

HYDRAULIC CONDUCTIVITY AND CATION EXCHANGE IN NON-PREHYDRATED AND PREHYDRATED BENTONITE PERMEATED WITH WEAK INORGANIC SALT SOLUTIONS

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Abstract—Sets of replicate hydraulic conductivity tests were conducted using 100 mM KCl and 20 and 40 mM CaCl₂ solutions to evaluate how changes in hydraulic conductivity are related to changes in the exchange complex and physical properties (water content and free swell) of prehydrated and non-prehydrated bentonite used for geosynthetic clay liners (GCLs). Essentially no change in hydraulic conductivity and water content (or void ratio) occurred during tests with the 100 mM KCl solution even though K⁺ was replacing Na⁺ on the exchange complex. In contrast, for the CaCl₂ solutions (20 mM and 40 mM), the hydraulic conductivity increased and the free swell and water content decreased as exchange of Ca²⁺ for Na⁺ occurred. Faster changes in hydraulic conductivity and the exchange complex occurred in the tests with the 40 mM CaCl₂ solution and the non-prehydrated bentonite (*i.e.* the hydraulic conductivity changed more rapidly when exchange occurred more rapidly). Even though exchange of Ca²⁺ for Na⁺ was essentially complete at the end of testing, the hydraulic conductivity obtained with the 20 mM CaCl₂ solution was less and the water content greater than obtained with the 40 mM CaCl₂ solution (2.6×10^{-8} cm/s *vs.* 6.7×10^{-8} cm/s, 122% *vs.* 111%, and 3.2 *vs.* 2.9). Similarly, the prehydrated bentonite had lower hydraulic conductivity (1.9×10^{-8} cm/s *vs.* 6.7×10^{-8} cm/s) and greater water content (167% *vs.* 111%) than the non-prehydrated bentonite at the end of testing, even though Ca-for-Na exchange was essentially complete.

Key Words—Bentonite, Cation Concentration, Cation Valence, Exchange Complex, Free Swell, Geosynthetic Clay Liner, Immobile Water, Interlayer, Leachate, Montmorillonite, Prehydration, Waste Containment.

INTRODUCTION

Thin bentonitic barriers called geosynthetic clay liners (GCLs) have become a popular component of lining systems used for waste containment facilities. They consist of a thin layer of Na-bentonite sandwiched between two geotextiles (thin porous polymeric fabrics) or glued to a geomembrane (thin non-porous plastic sheet). Geosynthetic clay liners are used in waste-containment facilities because of their low hydraulic conductivity ($<10^{-8}$ cm/s) to water, ease of installation, and perceived resistance to environmental distress (Estornell and Daniel, 1992; Koerner, 1997). For GCLs without a geomembrane, the bentonite is responsible for the low hydraulic conductivity. Most bentonites used for GCLs contain at least 70% montmorillonite, which is the component primarily responsible for the low hydraulic conductivity (Shackelford *et al.*, 2000; Egloffstein, 2001).

Leachates contained in most modern waste-containment facilities are aqueous solutions containing a

complex mixture of inorganic and organic species. Most organic species exist at concentrations low enough so that they do not alter the hydraulic conductivity of GCLs. However, inorganic species are known to interact with the bentonite in GCLs and can cause alterations in the hydraulic conductivity (Shackelford *et al.*, 2000). Consequently, there has been considerable interest in understanding how the hydraulic conductivity of bentonite used in GCLs is affected by the concentration and valence of cations in aqueous permeant solutions (Ruhl and Daniel, 1997; Petrov and Rowe, 1997; Shackelford *et al.*, 2000; Jo *et al.*, 2001; Shan and Lai, 2002).

The hydraulic conductivity of GCLs, and clay soils in general, depends on the fraction of water that is hydraulically mobile (*i.e.* 'free' water) and the size and tortuosity of the pathways through which the free water flows (Mesri and Olson, 1971). Na-bentonite typically has low hydraulic conductivity because a large fraction of the pore water is 'bound' to the clay surface (*i.e.* the water is immobile under a hydraulic gradient) and the free water is delegated to small and tortuous flow paths. Bound water molecules accumulate in the interlayer of the montmorillonite particles during hydration and are tightly held by electrical forces (van Olphen, 1991; McBride, 1994, 1997). A change in the fraction of the pore space filled with bound water results in a

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corresponding change in fraction of the pore space filled with free water, as well as changes in the flow paths. Thus, factors that affect the fraction of bound water directly affect the hydraulic conductivity of bentonite (McNeal and Coleman, 1966; Mesri and Olsen, 1971; Egloffstein, 1997; Shackelford *et al.*, 2000; Jo *et al.*, 2001).

For typical leachate compositions in North America, concentration, hydration energy, and valence of cations in the permeant liquid are the primary factors affecting the cations adsorbed on the montmorillonite, the amount of water bound in the interlayer space, and the hydraulic conductivity of GCLs (and bentonite in general) when the permeant liquid is an inorganic aqueous solution. Anion type can be important as well (McNeal and Coleman, 1966; Mesri and Olson, 1971; Alther *et al.*, 1985; Güven, 1993; Gleason *et al.*, 1997; Kashir and Yanful, 2001). For example, several studies have shown that the hydraulic conductivity of GCLs can be very high (10^{-5} to 10^{-7} cm/s) when GCLs are permeated with strong inorganic solutions (>500 mM) or very low ($\sim 10^{-9}$ cm/s) when permeated with weak inorganic solutions (<20 mM) or deionized water. Solutions containing divalent cations are also known to cause an increase in hydraulic conductivity that varies between a factor of 10 and 10,000 depending on the concentration (Alther *et al.*, 1985; Gleason *et al.*, 1997; Petrov *et al.*, 1997; Quaranta *et al.*, 1997; Ruhl and Daniel, 1997; Kolstad, 2000; Shackelford *et al.*, 2000; Egloffstein, 2001; Jo *et al.*, 2001; Vasko *et al.*, 2001; Shan and Lai, 2002). When GCLs containing Na-bentonite are permeated with weak (<20 mM) solutions with polyvalent cations, the hydraulic conductivity gradually increases by a factor of ~ 10 to 20 over a period of months or years (Shackelford *et al.*, 2000; Egloffstein, 2001; Jo *et al.*, 2005). The change in hydraulic conductivity is believed to occur slowly because the rate at which polyvalent cations replace Na^+ ions is controlled by the slow rate at which these cations diffuse into and out of the interlayer space (McBride, 1994; Jo, 2003).

To the authors' knowledge, data documenting the gradual changes in the exchange complex of bentonite from GCLs and the corresponding gradual changes in hydraulic conductivity have not been reported in the literature. Accordingly, the objective of this study was to evaluate how changes in the hydraulic conductivity of bentonites permeated with dilute inorganic salt solutions are related to the composition of the exchange complex, as well as related parameters such as free swell and water content. Tests were conducted on 'non-prehydrated' and 'prehydrated' bentonite to determine if different behavior would be obtained if the bentonite is prehydrated. Non-prehydrated bentonite is defined as bentonite that is hydrated and permeated using the same chemical solution, whereas prehydrated bentonite is defined as bentonite that is initially hydrated by permeation with deionized water, followed by permea-

tion with a chemical solution (Ruhl and Daniel, 1997; Shackelford *et al.*, 2000).

BACKGROUND

Bentonite and bound water

The hydraulic conductivity of bentonite changes in accordance with the fraction of the pore water that is bound to the montmorillonite surface (*i.e.* hydraulically immobile water). Concentration, cation valence and pH of permeant solution affect the fraction of water that is bound (Reeve and Ramaddoni, 1965; McNeal *et al.*, 1966; McNeal and Coleman, 1966; Mesri and Olson, 1971; Mitchell, 1993; Egloffstein, 1997; Petrov and Rowe, 1997; Shackelford *et al.*, 2000; Kolstad, 2000; Jo *et al.*, 2001). While water is bound both on external and interlayer surfaces of montmorillonite particles, most of the bound water is associated with the interlayer. The bound interlayer water forms in two phases: the 'crystalline' phase and the 'osmotic' phase (van Olphen, 1991; McBride, 1994; Prost *et al.*, 1998). The crystalline phase forms as the mineral surface and cations on the surface hydrate from a dry state, and continues until several monolayers of water molecules are bound in the interlayer. The osmotic phase follows the crystalline phase, but occurs only when the exchange sites contain monovalent cations (Norrish and Quirk, 1954; Kjellander *et al.*, 1988; McBride, 1994; Prost *et al.*, 1998). Bentonites that undergo both crystalline and osmotic hydration contain a greater fraction of bound water molecules, and have lower hydraulic conductivity than bentonites that only undergo crystalline swelling (Jo *et al.*, 2001).

In waste-containment applications, the Na-bentonite used in GCLs undergoes crystalline and osmotic swelling from a dry state as the bentonite adsorbs water from the atmosphere and from adjacent subgrade soils (Mitchell, 1993; Egloffstein, 1997; Vasko *et al.*, 2001; Jo *et al.*, 2001). Ion exchange often follows as solutions containing polyvalent cations gradually pass through the bentonite. The exchange process generally alters the hydraulic conductivity, most likely as a result of changes in interlayer spacing and redistribution of pore water between the bound and unbound phases (Jo *et al.*, 2005).

Long-term hydraulic conductivity tests on non-prehydrated GCLs

Shackelford *et al.* (2000) described the hydraulic conductivity of a non-prehydrated GCL containing natural Na-bentonite that was permeated with a 12.5 mM CaCl_2 solution for >4 y. The hydraulic conductivity initially was 1.3×10^{-9} cm/s, which was comparable to the hydraulic conductivity of an identical specimen permeated with deionized water. No change in hydraulic conductivity occurred until 5 pore volumes of flow (PVF) (220 d of permeation) had passed through

the specimen. After 5 PVF, the hydraulic conductivity began to increase gradually, eventually reaching 2.6×10^{-8} cm/s after ~200 PVF (600 d of permeation). No change in hydraulic conductivity occurred for the remainder of the test (*i.e.* 1100 PVF and 4.4 y).

Jo *et al.* (2005) conducted long-term hydraulic conductivity tests on non-prehydrated GCLs containing natural Na-bentonite for >2.5 y. Single-species inorganic salt solutions (*i.e.* NaCl, KCl, CaCl₂ and deionized water) were used as the permeant solutions. Hydraulic conductivities obtained using 100 mM NaCl and KCl solutions were comparable to those obtained using deionized water ($\sim 3.0 \times 10^{-9}$ cm/s) and varied by, at most, a factor of 1.8 throughout the test duration (>3 y). For CaCl₂ solutions of low concentration (≤ 20 mM), the hydraulic conductivity initially stabilized at $\sim 2.0 \times 10^{-9}$ cm/s after 3 to 15 PVF (~60 d), but then began to increase gradually to $\sim 3.0 \times 10^{-8}$ cm/s until the effluent and influent concentrations were essentially equal and the concentration of Na⁺ in the effluent was below the method detection limit (MDL). Approximately 300 to 400 PVF (600 to ~800 d) were required to achieve this condition. In contrast, GCLs permeated with CaCl₂ solutions having high concentration (>50 mM) reached equilibrium nearly immediately, with the hydraulic conductivity approximately two orders of magnitude higher than the hydraulic conductivity to deionized water. Examination of the exchange complex at the end of testing showed that the native cations (primarily Na⁺) were completely replaced by the cations in the permeant solution.

Hydraulic conductivity of prehydrated GCLs permeated with inorganic salt solutions

Prehydration has been suggested as a means to prevent the hydraulic conductivity of GCLs from being altered by permeation. Prehydration is hydration of the bentonite with a dilute solution (*e.g.* deionized, distilled, or tap water) by soaking or permeation prior to permeation by a chemical solution (Gleason *et al.*, 1997; Petrov and Rowe, 1997; Ruhl and Daniel, 1997; Shackelford *et al.*, 2000; Vasko *et al.*, 2001). Prehydration in the field may occur naturally due to migration of water from an underlying subgrade (as a result of capillary effects or vapor-phase diffusion) or may be intentional (*e.g.* spraying or inundating the GCL).

Ruhl and Daniel (1997) conducted hydraulic conductivity tests on non-prehydrated and prehydrated GCLs using a simulated municipal solid waste (MSW) leachate consisting of acetic acid (150 mM), sodium acetate (150 mM), and calcium chloride (25 mM). Prehydration was accomplished by permeating the GCLs with several pore volumes of flow (PVF) of distilled water. The hydraulic conductivity of the non-prehydrated GCLs ranged between 2.0×10^{-6} and 8.0×10^{-6} cm/s, whereas the hydraulic conductivity of

GCLs prehydrated with tap water was approximately four orders of magnitude lower. However, chemical equilibrium was not established when the tests on the prehydrated GCLs were terminated (Ruhl and Daniel, 1997). Thus, a definitive conclusion regarding the permanence of the prehydration effect was not possible.

Petrov and Rowe (1997) conducted hydraulic conductivity tests on non-prehydrated and prehydrated GCLs using NaCl solutions having concentrations between 10 mM and 2000 mM. The GCLs were prehydrated by permeation with distilled water for several PVF. Tests were conducted at effective confining stresses between 3.6 and 108.0 kPa. For higher concentrations (>600 mM), the hydraulic conductivity of GCLs prehydrated with distilled water was approximately one to two orders of magnitude lower than that of the non-prehydrated GCLs. For lower concentrations (≤ 100 mM), the prehydrated and non-prehydrated GCLs had essentially the same hydraulic conductivity (between 9.2×10^{-10} cm/s and 6.4×10^{-9} cm/s).

Vasko *et al.* (2001) investigated how partial prehydration affects the hydraulic conductivity of GCLs. CaCl₂ solutions having concentrations between 5 and 1000 mM were used as the permeant solutions. GCL specimens were prehydrated with deionized water to various water contents (9% to 250%) by capillarity and vapor diffusion to simulate hydration that occurs when a GCL is in contact with a subgrade. Hydraulic conductivities for the strongest solution (1000 mM) decreased from approximately 1.0×10^{-4} cm/s to 1.0×10^{-6} cm/s as the prehydration water content increased from 9% to 200%. Further increases in prehydration water content caused no additional decrease in hydraulic conductivity. For less concentrated solutions, prehydration water content had no effect on the hydraulic conductivity.

Egloffstein (2001) conducted hydraulic conductivity tests on two prehydrated GCL specimens having different dry mass per unit area (*i.e.* 4.7 kg/m² and 8.0 kg/m²) of Na-bentonite. The GCLs were initially permeated with deionized water and then permeated with a solution representing pore water in a natural soil. Egloffstein (2001) did not cite the composition of the solution, but indicates that the Ca concentration in the pore water of natural soils is comparable to that in a 15 mM CaCl₂ solution. The hydraulic conductivity was initially 2.0×10^{-9} cm/s for the specimen having low mass per unit area (4.7 kg/m²) and 4.0×10^{-9} cm/s for the specimen having high mass per unit area (8.0 kg/m²). No change in hydraulic conductivity occurred during one year of permeation. The hydraulic conductivity of both specimens then gradually increased by one order of magnitude and became steady after ~3 y. Egloffstein (2001) attributed the increase in hydraulic conductivity to gradual ion exchange (Ca²⁺ for Na⁺), but did not present data describing the exchange complex.

MATERIAL AND METHODS

Bentonite

The bentonite used in this study was obtained from a GCL containing natural granular Na-bentonite without chemical additives or adhesives. The average initial gravimetric water content of the bentonite was 9% and the specific gravity of solids was 2.65. Results of X-ray diffraction show that the bentonite consists primarily of montmorillonite (81%), but also contains quartz, opaline silica, feldspars, calcite and illite/mica. Sieve and sedimentation analyses (conducted per ASTM D 422 as described in ASTM, 2002) show that the dry bentonite consists of granules ranging from 0.1 mm to 0.4 mm and that the fraction of clay-size particles (<0.002 mm) is 88% (Figure 1). The liquid limit (LL) of the bentonite is 504 and the plastic index (PI) is 465, both of which are comparable to Atterberg limits reported by Mesri and Olson (1971) for Na-bentonite. The bentonite classifies as highly plastic clay (CH) in the Unified Soil Classification System (ASTM D 2487: ASTM, 2002).

The cation exchange capacity (CEC) of the bentonite was determined by the ammonium acetate method (Rhoades, 1982a). The pH and electrical conductivity (EC) of the bentonite were measured on pastes prepared with deionized water (Rhoades, 1982b). The CEC ranges between 65 and 75 meq/100 g, the paste pH is 8.9, and the paste EC is 300 mS/m. The exchange complex was determined as the difference between soluble salts extracted using the fixed-ratio extract method with deionized water (Rhoades, 1982b) and the total exchangeable cations extracted by the ammonium acetate method (Thomas, 1982). Chemical analysis of the extracts was conducted using a flame atomic absorption spectrometer (FAA) in accordance with USEPA Method 200.7. The exchange complex of the bentonite was dominated by Na when the GCL was new (Na = 43.8±16.8 meq/100 g, Ca = 16.5±5.4 meq/100 g, Mg = 6.0±3.4 meq/100 g and K = 0.8±0.4 meq/100 g).

Permeant solutions

The chemical properties of the permeant solutions used in the study are shown in Table 1. Tests were conducted with 100 mM KCl and 20 and 40 mM CaCl₂

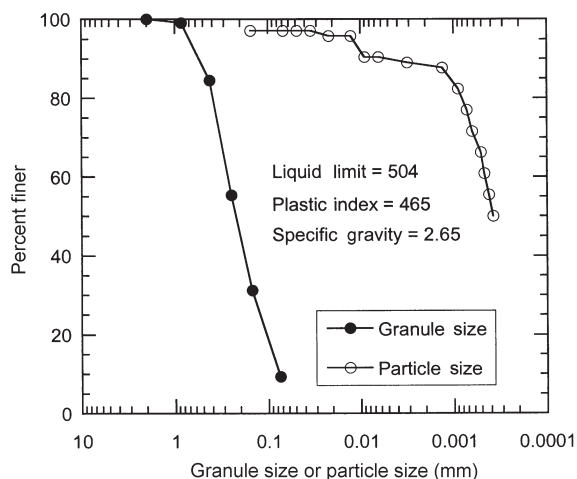


Figure 1. Granule- and particle-size distributions, Atterberg limits, and specific gravity of solids of bentonite.

solutions. The KCl and CaCl₂ solutions were used to investigate the effect of valence. Other cation species were not used. Kolstad *et al.* (2004) and Jo *et al.* (2001) show that cation species has no measurable effect on the hydraulic conductivity of the bentonite used in this study at a given concentration and ratio of monovalent and divalent cations. The solutions were prepared by dissolving powdered salts in deionized (DI) water (Type II water, EC <0.1 mS/m, as specified in ASTM D 1193: ASTM, 2002). The deionized water was also used for prehydration of the bentonite.

The 100 mM KCl and 40 mM CaCl₂ solutions have comparable ionic strength (100 mM *vs.* 120 mM) and were used to assess the effect of valence. The 20 mM and 40 mM CaCl₂ solutions were used to investigate the effect of concentration of divalent cations. Jo *et al.* (2005) show that these Ca solutions are strong enough to alter the hydraulic conductivity of the bentonite, but weak enough so that the changes in hydraulic conductivity occur gradually (*i.e.* >100 d of permeation).

Hydraulic conductivity tests

Hydraulic conductivity tests were conducted on thin layers of bentonite prepared with the same mass per unit

Table 1. Properties of permeant solutions.

| Compound used | Compound source and purity | Concentration (mM) | Cation concentration ^a (mg/L) | | pH ^b | | Electrical conductivity ^c EC (mS/m) | |
|-------------------|----------------------------|--------------------|--|------------|-----------------|------------|--|------------|
| | | | Mean ^d | σ^e | Mean | σ^e | Mean | σ^e |
| KCl | SIGMA Co. 99.0% | 100 | 3882 | 10.2 | 6.3 | 0.1 | 1288 | 4.0 |
| CaCl ₂ | SIGMA Co. 96.0% | 20 | 848 | 17.7 | 6.5 | 0.6 | 437 | 5.2 |
| | | 40 | 1606 | 12.1 | 6.1 | 0.3 | 833 | 0.3 |
| Deionized water | Type II ^f | — | — | — | 6.5 | 0.1 | 0.04 | 0.0 |

^a Measured by atomic absorption spectrometry; ^b measured using a pH meter; ^c measured by an electrical conductivity probe;

^d mean for measurements over the duration of study; ^e standard deviation over the duration of study; and ^f per ASTM D 1193.

area (4.5 kg/m^2) and dry thickness (7 mm) as the GCL. Thin layers of bentonite were used in lieu of GCL specimens so that the dry mass of bentonite in each specimen could be controlled precisely. Specimens were prepared following the procedure described by Jo *et al.* (2001). Dry granular bentonite was removed from a GCL panel and placed as a thin layer in an acrylic ring attached to the lower pedestal of a flexible-wall permeameter. The bentonite was moistened with permeant solution (non-prehydrated tests) or deionized water (prehydrated tests), using a spray bottle, to provide some cohesion. The ring was then removed and the top cap and membrane were installed.

The tests were conducted in flexible-wall permeameters using the falling-head method with constant tailwater level as described in ASTM D 5084 (ASTM, 2002). No backpressure was applied so that effluent samples for chemical analyses (*i.e.* pH, EC and cation concentrations) could be conveniently collected. Cell and influent pressures were applied using gravity reservoirs to minimize the potential for changes in effective stress or gradient that would occur during the long test durations. The effective stress ranged between 16.3 kPa and 17.0 kPa, and was 16.7 kPa on average. The hydraulic gradient ranged between 135 and 125, and was 130 on average. The average hydraulic gradient that was used is greater than gradients normally used for testing clayey soils, but is typical of tests conducted on GCLs (Shackelford *et al.*, 2000).

Non-prehydrated bentonite specimens were permeated directly with a salt solution. Prehydrated specimens were initially permeated with deionized water for 4 PVF (40 d), and then the permeant solution was switched to a salt solution. The specimens were hydrated with the salt solutions (non-prehydrated specimens) or deionized water (prehydrated specimens) in the permeameter for 48 h without application of a hydraulic gradient to allow some swelling of the bentonite before permeation. After 48 h, the hydraulic gradient was applied by opening the effluent valve.

A series of four to six replicate tests was conducted for each category of treatment (non-prehydrated bentonite: 100 mM KCl solution – four tests, 20 mM CaCl_2 solution – six tests, and 40 mM CaCl_2 solution – four tests; prehydrated bentonite: 40 mM CaCl_2 solution – six tests). All tests were conducted with the same effective stress and hydraulic gradient. The tests in each set were terminated sequentially after ~2, 5, 10, 20, 40 and 80 PVF to investigate how properties of the bentonite (*i.e.* water content, free swell and exchange complex) change with time. Because these tests are destructive, the specimens were not permeated again after being terminated to characterize the bentonite. Thus, the number of replicate tests decreased as the PVF increased. Effluent samples were regularly collected for chemical analysis during permeation. The pH, EC and salt concentrations of effluent samples were measured

using a pH meter, an electrical conductivity probe, and FAA using an air-acetylene flame. Mass-balance calculations, made using the mass of eluted Na^+ and the Na^+ on the exchange complex, showed that the mass-balance error was <1%.

After termination of each hydraulic conductivity test, the bentonite was characterized for final thickness, final water content, free swell, void ratio and composition of the exchange complex. The final thickness of the specimen was measured at six locations using a caliper. Free swell was measured per ASTM D 5890 (ASTM, 2002) using deionized water after air drying, grinding, and sieving. Soluble salts and exchangeable cations were measured using the methods described previously. Void ratio (defined as volume of voids per volume of solids) was computed using phase calculations from the measurements of specific gravity, water content and dry density.

RESULTS

Temporal behavior of the hydraulic conductivity, EC ratio (effluent EC \div influent EC), effluent pH, and the Ca and Na concentrations in the effluent are shown in Figures 2 to 5. The results of the hydraulic conductivity tests are summarized in Table 2, in which K_{max} and K_{min} are the highest and lowest hydraulic conductivity, respectively, measured in the replicate tests at a given PVF. The water content, exchange complex and free swell of the bentonite at various PVF are summarized in Table 3.

At a given PVF, hydraulic conductivities obtained from the replicate tests differed by at most a factor of 1.6 for the non-prehydrated bentonite specimens permeated with the 100 mM KCl solution, a factor of 2.1 for the non-prehydrated bentonite specimens permeated with the 20 and 40 mM CaCl_2 solutions, and a factor of 1.3 for the prehydrated bentonite specimens permeated with the 40 mM CaCl_2 solution (Table 2). The trend in hydraulic conductivity obtained from the replicate tests was generally very similar. In addition, similar effluent concentrations, EC ratio and effluent pH were obtained from the replicate tests (Figures 2 to 5), indicating good reproducibility. Thus, the hydraulic conductivity, free swell, water content and exchange-complex measurements made at different times on the replicate specimens are believed to be representative of the temporal changes in the bentonite for a given permeant solution, even though the measurements were made on separate specimens.

Hydraulic conductivity of non-prehydrated bentonite (KCl solution)

Four replicate tests were conducted on non-prehydrated bentonite specimens permeated with the 100 mM KCl solution. The tests were terminated sequentially at 3, 8, 23 and 43 PVF (Figure 2). After 3 PVF, the EC

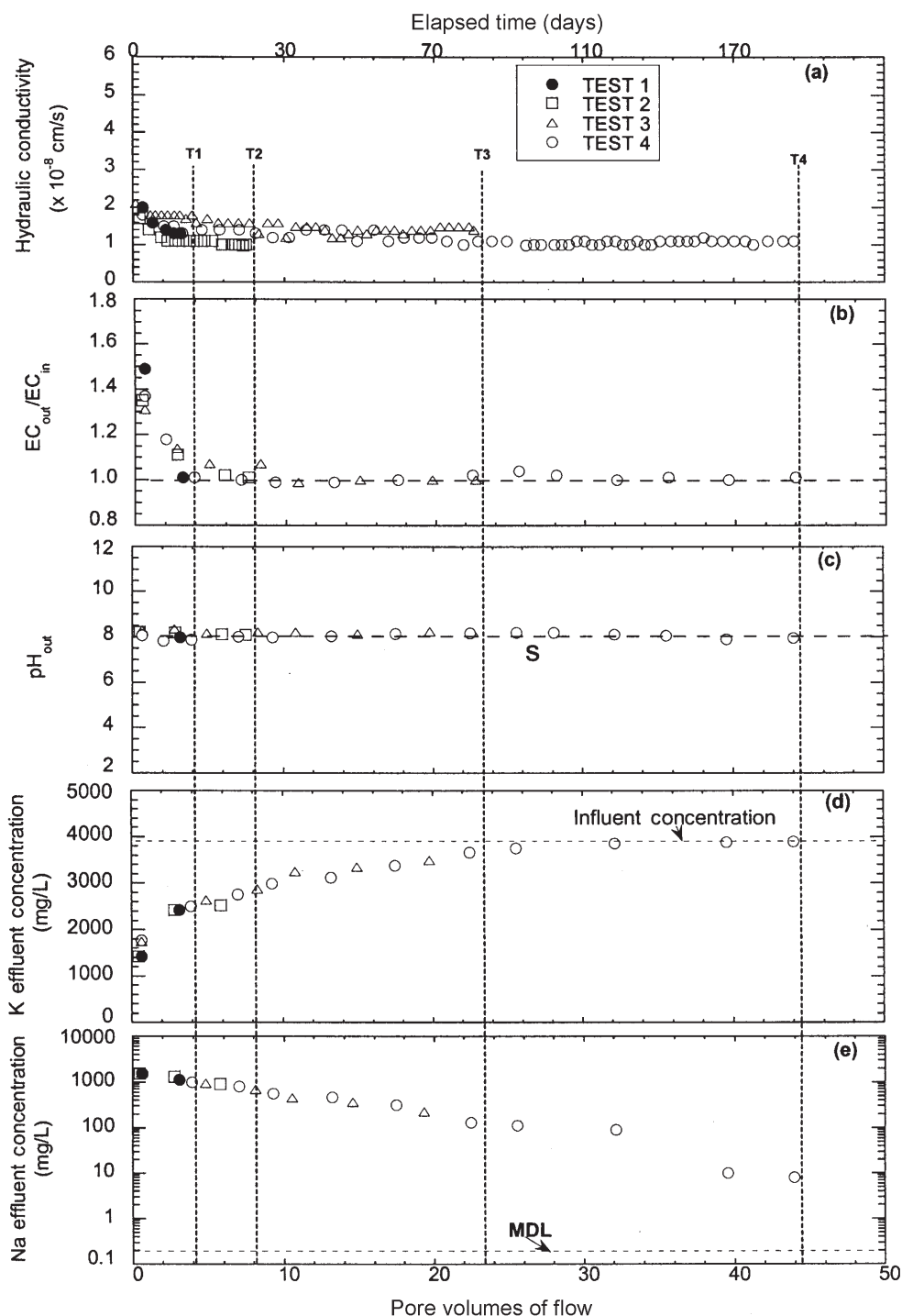


Figure 2. Hydraulic conductivity (a), EC ratio (b), effluent pH (c), effluent K concentration (d), and effluent Na concentration (e) for non-prehydrated specimens permeated with a 100 mM KCl solution as a function of PVF (T1, T2, T3 and T4 designate when each test was terminated). MDL = method detection limit for Na.

ratio was 1.0 ± 0.1 and the hydraulic conductivity was stable ($\sim 1.4 \times 10^{-8}$ cm/s). Only a small change (*i.e.* within a factor of 1.6) in hydraulic conductivity occurred during the tests (~ 200 d).

Hydraulic conductivity of non-prehydrated bentonite (CaCl₂ solutions)

Six replicate tests were conducted on non-prehydrated bentonite specimens with the 20 mM CaCl₂

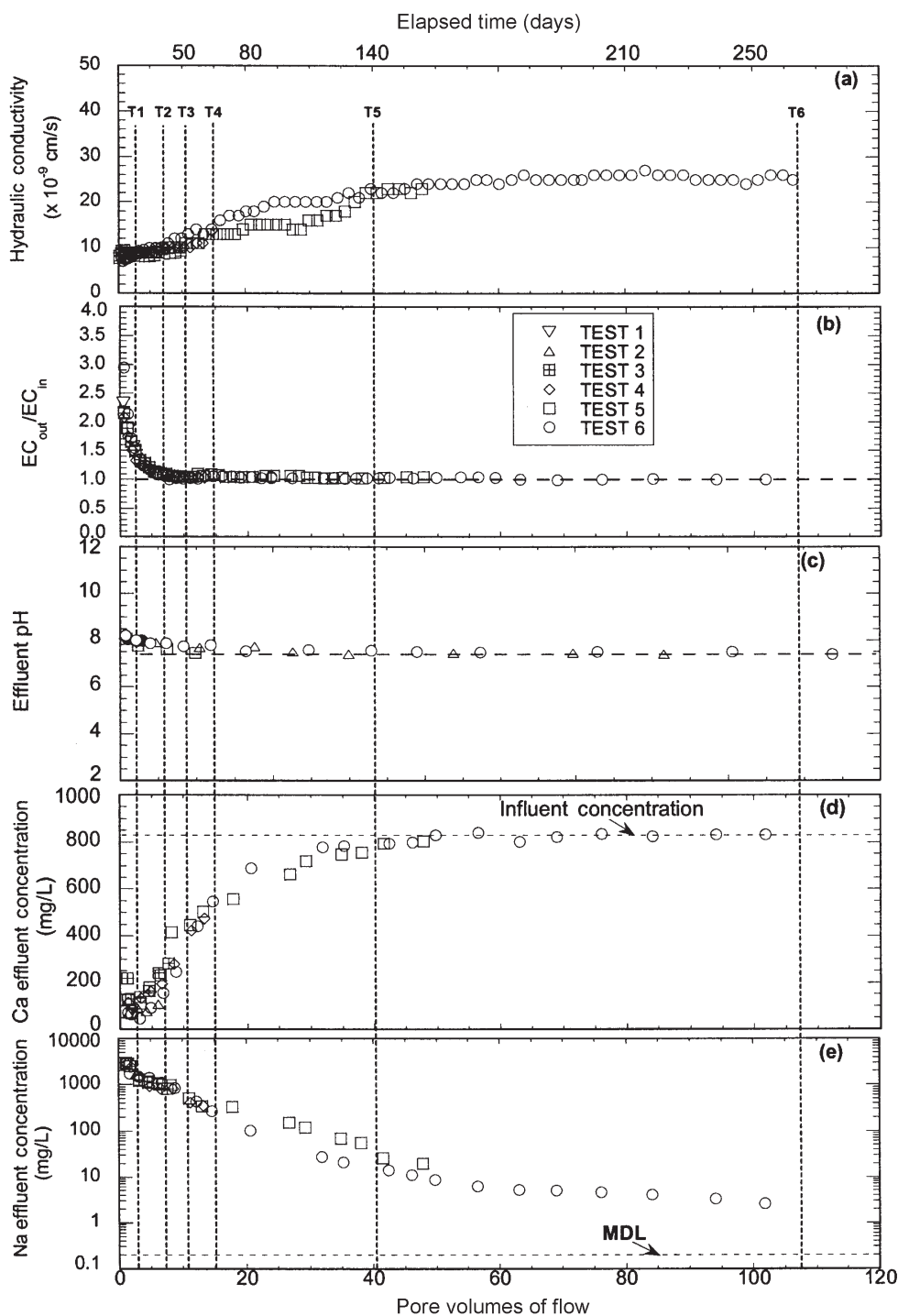


Figure 3. Hydraulic conductivity (a), EC ratio (b), effluent pH (c), effluent Ca concentration (d), and effluent Na concentration (e) for non-prehydrated specimens permeated with a 20 mM CaCl_2 solution as a function of PVF (T1, T2, T3, T4, T5 and T6 designate when each test was terminated). MDL = method detection limit for Na.

solution. The replicate tests were terminated sequentially at 2, 6, 10, 13, 48 and 106 PVF. Four replicate tests were conducted on non-prehydrated bentonite specimens permeated using the 40 mM CaCl_2 solution. These tests were terminated at 3, 10, 71 and 94 PVF.

Results of tests conducted with the 20 mM CaCl_2 are summarized in Figure 3. The hydraulic conductivity of the bentonite specimens was initially approximately constant (8.1×10^{-9} cm/s) within the first 3 PVF (15 d) (Figure 3a), but the EC and chemical composition of the

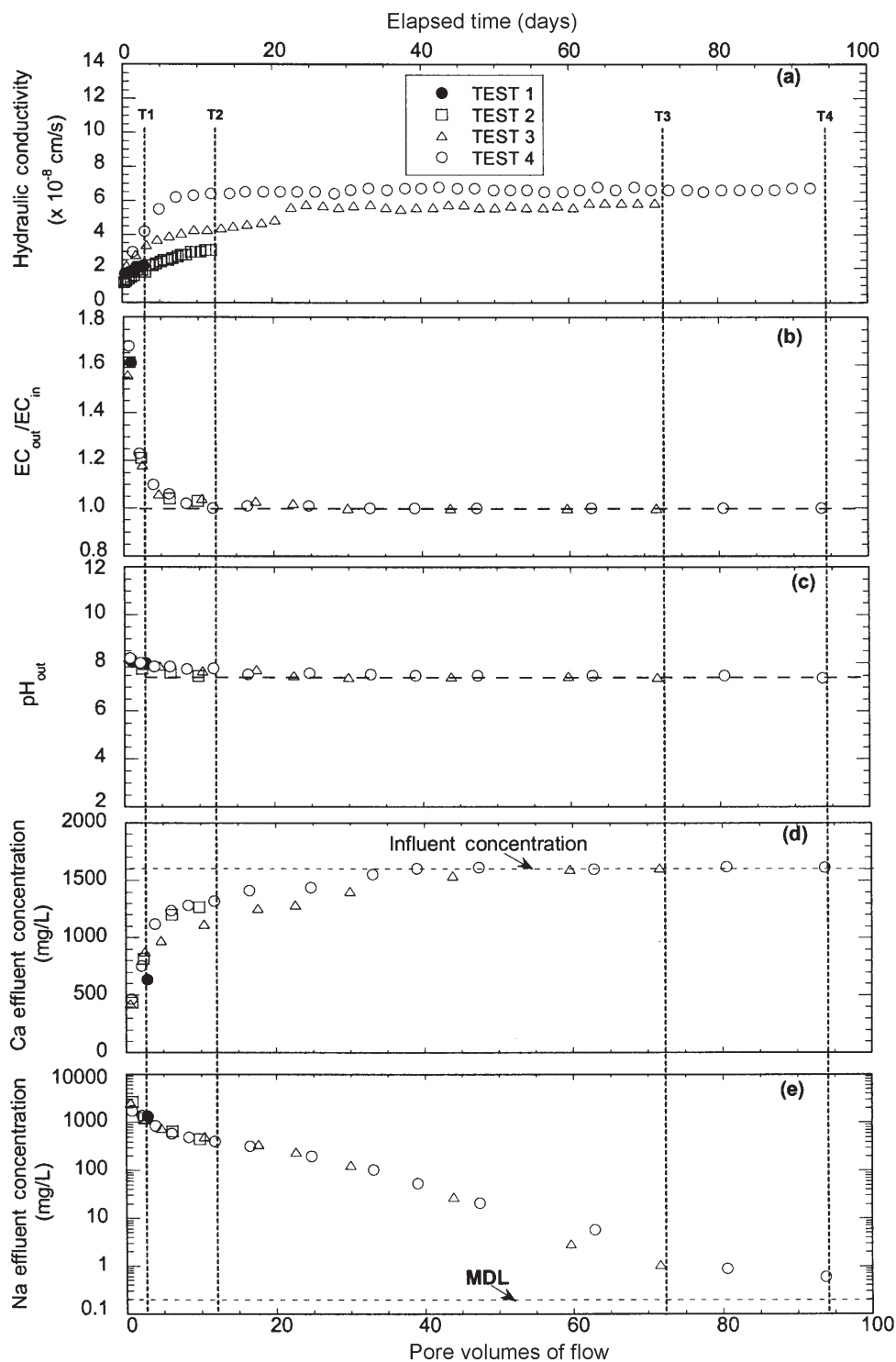


Figure 4. Hydraulic conductivity (a), EC ratio (b), effluent pH (c), effluent Ca concentration (d), and effluent Na concentration (e) for non-prehydrated specimens permeated with a 40 mM $CaCl_2$ solution as a function of PVF (T1, T2, T3 and T4 designate when each test was terminated). MDL = method detection limit for Na.

influent and effluent were appreciably different during this period (Figure 3b,d,e). Subsequently, the hydraulic conductivity gradually increased to 2.2×10^{-8} cm/s.

Concurrently, the Ca concentration in the effluent increased, the Na concentration decreased, and the EC ratio approached 1.0. Even after 100 PVF (~270 d), the

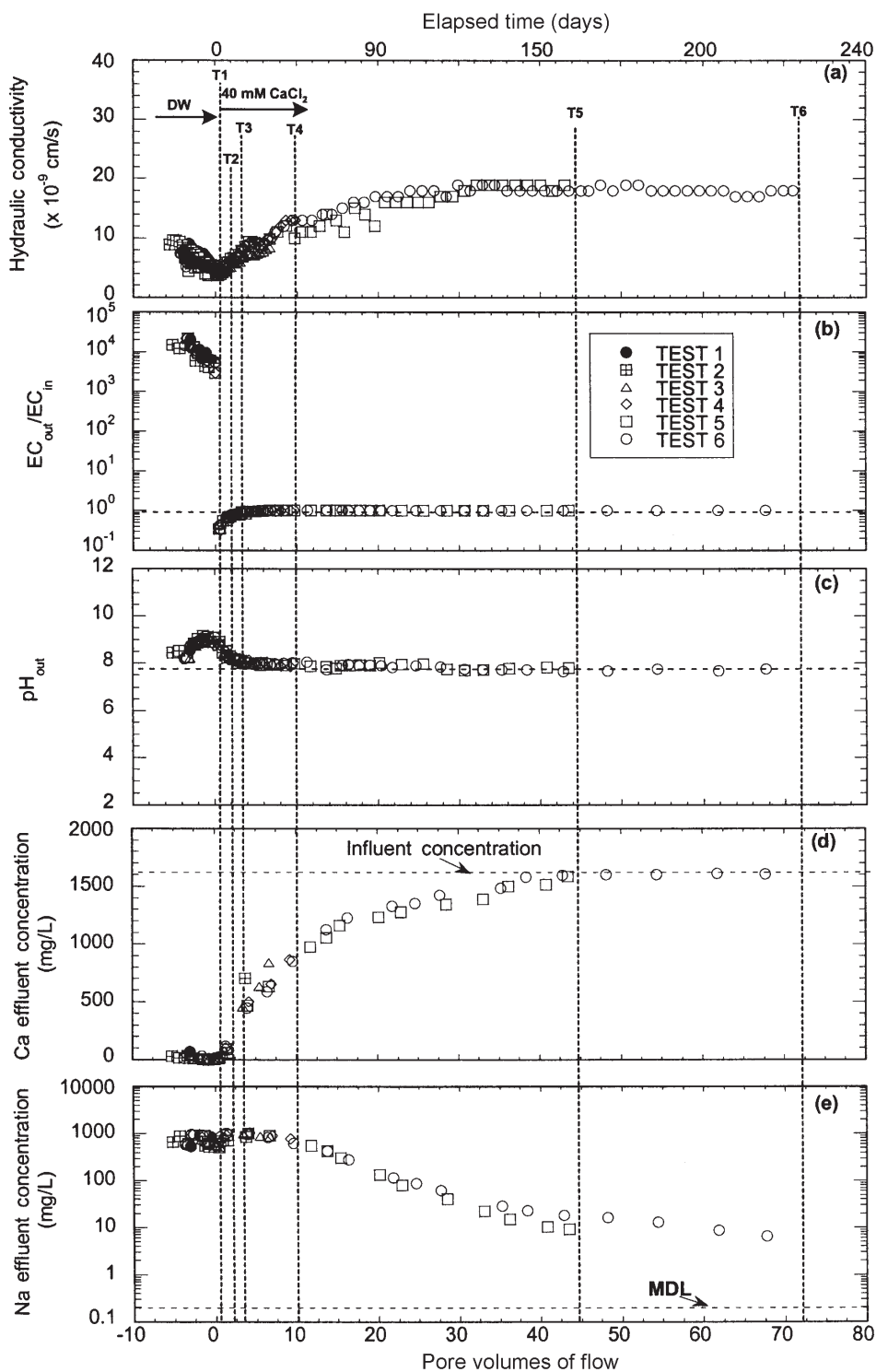


Figure 5. Hydraulic conductivity (a), EC ratio (b), effluent pH (c), effluent Ca concentration (d) and effluent Na concentration (e) for prehydrated specimens permeated with a 40 mM CaCl_2 solution as a function of PVF (T1, T2, T3, T4, T5 and T6 designate when each test was terminated). MDL = method detection limit for Na.

hydraulic conductivity continued to increase slightly and the Na concentration in the effluent remained at ~5 mg/L.

The results of the tests conducted with the 40 mM CaCl_2 solution are shown in Figure 4. The hydraulic conductivity was initially 2.9×10^{-8} cm/s after 3 PVF

Table 2. Summary of hydraulic conductivities.

| Type of specimen | Permeant liquid | Pore volumes of flow | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Test 6 | Median ^a | K_{\max}/K_{\min} ^b |
|------------------|-------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------------------|
| Non-prehydrated | 100 mM KCl | 3 | 1.3×10^{-8} | 1.1×10^{-8} | 1.8×10^{-8} | 1.5×10^{-8} | — | — | 1.4×10^{-8} | 1.6 |
| | | 8 | — | 1.0×10^{-8} | 1.6×10^{-8} | 1.3×10^{-8} | — | — | 1.3×10^{-8} | 1.6 |
| | | 23 | — | — | 1.4×10^{-8} | 1.1×10^{-8} | — | — | 1.3×10^{-8} | 1.3 |
| | | 43 | — | — | — | 1.1×10^{-8} | — | — | 1.1×10^{-8} | 1.0 |
| | 20 mM CaCl ₂ | 2 | 8.1×10^{-9} | 8.0×10^{-9} | 8.0×10^{-9} | 8.7×10^{-9} | 8.9×10^{-9} | 8.0×10^{-9} | 8.1×10^{-9} | 1.1 |
| | | 6 | — | 8.3×10^{-9} | 8.4×10^{-9} | 9.0×10^{-9} | 9.1×10^{-9} | 9.9×10^{-9} | 9.0×10^{-9} | 1.2 |
| | | 10 | — | — | 9.4×10^{-9} | 9.9×10^{-9} | 1.0×10^{-8} | 1.2×10^{-8} | 1.0×10^{-8} | 1.3 |
| | | 13 | — | — | — | 1.1×10^{-8} | 1.1×10^{-8} | 1.4×10^{-8} | 1.1×10^{-8} | 1.3 |
| | 40 mM CaCl ₂ | 48 | — | — | — | — | 2.3×10^{-8} | 2.4×10^{-8} | 2.4×10^{-8} | 1.0 |
| | | 106 | — | — | — | — | — | 2.6×10^{-8} | 2.6×10^{-8} | 1.0 |
| | | 3 | 2.3×10^{-8} | 1.8×10^{-8} | 3.4×10^{-8} | 3.9×10^{-8} | — | — | 2.9×10^{-8} | 1.7 |
| | | 10 | — | 3.0×10^{-8} | 4.3×10^{-8} | 6.3×10^{-8} | — | — | 4.3×10^{-8} | 2.1 |
| Prehydrated | 40 mM CaCl ₂ | 71 | — | — | 5.9×10^{-8} | 6.6×10^{-8} | — | — | 6.3×10^{-8} | 1.1 |
| | | 94 | — | — | — | 6.7×10^{-8} | — | — | 6.7×10^{-8} | 1.0 |
| | 40 mM CaCl ₂ | 0 | 5.0×10^{-8} | 5.3×10^{-8} | 4.8×10^{-8} | 5.1×10^{-9} | 5.2×10^{-9} | 4.7×10^{-9} | 5.1×10^{-9} | 1.1 |
| | | 4 | — | 9.0×10^{-9} | 7.3×10^{-9} | 9.0×10^{-9} | 8.7×10^{-9} | 7.4×10^{-9} | 8.7×10^{-9} | 1.2 |
| | | 6 | — | — | 8.4×10^{-9} | 9.4×10^{-9} | 8.9×10^{-9} | 8.8×10^{-9} | 8.9×10^{-9} | 1.1 |
| | | 10 | — | — | — | 1.3×10^{-8} | 1.0×10^{-8} | 1.3×10^{-8} | 1.3×10^{-8} | 1.3 |
| | | 44 | — | — | — | — | 1.9×10^{-8} | 1.8×10^{-8} | 1.9×10^{-8} | 1.1 |
| | | 71 | — | — | — | — | — | 1.8×10^{-8} | 1.9×10^{-8} | 1.0 |

^a Median hydraulic conductivity at a given PVF^b K_{\max} is the highest hydraulic conductivity at a given PVF and K_{\min} is the lowest hydraulic conductivity at a given PVF

(~7 d) had passed through the bentonite, and then increased rapidly. After 90 PVF (~90 d), the hydraulic conductivity had reached 6.7×10^{-8} cm/s and was still increasing slightly. This trend in hydraulic conductivity is consistent with that obtained with the 20 mM CaCl_2 solution, although the hydraulic conductivity increased more rapidly and ultimately was ~3 times higher with the 40 mM CaCl_2 solution. As was obtained using the test with the 20 mM solution, the Ca concentration in the effluent increased and the Na concentration in the effluent decreased as the hydraulic conductivity was changing. At the end of testing, elution of Na was still occurring (the Na concentration in the effluent was ~3 mg/L).

Long-term (>2.5 y) tests conducted on the GCL by Jo *et al.* (2005) using similar solutions yielded comparable hydraulic conductivities. Jo *et al.* (2005) report a long-term hydraulic conductivity of 2.3×10^{-8} cm/s for a 10 mM CaCl_2 solution and 2.9×10^{-8} cm/s for a 20 mM CaCl_2 solution. Thus, the thin bentonite layers are believed to be representative of conditions in a GCL.

Hydraulic conductivity of prehydrated bentonite (CaCl_2 solutions)

Six replicate tests were conducted on prehydrated bentonite specimens permeated with the 40 mM CaCl_2 solution. These tests were terminated sequentially at 0, 4, 6, 10, 44 and 71 PVF of the CaCl_2 solution (Figure 5). The PVF shown in Figure 5 corresponds to conditions after permeation with the CaCl_2 solution was initiated (*i.e.* the switch from deionized water to 40 mM CaCl_2 occurs at PVF = 0). The hydraulic conductivity of the bentonite specimens was 5.1×10^{-9} cm/s at the end of the prehydration period (*i.e.* permeation with deionized water for 30 d), comparable to the hydraulic conductivity to deionized water reported by Kolstad *et al.* (2004) and Jo *et al.* (2001, 2005).

After switching to the 40 mM CaCl_2 solution, the hydraulic conductivity initially decreased to 4.0×10^{-9} cm/s. After 2 PVF (~15 d), the hydraulic conductivity increased to 1.8×10^{-8} cm/s (a factor of 4.5) until ~40 PVF (~160 d). More gradual changes occurred thereafter. After approximately 70 PVF (~230 d), the hydraulic conductivity began to increase slightly. As with the other tests, the Ca concentration in the effluent increased and the Na concentration decreased during the test, and the Na concentration in the effluent was still appreciable (~10 mg/L) at the end of testing.

DISCUSSION

Effect of cation valence

Median hydraulic conductivities at a given PVF, free swell in deionized water, mole fractions of Na (X_{Na}), K (X_{K}) and Ca (X_{Ca}), water content, and void ratio of the bentonite after sequentially terminating the replicate

hydraulic conductivity tests are shown in Figure 6 for the non-prehydrated specimens permeated with the 100 mM KCl and 40 mM CaCl_2 solutions and in Figure 7 for the non-prehydrated specimens permeated with the 100 mM KCl and 40 mM CaCl_2 solutions. The mole fraction (X_i) is defined as the moles of cation *i* on the exchange complex relative to the total number of moles of cations on the exchange complex of bentonite. Void ratio is the total volume of voids per volume of mineral solid and is directly proportional to the water content when the soil is saturated.

The hydraulic conductivity obtained with the 100 mM KCl solution remains within a narrow range (1.1×10^{-8} to 1.4×10^{-8} cm/s) even though gradual exchange of K^+ for Na^+ occurs, indicating that the exchange of K^+ for Na^+ had no practical effect on the hydraulic conductivity of the bentonite (Figure 6a, 7a). By the end of the test, K^+ replaced essentially all of the Na^+ in the exchange complex. However, X_{K} remained <1.0 because of the Ca^{2+} originally in the exchange complex, which is preferred relative to K^+ (Figures 6c, 7c).

In contrast, the hydraulic conductivities obtained with the 40 mM and 20 mM CaCl_2 solutions gradually increase throughout the tests (40 mM: 2.9×10^{-8} to 6.7×10^{-8} cm/s vs. 20 mM: 8.9×10^{-9} to 2.6×10^{-8} cm/s), and the rate of change in the hydraulic conductivity is related to the rate of exchange of Ca^{2+} for Na^+ (*i.e.* the hydraulic conductivity changes more rapidly when the exchange complex is changing rapidly). Exchange of permeant cations for Na^+ occurs faster in the tests with the 40 mM Ca^{2+} solution than the 100 mM K^+ solution, which is probably due to the slightly higher ionic strength of the Ca^{2+} solution (120 mM vs. 100 mM) and the greater affinity of montmorillonite for Ca^{2+} . On the other hand, replacement of Na^+ occurs more slowly with the 20 mM Ca^{2+} solution than the 100 mM K^+ solution probably due to the greater ionic strength of the K^+ solution (100 mM vs. 60 mM) and its effect on diffusion into the interlayer space (Jo, 2003).

The trends in free swell data for Ca^{2+} reflect the gradual exchange of permeant cations for Na^+ . As Ca^{2+} replaces Na^+ , the osmotic component of free swell decreases, which is reflected in less free swell. Ultimately, the free swell at the end of testing for the specimen permeated with the CaCl_2 solutions is comparable to that of Ca-bentonite (~8 mL/2 g, Egloffstein, 1995; Jo *et al.*, 2005), which is also consistent with the nearly complete exchange of Ca^{2+} for Na^+ that was observed ($X_{\text{Ca}} = 0.93$, $X_{\text{Na}} = 0.02$ at the end of testing, Figures 6, 7). The water content and void ratio data also reflect this behavior. The water content and void ratio of the bentonite from tests with the Ca^{2+} solutions gradually decrease (40 mM: 127 to 111% and 3.4 to 2.9, 20 mM: 155 to 122% and 4.2 to 3.2), reflecting contraction of the interlayer space due to replacement of Na^+ by Ca^{2+} , *i.e.* increases in hydraulic conductivity incurred by permeation using a Ca^{2+}

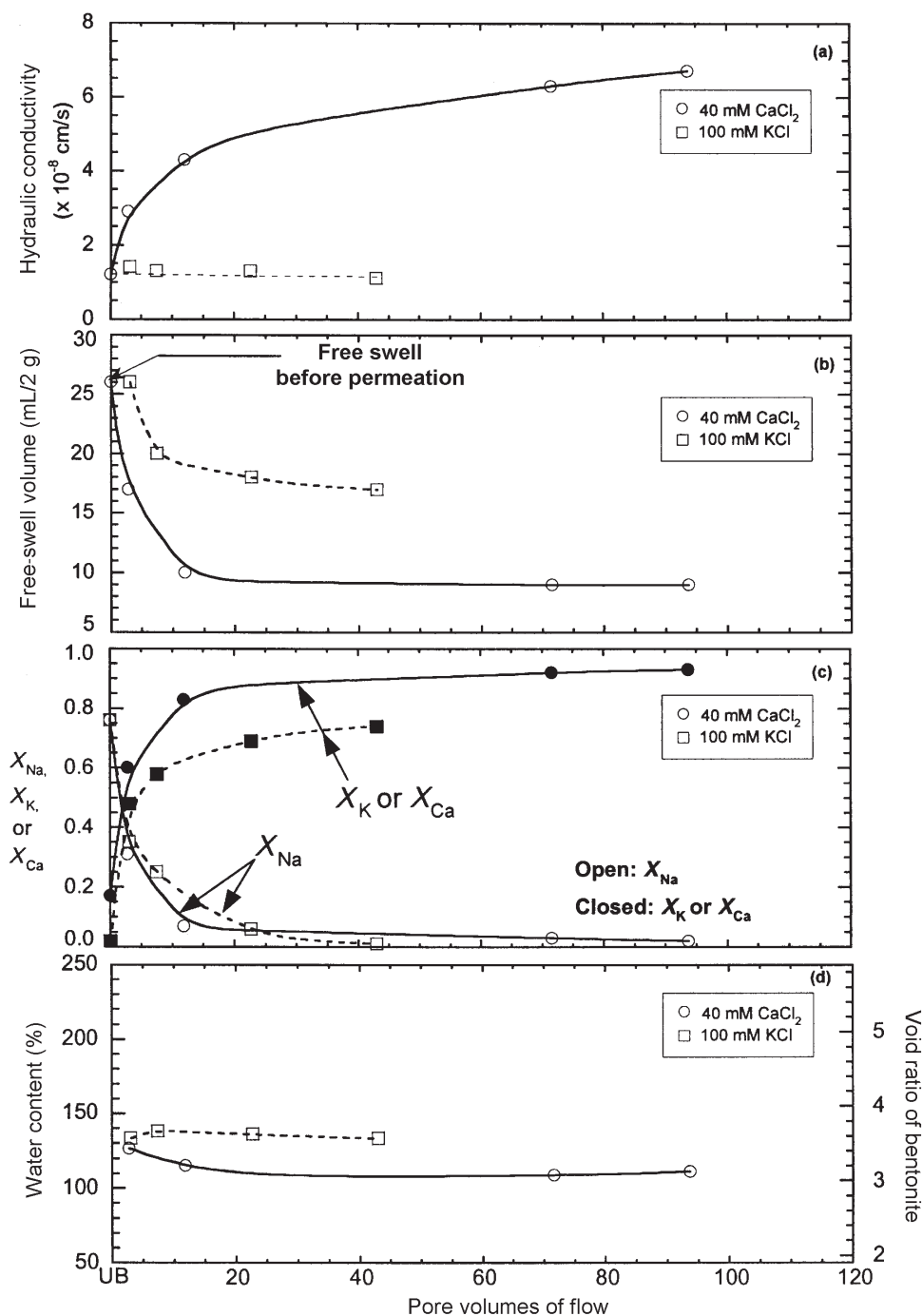


Figure 6. Hydraulic conductivity (a), free swell volume in deionized water (b), mole fractions of Na, K and Ca in the exchange complex (c), and water content and void ratio of bentonite (d) for non-prehydrated specimens after terminating hydraulic conductivity tests conducted using 100 mM KCl and 40 mM CaCl_2 solutions. X_{Na} = the mole fraction of Na on the exchange complex, X_{K} = the mole fraction of K on the exchange complex, X_{Ca} = the mole fraction of Ca on the exchange complex, and UB = unused bentonite.

solution are associated with decreases in void ratio (*i.e.* smaller total void space).

The trends in water content (or void ratio) for the bentonite permeated with the K^+ are also consistent with the trend in hydraulic conductivity. Essentially no

change in hydraulic conductivity, water content, or void ratio occurred during the test (Figure 6a,d) even though K^+ was replacing Na^+ (Figure 6c). However, the gradual reduction in free swell does reflect the K^+ -for- Na^+ exchange. The effect of exchange is evident in the

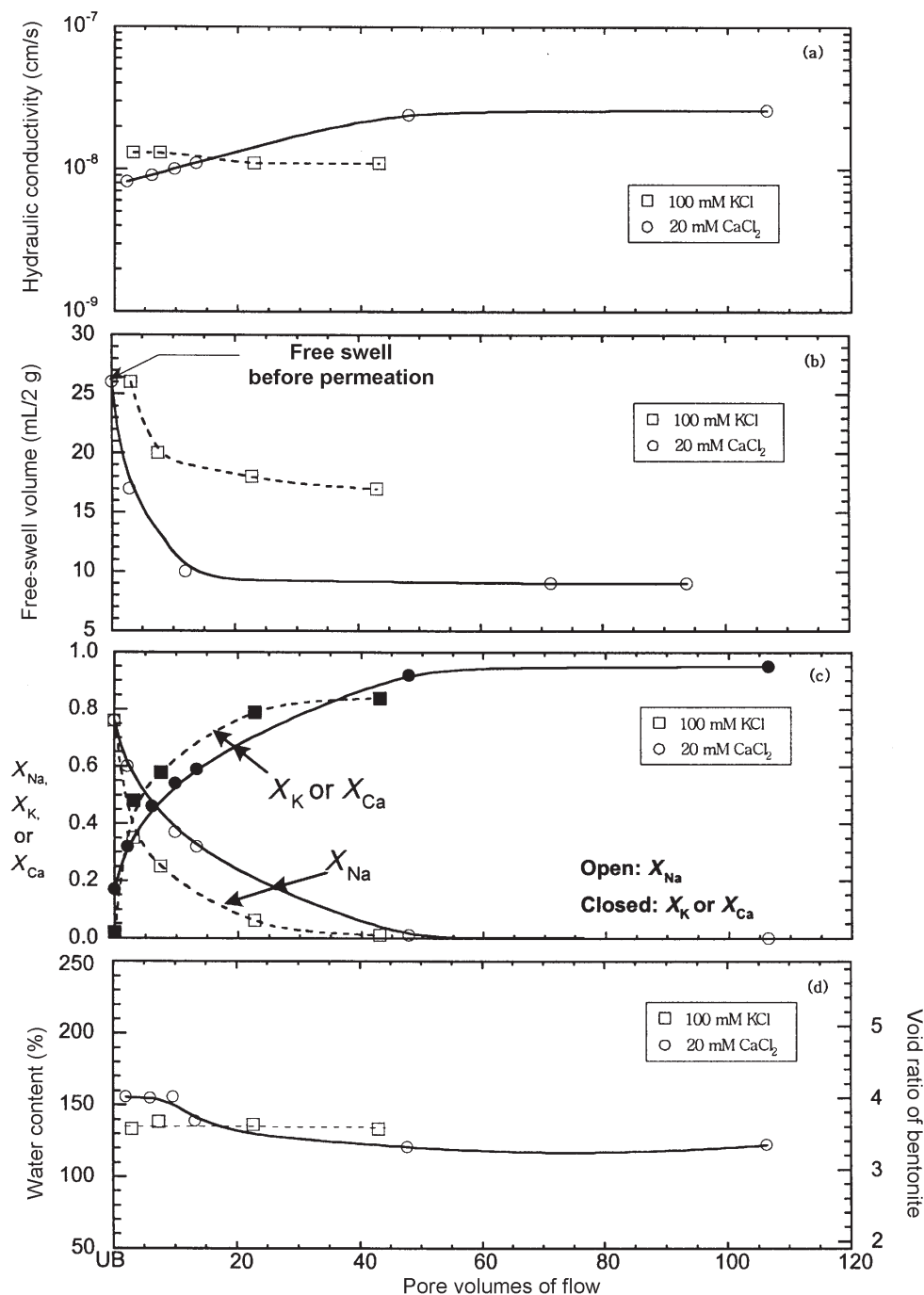


Figure 7. Hydraulic conductivity (a), free swell volume in deionized water (b), mole fractions of Na, K, and Ca in the exchange complex (c), and water content and void ratio of bentonite (d) for non-prehydrated specimens after terminating hydraulic conductivity tests conducted using 100 mM KCl and 20 mM CaCl_2 solutions. X_{Na} = the mole fraction of Na on the exchange complex, X_{K} = the mole fraction of K on the exchange complex, X_{Ca} = the mole fraction of Ca on the exchange complex, and UB = unused bentonite.

free swell data because the bentonite is dried, ground and then re-hydrated in deionized water for a free swell test, and K-bentonites exhibit lower free swell in deionized water than Na-bentonites when hydrated

from a dry state because of the smaller hydrated radius of K^+ resulting from a lower hydration energy (van Olphen, 1991; Güven, 1993; McBride, 1994; Jo *et al.*, 2001).

Effect of concentration

The effect of concentration is shown in Figure 8 using data from the tests conducted on non-prehydrated bentonite with 20 and 40 mM CaCl_2 solutions. For both solutions, hydraulic conductivity increases and free swell, water content and void ratio decrease as exchange of Ca^{2+} for Na^+ occurs. The rate of change in these

properties is reflected in the rate at which ion exchange occurs. Faster changes occur in the tests with the 40 mM CaCl_2 solution. More Ca^{2+} is available for exchange and the concentration gradient between the bulk pore water and interlayer space is larger.

At the end of both sets of tests, exchange of Ca^{2+} for Na^+ is essentially complete (Figure 8c). Nevertheless, the hydraulic conductivity obtained with the 20 mM

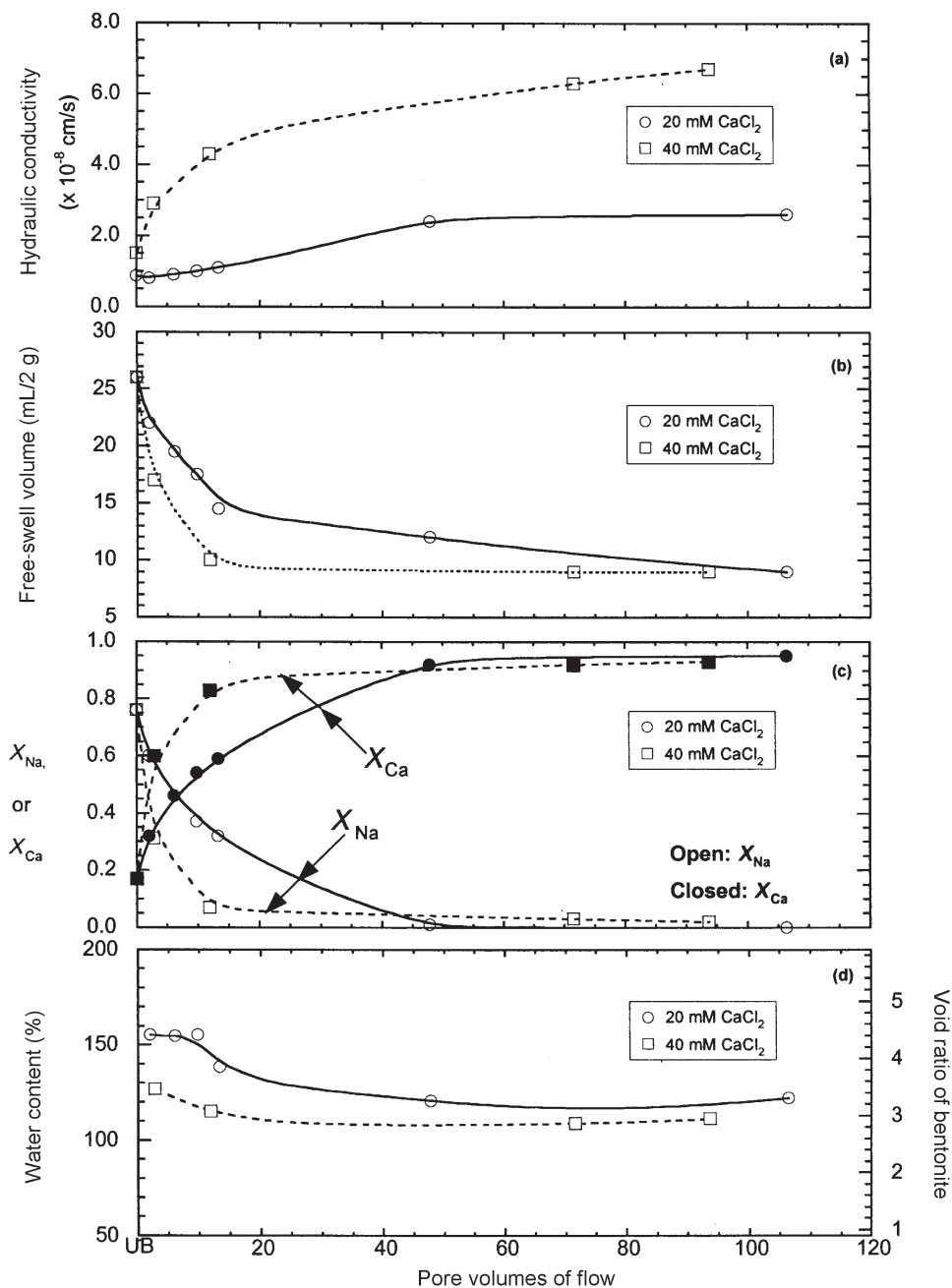


Figure 8. Hydraulic conductivity (a), free swell volume in deionized water (b), mole fractions of Na and Ca in the exchange complex (c), water content and void ratio of bentonite (d) for non-prehydrated specimens after terminating hydraulic conductivity tests conducted using 20 mM and 40 mM CaCl_2 solutions. X_{Na} = the mole fraction of Na on the exchange complex, X_{Ca} = the mole fraction of Ca on the exchange complex, and UB = unused bentonite.

CaCl_2 solution (2.6×10^{-9} cm/s) is less than that obtained with the 40 mM CaCl_2 (6.7×10^{-8} cm/s), whereas the water content (or void ratio) of bentonite from the tests with the 20 mM CaCl_2 solution is larger than the water content (or void ratio) of bentonite from the tests with the 40 mM CaCl_2 solution (122% vs. 111%, and 3.2 vs. 2.9) (Figure 8a,d). That is, more water is being retained in the bentonite permeated with the more dilute CaCl_2 solution, even though both bentonites are Ca-bentonites at the end of testing (*i.e.* both specimens should no longer exhibit an osmotic component to swell).

This difference in retention of water is not evident in the free swell data. When exchange is complete, free swell of the bentonite from both tests is similar (8.5 vs. 9.0 mL/2 g) regardless of concentration of the permeant solution (Figure 8b). However, a free-swell test is conducted on bentonite that has been dried, *i.e.* external energy (heat during drying) is used to extract water molecules from the interlayer space after exchange has occurred. In contrast, the osmotic gradient is the primary force for extracting water molecules during a hydraulic conductivity test. Apparently the osmotic gradient is counteracted by forces tending to retain water, such as electrostatic forces acting on the polar water molecules or correlation forces between the hydrated Ca^{2+} ions (McBride, 1997). As a result, complete compression of the interlayer space (*i.e.* to four layers of water molecules, as during hydration of dry Ca-bentonite) does not occur when ion exchange takes place during permeation. The exception could be when the permeant solution is concentrated enough to provide an osmotic force large enough to overcome forces in the interlayer space that tend to retain water molecules.

Effect of prehydration

The effects of prehydration are shown in Figure 9 using data from the tests on prehydrated and non-prehydrated bentonite permeated with the 40 mM CaCl_2 solution. Greater increases in hydraulic conductivity occur for the non-prehydrated bentonite, and the changes in hydraulic conductivity are more persistent (Figure 9a). For example, nearly all of the change in hydraulic conductivity of the prehydrated bentonite occurs within the first 10 PVF, whereas changes in hydraulic conductivity are evident throughout the test on the non-prehydrated bentonite. In both sets of tests, the rapid change in hydraulic conductivity, along with the rapid decrease in free swell, occurs in periods when most of the exchange of Ca^{2+} for Na^+ occurs (Figure 9a,b).

Exchange occurs more rapidly in the non-prehydrated bentonite than the prehydrated bentonite (Figure 9c). The retardation of exchange by prehydration is also evident in the free-swell data; free swell of the bentonite drops more rapidly than free swell of the prehydrated bentonite (Figure 9b). These differences may be due to

diffusion of Ca^{2+} into the interlayer space being inhibited by a greater amount of immobile water in the prehydrated bentonite.

Even when exchange is complete (at the end of testing), the prehydrated bentonite has lower hydraulic conductivity (1.9×10^{-8} cm/s) than the non-prehydrated bentonite (6.7×10^{-8} cm/s). Comparison of the free swell, water content, and void ratio data suggest that the lower hydraulic conductivity is due to retention of immobile water. The free swell obtained from dried bentonite for the prehydrated specimens is the same as that from dried bentonite for the non-prehydrated specimens (~ 8 mL/2 g); however, the prehydrated specimens have 55% higher water content and larger void ratio (4.4 vs. 2.9) than the non-prehydrated specimens (Figure 9d).

In a manner similar to that observed when comparing hydraulic conductivities of the non-prehydrated bentonites (*i.e.* Figure 9), the lower hydraulic conductivity of the prehydrated bentonite relative to that of non-prehydrated bentonite was not expected given that both bentonites effectively were Ca-bentonites at the end of the test. If exchange of Na^+ for Ca^{2+} is complete, then the interlayer space should collapse to a similar spacing regardless of concentration. This condition generally corresponds to little swell (crystalline swell only) and high hydraulic conductivity ($\sim 10^{-6}$ cm/s) because most of the pore water is free to flow rather than being bound to the mineral surface (McNeal *et al.*, 1966; McNeal and Coleman, 1966; Lagerwerff *et al.*, 1969; Mesri and Olson, 1971; Shackelford *et al.*, 2000; Jo *et al.*, 2001). However, most fundamental studies regarding the crystalline swell of bentonite consider hydration of a dry homoionic montmorillonite, which contains polyvalent cations on the exchange sites (Norris and Quirk, 1954; Posner and Quirk, 1964; Kjellander *et al.*, 1988; McBride, 1994; Prost *et al.*, 1998). In contrast, in this study the bentonite initially contained mainly Na^+ , and was hydrated into an osmotic state from a dry state with a permeant solution having low concentration of Ca^{2+} (*i.e.* non-prehydrated bentonite) or deionized water (prehydrated bentonite). Hydration then was followed by gradual exchange of Ca^{2+} for Na^+ . This process appears to result in a different swelling state, greater retention of water, and lower hydraulic conductivity than hydration of homoionic bentonite from the dry state using a solution with the same ionic composition.

Free swell and exchange complex

The similarity in the trends shown in Figures 6–8 between X_{Na} and PVF and free swell and PVF suggest that free-swell tests may be a convenient means to estimate X_{Na} . To evaluate this possibility, the relationship between X_{Na} and free swell is graphed using the data in Table 3, as shown in Figure 10. Linear relationships exist between X_{Na} and free swell, but the relationship is different for the KCl and CaCl_2 tests. Thus, a

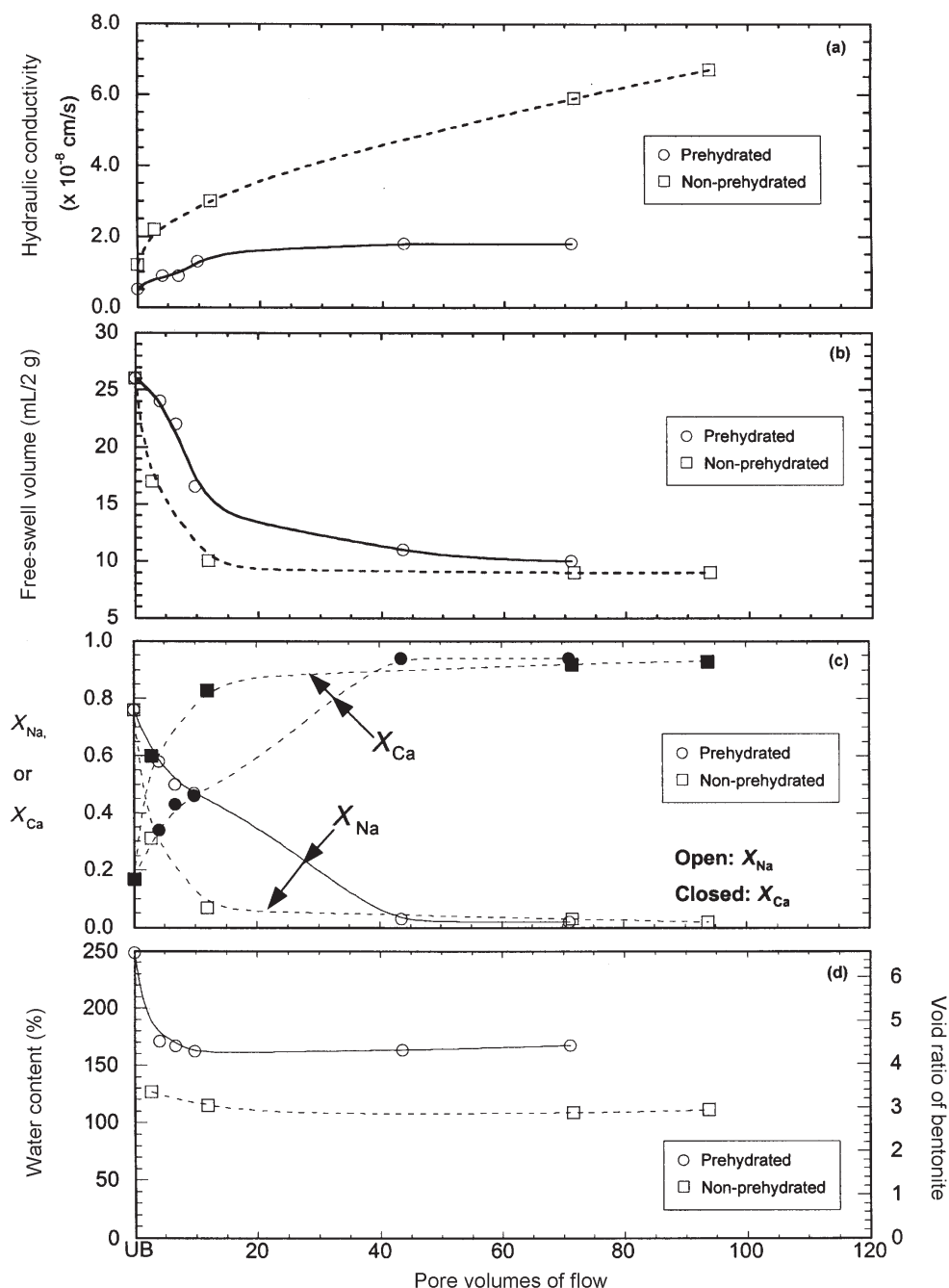


Figure 9. Hydraulic conductivity (a), free swell volume in deionized water (b), mole fractions of Na and Ca in the exchange complex (c), water content and void ratio of bentonite (d) for non-prehydrated and prehydrated specimens after terminating hydraulic conductivity tests conducted using a 40 mM CaCl_2 solution. X_{Na} = the mole fraction of Na on the exchange complex, X_{Ca} = the mole fraction of Ca on the exchange complex, and UB = unused bentonite.

solution-specific calibration curve is probably needed to estimate X_{Na} from free swell. Although not evaluated in this study, the calibration curve is probably sensitive to the properties of the bentonite as well.

The data for the Ca tests shown in Figure 10 were used to estimate the uncertainty associated with estimating X_{Na} from free-swell data (an assessment of

uncertainty was not made using the K^+ data because the data set for K^+ is sparse). For the Ca^{2+} dataset, linear regression of X_{Na} on free swell results in $R^2 = 0.96$ and a standard error (s_e) = 0.06. This error suggests that X_{Na} can be estimated ± 0.12 (i.e. $\pm 2s_e$) from a free-swell measurement, if a calibration curve that is specific to the bentonite and solution is available.

Table 3. Summary of water content, composition of exchange complex, and swell volume in deionized water of bentonite specimens after terminating hydraulic conductivity tests.

| Type of specimen | Permeant liquid | PVF* | Water content (%) | Exchange complex (meq/100 g) | | | | Swell volume in deionized water (mL/2 g) |
|------------------|-------------------------|------|-------------------|------------------------------|---------|----------|---------|--|
| | | | | Na | K | Ca | Mg | |
| Unused bentonite | — | — | 9.0 | 43.8±16.8 | 0.8±0.4 | 16.5±5.4 | 6.0±3.4 | 26.0 |
| Non-Prehydrated | 100 mM KCl | 3 | 133.3 | 20.2 | 27.8 | 15.1 | 5.3 | 20.0 |
| | | 8 | 138.3 | 14.1 | 32.2 | 13.9 | 5.3 | 19.0 |
| | | 23 | 136.0 | 3.9 | 48.0 | 12.7 | 5.3 | 17.0 |
| | | 43 | 133.3 | 0.9 | 47.1 | 12.2 | 3.3 | 16.0 |
| | 20 mM CaCl ₂ | 2 | 155.3 | 27.5 | 1.1 | 29.9 | 4.8 | 22.0 |
| | | 6 | 154.6 | 19.6 | 1.0 | 39.3 | 4.6 | 19.5 |
| | | 10 | 155.3 | 15.3 | 1.1 | 44.6 | 4.7 | 17.5 |
| | | 13 | 138.5 | 13.3 | 1.0 | 48.8 | 4.7 | 14.5 |
| | | 48 | 120.7 | 0.3 | 0.9 | 59.0 | 2.6 | 11.0 |
| | | 106 | 122.2 | 0.1 | 1.1 | 61.2 | 0.9 | 8.5 |
| | 40 mM CaCl ₂ | 3 | 126.8 | 11.4 | 0.9 | 44.8 | 5.0 | 17.0 |
| | | 10 | 115.1 | 2.2 | 0.8 | 53.3 | 4.6 | 10.0 |
| | | 71 | 108.9 | 0.9 | 0.8 | 57.0 | 1.9 | 9.0 |
| | | 94 | 111.3 | 0.7 | 0.7 | 57.0 | 1.1 | 9.0 |
| Prehydrated | 40 mM CaCl ₂ | 0 | 248.3 | 36.5 | 0.9 | 17.4 | 4.9 | 25.5 |
| | | 4 | 171.1 | 27.2 | 0.7 | 31.9 | 5.7 | 24.0 |
| | | 6 | 166.8 | 21.5 | 0.7 | 37.0 | 5.4 | 22.0 |
| | | 10 | 162.0 | 19.7 | 0.8 | 38.3 | 4.4 | 16.5 |
| | | 44 | 163.5 | 0.9 | 0.5 | 58.4 | 1.0 | 11.0 |
| | | 71 | 167.5 | 0.7 | 0.7 | 58.6 | 0.8 | 9.0 |

* PVF at the end of test.

SUMMARY AND CONCLUSIONS

Sets of replicate hydraulic conductivity tests were conducted on thin layers of prehydrated and non-prehydrated bentonite simulating GCLs using 100 mM KCl and 20 and 40 mM CaCl₂ solutions. The bentonite

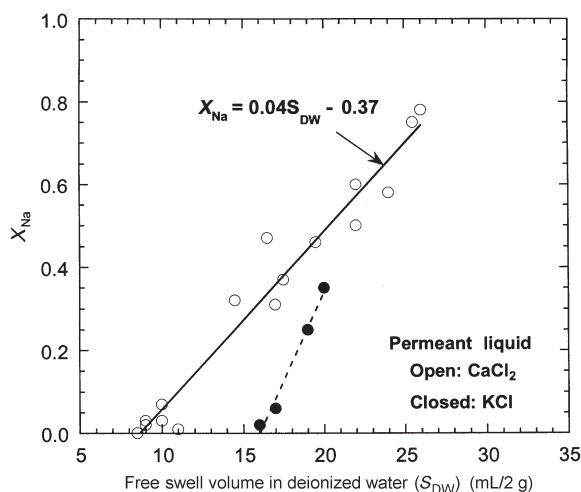


Figure 10. Relationship between mole fraction of Na on the exchange complex and free swell volume in deionized water for bentonite after terminating hydraulic conductivity tests using 100 mM KCl and 20 mM and 40 mM CaCl₂ solutions. S_{DW} = swell volume of the bentonite in deionized water and X_{Na} = the mole fraction of Na on the exchange complex of the bentonite.

was characterized for water content, free swell and exchange complex after termination of each hydraulic conductivity test. The objective was to evaluate how the gradual change in hydraulic conductivity of bentonite permeated with dilute inorganic salt solutions is related to the composition of the exchange complex, free swell, and water content (or void ratio) of prehydrated and non-prehydrated bentonite.

The test data show that changes in the exchange complex correspond with changes in the hydraulic conductivity, water content (or void ratio), and free swell of bentonite used in GCLs when the permeant solution contains divalent cations. In contrast, when the permeant solution contains monovalent cations, complete exchange for the native Na⁺ ions can occur with no noticeable change in hydraulic conductivity or water content (or void ratio). However, changes in the exchange complex caused by monovalent cations in the permeant solution are reflected in the free swell of the bentonite.

For permeant solutions with divalent cations, larger and more rapid changes in hydraulic conductivity and water content (or void ratio) occur as the concentration increases. This occurs as a result of more rapid replacement of sodium cations in the exchange complex by the divalent cations in the permeant solution. Moreover, the difference in physical properties persists, even though complete replacement of native Na ions in

the exchange complex is achieved by the end of the test regardless of the differences in concentration.

Hydration state at the onset of permeation with salt solutions also affects the rate of exchange, hydraulic conductivity, water content (or void ratio), and free swell in bentonites used in GCLs. More rapid exchange along with larger changes in hydraulic conductivity and water content (or void ratio) occur in non-prehydrated bentonite than in bentonite prehydrated with deionized water even if both bentonites are permeated with the same solution and complete exchange is achieved by the end of the test.

The lower hydraulic conductivity and higher water content (or void ratio) associated with prehydration or permeation with a solution with low divalent cation concentration is likely related to the degree to which water molecules can be displaced from the interlayer region during permeation. Permeant solutions having higher concentration probably cause more displacement of water molecules because the osmotic gradient between the bulk pore water and interlayer water is larger. Thus, the osmotic gradient is able to overcome more of the electrostatic forces retaining water molecules. More study is needed, however, to confirm this hypothesis.

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