 1995b). However, the most appropriate analytical transport model corresponding to the same boundary conditions upon which Eq. 11 is based is given as follows (Shackelford, 1995a,b):

\[
CMR = \frac{R_d}{2P_L} \left[ (\beta_4 - \beta_2) \text{erfc}(\beta_1) + (\beta_4 + \beta_2) \exp(\beta_2) \text{erfc}(\beta_1) \right]
\]  

(20)

where \( CMR = \) the dimensionless cumulative mass ratio, \( \beta_1, \beta_2, \) and \( \beta_3 \) are the same arguments as defined by Eq. 12, and \( \beta_4 \) is the dimensionless argument defined as follows:

\[
\beta_4 = \frac{TP_L}{R_d}
\]  

(21)

The CMR in Eq. 20 represents the cumulative solute mass in the effluent relative to the mass of the same solute in the pore water of the soil after steady-state transport, \( m_o \), or:

\[
CMR = \frac{\Sigma \Delta m}{m_o} = \frac{\Sigma \Delta m}{V_t C_o}
\]  

(22)

Based on Eq. 20, when the cumulative mass BTC is presented in the form of \( CMR \) versus \( T \) as shown in Fig. 17b, the slope of the BTC corresponding to steady-state transport is unity, and the value of \( T \) corresponding to the \( x- \) or \( T- \) axis intercept of the line representing steady-state transport, i.e., \( T_o \), represents \( R_d \). Alternatively, the dimensionless form of the cumulative mass BTC can be plotted as \( T-CMR \) versus \( T \) as illustrated in Fig. 17c, in which case the initial slope of the BTC corresponding to Stage 1 is unity, and the \( y- \) or \( T-CMR \)-axis intercept corresponding to steady-state transport, i.e., \( (T-CMR)_o \),
Zn\textsuperscript{2+} represents $R_d$.

Similar to the case where measured $RC$-versus-$T$ data are fitted using Eq. 11 to determine $R_d$ and $P_L$ as illustrated in Fig. 15, measured $CMR$-versus-$T$ data can be fitted using Eq. 20 to determine $R_d$ and $P_L$ (e.g., see Shackelford, 1995a; Hong and Shackelford, 2017b; 2019; Shackelford and Hong, 2020). Alternatively, $R_d$ can be determined directly from the measured data based on $R_d = T_o$ (Fig. 17b) or $R_d = (T - CMR)_o$ (Fig. 17c). However, as noted by Shackelford and Hong (2020), determining $R_d$ based on $(T - CMR)_o$ tends to be more accurate than doing so based on $T_o$, primarily because the establishment of steady-state transport is more readily apparent when the measured data are presented in the form of the BTC illustrated in Fig. 17c versus that illustrated in Fig. 17b.

### 4.3 Example results

The following results from Hong and Shackelford (2017a,b) and Shackelford and Hong (2020) help to illustrate the application of the fundamental considerations for cumulative mass column testing of clay-based barriers. The results pertain to a cumulative mass column test conducted on a sand-bentonite backfill that was consistent with those used for SB vertical cutoff walls. The backfill was prepared by first mixing sand with 4% (dry mass) sodium bentonite, and the resulting dry sand-bentonite mixture was further mixed with a 5% bentonite slurry (i.e., 5 g of bentonite suspended in 95 g of water) to achieve a slump of 125 mm in accordance with standard practice for SB backfills. The resulting, slumped backfill contained a total of 4.8% (dry mass) bentonite. A specimen of the slumped backfill then was placed in a flexible-wall cell (see Malusis et al., 2009; Hong et al., 2012), back-pressure saturated, and consolidated to an initial effective stress of 34.5 kPa prior to permeation. The specimen then was permeated at a constant flow rate of 8.00 mL/d using a flow-pump system as described by Hong and Shackelford (2017a).

The specimen was permeated first with deionized water (DIW) to flush soluble salts from the pore water, and then with a 20 mM ZnCl\textsubscript{2} solution (i.e., 20 mM Zn\textsuperscript{2+} and 40 mM Cl\textsuperscript{-}) to evaluate the transport of Cl\textsuperscript{-} and Zn\textsuperscript{2+}. Permeation with DIW lasted 85 d and resulted in a steady-state $k$ ($k_o$) of 3.8 x 10\textsuperscript{-10} m/s, whereas permeation with the 20 mM ZnCl\textsubscript{2} solution lasted 415 d and resulted in a steady-state $k$ ($k_r$) of 3.5 x 10\textsuperscript{-10} m/s. Thus, the specimen was compatible with the salt solution (i.e., $k_r/k_o = 0.92$). The resulting cumulative mass BTCs are shown in Fig. 18.

The cumulative mass BTC in the form of $CMR$ versus $T$ is shown in Fig. 18a. The measured data for both Cl\textsuperscript{-} and Zn\textsuperscript{2+} were fitted using Eq. 20, and the results of the fitting are shown in Fig. 18a. The fitted $R_d$ for Cl\textsuperscript{-} was 1.00, indicating that Cl\textsuperscript{-} was a nonadsorbing tracer and that there was no effective porosity effect (Hong and Shackelford, 2017b). In contrast, Zn\textsuperscript{2+} exhibited significant retardation ($R_d = 6.88$), which was attributed by Hong and Shackelford (2017b) to the cation exchange capacity of the bentonite component of the backfill. The values of $D_o$ for Cl\textsuperscript{-} and Zn\textsuperscript{2+} based on the fitted $P_L$ values shown in Fig. 18a were 5.00 x 10\textsuperscript{-10} m\textsuperscript{2}/s and 4.22 x 10\textsuperscript{-10} m\textsuperscript{2}/s, respectively (Hong and Shackelford, 2017b).

Since these $D_o$ values were within a typical range of $D^*$ values for these chemical species, i.e., $1.0 \times 10^{-10}$ m\textsuperscript{2}/s $\leq D^* \leq 1.0 \times 10^{-9}$ m\textsuperscript{2}/s based on Shackelford and Daniel (1991), Hong and Shackelford (2017b) concluded that diffusion dominated the transport of both Cl\textsuperscript{-} and Zn\textsuperscript{2+}, which is consistent with the low flow rate imposed in the test and the resulting long test duration (1.14 yr).

![Fig. 18. Cumulative mass column testing data for a sand-bentonite backfill: (a) nonlinear fitting analysis of measured $CMR$-versus-$T$ data; (b) $R_d = T_o$ analysis based on $CMR$-versus-$T$ data; (c) $R_d = (T - CMR)_o$ analysis based on $T$ - $CMR$-versus-$T$ data [$CMR$ = dimensionless cumulative mass ratio; $T$ = dimensionless cumulative time] (modified from Hong and Shackelford, 2017b, and Shackelford and Hong, 2020).](image)

The alternative forms of the cumulative mass BTCs for the same test data are shown in Figs. 18b,c (see Hong and Shackelford, 2020). The dashed lines in Fig. 18b represent linear regressions corresponding to the best estimate of the steady-state portion of the measured $CMR$-versus-$T$ data, and the resulting analysis for $R_d$ of Cl\textsuperscript{-} and Zn\textsuperscript{2+} based on $T_o$ yielded slightly higher $R_d$ values for Cl\textsuperscript{-} and Zn\textsuperscript{2+} relative to those based on the fitting analysis shown in Fig. 18a. In contrast, the analysis for $(T - CMR)_o$ from the measured $T$ - $CMR$-versus-$T$ data in Fig. 18c provided exactly the same $R_d$ for Cl\textsuperscript{-} as that based on fitting, i.e., $R_d = 1.00$, and an $R_d$ for Zn\textsuperscript{2+} of 6.91, which is only 0.44% higher than the $R_d$ of 6.88.
based on fitting. Thus, the values of \( R_d \) based on \((T - CMR)_{ss}\) were slightly more accurate than those based on \( T_o \), although both methods provided reasonably accurate \( R_d \) values.

One final observation with respect to the CMR-versus-\( T \) data shown in Fig. 18a is that there is essentially no scatter in the measured data, i.e., \( r^2 = 1.00 \), which is in stark contrast to the typical measured data for concentration-based BTCs (e.g., see Fig. 15). The reason for this difference is that integration under the concentration-based BTC to determine the cumulative solute mass essentially dampens out the scatter that typically is more prevalent with the concentration-based BTC (Shackelford, 1995a).

### 4.4 Advantages of cumulative mass approach

Shackelford (1995a) noted several advantages of the cumulative mass approach to column testing relative to the more traditional, concentration-based approach. First, the need to collect discrete, small effluent samples in the traditional approach to better approximate instantaneous effluent concentrations, \( C_o \), is eliminated from consideration. Instead, because the cumulative mass approach is based on solute mass, which is a more fundamental parameter than solute concentration, the sample period, \( \Delta t \), does not have to be short and the sampled effluent volume, \( \Delta V_o \), does not have to be small.

In fact, Shackelford (1995a) showed that relatively large volumes of effluent could be collected without affecting the results based on fitting of the measured data using Eq. 20. As a result, the number of effluent samples required can be significantly reduced using the cumulative mass approach relative to the traditional concentration-based approach, thereby reducing not only the frequency of sampling but also the required chemical analysis of collected samples. However, for the cumulative mass approach, all effluent must be collected. If discrete, small samples are collected in accordance with the traditional concentration-based approach, then the data should not be analyzed based on the cumulative mass approach, as doing so likely would result in significant error in the results.

Second, the desired concentration to be measured in the cumulative mass approach is the average concentration, \( C_{e,avg} \), because the accumulated solute mass in the effluent sample, \( \Delta V_o \), will be based on the average solute concentration over that time interval of sampling. Thus, the need to determine instantaneous effluent concentrations is removed from consideration.

However, since the results will depend on the accuracy of the measured \( C_{e,avg} \), the effluent sample should be well mixed (e.g., shaken) prior to recovering aliquots for chemical analysis. Also, if desired for accuracy, statistical information on the measured \( C_{e,avg} \) can be ascertained by collecting a sufficient number of aliquots for chemical analysis to establish the mean and standard deviation of each measured \( C_{e,avg} \).

Third, the value of \( R_d \) determined using the cumulative mass approach is the correct, mass-based value corresponding to the relative holdup (Eq. 18), regardless of the imposed flow rate. Thus, determining \( R_d \) in accordance with the cumulative mass approach always results in the correct value of \( R_d \), independent of the flow rate.

Fourth, the cumulative mass approach explicitly distinguishes between early breakthrough due to diffusion versus that due to an effective porosity effect. In the case where an effective porosity is present and diffusion is dominant, an \( R_d \) for the nonadsorbing tracer (e.g., Cl) that is less than unity truly represents the effective porosity ratio (i.e., \( R_d = n_e/n \)), independent of the effect of diffusion (e.g., see Shackelford, 1995a, for an example analysis illustrating this concept).

Fifth, as previously noted and as illustrated by Shackelford and Hong (2020), relatively accurate values of \( R_d \) can be determined directly from the measured cumulative mass data based on \( T_o \) and \((T - CMR)_{ss} \) (Figs. 17b,c), such that nonlinear fitting with Eq. 20 is not required. However, to determine accurate values of \( R_d \) using these approaches, steady-state transport must be clearly established in the test. In the case of cumulative mass column tests conducted with low-permeability, clay-based barriers, establishing steady-state transport can require lengthy test durations. If the test is terminated prior to establishing steady-state transport, the value of \( R_d \) based on \( T_o \) and \((T - CMR)_{ss} \) likely will be conservative, i.e., underestimated (see Shackelford and Hong, 2020).

### 5 SUMMARY AND CONCLUSIONS

The procedure for conducting a column test based on maintaining a constant solute source concentration was described. In brief, this method involves first establishing steady-state flow of solvent (e.g., water), then continuously introducing as the influent a chemical solution with one or more solutes of interest at constant-source concentrations, \( C_o \), and simultaneously monitoring the effluent to determine the effluent concentrations, \( C_e \), of the same solutes. The resulting values of \( C_e \), which range from zero to \( C_o \) (i.e., \( 0 \leq C_e \leq C_o \)) when the initial solute concentration within the column of soil, \( C_i \), is zero (\( C_i = 0 \)) or from \( C_i \) to \( C_o \) (i.e., \( C_i \leq C_e \leq C_o \)) when \( C_i > 0 \), plotted versus the elapsed time, \( t \), represent the measured breakthrough curve (BTC) for the given solute.

The shape of the resulting BTC can provide an indication of the physical, chemical, and/or biological processes governing the fate and transport of the solute(s) through the soil column. In particular, the shape of BTCs generally can be categorized as either sigmoidal symmetric about the effluent concentration \( C_e = 0.5C_o \) when \( C_i = 0 \) or \( C_e = 0.5(C_o + C_i) \) when \( C_i > 0 \), or sigmoidal asymmetric. Sigmoidal symmetric BTCs occur only in the limiting case when advection dominates solute transport and adsorption is linear,
instantaneous, and reversible. In contrast, sigmoidal asymmetric BTCs typically reflect diffusion-dominated transport even when adsorption is linear, instantaneous, and reversible, although sigmoidal asymmetric BTCs also may reflect nonlinear, equilibrium adsorption or nonequilibrium (kinetic) adsorption. Advective-dominated solute transport and, therefore, sigmoidal symmetric BTCs are unlikely in low-permeability, clay-based barriers used for chemical containment.

For traditional, concentration-based column testing, the theoretical BTC represents a continuous distribution of an infinite number of instantaneous concentrations. In contrast, the measured effluent concentrations represent average effluent concentrations, \( C_{e,\text{avg}} \), corresponding to a finite increment in solute mass, \( \Delta m \), relative to a finite volume of effluent, \( \Delta V_e \), collected over a finite period of time, \( \Delta t \), i.e., \( C_{e,\text{avg}} = \Delta m/\Delta V_e = \Delta m/\Delta q \Delta t \). To accurately approximate instantaneous concentrations, \( \Delta V_e \) needs to be as small as possible, but also sufficiently large to provide enough liquid for chemical analysis. In addition, a sufficient number of effluent samples must be collected at discrete intervals in time to provide a sufficient number of \( C_{e,\text{avg}} \) that is required to define the shape of the BTC. Finally, for convenience, the measured \( C_{e,\text{avg}} \) are plotted at the elapsed time, \( t \), corresponding to the middle of the sampling interval, \( t_m \), even though this approach represents an approximation.

The BTC commonly is plotted in terms of a dimensionless, relative concentration, \( RC = (C_e - C_i)/(C_o - C_i) \) and dimensionless time, \( T \), or pore volumes of flow, \( PVF \). However, the use of \( T \) or \( PVF \) in lieu of \( t \) implicitly assumes that the flow rate, \( q \), and seepage velocity, \( v_s \), are constant. Also, fitting of the measured solute BTC with an analytical solute transport model such as given by Eq. 11 to determine the transport properties, viz. \( D_h \) via \( P_t \) and \( R_d \), also requires that \( v_s \) is constant. However, hydraulic incompatibility between the chemical solution being used as the permeant liquid and the clay-based barrier being evaluated in a column test can lead to significant increase in the hydraulic conductivity based on permeation with the chemical solution, \( k_e \), relative to that based on permeation with water, \( k_w \), i.e., \( \log(k_e/k_w) > 1 \). Thus, since \( v_s = k_i/n \), if the constant hydraulic gradient (head) condition is used for hydraulic control, significant changes in \( k \) will correlate with significant changes in \( v_s \). In contrast, the use of a constant-flow condition (i.e., constant \( q \)) will maintain a relatively constant \( v_s \) even if/when significant changes in \( k \) are experienced. Therefore, use of the constant-flow condition is recommended when conducting column tests with engineered, clay-based barriers.

Incompatibility between the permeant liquid and the clay-based barrier also can result in shrinkage of the clay, which can lead to side-wall leakage and short circuiting of solute if rigid-wall cells (permeameters) are used in the column test. In contrast, use of flexible-wall cells can prevent side-wall leakage and solute short circuiting, and also provide for back-pressure saturation of the column specimen prior to testing as well as complete control of the state of stress. For these reasons, flexible-wall cells are recommended for use when conducting column tests with engineered, clay-based barrier materials.

For concentration-based column testing, \( T_{0.5} = R_d \) is valid only under advective-dominated transport when the solute BTC is sigmoidal symmetric. If the BTC is sigmoidal asymmetric, accurate estimates of \( R_d \) can be determined only by fitting the measured BTC versus an appropriate solute transport model (e.g., Eq. 11). In this case, the value of \( R_d \) based on fitting is likely to be greater than that based on \( T_{0.5} = R_d \).

Breakthrough for a nonadsorbing, nonreactive tracer under an advective-dominated transport condition should occur at one\( PVF \), i.e., \( T_{0.5} = 1.0 \), if all pores are conductive. However, if some pores are immobile, such as dead-end pores, then breakthrough will occur at less than one\( PVF \) such that the resulting value of \( T_{0.5} \) represents the effective porosity ratio, i.e., \( T_{0.5} = n_e/n < 1.0 \). Since diffusion-dominated transport also results in early breakthrough of a nonadsorbing tracer, consideration should be given to the relative roles of diffusion and effective porosity when interpreting the results of column tests conducted with low-permeability, clay-based barriers.

Semipermeable membrane behavior, which results from solutes being restricted through some pores (anion exclusion), is known to exist in clay-based barriers, especially those with an appreciable amount of bentonite. The existence of semipermeable membrane behavior also represents an effective porosity effect. However, when column tests are conducted on clay-based barriers that exhibit membrane behavior, the effect is to reduce the steady-state \( C_e \) to a value less than \( C_o \), with the steady-state value of \( C_e \) decreasing with increasing membrane efficiency, \( \omega \), such that, in the limit as \( \omega \to 1.0 \), \( C_e \to 0 \).

The cumulative mass approach to column testing differs from the more traditional, concentration-based approach in that the cumulative mass approach requires that all effluent is collected incrementally and sequentially and monitored for solute concentrations, which are converted into solute mass. This approach offers several advantages relative to the more traditional, concentration-based approach, including less frequent sampling and chemical analysis, the ability to distinguish explicitly between early breakthrough due to effective porosity versus diffusion, and the ability to provide the correct, mass-based value for \( R_d \) independent of the imposed flow rate. Also, the value of \( R_d \) can be determined simply by linear regression of the steady-state portion of the cumulative mass BTC. However, the values of \( R_d \) so determined will be accurate only if steady-state transport has been established, which can require excessively long test durations when low-
permeability, clay-based barriers are being tested at reasonably representative (i.e., low) flow rates.

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