Variability in Membrane Behavior of Geosynthetic Clay Liners

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ABSTRACT

Geosynthetic clay liners (GCLs) comprising sodium bentonite (NaB) have been shown to exhibit significant membrane behavior, whereby contaminants are restricted from passing through the clay due to electrostatic repulsion, potentially enhancing long-term containment performance. Recent membrane behavior research has focused on evaluating membrane efficiency (ω) of enhanced bentonites (e.g., bentonite polymer composites) and testing under more complex conditions (e.g., elevated temperatures, unsaturated conditions), often drawing comparisons with earlier published data on NaB-GCLs. However, the validity of comparing NaB-GCL results across studies and from earlier work remains unclear. No prior study has evaluated the variability in reported ω values for the same type of NaB-GCL manufactured in different years. In this study, multistage membrane behavior tests were performed on specimens of the same NaB-GCL type manufactured at different dates. One specimen (GCL1) was taken from a NaB-GCL roll manufactured in the last five years. Another specimen (GCL2) was taken from a NaB-GCL roll that had been stored in a laboratory since 2005. Values of ω were measured for both specimens, and also compared to results reported in 2002 for the same type of NaB-GCL (GCL3). To support interpretation of the results, cation exchange capacity, mass per unit area, and swell index tests also were performed. For the same salt solution concentrations, GCL2 exhibited significantly lower ω than GCL1 and GCL3. Lower values of ω corresponded to lower bentonite mass per unit area. The results have important implications regarding limitations in comparing results of current membrane behavior research on enhanced materials and testing conditions to commonly cited literature data.

INTRODUCTION AND BACKGROUND

Geosynthetic clay liners (GCLs) containing sodium bentonite (NaB) are widely used in hydraulic and chemical containment applications due to the high swelling capacity and low hydraulic conductivity (k) of NaB. In addition to low k, NaB-GCLs also have been shown to exhibit significant membrane behavior (e.g., Malusis and Shackelford 2002a; Shackelford and Lee 2003; Kang and Shackelford 2011; Meier et al. 2014; Shackelford et al. 2016). Membrane behavior occurs in clays due to electrostatic repulsion effects associated with the diffuse double layer. When electrostatic fields from adjacent clay minerals overlap, charged solutes may be repelled and restricted from passing through the pores (Kemper and Rollins 1966; Fritz 1986). This phenomenon (also known as anion exclusion) reduces the total contaminant flux occurring across the barrier into the environment, potentially enhancing long-term containment performance (Manassero and Dominijanni 2003; Dominijanni et al. 2013, 2018; Shackelford 2013; Li et al. 2014; Malusis et al. 2020; Tong and Sample-Lord 2022).

Membrane behavior is quantified by a membrane efficiency coefficient (ω) that generally ranges from $\omega = 0$ for no solute restriction to $\omega = 1$ for complete solute restriction (i.e., a "perfect" membrane) (Mitchell 1993). Values of ω for GCLs typically have been measured in the laboratory using a specialized closed-system apparatus similar to that described in detail by Malusis et al. (2001). Prior experimental studies on NaB-GCLs indicate that:

- NaB-GCL ω values decrease with increasing ionic strength, which has been attributed to reductions in diffuse double layer thickness (e.g., Di Emidio 2010; Meier et al. 2014);
- NaB-GCL ω values increase with increasing effective stress, and corresponding decreases in porosity (Kang and Shackelford 2011); and
- decreasing membrane behavior (lower ω) typically corresponds to concurrent increases in effective diffusion coefficients and increased contaminant flux (e.g., Malusis and Shackelford 2002b).

As research on membrane behavior of NaB-GCLs has become more established, recent studies have shifted focus to evaluating ω of enhanced bentonites and testing under more complex conditions (e.g., elevated temperatures, unsaturated conditions, GCLs exhumed from the field). For example, experimental studies have been performed to measure ω of bentonite-polymer composites (BPC) (e.g., Bohnhoff and Shackelford 2013), HYPER clay (Di Emidio 2010), multiswellable bentonite (e.g., Mazzieri et al. 2010), sodium hexametaphosphate (SHMP)-amended bentonite (Fu et al. 2021), and dense prehydrated GCLs (Malusis and Daniyarov 2016). Recent and future research directions also include evaluating membrane efficiency of NaB under unsaturated conditions (e.g., Sample-Lord and Shackelford 2018), elevated temperatures (Rahman et al. 2022), and for field exhumed GCLs (Yesiller et al. 2021). These studies often compare their results to earlier experimental findings reported for NaB-GCLs to draw conclusions regarding impacts of the bentonite amendment or different testing conditions. However, variability in reported ω values for the same type of NaB-GCL under the same test conditions has not been investigated. Thus, the validity of comparing recent findings to NaB-GCL results across studies and over multiple decades remains unclear.

In this study, membrane behavior tests were performed on specimens of the same NaB-GCL type, using the same type of testing apparatus and salt solutions. However, the NaB-GCL specimens were manufactured and tested at different times over the last two decades. All tests were performed with KCl solutions to allow for comparison with the existing literature. Variability in the measured ω values for the three GCLs were determined with supporting results for cation exchange capacity, swell index, bentonite mass per unit area, and hydraulic conductivity to water.

MATERIALS

All three GCL specimens were Bentomat® DN, a product manufactured by CETCO (Mineral Technologies Incorporated, Hoffman Estates, IL). The GCLs were needle-punched, nonwoven-nonwoven, with granular sodium bentonite. The bentonite in the GCL classified as high-plasticity clay, CH. GCL1 was manufactured in 2018, stored in the laboratory, and then tested in 2022. GCL2 was manufactured in approximately 2004 and then stored in the laboratory in sealed thick plastic film until testing in 2020. GCL3 was manufactured in the late 1990s and tested in 1999.

METHODS

Membrane Behavior Testing

The tests on the three GCL specimens were performed by three different researchers, using a similar testing apparatus and procedure as described in detail in Malusis et al. (2001). All test specimens were confined within custom-machined, rigid-wall acrylic cells (e.g., Fig. 1). To apply a concentration difference across the specimens, potassium chloride (KCl) solutions were circulated through a porous disk at the top boundary of the specimen while water was circulated through a disk across the bottom boundary. Syringe pumps were used to supply constant flow rates and to ensure a closed-system condition (i.e., no volume change allowed within the system).

Pressure transducers were used to measure the differential pressure that developed across the specimen in response to the applied concentration difference, and then the differential pressure was used to calculate ω (see Malusis et al. 2001 for further detail). The only significant difference between the testing methods was that the apparatus used for the tests performed on GCL1 and GCL2 had been modified to allow for automatic refilling of the syringes (Fig. 1), whereas the apparatus used for GCL3 required manual refilling of the syringes (Malusis et al. 2001).

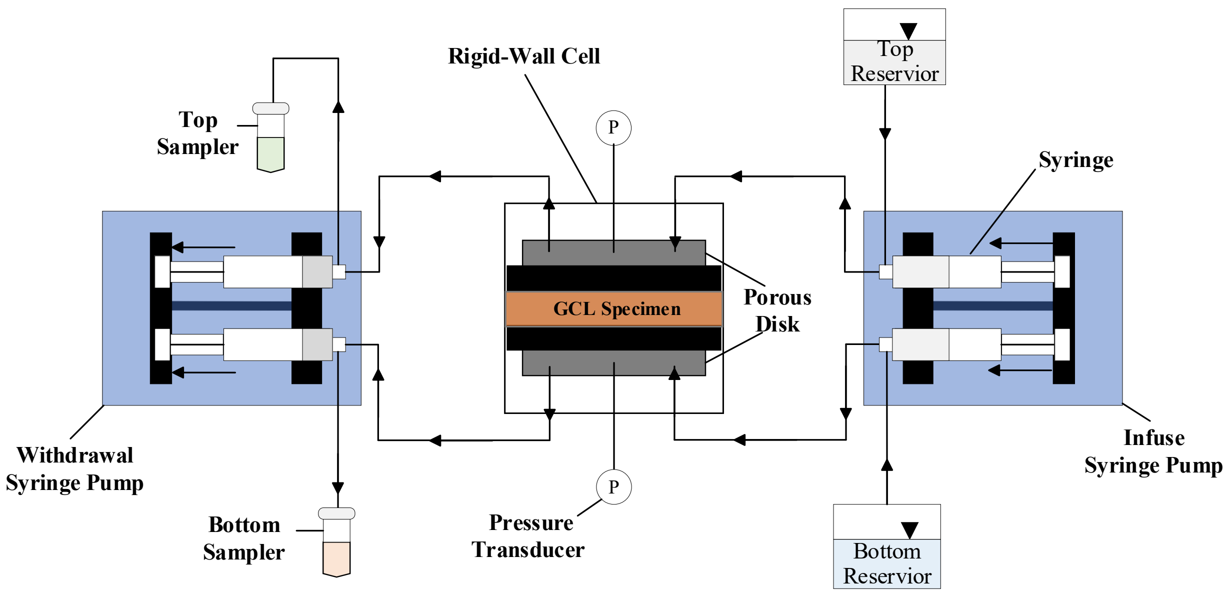

Figure 1. Example diagram of membrane behavior testing apparatus.

For all the tests, the GCL first was permeated with deionized water to saturate the specimen and flush the GCL of excess soluble salts. During this stage, the hydraulic conductivity to water also was recorded. Then, water was circulated across the top and bottom boundaries of the specimen to prepare the system and measure baseline pressures. To initiate the membrane behavior testing stage, the liquid circulating across the top boundary was switched to KCl solution and in a subsequent stage of testing, increased in chemical concentration. After steady-state conditions were achieved for the first concentration stage (e.g., 5 mM KCl), the solution concentration at the top boundary was increased to begin the next stage (e.g., 10 mM). The concentration stages and the duration of each testing stage are summarized in Table 1.

Table 1. Conditions for membrane behavior testing.

Specimen ID	Approximate Manufacture Date	Year of Testing	Specimen Thickness (mm)	Testing Stage Target Concentration (mM)	Testing Stage Actual Concentration (mM)	Stage Duration (d)
GCL1	2018	2022	6.7	5 10	4.6 11.3	36 39
GCL2	2004	2020	8.4	5 10	6 12	38 30
GCL3	late 1990s	1999	8.0[a]	4[a] 6[a] 10[a]	3.9[a] 6.0[a] 8.7[a]	7[a] 7[a] 7[a]

[a] Reported in Malusis and Shackelford (2002a).

Supplemental Testing

To support comparison of the membrane behavior results, the dry bentonite mass per area, free swell index, and cation exchange capacity of the GCLs also were considered. For GCL1 and GCL2, free swell index tests were performed on the bentonite in general accordance with ASTM D5890-19. Swell index data was not available for GCL3 from two decades ago. The mass per unit area was measured in general accordance with ASTM D5993-18, using duplicate samples. The cation exchange capacity (CEC) of GCL1 and GCL2 was determined based on ASTM D7503-18. The CEC of GCL3 was determined following the procedures described in Shackelford and Redmond (1995).

RESULTS AND DISCUSSION

Swell Index, Cation Exchange Capacity, and Mass per Unit Area

The results of the swell index, CEC, and mass per unit area tests for each GCL are summarized in Table 2. GCL1 (the most recently manufactured GCL) had a CEC of 96.7 cmol$^+$/kg, which was the highest CEC of the three specimens. The CEC for GCL3 was relatively low. The GCL3 CEC was measured using a different method during the 1990s, which may impact the comparison between the results. The mass per unit area for GCL1 and GCL2 was measured in accordance with ASTM D5993, whereas the mass per unit area for GCL3 was back-calculated from other properties reported in Malusis and Shackelford (2002).

Table 2. Measured properties of GCL test specimens.

Property	ASTM Standard	GCL1	GCL2	GCL3[a]
Swell Index (mL/2g)	D5890-19	20	23	Not reported
Cation Exchange Capacity (cmol$^+$/kg)	D7503-18	96.7	81.4	47.7[a,b]
Bentonite Mass Per Unit Area (kg/m^2)	D5993 -18	4.0	3.8	5.0[a]
Hydraulic Conductivity to Water, k_w (m/s)	permeation prior to first KCl stage for membrane test	1.1×10^{-11}	4.1×10^{-11}	3.9×10^{-12}

a. Calculated from data reported in Malusis and Shackelford (2002)

b. Measured using procedures described in Shackelford and Redmond (1995).

Membrane Behavior

The results of the multistage membrane behavior tests for the three GCLs are summarized in Figure 2. As expected, for all three GCL specimens, ω decreased as the concentration of the KCl test solution increased. This trend is consistent with the literature and has been attributed to decreased diffuse double layer thickness with increasing ionic strength of the solution in the pores of the clay (Shackelford 2013).

There was a significant difference in the measured values of ω for the same GCL product (all Bentomat® DN), at the same KCl concentrations, tested using the same type of apparatus and procedures. For instance, for a KCl concentration of ~6 mM, the ω values for GCL1, GCL2, and GCL3 are 0.51 (interpolated from Fig. 2), 0.69, and 0.34, respectively. These differences bring into question the validity of comparing results across different experimental studies to elucidate mechanisms impacting membrane behavior. For example, recent studies on membrane behavior of enhanced bentonites often compare their results with earlier published data for NaB-GCLs (e.g., GCL3 data) to draw conclusions regarding enhancements to containment performance (e.g., Mazzieri et al. 2010; Bohnhoff and Shackelford 2013; Sample-Lord and Tong 2022). However, the data in Figure 2 suggest that this type of comparison should be exercised with caution.

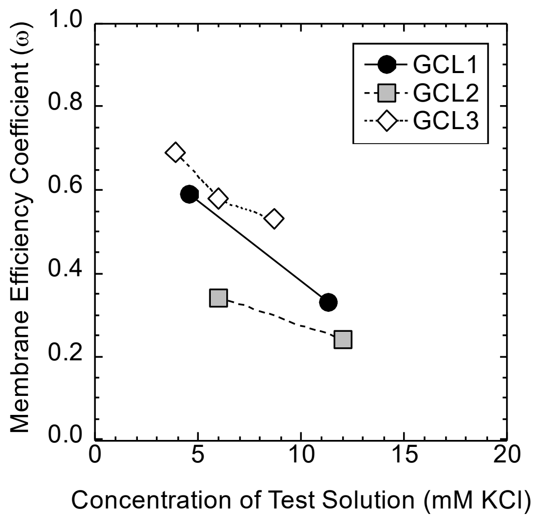

Figure 2. Membrane efficiency versus KCl concentration for the three GCL specimens.

To further investigate potential reasons for the significant differences observed between the GCL results presented in Figure 2, the values are ω are replotted versus the corresponding porosity of the specimen (Figure 3a) and versus the k_w measured for the GCL during the permeation stage (Figure 3b). The data series represent different KCl solution concentration ranges, as noted in the legend.

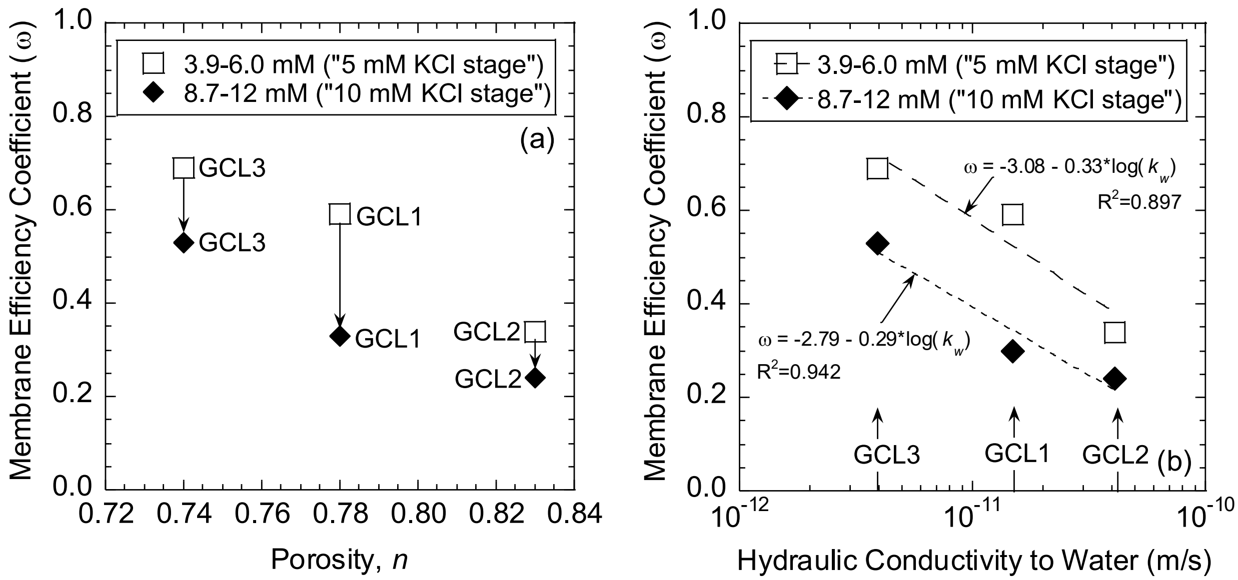

Figure 3. Membrane efficiency versus (a) porosity and (b) hydraulic conductivity to water measured for the three GCL specimens.

Decreases in porosity have previously been correlated to increases in GCL membrane efficiency (e.g., Kang and Shackelford 2011), consistent with current conceptual understanding of ion repulsion due to overlapping diffuse double layers. However, the porosity of an intact GCL specimen can be challenging to determine precisely using phase relationships, due to uncertainties in quantifying the contribution of the outer geotextiles and the needle-punched fibers to the overall mass and volume of the test specimen. Based on the specimen thicknesses in Table 1 and the bentonite masses per unit area in Table 2, the estimated porosities were 0.78 for GCL1, 0.83 for GCL2, and 0.74 for GCL3. Prior studies reporting increasing ω with decreasing *n* have been for experiments performed on specimens taken from the same GCL roll. As presented in Figure 3(a), correlation between *n* and ω across studies using different GCL rolls and sodium bentonite qualities may be valid. As expected, the GCL with the lowest *n* (GCL3 with *n* = 0.74) exhibited higher ω than the GCLs with the higher *n* (GCL1 and 2 with *n* = 0.78 and 0.83). The ω values for GCL2 were lower than those for GCL1 and GCL3. For example, for the same concentration stage of ~5 mM in Figure 3a, the ω values for GCL1 and GCL2 were 0.59 and 0.34, respectively. The results in Figure 3a suggest that even for GCLs of the same product type tested under similar conditions, care must be exercised in correlating ω to a single parameter (such as *C*) from data across multiple studies.

Membrane efficiency is a function of multiple factors, including both physical GCL properties (e.g., porosity, mass per unit area) as well as the quality of the bentonite (as indicated by parameters such as CEC and swell index). The combined impact of such factors may be better represented by observed trends in the hydraulic conductivity of the specimen. In Figure 3b, increasing ω correlates well to decreasing k_w, as would be expected as both properties are impacted by the porosity and osmotic swelling of the bentonite. The lower porosity of GCL3 is consistent with the lower k_w and higher ω for GCL3 relative to GCL1 and GCL2. The relationships between ω and k_w in Figure 3b appear consistent between the GCLs and for different concentrations. Thus, differences in k_w may also be a reliable indicator of the potential for variability in ω and should be considered when selecting literature data to compare ω results for GCLs.

CONCLUSIONS AND RECOMMENDATIONS

Membrane behavior of the same type of NaB-GCL samples with varying manufacturing dates and ages was determined and compared. All the GCL specimens exhibited membrane behavior, which may enhance long-term containment performance of the barrier. However, comparison of results from membrane behavior tests performed on the same type of NaB-GCL across different experimental studies revealed significant variability in the reported membrane efficiencies (e.g., by 25 percentage points, even for the same GCL type, concentration, and porosity). Although all the tests were performed using a similar apparatus and testing procedures, the GCLs had been manufactured at different times spanning a 20-year period and stored for different durations in the laboratory prior to testing. Increasing measured values of ω generally correlated with decreasing n of the GCL specimens. Values of ω correlated with measured k_w of the GCL, with ω increasing as k_w decreased. In future research where comparisons are drawn between membrane behavior of multiple GCL specimens, differences in k_w may be a useful indicator of expected variability in ω. For membrane behavior research that attempts to draw conclusions through comparisons with literature data for NaB-GCLs, caution should be exercised.

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