



Research paper

# Improving membrane performance via bentonite polymer nanocomposite

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## 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,  $\omega$ , for the BPN specimens were greater than those previously reported for specimens containing sodium bentonite under similar testing conditions. For example, 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), 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.

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## 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  $\text{Ca}^{2+}$ -for- $\text{Na}^{+}$  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; Eglhoffstein, 2001; James et al., 1997; Jo et al., 2001, 2004; Meer and Benson, 2007; Shackelford et al., 2000). The  $\text{Ca}^{2+}$  is derived from surrounding soils, and migrates into the GCL usually in response to hydraulic (suction) and/or chemical (diffusive) gradients.

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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 bentonites 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 organophilic 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 polyacrylamides) 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 Pappaspyrides, 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 Fisher Scientific, Rochester, NY). The pH and electrical conductivity,  $EC$ , of the solutions were measured using a pH meter (Accumet® AB15 meter; Fisher Scientific Co., 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 ( $Cl^-$ ) concentrations, and inductively coupled plasma-atomic emission spectrometry (IRIS® Advantage/1000 ICAP Spectrometer, Thermo Jarrel Ash Co., Franklin, MA) was used to measure potassium ( $K^+$ ) 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

**Table 1**  
Chemical properties of liquids used in study.

Liquid	Concentration		pH	Solution electrical conductivity, $EC_o$ (mS/m), @ 25 °C
	(mM)	(mg/L)		
De-ionized water	0	0	7.35	<0.1
KCl solutions	4.7	350	5.31	71
	9.3	690	5.20	139
	20	1500	5.28	276
	54	4000	5.24	661

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 2**  
Index properties of the conventional sodium bentonite used to create the bentonite polymer nanocomposite (BPN) and the BPN evaluated in this study.

Property	Standard	Average value or type [no. trials]	
		Sodium bentonite	Bentonite polymer nanocomposite (BPN)
Specific gravity	ASTM D 854	2.76	2.67
Soil classification	ASTM D 2487	CH [3]	CH [3] <sup>a</sup>
Percent clay (%)	ASTM D 422	78 [3]	96 [3]
Liquid limit, $LL$ (%)	ASTM D 4318	422 [3]	255 [2]
Plasticity index, $PI$ (%)	ASTM D 4318	384 [3]	NA
Swell index, $SI$ (mL/2 g)	ASTM D 5890	22 [3]	73 [5]
Solution retention capacity, SRC (mL/1 g)	<sup>b</sup>	7.3 [3]	11.0 [6]

NA = Not applicable.

<sup>a</sup> Based on grain-size distribution.

<sup>b</sup> Based on procedures in Lee and Shackelford (2005c) with centrifuge speed at 3000 rpm.

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