Research paper

Improving membrane performance via bentonite polymer nanocomposite

Gretchen L. Bohnhoff a,b, Charles D. Shackelford c,⁎

a Department of Civil & Environmental Engineering, 1 University Plaza, University of Wisconsin-Platteville, Platteville, WI 53818-3099, USA
b Department of Civil and Environmental Engineering, Colorado State University, USA
c Department of Civil and Environmental Engineering, 1372 Campus Delivery, Colorado State University, Fort Collins, CO 80523-1372, USA

Abstract

Traditional (non-treated) sodium bentonite has been shown to exhibit substantial semipermeable membrane behavior, or the ability to restrict the migration of solutes. However, partial or complete degradation of the membrane behavior due to diffusion of invading salt cations into the sodium bentonite also has been observed. In this study, a polyacrylate modified bentonite, referred to as a bentonite polymer nanocomposite, or BPN, was evaluated as a potential substitute for sodium bentonite for the purpose of providing increased resistance to salt degradation of membrane behavior. The membrane behavior of the BPN was measured in the laboratory by establishing differences in salt concentrations ranging from 4.7 to 54 mM KCl across specimens contained in either rigid-wall or flexible-wall cells under closed-system boundary conditions. The measured membrane efficiency coefficients, ω, for the BPN specimens were greater than those previously reported for specimens containing sodium bentonite under similar testing conditions. For example, the measured ω values for the BPN specimens ranged from 109% to 433% of those previously reported for the specimens containing traditional sodium bentonite, depending on the initial porosity or initial effective stress of the specimen, the concentration of KCl, and the type of test cell (rigid vs. flexible), and despite the BPN specimens not being flushed of soluble salts prior to membrane testing as in the case of the specimens containing sodium bentonite. Thus, the BPN exhibited substantially improved membrane behavior under conditions that presumably were more adverse with respect to soluble salts than those previously reported for specimens containing a sodium bentonite. However, the potential role that any excess low molecular weight polymer in the BPN may have played in affecting the results is uncertain, such that additional testing of the BPN is warranted to better understand the long-term behavior of the BPN.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Bentonite is commonly used to control liquid flow and contaminant transport for a variety of hydraulic containment applications, including groundwater cutoff walls, barriers for waste containment (e.g., landfills, wastewater ponds, manure lagoons, nuclear storage, etc.), secondary containment in tank farms, and seals in monitoring and water supply wells (Christman et al., 2002; Estornell and Daniel, 1992; Evans, 1993; Kajita, 1997; Katsumi et al., 2008; Smith et al., 2003). In nearly all of these applications, traditional sodium bentonite is used, meaning that sodium is the predominant cation associated with the exchange complex of the bentonite particles. The preference for sodium bentonite stems from desirable engineering properties, such as low hydraulic conductivity (k) to water (typically k < 10−10 m/s), and the existence of semipermeable membrane behavior, or the restriction of solutes during migration which gives rise to hyperfiltration, chemico-osmosis, and reduced diffusive solute mass flux (Malusis et al., 2003).

Unfortunately, sodium bentonite is thermodynamically unstable in environments where multivalent cations are present or predominant (Sposito, 1989), including most naturally occurring pore waters in earthen materials. Under such conditions, multivalent cations gradually replace monovalent cations originally dominating the exchange complex, thereby reducing or eliminating osmotic swelling of the sodium bentonite and the ability of sodium bentonite to function effectively, even if the sodium bentonite is prehydrated (Kolstad et al., 2004; Lee and Shackelford, 2005b; Vasko et al., 2001). For example, several field studies have shown that Ca2+-for-Na+ exchange can result in reduced swelling capability of the sodium bentonite contained in geosynthetic clay liners (GCLs) used in hydraulic containment applications upon hydration, and ultimately to poor hydraulic performance (ATU, 1992; Benson et al., 2007; Egloffstein, 2001; James et al., 1997; Jo et al., 2001, 2004; Meer and Benson, 2007; Shackelford et al., 2000). The Ca2+ is derived from surrounding soils, and migrates into the GCL usually in response to hydraulic (suction) and/or chemical (diffusive) gradients.
Recent laboratory studies have illustrated the deleterious effects of long-term cation exchange on both k and membrane behavior (Egloffstein, 2001; Jo et al., 2001, 2005; Kolstad et al., 2004; Lee and Shackelford, 2005a,b; Lin and Benson, 2000; Shackelford and Lee, 2003). For example, in terms of membrane behavior, a direct correlation between diffusion of invading cations into bentonite and either partial or complete destruction of membrane behavior has been shown (Malusis and Shackelford, 2002a; Shackelford and Lee, 2003). These field and laboratory data paint an unsettling picture regarding the long-term effectiveness of bentonites used for hydraulic containment applications. However, bentonites can be chemically modified to make the bentonite properties more compatible with the surrounding environment (e.g., Katsumi et al., 2008). For example, anionic polymers are added to bentonite to attain rheological properties needed for drilling fluids (Heller and Keren, 2003). Organobentonites also have been used for applications where an organophylic material is needed for adsorption or containment of organic compounds (e.g., Lo et al., 1996; Smith et al., 2003).

The objective of this study was to evaluate the potential use of a polyacrylate modified bentonite, referred to as a bentonite polymer nanocomposite, or BPN, for improving membrane behavior in the presence of simple salt solutions relative to traditional sodium bentonite that is commonly used in hydraulic containment barriers, such as GCLs (e.g., Kang and Shackelford, 2009; Malusis and Shackelford, 2002a), compacted soil–bentonite liners (Kang and Shackelford, 2010), and soil–bentonite backfills in vertical cutoff walls (Evans et al., 2008; Henning et al., 2006; Yeo et al., 2005). The BPN evaluated in this study is thought to be fundamentally different from other polymer–modified bentonites in that the organic molecules are polymerized after intercalation, resulting in the polymer bonding with sodium ions initially in the interlayer region and the surface of the bentonites, a process which is hypothesized to result in a stable structure where the layers are propped open in the state attained by osmotic swelling (Bohnhoff, 2012; Scalia, 2012). In contrast, conventional anionic polymer–modified bentonites employ long-chain anionic polymers (e.g., anionic polyacrylimides) that are electrostatically associated with the positively charged edges of the bentonite platelets (e.g., Boels and van der Wal, 1999; Heller and Keren, 2003; Pavlidou and Papaspyrides, 2008).

### 2. Materials and methods

#### 2.1. Liquids

The liquids used in this study included de-ionized water (DIW) and solutions of DIW with potassium chloride (KCl) (certified A.C.S.; Fisher Scientific, Fair Lawn, NJ). The KCl solutions were used as circulating liquids in the membrane tests to allow for direct comparison of results from this study with those previously reported for tests conducted on GCLs (Kang and Shackelford, 2009; Malusis and Shackelford, 2002a). Solutions were prepared and stored in 20-L carboys (Nalgene®; Thermo Scientific, Rochester, NY). The pH and electrical conductivity, EC, of the solutions were measured using a pH meter (Accumet® EC 84; Fisher Scientific, Pittsburgh, PA) and an EC probe (150 A = Conductivity meter; Thermo Orion, Beverly, MA), respectively. Ion chromatography (Dionex® 4000i IC Module, Dionex Co., Sunnyvale, CA) was used to measure chloride (Cl\(^{-}\)) and potassium (K\(^{+}\)) concentrations, and inductively coupled plasma–atomic emission spectrometry (IRIS® Advantage/1000 ICP Spectrometer, Thermo Jarrel Ash Co., Franklin, MA) was used to measure potassium (K\(^{+}\)) and chloride (Cl\(^{-}\)) concentrations. The measured EC and pH of the KCl solutions are given in Table 1.

#### 2.2. BPN

The BPN evaluated in this study was prepared by Colloid Environmental Technologies Co. (CETCO, Hoffman Estates, IL). The BPN was produced with polyacrylic acid (PAA) and a conventional sodium bentonite using methods similar to those used for the production of polymer nanocomposites (e.g., Muzny et al., 1996). First, a monomer solution was prepared by dissolving acrylic acid in water followed by neutralization with sodium hydroxide and addition of an initiator, sodium persulfate. Then, the sodium bentonite was added to the monomer solution in concentrations ranging from 30 to 50% by mass of the slurry to form a bentonite–monomer slurry. Polymerization was initiated by raising the temperature of the bentonite–monomer slurry above the decomposition temperature of the initiator molecule causing the initiator molecule to decompose into free radicals. The free radicals react with the acrylic acid monomer to form more free radicals, which in turn react with additional monomer to proliferate the polymer chain. Following polymerization, the BPN was oven dried at 105 °C, milled, and screened by CETCO (Scalia et al., 2011).

Based on the grain-size distributions from a hydrometer analysis (ASTM D 422), 100% of the sodium bentonite and the BPN were fine-grained (<0.075 mm) with the sodium bentonite and the BPN containing 78% and 96% of clay-sized (<5 mm) material, respectively. The sodium bentonite and the BPN classified as a highly plastic clay (or CH according to the Unified Soil Classification System (ASTM D 2487)). Mineralogical analyses conducted by Mineralogy, Inc., Tulsa, OK, using X-ray diffraction indicated that the sodium bentonite was comprised of 77% montmorillonite, 15% quartz, 4% plagioclase feldspar, 3% illite/mica, and 1% calcite, whereas BPN was comprised of 76% montmorillonite, 15% quartz, 7% plagioclase feldspar, and 2% illite/mica. Thus, despite polymerization, the mineralogy of the BPN was close to that of the sodium bentonite.

Index properties of the sodium bentonite and the BPN are included in Table 2. The Atterberg limits of the sodium bentonite and the BPN also were measured according to ASTM D 4318. The measured liquid limit, LL, was 255, which is significantly lower than the LL of 422 for the sodium bentonite that was used to create the BPN as well as other traditional sodium bentonites, with values of LL that typically vary from 400 to 700 (e.g., Ito, 2006; Kenney et al., 1992; Lee and Shackelford, 2005b). The values of LL for other treated bentonites also

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical properties of liquids used in study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>Concentration (nM)</td>
</tr>
<tr>
<td>De-ionized water</td>
<td>0</td>
</tr>
<tr>
<td>KCl solutions (mg/L)</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Index properties of the conventional sodium bentonite used to create the bentonite polymer nanocomposite (BPN) and the BPN evaluated in this study.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
<td>Standard</td>
</tr>
<tr>
<td>Sodium bentonite</td>
<td>Bentonite polymer nanocomposite (BPN)</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>ASTM D 854</td>
</tr>
<tr>
<td>Plasticity index, PI (%)</td>
<td>ASTM D 4318</td>
</tr>
<tr>
<td>Swell index, SI (mL/g)</td>
<td>ASTM D 5890</td>
</tr>
<tr>
<td>Solution retention capacity, SRC (mL/g)</td>
<td>7.3 [3]</td>
</tr>
</tbody>
</table>

NA = Not applicable.

* Based on grain-size distribution.

** Based on procedures in Lee and Shackelford (2005c) with centrifuge speed at 3000 rpm.
have been reported as being lower relative to those of traditional sodium bentonites. For example, Di Emidio (2010) reported a $LL$ of 375 for dense pre-hydrated GCL, which is a GCL containing sodium bentonite that is prehydrated with sodium-carboxymethylcellulose and methanol and densified via calendaring. In contrast, the values of the $LL$ for HYPER clay, an anionic polymer modified bentonite, and multi-swellable bentonite are reported by Di Emidio (2010) to be similar to those of traditional bentonites (e.g., 650 for HYPER clay and 554 for multi-swellable bentonite). McKory and Ashmawy (2005) reported increases and decreases in the $LL$ of five polymer treated clays with the value of $LL$ depending on the type of polymer (e.g., cationic, anionic), the weight percent of the polymer, and whether or not the clay was heated. For example, $LL$ for a bentonite modified with 1% cationic polymer was 291.

In contrast to the $LL$, the plastic limit, $PL$, of the BPN could not be determined. As shown in Fig. 1, the consistency of the BPN during the test for $PL$ was similar to “silly putty” at low gravimetric water contents (<150%), and the soil “worm” did not exhibit the same cracking pattern that a traditional sodium bentonite would exhibit as the water content approaches the $PL$. The initial polymer content of the BPN was calculated to be 28.5% by mass (Scalia, 2012). Therefore, this “silly putty” behavior is likely a result of the superabsorbent polymer in the BPN causing the BPN to act more like a polymer than a typical clay. As a result, the plasticity index, $PI$, of the BPN could not be determined.

Tests to measure both the swell index, $SI$, and the solution retention capacity, $SRC$, using DIW also were conducted. The $SI$ tests were conducted in general accordance with ASTM D 5890. Briefly, 2 g of oven-dried BPN were dusted over the test solution in 0.1-g increments. The $SI$ (mL/2 g) was monitored initially after 16 h and subsequently every 4 h thereafter up to a total elapsed time of 48 h, at which swelling had ceased. The $SRC$ tests were conducted following the procedures described in Lee and Shackelford (2005c), except that the centrifuge speed was set at 3000 rpm versus the 5000 rpm used by Lee and Shackelford (2005c) to allow for an increased sensitivity of the resulting measurements.

The resulting values of $SI$ and $SRC$ for the BPN were 73 mL/2 g and 11 mL/g, respectively. These values are noticeably higher than those typically reported for traditional sodium bentonite (e.g., Lee and Shackelford, 2005c). For example, values of $SI$ and $SRC$ for traditional sodium bentonite typically range from 25 to 36 mL/2 g and from 5.7 to 7.7 mL/g, respectively (Benson and Meer, 2009; Bohnhoff, 2012; Katsumi et al., 2007; Kenney et al., 1992; Kolstad et al., 2004; Lee and Shackelford, 2005b). Also, the values for the $SI$ and $SRC$ of the sodium bentonite that was used to create the BPN were 22 mL/2 g and 7.3 mL/g, respectively. The greater swelling behavior of the BPN compared to the sodium bentonite is in contrast to the $LL$ results, and likely is attributable to the contribution of the swelling resulting from the superabsorbent polymer portion of the BPN (Bohnhoff, 2012; Scalia, 2012; Scalia et al., 2011).

2.3. Membrane testing

A schematic of the overall testing apparatus is shown in Fig. 2a, and schematics of the rigid-wall and the flexible-wall cells used in the study are shown in Fig. 2b and c, respectively. The rigid-wall cell is similar to that described by Malusis et al. (2001), and the flexible-wall cell is similar to that described by Kang and Shackelford (2009). The rigid-wall cell is used to test specimens under constant-volume conditions throughout the test. As explained by Kang and Shackelford (2009), the flexible-wall cell also maintains constant specimen volume during the stages of the test devoted to measuring membrane behavior, as required by the constant-volume assumption inherent in the equation used to calculate the membrane efficiency (described subsequently). However, some volume change generally occurs during the brief (~5 min) liquid refilling and sampling periods that are required periodically between the longer (typically either 24 or 48 h) membrane testing periods. Also, the flexible-wall cell allows for back-pressure saturation of the specimen prior to membrane testing and for control of the stress conditions imposed on the specimen (Kang and Shackelford, 2009).

As shown in Fig. 2a, either a rigid-wall or a flexible-wall cell was connected via stainless steel tubing to a hydraulic control system consisting of a flow-pump with syringes (actuators) used to circulate chemical solutions across both the top and bottom boundaries of the specimen contained in the cell at the same, constant displacement rate (Kang and Shackelford, 2009; Malusis et al., 2001). Stainless steel tubing was used to minimize volume change within the testing apparatus and to provide chemical resistance to electrolyte solutions. Two in-line pressure transducers (model Nos. PX181-100G5V or PX209-015G10V, Omega Engineering Inc., Stamford, CT) were used to measure the pressures existing in the boundary liquids, and a differential pressure transducer (model DP15-64, Validyne Engineering Corp., Northbridge, CA) was used to measure the generation of pressure difference across the specimen due to specimen membrane behavior. These pressures were recorded via a data acquisition (DAQ) system consisting of a circuit board (SCB-68, National Instruments, Austin, TX), a DAQ device (National Instruments, Austin, TX), and the LabVIEW software (National Instruments, Austin, TX). Refilling and sampling reservoirs were used to replenish the syringes with fresh chemical solutions or DIW and to collect circulation outflows for measurement of chemical parameters (e.g., solute concentrations, electrical conductivity) during the aforementioned replenishment and sampling periods at the end of each circulation cycle.

The rigid-wall cell (Fig. 2b) consists of an acrylic cylinder with a 71.0-mm (2.8-in) inner diameter, a top piston, and a base pedestal. The acrylic cylinder slides over the base pedestal and the top piston slides into the acrylic cylinder. O-rings on both the base pedestal and top piston and vacuum grease provide a tight seal between the acrylic cylinder and the base pedestal and top piston. The top piston is used to control the thickness (i.e., volume) of the specimen and can be locked in place during testing. The base pedestal and top piston have three ports. The inflow and outflow ports allow circulation of liquids (e.g., electrolyte solutions) through the porous plastic disks (GenPore porous sheet TO-6, General Polymer Corp., Reading, PA) located along the top and bottom boundaries of the specimen, whereas third ports located in the center of the top piston and the base pedestal provide connections to the individual in-line pressure transducers for measurement of the boundary liquid pressures at the top and bottom of the specimen, or $u_{\text{top}}$ and $u_{\text{bottom}}$, respectively, and the differential pressure transducer used to measure the pressure difference, $\Delta P = u_{\text{bottom}} - u_{\text{top}}$, across the specimen.

![Fig. 1. Photograph of plastic limit "worms" for traditional (untreated) bentonite and bentonite polymer nanocomposite (BPN).](image-url)
The flexible-wall cell (Fig. 2c) is a triaxial cell with special top and bottom caps as described in Kang and Shackelford (2009). The cell consists of an acrylic outer cylinder, top and bottom plates, and top and bottom caps. Each top and bottom cap has three ports, i.e., one port to allow for a circulation inflow, one port to allow for circulation outflow, and a third port to allow for measurement of the boundary liquid pressures (i.e., $u_{\text{Top}}$ and $u_{\text{Bottom}}$) and the pressure difference across the specimen (i.e., $\Delta P$). The bottom cap is attached to a bottom plate.

For the flexible-wall tests, a test specimen with a diameter of 102 mm (4.0 in) was placed above a heat-bonded, 140 g/m², non-woven geotextile on the bottom cap followed by a top cap and a flexible (polymer) membrane that is sealed with o-rings. The flexible membrane separated the specimen from the cell water. The outer cylinder was filled with de-aired water, which may be pressurized to apply a confining pressure (i.e., total stress) to the specimen. A cell-water accumulator was connected to the cell water to monitor volume change. Backpressure was applied to the specimen through the inflow and outflow ports in the top and bottom caps.

The flow-pump system is essentially the same as that described by Malusis et al. (2001) and consists of a dual carriage syringe pump (Model 940 or 944, Harvard Apparatus, Holliston, MA), two stainless steel actuators (syringes), and stainless steel tubing. Stainless steel components are used to minimize corrosion and apparatus volume change. The syringes displace liquids at the same, constant rate into the top and bottom caps via the inflow port, the liquids circulate through the porous plastic disks, and then exit via the outflow ports. In addition, infusion and withdrawal of the liquids occur at constant rates, such that the incremental volume of liquid that enters the cell, $\Delta V_{\text{in}}$, is equal to the incremental volume of liquid that exits the cell, $\Delta V_{\text{out}}$. As a result, there is no volume change in the circulation
system during circulation, such that there can be no flow of liquid through the specimen during circulation. Thus, the circulation system represents a closed system, i.e., at least during the periods of the test devoted to measurement of the membrane behavior of the specimen.

Operation of the flow-pump system consists of a circulation (i.e., testing) phase and a sampling and refilling phase. During the testing phase, the syringes are open to the cell, but closed to the reservoirs by opening valves 1 and 3 and closing valves 6 and 7 (see Fig. 2a). The syringes circulate liquids (DIW or electrolyte solutions) through the top and bottom of the specimens, such that a constant concentration difference (ΔC) is maintained across the specimen. If the specimen behaves as a semipermeable membrane, then a pressure difference, ΔP, is generated in response to the ΔC to counteract the tendency for chemico-osmotic flow, which is prevented from occurring due to maintaining a constant volume during circulation. This pressure difference is measured both directly by the differential transducer and indirectly as the difference in pressures measured by the two in-line pressure transducers.

The circulation rate of the liquid is adjustable by changing the displacement rate for the syringes of the flow pump. The possible displacement rates for the pumps and syringes that were used in this study varied from 9.2 × 10⁻⁹ to 4.7 × 10⁻⁷ m³/s. The circulation rate was adjusted to mimic “perfectly flushing” boundary conditions such that a steady-state ΔP was achieved during the circulation period, i.e., the time between the sampling and refilling periods (e.g., see Malusis et al., 2001). The circulation rate used in this study was 2.3 × 10⁻⁹ m³/s, which amounted to a circulation of approximately 40 mL every two days, after which the syringes were sampled and refilled before the start of a new circulation cycle.

During the brief (~5 min) sampling and refilling periods, the syringes were closed to the cell and opened to the reservoirs by closing valves 1 and 3 and opening valves 6 and 7 (see Fig. 2a), and the directions of the syringe displacement were reversed. The front (inflow) chambers of the syringes were refilled with fresh circulation liquid from the refilling reservoirs, whereas the circulation outflow liquids from the back chambers of the syringes were emptied into the sampling reservoirs. The outflow liquids were collected and stored for subsequent analysis (e.g., EC and solute concentration, C).

The membrane tests consisted of two stages, a permeation stage and a chemico-osmotic testing stage. During the permeation stage, specimens were permeated for periods from weeks to months in order to saturate the specimens. Despite those durations of permeation, specimens were permeated for periods from weeks to months in order to saturate the specimens. Despite those durations of permeation, specimens were permeated for periods from weeks to months in order to saturate the specimens. Despite those durations of permeation, specimens were permeated for periods from weeks to months in order to saturate the specimens. Despite those durations of permeation, specimens were permeated for periods from weeks to months in order to saturate the specimens.

The membrane efficiency coefficient, \( \omega \), is defined as follows (Groenevelt and Elrick, 1976; Malusis et al., 2001):

\[
\omega = \frac{\Delta P}{\Delta \pi}
\]  

(1)

where ΔP (≤0, since the positive x-direction is assumed downward from the top of the specimen) is the measured chemico-osmotic pressure difference induced across the specimen as a result of prohibiting chemico-osmotic flux of liquid, and Δ\( \pi \) (≤0) is the theoretical chemico-osmotic pressure difference across an “ideal” semipermeable membrane (i.e., \( \omega = 1 \)) subjected to an applied difference in solute (electrolyte) concentration (e.g., Olsen et al., 1990). The value of Δ\( \pi \) can be calculated in accordance with the van’t Hoff expression in terms of either the source concentrations of KCl in the circulation inflows across the top and bottom of the specimen, or the average of the boundary salt concentrations (Malusis et al., 2001). The membrane efficiency coefficient in terms of the source KCl concentrations, designated as \( \omega_0 \), is given as follows (e.g., Kang and Shackelford, 2011):

\[
\omega_0 = \frac{\Delta P}{\Delta \pi_0} = \frac{\Delta P}{\nu RT \Delta C_0} = \frac{\Delta P}{\nu RT (C_{ob} - C_{at})} = \frac{\Delta P}{-\nu RT C_{at}}
\]  

(2)

where \( \nu \) is the number of ions per molecule of the salt (2 for KCl), \( R \) is the universal gas constant [8.314 J mol⁻¹ K⁻¹], \( T \) is the absolute temperature (293 K in this study corresponding to 20 °C), and \( C_{ob} \) (≥0) and \( C_{at} \) (≥0) are the initial concentrations of KCl (M) in the source solutions introduced across the top and bottom specimen boundaries, respectively. In terms of average KCl concentrations, the membrane efficiency coefficient, \( \omega_{ave} \), is given as follows (e.g., Kang and Shackelford, 2011):

\[
\omega_{ave} = \frac{\Delta P}{\Delta \pi_{ave}} = \frac{\Delta P}{\nu RT \Delta C_{ave}} = \frac{\Delta P}{\nu RT (C_{ob,ave} - C_{at,ave})}
\]  

(3)
where \( C_{\text{ave}} \) and \( C_{\text{ave}} \) are the average KCl concentrations across the top and bottom of the specimen boundaries defined as follows:

\[
C_{t, \text{ave}} = \frac{C_t + C_i}{2} ; \quad C_{b, \text{ave}} = \frac{C_{b} + C_{o}}{2}
\]

and \( C_t \) and \( C_i \) are the measured KCl concentrations via calibration with EC in the circulation outflows from the bottom and top of the specimen boundaries, respectively. Since \( C_{t, \text{ave}} < C_t \) and \( C_{b, \text{ave}} \geq C_{b} \), the magnitude of \( \Delta \pi \) will be greater than that of \( \Delta \pi_{\text{ave}} \). Thus, membrane efficiency coefficients based on source salt concentrations typically are more conservative (lower) than those based on average salt concentrations. However, in the limit as \( \omega \to 1 \), solutes can neither enter nor exit the specimen, such that \( C_{t, \text{ave}} \to C_t \), \( C_{b, \text{ave}} \to C_{b} \), and \( \omega_{\text{ave}} \to \omega \) (Kang and Shackelford, 2009).

2.5. Testing program

Multiple-stage membrane tests were conducted in this study by sequentially circulating four electrolyte solutions containing 4.7, 9.3, 20, and 54 mM KCl across the top boundary of the specimen for each test, while simultaneously circulating DIW across the bottom boundary of the specimen. After steady-state conditions were achieved for each stage of the test, i.e., after \( \Delta \pi \) and EC were constant, the source circulating solution was replaced with the subsequent solution containing a higher concentration of KCl and this process was repeated until all four stages were completed. This procedure resulted in test durations ranging from 96 to 154 d. The two rigid-wall membrane tests designated as RW1 and RW2 corresponded to specimen thicknesses, \( L \), of 16.7 mm and 8.6 mm and specimen total porosities, \( n \), of 0.92 and 0.80, respectively. The two flexible-wall membrane tests designated as FW1 and FW2 corresponded to initial effective stresses, \( \sigma' \), of 34.5 kPa (5 psi) and 103 kPa (15 psi), respectively, and initial values of \( n \) immediately after consolidation, but prior to membrane testing, of 0.95 and 0.84, respectively.

3. Results

3.1. Boundary electrical conductivity values

The measured EC of the circulation outflows versus time for the rigid-wall and flexible-wall membrane tests are presented in Fig. 3. The EC of the outflows from both the top and the bottom of the specimen increased as the solute concentration of the circulation liquid increased. The increase in EC at the bottom of the specimen can be attributed initially to diffusion of any remnant ions contained within the pores of the BPN specimens and eventually to diffusion of Cl\(^-\) and K\(^+\) completely through the specimen and eventually to diffusion of Cl\(^-\) and K\(^+\) through the specimen and eventually to diffusion of Cl\(^-\) and K\(^+\).

The differences in electrical conductivity, \( \Delta EC \), between the steady-state \( EC \) values measured in the circulation outflows across the top and the bottom of the specimens, or \( EC_t \) and \( EC_b \), respectively, relative to the respective limiting values of \( EC \) in the circulation inflows, i.e., \( \Delta EC = EC_t - EC_t \) and \( \Delta EC_b = EC_b - EC_b \), are plotted versus the average salt concentration across the specimen, \( C_{\text{ave}} \), in Fig. 4. The values of \( \Delta EC \) for the top of the specimen are negative, because \( EC_t < EC_t \) due to

![Fig. 3. Measured electrical conductivity across top and bottom boundaries of BPN specimens during membrane testing in (a,b) rigid-wall cells and (c,d) flexible-wall cells.](image-url)
diffusion of $K^+$ and $Cl^-$ ions into the specimen at the top, whereas the values of $\Delta EC$ for the base of the specimen are positive, because $EC_0 - EC_{ob}$ due to diffusion of any remnant ions initially in the pore waters of the specimens and eventually including $K^+$ and $Cl^-$ ions from the bottom of the specimens into the circulation outflows. As shown in Fig. 4, the magnitude of $\Delta EC$ (positive or negative) increases with an increase in $C_{ave}$ for all four tests due to the increase in concentration difference, $\Delta C$ across the specimens during the sequential circulation of higher concentration KCl solutions in the multistage tests. This trend of increasing $\Delta EC$ with increasing $C_{ave}$ is consistent with increased solute diffusion through the specimen due to an increasing concentration gradient across the specimen with increasing $C_{ave}$.

For example, consider the following form of Fick’s first law for steady-state diffusive solute mass flux, $J_d$, in saturated soil (Shackelford and Daniel, 1991):

$$J_d = -nD^* \frac{\Delta C}{L}$$

(5)

where $n$ is the porosity of the soil, $D^*$ is the effective diffusion coefficient of the diffusing chemical species, and $\Delta C$ is the difference in the concentration of chemical species across a specimen of length $L$. As defined by Shackelford and Daniel (1991), $D^*$ is the product of the aqueous-phase diffusion coefficient for a specific chemical species, $D_a$, and the apparent tortuosity factor, $\tau_a$, or $D^* = \tau_a D_a$, where $0 < \tau_a \leq 1$. As further defined by Malusis and Shackelford (2002b), $\tau_a$ equals the product of the matrix tortuosity factor, $\tau_m$ ($0 < \tau_m \leq 1$), representing the portion of the apparent tortuosity factor attributed to the geometry of the interconnected pore structure, and a restrictive tortuosity factor, $\tau_r$ ($0 < \tau_r \leq 1$), resulting from other factors that can affect solute diffusion through soil, such as anion exclusion and increased viscosity of the liquid adjacent to clay particles. In the case where semipermeable membrane behavior is evident, Manassero and Dominiャnij (2003) propose that $\tau_a$ be taken as an inverse linear function of the membrane efficiency coefficient, $\omega$, or $\tau_a = 1 - \omega$. This correlation is supported by the experimental results reported by Malusis and Shackelford (2002a) and Malusis et al. (2013), as well as by the theoretical model proposed by Dominиャnij and Manassero (2012). Thus, as $\omega$ approaches unity corresponding to a perfect membrane, $\tau_a, D^*$ and $J_d$ all approach zero as required by definition for ideal or perfect membrane behavior.

Of all the factors affecting $J_d$, $n$ and $L$ should be relatively constant for a given test specimen. In terms of $D^*$, results of numerous tests have clearly shown that $\omega$ decreases approximately semi-log linearly with increasing $C_{ave}$ (e.g., Shackelford et al., 2003). Thus, $J_d$ also would be expected to increase with increasing $C_{ave}$, since $D^*$ is expected to increase with decreasing $\omega$. Finally, when $C_{ave}$ is defined with respect to the initial source concentrations, such that $C_{ave} = (C_{in} + C_{ob})/2$ and $C_{ob}$ is zero (i.e., DIW), $\Delta C = (C_{in} - C_{ob})$ in Eq. (5) is directly related to $C_{ave}$, or $\Delta C = -C_{in} = 2C_{ave}$. Thus, as $C_{ave}$ increases, $\Delta C$ increases and, therefore, $J_d$ increases.

Based on the aforementioned considerations, as $\Delta C$ across the specimen increases from 4.7 to 54 mM during a given test, $J_d$ across the top and bottom boundaries increases into and out from the specimen, respectively, resulting in a parallel effect on the magnitude of the $\Delta EC$. In addition, the $\Delta EC$ is lower for the tests with lower porosity (i.e., $n = 0.80$ for RW2 vs. $n = 0.92$ for RW1) and for the test with a higher initial effective stress, $\sigma_e$ (i.e., $\sigma_e = 103$ kPa (15 psi) for FW2 vs. $\sigma_e = 34.5$ kPa (5 psi) FW1), also corresponding to a lower initial value of $n$ (i.e., $n = 0.84$ for FW2 vs. $n = 0.95$ for FW1). Finally, the $\Delta EC$ values for FW1 and FW2 are greater than those for RW1 and RW2, which is consistent with the lower membrane efficiencies (higher $D^*$ values) measured for the specimens in the flexible-wall cells, as discussed subsequently.

### 3.2. Chemico-osmotic pressures

The measured chemico-osmotic pressure differences ($-\Delta P > 0$) are presented in Fig. 5. The baseline differential pressure, $-\Delta P_{ave}$ induced during the circulation of DIW along both boundaries (i.e., $C_{in} = C_{ob} = 0$) varied from 6.7 kPa for RW2 to $-5.0$ kPa for FW2. As described in Malusis et al. (2001), possible reasons for a nonzero baseline differential pressure include slight differences in the hydraulic resistance of the porous plastic disks along the top and bottom of the specimen, which would result in different head losses within the disks between the points where the circulation liquids enter the disks and the middle of the disk where the pressure difference is measured, and slightly different flow rates across the top and bottom of the specimen due to slight differences in the machining of the syringes. Therefore, corrected or effective values of the differential pressure, $-\Delta P_{ave} = -\Delta P_{ave} - (\Delta P_h)$, as summarized in Table 3, were used to calculate $C_{ave}$ and $\omega_{ave}$.

The values of $-\Delta P_{ave}$ for test RW1 ($n = 0.92$) increased from 18.4 kPa during the circulation of 4.7 mM KCl across the top to the specimen to 59.0 kPa during the circulation of 54 mM KCl (see Fig. 5a). The $-\Delta P_{ave}$ for RW2 ($n = 0.80$) was higher than that for the RW1, in that the $-\Delta P_{ave}$ for RW2 increased from 21.3 kPa during the circulation of 4.7 mM KCl across the top to the specimen to 59.0 kPa during the circulation of 54 mM KCl for RW2 (see Fig. 5b). The steady-state $-\Delta P_{ave}$ for RW1 and RW2 during the circulation of 54 mM KCl was lower than the aforementioned peak value of $-\Delta P_{ave}$ as a result of post-peak degradation resulting from diffusion of solutes into and subsequently through the specimen (e.g., maximum $-\Delta P_{ave} = 59.0$ kPa versus steady-state $-\Delta P_{ave} = 44.3$ kPa for RW1). This time-dependent, post-peak degradation of $-\Delta P_{ave}$, especially at higher KCl concentrations, is consistent with the same trend previously reported by others (e.g., Malusis and Shackelford, 2002a), and has been attributed to progressive compression of the diffuse double layer surrounding individual clay particles due to increasing salt concentration within the pores resulting from diffusion of KCl from the upper boundary (Fritz, 1986; Malusis and Shackelford, 2002a; Mazzieri et al., 2010; Shackelford and Lee, 2003; Shackelford et al., 2003).

The values of $-\Delta P_{ave}$ for the flexible-wall membrane tests were lower than those for the rigid-wall tests, with $-\Delta P_{ave}$ for FW1 increasing from 12.4 kPa during circulation of 4.7 mM KCl to 14.6 kPa during circulation of 20 mM KCl (see Fig. 5c), and $-\Delta P_{ave}$ for FW2 increasing from 10.3 kPa during circulation of 4.7 mM KCl to 35.7 kPa during circulation of 20 mM KCl (see Fig. 5d). This trend of a slightly lower $-\Delta P_{ave}$ for the flexible-wall versus rigid-wall membrane tests also was observed by Kang and Shackelford (2009) for their tests performed using a specimen of a GCL, and was attributed to the different stress conditions and volume control conditions in the two types of cells.
Another possible explanation for the difference in membrane performance of the BPN specimens in the rigid-wall cells versus the flexible-wall cells may be the circumstances under which the BPN specimens were initially exposed to water. In the rigid-wall cell, the BPN specimens were permeated with water in the confined (fixed volume) cell that restricted swelling of the super absorbent polymer portion of the BPN and limited flushing of the excess low molecular weight polymer from the system, resulting in smaller hydraulically active pores (i.e., pores are smaller and more pores are clogged with excess low molecular weight polymer that exists in the BPN), as described by Scalia (2012). In contrast, the BPN specimens in the flexible-wall cells were permeated with water under an essentially constant, average value for \( \sigma' \) of 34.5 kPa (5 psi) or 103 kPa (15 psi), but the specimens were able to swell due to the propensity for montmorillonite and the super-absorbent polymer portion of the BPN to absorb water. This swelling resulted in larger hydraulically active pores and additional flushing of the excess low molecular weight polymer from the system and, therefore, less clogging of pores prior to the membrane testing stage of the test.

Fig. 5. Measured chemico-osmotic pressure differences across BPN specimens tested in rigid-wall cells (a,b) and flexible-wall cells (c,d) (\( n = \) initial specimen porosity; \( \sigma_c, u_{bp}, \) and \( \sigma' = \) confining stress, back pressure, and initial effective stress before membrane testing, respectively).
of system pressure. However, the calculated and differential pressures returned to the same values prior to loss of system pressure. Upon restoration of the system pressure, both the in-line and differential pressures returned to the same values prior to loss of system pressure. However, the calculated $\omega_b$ and $\omega_{ave}$ were lower than the expected values, in that the values of $\omega_b$ and $\omega_{ave}$ for test FW2 were expected to be greater than the same respective values for test FW1, because test FW2 was conducted at a higher effective stress than test FW1 [103 kPa (15 psi) vs. 34.5 kPa (5 psi), Table 3].

The values of $\omega_b$ and $\omega_{ave}$ for test FW2 with the 4.7 mM KCl solution are anomalous due to an unexpected loss of system pressure 14 d into the circulation of 4.7 mM KCl resulting in loss of the applied cell pressure. Upon restoration of the system pressure, both the in-line and differential pressures returned to the same values prior to loss of system pressure. However, the calculated $\omega_b$ and $\omega_{ave}$ were lower than the expected values, in that the values of $\omega_b$ and $\omega_{ave}$ for test FW2 were expected to be greater than the same respective values for test FW1, because test FW2 was conducted at a higher effective stress than test FW1 [103 kPa (15 psi) vs. 34.5 kPa (5 psi), respectively].

Finally, the approximate semi-log linear decrease in $\omega_b$ and $\omega_{ave}$ with increasing $C_{ave}$, which as previously noted is consistent with the results of several other membrane studies involving traditional sodium bentonite and KCl solutions, suggests that the mechanisms of the membrane behavior for the BPN specimens are consistent with those previously associated with traditional sodium bentonite, i.e., physico-chemical interactions between the salts in the pores of the diffuse double layers (DDL) surrounding the BPN particles, such that increase in concentration results in progressively greater collapse of the DDL, progressively larger pores, and subsequent decrease in observed membrane behavior (e.g., see Kang and Shackelford, 2011; Malusis and Shackelford, 2002a). If the mechanism for solute restriction had been physical clogging of the pores by excess polymer that was not flushed from the specimens during membrane testing, then this trend of decreasing $\omega_b$ and $\omega_{ave}$ with increasing log $C_{ave}$ would not necessarily have been expected, i.e., unless the physico-chemical

3.3. Membrane efficiency coefficients

The values of $\omega_b$ and $\omega_{ave}$ for the membrane tests based on Eqs. (2) and (3), respectively, are shown as a function of $C_{ave} (= \Delta C_\omega/2)$ in Fig. 6. With the exception of the values of $\omega_b$ and $\omega_{ave}$ for test FW2 with the 4.7 mM KCl solution, the results are consistent with previous results (e.g., Kang and Shackelford, 2009; Malusis and Shackelford, 2002a) in that (1) the values of $\omega_{ave}$ are generally greater than the values of $\omega_b$ for a given value of $C_{ave}$, (2) the values of both $\omega_b$ and $\omega_{ave}$ decrease approximately semi-log linearly with increasing $C_{ave}$, (3) the values of $\omega_b$ or $\omega_{ave}$ from the rigid-wall tests are greater than those from the flexible-wall tests, and (4) the values of $\omega_b$ or $\omega_{ave}$ are greater for specimens at higher initial effective stresses, $\sigma'$, and specimens with lower initial porosities, $n$.

The values of $\omega_b$ and $\omega_{ave}$ for test FW2 with the 4.7 mM KCl solution are anomalous due to an unexpected loss of system pressure 14 d into the circulation of 4.7 mM KCl resulting in loss of the applied cell pressure. Upon restoration of the system pressure, both the in-line and differential pressures returned to the same values prior to loss of system pressure. However, the calculated $\omega_b$ and $\omega_{ave}$ were lower than the expected values, in that the values of $\omega_b$ and $\omega_{ave}$ for test FW2 were expected to be greater than the same respective values for test FW1, because test FW2 was conducted at a higher effective stress than test FW1 [103 kPa (15 psi) vs. 34.5 kPa (5 psi), respectively].

Finally, the approximate semi-log linear decrease in $\omega_b$ and $\omega_{ave}$ with increasing $C_{ave}$, which as previously noted is consistent with the results of several other membrane studies involving traditional sodium bentonite and KCl solutions, suggests that the mechanisms of the membrane behavior for the BPN specimens are consistent with those previously associated with traditional sodium bentonite, i.e., physico-chemical interactions between the salts in the pores of the diffuse double layers (DDL) surrounding the BPN particles, such that increase in concentration results in progressively greater collapse of the DDL, progressively larger pores, and subsequent decrease in observed membrane behavior (e.g., see Kang and Shackelford, 2011; Malusis and Shackelford, 2002a). If the mechanism for solute restriction had been physical clogging of the pores by excess polymer that was not flushed from the specimens during membrane testing, then this trend of decreasing $\omega_b$ and $\omega_{ave}$ with increasing log $C_{ave}$ would not necessarily have been expected, i.e., unless the physico-chemical

### Table 3

Results of membrane testing on BPN using rigid-wall (RW) and flexible-wall (FW) cells.

<table>
<thead>
<tr>
<th>Test designation</th>
<th>Specimen porosity, $n$</th>
<th>Initial effective stress, $\sigma'$ [kPa (psi)]</th>
<th>Source KCl concentration, $C_{ave}$ (mM)</th>
<th>Maximum chemico-osmotic pressure difference, $\Delta\pi_b$ (kPa)</th>
<th>Effective (measured) chemico-osmotic pressure difference, $-\Delta\pi_b$ (kPa)</th>
<th>Membrane efficiency coefficient @ steady-state</th>
</tr>
</thead>
<tbody>
<tr>
<td>RW1</td>
<td>0.92</td>
<td>NA</td>
<td>4.7</td>
<td>22.9</td>
<td>21.9</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>45.3</td>
<td>43.6</td>
<td>30.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>97.4</td>
<td>83.2</td>
<td>41.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>54</td>
<td>263</td>
<td>206</td>
<td>44.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>97.4</td>
<td>88.0</td>
<td>47.5</td>
</tr>
<tr>
<td>RW2</td>
<td>0.80</td>
<td>NA</td>
<td>4.7</td>
<td>22.9</td>
<td>22.8</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>45.3</td>
<td>44.5</td>
<td>34.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>97.4</td>
<td>88.0</td>
<td>47.5</td>
</tr>
<tr>
<td>FW1</td>
<td>0.94–0.95</td>
<td>34.5 (5)</td>
<td>4.7</td>
<td>22.9</td>
<td>19.3</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>45.3</td>
<td>32.2</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>97.4</td>
<td>60.7</td>
<td>13.4</td>
</tr>
<tr>
<td>FW2</td>
<td>0.78–0.84</td>
<td>103 (15)</td>
<td>4.7</td>
<td>22.9</td>
<td>22.5</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>45.3</td>
<td>37.6</td>
<td>17.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>97.4</td>
<td>70.0</td>
<td>24.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>54</td>
<td>263</td>
<td>163</td>
<td>26</td>
</tr>
</tbody>
</table>

- Based on difference in initial (source) KCl concentrations.
- Based on difference in average, boundary KCl concentrations.

### Fig. 6

Steady-state membrane efficiency coefficients of BPN specimens during membrane testing in rigid-wall cells (RW1, RW2) and flexible-wall cells (FW1, FW2) as a function of average source salt (KCl) concentration across the specimen: (a) $\omega_b$ values based on initial (source) boundary concentrations, $C_{ave}$; (b) $\omega_b$ values based on average boundary concentrations, $C_{ave}$.
behavior of the polymer is the same as that of sodium bentonite. Instead, physical pore clogging by excess polymer likely would have resulted in an observed membrane behavior that was more independent of the \( C_{\text{inc}} \). Thus, the similarity in the membrane behavior of the BPN specimens with that previously shown for sodium bentonite under the same conditions suggest that the mechanism responsible for the membrane behavior observed for the BPN specimens in this study is that same as that previously reported for specimens of sodium bentonite.

3.4. Volume changes

As described in Kang and Shackelford (2009), although drainage was not allowed to occur during the circulation periods of the membrane tests conducted using the flexible-wall cells, drainage from the specimen did occur during the brief (~5 min) refilling and sampling periods of the test when the valves to the reservoirs and the cell (valves 1, 3, 6 and 7 in Fig. 2a) were simultaneously and temporarily opened to re-establish the backpressure. Kang and Shackelford (2009) attributed
the drainage to an increment in effective stress resulting from physico-chemical interactions between the pore water in the bentonite and the individual particles of bentonite. Theoretically, an increase in salt concentration in the pore water results in decrease in the repulsive electrical forces relative to the adsorptive forces between individual soil particles (i.e., so-called $R - A$ effect), such that the effective stress in the soil also increases resulting in compression of the soil (i.e., provided drainage is allowed). Such an increase in salt (KCl) concentration in the pore water is consistent with diffusion of the KCl into the specimens (e.g., Mitchell, 1976; Di Maio, 1996). Such an increase in salt concentration in the pore water results in decrease in the repulsive electrical forces relative to the adsorptive forces between individual soil particles (i.e., so-called $R - A$ effect), such that the effective stress in the soil also increases resulting in compression of the soil (i.e., provided drainage is allowed). Such an increase in salt (KCl) concentration in the pore water is consistent with diffusion of the KCl into the specimens (e.g., Mitchell, 1976; Di Maio, 1996). Such an increase in salt concentration in the pore water results in decrease in the repulsive electrical forces relative to the adsorptive forces between individual soil particles (i.e., so-called $R - A$ effect), such that the effective stress in the soil also increases resulting in compression of the soil (i.e., provided drainage is allowed).

Accordingly, volume changes were recorded for the membrane tests conducted in the flexible-wall cell using the cell-water accumulator attached to the flexible-wall cell (see Fig. 2c). The resulting measured values of incremental volume change, $\Delta V$, cumulative volumetric strain, $\sum (-\Delta V)/V_o$, are presented in Fig. 7 and the resulting differences in bulk specimen porosities are indicated in Table 4. The $\Delta V$ values generally were negative, indicating that the volume of the specimen decreased during the test (i.e., a final volume less than the initial volume). The magnitude of $-\Delta V$ increased with increasing concentration of KCl. For FW1 with $\sigma_w = 34.5$ kPa (5 psi), $-\Delta V$ was less than $+0.5$ ml during the circulation of DIW and 4.7 mM KCl, whereas $-\Delta V$ was as much as 3.2 ml during the circulation of 54 mM KCl (Fig. 7a). The $\Sigma (-\Delta V)$ was 46.3 ml (Fig. 7c), which corresponds with a cumulative volumetric strain, $\Sigma (-\Delta V)/V_o$, of 25% (see Fig. 7e). The incremental volumetric strains (not shown) for FW1 were less than $-0.5$ during the circulation of DIW, 4.7 mM KCl, and 9.3 mM KCl, but increased to as much as 1.7% during the circulation of 54 mM KCl, which is consistent with an increasing $R - A$ effect with an increasing salt concentration.

In contrast, for FW2 with $\sigma_w = 103$ kPa (15 psi), $-\Delta V$ was as much as $-2$ ml during circulation of DIW and 4.7 mM KCl, but $-\Delta V$ was less than 1.5 ml during circulation of 54 mM KCl (Fig. 7b). During the circulation of both DIW and the 4.7 mM KCl solution after the loss of cell pressure, the specimen swelled likely as a result of the affinity for water of the superabsorbent polymer portion of the BPN. However, during the remainder of the test, the specimen compressed, i.e., volume of the specimen decreased, which is similar to the results for FW1 and consistent with the $R - A$ effect with increasing salt concentrations. The $\Sigma (-\Delta V)$ was 20.7 ml (Fig. 7d), which corresponds to a value for $\Sigma (-\Delta V)/V_o$ of 27% (see Fig. 7f). The incremental volumetric strains (not shown) were as much as $-2.5$ during the circulation of DIW and 4.7 mM KCl after the loss of cell pressure, were generally less than 1.0% during the circulation of 9.3 mM KCl and 20 mM KCl, and then increased to as much as 2.0% during the circulation of 54 mM KCl.

### 3.5. Limits on membrane behavior

As previously described, an approximately semi-log linearly relationship between $\omega$ and $C_{ave}$ has been shown to exist on the basis of numerous experimental results (e.g., see Shackelford et al., 2003). This relationship is illustrated schematically in Fig. 8, where the slope of relationship is defined as the membrane index, $I_m$, and the limiting values of $C_{ave}$ are defined as the threshold concentration, $C_{ave, pm}$, corresponding to the concentration below which membrane behavior occurs (i.e., $\omega > 0$ for $C_{ave} < C_{ave, pm}$), and the perfect membrane concentration, $C_{ave, pm}$, corresponding to the concentration below which the material behaves as a perfect membrane (i.e., $\omega = 1$ for $C_{ave} < C_{ave, pm}$). As depicted in Fig. 8, the trend between $\omega$ versus $C_{ave}$ in reality likely becomes non-semi-log linear as the concentrations approach $C_{ave, pm}$ and $C_{ave, pm}$. However, the exact functional forms of this non-semi-log linear behavior are unknown, such that semi-log linear regressions can be used as a first approximation (Shackelford et al., 2003).

Accordingly, semi-log linear regressions to the data presented in Fig. 6 are shown in Fig. 9 along with the corresponding coefficients of determination, $r^2$, and the resulting regression coefficients are summarized in Table 5. The $r^2$ values indicate that the regressions are reasonable ($r^2 \geq 0.94$) over the range of measured data with somewhat better regressions based on the results of the rigid-wall tests (i.e., $r^2 \geq 0.99$) versus those for the flexible-wall tests (i.e., $r^2 \geq 0.94$). The threshold concentrations, $C_{ave, pm}$, range from 25 mM for FW1 based on $\omega_0$ to 68 mM for RW2 based on $\omega_ave$. The values for the membrane index, $I_m$, ranged from 0.60 to 0.67 for tests RW1 based on $\omega_ave$ and RW2 based on $\omega_ave$, respectively, whereas the $I_m$ values ranged from 0.38 to 0.55 for tests FW2 based on $\omega_0$ and FW1 based on $\omega_ave$, respectively. In general, the threshold concentrations based on the two flexible-wall tests were lower than those based on the two rigid-wall tests. The higher threshold concentrations for the rigid-wall tests indicate that the BPN under these test conditions will exhibit membrane behavior at higher $C_{ave}$, which is advantageous in practical applications. The increased performance of BPN in the rigid-wall cells relative to BPN in the flexible-wall cells cannot be attributed to the porosity alone, because the porosities of the RW and FW tests were similar (RW1 similar to FW1 and RW2 similar to FW2; see Table 5).

### 4. Discussion

#### 4.1. Comparison of the limits to membrane behavior

For comparison to the limits of membrane behavior for the BPN specimens as summarized in Table 5, the results of semi-log linear

---

**Table 4**

Bulk porosities of BPN specimens during membrane testing in flexible-wall (FW) cells.

<table>
<thead>
<tr>
<th>Stage of test</th>
<th>Test designation</th>
<th>FW1 [$\sigma_w = 34.5$ kPa (5 psi)]</th>
<th>FW2 [$\sigma_w = 103$ kPa (15 psi)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>After consolidation</td>
<td>0.95</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>After DIW circulation</td>
<td>0.95</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>After 4.7 mM KCl circulation</td>
<td>0.95</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>After 9.3 mM KCl circulation</td>
<td>0.95</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>After 20 mM KCl circulation</td>
<td>0.95</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>After 54 mM KCl circulation</td>
<td>0.94</td>
<td>0.78</td>
<td></td>
</tr>
</tbody>
</table>

Note: $\sigma_w$ is initial effective stress in specimen after consolidation but prior to DIW circulation.

---

**Figure 8.** Schematic illustration of limiting concentrations and slope of approximate semi-logarithmic relationship between membrane efficiency, $\omega$, and average boundary salt concentration (redrawn after Shackelford et al., 2003). [Note: $\omega_{ave}$ = reference membrane efficiency coefficient at log $C_{ave} = 0$; $C_{ave, pm}$ = threshold concentration corresponding to $\omega = 0$; $C_{ave, pm}$ = perfect membrane concentration corresponding to $\omega = 1$; $I_m$ = the membrane index].
regressions to the measured values of $\omega$ versus logarithm of $C_{\text{ave}}$ reported by Kang and Shackelford (2009) and Malusis and Shackelford (2002a) for traditional GCL containing sodium bentonite are summarized in Table 6. The threshold concentrations, $C_{\text{ave},L}$, for the BPN specimens were greater than those for the GCL specimens tested in both rigid-wall cells and flexible-wall cells. For example, the highest $C_{\text{ave},L}$ determined for a BPN specimen in a rigid-wall cell of 67.7 mM is 1.41 times greater than the value of 48.0 mM for the GCL specimen, whereas the highest value for $C_{\text{ave},L}$ of 62.2 mM determined for a BPN specimen in a flexible-wall cell with $\sigma = 103$ kPa (15 psi) is 2.38 times the value of 26.1 mM reported for the GCL specimen tested under similar stress conditions.

As previously mentioned, the higher $C_{\text{ave},L}$ values for the BPN compared to the GCL suggest that the BPN would presumably exhibit membrane behavior at higher concentrations. The superior membrane performance of the BPN compared to a GCL is likely due, in part, to the superabsorbent polymer portion of the BPN resulting in higher swell and smaller hydraulically active pores resulting in enhanced membrane behavior (Scalia, 2012). Also, clogging of any hydraulically active pores by excess low molecular weight polymer also may have contributed to the enhanced membrane behavior of the BPN relative to that of a GCL containing traditional bentonite (Scalia, 2012). However, the long-term sustainability of the possible contribution of any excess low molecular weight polymer to the enhanced membrane behavior of the BPN is unknown. Additional studies on BPN specimens that have been flushed to remove the excess low molecular weight polymer may answer this issue, although available evidence (e.g., Scalia, 2012) indicates that several years likely will be required to flush any excess polymer prior to membrane testing, i.e., assuming flushing by permeation.

### 4.2. Comparison of membrane efficiency coefficients

The measured values of $\omega$ from this study are compared with those previously reported for tests conducted using GCLs (Kang and Shackelford, 2009; Malusis and Shackelford, 2002a) in Fig. 10. For the rigid-wall membrane tests performed using the BPN, values of both $\omega_0$ and $\omega_{\text{ave}}$ are higher than those reported by Malusis and Shackelford (2002a) for a GCL that was 8-mm thick (i.e., $L = 8$ mm) with a lower porosity of 0.74 (see Fig. 10a,b). Also, values of both $\omega_0$ and $\omega_{\text{ave}}$ for the flexible-wall membrane tests conducted in this study are higher than those reported by Kang and Shackelford (2009) for a GCL under similar effective confining stresses of 34.5 kPa (5 psi) and 103 kPa (15 psi) (see Fig. 10c,d). In addition, unlike the GCL specimens that were flushed (leached) of soluble salts by permeation with DIW prior to membrane testing to enhance the potential for significant membrane efficiency, the higher values of $\omega_0$ and $\omega_{\text{ave}}$ for the tests performed in this study using the BPN were achieved without flushing (leaching) of soluble salts from the BPN specimens prior to membrane testing. Thus, the BPN specimens not only reflected greater membrane efficiencies than previously reported for specimens of a GCL containing a traditional bentonite, but also did so presumably under more disadvantageous initial conditions in terms of soluble salts. However, the long-term membrane behavior of a flushed BPN specimen may be temporarily variable as the excess low molecular weight polymer may be removed from the material with time resulting in a decrease in the observed membrane behavior. Thus, even though the trends in the observed membrane behaviors with increasing KCl concentrations for the BPN specimens shown in Fig. 10 are similar to those for the GCL, suggesting that the mechanisms responsible for the membrane

---

### Table 5

<table>
<thead>
<tr>
<th>Test designation</th>
<th>Specimen porosity, n</th>
<th>Initial effective stress, $\sigma$ [kPa (psi)]</th>
<th>Definition of membrane efficiency coefficient$^a$</th>
<th>Regression results: $\omega = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</th>
<th>Limiting average concentrations, $C_{\text{ave}}$ (mM)</th>
<th>$\omega = 0$, $C_{\text{ave},L}$ $\omega = 1$, $C_{\text{ave},P}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RW1</td>
<td>0.92</td>
<td>NA</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
</tr>
<tr>
<td>RW2</td>
<td>0.80</td>
<td>NA</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
</tr>
<tr>
<td>FW1</td>
<td>0.94–0.95</td>
<td>34.5 (5)</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
</tr>
<tr>
<td>FW2</td>
<td>0.78–0.84</td>
<td>103 (15)</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
<td>$\omega_{\text{ave}} = \omega_{\text{ref}} - I_n \cdot \log C_{\text{ave}}$</td>
</tr>
</tbody>
</table>

$^a$ $\omega_{\text{ave}}$ = membrane efficiency coefficient based on average (source) salt concentrations; $\omega_{\text{ave}} = \omega_{\text{ave}}$ = membrane efficiency coefficient based on average boundary salt concentrations.

$^b$ $\omega_{\text{ave}}$ = reference membrane efficiency coefficient corresponding to $\log C_{\text{ave}} = 0$; $I_n$ = the membrane index as defined by Shackelford et al. (2003) and illustrated schematically in Fig. 8.
behaviors in both the BPN and the GCL are also similar, additional long-term tests on flushed BPN specimens may be required to more fully understand the behavior of the BPN under these conditions.

The ratios of the values of $\omega$ for the BPN specimens measured in this study to the previously reported values of $\omega$ for the GCL specimens, or $R_{\omega, \text{BPN/GCL}}$, are shown in Fig. 11. Because of slight differences between the values of $C_{\text{ave}}$ used in the previous studies for the GCL specimens, the values of $\omega$ used to calculate the values of $R_{\omega, \text{BPN/GCL}}$ shown in Fig. 11 were based on the regressed semi-log linear expressions given in Tables 4 and 5. The resulting values of $R_{\omega, \text{BPN/GCL}}$ should be reasonably accurate given the high values of $r^2$ for the regressions as previously noted. Several observations are apparent based on the results shown in Fig. 11.

First, regardless of type of cell (i.e., rigid-wall vs. flexible-wall) or the basis for calculating $\omega$ (i.e., $\omega_b$ vs. $\omega_{\text{ave}}$), the values of $R_{\omega, \text{BPN/GCL}}$ increase with increasing $C_{\text{ave}}$. This trend occurs as a result of the trend of decreasing $\omega$ with increasing $C_{\text{ave}}$ (e.g., Fig. 10). Thus, the improvement

<table>
<thead>
<tr>
<th>Type of cell</th>
<th>Porosity, $n$</th>
<th>Initial effective stress, $\sigma'$ [kPa (psi)]</th>
<th>Definition of membrane efficiency coefficient$^a$</th>
<th>Regression results for: $\omega = \omega_{\text{ref}} - I_0 \cdot \log C_{\text{ave}}$</th>
<th>Limiting average concentrations, $C_{\text{ave}}$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid-wall$^b$</td>
<td>0.74</td>
<td>NA</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ref}}$</td>
<td>$I_0$</td>
</tr>
<tr>
<td>Flexible-wall$^c$</td>
<td>0.79–0.81</td>
<td>34.5 (5)</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ref}}$</td>
<td>0.81</td>
</tr>
<tr>
<td>Flexible-wall$^d$</td>
<td>0.79–0.80</td>
<td>103 (15)</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ref}}$</td>
<td>0.83</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Membrane Efficiency Coefficient$^a$</th>
<th>Membrane Efficiency Coefficient$^a$</th>
<th>Membrane Efficiency Coefficient$^a$</th>
<th>Membrane Efficiency Coefficient$^a$</th>
<th>Membrane Efficiency Coefficient$^a$</th>
<th>Membrane Efficiency Coefficient$^a$</th>
<th>Membrane Efficiency Coefficient$^a$</th>
<th>Membrane Efficiency Coefficient$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
</tr>
<tr>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
</tr>
<tr>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
<td>$\omega_{\text{ave}}$</td>
</tr>
</tbody>
</table>

$^a$ $\omega_{\text{ave}}$ = membrane efficiency coefficient based on initial (source) salt concentrations; $\omega_{\text{ave}}$ = membrane efficiency coefficient based on average boundary salt concentrations.

$^b$ $\omega_{\text{ave}}$ = reference membrane efficiency coefficient corresponding to log $C_{\text{ave}} = 0$; $I_0$ = the membrane index as defined by Shackelford et al. (2003) and illustrated schematically in Fig. 8.

$^c$ From Malusis and Shackelford (2002a).

$^d$ From Kang and Shackelford (2011).
Changes that occur during the tests conducted using rigid-wall cells, as previously described (e.g., see Fig. 7).

Overall, the BPN specimens exhibited substantially improved membrane performance relative to the GCL specimens, with values of \( R_{\text{m, BPN/GCL}} \) ranging from 128 to 294% for tests conducted using rigid-wall cells and from 109 to 433% for tests conducted using flexible-wall cells. There are at least two possible mechanistic explanations for the improved performance of the BPN compared to the sodium bentonite in a GCL (e.g., Scalia, 2012; Scalia et al., 2011). First, the superabsorbent polymer portion of the BPN swells in low EC solutions, resulting in osmotic swelling and smaller hydraulically active pores than those in the sodium bentonite typically found in GCLs. Second, an excess of low molecular weight polymer in the BPN during the manufacturing process resulting from incomplete polymerization (chain termination) likely results in clogging the interconnected pores of the BPN. Regardless of the exact mechanisms, the BPN evaluated in this study exhibited substantially improved membrane behavior relative to the GCL containing traditional sodium bentonite.

4.3. Comparison of volume changes

The extent of the volume changes that occurred with the BPN specimens in this study was far greater than that previously reported for membrane tests in flexible-wall cells using GCL containing traditional bentonites (Kang and Shackelford, 2009, 2011). For example, the cumulative volume change, \( \Sigma (\Delta V) \), for a traditional GCL tested at \( \sigma' = 34.5 \text{ kPa} \) (5 psi) as reported by Kang and Shackelford (2011) was 5.98 mL, whereas the \( \Sigma (\Delta V) \) for BPN tested at the same effective stress in this study was 46.3 mL, or almost eight times greater. However, similar to the traditional GCL, the \( \Sigma (\Delta V) \) for the BPN decreased with increased \( \sigma' \) (e.g., \( \Sigma (\Delta V) = 20.7 \text{ mL versus 46.3 mL for } \sigma' = 103 \text{ kPa (15 psi)} \) and \( \sigma' = 34.5 \text{ kPa (5 psi)} \), respectively).

The volume changes observed for the traditional GCL were attributed to compression of the diffuse double layers as the concentration of the salts in the pore water increased (Kang and Shackelford, 2009). In addition to this possibility, the increased volume change of the BPN may be attributed, in part, to the unique properties of the BPN. The initial volume, \( V_0 \), of the BPN specimen was greater than that of the GCL (e.g., 191 mL versus 75.5 mL, respectively) for tests conducted at \( \sigma' = 34.5 \text{ kPa (5 psi)} \), because of the greater swelling of the BPN versus a traditional GCL (\( 73 \text{ mL/g versus 25 to 35 mL/g} \)). This increased swelling for the BPN is a result of the superabsorbent polymer portion of the BPN (Scalia et al., 2011), which likely caused greater volume changes throughout the membrane test compared to that of a GCL.

The swelling capacity of the superabsorbent polymer portion of the BPN is affected by the applied load (i.e., \( \sigma' \)) and the salt concentration in the pores (Buchholz and Graham, 1998). In addition, for superabsorbent polymers, the effect of the salt concentration in the pores on the swelling capacity decreases with increasing load (Buchholz and Graham, 1998). These properties of superabsorbent polymer correlate with the observed volume changes of the BPN. For example, for the test conducted at the higher \( \sigma' \) (i.e., \( \sigma' = 103 \text{ kPa (15 psi)} \) for FW 2), the specimen swelled less resulting in a lower \( V_0 \) (75 mL versus 191 mL for FW2 and FW1, respectively), and consequently less volume change throughout the test (i.e., \( \Sigma (\Delta V) = 20.7 \text{ mL versus 46.3 mL for FW2 vs. FW1, respectively} \)). In addition, the volume change of the BPN decreased with increasing \( \sigma' \). For example, the value of \( \Sigma (\Delta V) \) was less than 1.5 mL during circulation of 54 mM KCI for FW2 \( [\sigma' = 103 \text{ kPa (15 psi)}] \), whereas for FW1 \( [\sigma' = 34.5 \text{ kPa (5 psi)}] \) was as much as 3.2 mL during the circulation of 54 mM KCl.

4.4. Effect of effective stress and boundary salt concentration

The ratio of the membrane efficiency coefficient at any \( \sigma' \), relative to that at \( \sigma' = 34.5 \text{ kPa (5 psi)} \), or \( R_{\text{m, BPN/GCL}} = \omega_{\sigma} \sigma' / \omega_{\sigma} \sigma' = 34.5 \text{ kPa (5 psi)} \), is plotted as a function of \( C_{\text{ave}} \) for the BPN and a GCL (Kang and...
specimen. However, this increase is greater with higher average source concentrations across the specimen, \(C_{\text{ave}}\) (Kang and Shackelford, 2011). In addition, the effect of increasing \(\sigma'\) tends to offset the effect of an increase in \(C_{\text{ave}}\). As described in Kang and Shackelford (2011), the pore sizes decrease with increasing \(\sigma'\), which tends to offset the effect of an increase in \(C_{\text{ave}}\) on the membrane efficiency. The lower increase in values of \(R_{\text{def}}\) for the BPN specimens relative to that of the GCL suggests that the BPN is less sensitive to \(C_{\text{ave}}\) than the GCL, likely due, in part, to the differences in the compressibility of the BPN relative to that of the GCL. As previously discussed, the compressibility of the BPN is greater than that of the GCL as a result of the superabsorbent polymer portion of the BPN.

5. Conclusions

The results of a laboratory experimental program to determine the existence of semipermeable membrane behavior for a polycrylate modified bentonite material known as a bentonite polymer nanocomposite, or BPN, were presented. The results indicated that the BPN exhibited membrane behavior when exposed to KCl with initial concentration differences ranging from 4.7 to 54 mM. A comparison of the measured membrane behavior for the BPN with that previously reported for sodium bentonite contained in a GCL showed that the BPN exhibited greater membrane behavior.

For example, the membrane efficiency coefficient, \(\omega\), for a specimen of the BPN with a porosity, \(n\), of 0.92 contained within a rigid-wall cell was 0.43 based on an initial concentration difference of 20 mM KCl, whereas \(\omega\) for a GCL specimen with a lower (more favorable) porosity of 0.74 also contained within a rigid-wall cell and subjected to the same initial concentration difference was only 0.30. Similarly, the \(\omega\) for a specimen of the BPN contained within a flexible-wall cell at an initial effective stress of 34.5 kPa (5 psi) and subjected to an initial concentration difference of 9.3 mM KCl was 0.32, whereas \(\omega\) for a GCL specimen also contained within a flexible-wall cell at the same initial effective stress but subjected to a slightly lower (more favorable) concentration difference of 8.7 mM KCl was only 0.20. Overall, the measured \(\omega\) values for the BPN specimens ranged from 109% to 433% of those previously reported for the specimens containing traditional sodium bentonite, depending on the initial porosity or initial effective stress of the specimen, the concentration of KCl, and the type of test cell (rigid vs. flexible), despite the BPN specimens not being flushed of soluble salts prior to membrane testing as in the case of the specimens containing sodium bentonite. Finally, the BPN exhibited membrane behavior over a wider range in concentrations than those for the GCL. Thus, relative to values of \(\omega\) previously reported for GCL specimens containing a traditional sodium bentonite, the BPN evaluated in this study exhibited improved membrane behavior under conditions that presumably were more adverse with respect to soluble salts to those for the GCL specimens. However, additional testing of the BPN is warranted to better understand the long-term behavior of the BPN and to investigate the sustainability of the membrane behavior with other solutions containing divalent cations such as CaCl₂.

Acknowledgment

Financial support for this project, which was a collaboration among Colorado State University (CSU), the University of Wisconsin-Madison (UW-Madison), and Colloid Environmental Technologies Co. (CETCO), was provided by the U.S. National Science Foundation (NSF), Arlington, VA under Grant No. CMMI-0757815. The opinions expressed in this paper are solely those of the authors and are not necessarily consistent with the policies or opinions of the NSF. The authors thank CETCO for providing the bentonites used in this study, the assistance of all the collaborators including Craig Benson, Tuncer Edil, and Joe Scalia at UW-Madison and Mike Donovan and Jerry Darlington of CETCO, Kristin Sample-Lord and Catherine Soo Jung Hong of CSU for assistance with the membrane tests, and Thomas Borch of CSU for the use of the ion chromatograph for anion concentration analyses.

References


