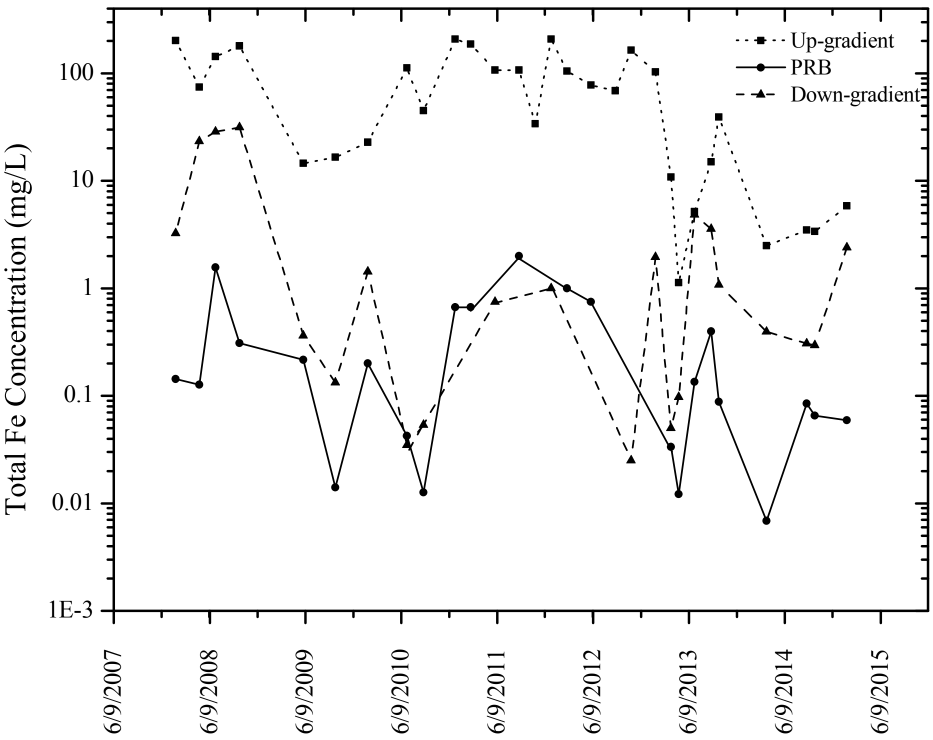

FIG. 6. Total Fe concentration in the up-gradient, PRB and down-gradient.

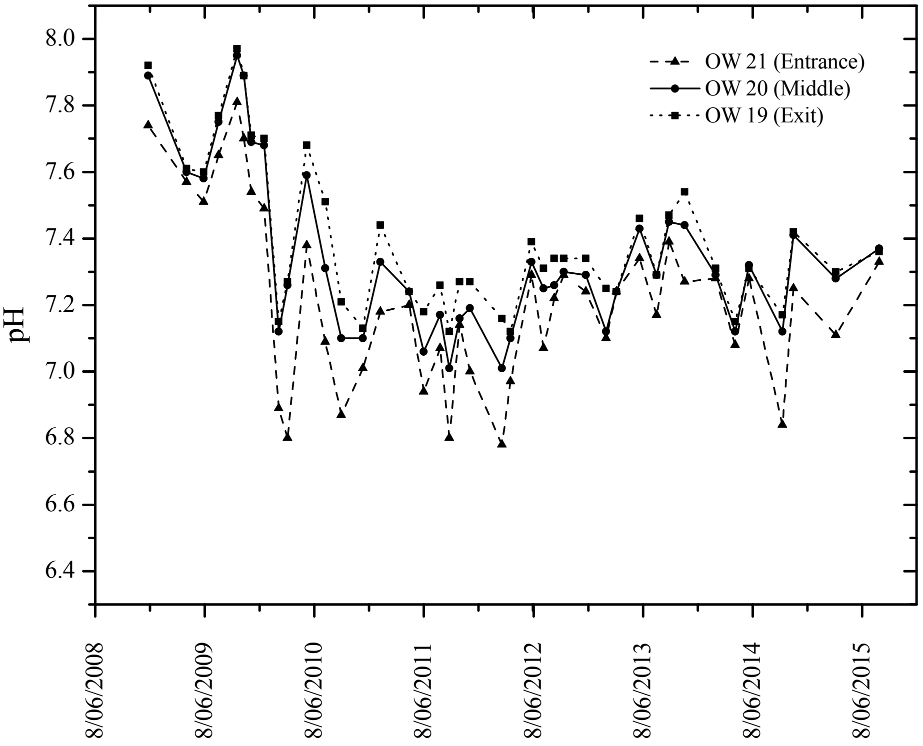

FIG. 7. pH along a centre-line of PRB (OW21-Entrance, OW20-Middle, OW19-Exit).

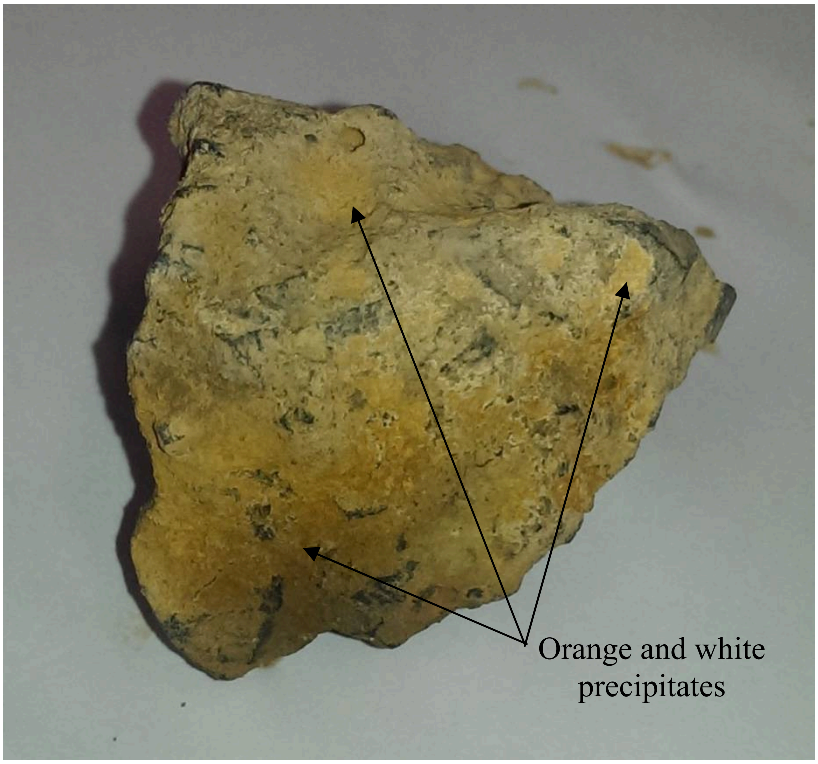

FIG. 8. Recycled concrete sample exhumed from the entrance zone of PRB.

LONGEVITY PREDICTION OF THE PRB

Permeable reactive barriers are expected to serve for a longer time compared to other subsurface groundwater remediation methods. The performance of pilot-scale PRBs, has hindered its efficacy mainly due to the secondary mineral precipitation on reactive surfaces of the PRB material (Duran et al., (2000); Furukawa et al., (2002); Gavaskar et al., (2000); Morrison (2003); Nafts et al., (2002); Phillips et al., (2000); Puls et al., 1999a; Puls et al., 1999b; Puls et al., (2000); Sarr, (2001); USEPA (2004); Vogan et al., (1999); Wilkin et al., (2003)). In the current study, longevity prediction was carried out by considering the usage of reactive material and the rate of precipitation of secondary minerals with reference to groundwater flow at the field site.

Acid neutralisation capacity (ANC) is reduced by the continuous mineral precipitation on reactive media. The ANC was reduced by 54% due to the secondary mineral precipitation for the current study (Pathirage 2014). This PRB has 80 tonnes of recycled concrete particles (d_{50} = 40 mm). Therefore, this PRB has 11.7 tonnes of ANC from the alkalinity generating minerals of 146 g/kg. With an average groundwater flow of 0.05 m/day, the average acidic groundwater flow through the barrier would be 4.85×10^5 L/year. Therefore, the averaged alkalinity consumption would be 0.274 t/year, attributed to a mean acidity of 565 mg/L (equivalent to $CaCO_3$) (Pathirage and Indraratna, 2015). These averaging values lead to 42.7 years of longevity considering the neutralisation process alone. Therefore, when the armouring effect and the corresponding reduction of ANC of 54% are brought to the calculation, longevity of this PRB would be 19.5 years for an average groundwater flow of 0.05 m/day (Pathirage and Indraratna 2015). Predicted longevity could vary according to the groundwater flow and associated usage of alkalinity from the PRB.

CONCLUSIONS

The performance of the pilot-scale PRB was monitored over 8 years. The PRB has proven to maintain a groundwater pH of 7 inside the PRB and a pH of 6 in the down-gradient of the PRB. In terms of removing heavy metals- Al and Fe, PRB has shown great efficiency and removed 99% of the above from groundwater. pH at the entrance phase has being decreasing slightly, because of the exhaustion of alkalinity minerals and armouring effect by secondary mineral precipitation. Therefore, the reduction in hydraulic conductivity was 3% for 8 years of operation. The predicted longevity of this PRB is 19.5 years for an average groundwater flow of 0.05 m/day.

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Advances in the Membrane Behavior of Bentonite-Based Barriers

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Abstract: Sodium bentonite (Na-bentonite) commonly is used as a barrier or a component of a barrier to limit contaminant migration into the environment. Results of experimental research to date indicate that Na-bentonite may exhibit significant membrane behavior resulting in restricted solute migration (also known as anion exclusion) and development of chemico-osmosis, leading to reductions in both liquid and contaminant flux through the bentonite. Thus, bentonite-based engineered barriers may exhibit improved containment performance, which has motivated the development of laboratory research to further evaluate and quantify membrane behavior. The purpose of this paper is to provide a summary of recent and current advances in the ongoing evaluation of the significance of membrane behavior in bentonites, including chemically modified bentonites (e.g., dense pre-hydrated geosynthetic clay liners, multiswellable bentonite, bentonite polymer nanocomposite, HYPER-clay) and bentonite-amended clays. In addition, the development of an innovative apparatus to measure membrane behavior under unsaturated conditions is described. Recent research regarding the limiting concentrations at which membrane behavior continues to persist is summarized. Finally, recommendations for future research on the relevance of membrane behavior in practical applications are provided.

INTRODUCTION

Bentonite-based barriers commonly are used to control the migration or flux of contaminants into the environment. In addition to a low hydraulic conductivity, *k*, to dilute aqueous solutions, bentonite and soil mixtures containing bentonite also have been shown to exhibit semipermeable membrane behavior resulting in restricted solute migration and chemico-osmosis. The existence of membrane behavior is potentially advantageous, as the membrane behavior results in reduced contaminant transport through the barrier (Shackelford 2013).

A variety of bentonite-based barriers are used for chemical containment applications, ranging from geosynthetic clay liners (GCLs) containing 100 % sodium bentonite (Na-bentonite), to natural clay soils amended with low amounts of bentonite (~5 % by dry mass) and soil-bentonite backfills used in vertical cutoff walls. Membrane behavior has been shown to exist in all of these barrier types (Malusis and Shackelford 2002, Yeo et al. 2005, Henning et al. 2006, Evans et al. 2008, Kang and Shackelford 2010, Shackelford 2013).

Membrane behavior is quantified in terms of the membrane or chemico-osmotic efficiency coefficient, ω. In general, ω ranges from zero indicating no membrane behavior to unity ($0 \leq \omega \leq 1$) indicating perfect or ideal membrane behavior where no solute flux occurs. The ω of bentonite-based barrier materials that exhibit membrane behavior typically lies between zero and unity ($0 < \omega < 1$) due to the variety of pore sizes (i.e., some pores are restrictive while others are not). Thus, these barriers are considered semipermeable membranes in that some but not all of the solute flux is restricted.

The existence and magnitude of membrane behavior is dependent on the composition and properties of the barrier material and the concentration and constituents in the liquid to which the barrier is exposed. Variables that affect membrane behavior in bentonite-based barriers include, but are not limited to, the composition of the clay or clay mixture (e.g., mineralogy of the clay, percentage of bentonite in the mixture), porosity (n), degree of water saturation (S), and the concentration, pH and chemical composition of the liquid in the pore space (i.e., pore liquid).

Significant research has been performed over the past approximate two decades to further evaluate and quantify the effects of these variables on membrane behavior measured in the laboratory. Barrier materials containing high swelling smectite-based minerals, such as montmorillonite in Na-bentonite, generally have been shown to exhibit substantial membrane behavior. For example, Malusis and Shackelford (2002) measured ω values as high as 0.7 for a GCL containing Na-bentonite ($n >$ 0.75) when exposed to KCl solutions. Kang and Shackelford (2010) measured a value for ω of 0.76 for a compacted clay specimen amended with 5 % bentonite. However, Yeo et al. (2005) reported lower values of ω, ranging from 0.12 to 0.16, for sand-bentonite backfills of vertical cutoff walls with a bentonite content of 7.2 % (dry mass). In addition, ω increases as n decreases, as the effective stress (σ') increases, and/or as the concentration (C) or ionic strength of the pore liquid decreases (e.g., Kang and Shackelford 2011, Yeo et al. 2005). Kang and Shackelford (2011) calculated the ratio of ω for a GCL at σ' of 241 kPa (35 psi) relative to that at σ' of 34.5 kPa (5 psi) to be as high as 7.9. The ω for electrolyte solutions containing monovalent cations (such as KCl) is greater than that for electrolyte solutions containing divalent cations (such as $CaCl_2$). For example, Shackelford and Lee (2003) showed that continuous exposure of a GCL to a 5 mM $CaCl_2$ solution resulted in a decrease in membrane efficiency of the GCL from 52 % ($\omega = 0.52$) after 9 d to practically nil ($\omega \approx 0$) after 35 d due to diffusion of Ca^{2+} into the GCL and time-dependent collapse of the diffuse double layers associated with the bentonite particles.

Why is membrane behavior significant? As described in Shackelford (2013), the existence of membrane behavior can improve significantly the containment function of a barrier. This improved containment performance results from solute restriction, chemico-osmotic counter flow, and reduced diffusive flux through the barrier. However, as previously noted (e.g., Shackelford and Lee 2003), partial or complete destruction of the membrane behavior in Na-bentonite by invading salt cations has been observed. For this reason, the membrane behavior for novel and alternative barrier materials that are potentially more chemical resistant, such as chemically modified bentonites, has been the subject of recent research. In addition, the advancement of testing conditions including measurement of membrane behavior under unsaturated conditions and at the limiting concentrations (i.e., the concentration at which ω reaches zero) has been evaluated relatively recently.

EVALUATION OF NOVEL AND ALTERNATIVE BARRIER MATERIALS

Chemically Modified Bentonites

The investigation into the possible substitution of chemically modified bentonites, or CMBs (e.g., bentonites amended with organic modifiers, such as polymers) in engineered barriers has gained momentum, because CMBs may provide greater resistance to degradation of the membrane behavior by invading salts. The membrane behavior and diffusive properties of several CMBs exposed to solutions of KCl and $CaCl_2$ are described in this section. The CMBs considered include a dense pre-hydrated geosynthetic clay liner (DPH-GCL), multiswellable bentonite (MSB), bentonite polymer nanocomposite (BPN), and HYPER-clay.

To create DPH-GCLs, bentonite is prehydrated with dilute solutions of sodium carboxylmethyl cellulose (Na-CMC) and sodium polyacrylate, and then vacuum extruded to densify the hydrated bentonite (Malusis and Daniyarov 2014). The MSB is a sodium-rich montmorillonite modified with propylene carbonate (Mazzieri et al. 2010). Formation of BPN, also referred to as a bentonite polymer alloy (BPA) and bentonite polymer composite (BPC), occurs through polymerization of an organic monomer in a bentonite slurry (see Bohnhoff and Shackelford 2013). HYPER-clay (HC) is another polymerized bentonite that is modified with 2 % or more by dry weight of the Na-CMC anionic polymer (Di Emidio et al. 2015).

Enhanced membrane behavior has been reported for several of the CMBs. In general, values of ω measured for CMB specimens are higher than those of conventional Na-bentonite specimens tested using solutions containing the same type and concentration of salt and similar testing conditions (i.e., rigid-wall (RW) versus flexible-wall (FW) cell and/or similar n). For example, as shown in Figure 1a, the values of ω based on membrane tests performed using a RW cell for BPN (BPN-RW) from Bohnhoff and Shackelford (2013) and DPH-GCL from Malusis and Daniyarov (2014) were higher than the values of ω for conventional Na-bentonite in GCLs (GCL-RW) from Malusis and Shackelford (2002) over nearly the entire range of KCl concentrations evaluated. For both the CMB and the Na-bentonite, ω decreased as the salt concentration increased, which is consistent with expectations based on classical diffuse-double layer theory (Fritz 1986). However, the ω of the CMB remained greater than the ω of the Na-bentonite specimens at the highest KCl concentrations investigated. For example, at a source KCl concentration, C_{ot}, of 47 mM, ω was 0.14 and 0.26 for GCL and DPH-GCL, respectively, indicating higher limiting or threshold concentrations (i.e., the concentration at which ω → 0) for the CMB. The values of ω for the BPN in the flexible wall cell (i.e., BPN-FW) were lower than those of the Na-bentonite in a rigid wall cell (i.e., GCL-RW). However, when compared with the ω of Na-bentonite under similar testing conditions, e.g., GCL-FW (n = 0.79-0.81), the ω of the BPN-FW were higher for the range of KCl concentrations investigated. As a result of the manufacturing process, the n of the DPH-GCL was considerably lower than the n of most GCLs that have been investigated. Malusis and Daniyarov (2014) attributed the higher ω for a given KCl concentration to the lower n of the DPH-GCL. However, the values of ω for the DPH-GCL were still higher than the ω for a GCL (GCL-FW, n = 0.66-0.71) with an n approaching those of the DPH-GCL, indicating that other factors such as the presence of CMC may be contributing to this behavior.

For several of the CMBs, the membrane behavior persisted ($\omega > 0$) at higher salt concentrations than those that caused complete degradation of membrane behavior (i.e., $\omega = 0$) in Na-bentonite (Figure 1b). Most of the CMBs (BPN, DHP-GCL, and HYPER-clay) exhibited membrane behavior at low concentrations of $CaCl_2$. However, for exposure to 1 mM $CaCl_2$, the ω of 0.27 for the DPH-GCL (Di Emidio 2010) was slightly lower than the ω of 0.29 for the Na-bentonite (Di Emidio et al. 2010) The values of ω for the BPN (Bohnhoff et al. 2014) and HYPER-clay (Di Emidio et al. 2015) exposed to 5mM $CaCl_2$ were greater than zero, whereas the values of ω for Na-bentonite and a GCL (Shackelford and Lee 2003) reached zero at steady-state. These results indicated improved performance of some of the CMBs compared to that of Na-bentonite. However, complete (or nearly so) degradation of the membrane behavior eventually occurred as the CMB specimens were exposed to solutions containing increasingly higher concentrations of $CaCl_2$.

These results raise lingering questions regarding the long-term integrity of CMBs due to issues such as the potential for the organic (polymer) amendment to be eluted out of the material over time. Therefore, additional testing is warranted to better understand the long-term behavior of the CMBs and the membrane behavior with other solutions and higher concentration solutions.

Bentonite-Amended Soils

The performance of clay barriers has been shown to improve when amended with bentonite. Not only is the k of the barrier reduced, but also the membrane behavior can be enhanced. For example, Tang et al. (2014) investigated the membrane behavior of local Fukakusa Clay (FC) amended with 5 % to 20 % bentonite (by dry weight). As expected, the ω increased with increasing bentonite amendment. For example, the ω for the FC amended with 5 % bentonite was 0.39 whereas ω for the FC without amendment (0 % bentonite) was 0.11. In addition, the ω increased as the

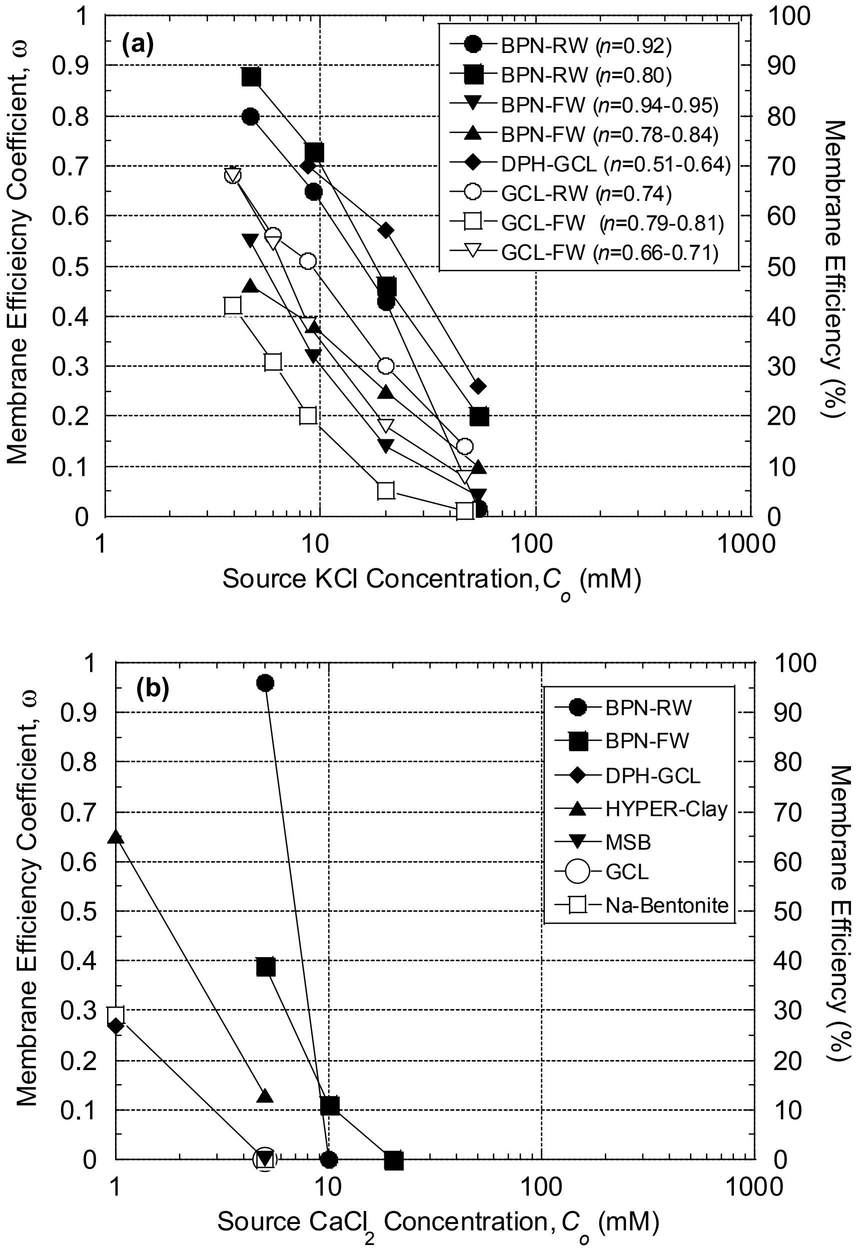

FIG. 1. Comparison of the membrane efficiency coefficients for specimens of chemically modified bentonites (closed symbols) and traditional sodium bentonite (open symbols) as a function of (a) source KCl concentration and (b) source $CaCl_2$ concentration. BPN using rigid-wall and flexible-wall cells (BPN-RW, BPN-FW) from Bohnhoff and Shackelford (2013) and Bohnhoff et al. (2014), dense prehydrated GCL (DPH-GCL) from Di Emidio (2010) and Malusis and Daniyarov (2014) and multi-swellable bentonite (MSB) from Mazzieri et al. (2010), Hyper-clay from Di Emidio et al. (2015), and a GCL containing a traditional Na-bentonite (GCL) from Shackelford and Lee (2003), Malusis and Shackelford (2002), and Kang and Shackelford (2011), and a traditional (unmodified) Na-bentonite from Di Emidio (2010).

concentration of the KCl solution decreased (e.g., ω = 0.04 for a KCl concentration of 50 mM versus ω = 0.88 for a KCl concentration of 0.5 mM), which was consistent with trends reported in previous membrane behavior research for Na-bentonite (described previously). However, comparison of the results from Tang et al. (2014) with those existing in literature for other amended clays (e.g., Kang and Shackelford 2010) indicate very high ω values, despite the relatively high values of *k* (~ 1 x 10^{-9} m/s for FC amended with 5 % bentonite) reported for the mixtures. These higher values of ω may have been due, in part, to differences in the testing conditions used by Tang et al. (2014) relative to other membrane literature. For example, the base of the test cell used by Tang et al. (2014) was open to the atmosphere whereas Kang and Shackelford (2010) maintained a closed-system at the base of the cell allowing for measurement of pressures induced by membrane behavior at the bottom boundary of the specimen. Further research is required regarding the effectiveness of bentonite amendment to improve membrane behavior in natural clay liners, soil-bentonite backfills, and compacted sand-bentonites.

ADVANCEMENTS IN TESTING CONDITIONS

Unsaturated Barriers

Until recently, experimental studies have focused on measurement of ω almost exclusively under fully saturated conditions ($S = 1.0$). However, clay barriers may exist at varying degrees of water saturation ($S < 1.0$), such as in barriers being proposed for long-term disposal of high level radioactive waste (HLRW) (Yong et al. 2010). Based on our conceptual understanding of the mechanisms causing membrane behavior in clays, the influence of membrane behavior on solute transport is likely to be even more significant in clays under unsaturated conditions due to air occupying a portion of the pore space. That is, as *S* decreases, the pore space accessible to dissolved solutes decreases and ω is expected to increase (see Sample-Lord and Shackelford 2014, Sample-Lord 2015).

Sample-Lord and Shackelford (2014) described the development of an innovative, closed-system testing apparatus to allow for the simultaneous measurement of membrane behavior and diffusion in unsaturated Na-bentonite. In contrast to previous closed-system testing apparatuses used for measurement of membrane behavior in saturated clays, the rigid-wall test cell included ceramic, high air-entry disks at the boundaries of the specimen to maintain constant water content and *S* throughout testing. An air pressure was applied to the specimen to maintain positive pore-water pressures under unsaturated conditions (i.e., axis-translation technique), and a flexible membrane was included between the specimen and the rigid sidewall to prevent short-circuiting along the perimeter. Sample-Lord (2015) reported values of ω measured for bentonite specimens ($0.87 \leq n \leq 0.89$) with *S* ranging from 0.79 to 1.0 and exposed to multiple concentrations of KCl solutions (20 mM, 30 mM, and 50 mM). For all values of *S*, a decrease in *S* correlated with an increase in ω. For example, for a source concentration of 20 mM KCl, ω increased from 0.61 to 0.71 as *S* decreased from 1.0 to 0.84. While the results of the studies by Sample-Lord and Shackelford (2014) and Sample-Lord (2015) advanced our fundamental understanding of solute