Limiting Membrane and Diffusion Behavior of a Geosynthetic Clay Liner

By

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Abstract: Bentonite based geosynthetic clay liners (GCLs) are commonly used as chemical containment barriers to minimize liquid flow and contaminant transport. The preference for GCLs relative to other materials for chemical containment include economy of use and superior engineering properties, including low hydraulic conductivity (k) and the ability to exhibit semipermeable membrane behavior that restricts the migration of solutes through the bentonite. In the case of low k (e.g., $\leq 10^{-10}$ m/s), diffusion is likely to be a significant, if not dominant, mechanism of chemical transport. The objective of this study was to evaluate the membrane and diffusion behavior of a GCL in the limit as the salt (KCl) concentration increased to the extent that any observed membrane behavior was destroyed. The results indicated that the observed membrane behavior for the GCL was essentially destroyed when the average KCl concentration across the GCL specimen, C_{ave} , reached 200 mM KCl, which was greater than the value of C_{ave} that would have been predicted on the basis of previous results. The results also indicated that the value of the effective diffusion coefficient, D^* , for Cl^- at this limiting value for C_{ave} of 200 mM KCl was greater than the value of D^* that would have been predicted on the basis of the use of lower values of C_{ave} . However, the differences between the measured and predicted values of D^* were relatively minor ($\leq 11.3\%$), such that the differences likely would be insignificant for most practical applications.

KEY WORDS: Diffusion; Geosynthetic clay liner; Membrane efficiency; Semipermeable; Tortuosity

1. Introduction

Bentonite based geosynthetic clay liners (GCLs) have been used extensively as hydraulic and chemical barriers for a wide variety of containment applications, including liners and covers for solid municipal and hazardous waste landfills, surface impoundments (e.g., lakes and ponds, aeration lagoons, fly ash lagoons, mine tailings impoundments, etc.), canals, storage tanks, and secondary containment of above-grade fuel storage tanks (e.g., Bouazza, 2002; Rowe, 2006, 2007, 2014). The preference for GCLs relative to other materials for such containment applications stems primarily from an economy of use and the possibility of a low hydraulic conductivity, k (e.g., $\leq 10^{-10}$ m/s), although the potential for incompatibility between the bentonite comprising the GCL and the chemicals to be contained can result in significant increases in k , i.e., $\Delta k \gg 0$ (e.g., Shackelford et al., 2000; Jo et al., 2001; Kolstad et al., 2004; Jo et al., 2005; Lee and Shackelford, 2005a,b; Lee et al., 2005; Shackelford et al., 2010; Liu et al., 2013, 2014, 2015; Ishimori and Katsumi, 2012; Rosin-Paumier and Touze-Foltz, 2012; Mazzieri et al., 2013; Bouazza and Gates, 2014; Makusa et al., 2014). In cases where significant increases in k are deemed likely, consideration has been given to the potential use of chemically modified bentonites in GCLs for the primary purpose of mitigating any such incompatibility in order to maintain a low k (e.g., Onikata et al., 1999; Katsumi et al., 2008; Di Emdio, 2010; Mazzieri et al., 2010; Bohnhoff, 2012; Scalia, 2012; Bohnhoff et al., 2013; Bohnhoff and Shackelford, 2014; Di Emdio et al., 2015; Mazzieri and Di Emdio, 2015). However, even when GCLs are able to maintain a low k upon exposure to chemical solutions, diffusion is likely to be a significant, if not dominant, mechanism of chemical transport through the GCLs due to the low k and the relative thinness of GCLs

(typically ≤ 15 mm) (e.g., Shackelford 2013). As a result, a significant number of studies have focused on the transport, in general, and diffusion, in particular, of chemicals through GCLs both individually and as components of composite barriers (e.g., Lake and Rowe, 2000; Malusis and Shackelford, 2002b; El-Zein et al. , 2012; Mendez et al., 2013; Shackelford, 2013; Xie et al., 2013; Hosney and Rowe, 2014; Chen et al., 2015).

In addition to economy of use and the potential for low k , GCLs have been shown to exhibit semipermeable membrane behavior, which refers to the ability of clays to restrict the migration of dissolved chemical species or solutes (e.g., Malusis and Shackelford, 2002a; Kang and Shackelford, 2011; Malusis et al., 2015; Malusis and Daniyarov, 2016). Solute restriction is a function of the sizes of the clay pores, with smaller pore sizes resulting in greater solute restriction. In bentonites, solute restriction is attributed to electrostatic repulsion of the solutes due to interaction of the electric fields associated with the diffuse double layers (DDLs) of adjacent clay particles in close proximity (Fritz, 1986). Because the sizes of the pores in clays vary, the extent of solute restriction in clays that behave as membranes also varies, such that some pores restrict solute migration while others do not. However, the mass flux resulting from solute migration through clay membranes is reduced relative to that in the absence of solute restriction. As a result, the chemical containment function of a GCL can be enhanced by the existence of membrane behavior (Malusis et al., 2003; Shackelford et al., 2003; Kang and Shackelford, 2010; Shackelford, 2013; Malusis and Daniyarov, 2016).

The ability of GCLs to restrict solute migration also is known to decrease as the salt concentration within the pore water of the bentonite contained within the GCL increases (Malusis and Shackelford, 2002a; Shackelford et al., 2003; Kang and

Shackelford, 2010; Shackelford, 2011, 2013; Malusis and Daniyarov). This trend of decreasing solute restriction with increasing solute concentration occurs because, as the concentration of the solutes in the pore water increases, the thicknesses of the DDLs and associated electric fields controlling solute restriction decrease, resulting in progressively larger pores and correspondingly lesser solute restriction (Fritz, 1986). In this regard, knowledge of the solute concentration at which solute restriction (i.e., membrane behavior) ceases to exist, commonly referred to as the threshold concentration (Shackelford et al., 2003), is important from the viewpoint of knowing whether or not the beneficial aspects of membrane behavior will be prevalent.

Unfortunately, very few experimental studies have been conducted using solute concentrations that were sufficiently high so as to result in complete destruction of membrane behavior, such that the threshold concentrations typically have been determined by extrapolation. However, such extrapolations are suspect, as the trend in solute restriction (membrane behavior) versus logarithm of the average solute concentration has been shown to become non-linear in the limit as the solute concentration approaches the threshold concentration (e.g., Kemper and Rollins, 1966; Dominijanni et al., 2013).

For example, Kemper and Rollins (1966) measured osmotic (membrane) efficiency coefficients, designated as σ , for specimens of a sodium bentonite at several different volumetric water contents, θ (0.80, 0.84, 0.91), exposed to several different salts (NaCl, CaCl₂, Na₂SO₄, CaSO₄) over a range of average salt concentrations, C_{ave} , across the specimens. In general, values of σ range from zero for no solute restriction (no membrane behavior) to unity for complete or 100 % solute restriction corresponding

to ideal membrane behavior. Kemper and Rollins (1966) established that σ decreased as C_{ave} increased for any given salt and value of θ . More importantly, they performed their tests using a wide range of salt concentrations (e.g., $0.0006 \text{ N} \leq C_{ave} \leq 0.2 \text{ N}$), which allowed them to measure values of σ that were either very close to or at zero. However, their study did not include any results pertaining to diffusion of the salts through the bentonite.

Shackelford and Lee (2003) measured the membrane and diffusion behaviors of a specimen of a GCL bounded by a 5 mM calcium chloride (CaCl_2) solution on one side and de-ionized water (DIW) on the other side. They observed an initial development of a chemico-osmotic pressure difference, ΔP , which is directly proportional to the membrane efficiency coefficient, of 19.3 kPa, suggesting the existence of significant membrane behavior in the GCL. However, the magnitude of ΔP subsequently decreased to zero as the test progressed. The decrease in ΔP was attributed to reduction in the solute restriction resulting from continual diffusion of Ca^{2+} into the pores of the bentonite, which led to the progressive collapse of the DDLs surrounding the bentonite particles and a concomitant increase in the sizes of the pores. They concluded that the eventual destruction of the initially observed membrane behavior correlated well with the time required to achieve steady-state diffusion of Ca^{2+} . However, their test involved only one concentration (5 mM) and one salt (CaCl_2).

Meier et al. (2014) evaluated the persistence of membrane behavior for a GCL specimen by exposing the specimen to increasingly higher concentrations of potassium chloride (KCl) until any observed membrane behavior was essentially destroyed. They found that the membrane behavior of the GCL specimen persisted until the specimen

was exposed to a KCl concentration of 400 mM (i.e., $C_{ave} = 200$ mM KCl), which was well beyond the salt concentrations used in any previous study evaluating the membrane behavior of GCLs. They concluded that the results of their study represented the first evaluation of the persistence of membrane behavior of a GCL exposed to simple monovalent salt solutions. However, their study did not include an evaluation of the diffusion of the KCl.

The purpose of this paper is to extend the results previously reported by Meier et al. (2014) by including the diffusion behavior of the same GCL with respect to the same boundary concentrations of KCl. The results reported in this paper are believed to provide the first experimental evidence pertaining to quantifying the limiting membrane and diffusion behavior of a GCL.

2. Materials and Methods

2.1 Materials

The GCL evaluated in this study was Bentomat[®] (Colloid Environmental Technologies Company (CETCO), Hoffman Estates, Illinois, USA). The mineralogy, cation exchange capacity (CEC), and index properties of the bentonite in the GCL were reported by Malusis and Shackelford (2002a) and are summarized in Table 1. The mineralogy includes 71 % smectite (montmorillonite), 15 % quartz, 7 % mixed layer illite/smectite minerals, and 7 % other minerals. The measured CEC was 47.7 meq/100 g, with 53 % of the exchange complex comprised of exchangeable sodium. The liquid limit (*LL*) and plastic limit (*PL*) measured in accordance with ASTM D4318, were 478 % and 39 %, respectively. Based on the Unified Soil Classification System (USCS, ASTM

D2487), the bentonite classified as a high plasticity clay (CH). Further details on the chemical and physical properties of the bentonite in the GCL can be found in Malusis and Shackelford (2002a) and Meier et al. (2014).

The liquids used in this study included DIW and solutions of KCl (certified A.C.S.; Fisher Scientific, Fair Lawn, NJ) with target (desired) KCl concentrations, designated as C_{ot} , of 20, 35, 50, 100, 200, and 400 mM. The measured values of the electrical conductivity (EC) and pH for the DIW were approximately zero (≤ 0.2 mS/m) and 7.0, respectively, whereas the measured values of EC and pH for each of the KCl solutions are summarized in Table 2. The actual, measured concentrations of KCl for each of the KCl solutions also are summarized in Table 2. As noted in Table 2, the measured concentrations of KCl were higher than the target concentrations of KCl. Only the measured concentrations were used in any relevant calculations.

2.2 Testing Apparatus and Procedures

The testing apparatus and procedures used in this study were similar to those described in detail by Malusis et al. (2001), Shackelford and Lee (2003), and Bohnhoff and Shackelford (2013). A 90-mm-diameter specimen of the GCL with a dry thickness of 8 mm and a porosity, n , of 0.79, was placed within a rigid-wall cell (see Fig. 1). After assembling the cell, the specimen was permeated with DIW to measure the k prior to membrane testing. The use of DIW as the permeant liquid typically results in the lowest value of k , which is unconservative for containment applications (e.g., Daniel, 1994; Shackelford, 1994). However, most, if not all, previous studies evaluating the membrane behavior of GCL specimens have involved the use of DIW as a permeant liquid for the

purpose of flushing soluble salts from the pore water of the bentonite in the GCL specimens (Shackelford, 2013). Thus, the use of DIW as the permeant liquid in this study was deemed necessary so as to provide a consistent basis for comparison of the results of this study with those of previous studies. The measured *EC* of the effluent during permeation decreased from 229 mS/m to 30 mS/m, indicating the removal of soluble salts from the pores of the specimen, and the final measured value of *k* for the GCL specimen at the end of permeation was 9.0×10^{-12} m/s. Further details of the specimen preparation procedure are provided by Meier et al. (2014).

After permeation, the specimen was isolated (via valves) in a closed system that allowed circulation of liquids across the top and bottom of the specimen at the same rate, such that no volume change within the system could occur (see Fig. 1). Then, DIW was circulated through porous disks along both the top and bottom of the specimen (i.e., $C_{ot} = C_{ob} = 0$, where C_{ob} is the concentration of the bottom inflow) for a period of about 25 d to establish baseline conditions. Following this initial period of circulation with DIW, the liquid in the top circulation loop was changed from DIW to a KCl solution (i.e., $C_{ot} > 0$), while circulation of DIW ($C_{ob} = 0$) continued along the base of the specimen to establish a concentration difference, $\Delta C_o (= C_{ob} - C_{ot} < 0)$, across the specimen. Since the system was closed during the liquid circulation stage, chemico-osmotic liquid flow from the bottom to the top of the specimen (i.e., from low concentration to high concentration) was prevented. As a result, a chemico-osmotic pressure built up on the high concentration side (i.e., top) of the specimen to counteract the tendency for chemico-osmotic liquid flow (e.g., see Malusis et al., 2001; Shackelford, 2013).

The difference in pressure across the specimen, ΔP , was measured using a differential pressure transducer (Model PX26, Omega Engineering Inc., Stamford, CT), as illustrated in Fig. 1. The value of ΔP measured during initial circulation of DIW at both boundaries, ΔP_{DIW} , provided the baseline value of ΔP for subsequent test stages. The ratio of the effective pressure difference, ΔP_e , defined as the difference between the steady-state value of ΔP based on circulation of a KCl solution across the top of the specimen, ΔP_{ss} , and ΔP_{DIW} (i.e., $\Delta P_e = \Delta P_{ss} - \Delta P_{DIW}$), relative to the maximum chemico-osmotic pressure difference, $\Delta \pi$, based on the difference in boundary salt concentrations equates to the magnitude of the membrane efficiency coefficient, ω ($= \Delta P_e / \Delta \pi$) (Groenevelt and Elrick, 1976; Malusis et al., 2001). Note that ω is the same as σ reported in the study by Kemper and Rollins (1966). However, ω is preferred in the engineering literature because σ is more commonly used to represent stress (e.g., Malusis and Shackelford, 2002a). Thus, values of ω vary from zero for no solute restriction (i.e., no membrane behavior) to unity for complete solute restriction (i.e., ideal membrane behavior), with most natural clays exhibiting values of ω less than unity ($0 \leq \omega < 1$) because of the variation in pore sizes (i.e., non-ideal membrane behavior).

2.3 Measurement of Diffusion Coefficients

For specimens that do not behave as ideal membranes (i.e., $\omega < 1$), solutes diffuse from the top to the bottom of the specimen (i.e., from high to low concentration), because some of the pores within the specimen are not restrictive (see Fig. 1). If the concentration boundaries are maintained reasonably constant, then solute diffusion

through a specimen eventually will reach a steady-state diffusive mass flux. This diffusive mass flux then can be used to determine diffusion coefficients for the solutes. This approach for measuring diffusion coefficients traditionally has been referred to as the steady-state, time-lag, or through-diffusion method (e.g., Shackelford, 1991; Malusis et al., 2001).

In the present study, diffusion of Cl^- and K^+ into the specimen from the top boundary resulted in concentrations of Cl^- and K^+ in the circulation outflow from the top of the specimen, C_t , that were lower than those in the circulation inflow at the top of the specimen, i.e., $C_t < C_{ot}$ (see Fig. 1). The Cl^- and K^+ that entered the top of the specimen eventually diffused all the way through the specimen, such that the concentrations of Cl^- and K^+ in the circulation outflow from the base of the specimen, C_b , eventually became greater than those in the circulation inflow to the specimen base, i.e., $C_b > C_{ob}$ (see Fig. 1). The resulting values of C_b were measured as a function of time, using inductively coupled plasma-atomic emission spectrometry or ICP-AES (IRIS[®] Advantage/1000 ICAP Spectrometer, Thermo Jarrel Ash Co., Franklin, MA) for K^+ and ion chromatography or IC (Dionex[®] 4000i IC Module, Dionex Co., Sunnyvale, CA) for Cl^- . The measured values of C_b then were converted to the area normalized cumulative mass (Q_t) for each solute, as follows (e.g., Malusis et al., 2001; Malusis and Shackelford, 2002b; Shackelford and Lee, 2003; Bohnhoff and Shackelford, 2015):

$$Q_t = \frac{1}{A} \sum_{i=1}^{N_s} \Delta m_i = \frac{1}{A} \sum_{i=1}^{N_s} C_{b,i} \Delta V_i \quad (1)$$

where A is the cross-sectional area of the specimen, Δm_i is the incremental mass of the

solute species collected over a time increment, Δt , $C_{b,i}$ is the mass concentration of the solute species in the incremental volume, ΔV_i , of the circulation outflow from the base of the pedestal corresponding to the Δt , i is an index designating the incremental sample, and N_s is the total number of incremental samples corresponding to the total elapsed time, t . An important constraint in the use of Eq. 1 is that all solute mass must be included, such that sampling must be continuous, although the magnitude of ΔV_i can vary.

The resulting values of Q_t were plotted versus the cumulative elapsed time, t . Such plots generally are nonlinear during the initial, transient stage of the test, and then become linear corresponding to a steady-state stage representing constant diffusive solute mass flux (Shackelford, 1991; Malusis et al., 2001; Shackelford and Lee, 2003; Shackelford and Moore, 2013). Thus, linear regression of the steady-state portion of the Q_t -versus- t data for each solute can be used to determine the values of the effective diffusion coefficient, D^* , based on the following expression (Shackelford, 1991; Malusis et al., 2001; Bohnhoff and Shackelford, 2015):

$$D^* = -\left(\frac{\Delta Q_t}{\Delta t}\right)\left(\frac{L}{nw_A\Delta C}\right) \quad (2)$$

where $\Delta Q_t/\Delta t$ represents the slope of the linear regression of the Q_t -versus- t data, L is the specimen thickness, n is the specimen porosity, w_A is the atomic weight of the diffusing solute (i.e., 35.453 g/mol for Cl^- and 39.0983 g/mol for K^+), and ΔC is the molar concentration difference of the solute across the specimen. In applying Eq. 2, a

sequential linear regression was conducted on the measured Q_t -versus- t data to establish the number of measured data representing the steady-state diffusive mass flux as described by Shackelford and Lee (2003).

The parameter D^* determined using Eq. 2 for each solute species (i.e., Cl^- or K^+) is defined as follows (Shackelford and Daniel, 1991; Malusis et al., 2012; Shackelford and Moore 2013):

$$D^* = D_o \tau_a = D_o \tau_m \tau_r = D_p \tau_r \quad (3)$$

where D_o is the aqueous-phase or free-solution diffusion coefficient of the solute, τ_a is an apparent tortuosity factor ($0 \leq \tau_a \leq 1$) representing the product of the actual matrix (geometric) tortuosity factor, τ_m , and a restrictive tortuosity factor, τ_r , and $D_p (= D_o \tau_m)$ is known as the "pore diffusion coefficient" (e.g., see Shackelford and Moore, 2013). The restrictive tortuosity factor takes into account all factors other than the matrix tortuosity related to the interconnectivity of the pores, such as anion exclusion, increased water viscosity near the surface of clay particles, etc. (Shackelford and Daniel, 1991; Malusis and Shackelford, 2002b; Shackelford and Moore, 2013).

The test conducted in this study was a multiple-stage membrane/diffusion test as described by Bohnhoff and Shackelford (2015). In this test, KCl solutions with increasingly higher (target) source concentrations, C_{ot} , of 20, 35, 50, 100, 200, and 400 mM were circulated sequentially across the top boundary of the specimen, while simultaneously circulating DIW across the bottom boundary of the specimen (i.e., $C_{ob} = 0$). With each increase in C_{ot} , a greater diffusive solute mass flux occurred as a result of

the greater concentration gradient imposed across the specimen (i.e., $\Delta C/L$), such that the slope of Q_t versus t increased with increasing C_{ot} . Thus, net values of Q_t and t , or Q_t' and t' , respectively, pertaining to each individual stage (i.e., each value of C_{ot}) were used to evaluate D^* for each solute. The use of Q_t' and t' for each stage of the test essentially amounts to resetting Q_t and t to zero for the evaluation of D^* for each subsequent stage of the test. As previously described, the membrane efficiency coefficient, ω , also was measured simultaneously, as reported by Meier et al. (2014).

3. Results

3.1 Membrane Behavior

The measured data required for determination of the values of ω for the GCL evaluated in this study are provided in Meier et al. (2014), and the measured values of ω are summarized in Table 3. However, unlike Meier et al. (2014), two different values of ω are distinguished in Table 3, i.e., values of ω designated as ω_o that were calculated using the source concentrations (i.e., C_{ot} and C_{ob}), and values of ω designated as ω_{ave} that were calculated using the averages of the top and bottom boundary concentrations defined as follows (Malusis et al., 2001; Malusis and Shackelford, 2002a; Shackelford, 2013; Malusis and Daniyarov, 2016):

$$C_{t,ave} = \frac{C_{ot} + C_t}{2} \quad ; \quad C_{b,ave} = \frac{C_{ob} + C_b}{2} = \frac{C_b}{2} \Big|_{C_{ob}=0} \quad (4)$$

As explained by Malusis and Shackelford (2002a), values of ω_o are typically lower

relative to values of ω_{ave} , because the $\Delta\pi$ based on the average boundary concentrations, $\Delta\pi_{ave}$, is typically lower than $\Delta\pi$ based on the source concentrations, $\Delta\pi_o$ (e.g., see Table 3). Thus, although ω_{ave} is likely more accurate, ω_o is typically more conservative.

As indicated in Table 3, the values of ω_o and ω_{ave} decrease with increasing values of C_{ot} , which is consistent with the results of previous studies (e.g., Malusis and Shackelford, 2002a; Kang and Shackelford, 2009, 2011; Bohnhoff and Shackelford, 2013; Malusis and Daniyarov, 2016). This behavior has been explained in terms of classical DDL theory, whereby an increase in C_{ot} results in an increase in the salt concentration in the pore water of the bentonite which, in turn, results in compression of the DDLs surrounding the individual clay particles, an increase in the sizes of the pores, and a decrease in solute restriction (Fritz, 1986). More significantly, the low value for $-\Delta P_e$ of 0.17 kPa corresponding to the stage of the testing involving the KCl solution with a C_{ot} of 400 mM equates to values of ω_o and ω_{ave} that are zero to three decimal places. Thus, the C_{ot} value of 400 mM KCl can be considered to represent the threshold concentration, or the concentration representing the transition from the existence of membrane behavior (i.e., $\omega > 0$) to no membrane behavior (i.e., $\omega = 0$) (e.g., Shackelford et al., 2003).

The results of this study (Table 3) are compared in Fig. 2 with those from the literature for other GCL specimens exposed to KCl solutions. Note that the results in Fig. 2 also include tests conducted using flexible-wall cells. Several observations are readily apparent from the data shown in Fig. 2. First, the test conducted in this study included KCl concentrations that were significantly greater than those used in previous

studies involving GCL specimens, such that the GCL specimen evaluated in this study was the only GCL specimen that has been tested until the observed membrane behavior was completely destroyed. Second, the relationship between ω_o or ω_{ave} and the logarithm of the average source KCl concentration, $C_{o,ave}$ ($= C_{ot}/2$), is non-linear over the range of KCl concentrations evaluated in this study. This result is supported by the aforementioned experimental results shown by Kemper and Rollins (1966), and by theoretical considerations proposed by Dominijanni et al. (2013). A similar, non-linear trend is evident in some of the results based on the use of flexible-wall cells, but this behavior has been attributed to slight volume changes that occur in the specimens during the sampling period between the membrane testing stages (Kang and Shackelford, 2009), i.e., as opposed to specimens tested in rigid-wall cells that do not undergo volume change. Third, the resulting threshold value of $C_{o,ave}$ for the GCL evaluated in this study of approximately 200 mM KCl (i.e., $C_{ot} = 400$ mM KCl) was greater than the threshold values of $C_{o,ave}$ that would have been obtained from an extrapolation of the semi-log linearly trends in the data from the literature for the other GCL specimens. Based primarily on this third observation, Meier et al. (2014) concluded that the membrane behavior in the GCL was more persistent than would have been predicted on the basis of the previous results.

3.2 Diffusion Results

The measured values of C_b that were used to determine D^* for Cl^- and K^+ via Eq. 1, as well as the other major soluble and bound cations initially associated with the bentonite of the GCL (Table 1), are shown for each stage of the test (i.e., each C_{ot}) in

373 Fig. 3. As indicated in Fig. 3, Cl^- was the dominant ionic species throughout the test, as
 374 expected on the basis that Cl^- was being introduced continuously into the system via the
 375 source KCl solution and, as a conservative, nonreactive (nonadsorbing) chemical
 376 species, Cl^- diffused through the GCL relatively rapidly. In contrast, diffusion of the K^+
 377 through the GCL specimen initially was slowed or retarded relative to that of Cl^- ,
 378 primarily due to the initially high concentrations of Na^+ in the pore water of the bentonite
 379 (Table 1), which initially dominated the requirement for electroneutrality (i.e., $\Sigma \text{anionic}$
 380 $\text{charge} = \Sigma \text{cationic charge}$), and the preferential sorption of K^+ relative to Na^+ via cation
 381 exchange (e.g., van Olphen, 1963; Huertas et al., 2001; Sparks, 2003). As the amount
 382 of K^+ in the pore water of the bentonite in the GCL specimen increased via diffusion
 383 from the top boundary, the K^+ displaced a progressively greater amount of bound Na^+
 384 via cation exchange, such that the Na^+ concentration in the circulation outflow from the
 385 bottom of the specimen diminished to a negligible value towards the end of the second
 386 stage of the test (i.e., $C_{ot} = 35 \text{ mM KCl}$). This decrease in Na^+ concentration was
 387 matched by a concomitant increase in the K^+ concentration to satisfy electroneutrality,
 388 such that the values of C_b for K^+ approached the values of C_b for Cl^- towards the end of
 389 the first stage ($C_{ot} = 20 \text{ mM KCl}$), and thereafter remained close to, but slightly lower
 390 than, the values of C_b for Cl^- . The slight differences between the concentrations of Cl^-
 391 and K^+ can be attributed to the progressively greater amounts of Ca^{2+} and Mg^{2+}
 392 appearing in the bottom circulation outflow, presumably due to an increasing extent of
 393 exchange of K^+ for bound Ca^{2+} and Mg^{2+} with increasing source concentration of K^+
 394 (i.e., due to a mass action effect). Overall, the temporal trends in the measured values
 395 of C_b for each of the major ionic species noted in Fig. 3 are consistent with the

knowledge of the concentrations of soluble and bound metals initially within the bentonite (Table 1), the increasing amounts of Cl^- and K^+ diffusing into the GCL specimen from the top boundary, the requirement for electroneutrality in solution, and the preferential sorption of K^+ .

The temporal values of Q_t for Cl^- and K^+ for the entire test are shown in Fig. 4. As indicated in Fig. 4, the slopes in the data of Q_t versus elapsed time, t , or $\Delta Q_t / \Delta t$, increase with each stage of the test. This trend is expected on the basis that $\Delta Q_t / \Delta t$ represents the diffusive mass flux which, based on Fick's first law, is proportional to the concentration gradient across the specimen, i.e., $-\Delta C / L$ (> 0), where L is the length or thickness of the specimen (e.g., see Eq. 2). Thus, as C_{ot} increases, $-\Delta C$ increases resulting in an increase in $\Delta Q_t / \Delta t$.

As previously noted, for a multiple stage membrane/diffusion test such as conducted in this study, the values of D^* are based on the net values of Q_t and t , or Q_t' and t' , for each stage of the test, as shown in Fig. 5. The slopes of these trends in Q_t' versus t' are used together with the respective concentration differences, ΔC , in Eq. 2 to calculate the effective diffusion coefficients, D^* for both Cl^- and K^+ for each stage of the test. However, as noted by Shackelford (2013), there are two possible values of ΔC that can be used to calculate D^* , viz., the value of ΔC based on the source concentrations, i.e., $\Delta C_o = C_{ob} - C_{ot}$ (< 0), and the value of ΔC based on the average boundary concentrations defined in accordance with Eq. 4, i.e., $\Delta C_{ave} = C_{b,ave} - C_{t,ave}$ (< 0). Thus, two different values of D^* were calculated for each solute (Cl^- and K^+), one based on ΔC_o that is designated as D^*_{o} , and one based on ΔC_{ave} that is designated as D^*_{ave} . The resulting values of D^*_{o} and D^*_{ave} for both Cl^- and K^+ are shown in Fig. 6 as a function of

the measured value of C_{ot} . Several observations are evident by the data shown in Fig. 6.

First, all of the D^* values in Fig. 6 increase with increasing C_{ot} . The same trend has been noted in previous studies (e.g., Malusis and Shackelford, 2002b), and has been attributed to increasing size and number of pores that are available for diffusion with increasing C_{ot} due to progressively greater compression of the DDLs. However, the increase in the D^* values over the range of measured C_{ot} (i.e., $21.1 \leq C_{ot} \leq 408$ mM KCl) is minimal, with values for both D_o^* and D_{ave}^* increasing by factors of only 1.6 and 2.0 for Cl^- and K^+ , respectively.

Second, the values of D_{ave}^* for Cl^- and K^+ are greater than the respective values of D_o^* for Cl^- and K^+ . This difference is a direct result of the use of Eq. 2 to calculate D^* , in that lower values of ΔC result in higher values of D^* , all other factors being equal, and the values of ΔC_{ave} were lower than the values of ΔC_o (see Table 3). In that the average concentrations across the top and bottom boundaries of the specimen are considered to be more accurate than the source concentrations, the values of D_{ave}^* are likely more accurate than are the values of D_o^* . Thus, similar to the case of ω , the use of ΔC_o results in lower calculated values of D^* . However, unlike the situation with ω , where lower values are more conservative from the viewpoint of assessing the performance of GCLs for chemical containment, lower values of D^* are less conservative. This result suggests that D_{ave}^* values should be used to provide accurate estimates of the diffusive mass flux.

Third, for a given C_{ot} , the D^* values for Cl^- (i.e., D_o^* or D_{ave}^*) are greater than the respective D^* values for K^+ . This trend also has been noted previously by Bohnhoff and

Shackelford (2015), and can be attributed to the likelihood that steady-state diffusive mass flux for K^+ had not been achieved during each stage of the test due to the continual exchange of K^+ initially for Na^+ and subsequently for Ca^{2+} and Mg^{2+} . Bohnhoff and Shackelford (2015) also note that, for the case where Cl^- and K^+ are the only diffusing ions, the diffusive molar fluxes (moles/ m^2 -d) of both Cl^- and K^+ must be equal at true steady state due to the requirement for charge balance (electroneutrality), i.e., since both of these ionic species are monovalent. In this case, the diffusive mass flux (mg/ m^2 -d) for K^+ at steady state must be a factor of 1.10 greater than that for Cl^- at steady state, since the atomic weight for K^+ is 1.10 times greater than that for Cl^- (i.e., $39.0983/35.453 \approx 1.10$). Observation of the data shown in Figs. 4 and 5 indicate that the diffusive mass flux for Cl^- in this study actually was greater than that for K^+ in each stage of the test. Thus, despite the apparent linear trends in diffusive mass flux for K^+ shown in Fig. 5 (i.e., $r^2 = 0.999$), the K^+ likely had not achieved true steady-state conditions, resulting in the D^* values for K^+ (i.e., D_o^* or D_{ave}^*) being lower than the respective D^* values for Cl^- .

4. Discussion

4.1 Limiting Membrane and Diffusion Behavior

The values of D_o^* and D_{ave}^* for Cl^- are summarized in Table 4 and shown in Fig. 7 as a function of the values of ω_o and ω_{ave} (Table 3), respectively. As noted in previous studies (e.g., Malusis and Shackelford, 2002b; Bohnhoff and Shackelford, 2015), the general trend of increasing D^* with decreasing ω is evident in the results shown in Fig. 7. However, unlike previous studies, the limiting behavior wherein the value of D^*

approaches the pore diffusion coefficient, D_p (Eq. 3), as the value of ω approaches zero (i.e., $D^* \rightarrow D_p$ as $\omega \rightarrow 0$) is directly evident in Fig. 7, because the GCL evaluated in this study was tested until the membrane behavior was essentially destroyed. The aforementioned previous studies relied on linear extrapolation of the observed trends in ω versus D^* to determine D_p , because the KCl concentrations used in those studies were not sufficiently high so as to provide directly the limiting value of D^* . In the current study, the resulting limiting values of D_o^* and D_{ave}^* , or $D_{p,o}$ and $D_{p,ave}$, were $1.42 \times 10^{-10} \text{ m}^2/\text{s}$ and $1.83 \times 10^{-10} \text{ m}^2/\text{s}$, respectively, as shown in Fig. 7a. The value of $D_{p,ave}$ is greater than that of $D_{p,o}$ because, as previously noted, D_{ave}^* is greater than D_o^* . The value for $D_{p,ave}$ of $1.83 \times 10^{-10} \text{ m}^2/\text{s}$ likely represents the more accurate limiting diffusion coefficient.

For the current study, the error associated with extrapolating the trend in D^* versus ω is illustrated in Fig. 7b, where linear extrapolations in the trends result in extrapolated values for $D_{p,o}$ and $D_{p,ave}$ of $1.26 \times 10^{-10} \text{ m}^2/\text{s}$ and $1.72 \times 10^{-10} \text{ m}^2/\text{s}$, respectively. These extrapolated values for $D_{p,o}$ and $D_{p,ave}$ underestimated the measured (true) values for $D_{p,o}$ and $D_{p,ave}$ by 11.3 % and 6.0 %, respectively. Thus, although the extrapolated values for $D_{p,o}$ and $D_{p,ave}$ were unconservative (low) relative to the measured values for $D_{p,o}$ and $D_{p,ave}$, the differences likely would be insignificant for most practical applications.

4.2 Tortuosity Factors

In accordance with Eq. 3, values of the apparent tortuosity factor, τ_a , can be calculated as the ratio of the measured D^* values for the nonreactive tracer, which is Cl^-

in the current study, to the aqueous or free-solution diffusion coefficient, D_o (i.e., $\tau_a = D^*/D_o$). Although a common practice is to use the value of D_o corresponding to the self-diffusion coefficient for Cl^- at infinite dilution (i.e., $2.03 \times 10^{-9} \text{ m}^2/\text{s}$), this value assumes that Cl^- is diffusing in the absence of any constraints by any co-diffusing ions, such as K^+ , Na^+ , Ca^{2+} , and Mg^{2+} (Shackelford and Daniel, 1991). In most realistic situations, including the current study, the ideal scenario of infinite dilution is not valid, such that consideration of electroneutrality is required. In this case, a more representative value for D_o is the value for the salt, KCl, of $1.993 \times 10^{-9} \text{ m}^2/\text{s}$, which takes into account the drag on the diffusion of Cl^- in aqueous solution resulting from the slower diffusing K^+ (Shackelford and Daniel, 1991). Thus, values of τ_a in this study were calculated as the measured values for D^* , i.e., D_o^* and D_{ave}^* , divided by the D_o value for KCl of $1.993 \times 10^{-9} \text{ m}^2/\text{s}$. The resulting values of $\tau_{a,o}$ and $\tau_{a,ave}$ are summarized in Table 4.

As shown in Table 4, the values of $\tau_{a,o}$ and $\tau_{a,ave}$ increase from 0.045 to 0.071 and from 0.056 to 0.092, respectively, as C_{ot} (target) increases from 20 to 400 mM KCl. This trend is directly related to the previously noted trends in the measured D^* values for Cl^- with increasing C_{ot} (see Fig. 6). Also, the values of $\tau_{a,ave}$ likely are more accurate than the values of $\tau_{a,o}$ because, as previously noted, the values of D_{ave}^* are likely more accurate than the values of D_o^* .

In accordance with Eq. 3, the apparent tortuosity factor, τ_a , is the product of the matrix tortuosity factor, τ_m , and the restrictive tortuosity factor, τ_r (i.e., $\tau_a = \tau_m \tau_r$). The matrix, or geometric, tortuosity factor takes into account the interconnectivity of the network of pores within the porous medium, without regard to any additional factors affecting solute diffusion, and can be determined as the ratio of the limiting value of D^*

at $\omega = 0$ (i.e., D_p) to D_o (i.e., $\tau_m = D_p/D_o$). The resulting values of $\tau_{m,o}$ and $\tau_{m,ave}$ corresponding to the measured values for $D_{p,o}$ and $D_{p,ave}$, of $1.42 \times 10^{-10} \text{ m}^2/\text{s}$ and $1.83 \times 10^{-10} \text{ m}^2/\text{s}$, respectively, are 0.071 and 0.092, respectively. Unlike τ_a , τ_m is considered to be unique for a given porous medium, i.e., provided there is no volume change for the specimen, such that τ_m should be independent of C_{ot} and, therefore, ω . For the same reason as previously noted, the $\tau_{m,ave}$ value of 0.092 likely provides a more accurate estimate of the true matrix tortuosity for the GCL specimen evaluated in this study.

The restrictive tortuosity factor, τ_r , takes into account factors other than the interconnectivity of the network of pores that can affect solute diffusion, such as solute restriction resulting from membrane behavior. Values of τ_r can be determined as the ratio of τ_a to τ_m or the ratio of D^* to D_p (i.e., $\tau_r = \tau_a/\tau_m = D^*/D_p$). The resulting values of τ_r for this study based on the source and average boundary concentrations, or $\tau_{r,o}$ and $\tau_{r,ave}$, respectively, are summarized in Table 4.

As shown in Table 4, the values of $\tau_{r,o}$ and $\tau_{r,ave}$ increased from 0.63 to 1.00 and from 0.61 to 1.00, respectively, as target values of C_{ot} increased from 20 to 400 mM KCl. Although the values of $\tau_{r,ave}$ generally are lower than those of $\tau_{r,o}$, the differences between $\tau_{r,o}$ and $\tau_{r,ave}$ are relatively minor. Manassero and Dominijanni (2003) and Malusis et al. (2012) have shown that τ_r equates to an effective porosity ratio defined as the ratio of the effective porosity, n_e , to the total porosity (i.e., $\tau_r = n_e/n$). Thus, another interpretation of the values of τ_r shown in Table 4 is that the percentage of the total porosity of the GCL specimen that was effective in allowing diffusion of Cl^- was reduced to as low as approximately 60 % due to the existence of membrane behavior in the

GCL.

Finally, Manassero and Dominijanni (2003) also proposed the correlation, $\tau_r = 1 - \omega$, as a method to estimate the effect of membrane behavior on solute diffusion based on the results of measurements of ω . Further, justification for this proposed correlation has been provided by Dominijanni and Manassero (2012a,b) and Dominijanni et al. (2013). Accordingly, the measured values of $\tau_{r,0}$ and $\tau_{r,ave}$ from this study shown in Table 4 are compared with this linear correlation between τ_r and $1 - \omega$ in Fig. 8. As shown, the linear correlation tends to overestimate the measured values for τ_r over the range of ω values measured in this study. Thus, the linear correlation between τ_r and $1 - \omega$ would result in conservative (high) estimates of D^* , all other factors being the same.

However, another possible explanation for the overestimation in the measured τ_r values based on the correlation $\tau_r = 1 - \omega$ as shown in Fig. 8 is that changes in τ_a at the higher KCl concentrations used in this study may have been due to changes in τ_m instead of changes in τ_r . For example, based on the results of a previous study by Malusis and Shackelford (2002a) involving the measurement of ω for a GCL using solutions with KCl concentrations ranging from 3.9 to 47 mM (see Fig. 2), Malusis and Shackelford (2002b) concluded that membrane behavior would be negligible at source (C_{ot}) KCl concentrations greater than the estimated threshold concentration of 100 mM, such that the value of τ_r would be unity (i.e., $\tau_r = 1$) for values of C_{ot} greater than 100 mM KCl. Malusis and Shackelford (2002b) further noted that the results of the study by Lake and Rowe (2000) involving the measurement of values of D^* for NaCl diffusing through a GCL based on NaCl source concentrations ranging from 80 to 2000 mM increased with increasing NaCl concentration, even though membrane behavior for the

GCL was not observed. Thus, Malusis and Shackelford (2002b) concluded that the measured increases in the values of D^* for NaCl reported by Lake and Rowe (2000) must have been due to increases in τ_m resulting from further compression of the electrostatic diffuse double layers surrounding individual bentonite particles with increasing NaCl concentrations, which would have changed the micro-fabric of the interconnected pores (also see Shackelford 2013).

If the aforementioned observations made by Malusis and Shackelford (2002b) are applied to the current study, then the observed increases in τ_a with increasing C_{ot} of KCl used in this study (Table 4), especially those associated with the higher values of C_{ot} , can be attributed to increases in τ_m instead of increases in τ_r , such that the correlation $\tau_r = 1 - \omega$ would only be applicable to the values of τ_a corresponding to the lower values of C_{ot} . However, the conditions for the study by Malusis and Shackelford (2002a,b), although similar, were not exactly the same as those for the current study, and the threshold C_{ot} of 100 mM KCl reported by Malusis and Shackelford (2002a,b) was based on a liner extrapolation in the ω -versus- C_{ot} data (e.g., see Shackelford 2013), which likely underestimates the true threshold concentration as previously noted. Nonetheless, the results of this study suggest that the typical assumption of a constant τ_m for GCLs that behave as semipermeable membranes may not be valid over the range of C_{ot} values associated with the limiting membrane behavior.

5. Conclusions

The objective of this study was to evaluate simultaneously the membrane and diffusion behaviors of a GCL in the limit as the salt (KCl) concentration increased to the

extent that any observed membrane behavior was destroyed. The results indicated the membrane behavior of the GCL specimen persisted until the specimen was exposed to a KCl concentration of 400 mM, which is well beyond the salt concentrations used in any previous study evaluating the membrane behavior of GCLs. In addition, the results clearly showed that the relationship between the membrane efficiency coefficient (ω) and the logarithm of the average salt concentration across the specimen ($\log C_{ave}$) becomes nonlinear with increasing salt concentration, a trend that previously had been observed on the basis of limited experimental data. Thus, the results of this study represent the first evaluation of the limit in the membrane behavior of a GCL exposed to simple monovalent salt solutions.

The behavior of the GCL with respect to diffusion of Cl^- and K^+ also was measured simultaneously. The results indicated that the effective diffusion coefficients, D^* , for both Cl^- and K^+ increased by factors of 1.6 and 2.0 for Cl^- and K^+ , respectively, as the measured source KCl concentration, C_{ot} , increased from 21.1 to 408 mM KCl, which is consistent with a decrease in ω with increasing C_{ave} and C_{ot} . Also, the limiting values of D^* for Cl^- (i.e., the values of D^* corresponding to $\omega = 0$) determined by the typical approach based on extrapolating the trend in ω versus D^* were found to be lower (unconservative) relative to the measured or true limiting values. However, the differences between the extrapolated and measured values of D^* for Cl^- were relatively minor ($\leq 11.3\%$), such that the differences likely would be insignificant for most practical applications. Finally, the percentage of the total porosity of the GCL specimen that was effective in allowing diffusion of Cl^- was reduced to as low as approximately 60 % due to the existence of membrane behavior in the GCL.

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820

821 **Tables**

822 Table 1. Measured properties of the bentonite contained in the GCL evaluated in this study.

Property	Standard	Value
Liquid Limit, <i>LL</i> (%)	ASTM D4318	478
Plasticity Index, <i>PI</i> (%)	ASTM D4318	439
Specific Gravity, <i>G_s</i>	ASTM D854	2.68
Principal Minerals (%):	a	
Montmorillonite		71
Mixed-Layer Illite/Smectite		7
Quartz		15
Other		7
Cation Exchange Capacity, <i>CEC</i> (cmol _c /kg)	b	47.7
Exchangeable Metals (cmol _c /kg):	b	
Na ⁺		31.0
Ca ²⁺		20.8
Mg ²⁺		6.4
K ⁺		0.8
Sum		59.0
Soluble Metals (mg/kg):	b, c	
Na ⁺		4636
Ca ²⁺		443
Mg ²⁺		407
K ⁺		263
Soil pH	b, d	9.2
Electrical Conductivity, <i>EC</i> (mS/m) @ 25°C	b, d	120

823 ^a Based on x-ray diffraction analyses performed by Mineralogy Inc., Tulsa, OK.

824 ^b Based on procedures described in Shackelford and Redmond (1995).

825 ^c Measured from a 1 g:20 mL clay-water extract.

826 ^d Measured on a saturated soil paste.

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828 Table 2. Chemical properties of the potassium chloride (KCl) solutions used in this study.

829

KCl Source Concentration, C_{ot} (mM)		Electrical Conductivity, EC (mS/m), @ 25° C	pH
Target	Measured		
20	21.1	281	4.9
35	35.2	483	5.7
50	54.9	747	5.8
100	108	1418	6.0
200	240	2858	6.0
400	408	5280	6.1

830 Table 3. Measured GCL membrane properties.

Target Source KCl Concentration, C_{ot} (mM)	Measured Concentration Difference, $-\Delta C$ (mM)		Maximum Chemico- osmotic Pressure difference, $-\Delta\pi$ (kPa)		Measured Effective Chemico- osmotic Pressure Difference, $-\Delta P_e$ (kPa)	Measured Membrane Efficiency Coefficient, $\omega (= \Delta P_e / \Delta\pi)$	
	$-\Delta C_o$ ($= C_{ot} - C_{ob}$)	$-\Delta C_{ave}$ ($= C_{t,ave} - C_{b,ave}$)	$-\Delta\pi_o$	$-\Delta\pi_{ave}$		ω_o	ω_{ave}
20	21.1	17.0	103	83.2	9.97	0.097	0.120
35	35.2	28.1	172	137	9.27	0.054	0.067
50	54.9	43.6	269	213	9.20	0.034	0.043
100	108	90.1	528	441	7.79	0.015	0.018
200	240	183	1170	895	5.00	0.004	0.006
400	408	316	2000	1550	0.17	0.000	0.000

831 Notes:

832 C_{ot} = source KCl concentration at top of specimen

833 C_{ob} = source KCl concentration at bottom of specimen (= 0)

834 $C_{t,ave}$ = average KCl concentration at top of specimen

835 $C_{b,ave}$ = average KCl concentration at bottom of specimen

836 $\Delta\pi_o$, ω_o = values based on ΔC_o

837 $\Delta\pi_{ave}$, ω_{ave} = values based on ΔC_{ave}

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839 Table 4. Effective diffusion coefficients and tortuosity factors based on chloride diffusion.

Target Source KCl Concen- tration, C_{ot} (mM)	Measured Concentration Difference, $-\Delta C$ (mM)		Effective Diffusion Coefficient, D^* ($\times 10^{-10}$) (m^2/s)		Apparent Tortuosity Factor, τ_a		Restrictive Tortuosity Factor, τ_r	
	$-\Delta C_o$ ($= C_{ot} - C_{ob}$)	$-\Delta C_{ave}$ ($= C_{t,ave} - C_{b,ave}$)	D_o^*	D_{ave}^*	$\tau_{a,o}$ $[D_o^*/D_o]$	$\tau_{a,ave}$ $[D_{ave}^*/D_o]$	$\tau_{r,o}$ $[D_o^*/D_{p,o}]$	$\tau_{r,ave}$ $[D_{ave}^*/D_{p,ave}]$
20	21.1	17.0	0.89	1.11	0.045	0.056	0.63	0.61
35	35.2	28.1	1.08	1.35	0.054	0.068	0.76	0.74
50	54.9	43.6	1.17	1.47	0.059	0.074	0.82	0.80
100	108	90.1	1.26	1.52	0.063	0.076	0.89	0.83
200	240	183	1.26	1.65	0.063	0.083	0.89	0.90
400	408	316	1.42	1.83	0.071	0.092	1.00	1.00

840 Notes:

841 C_{ot} = source KCl concentration at top of specimen

842 C_{ob} = source KCl concentration at bottom of specimen (= 0 for de-ionized water)

843 $C_{t,ave}$ = average KCl concentration at top of specimen

844 $C_{b,ave}$ = average KCl concentration at bottom of specimen

845 D_o^* , $\tau_{a,o}$, $\tau_{r,o}$ = values based on $-\Delta C_o$

846 D_{ave}^* , $\tau_{a,ave}$, $\tau_{r,ave}$ = values based on $-\Delta C_{ave}$

847 $D_{p,o} = 1.42 \times 10^{-10} m^2/s$; $D_{p,ave} = 1.83 m^2/s \times 10^{-10}$; D_o (KCl) = $1.993 \times 10^{-9} m^2/s$

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Figure No.	Figure Caption
1	Schematic drawing illustrating circulation system for simultaneous measurement of membrane behavior and solute diffusion through a GCL specimen contained in a rigid-wall cell (after Malusis et al. 2001 and Bohnhoff and Shackelford 2013) [C = concentration; P = pressure].
2	Steady-state membrane efficiency coefficients for GCL specimens at different porosities (n) as a function of the average (measured) source concentration of KCl: (a) values based on the initial (source) boundary concentrations, ω_o ; (b) values based on the average boundary concentrations, ω_{ave} (modified after Meier et al. 2014).
3	Temporal concentrations of major ions in the circulation outflow from the bottom reservoir.
4	Cumulative mass data for chloride (Cl^-) and potassium (K^+) diffusing through a geosynthetic clay liner for different source concentrations (C_{ot}) of potassium chloride (KCl).
5	Individual stage cumulative mass data corresponding to different source concentrations, C_{ot} : (a) 20 mM KCl; (b) 35 mM KCl; (c) 50 mM KCl; (d) 100 mM KCl; (e) 200 mM KCl; (f) 400 mM KCl.
6	Effective diffusion coefficients for chloride (Cl^-) and potassium (K^+) based on the difference in the average boundary KCl concentrations (D_{ave}^*) and the difference in the source KCl concentrations (D_o^*) as a function of the measured source KCl concentration.
7	Effective diffusion coefficients for chloride as a function of the steady-state membrane efficiency coefficients based on source concentrations (D_o^* , ω_o) and average of the boundary concentrations (D_{ave}^* , ω_{ave}): (a) all measured values of ω ; (b) reduced range of ω values.
8	Restrictive tortuosity factors based on the measured effective diffusion coefficients (D^*) and pore diffusion coefficients (D_p) for chloride.

Figure 1. Schematic drawing illustrating the circulation system for simultaneous measurement of membrane behavior and solute diffusion through a GCL specimen contained in a rigid-wall cell (after Malusis et al. 2001 and Bohnhoff and Shackelford 2013) [C = concentration; P = pressure].

Figure 2. Steady-state membrane efficiency coefficients for GCL specimens at different porosities (n) as a function of the average (measured) source concentration of KCl: (a) values based on the initial (source) boundary concentrations, ω_o ; (b) values based on the average boundary concentrations, ω_{ave} (modified after Meier et al. 2014).

Figure 3. Temporal concentrations of major ions in the circulation outflow from the bottom reservoir.

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875 Figure 4. Cumulative mass data for chloride (Cl⁻) and potassium (K⁺) diffusing through a
 876 geosynthetic clay liner for different source concentrations (C_{0t}) of potassium chloride (KCl).

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Figure 5. Individual stage cumulative mass data corresponding to different source concentrations, C_{or} : (a) 20 mM KCl; (b) 35 mM KCl; (c) 50 mM KCl; (d) 100 mM KCl; (e) 200 mM KCl; (f) 400 mM KCl.

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887 Figure 6. Effective diffusion coefficients for chloride (Cl^-) and potassium (K^+) based on the
888 difference in the average boundary KCl concentrations (D_{ave}^*) and the difference in the source
889 KCl concentrations (D_o^*) as a function of the measured source KCl concentration.

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Figure 7. Effective diffusion coefficients for chloride as a function of the steady-state membrane efficiency coefficients based on source concentrations (D^*_o , ω_o) and average of the boundary concentrations (D^*_{ave} , ω_{ave}): (a) all measured values of ω ; (b) reduced range of ω values.

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898 Figure 8. Restrictive tortuosity factors based on the measured effective diffusion coefficients (D^*)
 899 and pore diffusion coefficients (D_p) for chloride.

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