

Diffusion and membrane behavior of an exhumed geosynthetic clay liner

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ABSTRACT: A composite bottom liner system consisting of a geomembrane over a geosynthetic clay liner (GCL) was constructed for a municipal solid waste landfill in California, USA, in 2004. The liner system then was left exposed without placement of overlying waste for over a decade. In 2016, samples of the GCL were exhumed from the sideslopes for laboratory testing. To investigate the impact of field exposure on the diffusion and membrane behavior properties of the bentonite, multi-stage through-diffusion tests were performed on the exhumed GCLs and a virgin specimen of the same GCL product. Membrane efficiency coefficients (ω) and effective diffusion coefficients (D^*) were measured for potassium chloride (KCl) source solutions. Preliminary results are presented to assess the impact of the long-term field exposure on diffusion and membrane properties of the GCL. Comparisons are drawn with the existing literature for diffusion and membrane behavior, which to date has been limited to testing of virgin GCLs.

1 INTRODUCTION

Geosynthetic clay liners (GCLs) are widely used as barriers in hydraulic and chemical containment applications (e.g., landfills, impoundments). GCLs have been shown to exhibit low hydraulic conductivity, k , to water (i.e., $< 10^{-10}$ m/s), limiting advective flux of contaminants through the liner (Rowe et al. 2004). Laboratory studies have shown that GCLs also exhibit semipermeable membrane behavior and have low effective diffusion coefficients, D^* , further enhancing the long-term performance of the barrier system to restrict migration of contaminants into the environment (e.g., Malusis and Shackelford 2002a, Manassero and Dominijanni 2003).

The existence of membrane behavior in a GCL results in restriction of charged inorganic solutes from entering the pores of the bentonite, thereby reducing the total contaminant flux through the GCL and enhancing the barrier performance (Shackelford 2012). This phenomenon occurs due to electrostatic repulsion of anions from electrical fields surrounding adjacent bentonite particles (Fritz 1986). The membrane behavior of GCLs is quantified by the membrane efficiency coefficient, ω , which ranges from a value of 0 (no solute restriction) to 1.0 or 100% (complete or perfect chemical restriction) (Mitchell 1991). Experimental studies indicated significant membrane behavior in GCLs comprising sodium bentonite (NaB) (e.g., $\omega = 0.7$ in Malusis and Shackelford 2002b). Polymer-enhanced bentonites for GCLs also exhibited membrane behavior (Bohnhoff et al. 2014; Di Emidio et al. 2015; Tong and Sample-Lord 2022). In addition, multiple studies on NaB and GCLs measured ω and diffusion simultaneously, and reported an inverse correlation between ω and D^* for chloride (e.g., Dominijanni et al. 2013, Shackelford et al. 2016).

Experimental diffusion and membrane behavior research to date has focused solely on virgin GCLs (i.e., GCLs that have never been exposed to field conditions). Processes that have been identified to adversely affect GCL performance in the field, such as cation exchange and downslope bentonite migration, may also degrade membrane behavior and diffusion performance. However, aside from the preliminary work of the authors, no known studies have attempted to measure membrane behavior and diffusion properties of GCLs that have been exhumed from field

sites. Thus, performance-based modeling capabilities and understanding of coupled flows in clay barriers are limited by current datasets of potentially unrepresentative values of ω and D^* obtained from laboratory testing of virgin GCLs.

The experimental study described in this paper included measurement of ω and D^* for GCL samples exhumed from a liner system in San Luis Obispo, California, USA after 12-years of field exposure. Testing was performed on GCL samples exhumed from the top and bottom of a landfill sideslope, as well as on a virgin GCL that was manufactured during the same time period as the installed liner. Results were compared between the exhumed and virgin specimens under the same testing conditions, as well as values reported in the literature for virgin GCLs that utilized similar testing methodologies.

2 MATERIALS AND METHODS

2.1 Exhumed and Virgin GCL Samples

The virgin and exhumed GCL samples were both Bentomat DN (CETCO, USA). Bentomat DN is a needle-punched nonwoven-nonwoven product made with sodium bentonite. Properties of the GCL determined through conformance testing included a bentonite mass per unit area of 4.9 kg/m² and k of 2.8×10^{-11} m/s. The average swell index (SI) reported by the manufacturer was 26.0 mL/2g.

The exhumed samples were obtained from a geomembrane-GCL composite bottom liner system that was installed at a municipal solid waste landfill in San Luis Obispo, California (USA) in 2004. The geomembrane was 1.5 mm-thick black HDPE. The composite liner system was left uncovered for 12 years (Fig. 1a), after which point the GCL samples were exhumed in 2016. A utility knife was used to cut a strip sample from the corner of the east and south slopes. For the membrane behavior and diffusion testing program, sub-samples (300 mm x 300 mm) were cut from the strip sample from near the top and bottom of the slope (Fig. 1b). Details of the liner exhumation are provided in Hanson and Yesiller (2019).

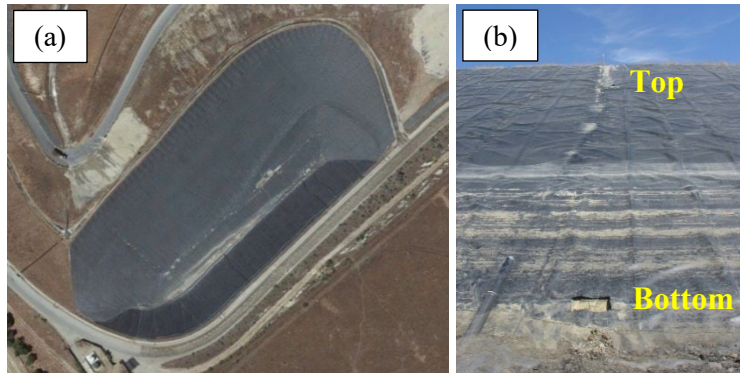


Figure 1. Photographs of: (a) site in San Luis Obispo, California, USA; (b) example “top” and “bottom” of slope exhumed sample locations.

The SI , bentonite mass per unit area, and k also were measured for GCL samples exhumed from the top and bottom of the slope. The SI of the sample exhumed from the top of the slope was 25.5 mL/2g, which was similar to the original SI reported by the manufacturer. However, the SI of the sample exhumed from the bottom of the slope had decreased to 9.5 mL/2g, suggesting significant cation exchange occurred between the NaB and subsoil for the GCL located near the bottom of the slope over the exposure period. The GCL exhumed from the top of the slope had a bentonite mass per unit area of 3.9 kg/m² and average thickness of 6.0 mm. In contrast, the GCL exhumed from the bottom of the slope had a bentonite mass per area of 4.9 kg/m² and average thickness of 11.7 mm. These mass/area results supported field observations that significant downslope bentonite erosion had occurred. The k of the GCL samples exhumed from both the top ($k = 7.7 \times 10^{-7}$ m/s) and bottom ($k = 1.2 \times 10^{-8}$ m/s) of the slope had increased by 3-4 orders of magnitude above the original values reported from the manufacturer and conformance testing. The increase in k for

the top sample likely was due to bentonite loss, whereas the increase in k for the bottom sample was attributed to reduced swell.

The virgin sample was obtained from a Bentomat DN GCL roll that was manufactured around the same time period as the field installation. This GCL remained stored in a laboratory setting at California Polytechnic State University-San Luis Obispo.

2.2 Diffusion and Membrane Behavior Testing

Membrane efficiency (ω) and chloride effective diffusion coefficients (D^*) were measured simultaneously using a closed-system, through-diffusion apparatus as described in detail in Malusis et al. (2001) and depicted in Figure 2. The apparatus includes a hydraulic control system with a double-syringe flow pump to circulate solutions, an acrylic cell to contain the specimen and porous disks, pressure transducers to monitor pressures at the specimen boundaries, and stainless steel connections throughout the apparatus (to prevent corrosion or volume change). The apparatus is used to simultaneously circulate a higher concentration solution across the top boundary of the specimen and a lower concentration solution across the bottom boundary, thus creating a concentration difference (ΔC) across the specimen. If a GCL exhibits membrane behavior, a hydraulic pressure difference (ΔP) will develop across the specimen due to the applied ΔC . The ΔP is measured via pressure transducers at the boundaries of the specimen and used to quantify the membrane efficiency as (Malusis et al. 2001):

$$\omega = \frac{\Delta P}{\Delta \pi} \quad (1)$$

where, $\Delta \pi$ is the theoretical maximum value of ΔP that would result across an ideal membrane subjected to the same ΔC . Values of $\Delta \pi$ for single-salt solutions can be determined in accordance with the van't Hoff expression (Katchalsky and Curran 1965).

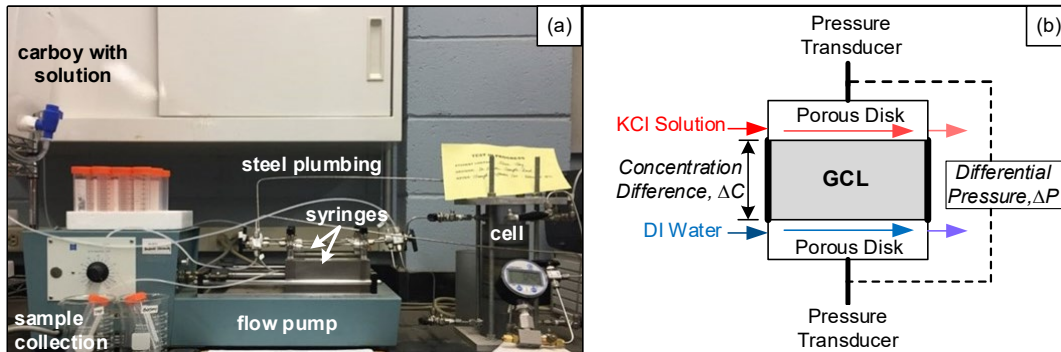


Figure 2. (a) Photograph of one of the closed-system apparatuses to simultaneously measure membrane behavior and diffusion; (b) schematic of conditions within the cell.

In preparation for testing, all specimens were trimmed to a diameter of 71 mm. The test specimen thicknesses for the virgin GCL, GCL exhumed from the top of the slope, and GCL exhumed from the bottom of slope were 7.1 mm, 6.8 mm, and 11.8 mm, respectively. Prior to introducing salt solution to start the diffusion and membrane behavior testing, deionized water (DIW) was circulated across both boundaries of the specimen. The purpose of this DIW stage is to establish steady baseline conditions before introducing the concentration difference, and measure any initial ΔP that exists across the specimen with $\Delta C = 0$ condition (referred to as the baseline pressure difference, ΔP_o). After completion of the DIW stage, the top solution was switched to 5 mM KCl to commence diffusion and membrane behavior measurements. After steady-state diffusion and pressure conditions were achieved for the 5 mM KCl stage, the top boundary solution was then increased to 10 mM KCl. Each KCl stage typically took three to five weeks to complete.

Recorded ΔP values that developed due to membrane behavior were corrected for ΔP_o (i.e., effective pressure difference, $\Delta P_e = \Delta P - \Delta P_o$) and then used to calculate membrane efficiency in accordance with Equation 1. Samples of the top and bottom boundary outflows were collected every 2 days and subsequently analyzed for EC , pH, temperature, and ion concentrations (Cl^- , K^+ , Na^+ , Ca^{2+} , Mg^{2+}). The Cl^- concentrations in the bottom boundary outflows were used to determine D^* values based on the commonly used “steady-state method” analysis procedure (e.g., Dutt and

Low 1962; Olsen et al. 1965; Shackelford 1991):

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

where L is the specimen thickness, A is cross-sectional area, n is porosity, Δt is the time increment over which the liquid outflow sample was collected from the bottom boundary (2 days for this testing), and Δm is the mass of Cl^- that diffused through the specimen over the time interval (calculated as the Cl^- concentration of the outflow sample $\times$ volume of the outflow sample).

This paper presents the preliminary results from the first two salt concentration stages (5 mM and 10 mM KCl) for the virgin and exhumed GCLs. The results of the subsequent higher concentration stages (up to 50 mM) are beyond the scope of this paper. The purpose of using KCl (vs. another salt) and solutions within that concentration range was to allow for comparison of the results with most of the literature data for similar tests on virgin GCLs.

3 PRELIMINARY RESULTS

The measured steady-state effective differential pressures (ΔP_e) and calculated membrane efficiency coefficients (ω) for each test stage are presented in Table 1. For all of the specimens, ω decreased as the source salt concentration increased, which has been widely observed in the membrane behavior literature and attributed to diffuse double layer compression as salt diffuses into the bentonite pores (Fritz 1986; Shackelford et al. 2003; Di Emidio et al. 2015; Dominijanni et al. 2018).

Table 1. Summary of membrane behavior test results.

GCL Specimen	Source KCl Concentration, C_o mM	Effective Pressure Difference, ΔP_e kPa	Membrane Efficiency Coefficient, ω %
Virgin	5	10.3	51.2
	10	8.6	23.6
Exhumed from Top of Slope	5	1.0	3.7
	10	2.8	5.3
Exhumed from Bottom of Slope	5	2.0	8.9
	10	0.56	0.95

The values of ω for the virgin GCL in Table 1 are consistent with ω ranges reported in the literature for other virgin GCLs. For example, Malusis and Shackelford (2002b) reported ω values of 52 % and 42 % for a similar Bentomat GCL (porosity, $n = 0.86$) from a multi-stage test with 3.9 mM and 8.7 mM KCl concentrations, respectively.

In contrast, values of ω for the exhumed GCLs were substantially lower than those for the virgin GCL in this study. Comparison of ω for the virgin and exhumed GCL specimens is presented graphically in Figure 3. The ω values of the GCL exhumed from the top of the slope were lower than the virgin GCL ω values by factors of 13.8 and 4 for the 5 mM and 10 mM stages, respectively. The reduced ω for the GCL exhumed from the top of the slope was likely due to the lower bentonite mass per area (3.9 kg/m^2), which had been attributed to downslope erosion based on field observations.

The ω values of the GCL exhumed from the bottom of the slope were lower than the virgin GCL ω values by factors of 5.7 and 25 for the 5 mM and 10 mM stages, respectively. Unlike the GCL at the top of the slope, the GCL from the bottom of the slope had experienced an increase in bentonite mass per area (4.9 kg/m^2). The increase in bentonite mass per area would have been expected to maintain (or potentially increase) the original membrane behavior. The destruction of membrane behavior for the GCL at the bottom of the slope likely was due to cation exchange. Evidence of cation exchange occurring at the bottom of the slope was supported by the lower SI .

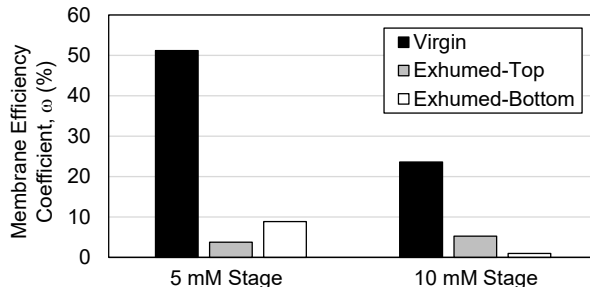


Figure 3. Membrane efficiency coefficients for the virgin and exhumed GCL specimens.

Figure 4 presents the ion concentrations measured in the liquid outflow samples collected during the diffusion and membrane behavior tests. As shown in Figure 4a for the virgin GCL and Figure 4b for the exhumed GCL from the top of the slope, the outflow samples had higher concentrations of Na^+ than Ca^{2+} or Mg^{2+} . This observation is consistent with the high SI values of the virgin and top GCL ($SI = 25\text{--}26 \text{ mL}/2\text{g}$), representative of a bentonite with significant Na^+ occupying the exchange complex. In contrast, Figure 4c for the exhumed GCL from the bottom of the slope shows Na^+ concentrations that are an order of magnitude lower than the Ca^{2+} and Mg^{2+} concentrations. This observation further supports the hypothesis that cation exchange was the primary cause of the reduction in ω for the GCL at the bottom of the slope. Future testing will include measurement of cation exchange capacity and bound cation composition for detailed explanation of the observed behavior.

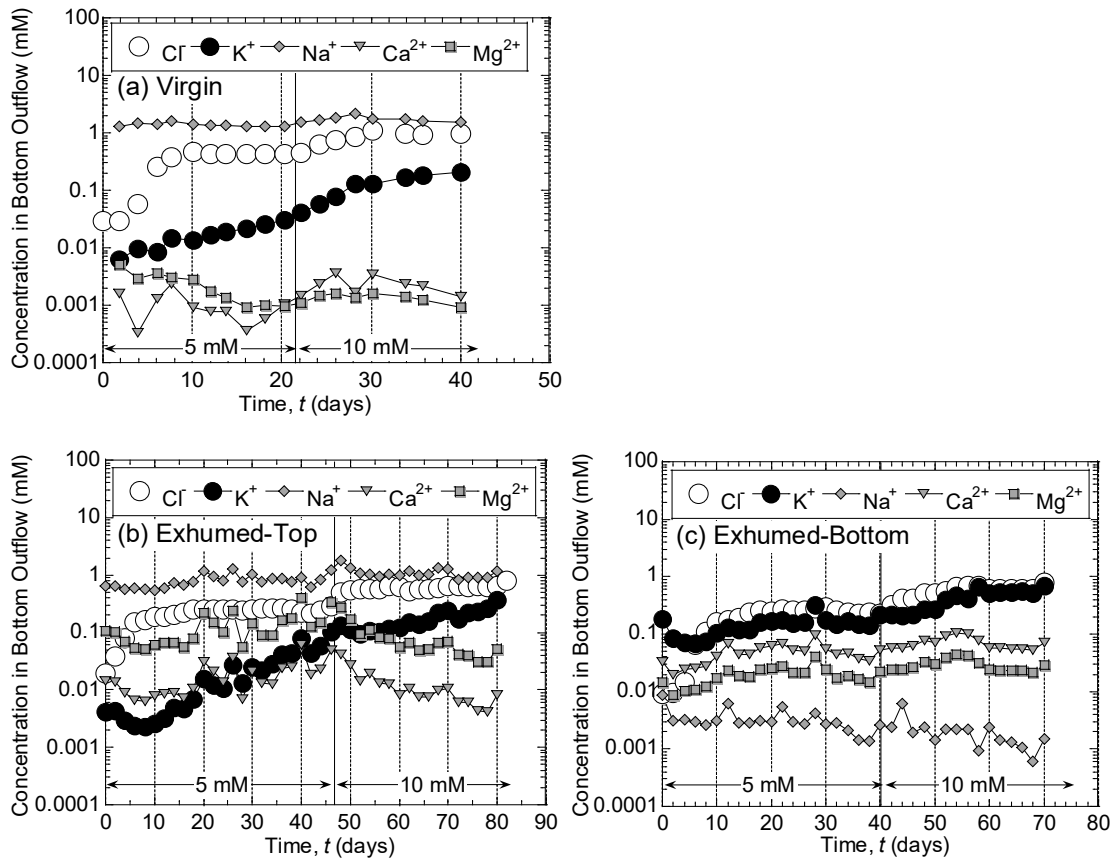


Figure 4. Measured ion concentrations in the bottom outflow samples with time for the (a) virgin GCL specimen, and GCL specimens exhumed from the (b) top and (c) bottom of the slope.

The concentrations in Figure 4 were used to determine the cumulative mass of Cl^- that had diffused through the specimens with time (normalized to specimen area), as shown in Figure 5.

Values of D^* were calculated in accordance with Equation 2. For the 5 mM KCl stage, D^* values for the virgin, top exhumed, and bottom exhumed GCL specimens were $6.29 \times 10^{-11} \text{ m}^2/\text{s}$, $2.43 \times 10^{-11} \text{ m}^2/\text{s}$, and $1.02 \times 10^{-10} \text{ m}^2/\text{s}$. For the 10 mM KCl stage, D^* values for the virgin, top exhumed, and bottom exhumed specimens were $7.97 \times 10^{-11} \text{ m}^2/\text{s}$, $3.24 \times 10^{-11} \text{ m}^2/\text{s}$, and $1.03 \times 10^{-10} \text{ m}^2/\text{s}$.

For all of the specimens, D^* increased as C_o increased, consistent with the literature for diffusion in bentonite and expectations based on diffuse double layer effects. However, unlike the membrane behavior results, differences between the D^* values for the virgin GCL versus the exhumed GCLs appeared to be minimal to insignificant. Comparison of D^* values may have been complicated by the presence of other ionic species that were not included in the chemical analysis presented in Figure 4. For example, diffusion of chloride may have been impacted by simultaneous diffusion of other anionic species (e.g., sulfate). Additional testing is required to refine conclusions being drawn regarding the impact of the field exposure on the GCL diffusion properties.

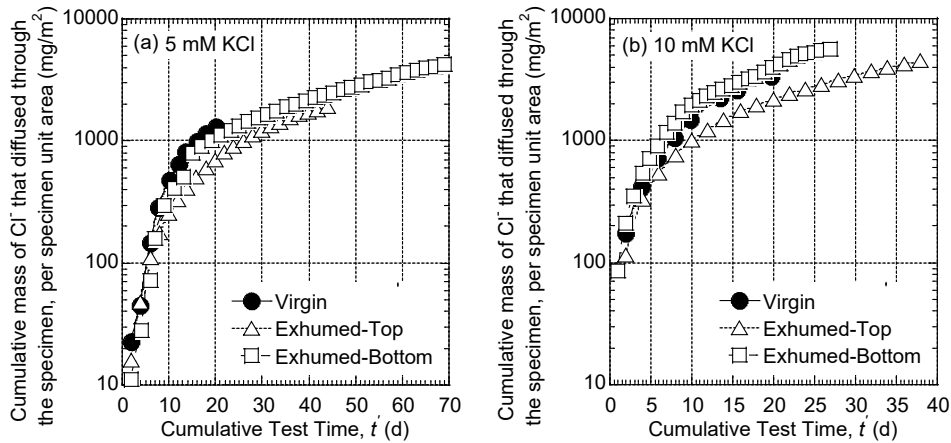


Figure 5. Cumulative mass of chloride (per unit area, per time) that diffused through each of the GCL specimens for the (a) 5 mM and (b) 10 mM test stages.

4 CONCLUSIONS

The study represents the first experimental evaluation of coupled membrane behavior and diffusion properties of GCLs exhumed from the field. The membrane behavior was determined to be highly impacted by the field exposure, exhibiting significant decreases in ω , which were attributed to downslope bentonite migration and cation exchange with the subsurface. Impacts of the field exposure on diffusion properties were less apparent, with no consistent trend in D^* observed for the virgin versus exhumed GCL specimens. Further study is underway to confirm the extent of cation exchange that occurred in the bottom GCL and to perform more comprehensive diffusion analysis.

Available data in the literature for ω and D^* values of GCLs are primarily based on laboratory studies of virgin GCLs. The results of this study suggest that predictions of long-term performance using coupled transport models, which consider membrane behavior likely underestimate the total contaminant mass flux transporting through the barrier if virgin GCL properties are used.

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