

Development of Cation Exchange Processes in Geosynthetic Clay Liners

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ABSTRACT

An investigation was conducted to systematically analyze the cation exchange characteristics of a conventional GCL as a function of time and concentration of hydration liquid under typical laboratory conditions. GCL specimens were hydrated using DI water and 2 mM, 50 mM, and 200 mM CaCl₂ solutions for 4 and 8 hours, and 1, 2, 4, 8, 16, and 32 days. Significant and rapid variations occurred in the amount and relative proportions of the bound cations in the exchange complex of the bentonite for the relatively high concentration solutions (50 mM and 200 mM CaCl₂). The exchange complex was relatively unaffected in the tests with DI water and 2 mM CaCl₂ solution. The highest changes occurred in the Na⁺ and Ca²⁺ fractions with relatively low changes in K⁺ and Mg²⁺. The majority of the exchange processes were completed within days (approximately ≤ 8 days) at the high concentration hydration conditions.

INTRODUCTION

Geosynthetic clay liners (GCLs) are multi-component materials that are used commonly in barrier systems in applications ranging from different types of landfills to waste ponds to additional liquid containment applications. Conventional GCLs consist of a thin layer of montmorillonite clay (i.e., bentonite) encased between typically two geotextile layers and in some cases an additional geofilm

layer attached to one of the geotextile layers. Sodium (Na) montmorillonite (i.e., Na-bentonite) is the main clay mineral in GCLs manufactured and used in North America. GCLs provide high resistance to transport of water. However, these materials are strongly affected by the chemistry of other liquids such as liquids containing cations with higher charges than that of sodium due to the highly active montmorillonite mineral (Mitchell and Soga 2005). The barrier function of the GCLs may be significantly impacted when in contact with highly concentrated solutions (NRC 2007, Benson et al. 2011).

Replacement of monovalent sodium (Na^+) with polyvalent cations (e.g., Ca^{2+} , Mg^{2+} , Fe^{3+}) through a cation exchange process significantly affects the material properties of the soil component of the GCLs and the overall engineering properties of GCLs. Adverse impacts of cation exchange on both fully saturated and variable saturated GCLs have been well demonstrated in the literature (e.g., Kolstad et al. 2004, Jo et al. 2005, Scalia and Benson 2011, Yesiller et al. 2019). While various studies have investigated effects of cation exchange on GCL behavior, studies on timing and rate of exchange processes are limited. Data and analysis have been provided for GCLs hydrated on/between different soils (type, water content, density/compaction conditions) including determination of cation exchange properties (e.g., Rowe and Abdelatty 2012, Bradshaw et al. 2013, Bradshaw and Benson 2014). However, temporal development of the cation exchange processes has not been widely investigated. Therefore, a comprehensive investigation is underway to systematically analyze the cation exchange characteristics of a GCL as a function of time, concentration of hydration liquid, temperature, and applied stress. Results of the time-dependent analysis conducted at 20°C with hydration liquids of variable concentrations under no stress conditions is presented herein.

EXPERIMENTAL TEST PROGRAM

Materials

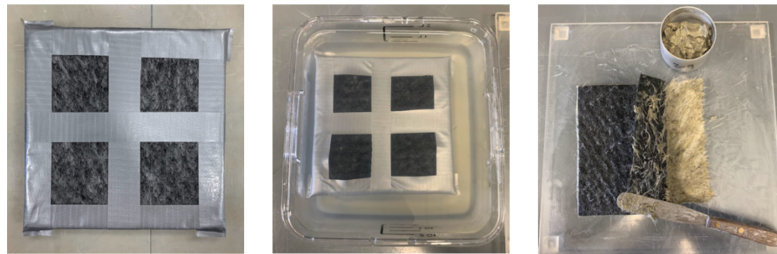
Experimental analysis is conducted on a conventional medium-weight needlepunched nonwoven-nonwoven GCL with granular bentonite that is used commonly in the U.S. The minimum bentonite dry mass per unit area (ASTM D5993), index flux (ASTM D5887), and maximum hydraulic conductivity (ASTM D5887) based on manufacturer data for the GCL are 3600 g/m², 1×10^{-8} (m³/m²)/s, and 5×10^{-11} m/s, respectively. The hydration solutions used in the experiments are deionized (DI) water, 2 mM CaCl_2 , 50 mM CaCl_2 , and 200 mM CaCl_2 . The calcium chloride solutions were made by mixing appropriate masses of American Chemical Society reagent-grade CaCl_2 crystals with deionized water. The 2 mM, 50 mM, and 200 mM CaCl_2 solutions represent typical soil pore liquid, mild landfill leachate, and harsh landfill leachate, respectively (Bradshaw and Benson 2014, Tian et al. 2019).

Methods

Tests were conducted on 150 mm x 150 mm square specimens of the GCL (Figure 1a). The edges of the specimens were wrapped in duct tape to prevent bentonite loss. The specimens also were

taped across the mid lengths along both sides to aid in maintaining relatively uniform hydration conditions (i.e., prevent high swelling in the middle and low swelling near the edges). Each specimen was fully submerged in a plastic tub with 2 L of hydration solution. The individual tubs were placed in a temperature-controlled bath (Figure 1b) for the testing program. A total of 12 tubs were placed in the temperature bath (maintained at 20°C) at a given time. The GCLs were hydrated over 8 distinct periods: 4 hours, 8 hours, 1 day, 2 days, 4 days, 8 days, 16 days, and 32 days.

Measurements made on the GCL specimens included determination of physical characteristics, length, width, thickness, and mass before and after each hydration period. Water content of the GCL was determined in the immediate vicinity of the locations where the GCL specimens were removed from the GCL roll for approximately every 12 specimens prior to testing. After hydration testing, water content for each specimen was determined by peeling of the cover geotextile and carefully removing the bentonite component of the GCLs (Figure 1a). Also, swell index of the bentonite component of the GCLs was determined using DI water (ASTM D5890) for all specimens after completion of each hydration period. Swell index (SI) data also was obtained on the virgin GCL that was not subjected to any of the hydration fluids. Daily measurements were conducted on the hydration fluid and included determination of electrical conductivity (EC), total dissolved solids (TDS), sodium cation concentration, and temperature. Calcium concentration was monitored for the DI water and 2 mM CaCl_2 hydration solution tests. Bulk GCL void ratio was calculated using the approach in Petrov et al. (1997). All testing and post-conditioning sampling were conducted in regions associated with fully exposed conditions (i.e., not covered by duct tape).



(a) Configuration and processing of GCL specimens.



(b) Constant-temperature bath.

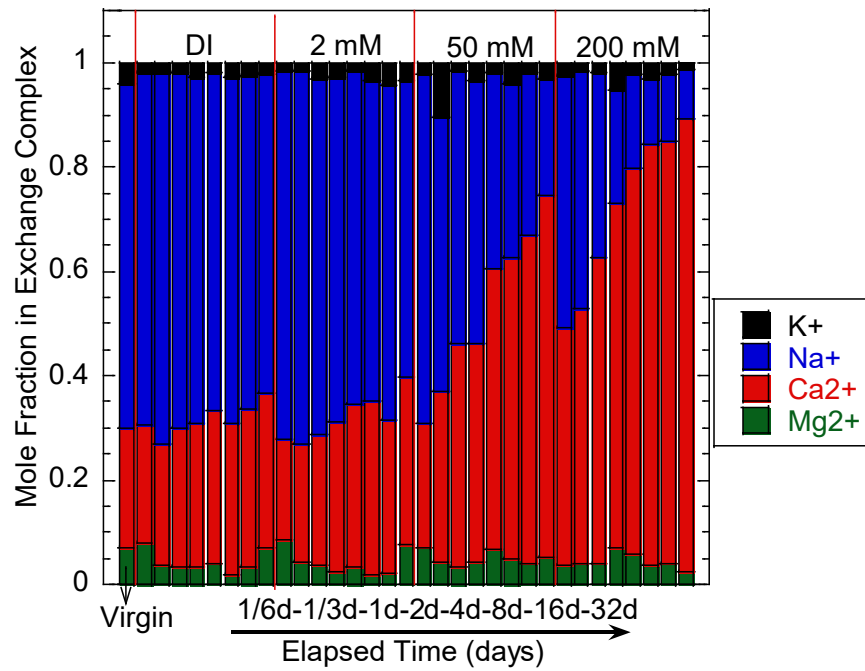
Figure 1. Temperature-dependent laboratory hydration tests.

After each hydration period, the bound cations (BC) and cation exchange capacity (CEC) were determined for the bentonite component of the GCL specimens. BC and CEC also were determined on the virgin GCL that was not subjected to any of the hydration fluids. Soluble cations (SC) and bound cations (BC) were determined using the procedure outlined in ASTM D7503. For sampling of bentonite from the GCL specimens for these tests, the bentonite was first dried in a microwave oven to arrest any further cation exchange in a timely manner to maintain representative conditions for the given hydration period. Bentonite specimens were filtered through a 0.45- μm filter and then analyzed for concentrations of major cations (Na, Ca, Mg, and K) using inductively coupled plasma/optical emission spectrophotometry (ICP-OES). Tests were conducted using SPECTROBLUE FMT36 (Mahwah, New Jersey) following USEPA SW-846 Test Method 6010B (USEPA 2018). Cation Exchange Capacity (CEC) was determined using the procedure outlined in ASTM D 7503. Nitrogen (mg/L) concentrations extracted from KCl were determined by Orion Dual Star pH/ISE ROSS Meter Kit (Cat. No. 2115101) using Ammonia Gas Sensing Combination ISE Electrode (Cat. No. 9512BNWP).

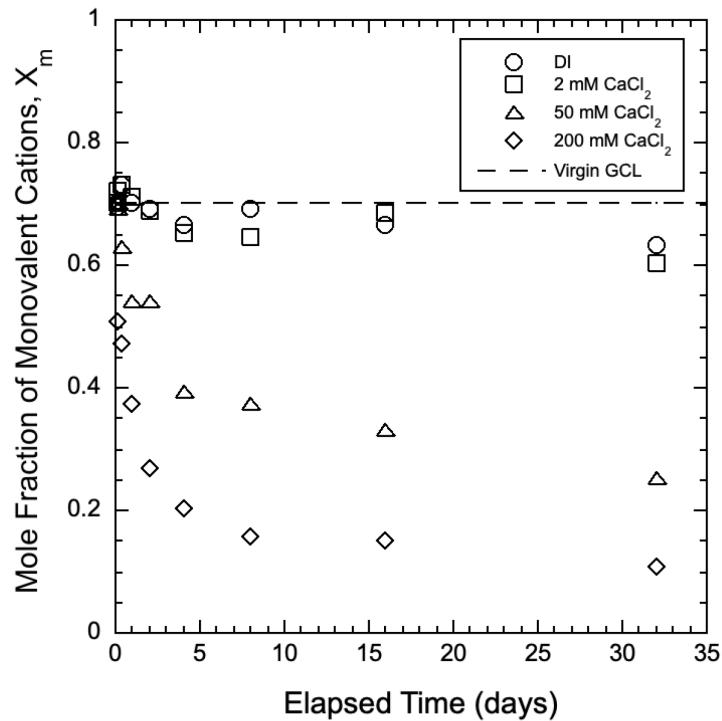
RESULTS

The cation exchange capacity of the GCL specimens varied from 70.4 cmol^+/kg (average for 2 mM CaCl_2 solution) to 70.5 cmol^+/kg (average for DI water). The CEC for the virgin GCL was 72 cmol^+/kg and the average CEC for the 32 specimens hydrated in the variable solutions was 70.5 cmol^+/kg . These values are similar to CEC reported for similar conventional GCLs in previous studies (e.g., Bradshaw and Benson 2014). Variations of bound cations with time and concentration of hydration solution are presented in Figures 2 and 3 with focus on relative fractions and time variability, respectively. The main variations in bound cations were for Na^+ and Ca^{2+} with low variations in the relative bound fractions of K^+ and Mg^{2+} . The sodium in the bentonite is replaced increasingly with the calcium in the hydration solution with increasing CaCl_2 concentration. The relative fraction of Na^+ in the virgin GCL was 66%, which decreased to 9% for the GCL hydrated with the 200 mM CaCl_2 solution for 32 days. The relative fraction of Ca^{2+} in the virgin GCL was 23%, which increased to 87% for the GCL hydrated with the 200 mM CaCl_2 solution for 32 days. The amount of bound Ca^{2+} in the bentonite increased rapidly for the 200 mM CaCl_2 solution followed by the 50 mM CaCl_2 solution with negligible variations over time for the DI water and 2 mM CaCl_2 solutions. Similarly, the amount of bound Na^+ in the bentonite decreased rapidly for the 200 mM CaCl_2 solution followed by the 50 mM CaCl_2 solution with negligible variations over time for the DI water and 2 mM CaCl_2 solutions. For the 200 mM CaCl_2 solution, the maximum decrease in the relative fraction of Na^+ was 14 percentage points and occurred for 1- and 2-day tests and the maximum increase in the relative fraction of Ca^{2+} was 10 percentage points and occurred for 8-hour and 1-day tests. For the 50 mM CaCl_2 solution, the maximum decrease in the relative fraction of Na^+ was also 14 percentage points and occurred for 4- and 8-hour tests and the maximum increase in the relative fraction of Ca^{2+} was 12 percentage points and

occurred for 2- and 4-day tests. The variation in BC reduced significantly after 4 to 8 days for the 2 relatively high CaCl_2 solutions used in the test program.



(a) All cations.



(a) Monovalent cations.

Figure 2. Variation of relative fraction of bound cations with time.

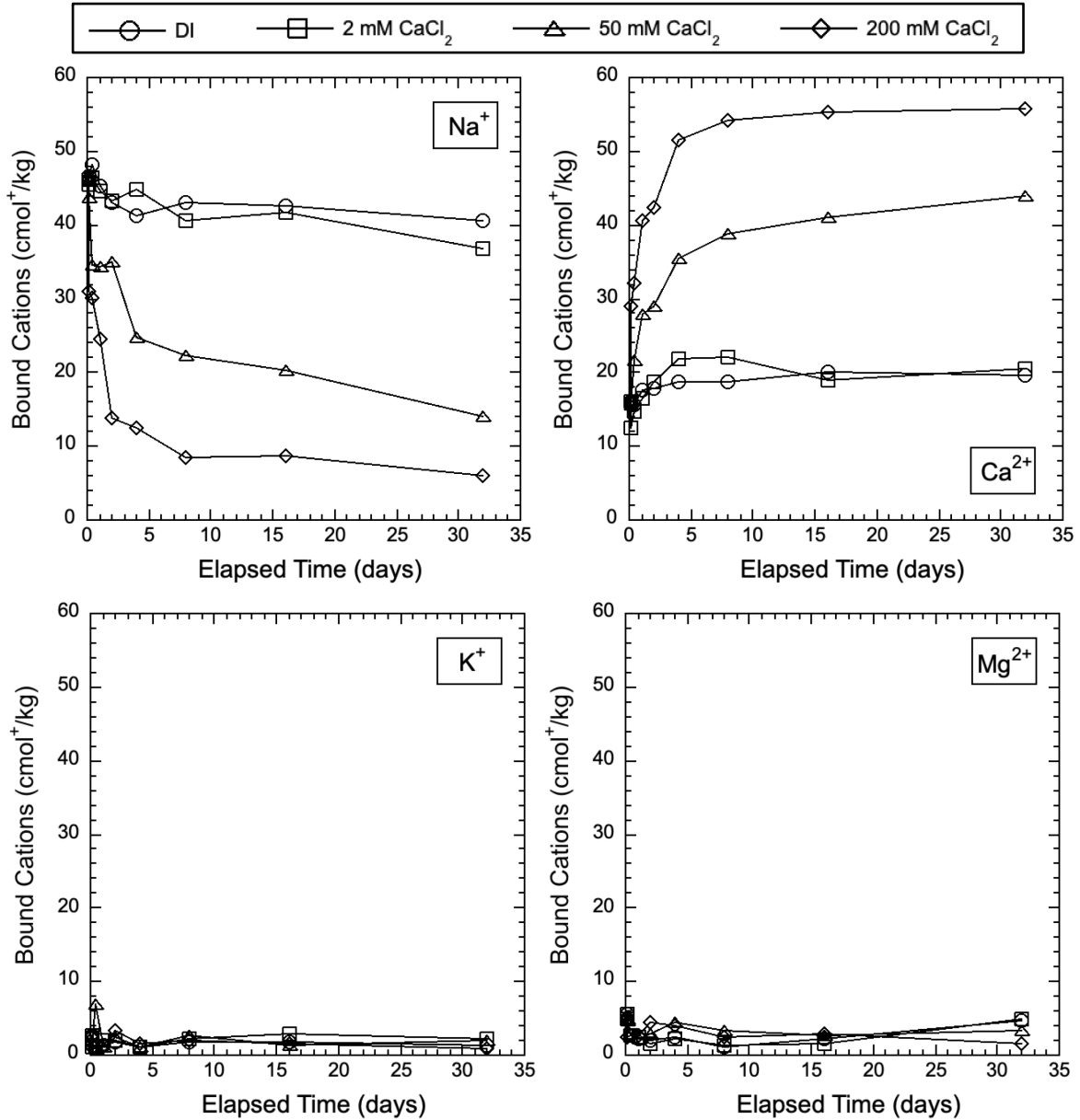


Figure 3. Variation of individual bound cation species with time.

Correlations between swell index and amount of bound Na⁺ and Ca²⁺ in the conditioned bentonite are presented in Figures 4 and 5. Swell index increased with increasing Na⁺ and decreasing Ca²⁺ concentrations (Figure 4). Swell index has been demonstrated to be inversely proportional to CaCl₂ solution concentration used for testing in previous studies (Scalia et al. 2014). Results of this investigation demonstrate the permanence of the modified GCL structure upon cation exchange by providing similar trends for conditioned specimens when DI water is used for the swell index tests. To attain swell index higher than 19 mL/2 g, more than 35 cmol⁺/kg Na⁺ and less than 35 cmol⁺/kg of Ca²⁺ were required in the bound cations in this test program. The variation of swell index with time was in line and character with the time-dependent variation of

the BCs as presented in a double y-axis plot in Figure 5. For the two solutions with high calcium concentration (50 and 200 mM CaCl_2 solutions), the timing for the significant changes in swell index and bound Na^+ and Ca^{2+} concentrations were generally consistent yet the timings for maximum Ca^{2+} and minimum Na^+ fractions were not exactly the same as individual sacrificial specimens were used in the test program.

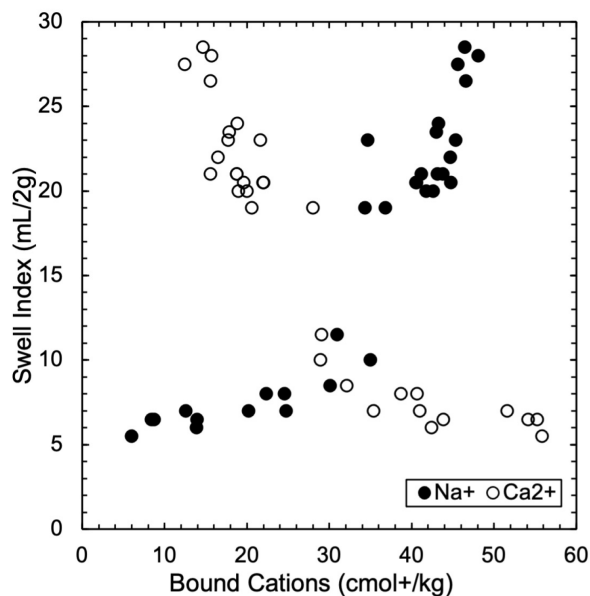


Figure 4. Variation of swell index with concentration of bound cations (Na^+ and Ca^{2+}).

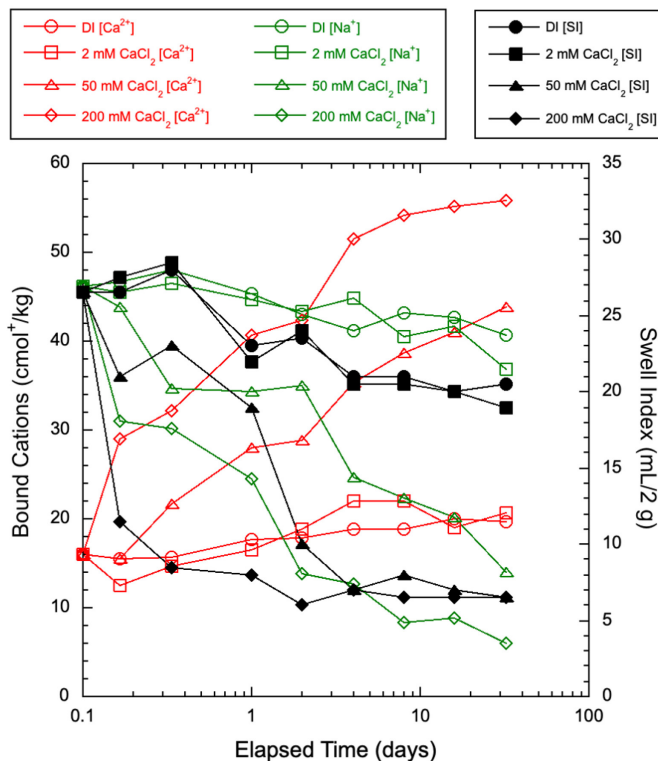


Figure 5. Combined variation of bound cations (Na^+ and Ca^{2+}) and swell index with time.

Variation of electrical conductivity with time is presented in Figure 6. The EC was determined to be relatively unchanged during the hydration tests irrespective of the concentration of the hydration solution. Electrical conductivity as an indication of chemical equilibrium between influent and effluent is used in experimental determination of hydraulic properties of GCLs with aqueous solutions (ASTM D6766). A low threshold variability between influent and effluent EC serves as termination criteria for GCL flux/hydraulic conductivity tests. In this test program, EC did not provide an indication of the variation of cation exchange processes and bound cation fractions in the GCL specimens and thus the use of EC may not be an appropriate indication of attainment of chemical equilibrium.

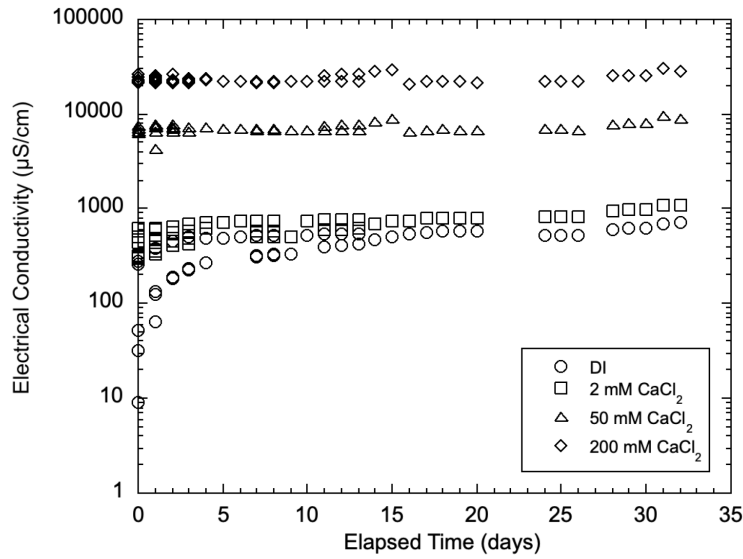


Figure 6. Variation of EC of hydration fluid with time.

CONCLUSIONS

This investigation was conducted to systematically analyze the cation exchange characteristics of a conventional GCL as a function of time and concentration of hydration liquid at 20°C. Tests were conducted on 150 mm x 150 mm square specimens of the GCL, which was a medium-weight needlepunched nonwoven-nonwoven product with granular bentonite. The GCL specimens were hydrated over 8 conditioning periods: 4 and 8 hours, and 1, 2, 4, 8, 16, and 32 days in 4 hydration solutions: DI water and 2 mM, 50 mM, and 200 mM CaCl₂ solutions.

The average cation exchange capacity of the GCL specimens was determined to be 70.5 cmol⁺/kg. The concentration of hydration fluid and conditioning time affected cation exchange behavior of the GCL. For the 50 mM and 200 mM CaCl₂ solutions, variations were significant, where the amount of bound Ca²⁺ in the bentonite increased rapidly and the amount of bound Na⁺ in the bentonite decreased rapidly, with negligible variations over time for the DI water and 2 mM CaCl₂ solutions. The majority of the exchange processes were completed within days

(approximately ≤ 8 days) at these relatively high calcium chloride solution hydration/exposure conditions. Relatively low changes in bound K^+ and Mg^{2+} concentrations were observed. Electrical conductivity of the hydration solutions did not provide good indication of the physicochemical processes occurring in the GCLs. The timing of cation exchange processes is critical for various applications ranging from laboratory and field testing for fluid transport characteristics of GCLs to maintaining integrity of GCL characteristics in field applications with timely cover of constructed liners, potential prehydration, and/or first/repeated exposure to contained liquids. This test program provides worst-case scenario conditions for timing of exchange processes. The timing of exchange processes may be different under different exposure conditions such as different hydration solutions and hydration over/under/between different variably saturated soils. The findings from this investigation improve understanding of the fundamental behavior of GCLs in the presence of chemical solutions.

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