DISSERTATION

LONG-TERM HYDRAULIC PERFORMANCE OF GEOSYNTHETIC CLAY LINERS SUBJECTED TO INORGANIC SALT SOLUTIONS

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY JAE-MYUNG LEE ENTITLED "LONG-TERM HYDRAULIC PERFORMANCE OF GEOSYNTHETIC CLAY LINERS SUBJECTED TO INORGANIC SALT SOLUTIONS" BE ACCEPTED AS FULFILLING, IN PART, THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

LONG-TERM HYDRAULIC PERFORMANCE OF GEOSYNTHETIC CLAY LINERS SUBJECTED TO INORGANIC SALT SOLUTIONS

Specimens of two geosynthetic clay liners (GCLs) containing sodium bentonite, commonly used as liners or liner components in waste containment, are permeated with water and inorganic salt solutions containing from 5 mM to 500 mM calcium chloride ($CaCl_2$) for the purpose of evaluating the long-term hydraulic performance of the GCLs. The results are evaluated in terms of criteria commonly used to terminate hydraulic conductivity tests involving non-standard permeant liquids (i.e., liquids other than water), the potential effects of quality of bentonite and prehydration on the hydraulic conductivities, and the potential correlation between index properties of the bentonite and hydraulic conductivity of the GCLs. All hydraulic conductivity tests involving $CaCl_2$ solutions were conducted until equilibrium between the effluent and influent chemistry was achieved, resulting in test durations ranging from less than 1 day to more than 900 days, with longer test durations associated with lower $CaCl_2$ concentrations. In addition, a new index property, referred to as the solution retention capacity (SRC) is developed and evaluated as an alternative to the use of the swell index approach for providing a qualitative indication of the relative impact of $CaCl_2$ solutions on the hydraulic performance of the GCLs. Finally, the potential effect of Ca^{2+} diffusion on the

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semipermeable membrane behavior is evaluated on the basis of a combined chemico-osmotic/diffusion test conducted on one of the GCLs.

In terms of termination criteria, only equilibrium between influent and effluent Ca^{2+} results in equilibrium in hydraulic conductivity, regardless of prehydration or quality of bentonite, particularly for the influent concentrations $\leq$ 20 mM $CaCl_2$. Also, the GCL containing the higher quality bentonite (GCL-HQB) is found to be more susceptible to incompatibility in hydraulic conductivity than the GCL with the lower quality bentonite (GCL-LQB) when permeated with $CaCl_2$ solutions. In fact, measured hydraulic conductivity values range from 2.4×10^{-9} cm/s to 1.9×10^{-6} cm/s for GCL-LQB and from 7.0×10^{-10} cm/s to 6.2×10^{-5} cm/s for GCL-HQB, respectively, when permeated with solutions containing from 0 (water) to 500 mM $CaCl_2$. The results also indicate that prehydration has little, if any, effect on hydraulic conductivity of GCL-LQB when permeated with solutions containing $\leq$ 50 mM $CaCl_2$, i.e., as long as the tests are conducted until equilibrium between the effluent and influent Ca^{2+} is achieved. Also, a strong correlation between the SRC and swell index is shown over the full range of $CaCl_2$ concentrations used in the study, suggesting that the SRC approach may be used as an alternative to the swell index approach. In general, correlations between the magnitude of the change in index property (e.g., liquid limit, sedimentation volume) when subjected to a $CaCl_2$ solution relative to that based on water and a change in hydraulic conductivity when permeated with the same $CaCl_2$ solution relative to permeation with water are shown to be a function of the magnitude of the change in hydraulic conductivity being considered (e.g., 10X or 100X), the index property, and the bentonite quality. Finally, time-dependent membrane efficiency is observed for a specimen of GCL-LQB, and the

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time required for effective destruction of semipermeable membrane property of the GCL correlates well with the time required to achieve steady-state Ca^{2+} diffusion.

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LIST OF SYMBOLS

A = cross-sectional area of specimen [L^2]
C = solute concentration [$M \cdot L^{-3}$ or $mol \cdot L^{-3}$]
C_o = source solute concentration [$mol \cdot L^{-3}$]
C_s = salt concentration [$M \cdot L^{-3}$]
D^* = effective diffusion coefficient [$L^2 t^{-1}$]
e = void ratio [dimensionless]
g = acceleration of gravity [Lt^{-2}]
G_s = specific gravity [dimensionless]
H or L = specimen thickness [L]
J_i = diffusive flux of solute i [$mol \cdot L^{-2} t^{-1}$]
k = hydraulic conductivity [Lt^{-1}]
m or M = mass [M]
n = specimen porosity [dimensionless]
P = hydraulic (or liquid) pressure [$ML^{-1}t^{-2}$]
Q = volumetric flow ratio [$L^3 t^{-1}$]
Q_t = cumulative solute mass per unit cross-sectional area [ML^{-2}]
R = universal gas constant [$8.314\ J \cdot mol^{-1} \cdot K^{-1}$]
R_d = retardation factor [dimensionless]
s = subscript denoting "salt"
ss = subscript denoting "steady state"
t = elapsed time [t]
t_R = residence or retention time [t]
t_{ss} = elapsed time to steady state [t]
T = absolute temperature [K]
t_L = time lag [t]
V = volume [L^3]
w = subscript denoting "water" or gravimetric water content [dimensionless]
x = generic distance [L]
z_i = charge or ion valence of solute i [dimensionless]
ν = number of ions per molecule of salt
π = chemico-osmotic pressure [$ML^{-1}t^{-2}$]
ρ_d = soil dry (bulk) density [ML^{-3}]
ρ_{sol} = solution density [ML^{-3}]
ρ_w = water density [ML^{-3}]
ω or σ = chemico-osmotic efficiency coefficient [dimensionless]

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 Geosynthetic Clay Liners

Geosynthetic clay liners (GCLs) are manufactured hydraulic barriers consisting of a thin layer (~ 5 to 10 mm) of natural or treated sodium bentonite sandwiched between two geotextiles or glued to a geomembrane (Daniel 1993, Koerner 1994). The primary differences between GCLs are the mineralogy (e.g., high vs. low content of montmorillonite) and form (e.g., powdery vs. granular) of bentonite used in the GCL, the type of geotextile (e.g., woven vs. non-woven), the hydration condition (e.g., non-prehydrated vs. prehydrated), and the bonding method (Daniel 1993, Koerner 1994, Shackelford et al. 2000). The structural integrity of GCLs is maintained by one of several bonding methods, such as by stitching, needle punching, and/or adding a chemical adhesive to the bentonite to provide protected handling and installation and enforced in-plane shear strength (Estornell and Daniel 1992, Daniel 1993). The use of GCLs as liners for waste containment has increased over the past decade due to several advantages, including relatively easy installation, invulnerability to weathering, low cost, and low hydraulic conductivity to water (i.e., $\leq 10^{-8}$ cm/s) (Estornell and Daniel 1992, Daniel 1993, Koerner 1994).

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1.1.2 Compatibility of GCLs

In the absence of a geomembrane component, the low hydraulic conductivity to water of GCLs is primarily attributed to swelling of bentonite upon hydration with water (Mitchell 1993, Egloffstein 1995, Shackelford et al. 2000, Kashir and Yanful 2001). Because the performance of GCLs as hydraulic barriers depends primarily on the bentonite, the hydraulic conductivity of GCLs based upon permeation with chemical solutions can be significantly higher than that based on water permeation due to chemical interactions between the solutions and the bentonite (Daniel et al. 1993, Gleason et al. 1997, James et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001). The potential effect of a non-standard permeant liquid (i.e., liquid other than water) on the hydraulic conductivity of a clay barrier usually is assessed by permeating the clay barrier material with the actual liquid to be contained or a simulated liquid with characteristics similar to the expected actual liquid. Since the primary objective of the test is to determine if the barrier material (e.g., bentonite in GCLs) and the permeant liquid are compatible such that no significant change in hydraulic conductivity occurs, this type of test often is referred to as a compatibility test (Shackelford 1994, Shackelford et al. 2000).

In cases where GCLs have been permeated with inorganic salt solutions containing relatively high concentrations of polyvalent cations (i.e., $\geq$ 50 mM), several studies have shown significant increases in the hydraulic conductivity (> 10X) of GCLs over relatively short test durations (i.e., $\leq$ 0.5 yr) (Ruhl and Daniel 1997, Kolstad 2000,

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Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001). In contrast, for cases involving permeation with inorganic salt solutions containing relatively low concentrations of polyvalent cations (i.e., < 50 mM), the GCLs typically have exhibited compatibility over relatively short durations, but incompatibility after longer durations of permeation (i.e., > 1 yr) (e.g., Dobras and Elzea 1993, Didier and Comeaga 1997, James et al. 1997, Petrov and Rowe 1997, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001, Melchior 2002). This apparent time-dependent compatibility of GCLs implies that the potential chemical interactions between the solutions and bentonites in the GCLs may not have been complete when the tests performed using permeant liquids containing relatively low salt concentrations were terminated (Shackelford et al. 2000). Thus, longer test durations may be required to fully evaluate the long-term compatibility of GCLs, particularly in the case of containment of solutions containing relatively low concentrations of polyvalent cations.

1.1.3 Effect of Prehydration

Several investigators have reported that prehydration of bentonite mixtures and/or GCLs with water prior to permeation with actual permeant liquids can have a significant effect on hydraulic conductivity (e.g., Shan and Daniel 1991, Daniel et al. 1993, Shackelford 1994, Didier and Comeaga 1997, Gleason et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a, Quaranta et al. 1997, Ruhl and Daniel 1997, Stern and Shackelford 1998, Lin and Benson 2000, Shackelford et al. 2000, Vasko et al. 2001, Shan and Lai 2002). This effect has been referred to as the "first exposure effect" (Shackelford 1994,

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Stern and Shackelford 1998) or the "prehydration effect" (e.g., Daniel et al. 1993, Didier and Comeaga 1997, Gleason et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a, Quaranta et al. 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Vasko et al. 2001, Ashmawy et al. 2002, Shan and Lai 2002). As a result of this effect, the hydraulic conductivity of GCLs permeated directly with chemical solutions typically has been found to be significantly higher (i.e., > 10X) than the hydraulic conductivity of GCLs permeated with the same chemical solutions after prehydration with water.

In the field, prehydration may occur naturally, such as by either precipitation or adsorption of water from adjacent soils (Daniel et al. 1993, Bonaparte et al. 1996, Petrov and Rowe 1997), or may be imposed either by spraying water (Vasko et al. 2001) or, in the case of GCLs, by installing commercially available prehydrated GCLs (e.g., RawMat® HDB, Rawell Water Control Systems Limited, Wirral, Merseyside, UK). For laboratory experiments, prehydration has been imposed either by spraying or soaking the specimens with water (e.g., Daniel et al. 1993, Didier and Comeaga 1997, Vasko et al. 2001), or by permeating the specimens with water (e.g., Shan and Daniel 1991, Shackelford 1994, Bonaparte et al. 1996, Gleason et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Stern and Shackelford 1998, Shackelford et al. 2000).

1.1.4 Effect of Bentonite Quality

Since the low hydraulic conductivity to water of bentonite is primarily attributed to swelling capacity upon hydration with water (Mesri and Olson 1971, Mitchell 1993, Egloffstein 1995, Shackelford et al. 2000, Jo et al. 2001, Kashir and Yanful 2001, Vasko

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et al. 2001), the quality of the bentonite can significantly affect the hydraulic conductivity of the bentonite when permeated with water (Shackelford et al. 2000). The quality of a bentonite is affected by several factors, including the mineralogical composition of the bentonite, the surface area of the bentonite, the surface charge deficiency of the bentonite, and the composition of the exchange complex (e.g., Shackelford et al. 2000, Ashmawy et al. 2002). In general, the quality of the bentonite increases with increase in montmorillonite content, surface area (decrease in particle size), surface charge deficiency, and/or percentage of Na^+ on the exchange complex.

However, since bentonites also are sensitive to chemical composition of the pore liquid that influences the thickness of the adsorbed layer, liquids that cause the adsorbed layer to collapse also cause the hydraulic conductivity to increase (Mesri and Olson 1971, Daniel et al. 1993, Gleason et al. 1997, James et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Daniel 2000, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001). Consequently, the higher the quality of the bentonite used in the GCL, the more vulnerable the GCL to chemical attack and, therefore, incompatibility, i.e., provided all other GCL properties (e.g., bentonite dosage) are the same (e.g., Shackelford et al. 2000).

1.1.5 Correlation with Index Properties

Several investigators have emphasized the need to perform compatibility tests until complete chemical equilibrium between the effluent and influent has been established (e.g., Bowders and Daniel 1987, Daniel 1994, Shackelford 1994, Shackelford et al 2000). However, due to the low hydraulic conductivity for barrier soils (i.e., $\leq 10^{-7}$

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cm/s), the test durations required to achieve chemical equilibrium may require several months or even years (e.g., Dobras and Elzea 1993, Daniel 1994, Imamura et al. 1996, James et al. 1997, Shackelford et al. 2000, Egloffstein 2001, Melchior 2002). As a result, an alternative approach has been proposed whereby changes in the index properties of the barrier soil (e.g., Atterberg limits, swell index, etc.) in the presence of the containment liquids relative to water are used as a qualitative, yet more rapid, indicators of the potential for incompatibility in hydraulic conductivity (Dunn and Mitchell 1984, Bowders et al. 1986, Bowders and Daniel 1987, Daniel et al. 1988, Acar and Olivieri 1989, Shackelford 1994, Narejo and Memon 1995, Shackelford et al. 2000, Jo et al. 2001).

For example, several investigators have performed Atterberg limit tests that were modified by using non-standard liquids (i.e., liquids other than water) to provide a qualitative indication of the effect of the liquid on the hydraulic conductivity of the soil (Bowders et al. 1986, Sridharan et al. 1986, Daniel et al. 1988, Acar and Olivieri 1989, Shackelford 1994, Gleason et al. 1997, Petrov and Rowe 1997, Lin and Benson 2000, Sridharan and Prakash 2000). In some cases, sedimentation tests have been performed to discern the effects of non-standard liquids on the sedimentation rate of clay soils as an indirect indication of the potential for the non-standard liquid to adversely affect the hydraulic conductivity of the soil (Dunn and Mitchell 1984, Bowders et al. 1986, Bowders and Daniel 1987, Ryan 1987, Shackelford 1994). Several studies also have shown that the swell index of bentonite is directly correlated with the hydraulic behavior of bentonite-based GCLs (Narejo and Memon 1995, Didier and Comeaga 1997, Petrov

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and Rowe 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Shan and Lai 2002).

1.1.6 Existence of Membrane Behavior

Since the primary objective of the barrier is to maintain a contaminant concentration at the outer boundary of the barrier that is lower than the source concentration of the same contaminant, the existence of membrane behavior may be important in terms of evaluating the hydraulic and contaminant transport performance of the containment barrier. For example, in the case where the clay containment barrier acts as a semipermeable membrane, both chemico-osmotic counter flow and contaminant (solute) restriction would act to reduce the outward contaminant flux (Malusis et al. 2001, Shackelford et al. 2001). Thus, a clay containment barrier that behaves as a semipermeable membrane is expected to perform better than one that does not exhibit membrane behavior.

In the case of electrolyte solutions, membrane behavior in clays generally is attributed to electrostatic repulsion of the ions by electric fields associated with the adsorbed layer of adjacent clay particles (e.g., Hanshaw and Coplen 1973, Fritz 1986). Thus, the factors that tend to cause an increase in the thickness of adsorbed layer (i.e., at constant porosity), such as decreasing ion concentration and/or decreasing ion valence, also tend to enhance the membrane efficiency of clays that behave as semipermeable membranes (see Kemper and Rollins 1966, Kemper and Quirk 1972). However, an increasing ion concentration and/or ion valence also may result in a reduction in membrane efficiency.

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1.2 GOAL AND OBJECTIVES OF RESEARCH

As a result of the aforementioned considerations, the primary goal of this research is to evaluate the long-term hydraulic performance of geosynthetic clay liners permeated with inorganic salt solutions containing divalent calcium ions (Ca^{2+}) at a range of concentrations. This goal will be achieved by accomplishing the following objectives:

(1) to evaluate the hydraulic performance of a GCL based on permeation with water and inorganic salt solutions containing from 5 to 500 mM $CaCl_2$ within the context of criteria commonly used to terminate laboratory compatibility tests;

(2) to evaluate the potential effect of prehydration on the hydraulic performance of a GCL based on permeation with water and inorganic salt solutions containing from 5 to 100 mM $CaCl_2$;

(3) to ascertain the potential difference in the hydraulic performance of two GCLs containing different qualities of bentonite based on permeation with water and inorganic salt solutions containing from 5 to 500 mM $CaCl_2$;

(4) to develop a new index property, referred to as the solution retention capacity (SRC), as an alternative to the use of the swell index approach for providing a qualitative indication of the relative impact of $CaCl_2$ solutions on the hydraulic performance of the GCLs;

(5) to assess the use of modified index properties (i.e., index properties based on use of testing liquids other than water) as indirect indicators of the long-term

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hydraulic performance of GCLs permeated with water and inorganic salt solutions containing from 5 to 500 mM $CaCl_2$;

(6) to evaluate the effect of Ca^{2+} diffusion on the semipermeable membrane behavior of a GCL in the presence of a $CaCl_2$ solution; and

(7) to ascertain the potential dependency of termination criteria for compatibility testing on prehydration and bentonite quality for GCLs based on permeation with water and inorganic salt solutions containing from 5 to 100 mM $CaCl_2$.

1.3 POTENTIAL IMPACT OF RESEARCH

The results of this research may have significant ramifications with respect to not only the long-term hydraulic performance of GCLs, but also the procedures for laboratory compatibility testing currently being used to evaluate such performance. In addition, the results may have significant implications with respect to the use of prehydration to minimize alterations in the hydraulic performance of GCLs as well as the use of GCLs containing a higher quality bentonite to enhance hydraulic performance of GCLs used in waste containment applications. Finally, the results also may have significant implications with respect to the ability of the GCL to act as a semipermeable membrane.

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CHAPTER 2

LONG-TERM COMPATIBILITY OF A GEOSYNTHETIC CLAY LINER PERMEATED WITH CALCIUM CHLORIDE SOLUTIONS

ABSTRACT: The long-term compatibility of a geosynthetic clay liner (GCL) containing sodium bentonite is evaluated by permeation with calcium chloride ($CaCl_2$) solutions within the context of a wide range of termination criteria for laboratory compatibility testing. Hydraulic conductivity values for specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions are comparable with those for specimens permeated with water ($\sim 10^{-9}$ cm/s) during short test durations (< 3 to 6 months), and then increase from approximately 5X to 10X to a value of $\sim 8.5 \times 10^{-9}$ cm/s regardless of the influent concentration after 0.4 yr to 1.6 yrs of permeation. In contrast, hydraulic conductivity values for specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions are about 2X, 40X, and 200X higher, respectively, than the hydraulic conductivity of $\sim 8.5 \times 10^{-9}$ cm/s for specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. Termination criteria based on volumetric flow ratio and steady hydraulic conductivity per ASTM D 5084, two pore volumes of flow, constant thickness of specimen, and pH and electrical conductivity equilibrium are found to be inapplicable, particularly for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. For these specimens, a statistically zero slope in

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hydraulic conductivity versus time or pore volumes of flow is not established until Ca^{2+} concentrations in the effluent and influent are similar.

Key Words: compatibility, geosynthetic clay liners, hydraulic conductivity, long-term testing, termination criteria

2.1 INTRODUCTION

Geosynthetic clay liners (GCLs) are manufactured hydraulic barriers consisting of a thin layer (~ 5 to 10 mm) of natural or treated sodium bentonite sandwiched between two geotextiles or glued to a geomembrane (Daniel 1993, Koerner 1994). The structural integrity of GCLs is maintained by one of several bonding methods, such as by stitching, needle punching, and/or adding a chemical adhesive to the bentonite (Estornell and Daniel 1992, Daniel 1993). The use of GCLs as liners for waste containment has increased over the past decade due to several advantages, including relatively easy installation, invulnerability to weathering, low cost, and low hydraulic conductivity to water (i.e., $\leq 10^{-8}$ cm/s) (Estornell and Daniel 1992, Daniel 1993, Koerner 1994).

The low hydraulic conductivity to water of GCLs, in the absence of a geomembrane component, is primarily attributed to swelling of bentonite upon hydration with water (Mitchell 1993, Egloffstein 1995, Shackelford et al. 2000, Kashir and Yanful 2001). Because the performance of GCLs as hydraulic barriers depends primarily on the bentonite, technical equivalency has focused primarily on the low hydraulic conductivity of GCLs permeated with water. However, the hydraulic conductivity of GCLs based on permeation with chemical solutions can be significantly higher than that based on

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permeation with water due to chemical interactions between the solutions and the bentonite (Daniel et al. 1993, Gleason et al. 1997, James et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001).

The potential effect of a non-standard permeant liquid (i.e., liquid other than water) on the hydraulic conductivity of a clay barrier usually is assessed by permeating the clay barrier with the actual liquid to be contained or, in the absence of the actual liquid, a simulated liquid with characteristics similar to those expected for the actual liquid. This type of test often is referred to as compatibility testing, since the primary objective of the test is to determine if the soil (e.g., bentonite in GCLs) and the permeant liquid are compatible (Shackelford et al. 2000).

The results of several studies based on compatibility testing have shown that the concentration and type of solutes can significantly increase the hydraulic conductivity (> 10X) of bentonitic barriers (Alther et al. 1985, Imamura et al. 1996, James et al. 1997, Melchior 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Kolstad 2000, Shan and Lai 2002). These results are also consistent with several studies that indicate significant increase in the hydraulic conductivity of sand-bentonite mixtures and GCLs upon permeation with solutions containing divalent cations at concentrations ≥ 50 mM (Shackelford 1994, Gleason et al. 1997, Ruhl and Daniel 1997, Stern and Shackelford 1998, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001).

In the case of GCLs permeated using solutions containing divalent cations at concentrations < 50 mM, some studies have reported hydraulic conductivities that are comparable to the hydraulic conductivities based on permeation with water (i.e., $\leq 10^{-8}$

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cm/s) (e.g., Didier and Comeaga 1997, Petrov and Rowe 1997, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Jo et al. 2001, Vasko et al. 2001). However, other studies have shown incompatibility of GCLs permeated with solutions containing divalent cations at concentrations < 50 mM, with hydraulic conductivity values as much as 200X higher than those based on permeation with water (Dobras and Elzea 1993, Imamura et al. 1996, James et al. 1997, Shackelford et al. 2000, Egloffstein 2001, Melchior 2002). Most of the studies showing compatibility were based on the results of tests performed over relatively short durations (≤ 0.5 yr), whereas the studies reporting incompatibility generally were performed over longer periods of time (> 1 yr). However, since most waste containment facilities are designed to last several decades, such short-term test results may not necessarily reflect the long-term field performance of GCLs, because chemical equilibrium may not be established within the test duration (Shackelford et al. 2000). Thus, longer test durations may be required to fully evaluate the long-term compatibility of GCLs, particularly in the case of containment of solutions containing relatively low concentrations (< 50 mM) of polyvalent cations.

As a result of the aforementioned considerations, the objective of this study is to evaluate the compatibility of a GCL permeated with $CaCl_2$ solutions containing various concentrations within the context of criteria commonly used to terminate laboratory compatibility tests. The results of this evaluation may have significant ramifications with respect to not only the long-term performance of GCLs used in waste containment applications, but also the laboratory compatibility test procedures currently used to evaluate such performance.

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2.2 MATERIALS AND METHODS

2.2.1 Geosynthetic Clay Liner

The geosynthetic clay liner (GCL) used in this study consists of a layer of granular sodium bentonite sandwiched between woven and non-woven polypropylene geotextiles held together by needle-punched fibers. The GCL is approximately 6-mm thick in an air-dried condition, and the gravimetric water content of bentonite ranges from 2 % to 6 %. The physical and chemical properties and the mineralogical composition for the bentonite portion of the GCL are given in Table 2.1. The air-dried bentonite consists of 20 % medium sand-sized (425 to 2000 μm) and 72 % fine sand-sized granules (75 to 425 μm) based on mechanical sieve analyses, whereas approximately 90 % of particles are clay sized (< 5 μm) based on hydrometer analyses (ASTM D 421, D 422).

2.2.2 Permeant Liquids

Kolstad (2000) and Jo et al. (2001) showed that salt solutions containing different divalent cations had little effect on hydraulic conductivity of GCLs provided the concentration of the cation in the solution was the same. In addition, the exchange of calcium for sodium in the adsorbed layer of sodium bentonite has been shown to cause an increase in hydraulic conductivity (Shackelford 1994, Gleason et al. 1997, Ruhl and Daniel 1997, Stern and Shackelford 1998, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001). As a result, the permeant liquids used in this study consist of tap water that is processed to remove ions by passing through three Barnstead® ion exchange columns in series (pH ~ 5.6, electrical conductivity, EC, at 25 °C ~ 0.2 mS/m) resulting in Type IV

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deionized water (DIW) as per ASTM D 1193, and chemical solutions containing 5, 10, 20, 50, 100, and 500 mM $CaCl_2$. The $CaCl_2$ solutions were prepared by dissolving $CaCl_2$ (powdered, > 96 % pure, Sigma-Aldrich Co., St. Louis, MO) in the DIW. Each solution was mixed in a 20-L carboy, and pH, EC, and solute concentrations of the permeant liquids were monitored with time using a pH meter (Accumet® AB15 meter, Fisher Scientific Co., Pittsburgh, PA), an EC probe (Accumet® AB30 meter, Fisher Scientific Co., Pittsburgh, PA), an ion chromatograph (Dionex® 4000i IC Module, Dionex Co., Sunnyvale, CA) for chloride (Cl^-) concentrations, and an inductively coupled plasma – atomic emission spectrometer (IRIS® Advantage/1000 ICAP Spectrometer, Thermo Jarrell Ash Co., Franklin, MA) for calcium (Ca^{2+}) concentrations. The measured properties of the permeant liquids are given in Table 2.2. As expected, the measured solute concentrations for the DIW were below the method detection limits (MDLs) of 0.02 mg/L for Ca^{2+} (EPA Method 200.7) and 0.04 mg/L for Cl^- (EPA Method 300.0).

The EC and solute concentrations of the permeant liquids remained relatively constant, whereas the pH of each solution slowly decreased over time (e.g., from 6.5 to 5.5 for DIW over 1.5 yrs). The decrease in pH is probably due to time-dependent dissolution of carbon dioxide (CO_2) from the atmosphere into the solutions. Nevertheless, any effect of decreasing source solution pH on the measured hydraulic conductivity likely was negligible relative to the effects caused by the various $CaCl_2$ solutions, because the range of measured pH (i.e., 5.0 to 7.0) was relatively narrow and close to neutral pH (Shackelford 1994, Jo et al. 2001, Shan and Lai 2002).

2.2.3 Hydraulic Conductivity Tests

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Specimens of the GCL with nominal diameters of 102 mm were permeated using the falling-head procedure with flexible-wall permeameters in accordance with ASTM D 5084 in a temperature-controlled laboratory (23.0 ± 0.5 °C). Although Petrov et al. (1997a) indicate that the type of permeameter is not particularly important when testing GCLs, the flexible-wall permeameter is the most reliable device for testing GCLs, and provides the greatest assurance that sidewall leakage does not affect the test results (Lin and Benson 2000, Shackelford et al. 2000). In addition, even though the falling-head procedure results in variations in the effective stress of the specimen during the test, the stress changes were within ± 5 % of the average effective stress of ~ 23.5 kPa (3.4 psi) applied for all the tests performed in this study. All hydraulic conductivity tests were duplicated for each permeant liquid.

Specimens were trimmed and assembled in the permeameters using the procedures described by Daniel et al. (1997) to prevent the possibility of short-circuiting through the geotextiles at the edge of the GCL specimens due to loss of bentonite and pinching of the geotextiles. The specimens in the permeameter initially were exposed to a permeant liquid for at least 48 hrs without applying a hydraulic gradient. Backpressure was not used so that effluent samples could be conveniently collected for pH, EC, and solute concentration measurements. The influent was refilled and the effluent was collected for each influent volume of 30 ± 5 mL. The pH and EC of some of the samples from the collected effluent were measured within minutes after collection, whereas others samples were stored in a refrigerator at 4.0 ± 1.0 °C for future measurements of solute concentrations.

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The thickness of specimens was measured before, during, and after the hydraulic conductivity testing using a caliper, a cathetometer, and a ruler. The measured thickness at the start of permeation was used to estimate the pore volume for each specimen, whereas the final GCL bulk void ratio was estimated based on the description given by Petrov et al. (1997b). An additional influent burette (50 mL) and effluent cylinder (100 mL) filled with water, but not connected to a permeameter, were used to measure evaporation rate of both influent (~ 0.094 mL/day) and effluent (~ 0.048 mL/day). The difference between two evaporation rates was due to the different cover system, i.e., a plastic cap for the influent burette and parafilm for the effluent cylinder.

All the specimens were permeated at an average hydraulic gradient of ~ 200. While this hydraulic gradient is significantly higher than the maximum gradient (i.e., 30) stipulated in ASTM D 5084, Shackelford et al. (2000) note that hydraulic gradients ranging from 50 to 600 typically are used for measuring the hydraulic conductivity of GCLs, and that the hydraulic conductivity of GCLs is affected more by average effective stress than by the magnitude of the hydraulic gradient due to the relative thinness of GCLs. For example, Petrov et al. (1997b) showed that the hydraulic conductivity of a needle-punched GCL decreased from ~ 4×10^{-9} cm/s to ~ 8×10^{-10} cm/s as the confining stress increased from 3 kPa to 117 kPa. However, essentially no change in hydraulic conductivity was observed for tests performed at hydraulic gradients ranging from 144 to 590. In addition, since GCLs are very thin (~ 5 to 10 mm), a moderate depth of liquid can result in a substantial hydraulic gradient (> 30) in field applications involving GCLs.

A wide range in common termination criteria used for compatibility tests were considered in this study (e.g., Shackelford et al. 2000). In particular, the following

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termination criteria were considered: (1) at least four consecutive volumetric flow ratios of effluent relative to influent fall within 1.00 ± 0.25 (e.g., ASTM D 5084), (2) at least four consecutive hydraulic conductivity (k) values fall within ± 25 % of the mean value for $k \geq 1 \times 10^{-8}$ cm/s or within ± 50 % for $k < 1 \times 10^{-8}$ cm/s (e.g., ASTM D 5084), (3) a minimum of two pore volumes of flow (PVF) have passed through the specimen (e.g., Bowders et al. 1986, Daniel 1994, Shackelford et al. 2000, ASTM D 6766), (4) the thickness of the specimen is constant (e.g., Petrov et al. 1997a), (5) the pH and EC ratio of effluent relative to influent fall within 1.00 ± 0.10 (e.g., Shackelford 1994, Shackelford et al. 1999, 2000, ASTM D 6766), and (6) the solute (i.e., Cl^- and Ca^{2+}) concentration equilibrium between effluent and influent is established (e.g., Bowders et al. 1986, Bowders and Daniel 1987, Bowders 1988, Daniel 1994, Shackelford 1994, Shackelford et al. 1999, 2000).

2.3 RESULTS

2.3.1 Results with Water

Results of the hydraulic conductivity tests performed using deionized water as the permeant liquid are shown in Fig. 2.1. The hydraulic conductivity values of duplicate specimens permeated with water initially decreased to about 2.0×10^{-9} cm/s within 10 days (~ 1 PVF) of permeation, and thereafter eventually increased by 1.5X to ~ 3.0×10^{-9} cm/s after ~ 2.3 yrs (~ 50 PVF) of permeation. The effluent calcium (Ca^{2+}) and chloride (Cl^-) concentrations initially were > 20 mg/L, and then decreased gradually to approximately 0.3 mg/L and 0.2 mg/L, respectively, over the same time frame, whereas

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the effluent sodium (Na^+) concentrations initially were > 1200 mg/L, and then decreased gradually to ~ 40 mg/L after ~ 2.3 yrs of permeation.

The gradual decrease in effluent Na^+ concentrations can be attributed, in part, to rate-limited diffusive mass transport of soluble Na^+ from the interlayer region of the bentonite particles to the interparticle and interclod migration pathways (Coats and Smith 1964, van Genuchten and Wierenga 1976, Rao et al. 1980, Tang et al. 1981, van Eijkeren and Loch 1984, Parker and Valocchi 1986, Pusch 1999, Pusch and Schomburg 1999). This slow leaching process also is responsible for significantly high ratios of effluent to influent EC (i.e., > 60) throughout the tests, and analogous to the process of reverse matrix diffusion that has attributed, in part, to the inability of pump-and-treat remediation systems to reach cleanup goals for contaminated aquifers (Feenstra et al. 1984, Parker et al. 1994, Shackelford and Jefferis 2000).

2.3.2 Results with 5, 10, and 20 mM $CaCl_2$ Solutions

Results of the hydraulic conductivity tests performed using 5, 10, and 20 mM $CaCl_2$ solutions as the permeant liquids are shown in Figs. 2.2 to 2.4, respectively. The hydraulic conductivity values for duplicate specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions initially decreased to ~ 10^{-9} cm/s after ~ 1 month (< 5 PVF) of permeation, and then began to increase after ~ 3 months to 6 months (~ 5 to 10 PVF). Thereafter, the hydraulic conductivity values increased from ~ 5X to 10X to a value of ~ 8.5 x 10^{-9} cm/s regardless of the influent concentration at times corresponding to ~ 1.6 yrs (~ 66 PVF), 1.0 yr (~ 33 PVF), and 0.4 yr (~ 16 PVF) for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively. However, a decrease in hydraulic

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conductivity was observed after ~ 1.4 yrs (~ 75 PVF) and 1.1 yrs (~ 60 PVF) of permeation for the duplicate specimens permeated with the 10 mM $CaCl_2$ solution, and after ~ 1.1 yrs (~ 90 PVF) and 0.7 yr (~ 70 PVF) for the duplicate specimens permeated with the 20 mM $CaCl_2$ solution, possibly due to biological and/or chemical clogging (Ruhl and Daniel 1997).

Consequently, the tests performed using 10 and 20 mM $CaCl_2$ solutions as the permeant liquids were disassembled and re-assembled (i.e., cleaning/replacing porous materials and all the parts including the tubing of the permeameter) to minimize and prevent any potential clogging processes due to prolonged permeation. The specimens were covered with a paper towel wetted by the permeant liquid during the disassembly and re-assembly procedure, which lasted < 2 hrs. Even though no clogging tendency was observed for the duplicate tests performed using the 5 mM $CaCl_2$ solution as the permeant liquid, these tests also were disassembled and re-assembled to see if any post re-assembly changes in the hydraulic conductivity could be attributed to specimen disturbance. However, no significant change (i.e., $\leq$ 45 %) in the hydraulic conductivities is apparent after the re-assembly in all the tests except for one test performed using the 10 mM $CaCl_2$ solution as the permeant liquid, in which the hydraulic conductivity increased by ~ 2.2X, probably due to the disturbance resulting from the additional re-assemblies required for this test relative to the other tests (i.e., 3 vs. 1). At the end of the tests performed using 5, 10, and 20 mM $CaCl_2$ solutions as the permeant liquids (i.e., ~ 2.7 yrs of permeation), the effluent Na^+ concentrations were ~ 0.65 mg/L, which is still higher than the MDL for Na^+ of 0.2 mg/L (EPA Method 200.7).

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2.3.3 Results with 50, 100, and 500 mM $CaCl_2$ Solutions

Results of the hydraulic conductivity tests performed using 50, 100, and 500 mM $CaCl_2$ solutions as the permeant liquids are shown in Figs. 2.5 to 2.7, respectively. For the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, the hydraulic conductivity values stabilized within 3 hrs to 5 days (< 10 PVF) depending on the influent concentration, and were always greater than 1.3×10^{-8}, 1.3×10^{-7}, and 1.1×10^{-6} cm/s for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, respectively. In contrast to the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, the hydraulic conductivity for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions changed by less than 3.5X throughout the tests. In fact, the final hydraulic conductivity values at the end of the tests were approximately 1.6×10^{-8}, 3.6×10^{-7}, and 1.4×10^{-6} cm/s for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, respectively. The effluent Na^+ concentrations were ~ 10 mg/L at the end of all the tests performed using 50, 100, and 500 mM $CaCl_2$ solutions as the permeant liquids.

2.3.4 Final Hydraulic Conductivity and Properties of Specimens

The hydraulic conductivity values at the end of tests (k_f) are shown in Fig. 2.8 as a function of influent $CaCl_2$ concentration. Since the measured Ca^{2+} concentrations for the water were below the MDL of 0.02 mg/L for Ca^{2+}, the MDL is used to represent the Ca^{2+} concentration for the water of this study. The average of the k_f values for the duplicate specimens permeated with water (i.e., 2.5×10^{-9} cm/s vs. 3.4×10^{-9} cm/s) is ~ 3.0×10^{-9} cm/s. For the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, all k_f values are close to 1.0×10^{-8} cm/s regardless of the influent concentration, except for one of the

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specimens permeated with the 10 mM $CaCl_2$ solution where the k_f value is ~ 1.5 x 10^{-8} cm/s probably due to the two additional re-assemblies. In general, the k_f values for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions are ~ 3.5X higher than those for the specimens permeated with water.

In contrast, the k_f values for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions are ~ 1.6 x 10^{-8}, 3.6 x 10^{-7}, and 1.4 x 10^{-6} cm/s, respectively. These values are ~ 5.5X, 120X, and 460X higher than the average value for the duplicate specimens permeated with water (i.e., ~ 3.0 x 10^{-9} cm/s), respectively. In addition, the greatest increase in k_f (i.e., ~ 20X) occurred when the influent $CaCl_2$ concentration increased from 50 mM to 100 mM.

The final bentonite gravimetric water content ($w_{b,f}$), bentonite void ratio ($e_{b,f}$), and GCL bulk void ratio ($e_{B,f}$) of the GCL specimens after permeation are shown in Figs. 2.9 and 2.10. As the $CaCl_2$ concentration in the permeant liquid increases from 0 (water) to 500 mM, $w_{b,f}$ decreases from ~ 189 % to 73 %, and $e_{b,f}$ decreases from ~ 5.2 to 2.0. Similarly, $e_{B,f}$ decreases from ~ 4.4 to 1.7 for the same range in $CaCl_2$ concentrations. In fact, the greatest decreases in $w_{b,f}$, $e_{b,f}$, and $e_{B,f}$ of ~ 1.8X occur as the influent $CaCl_2$ concentration increases from 0 (water) to 5 mM. Further increases in the $CaCl_2$ concentration of the permeant liquid also result in decreases in $w_{b,f}$, $e_{b,f}$, and $e_{B,f}$, but to a lesser extent.

2.4 DISCUSSION

2.4.1 Clogging

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As previously noted, clogging after approximately 1 yr of permeation with 10 and 20 mM $CaCl_2$ solutions resulted in an observed decrease in the hydraulic conductivity. Several studies have shown that the hydraulic conductivity of a saturated porous medium can be affected by clogging through microbiological activity (e.g., McNeal and Coleman 1966, Olson and Daniel 1981, Ilgenfritz et al. 1988, Klecka et al. 1990, Taylor and Jaffe 1990, Vandevivere and Baveye 1992, Baveye et al. 1998, Herbert et al. 1998, Kamon et al. 2002). The reduction in hydraulic conductivity can occur via a direct effect due to biological clogging, such as clogging of pores by bacterial cells, or an indirect effect resulting from biologically induced clogging, such as metals precipitation due to sulfate reducing bacteria (SRB) (e.g., McCalla 1945, 1950, Gupta and Swartzendruber 1962, Mitchell and Younger 1967, Ford and Beville 1968, Ford et al. 1968, Wood and Bassett 1975, van Beek and van der Kooij 1982, van Beek 1984). For example, the direct effect recently has been explored as a potential method for creating biobarriers for *in situ* containment of contaminated ground water (e.g., Dennis and Turner 1998), whereas the indirect effect currently is being evaluated for *in situ* remediation of metal-contaminated ground water in permeable reactive zones (e.g., Benner et al. 1999, Mayer et al. 1999, Blowes et al. 2000, Mayer et al. 2001, Benner et al. 2002).

The clogging observed in the tests of this study may be due to either or both types of clogging. However, the tendency for significant clogging with increasing source $CaCl_2$ concentration (see Figs. 2.2 to 2.4) suggests that the increased concentration of Ca^{2+} in the source solution plays a role in terms of the observed clogging. In this case, indirect clogging mediated by SRB under reducing conditions (i.e., anaerobic conditions) is more

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likely, since the direct clogging of pores by microbiological activity is not necessarily dependent on the source metal (i.e., Ca^{2+}) concentration.

2.4.2 Statistical Analysis on Hydraulic Conductivity

In general, hydraulic conductivity values for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions increased from ~ 5X to 10X to a value of ~ 8.5 x 10^{-9} cm/s after ~ 1.6 yrs (~ 66 PVF), 1.0 yr (~ 33 PVF), and 0.4 yr (~ 16 PVF) of permeation, respectively. Thereafter, the hydraulic conductivities for the duplicate specimens permeated with the 5 mM $CaCl_2$ solution stabilize, whereas the hydraulic conductivities for the specimens permeated with the 10 and 20 mM $CaCl_2$ solutions decrease after ~ 1.3 yrs (~ 66 PVF) and 0.9 yr (~ 80 PVF) of permeation, respectively, probably due to clogging. Due to the resulting ambiguity in the hydraulic conductivities, determination of equilibrium in hydraulic conductivity was based on the method proposed by Peirce and Witter (1986), whereby the slope of hydraulic conductivity versus number of PVF is analyzed statistically using linear regression based on the t-test at a 5 % significance level. In this study, the statistically zero slope of hydraulic conductivity was determined through analyzing the slope of five successive data points in series.

As shown in Fig. 2.11, all of the hydraulic conductivities for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions initially appear to stabilize within 10 PVF, and then begin to increase. As a result, the criterion based on statistical analyses by Peirce and Witter (1986) also is met for the initial stage of the compatibility tests, particularly for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. However, as noted by Bowders (1988), the establishment of hydraulic conductivity

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equilibrium based on the statistical approach recommended by Peirce and Witter (1986) is a necessary but not sufficient condition to ensure true equilibrium in the case of compatibility testing, since hydraulic conductivity equilibrium is truly established only after chemical equilibrium between effluent and influent has been achieved. Thus, even though the statistical approach is useful to determine the establishment of equilibrium in hydraulic conductivity, the statistical approach is meaningful only in conjunction with knowledge of the mechanisms involved in the compatibility tests (e.g., see Bowders 1988).

Consequently, the use of the statistical approach to determine the equilibrium in hydraulic conductivity was considered valid only after the initial stage of the compatibility tests. In fact, the slope of hydraulic conductivity versus the PVF is statistically zero (hereafter referred to as "zero slope") at approximately 54, 26, and 13 PVF for the first specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively (see Fig. 2.11). In addition, as shown in Fig. 2.12, the differences between the hydraulic conductivity at the zero slope and the final hydraulic conductivity at the end of tests are not significant (i.e., ≤ 45 %) for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, except for one specimen permeated with the 10 mM $CaCl_2$ solution.

2.4.3 Physical Termination Criteria

The test results based on the physical termination criteria, including the volumetric flow ratio and steady hydraulic conductivity per ASTM D 5084, 2 PVF, and constant thickness of specimen, are summarized in Table 2.3. The hydraulic conductivity, elapsed time, and PVF based on each physical termination criterion also are compared

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with those at the zero slope (or $k_{\Delta k \sim 0}$) in Figs. 2.13 to 2.15, respectively. For the specimens permeated with water and 50, 100, and 500 mM $CaCl_2$ solutions, the hydraulic conductivity based on overall physical termination criteria is not significantly lower (i.e., < 40 %) than the hydraulic conductivity at zero slope (or $k_{\Delta k \sim 0}$). However, for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, the hydraulic conductivity based on each physical termination criterion is at most ~ 7X lower than the hydraulic conductivity at the zero slope (or $k_{\Delta k \sim 0}$).

For example, the hydraulic conductivity based on the establishment of steady hydraulic conductivity per ASTM D 5084 is from ~ 3X to 6X lower than the hydraulic conductivity at the zero slope (or $k_{\Delta k \sim 0}$) for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In other words, significantly more PVF (i.e., 10 to 76 more) are required to achieve the statistically zero slope in hydraulic conductivity than are indicated by the physical termination criteria. Thus, none of the physical termination criteria appears to be adequate for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, whereas the overall physical termination criteria tend to ensure equilibrium in hydraulic conductivity for the specimens permeated with water and 50, 100, and 500 mM $CaCl_2$ solutions.

2.4.4 Chemical Termination Criteria

The results of the compatibility tests based on the chemical termination criteria, including pH, EC, and solute concentration equilibrium, are summarized in Table 2.4. The hydraulic conductivity, elapsed time, and PVF based on each chemical termination criterion also are compared with those at the zero slope (or $k_{\Delta k \sim 0}$) in Figs. 2.16 to 2.18,

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respectively. The termination criterion based on pH equilibrium was found to be inapplicable in this study, because the pH ratio (i.e., pH_{out}/pH_{in}) never reached the acceptable range (i.e., 1.00 ± 0.10) throughout the tests (Figs. 2.2 to 2.7), except for the tests performed using the 500 mM $CaCl_2$ solution as the permeant liquid. Since the pH of saturated bentonite paste is relatively high (~ 8.9), the influent pH (i.e., 5.0 to 7.0) is buffered, in part, by the bentonite, and consequently the effluent pH is expected to be higher than the influent pH (Shackelford et al. 1999). However, the buffering capacity of bentonite will be exhausted gradually by the slow leaching process (e.g., Shan and Lai 2002). In addition, the decrease in pH of the influent over time may result in an increase in the pH ratio.

Furthermore, if the liquid accumulated in the effluent reservoir is open to the atmosphere, then the release of aqueous-phase carbon dioxide ($CO_{2(aq)}$) into the atmosphere will result in a continual increase in the effluent pH with time (Shackelford 1994), as illustrated in Fig. 2.19. Also, in closed systems such as the flexible-wall apparatus used in this study, the concentration of the $CO_{2(aq)}$ in the pore liquid of a soil likely increases due to respiration by microorganisms under anaerobic conditions (Shackelford 1994). As a result, an increase in effluent pH is expected due to release of $CO_{2(aq)}$ as equilibrium with the atmosphere is established. Finally, the existence of sulfate reducing bacteria within the soil can result in an increase in pH and metals precipitation under anaerobic conditions (e.g., Kamon et al. 2002).

2.4.4.1 Electrical Conductivity Equilibrium

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Two termination criteria based on EC equilibrium were considered to evaluate the effect of the tolerance on EC, viz., $EC_{out}/EC_{in} = 1.00 \pm 0.10$ and $EC_{out}/EC_{in} = 1.00 \pm 0.05$. As shown in Fig. 2.16, the hydraulic conductivity based on either EC tolerance generally is always lower than the hydraulic conductivity at the zero slope (or $k_{\Delta k \sim 0}$) regardless of the influent concentration for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In fact, the hydraulic conductivity based on the EC ratio of 1.00 ± 0.10 and 1.00 ± 0.05 are ~ 5X and 2X lower than the hydraulic conductivity at the zero slope (or $k_{\Delta k \sim 0}$), respectively. On the other hand, for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, the hydraulic conductivity based on both tolerances in the EC ratio is not significantly different (i.e., < 45 %) to the hydraulic conductivity at the zero slope (or $k_{\Delta k \sim 0}$). Thus, equilibrium in EC between effluent and influent is a necessary, but not a sufficient, condition to ensure equilibrium in hydraulic conductivity for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, whereas EC equilibrium tends to ensure hydraulic conductivity equilibrium for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions.

2.4.4.2 Solute Concentration Equilibrium

As shown in Fig. 2.16, the hydraulic conductivity values based on chloride (Cl^-) concentration equilibrium between effluent and influent (i.e., $C_{Cl,out}/C_{Cl,in} = 1.00 \pm 0.10$) are from ~ 3X to 10X lower than the hydraulic conductivity value at zero slope (or $k_{\Delta k \sim 0}$), and are established within 15 PVF for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. Thus, the Cl^- concentration equilibrium is not a sufficient condition to ensure hydraulic conductivity equilibrium for the specimens permeated with 5, 10, and 20

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mM $CaCl_2$ solutions. However, as shown in Fig. 2.16, the closeness between the hydraulic conductivity at zero slope (or $k_{\Delta k \sim 0}$) and hydraulic conductivity based on Ca^{2+} concentration equilibrium (i.e., $C_{Ca,out}/C_{Ca,in} = 1.00 \pm 0.10$) supports the applicability of salt concentration equilibrium as a termination criterion for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. For the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, the hydraulic conductivity based on either Cl^- or Ca^{2+} concentration equilibrium is not significantly different (i.e., < 45%) to the hydraulic conductivity at zero slope (or $k_{\Delta k \sim 0}$).

2.4.4.3 Implications of Effluent Sodium

Since Ca^{2+} exchange for Na^+ is believed to be the primary mechanism that increases the hydraulic conductivity of sodium bentonite specimens permeated with low-concentration (< 50 mM) $CaCl_2$ solutions (Dobras and Elzea 1993, James et al. 1997, Shackelford et al. 2000, Egloffstein 2001, Melchior 2002), the effluent Na^+ concentration may also be considered as an indicator of equilibrium. However, even though Na^+ is the dominant exchangeable cation for sodium bentonite, cations other than Na^+ also exist on the exchangeable sites (Table 2.1). Nonetheless, any effect of the Ca^{2+} exchange for divalent cations (e.g., magnesium, Mg^{2+}) on hydraulic conductivity likely is negligible, and Ca^{2+} exchange for any other monovalent cations (e.g., potassium, K^+) will occur concomitantly with the Ca^{2+} exchange for Na^+. Therefore, the time required to reach an effluent Na^+ concentration below the method detection limit (MDL) of 0.2 mg/L probably is the most appropriate condition to ensure true equilibrium in the system.

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However, in the current study, the effluent Na^+ concentrations for all the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions were significantly higher (i.e., > 25X) than the MDL for Na^+ when chemical equilibrium was established (see Figs. 2.2 to 2.4). Even at the end of the tests (~ 2.7 yrs and 250 PVF), the effluent Na^+ concentrations (~ 0.65 mg/L) still were ~ 3X higher than the MDL. The long durations required for elution of the Na^+ probably are due to diffusion-limited leaching of Na^+ from the immobile phase of bentonite resulting from the relatively slow flow rate for the tests even after Ca^{2+} exchange for Na^+ is effectively completed (Coats and Smith 1964, van Genuchten and Wierenga 1976, Pusch 1999).

In order to assess the percentage of the cumulative mass of Na^+ released at each termination criterion (hereafter referred to as "percentage of Na^+ released"), the cumulative mass of effluent Na^+ is compared with the total Na^+ released throughout the test, as shown in Figs. 2.20 to 2.22. For the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, the percentage of Na^+ released was < 50 % for all the physical termination criteria, which required < 5 PVF. In contrast, the percentage of Na^+ released was ≥ 94 % for the Ca^{2+} concentration equilibrium (i.e., $C_{Ca,out}/C_{Ca,in} = 1.00 \pm 0.10$), which still required significantly less PVF than the PVF at the end of tests (i.e., < 80 PVF vs. > 190 PVF). Also, the percentages of Na^+ released at the time corresponding to the zero-slope criterion (i.e., slope of k ~ 0) were approximately 97, 94, and 86 % for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively (see Figs. 2.11 and 2.20). Furthermore, the additional 200 PVF increased the percentage of Na^+ released by only about 5 %, possibly due to extremely slow leaching process (see Fig. 2.20).

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Therefore, the use of the MDL for the effluent Na^+ concentration as an indicator for chemical equilibrium appears to be neither practical (i.e., due to extensive test durations and cost of chemical analysis) nor necessary (i.e., based on the cumulative mass analyses). On the other hand, for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, the percentages of Na^+ released were similar to those for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, even though the amounts of the Na^+ released were lower likely due to shorter test durations (i.e., < 3 months and < 50 PVF).

2.5 CONCLUSIONS

The influence of the $CaCl_2$ concentration in the permeant liquid on the long-term hydraulic conductivity of GCL specimens was evaluated in this study. Hydraulic conductivity values of the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions were comparable to those of the specimens permeated with water ($\sim 10^{-9}$ cm/s) during short-test durations (< 3 to 6 months). However, the hydraulic conductivity values then increased from about 5X to 10X to a value of $\sim 8.5 \times 10^{-9}$ cm/s regardless of the influent $CaCl_2$ concentration after ~ 0.4 yr to 1.6 yrs of permeation. In contrast, GCL specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions were approximately 2X, 40X, and 200X more permeable than specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively.

In terms of termination criteria, none of the physical criteria, including volumetric flow ratio and steady hydraulic conductivity per ASTM D 5084, 2 pore volumes of flow, and constant thickness of specimen, was adequate for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions in this study because equilibrium in hydraulic conductivity

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had not been established at the times corresponding to those criteria. In addition, since the pH ratio (i.e., pH_{out}/pH_{in}) was never within the acceptable range (i.e., 1.00 ± 0.10) throughout the tests, except for the tests performed using the 500 mM $CaCl_2$ solution as the permeant liquid, the termination criterion based on pH equilibrium was not applicable in this study. Also, the hydraulic conductivity values based on $EC_{out}/EC_{in} = 1.00 \pm 0.10$ and 1.00 ± 0.05 were always ~ 5X and 2X lower, respectively, than those at the statistically zero slope of hydraulic conductivity, regardless of influent concentration for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

In fact, the statistically zero slope of hydraulic conductivity was not established until the Ca^{2+} concentrations in the effluent and influent were similar (i.e., $C_{Ca,out}/C_{Ca,in} = 1.00 \pm 0.10$) for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. On the other hand, for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, all of the termination criteria were established relatively rapidly (< 1 month and < 10 PVF). Finally, the potential application of the MDL for the effluent Na^+ concentration as an indicator for true chemical equilibrium is likely to be neither necessary nor practical.

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Table 2.1 – Properties of bentonite in a geosynthetic clay liner.

Property	Standard	No. of Trials	Average Value [Max, Min]
Specific Gravity	ASTM D 854[a]	3	2.74 [2.74, 2.74]
Soil Classification:	ASTM D 2487		
Sieve Analysis (Air-Dried)		3	SP
Hydrometer		7	CH
Atterberg Limits (%):	ASTM D 4318	1	
Liquid Limit, LL			430
Plasticity Index, PI			393
Swell Index (mL/2 g)	ASTM D 5890	17	27.5 [29.5, 25.5]
Bentonite Mass (kg/m^2)	ASTM D 5993	5	5.1 [5.3, 4.7]
Principal Minerals (%):	b	3	
Montmorillonite			77.2 [79.6, 74.0]
Cristobalite			10.3 [15.0, 6.8]
Plagioclase Feldspar			5.1 [7.4, 4.0]
Quartz			3.4 [4.0, 3.0]
Others			4.0 [6.0, 2.9]
Cation Exchange Capacity, CEC (meq/100 g)	c	3	63.9 [73.5, 53.1]
Exchangeable Metals (meq/100 g):	c	3	
Ca^{2+}			11.5 [15.7, 6.9]
Mg^{2+}			3.7 [4.8, 2.2]
Na^{+}			45.8 [56.1, 40.0]
K^{+}			0.7 [0.8, 0.6]
Sum			61.7 [72.7, 51.2]
Soluble Metals (mg/kg):	c, d	3	
Ca^{2+}			218 [241, 174]
Mg^{2+}			24 [29, 14]
Na^{+}			3365 [3766, 3451]
K^{+}			48 [52, 43]
Saturated Soil Paste:	c	3	
pH			8.9 [8.9, 8.8]
EC[e] (mS/m)			305 [315, 290]

[a] Using a magnetic stirring device for de-airing.

[b] Based on X-ray diffraction (XRD) analyses performed by Mineralogy Inc., Tulsa, OK and GeoServices Inc., Argyle, TX.

[c] Based on procedures described in Shackelford and Redmond (1995).

[d] Measured from a 1 g:20 mL clay-water extract.

[e] Electrical conductivity at 25 °C.

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Table 2.2 – Properties of permeant liquids.

Permeant Liquid	Salt Concentration (mM)		Measured Solute Concentrations (mg/L)		Measured pH [No. of Trials]	Measured EC[c] (mS/m) [No. of Trials]
	Target	Measured [No. of Trials]	Calcium (Ca^{2+}) [No. of Trials]	Chloride (Cl^-) [No. of Trials]		
DIW[a]	0	< 0.0005[b] [10]	< 0.02[b] [10]	< 0.04[b] [10]	5.6 ± 0.5 [19]	0.21 ± 0.11 [19]
$CaCl_2$ (Sigma Co., 96 %)	5	5.1 ± 0.2 [14]	216 ± 10 [14]	377 ± 38 [14]	5.7 ± 0.5 [25]	123 ± 2.1 [25]
	10	10.1 ± 0.2 [13]	436 ± 30 [13]	756 ± 65 [13]	6.0 ± 0.3 [19]	234 ± 2.6 [19]
	20	20.1 ± 0.6 [13]	872 ± 77 [13]	1457 ± 110 [13]	6.1 ± 0.3 [17]	445 ± 7.3 [17]
	50	50.7 ± 1.4 [9]	2055 ± 63 [9]	3548 ± 69 [9]	5.7 ± 0.1 [18]	1041 ± 26 [18]
	100	100 ± 2.6 [6]	4072 ± 126 [6]	7030 ± 95 [6]	5.8 ± 0.1 [13]	1958 ± 48 [13]
	500	505 ± 10 [5]	20289 ± 474 [5]	35755 ± 710 [5]	6.5 ± 0.2 [12]	7693 ± 25 [12]

[a] Deionized water.

[b] Method detection limit (MDL).

[c] Electrical conductivity at 25 °C.

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Table 2.3 – Summary for results of hydraulic conductivity tests based on physical termination criteria.[a]

Permeant Liquid	Test No.	Slope of k ~ 0[b]		End of Test		Physical Termination Criteria							
						ASTM D 5084				2 PVF		Constant Thickness	
						Q Ratio		Steady k					
		$PVF_{\Delta k\sim0}$ $[t_{\Delta k\sim0}]$*	$k_{\Delta k\sim0}$ (cm/s)	PVF_f $[t_f]$*	k_f (cm/s)	PVF_Q $[t_Q]$*	$k_Q/k_{\Delta k\sim0}$	PVF_k $[t_k]$*	$k_k/k_{\Delta k\sim0}$	$[t_{2PVF}]$*	$k_{2PVF}/k_{\Delta k\sim0}$	PVF_H $[t_H]$*	$k_H/k_{\Delta k\sim0}$
Deionized Water	1	53 [860]	3.4×10^{-9}	53 [860]	3.4×10^{-9}	1.1 [13]	0.65	1.3 [16]	0.69	[37]	0.67	6.1 [114]	0.78
	2	49 [843]	2.5×10^{-9}	49 [843]	2.5×10^{-9}	1.2 [26]	0.68	1.2 [26]	0.88	[50]	0.66	5.1 [113]	0.84
5 mM $CaCl_2$	3	54 [494]	8.3×10^{-9}	274 [1026]	1.1×10^{-8}	1.5 [5.5]	0.32	2.8 [25]	0.24	[15]	0.21	2.2 [15]	0.21
	4	78 [774]	9.1×10^{-9}	195 [1060]	1.1×10^{-8}	1.7 [26]	0.19	1.7 [26]	0.24	[37]	0.16	1.2 [16]	0.22
10 mM $CaCl_2$	5	26 [376]	6.8×10^{-9}	265 [1028]	1.5×10^{-8}	2.6 [8.6]	0.37	3.9 [36]	0.28	[3.0]	1.92	3.4 [23]	0.28
	6	38 [304]	9.8×10^{-9}	268 [1018]	9.2×10^{-9}	3.7 [28]	0.18	4.4 [39]	0.21	[5.2]	1.15	3.7 [28]	0.18
20 mM $CaCl_2$	7	13 [136]	7.8×10^{-9}	269 [1002]	1.1×10^{-8}	2.5 [30]	0.29	2.5 [30]	0.35	[22]	0.30	0.87 [7.6]	0.48
	8	18 [147]	9.5×10^{-9}	284 [927]	9.5×10^{-9}	3.2 [47]	0.15	3.9 [59]	0.16	[34]	0.14	1.1 [9.6]	0.28
50 mM $CaCl_2$	9	7.0 [12]	1.6×10^{-8}	43 [68]	1.5×10^{-9}	3.0 [5.6]	0.85	3.0 [5.6]	0.86	[4.2]	0.80	1.5 [2.7]	0.83
	10	4.8 [8.9]	1.8×10^{-8}	41 [66]	1.8×10^{-9}	2.7 [5.5]	0.86	2.7 [5.5]	0.84	[4.2]	0.81	1.3 [2.6]	0.83
100 mM $CaCl_2$	11	9.1 [0.98]	3.4×10^{-7}	46 [3.9]	3.1×10^{-7}	3.0 [0.39]	0.58	3.0 [0.39]	0.61	[0.29]	0.59	1.5 [0.19]	0.69
	12	5.3 [0.54]	3.5×10^{-7}	45 [3.3]	4.0×10^{-7}	3.0 [0.37]	0.89	3.7 [0.43]	0.83	[0.31]	0.82	0.75 [0.15]	0.38
500 mM $CaCl_2$	13	7.5 [0.12]	1.8×10^{-6}	41 [0.57]	1.5×10^{-6}	3.4 [0.06]	0.63	4.2 [0.08]	0.63	[0.04]	0.62	2.6 [0.04]	0.62
	14	6.3 [0.09]	1.9×10^{-6}	39 [0.59]	1.3×10^{-6}	3.2 [0.05]	0.71	4.0 [0.06]	0.79	[0.03]	0.74	1.6 [0.02]	0.92

[a] k = hydraulic conductivity; Q = volumetric flow rate; PVF = pore volumes of flow.

[b] When the slope of k vs. number of PVF is statistically zero (Peirce & Witter 1986) except for the tests performed with deionized water, in which values are those at the end of the tests.

* Elapsed time [days].

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Table 2.4 – Summary for results of hydraulic conductivity tests based on chemical termination criteria.[a]

Permeant Liquid	Test No.	$k_{\Delta k\sim0}$[b] (cm/s)	Chemical Termination Criteria									
			ASTM D 6766				EC Ratio[c] (1.00 ± 0.05)		C_{Cl} Ratio[c] (1.00 ± 0.10)		C_{Ca} Ratio[c] (1.00 ± 0.10)	
			pH Ratio[c] (1.00 ± 0.10)		EC Ratio[c] (1.00 ± 0.10)							
			$PVF_{pH0.1}$ $[t_{pH0.1}]$*	$k_{pH0.1}/k_{\Delta k\sim0}$	$PVF_{EC0.1}$ $[t_{EC0.1}]$*	$k_{EC0.1}/k_{\Delta k\sim0}$	$PVF_{EC0.05}$ $[t_{EC0.05}]$*	$k_{EC0.05}/k_{\Delta k\sim0}$	$PVF_{Cl0.1}$ $[t_{Cl0.1}]$*	$k_{Cl0.1}/k_{\Delta k\sim0}$	$PVF_{Ca0.1}$ $[t_{Ca0.1}]$*	$k_{Ca0.1}/k_{\Delta k\sim0}$
5 mM $CaCl_2$	3	8.3×10^{-9}	d	d	24 [338]	0.26	32 [403]	0.39	6.3 [80]	0.18	57 [502]	1.04
	4	9.1×10^{-9}			27 [498]	0.20	40 [623]	0.43	5.0 [104]	0.11	79 [779]	0.95
10 mM $CaCl_2$	5	6.8×10^{-9}	d	d	14 [280]	0.30	20 [341]	0.64	11 [234]	0.22	30 [397]	0.98
	6	9.8×10^{-9}			11 [155]	0.20	21 [244]	0.50	15 [200]	0.25	36 [297]	0.98
20 mM $CaCl_2$	7	7.8×10^{-9}	d	d	3.8 [49]	0.24	8.4 [112]	0.54	7.0 [100]	0.37	21 [164]	1.03
	8	9.5×10^{-9}			4.6 [70]	0.17	12 [127]	0.61	1.8 [21]	0.17	31 [178]	0.99
50 mM $CaCl_2$	9	1.6×10^{-8}	d	d	3.0 [5.6]	0.85	3.8 [7.0]	0.91	2.2 [4.2]	0.80	9.3 [16]	1.03
	10	1.8×10^{-8}			2.7 [5.5]	0.86	3.4 [6.6]	0.91	2.0 [4.2]	0.81	8.9 [15]	1.06
100 mM $CaCl_2$	11	3.4×10^{-7}	d	d	3.0 [0.39]	0.58	3.8 [0.48]	0.62	2.3 [0.29]	0.59	6.8 [0.80]	0.87
	12	3.5×10^{-7}			2.2 [0.31]	0.82	3.7 [0.43]	0.96	1.5 [0.24]	0.65	6.0 [0.59]	1.07
500 mM $CaCl_2$	13	1.8×10^{-6}	0.9 [0.01]	1.03	0.87 [0.01]	1.03	0.87 [0.01]	1.03	1.7 [0.03]	0.64	1.7 [0.03]	0.64
	14	1.9×10^{-6}	0.8 [0.01]	1.41	0.79 [0.01]	1.41	2.4 [0.03]	0.74	2.4 [0.03]	0.74	1.6 [0.02]	0.92

[a] k = hydraulic conductivity; PVF = pore volumes of flow.

[b] When the slope of k vs. number of PVF is statistically zero (Peirce & Witter 1986).

[c] EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium; ratio = effluent relative to influent.

[d] Not established throughout the test.

* Elapsed time [days].

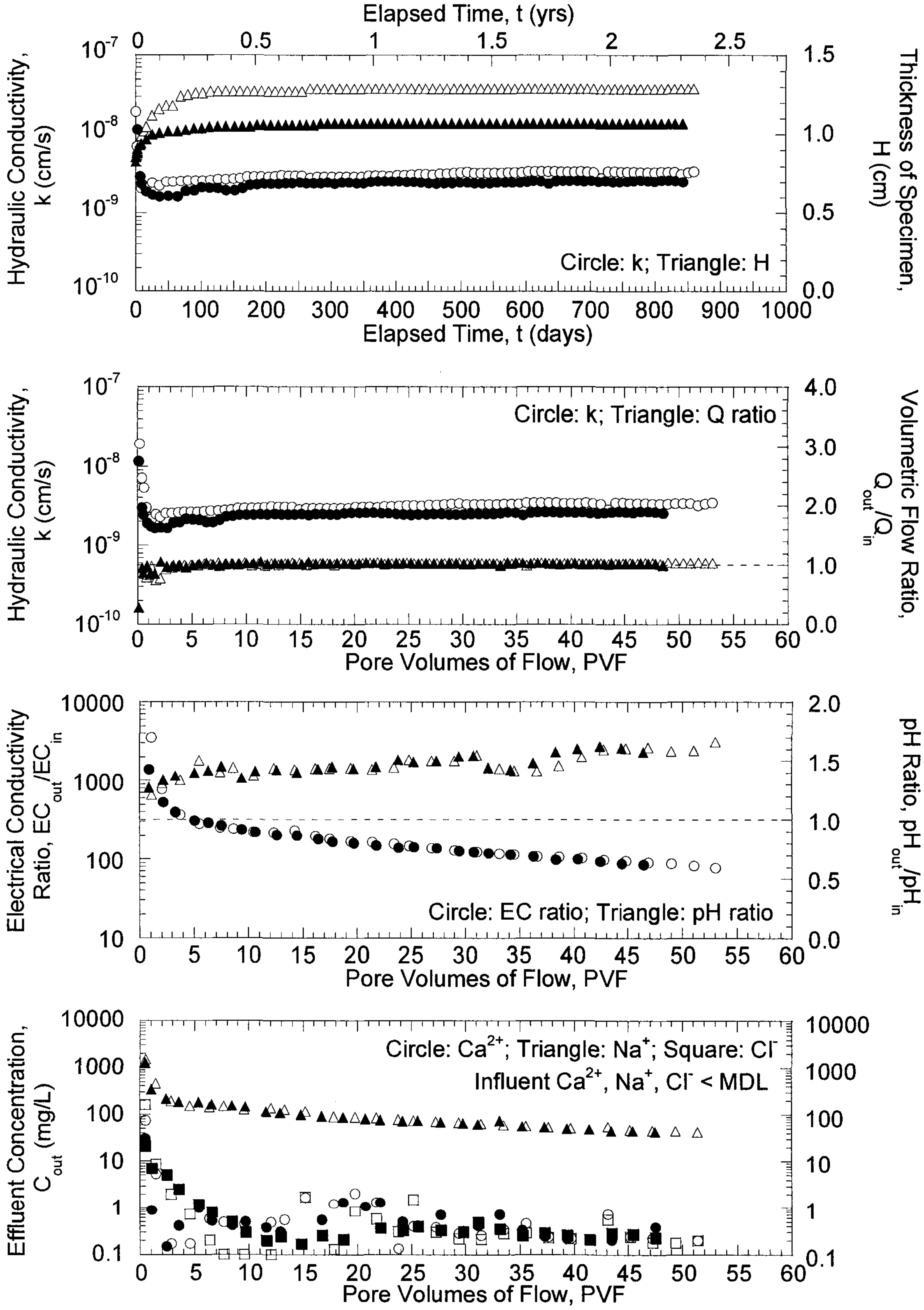

Fig. 2.1 – Test results for duplicate specimens permeated with water (MDL = method detection limit; MDL for Ca^{2+}, Na^{+}, Cl^{-} = 0.02, 0.2, 0.04 mg/L).

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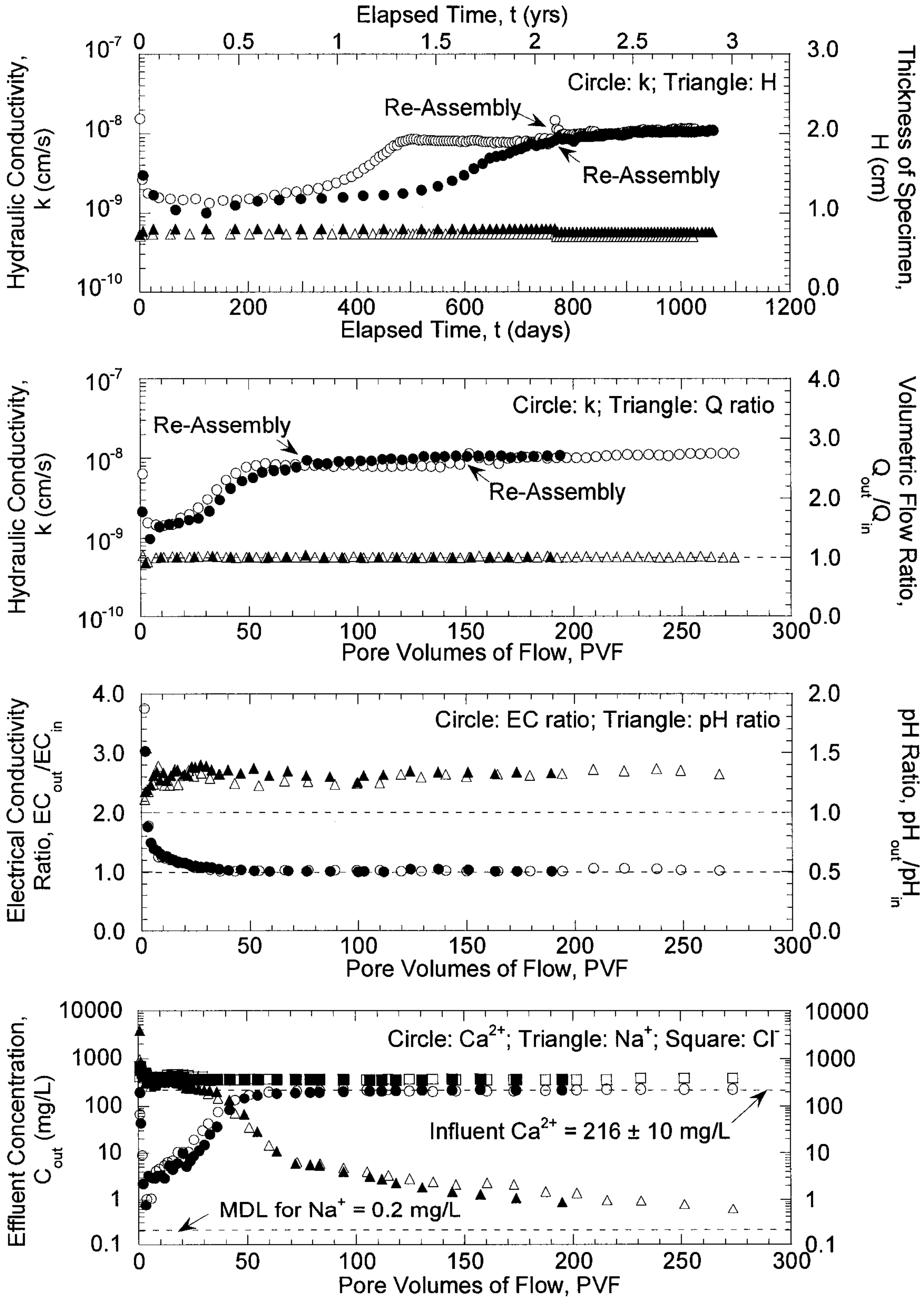

Fig. 2.2 – Test results for duplicate specimens permeated with 5 mM $CaCl_2$ solution (MDL = method detection limit).

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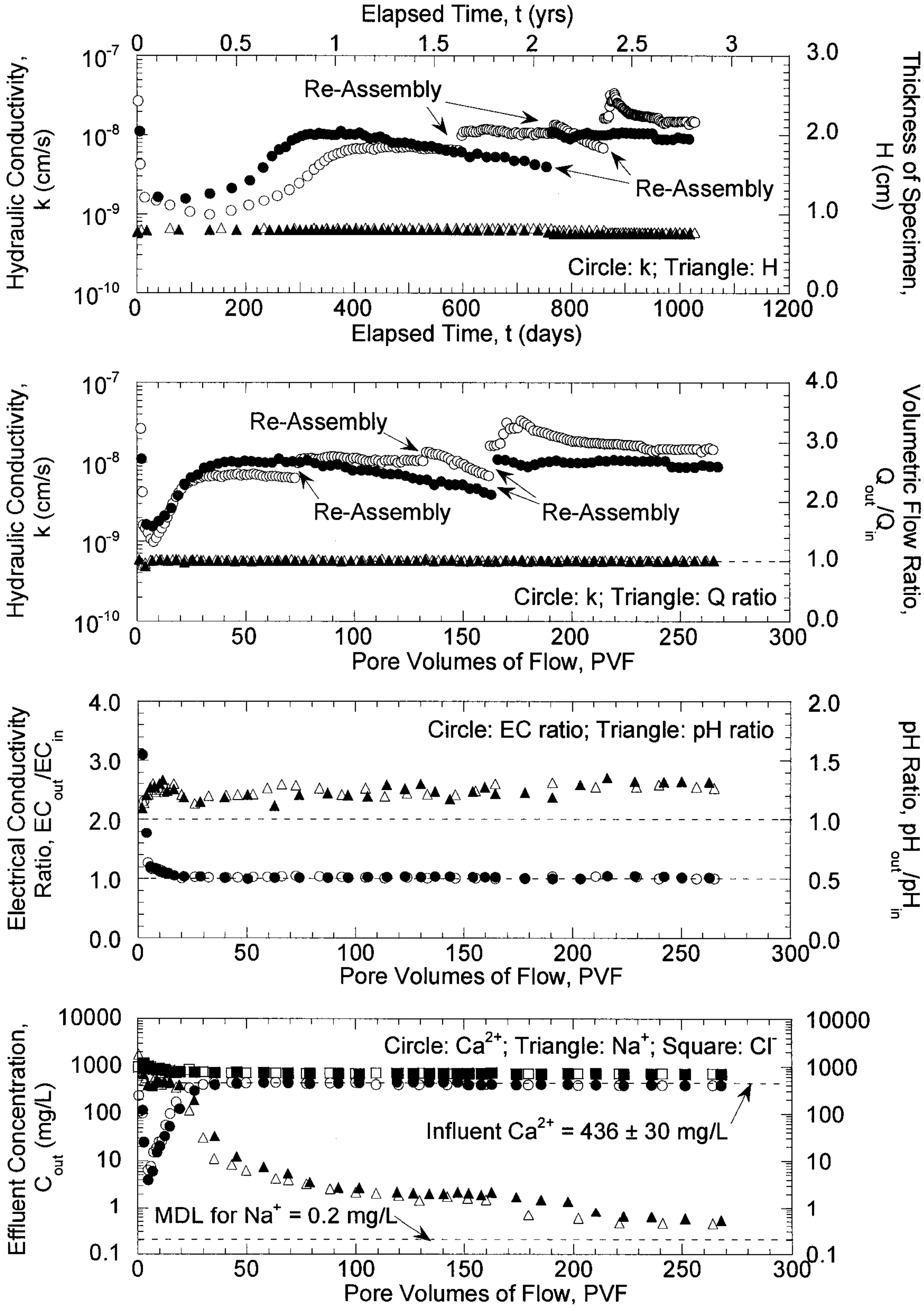

Fig. 2.3 – Test results for duplicate specimens permeated with 10 mM $CaCl_2$ solution (MDL = method detection limit).

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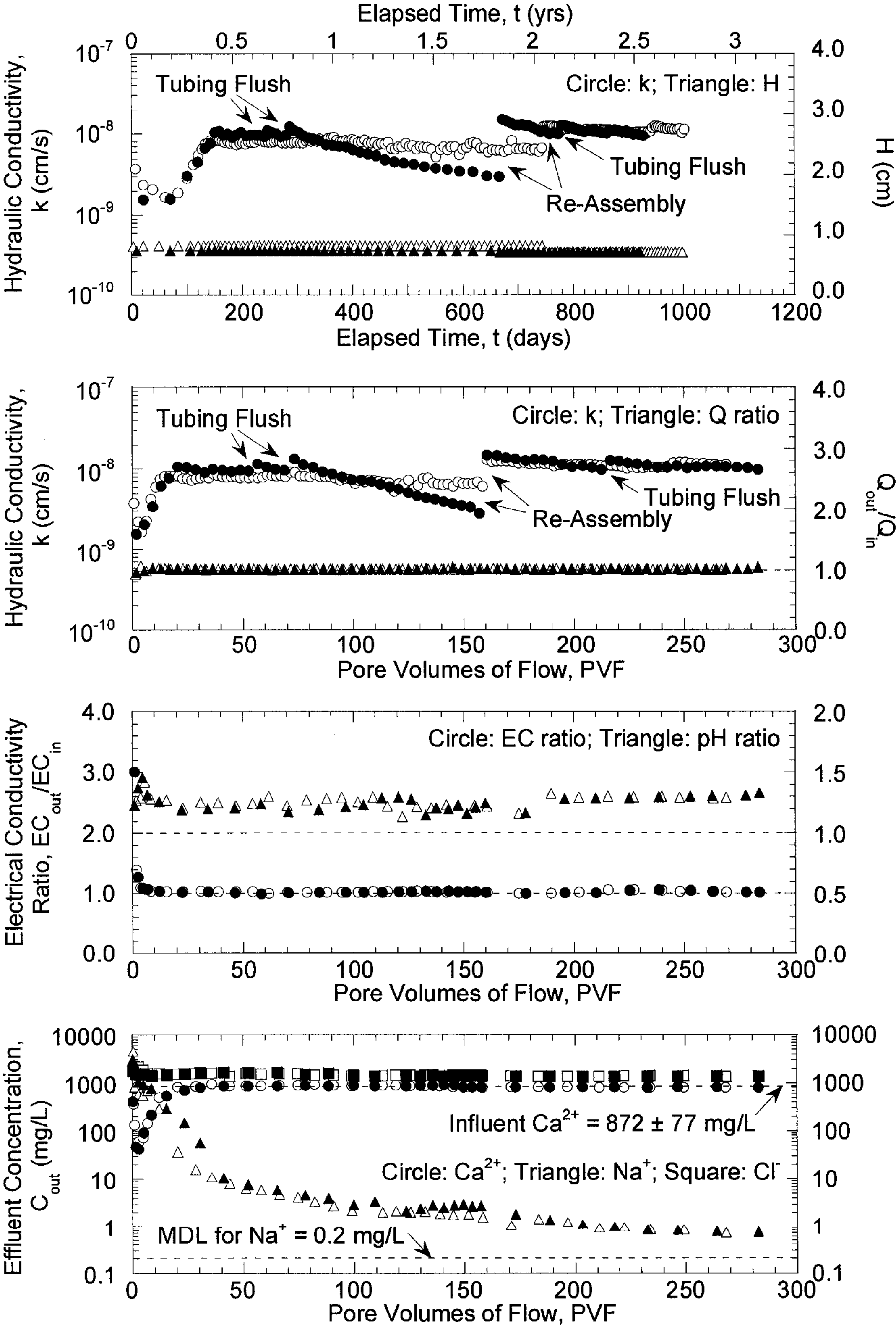

Fig. 2.4 – Test results for duplicate specimens permeated with 20 mM $CaCl_2$ solution (MDL = method detection limit).

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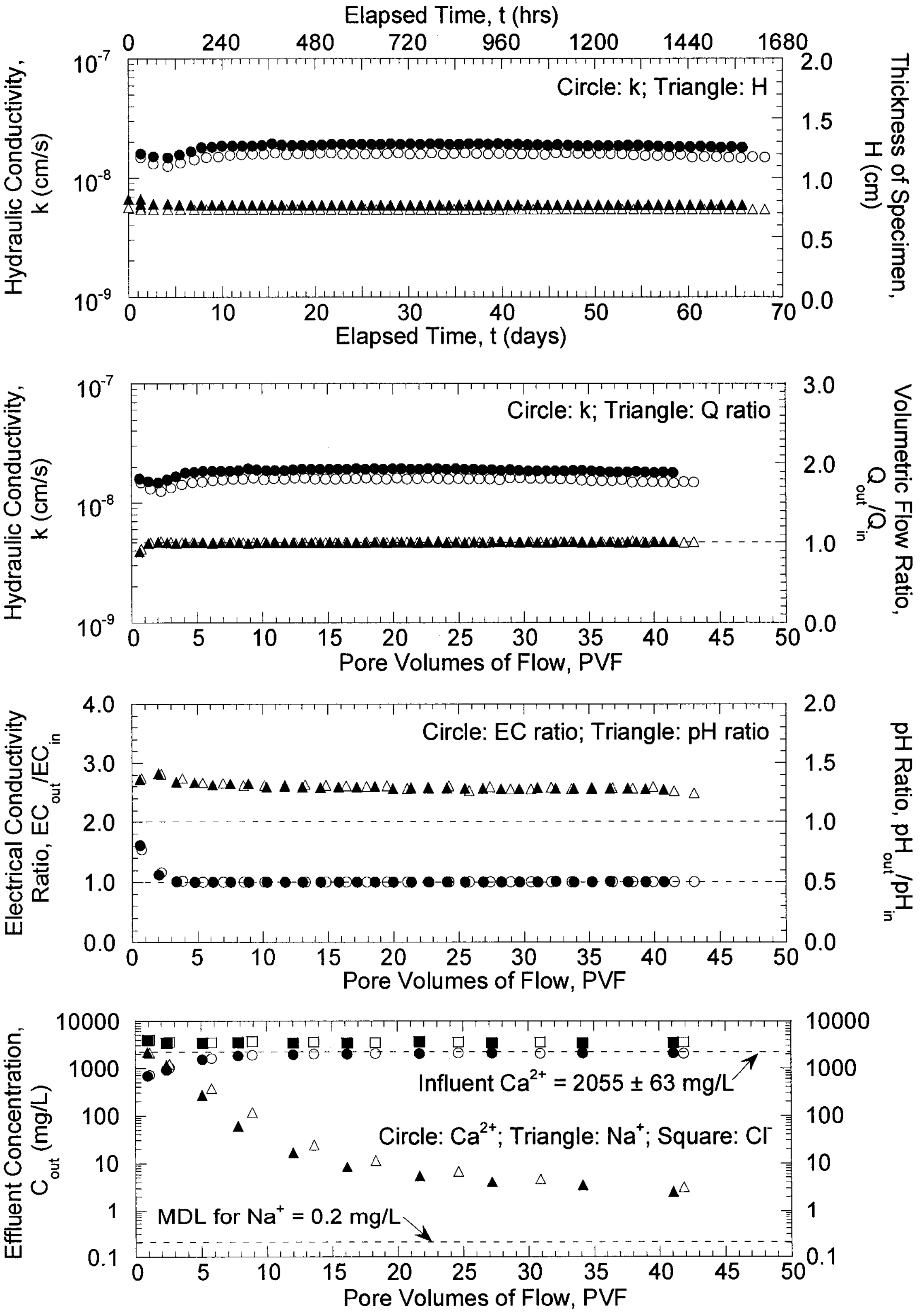

Fig. 2.5 – Test results for duplicate specimens permeated with 50 mM $CaCl_2$ solution (MDL = method detection limit).

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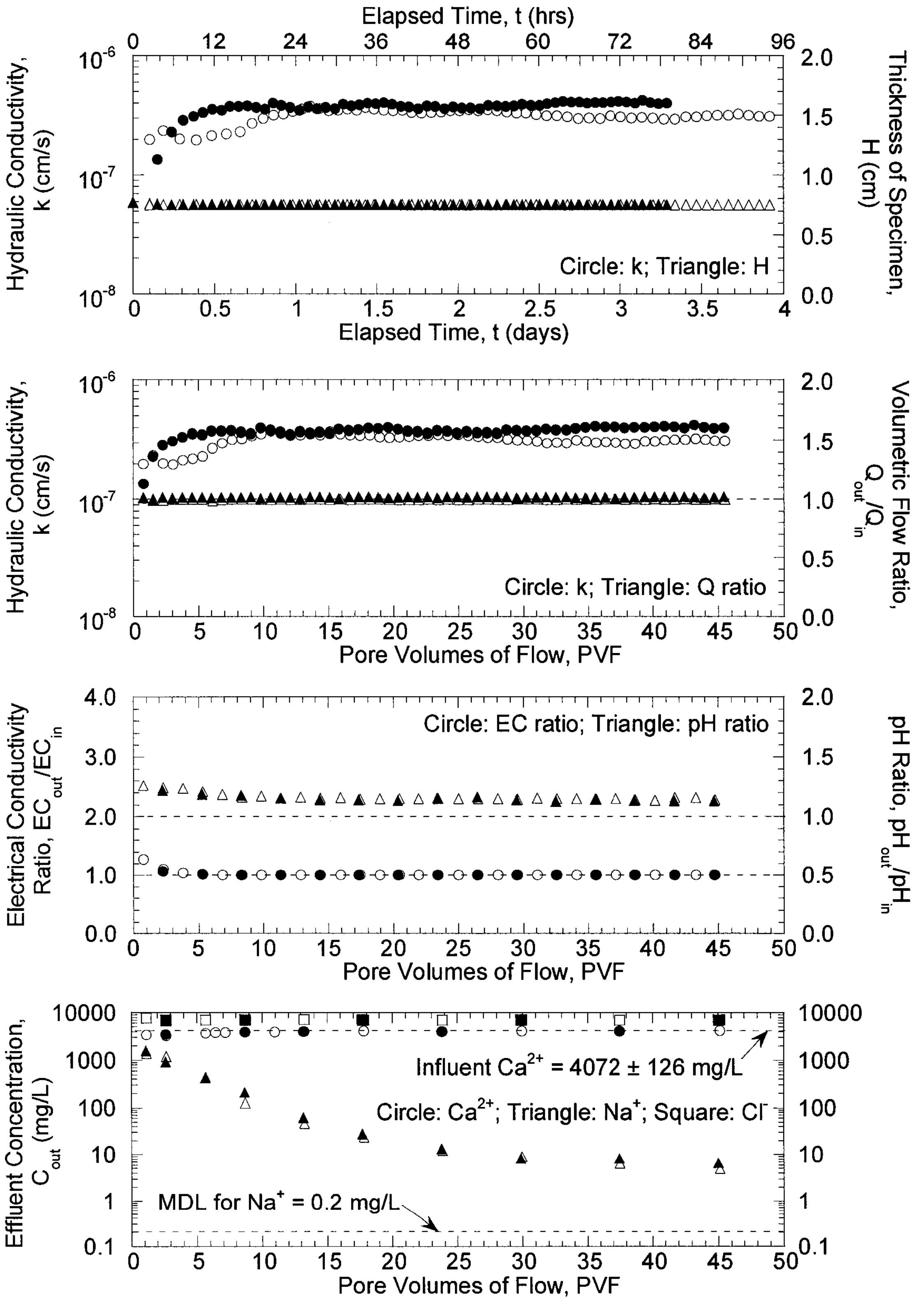

Fig. 2.6 – Test results for duplicate specimens permeated with 100 mM $CaCl_2$ solution (MDL = method detection limit).

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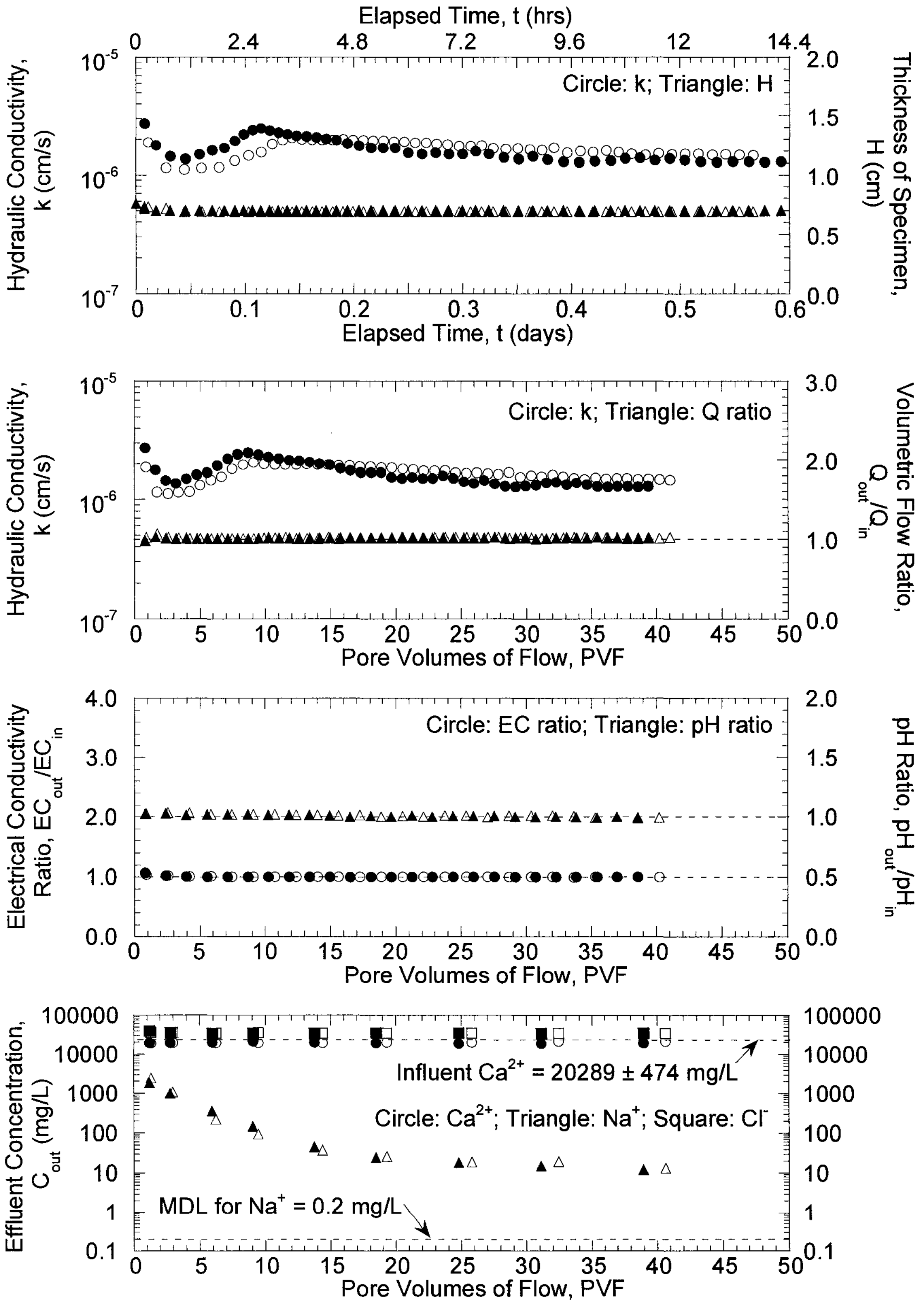

Fig. 2.7 – Test results for duplicate specimens permeated with 500 mM $CaCl_2$ solution (MDL = method detection limit).

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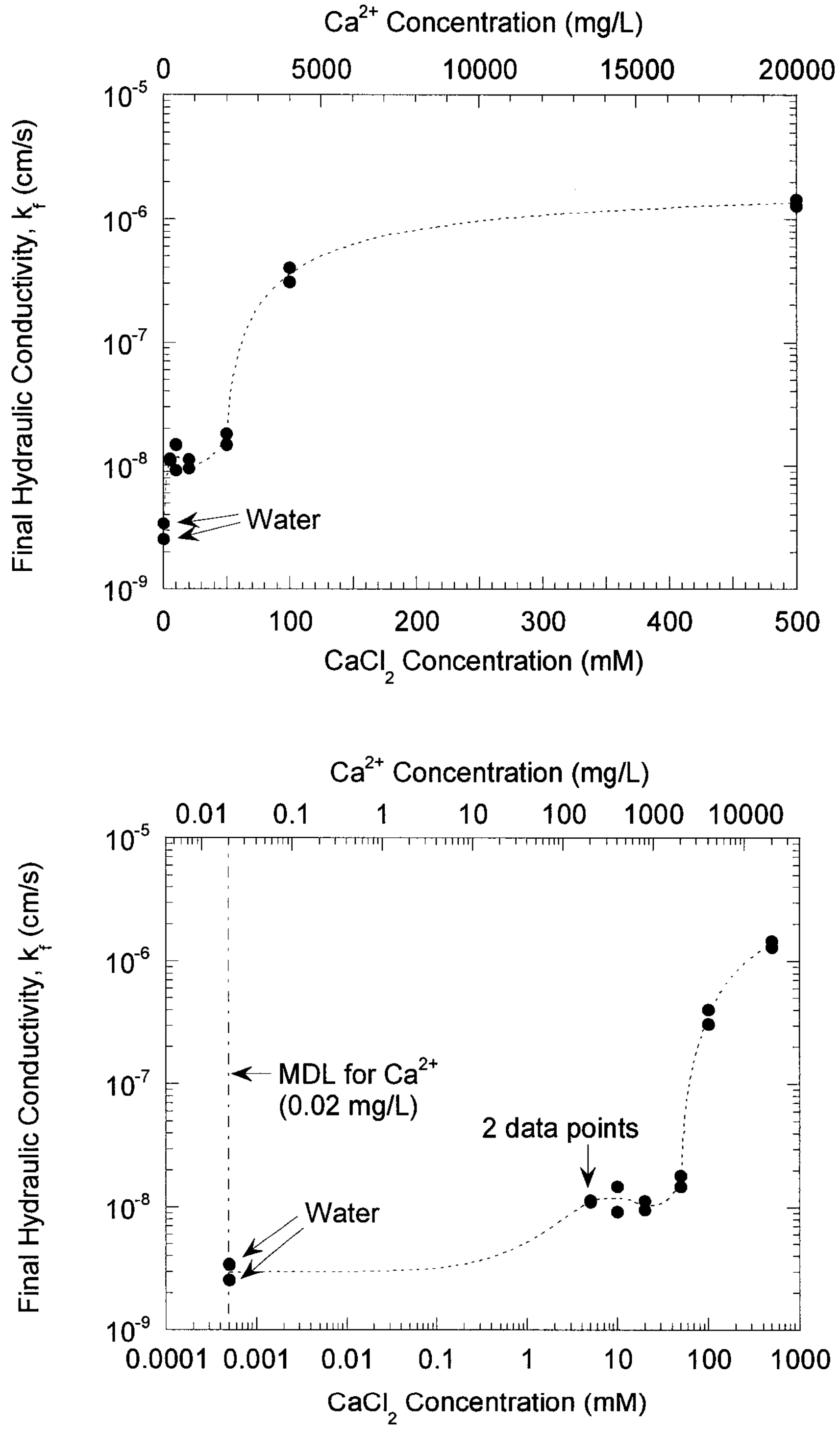

Fig. 2.8 – Final hydraulic conductivity at the end of permeation as a function of influent $CaCl_2$ concentration (MDL = method detection limit).

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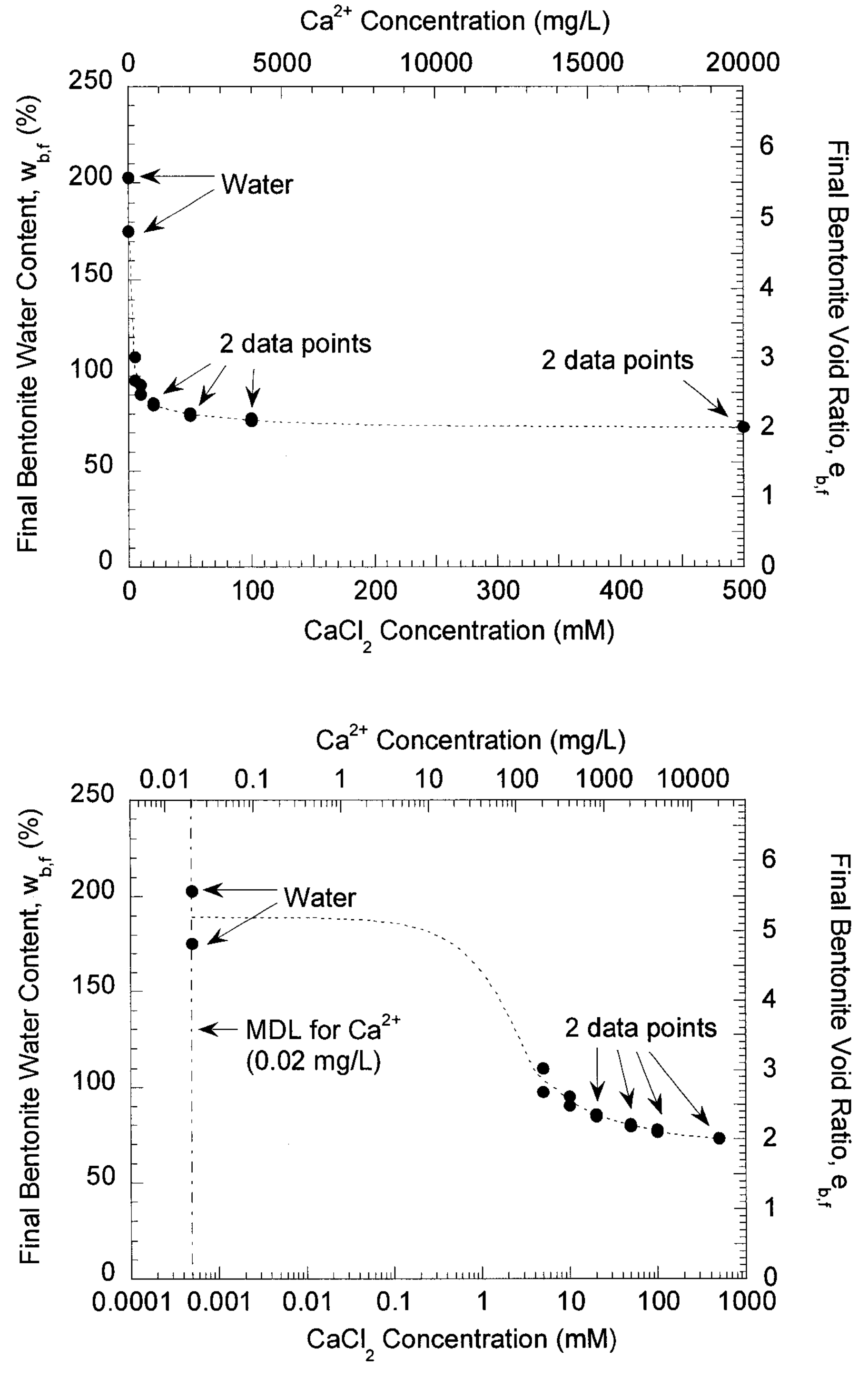

Fig. 2.9 – Final bentonite gravimetric water content and void ratio after permeation as a function of influent $CaCl_2$ concentration (MDL = method detection limit).

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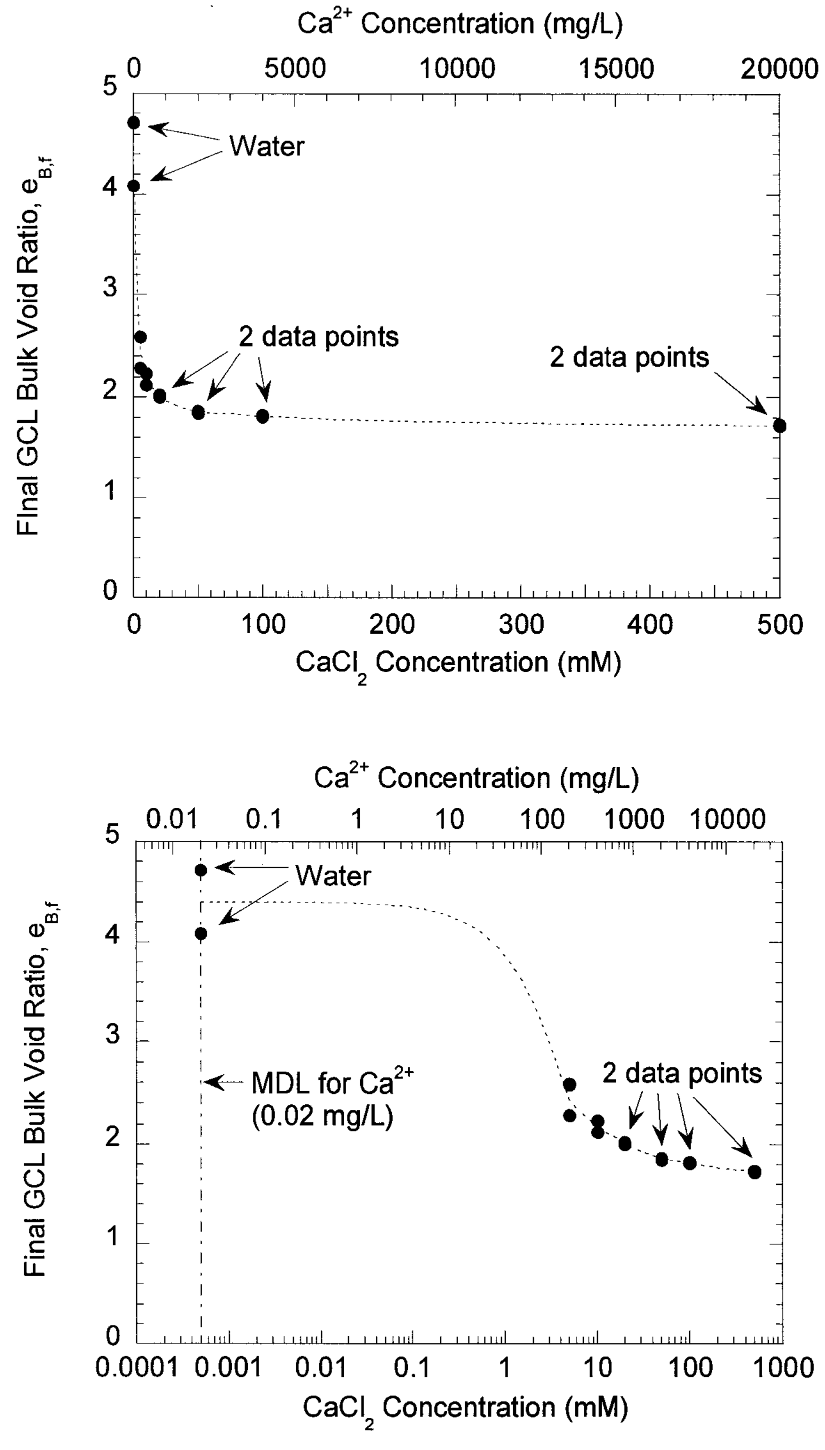

Fig. 2.10 – Final GCL bulk void ratio after permeation as a function of influent $CaCl_2$ concentration (MDL = method detection limit).

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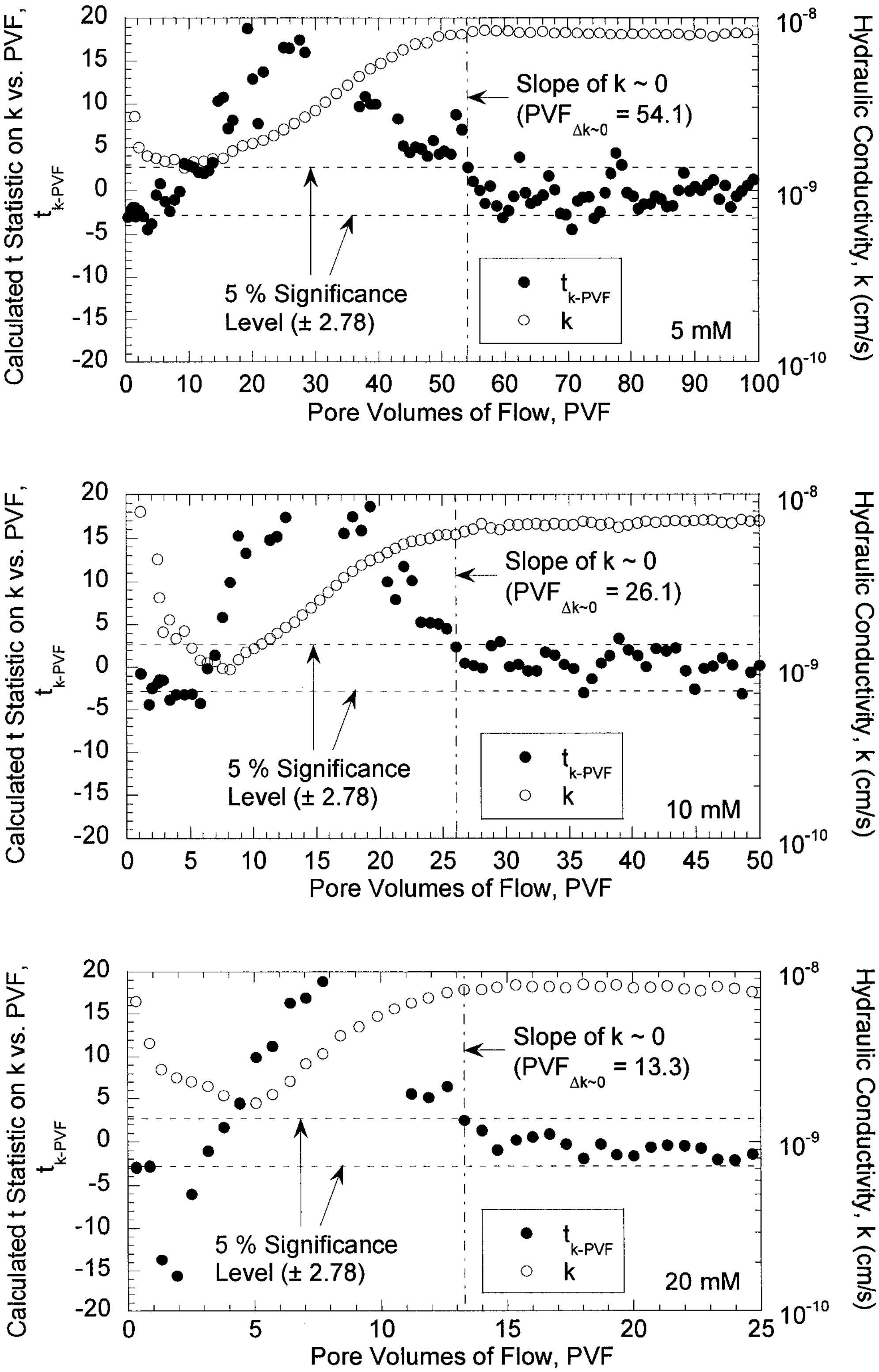

Fig. 2.11 – Pore volumes of flow at which the slope of hydraulic conductivity versus number of pore volumes of flow is statistically zero (i.e., slope of k ~ 0) for the first specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

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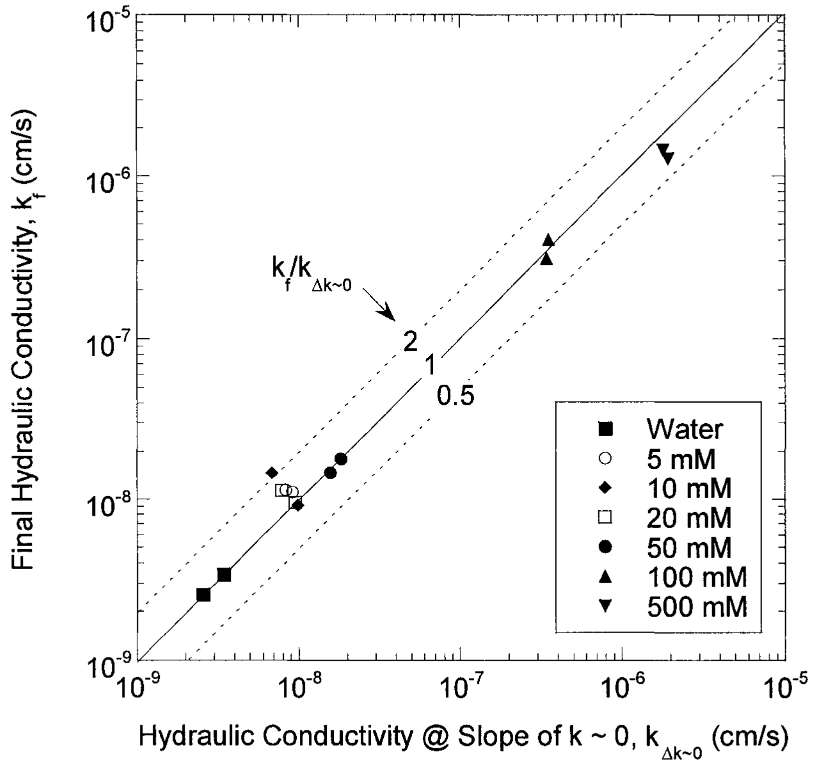

Fig. 2.12 – Final hydraulic conductivity versus hydraulic conductivity at the slope of k ~ 0 for the specimens permeated with water and $CaCl_2$ solutions ($k_{\Delta k\sim0}$ for water = k_f).

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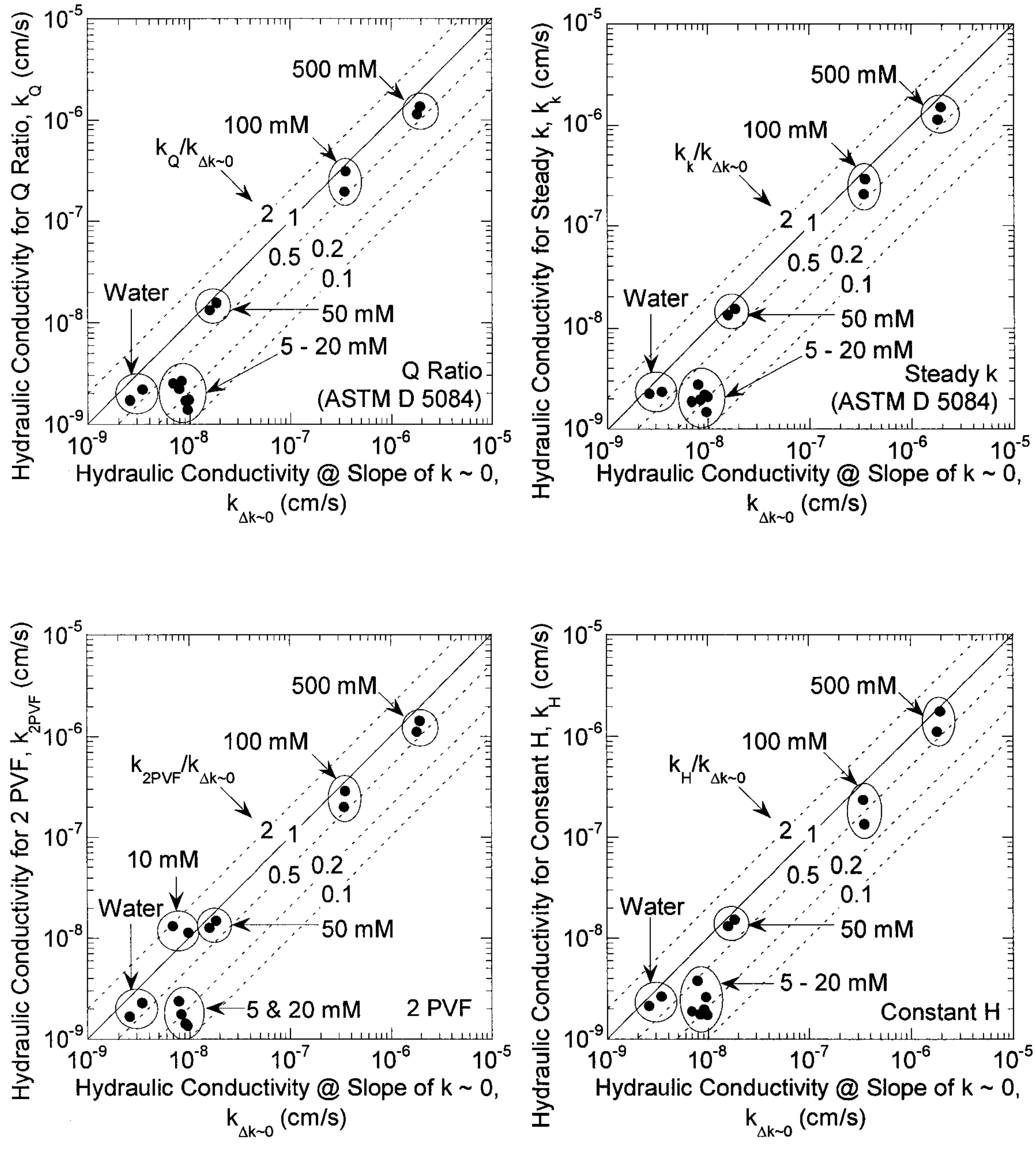

Fig. 2.13 – Hydraulic conductivity for physical termination criteria versus hydraulic conductivity at the slope of k ~ 0 (Q = volumetric flow rate; PVF = pore volumes of flow; H = thickness of specimen; $k_{\Delta k\sim 0}$ for water = final k at the end of test).

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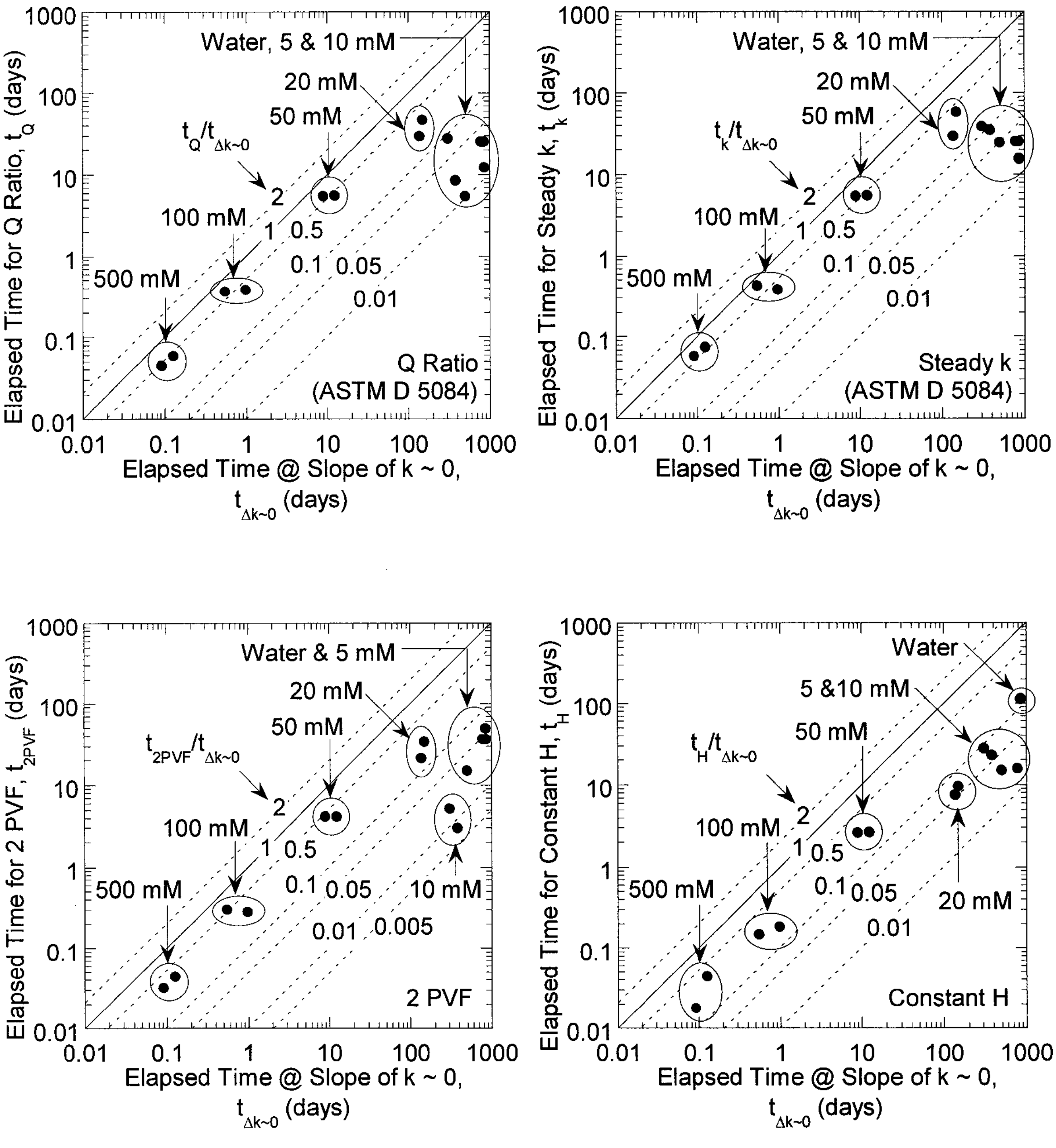

Fig. 2.14 – Elapsed time required to achieve physical termination criteria versus elapsed time at the slope of hydraulic conductivity (k) ~ 0 (Q = volumetric flow rate; PVF = pore volumes of flow; H = thickness of specimen; $t_{\Delta k\sim0}$ for water = final t at the end of test).

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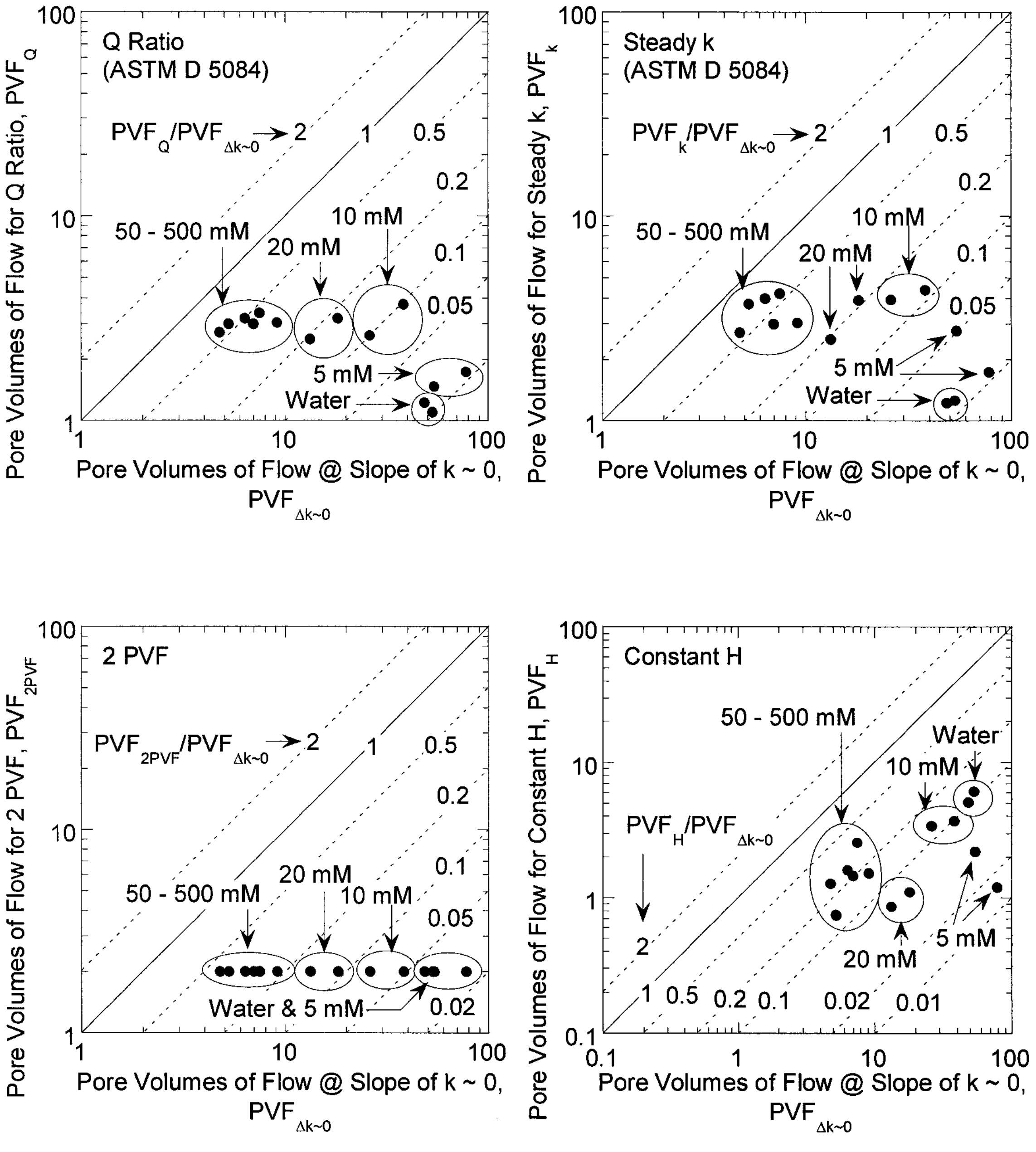

Fig. 2.15 – Pore volumes of flow (PVF) required to achieve physical termination criteria versus PVF at the slope of hydraulic conductivity (k) ~ 0 (Q = volumetric flow rate; H = thickness of specimen; PVF $_{\Delta k\sim 0}$ for water = final PVF at the end of test).

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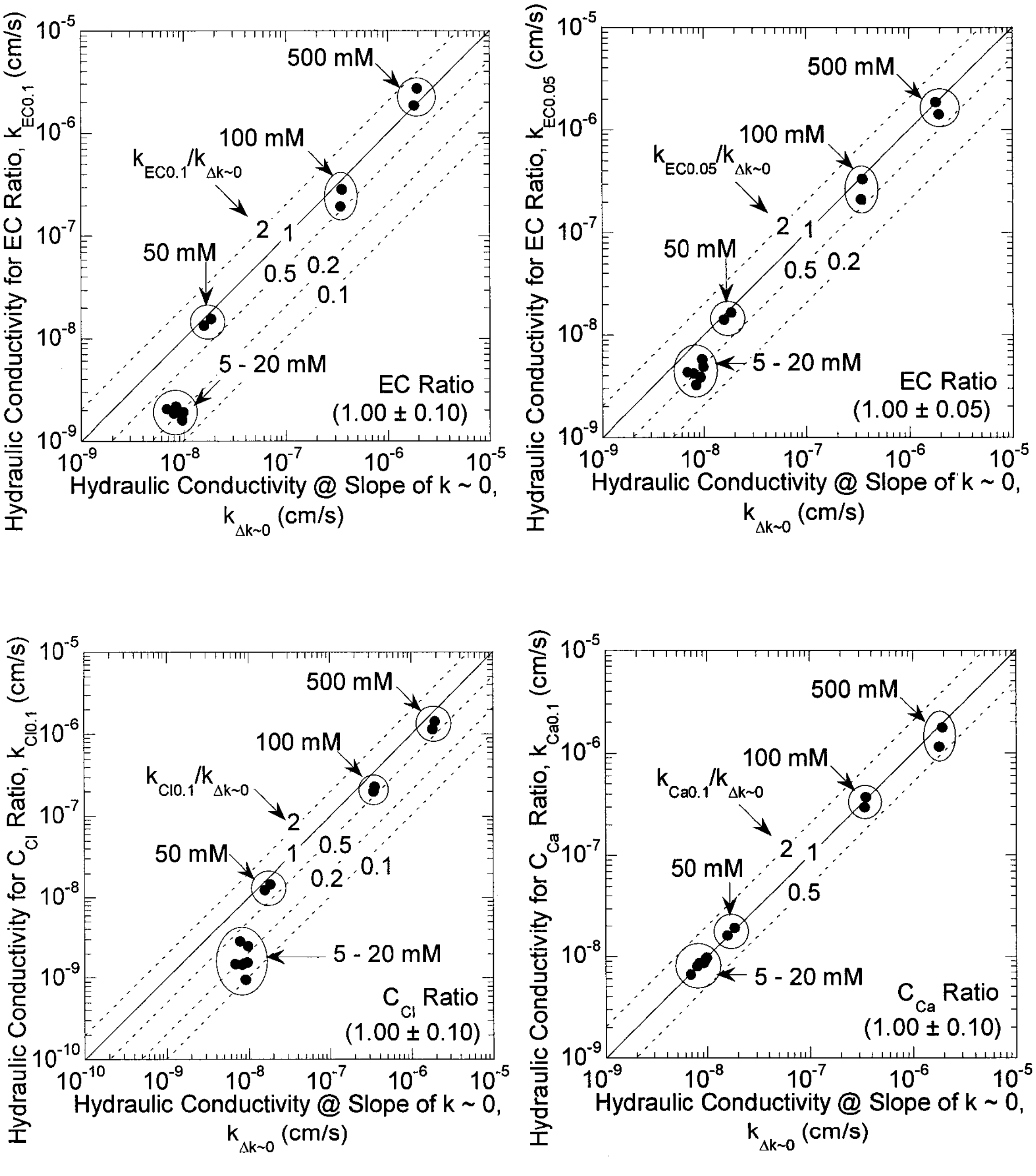

Fig. 2.16 – Hydraulic conductivity for chemical termination criteria versus hydraulic conductivity at the slope of k ~ 0 (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium; ratio = effluent relative to influent).

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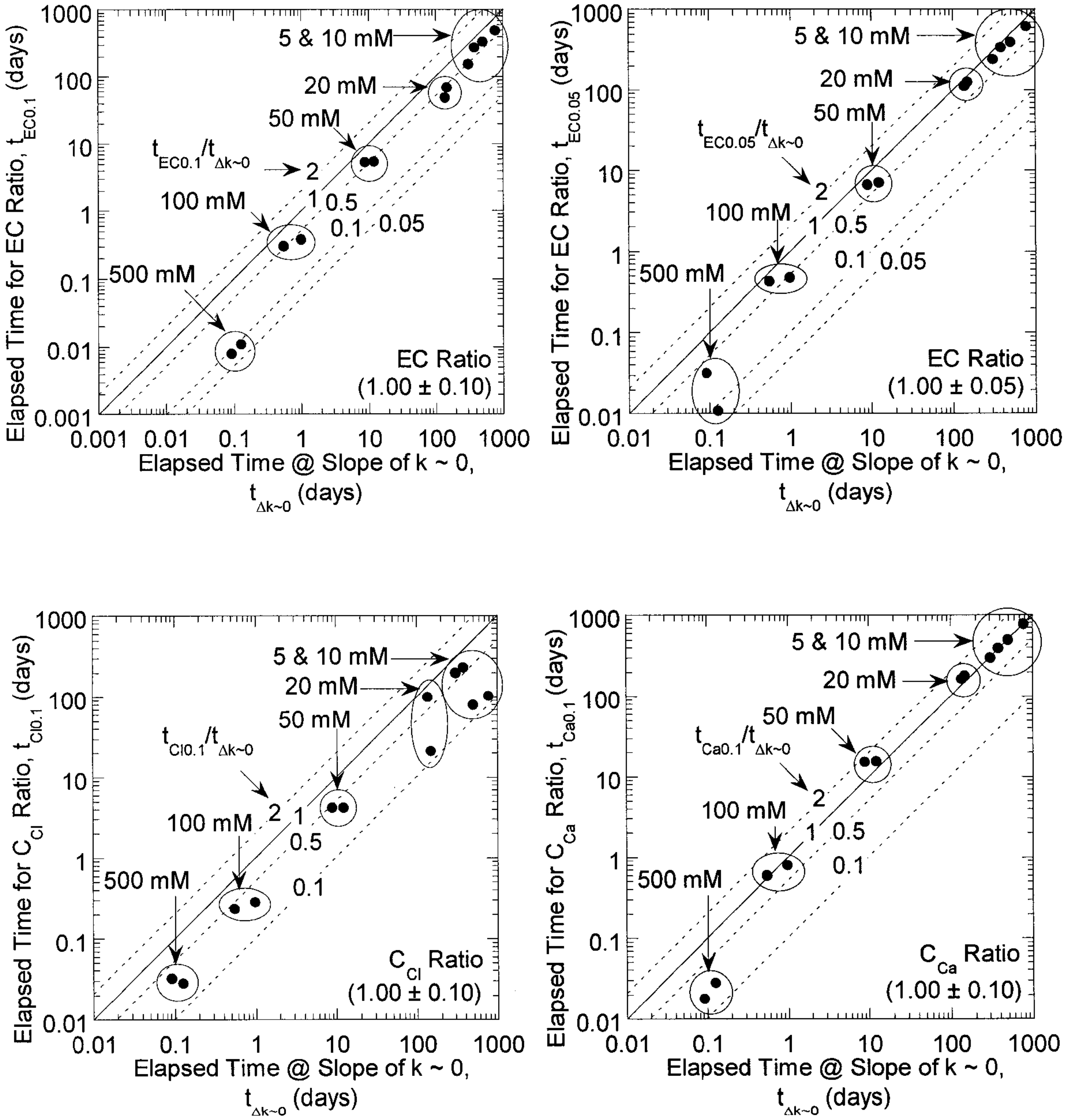

Fig. 2.17 – Elapsed time required to achieve chemical termination criteria versus elapsed time at the slope of hydraulic conductivity ~ 0 (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium; ratio = effluent relative to influent).

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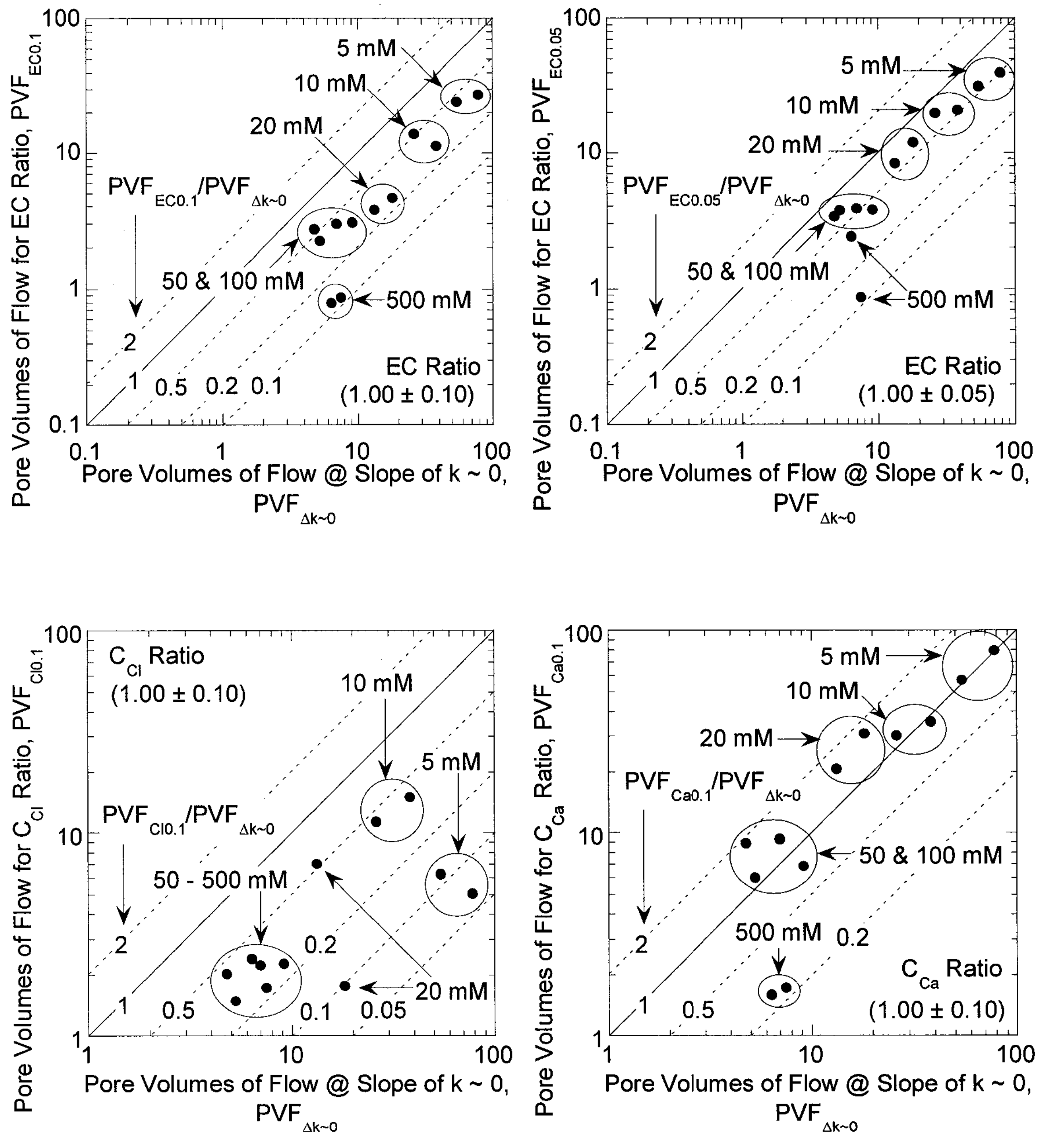

Fig. 2.18 – Pore volumes of flow (PVF) required to achieve each chemical termination criterion versus PVF at the slope of hydraulic conductivity ~ 0 (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium; ratio = effluent relative to influent).

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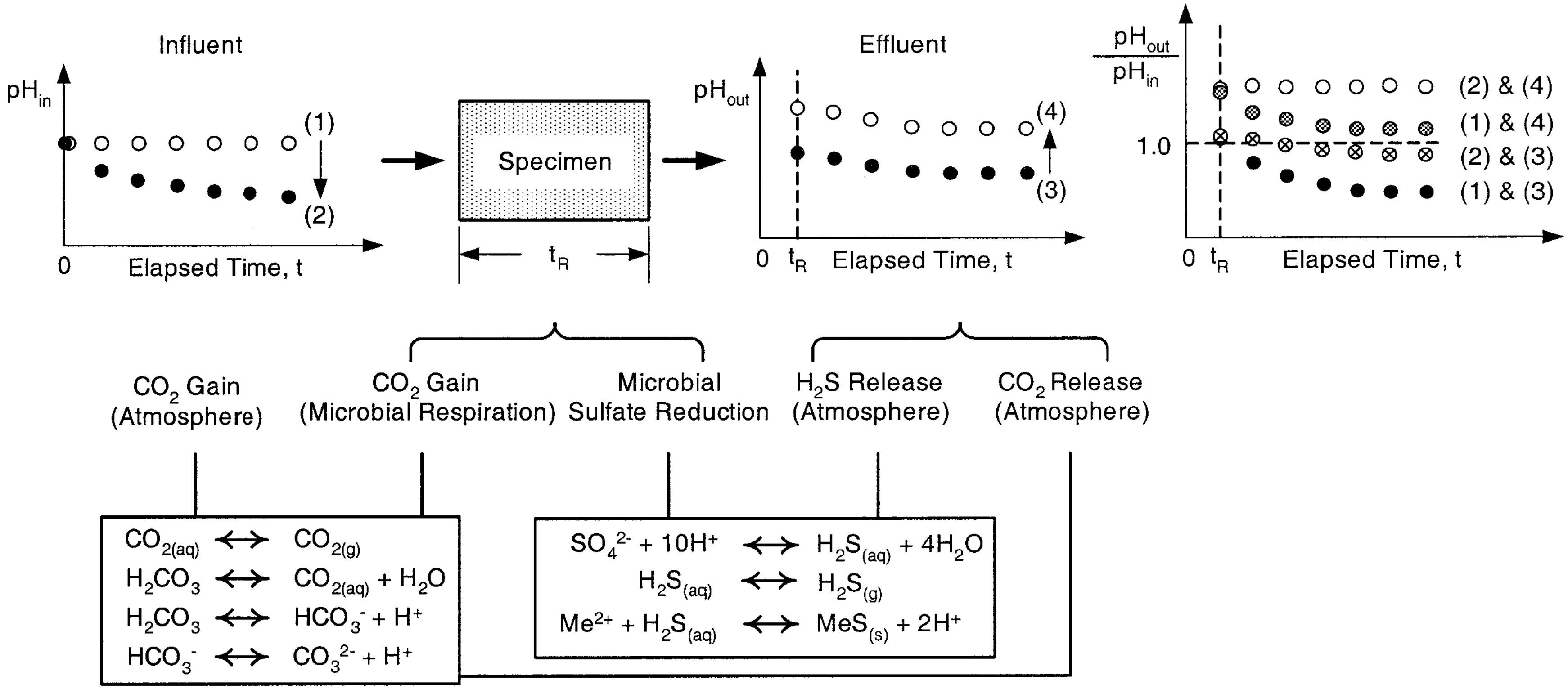

Notes: (1) the case for real-time preparation or closed-system storage of influent;
(2) the case for open-system storage of influent;
(3) the case for real-time measurement in a closed-system test;
(4) the case for a open-system test or open-system storage of effluent;
t_R = the residence (retention) time; and
Me = metal.

Fig. 2.19 – Potential mechanisms controlling pH in hydraulic conductivity tests.

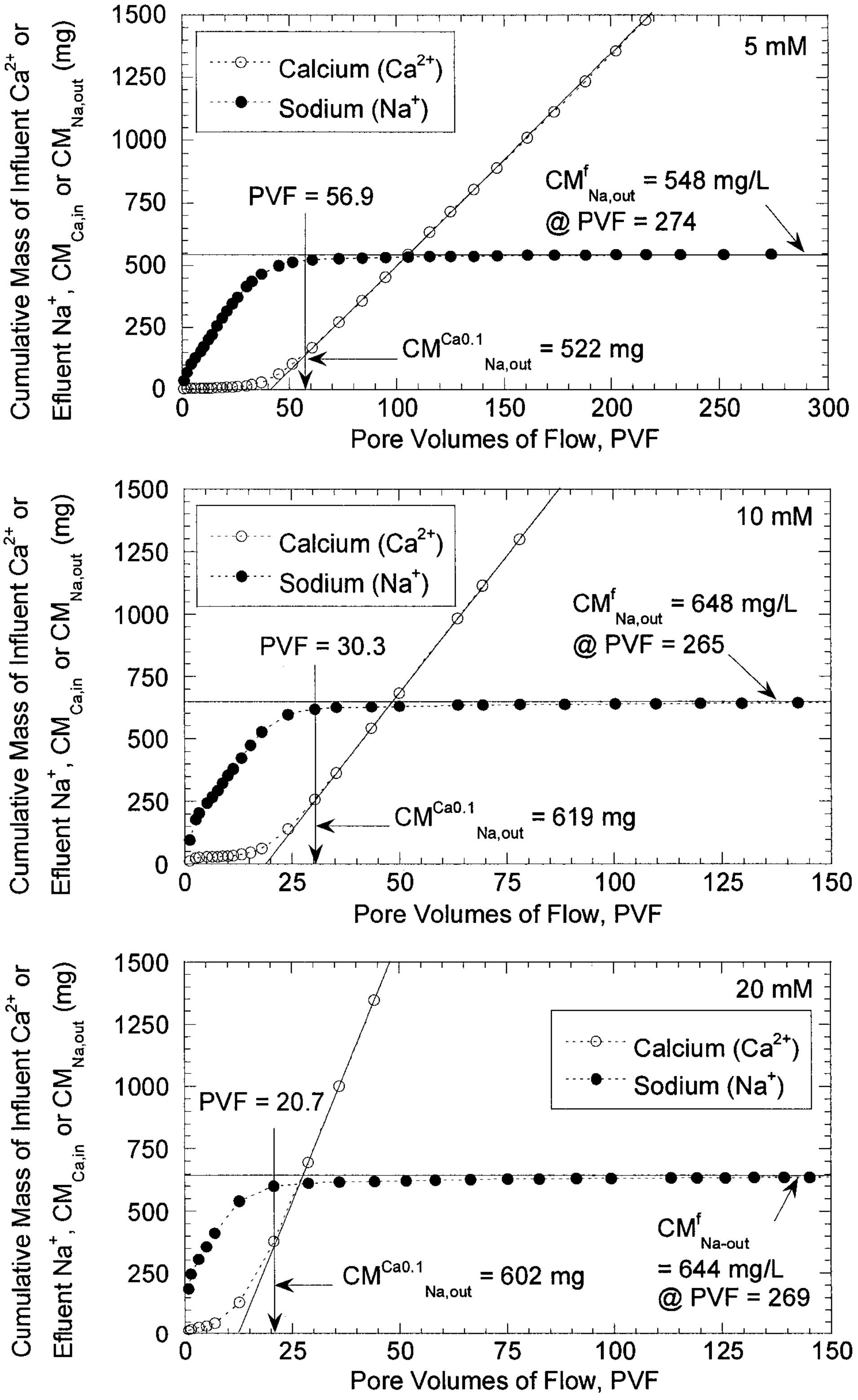

Fig. 2.20 – Cumulative mass of influent calcium and effluent sodium versus pore volumes of flow for the first specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions ($CM^{Ca0.1}_{Na,out}$ = $CM_{Na,out}$ for C_{Ca} ratio of 1.00 ± 0.10; $CM^{f}_{Na,out}$ = $CM_{Na,out}$ at the end of test).

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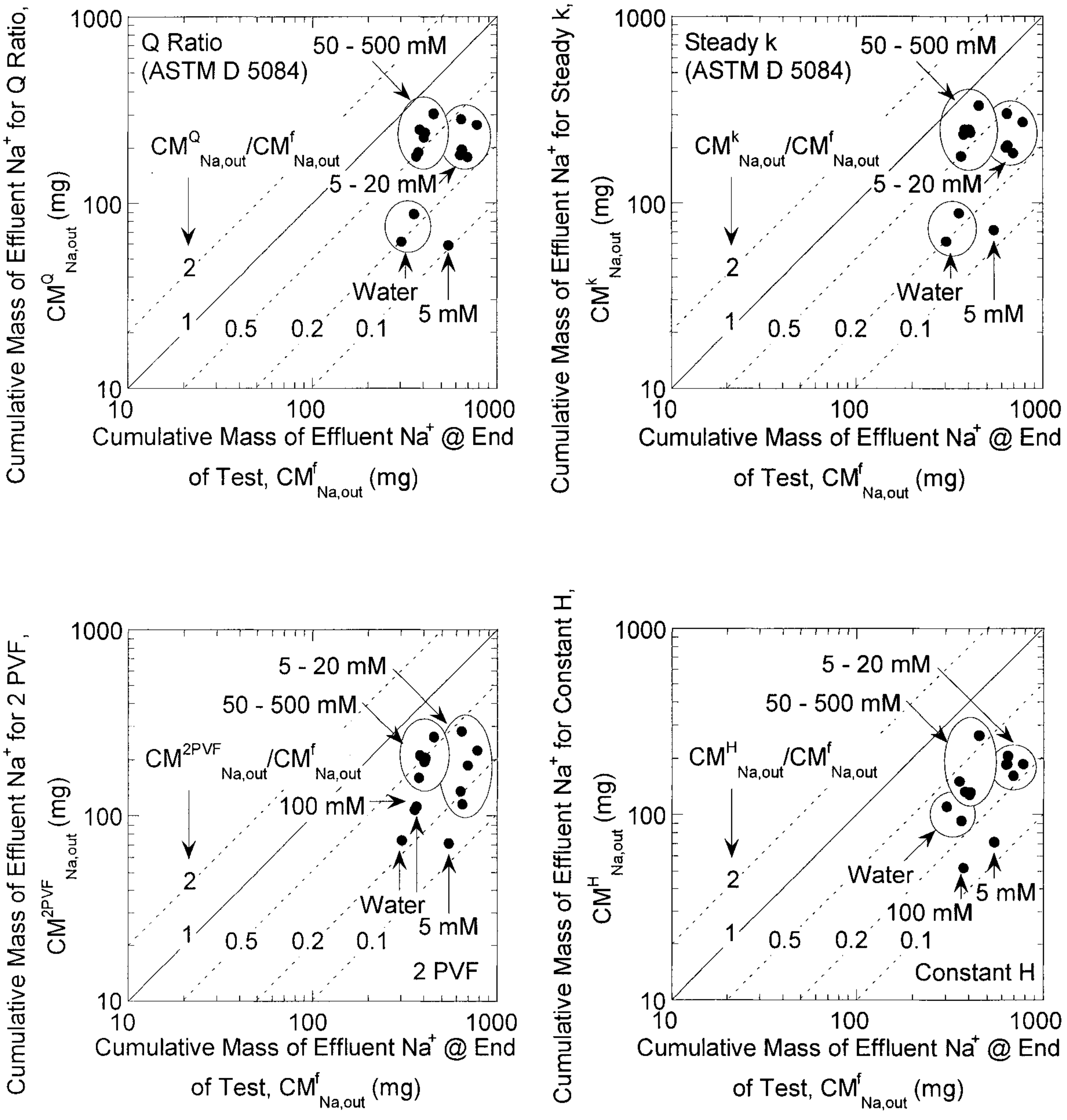

Fig. 2.21 – Cumulative mass of effluent sodium for physical termination criteria versus final cumulative mass of effluent sodium at the end of tests (Q = volumetric flow rate; k = hydraulic conductivity; PVF = pore volumes of flow; H = thickness of specimen).

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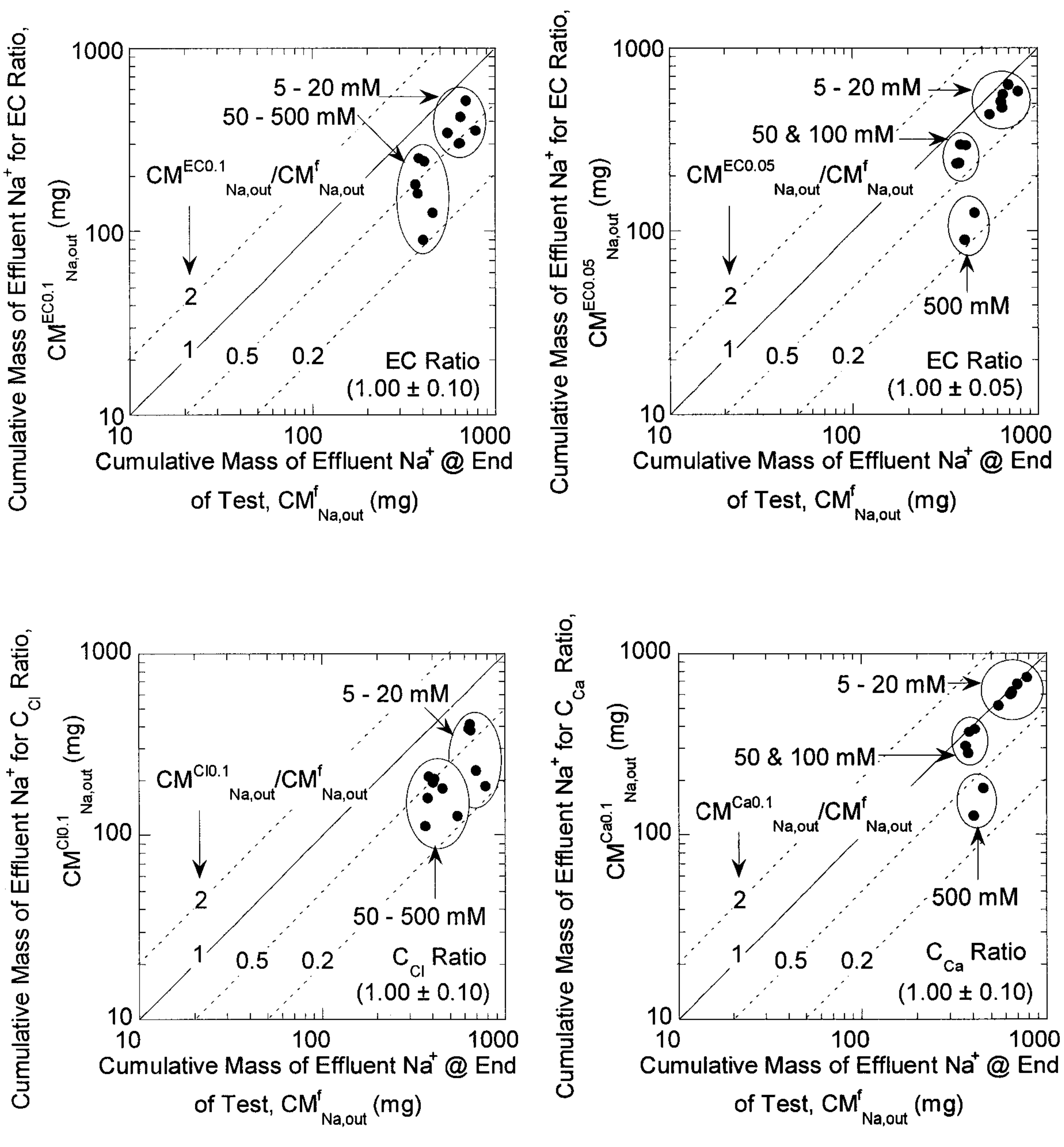

Fig. 2.22 – Cumulative mass of effluent sodium for chemical termination criteria versus final cumulative mass of effluent sodium at the end of tests (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium; ratio = effluent relative to influent).

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CHAPTER 3

CONCENTRATION DEPENDENCY OF THE PREHYDRATION EFFECT FOR A GEOSYNTHETIC CLAY LINER

ABSTRACT: Hydraulic conductivity tests are performed on both non-prehydrated and prehydrated specimens of a geosynthetic clay liner (GCL) with chemical solutions containing 5, 10, 20, 50, and 100 mM calcium chloride ($CaCl_2$). The tests are terminated only after chemical equilibrium between the influent and effluent solutions has been established, resulting in test durations ranging from 14 hrs to 500 days depending on the $CaCl_2$ concentration. The results are presented in the form of the first exposure ratio, FER, defined as the ratio of the hydraulic conductivity of a non-prehydrated specimen relative to the hydraulic conductivity of a separate but identical prehydrated specimen permeated with the same chemical solution. The results indicate that prehydration has little, if any, effect on hydraulic conductivity of the GCL for specimens permeated with solutions containing 5 to 50 mM $CaCl_2$ (i.e., $0.5 \leq FER \leq 1.1$), whereas prehydration has a more significant effect on hydraulic conductivity of the GCL for specimens permeated with the 100 mM $CaCl_2$ solution (i.e., FER ~ 3.0). The results represent the first evidence that the previously reported prehydration or first exposure effect based on fully prehydrated specimens is concentration dependent, and may be insignificant when the permeant liquid contains relatively low concentrations of inorganic solutes.

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Key Words: geosynthetic clay liners, hydraulic conductivity, prehydration, chemical equilibrium, termination criteria

3.1 INTRODUCTION

Several investigators have reported that prehydration of bentonite mixtures and/or geosynthetic clay liners (GCLs) with water prior to permeation with actual permeant liquids can have a significant effect on hydraulic conductivity (e.g., Shan and Daniel 1991, Daniel et al. 1993, Shackelford 1994, Didier and Comeaga 1997, Gleason et al. 1997, Kajita 1997, Petrov and Rowe 1997, Petrov et al. 1997a, Quaranta et al. 1997, Ruhl and Daniel 1997, Stern and Shackelford 1998, Lin and Benson 2000, Shackelford et al. 2000, Vasko et al. 2001, Ashmawy et al. 2002, Shan and Lai 2002). This effect commonly is referred to as the "first exposure effect" (Shackelford 1994, Stern and Shackelford 1998) or the "prehydration effect" (e.g., Daniel et al. 1993, Didier and Comeaga 1997, Gleason et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a, Quaranta et al. 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Vasko et al. 2001, Ashmawy et al. 2002, Shan and Lai 2002). As a result of this effect, the hydraulic conductivity of GCLs permeated directly with chemical solutions typically has been found to be significantly higher (i.e., > 10X) than the hydraulic conductivity of same GCLs permeated with the same chemical solutions after prehydration with water.

In the field, prehydration may occur naturally, such as by either precipitation or adsorption of water from adjacent soils (Daniel et al. 1993, Bonaparte et al. 1996, Petrov and Rowe 1997), or may be imposed either by spraying water (Vasko et al. 2001) or, in

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the case of GCLs, by installing commercially available prehydrated GCLs (e.g., RawMat® HDB, Rawell Water Control Systems Limited, Wirral, Merseyside, UK). For laboratory experiments, prehydration has been imposed either by spraying or soaking the specimens with water (e.g., Daniel et al. 1993, Didier and Comeaga 1997, Vasko et al. 2001), or by permeating the specimens with water (e.g., Shan and Daniel 1991, Shackelford 1994, Bonaparte et al. 1996, Gleason et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Stern and Shackelford 1998, Shackelford et al. 2000).

The degree of prehydration may be complete or partial depending on the degree of saturation upon prehydration (e.g., Daniel et al. 1993, Vasko et al. 2001). For example, Daniel et al. (1993) found that the degree of prehydration is not particularly important in terms of the hydraulic conductivity of GCLs permeated with different organic liquids (i.e., benzene, gasoline, methanol, methyl tertiary-butyl ether [MTBE], and trichloroethylene [TCE]) when the gravimetric water content of the bentonite after prehydration is 100 % or greater. However, the tests performed by Daniel et al. (1993) were relatively short-term tests (i.e., < 2 pore volumes of flow and < 2 months in duration), with no evidence of chemical equilibrium between the influent and effluent having been established. Similarly, Vasko et al. (2001) also found that the degree of prehydration had no apparent effect on the hydraulic conductivity of GCLs permeated with weak and intermediate $CaCl_2$ solutions (i.e., ≤ 25 mM). However, the hydraulic conductivity of GCL specimens permeated with strong $CaCl_2$ solutions (i.e., ≥ 100 mM $CaCl_2$) decreased from ~ 1×10^{-4} cm/s to ~ 3×10^{-7} cm/s as the prehydration water content increased from 9 % (air-dried) to 150 %, and no further increase in hydraulic conductivity occurred with further increase

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in the prehydration water content above 150 %. In contrast to the study by Daniel et al. (1993), the tests performed by Vasko et al. (2001) were continued until chemical equilibrium in terms of the electrical conductivity (EC) between the influent and effluent was established.

Gleason et al. (1997) found that the hydraulic conductivity of a prehydrated Ca-bentonite specimen (i.e., ~ 7 x 10^{-9} cm/s) permeated with a 250 mM $CaCl_2$ solution was half an order-of-magnitude lower than the hydraulic conductivity of a non-prehydrated Ca-bentonite specimen (i.e., ~ 3 x 10^{-8} cm/s) permeated with same solution. However, prehydration of compacted sand-bentonite mixtures (i.e., 5 % Na-bentonite) appeared to have little effect on the hydraulic conductivity (i.e., ~ 10^{-6} cm/s) to the same solution. This lack of agreement between the two results may have been due, in part, to the difference in specimen composition (i.e., sand-bentonite mixtures vs. pure bentonite) and/or the types of primary exchangeable cation of bentonite (i.e., Na-bentonite vs. Ca-bentonite).

Shan and Daniel (1991) and Rad et al. (1994) found that the hydraulic conductivities of prehydrated GCL specimens permeated with pure alcohols (i.e., ethanol or methanol) were similar to the hydraulic conductivities obtained from the tests performed with water. In contrast, Petrov et al. (1997b) found that the hydraulic conductivities of prehydrated GCL specimens permeated with pure ethanol were significantly higher (i.e., > 10X) than those based on permeation with water when the tests were continued until chemical equilibrium had been achieved. They also noted that the hydraulic conductivities reported by Shan and Daniel (1991) and Rad et al. (1994)

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probably would have been higher had the tests been continued until chemical equilibrium was reached.

As a result of the potential importance of prehydration in the case of the performance of bentonite-based barrier materials, such as GCLs, and the apparent inconsistencies regarding the effect of prehydration on hydraulic conductivity, the objective of this study is to evaluate the effect of prehydration on the hydraulic performance of a GCL permeated with inorganic solutions containing a wide range of $CaCl_2$ concentrations. In order to achieve this objective, hydraulic conductivity tests are performed on both non-prehydrated and prehydrated GCL specimens until chemical equilibrium between influent and effluent is established in terms of electrical conductivity (EC) and solute concentrations. In some cases, such as when low-concentration (5, 10, and 20 mM $CaCl_2$) solutions were used, establishing chemical equilibrium required in excess of 1 yr of permeation. The results of this study may have significant implications with respect to the use of prehydration to minimize alterations in the hydraulic performance of GCLs used in waste containment applications.

3.2 MATERIALS AND METHODS

3.2.1 Geosynthetic Clay Liner

The geosynthetic clay liner (GCL) used in this study consists of a layer of granular sodium bentonite sandwiched between woven and non-woven polypropylene geotextiles held together by needle-punched fibers. The GCL is ~ 6-mm thick in an air-dried condition, and the average gravimetric water content of bentonite is ~ 4 %. The physical and chemical properties and the mineralogical composition for the bentonite

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portion of the GCL are given in Table 3.1. The air-dried bentonite consists of 20 % medium sand-sized (425 – 2000 μm) and 72 % fine sand-sized granules (425 – 75 μm) based on mechanical sieve analyses, whereas approximately 90 % of particles are clay sized (< 5 μm) based on hydrometer analyses (ASTM D 421, D 422).

3.2.2 Permeant Liquids

The permeant liquids used in the experiment consist of tap water that is processed by passage through three Barnstead® ion exchange columns in series (pH ~ 5.6, electrical conductivity, EC, at 25 °C ~ 0.2 mS/m) and solutions containing 5, 10, 20, 50, and 100 mM calcium chloride ($CaCl_2$). The processed tap water classifies as Type IV deionized water (DIW) as per ASTM D 1193. Calcium chloride was chosen primarily because previous studies involving permeation of bentonite-based hydraulic barrier materials (e.g., GCLs, sand-bentonite mixtures) with $CaCl_2$ solutions have shown significant effects of the solutions on the hydraulic conductivity of these materials (Alther et al. 1985, Daniel et al. 1993, Shackelford 1994, Imamura 1996, Gleason et al. 1997, James et al. 1997, Melchior 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001, Shan and Lai 2002).

The $CaCl_2$ solutions were prepared by dissolving $CaCl_2$ (powdered, > 96 % pure, Sigma-Aldrich Co., St. Louis, MO) in the DIW. Each solution was mixed in a 20-L carboy, and pH, EC, and solute concentrations of the permeant liquids were monitored with time using a pH meter (Accumet® AB15 meter, Fisher Scientific Co., Pittsburgh, PA), an EC probe (Accumet® AB30 meter, Fisher Scientific Co., Pittsburgh, PA), an ion

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chromatograph (Dionex® 4000i IC Module, Dionex Co., Sunnyvale, CA) for chloride concentrations, and an inductively coupled plasma – atomic emission spectrometer (IRIS® Advantage/1000 ICAP Spectrometer, Thermo Jarrell Ash Co., Franklin, MA) for calcium concentrations, respectively. The measured properties of the permeant liquids are given in Table 3.2.

The EC and solute concentrations of the permeant liquids remained relatively constant, whereas the pH of each solution slowly decreased over time (e.g., from 6.3 to 5.9 for 20 mM $CaCl_2$ solution over 1.5 yrs). The decrease in pH is probably due to time-dependent dissolution of carbon dioxide (CO_2) from the atmosphere into the solutions. Nevertheless, the range of measured pH (i.e., 5.0 to 7.0) likely had little, if any, effect on the measured hydraulic conductivity values relative to the effects caused by the various concentrations of $CaCl_2$ solutions (Ruhl and Daniel 1997, Shackelford et al. 2000, Jo et al. 2001, Shan and Lai 2002).

3.2.3 Hydraulic Conductivity Tests

Both non-prehydrated and prehydrated specimens of the GCL with nominal diameters of 102 mm were permeated with each of the permeant liquids. Prehydration was achieved by permeating GCL specimens with the DIW. The specimens were permeated using the falling-head procedure with flexible-wall permeameters in accordance with ASTM D 5084 in a temperature-controlled laboratory (23.0 ± 0.5 °C) (see Fig. 3.1).

Specimens were trimmed and assembled in the permeameters using the procedures described by Daniel et al. (1997) to prevent the possibility of short-circuiting

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through the geotextiles at the edge of the GCL specimens due to loss of bentonite and pinching of the geotextiles. The specimens were exposed to a permeant liquid in the permeameter for at least 48 hrs without applying a hydraulic gradient. Backpressure was not used so that effluent liquids could be conveniently collected for pH, EC, and solute concentration measurements. Thickness of specimens was measured before, during, and after the hydraulic conductivity test using a caliper, a cathetometer, and a ruler. The measured thickness at the start of permeation was used to estimate the pore volume for each specimen, whereas the final GCL bulk void ratio was estimated based on the description given by Petrov et al. (1997b).

All the specimens were permeated at an average effective stress of ~ 23.5 kPa (~ 3.4 psi) and at an average hydraulic gradient of ~ 200. While this hydraulic gradient is significantly higher than the maximum gradient (i.e., 30) stipulated in ASTM D 5084, hydraulic gradients ranging from 50 to 600 typically are used for measuring the hydraulic conductivity of GCLs (e.g., Shan and Daniel 1991, Daniel et al. 1993, Didier and Comeaga 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Petrov and Rowe 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Shackelford et al. 2000). Results of these studies indicate that the hydraulic conductivity of GCLs is affected to a greater extent by average effective stress than by the magnitude of hydraulic gradient (Shackelford et al. 2000). All the tests were continued until chemical equilibrium (i.e., EC and solute concentrations) between influent and effluent was established (e.g., Daniel 1994, Shackelford et al. 1999, 2000).

Hydraulic conductivity tests performed on non-prehydrated specimens using solutions with relatively high $CaCl_2$ concentrations (i.e., 50 and 100 mM) were

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duplicated because the test durations were relatively short, allowing for the re-use of the permeameters. However, because the durations for the tests using solutions containing relatively low $CaCl_2$ concentrations (i.e., 5, 10, and 20 mM) required more than 4 months to establish chemical equilibrium, these tests could not be duplicated due to the limited number of permeameters available for testing.

3.3 RESULTS

3.3.1 Results with 5, 10, and 20 mM $CaCl_2$ Solutions

Results of the hydraulic conductivity tests performed using 5, 10, and 20 mM $CaCl_2$ solutions as the permeant liquids are shown in Figs. 3.2 to 3.4, respectively, for both non-prehydrated and prehydrated GCL specimens. The hydraulic conductivity values for the non-prehydrated specimens initially decreased to ~ 10^{-9} cm/s after ~ 1 month (< 5 PVF), and then began to increase after ~ 3 to 6 months (~ 5 to 10 PVF). Finally, the hydraulic conductivity values increased by ~ 7X when chemical equilibrium was established, corresponding to ~ 1.4 yrs (~ 57 PVF), ~ 1.1 yrs (~ 31 PVF), and ~ 0.4 yr (~ 21 PVF) for the non-prehydrated specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively. Even after establishment of chemical equilibrium, the effluent sodium (Na^+) concentrations still were > 5 mg/L at the end of all the non-prehydrated specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

On the other hand, the hydraulic conductivity values for all of the prehydrated specimens were ~ 2.4 x 10^{-9} cm/s at the end of prehydration (i.e., permeation with water). In addition, the effluent Na^+ concentration was > ~ 68 mg/L, even after ~ 1 yr (~ 20 PVF) of permeation with the water, whereas the effluent calcium (Ca^{2+}) and chloride (Cl^-)

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concentrations were < 1.0 mg/L at the end of prehydration period. The relatively high concentration of the effluent Na^+ even after ~ 1 yr (~ 20 PVF) of permeation with water probably were due to diffusion-limited leaching of soluble Na^+ from the interlayer region of the bentonite particles to the interparticle and interclod migration pathways resulting from the relatively slow flow rate during the prehydration period (Coats and Smith 1964, van Genuchten and Wierenga 1976, Pusch 1999). After switching the influent from water to the $CaCl_2$ solutions, the hydraulic conductivity values began to increase corresponding to < 3 months (~ 10 PVF) of permeation with the $CaCl_2$ solutions, whereas the thicknesses of specimens, which were always greater than those of non-prehydrated specimens, remained constant. When the chemical equilibrium between influent and effluent was established, the hydraulic conductivity values increased by ~ 3.5X after ~ 1.0 yr (~ 58 PVF), ~ 1.0 yr (~ 35 PVF), and ~ 0.3 yr (~ 16 PVF) for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively. At the end of the tests, the effluent Na^+ concentrations were $\geq$ 10 mg/L for all the prehydrated specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, similar to the cases for the non-prehydrated specimens.

3.3.2 Results with 50 and 100 mM $CaCl_2$ Solutions

Results of the hydraulic conductivity tests performed using 50 and 100 mM $CaCl_2$ solutions as the permeant liquids are shown in Figs. 3.5 and 3.6, respectively, for both non-prehydrated and prehydrated GCL specimens. For the duplicate non-prehydrated specimens permeated with 50 and 100 mM $CaCl_2$ solutions, the hydraulic conductivity values stabilized within 1 month (~ 10 PVF) at ~ 1.8×10^{-8} and 3.4×10^{-7} cm/s,

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respectively. Within the same time frame, the chemical equilibrium also was established for all of the specimens permeated with 50 and 100 mM $CaCl_2$ solutions. These hydraulic conductivity values at chemical equilibrium are ~ 2.3X higher for permeation with the 50 mM $CaCl_2$ solution and ~ 43X higher for permeation with the 100 mM $CaCl_2$ solution than the hydraulic conductivity values for the non-prehydrated specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

For the prehydrated specimens, the hydraulic conductivity values immediately began to increase when the influent was switched from water to the $CaCl_2$ solutions. Finally, the hydraulic conductivity values increased by ~ 14X and ~ 49X when chemical equilibrium was established, corresponding to ~ 24 days (~ 11 PVF)) and ~ 10 days of permeation (~ 10 PVF) for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions, respectively. The thickness of both prehydrated specimens permeated with 50 and 100 mM $CaCl_2$ solutions eventually decreased by ~ 15 % relative to the thickness at the end of prehydration with water, but always higher than that of non-prehydrated specimens permeated with same solutions. The effluent Na^+ concentrations were ~ 5 mg/L at the end of all the tests (i.e., both non-prehydrated and prehydrated) performed using 50 and 100 mM $CaCl_2$ solutions as the permeant liquids.

3.3.3 Summary of Test Results

All the test results are summarized in Table 3.3. Also included in Table 3.3 are the values for three hydraulic conductivity ratios as defined by Stern and Shackelford (1998). With respect to the schematic illustration in Fig. 3.7, the three ratios are: (1) the hydraulic conductivity ratio, KR1 (= k_P/k_W), which pertains to the effect of permeation with the

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chemical solution after initial permeation of the same specimen with water; (2) the hydraulic conductivity ratio, KR2 (= k_{NP}/k_w), which pertains to the effect of initial permeation with the chemical solution relative to initial permeation with water on two separate but identical test specimens; and (3) the first exposure ratio, FER (= KR2/KR1), which represents the ratio of the hydraulic conductivity of the specimen permeated initially with the chemical solution to the hydraulic conductivity of a separate but identical specimen permeated with the same chemical solution after initial permeation with water.

The three hydraulic conductivity values (i.e., k_w, k_P, and k_{NP}) as summarized in Table 3.3 are shown in Figs. 3.8 and 3.9 as a function of influent $CaCl_2$ concentration. As shown in Fig. 3.8, the hydraulic conductivity values based on permeation with water (i.e., k_w) for the five independent specimens are all ~ 2.4 x 10^{-9} cm/s and in close agreement (i.e., $\leq$ 5 % difference). Daniel et al. (1997) also reported similar results and reproducibility based on round-robin tests (i.e., 18 different laboratories) performed with water for a single type and make of GCL. As shown in Fig. 3.9, all of the hydraulic conductivity values based on permeation with 5, 10, and 20 mM $CaCl_2$ solutions for the prehydrated specimens (i.e., k_P) are similar (i.e., ~ 7.6 x 10^{-9} cm/s), regardless of influent $CaCl_2$ concentration. In contrast, for the prehydrated specimens permeated with 50 and 100 mM $CaCl_2$ solutions, an increase of influent $CaCl_2$ concentration results in a relatively significant change in the hydraulic conductivity at chemical equilibrium. In fact, the hydraulic conductivity values at chemical equilibrium are ~ 3.5 x 10^{-8} and ~ 1.1 x 10^{-7} cm/s for the prehydrated specimens permeated with 50 and 100 mM $CaCl_2$ solutions, respectively.

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Similarly, all of the hydraulic conductivity values based on permeation with 5, 10, and 20 mM $CaCl_2$ solutions for the non-prehydrated specimens (i.e., k_{NP}) are similar to ~ 7.8 x 10^{-9} cm/s, regardless of influent $CaCl_2$ concentration (see Fig. 3.9). However, the hydraulic conductivity values at chemical equilibrium for the non-prehydrated specimens permeated with 50 and 100 mM $CaCl_2$ solutions are ~ 2.3X and ~ 43X higher, respectively, than the hydraulic conductivity of ~ 7.8 x 10^{-9} cm/s for the non-prehydrated specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

3.4 DISCUSSION

3.4.1 Prehydration Effect on Hydraulic Conductivity

The previously defined three hydraulic conductivity ratios (i.e., KR1, KR2, and FER) as summarized in Table 3.3 are shown in Figs. 3.10 and 3.11 as a function of $CaCl_2$ concentration of the permeant liquid. For both non-prehydrated and prehydrated specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, the KR1 and KR2 values range from 2.5 to 3.9, and the resulting FER is within 10 % of unity (i.e., 1.0 ± 0.1). In other words, the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions are ~ 3.5X more permeable than those permeated with water regardless of prehydration. Thus, prehydration has little, if any, effect on hydraulic conductivity at chemical equilibrium for solutions containing 5, 10, and 20 mM $CaCl_2$.

On the other hand, the KR1 and KR2 values are ~ 14 and ~ 7.1, respectively, for the specimens permeated with the 50 mM $CaCl_2$ solution, and the resulting FER is ~ 0.5. Thus, prehydration has no distinctive effect on hydraulic conductivity based on chemical equilibrium for the 50 mM $CaCl_2$ solution, although the hydraulic conductivity values are

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~ 10X higher than those based on permeation with water. For the specimens permeated with the 100 mM $CaCl_2$ solution, the KR1 and KR2 values are ~ 49 and ~ 148, respectively, and the resulting FER is ~ 3.0. As a result, the hydraulic conductivity for the prehydrated specimen permeated with the 100 mM $CaCl_2$ solution are ~ 50X higher than that based on permeation with water, whereas the hydraulic conductivity for the non-prehydrated specimen permeated directly with the same solution are ~ 150X higher than that based on permeation with water. Therefore, prehydration has relatively significant effect on hydraulic conductivity at chemical equilibrium for the tests performed with the 100 mM $CaCl_2$ solution.

In general, prehydration has little, if any, effect on hydraulic conductivity of the GCL specimens tested in this study for solutions containing $\leq$ 50 mM $CaCl_2$ concentration (i.e., $0.5 \leq$ FER ≤ 1.1), provided the tests are continued until chemical equilibrium is established. Vasko et al. (2001) report similar results based on their tests in which a GCL was permeated with $\leq$ 25 mM $CaCl_2$ solutions, even though prehydration was imposed without confinement in the tests by Vasko et al. (2001). For the tests performed using the 100 mM $CaCl_2$ solution as the permeant liquid in this study, prehydration had a relatively significant effect on hydraulic conductivity (i.e., FER ~ 3.0). However, based on the results by Vasko et al. (2001) for the tests performed with a 100 mM $CaCl_2$ solution on both the non-prehydrated specimen and the specimen prehydrated with a confining stress of ~ 8 kPa, the resulting FER was ~ 230, which is ~ 77X higher than the FER from this study. This significant discrepancy in the FER between the two studies based on permeation with 100 mM $CaCl_2$ solutions is possibly due to the differences of test condition applied in between the study by Vasko et al. (2001) and this

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study, such as the confinement method during prehydration (i.e., uniaxial vs. triaxial), the average confining stress applied during prehydration (i.e., ~ 8 kPa vs. ~ 23.5 kPa), and the average effective stress applied during permeation (i.e., ~ 20 kPa vs. ~ 23.5 kPa).

3.4.2 Prehydration Effect on Equilibrium Time

As shown in Fig. 3.12, for the tests performed with the 5 mM $CaCl_2$ solution, the time required to achieve chemical equilibrium between influent and effluent (i.e., EC_{out}/EC_{in} and $C_{out}/C_{in} = 1.00 \pm 0.10$) for the non-prehydrated specimen was ~ 150 days longer than that required for the prehydrated specimen. Similarly, the non-prehydrated specimen required ~ 40 days longer than the prehydrated specimen to reach chemical equilibrium for the tests performed with 10 and 20 mM $CaCl_2$ solutions. For the tests with 50 and 100 mM $CaCl_2$ solutions, the prehydrated specimens required significantly longer time to establish chemical equilibrium than the non-prehydrated specimens, because chemical equilibrium for the non-prehydrated specimens was achieved within relatively short test durations (i.e., ~ 15 days and 1 day, respectively). Nonetheless, less time is required to achieve chemical equilibrium with increasing $CaCl_2$ concentration of the permeant liquid for both prehydrated and non-prehydrated specimens.

Similarly, as shown in Fig. 3.11, the pore volumes of flow (PVF) required to achieve chemical equilibrium decreases with increasing $CaCl_2$ concentration of the permeant liquid. For example, both prehydrated and non-prehydrated specimens required ~ 60, ~ 33, and ~ 19 PVF in order to establish chemical equilibrium for the tests performed with 5, 10, and 20 mM $CaCl_2$ solutions, respectively. In fact, the required PVF for the prehydrated specimens are relatively close to those for the non-prehydrated

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specimens (i.e., < 30 % difference). On the other hand, the prehydrated specimens required slightly greater PVF by a factor of 2 to 4 than the non-prehydrated specimens for permeation with 50 and 100 mM $CaCl_2$ solutions. This difference results from the need to displace the initial pore liquid (i.e., water) with the $CaCl_2$ solution for the prehydrated specimens and the subsequent chemical interactions that occur between the solution and the bentonite in the specimens.

3.4.3 Prehydration Effect on Final Properties of Specimens

The final bentonite gravimetric water content (w_b), bentonite void ratio (e_b), and GCL bulk void ratio (e_B) of both prehydrated and non-prehydrated GCL specimens after permeation are shown in Figs. 8.14 and 8.15. As the $CaCl_2$ concentration in the permeant liquid increases from 5 mM to 100 mM, w_b decreases from ~ 122 % to 102 % for the prehydrated specimen (i.e., $w_{b,P}$) and from ~ 97 % to 78 % for the non-prehydrated specimen (i.e., $w_{b,NP}$), and e_b decreases from ~ 3.3 to 2.8 for the prehydrated specimen (i.e., $e_{b,P}$) and from ~ 2.7 to 2.1 for the non-prehydrated specimen (i.e., $e_{b,NP}$). Similarly, e_B decreases from ~ 2.8 to 2.4 for the prehydrated specimen (i.e., $e_{B,P}$) and from ~ 2.3 to 1.8 for the non-prehydrated specimen (i.e., $e_{B,NP}$) for the same range in $CaCl_2$ concentrations. However, the overall trend in w_b, e_b, and e_B as a function of influent $CaCl_2$ concentration of the permeant liquid is similar for both prehydrated and non-prehydrated specimens, such that the lower the influent $CaCl_2$ concentration, the greater the change in w_b, e_b, and e_B. In general, the values for w_b, e_b, and e_B of the prehydrated specimens (i.e., $w_{b,P}$, $e_{b,P}$, and $e_{B,P}$) are always greater by 22 % to 34 % than those of the non-prehydrated specimens (i.e., $w_{b,NP}$, $e_{b,NP}$, and $e_{B,NP}$). These relative differences are

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consistent with the measured thickness of specimens during permeation with $CaCl_2$ solutions, i.e., greater thickness for prehydrated specimens than non-prehydrated specimens (see Figs. 3.2 to 3.6). Vasko et al (2001) reported similar results for final bentonite void ratios of non-prehydrated and prehydrated GCL specimens.

The hydraulic conductivity values are correlated with the GCL bulk void ratios (e_B) in Fig. 3.16. For the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, all of the hydraulic conductivity values are approximately 8 x 10^{-9} cm/s, regardless of the influent $CaCl_2$ concentration or the prehydration condition, whereas e_B decreases by ~ 6.0 % for the prehydrated specimen (i.e., $e_{B,P}$) and ~ 14 % for the non-prehydrated specimen (i.e., $e_{B,NP}$) as the influent $CaCl_2$ concentration increases from 5 mM to 20 mM. However, e_B for prehydrated specimens (i.e., $e_{B,P}$) is always higher than e_B for non-prehydrated specimens (i.e., $e_{B,NP}$) at a given hydraulic conductivity value, indicating a larger void space for the prehydrated specimens with a thicker adsorbed layer resulting from initial hydration with water (e.g., Shackelford et al. 2000, Vasko et al. 2001). In contrast, for both prehydrated and non-prehydrated specimens, the greatest increase in hydraulic conductivity (i.e., 3.5X and 21X, respectively) and the lowest decrease in e_B (i.e., 1.2 % and 2.0 %, respectively) occur as the influent $CaCl_2$ concentration increases from 50 mM to 100 mM.

3.5 SUMMARY AND CONCLUSIONS

The influence of prehydration on the hydraulic conductivity of GCL specimens is evaluated in this study. The hydraulic conductivity tests are performed on both non-prehydrated and prehydrated GCL specimens until chemical equilibrium between influent

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and effluent in terms of electrical conductivity (EC) and solute concentrations is established. The results are presented in the form of three hydraulic conductivity ratios to evaluate quantitatively the first exposure or prehydration effect. The hydraulic conductivity ratio, KR1, pertains to the effect of permeation with the chemical solution after initial permeation of the same specimen with water. The hydraulic conductivity ratio, KR2, pertains to the effect of initial permeation with the chemical solution relative to initial permeation with water on two separate but identical test specimens. The first exposure ratio, FER, represents the ratio of the hydraulic conductivity of the specimen permeated initially with the chemical solution to the hydraulic conductivity of the specimen permeated with the chemical solution after initial permeation with water.

For the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, the KR1 and KR2 values are between 2.5 and 3.9, and the resulting FER is close to unity (i.e., 1.0 ± 0.1). On the other hand, the KR1 and KR2 values are ~ 14 and 7.1, respectively, for the specimens permeated with the 50 mM $CaCl_2$ solution, and the resulting FER is ~ 0.5. For the specimens permeated with the 100 mM $CaCl_2$ solution, the KR1 and KR2 values are ~ 49 and 148, respectively, and the resulting FER is ~ 3.0. Therefore, prehydration has little, if any, apparent effect on hydraulic conductivity for solutions containing 5 to 50 mM $CaCl_2$, i.e., provided the tests are continued until chemical equilibrium is established. In contrast, prehydration has relatively significant effect on the hydraulic conductivity of the GCL when permeated with the 100 mM $CaCl_2$ solution.

In terms of equilibrium time, less elapsed time and pore volumes of flow (PVF) are required to establish chemical equilibrium with increase in $CaCl_2$ concentration of the permeant liquid for both prehydrated and non-prehydrated specimens. For the tests

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performed with 5, 10, and 20 mM $CaCl_2$ solutions, more elapsed time is required for the non-prehydrated specimens than required for the prehydrated specimens, while the required PVF for prehydrated specimens are relatively close to those for the non-prehydrated specimens. Also, establishment of chemical equilibrium required less elapsed time and PVF for the non-prehydrated specimens than required for the prehydrated specimens when permeated with the 50 and 100 mM $CaCl_2$ solutions. On the other hand, the GCL bulk void ratio for the prehydrated specimens is always greater than that that for the non-prehydrated specimens regardless of the influent $CaCl_2$ concentration. However, the overall trend in the GCL bulk void ratio as a function of influent $CaCl_2$ concentration is similar for both prehydrated and non-prehydrated specimens, such that the lower the influent $CaCl_2$ concentration, the greater the change in the GCL bulk void ratio.

ACKNOWLEDGEMENT

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Table 3.1 – Properties of bentonite in a geosynthetic clay liner.

Property	Standard	No. of Trials	Average Value [Max, Min]
Specific Gravity	ASTM D 854[a]	3	2.74 [2.74, 2.74]
Soil Classification:	ASTM D 2487		
Sieve Analysis (Air-Dried)		3	SP
Hydrometer		7	CH
Atterberg Limits (%):	ASTM D 4318	1	
Liquid Limit, LL			430
Plasticity Index, PI			393
Swell Index (mL/2 g)	ASTM D 5890	17	27.5 [29.5, 25.5]
Bentonite Mass (kg/m^2)	ASTM D 5993	5	5.1 [5.3, 4.7]
Principal Minerals (%):	b	3	
Montmorillonite			77.2 [79.6, 74.0]
Cristobalite			10.3 [15.0, 6.8]
Plagioclase Feldspar			5.1 [7.4, 4.0]
Quartz			3.4 [4.0, 3.0]
Others			4.0 [6.0, 2.9]
Cation Exchange Capacity, CEC (meq/100 g)	c	3	63.9 [73.5, 53.1]
Exchangeable Metals (meq/100 g):	c	3	
Ca^{2+}			11.5 [15.7, 6.9]
Mg^{2+}			3.7 [4.8, 2.2]
Na^+			45.8 [56.1, 40.0]
K^+			0.7 [0.8, 0.6]
Sum			61.7 [72.7, 51.2]
Soluble Metals (mg/kg):	c, d	3	
Ca^{2+}			218 [241, 174]
Mg^{2+}			24 [29, 14]
Na^+			3365 [3766, 3451]
K^+			48 [52, 43]
Saturated Soil Paste:	c	3	
pH			8.9 [8.9, 8.8]
EC[e] (mS/m)			305 [315, 290]

[a] Using a magnetic stirring device for de-airing.

[b] Based on X-ray diffraction (XRD) analyses performed by Mineralogy Inc., Tulsa, OK and GeoServices Inc., Argyle, TX.

[c] Based on procedures described in Shackelford and Redmond (1995).

[d] Measured from a 1 g:20 mL clay-water extract.

[e] Electrical conductivity at 25 °C.

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Table 3.2 – Properties of permeant liquids.

Permeant Liquid	Salt Concentration (mM)		Measured Solute Concentrations (mg/L)		Measured pH [No. of Trials]	Measured EC[c] (mS/m) [No. of Trials]
	Target	Measured [No. of Trials]	Calcium (Ca^{2+}) [No. of Trials]	Chloride (Cl^-) [No. of Trials]		
DIW[a]	0	< 0.0005[b] [10]	< 0.02[b] [10]	< 0.04[b] [10]	5.6 ± 0.5 [19]	0.21 ± 0.11 [19]
$CaCl_2$ (Sigma Co., 96 %)	5	5.1 ± 0.2 [14]	216 ± 10 [14]	377 ± 38 [14]	5.7 ± 0.5 [25]	123 ± 2.1 [25]
	10	10.1 ± 0.2 [13]	436 ± 30 [13]	756 ± 65 [13]	6.0 ± 0.3 [19]	234 ± 2.6 [19]
	20	20.1 ± 0.6 [13]	872 ± 77 [13]	1457 ± 110 [13]	6.1 ± 0.3 [17]	445 ± 7.3 [17]
	50	50.7 ± 1.4 [9]	2055 ± 63 [9]	3548 ± 69 [9]	5.7 ± 0.1 [18]	1041 ± 26 [18]
	100	100 ± 2.6 [6]	4072 ± 126 [6]	7030 ± 95 [6]	5.8 ± 0.1 [13]	1958 ± 48 [13]

[a] Deionized water.

[b] Method detection limit (MDL).

[c] Electrical conductivity at 25 °C.

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Table 3.3 – Summary of test results to evaluate prehydration effect.[a]

Permeant Liquid	Test No.	Pre-hydration	Permeation w/Water[b]		Permeation w/$CaCl_2$ Solution[c]		Hydraulic Conductivity Ratios		
			PVF_w [t_w (days)]	k_w (cm/s)	$PVF_{NP\ or\ P}$ [$t_{NP\ or\ P}$ (days)]	$k_{NP\ or\ P}$ (cm/s)	KR1 (k_P/k_w)	KR2 (k_{NP}/k_w)	FER (k_{NP}/k_P or KR2/KR1)
5 mM $CaCl_2$	1	No	26 [379]	2.4×10^{-9}	57 [502]	8.6×10^{-9}	3.3	3.6	1.1
	2	Yes			58 [358]	7.8×10^{-9}			
10 mM $CaCl_2$	3	No	21 [379]	2.5×10^{-9}	30 [397]	6.7×10^{-9}	2.5	2.7	1.1
	4	Yes			35 [360]	6.2×10^{-9}			
20 mM $CaCl_2$	5	No	17 [379]	2.2×10^{-9}	21 [164]	8.1×10^{-9}	3.9	3.6	0.9
	6	Yes			16 [120]	8.8×10^{-9}			
50 mM $CaCl_2$	7	No	24 [439]	2.5×10^{-9}	9.3 [16]	1.6×10^{-8}	14	7.1[d]	0.5[d]
	8	No			8.9 [15]	1.9×10^{-8}			
	9	Yes			11 [24]	3.5×10^{-8}			
100 mM $CaCl_2$	10	No	26 [406]	2.3×10^{-9}	6.8 [0.80]	3.0×10^{-7}	49	148[d]	3.0[d]
	11	No			6.0 [0.59]	3.7×10^{-7}			
	12	Yes			10 [10]	1.1×10^{-7}			

[a] k = hydraulic conductivity; PVF = pore volumes of flow; t = elapsed time.

[b] Values at the end of prehydration with water.

[c] Values at chemical equilibrium in terms of both electrical conductivity (EC) and solute concentrations (i.e., $EC_{out}/EC_{in} = 1.00 \pm 0.10$ and $C_{out}/C_{in} = 1.00 \pm 0.10$); NP = non-prehydrated; P = prehydrated specimen.

[d] Based on average k_{NP} values.

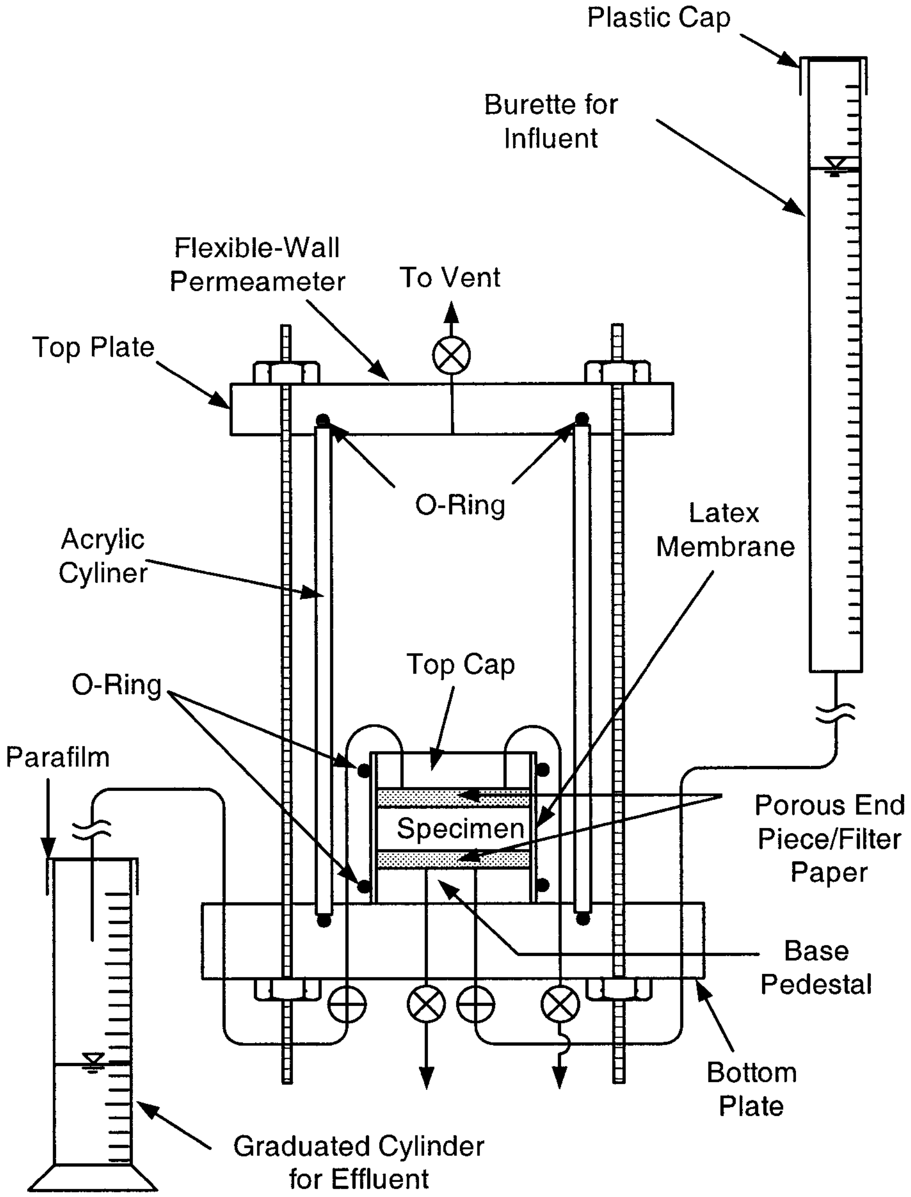

Fig. 3.1 – A schematic diagram of the hydraulic conductivity test setup.

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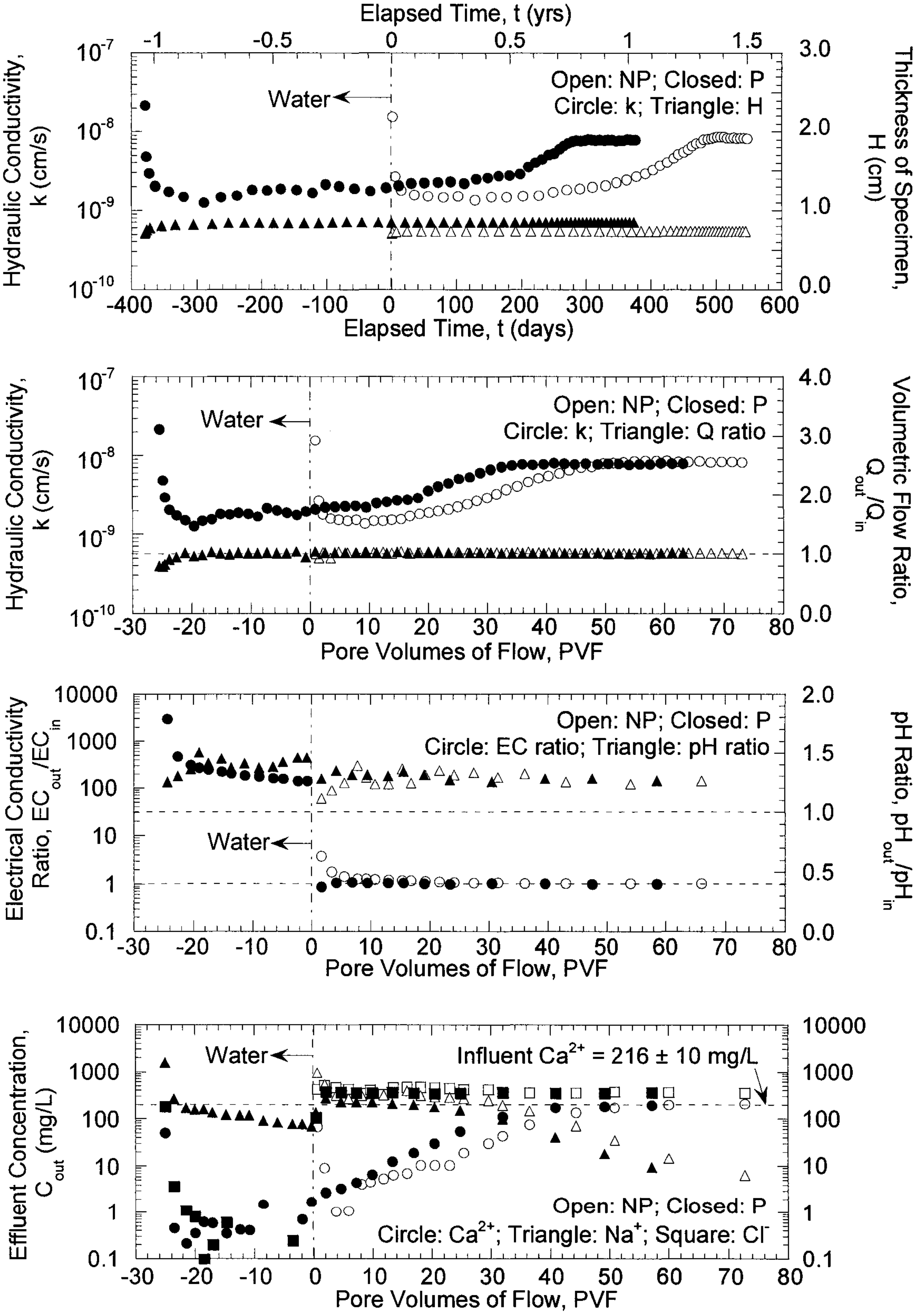

Fig. 3.2 – Test results for both non-prehydrated (NP) and prehydrated (P) specimens permeated with 5 mM $CaCl_2$ solution.

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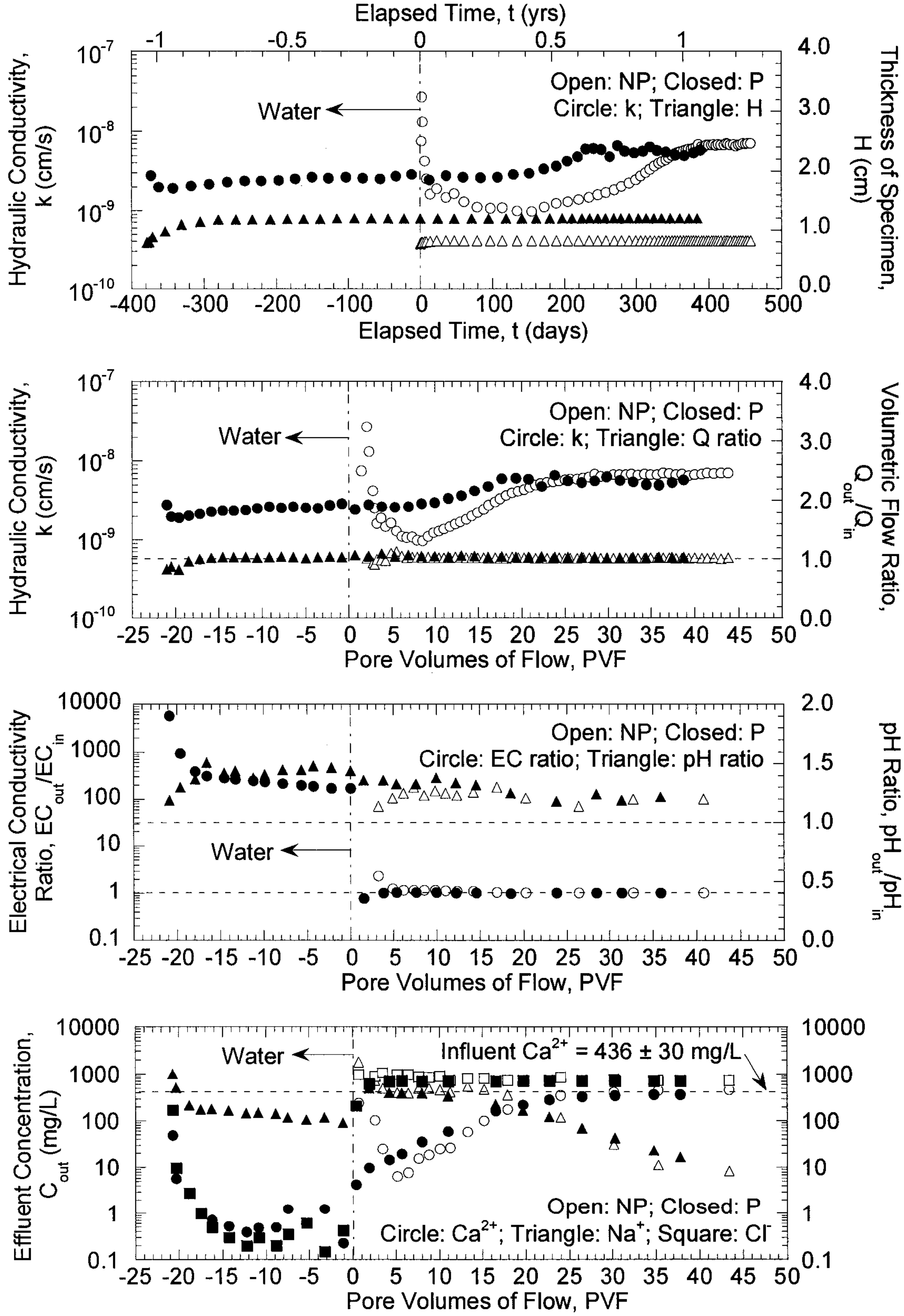

Fig. 3.3 – Test results for both non-prehydrated (NP) and prehydrated (P) specimens permeated with 10 mM $CaCl_2$ solution.

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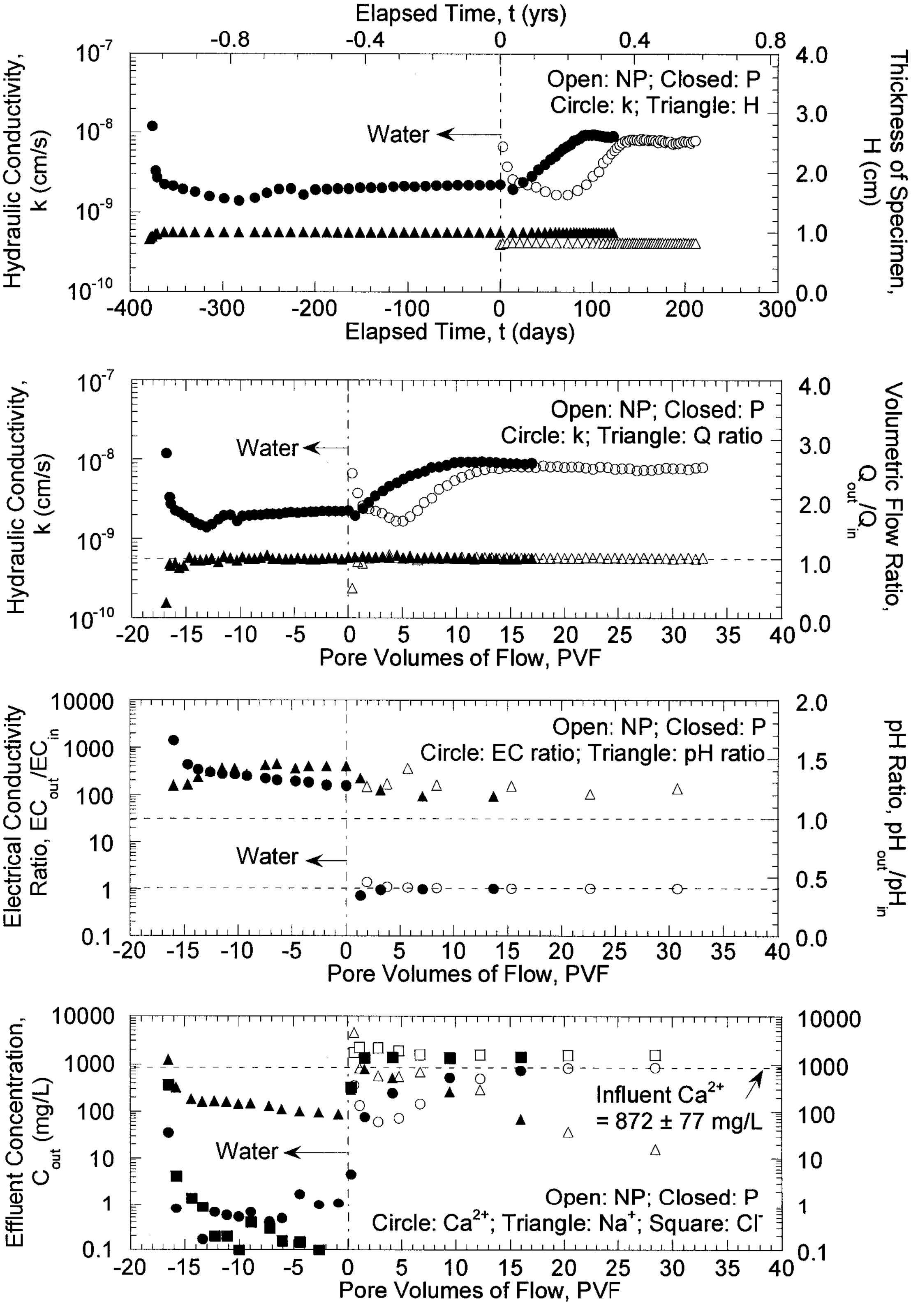

Fig. 3.4 – Test results for both non-prehydrated (NP) and prehydrated (P) specimens permeated with 20 mM $CaCl_2$ solution.

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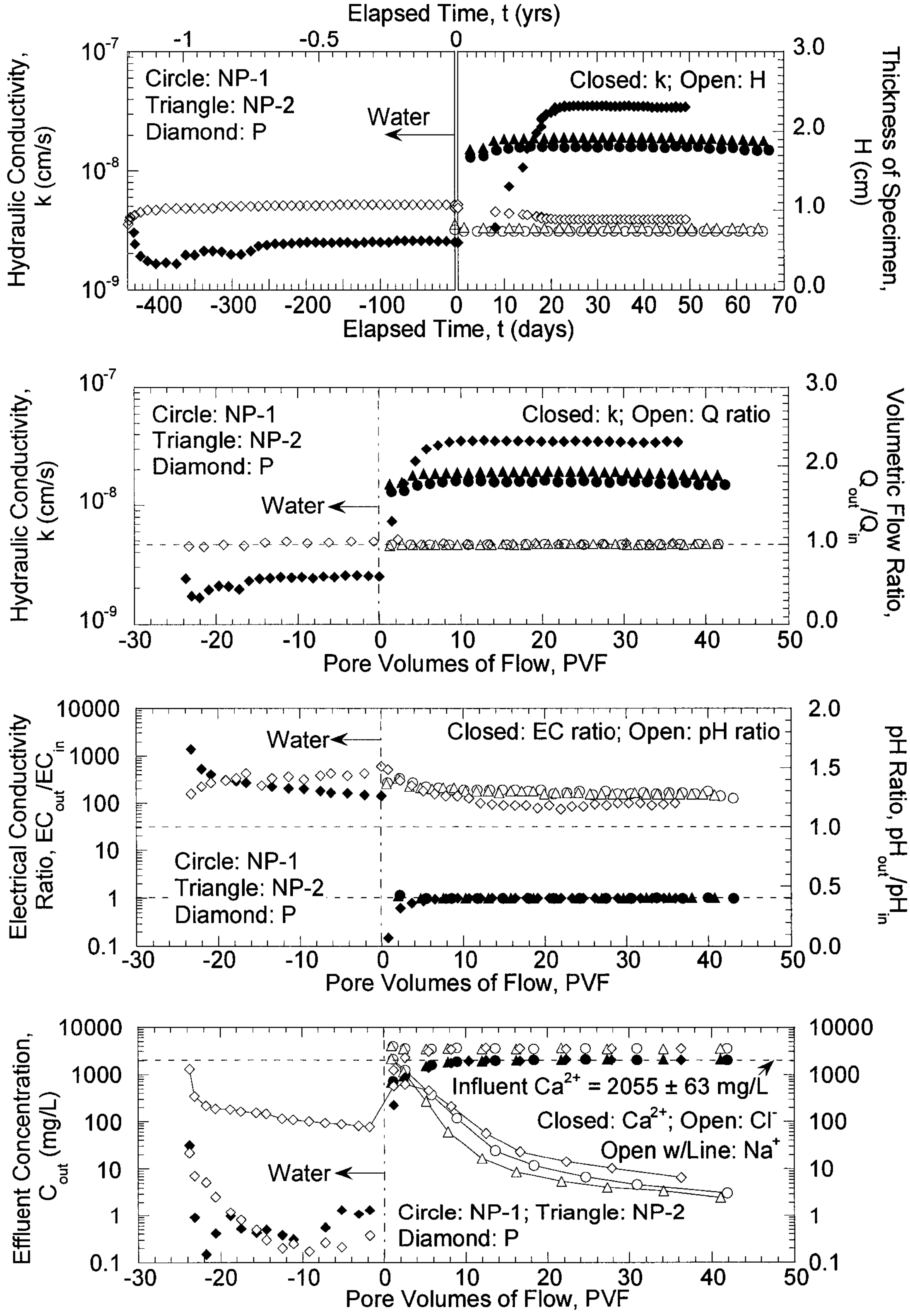

Fig. 3.5 – Test results for both duplicate non-prehydrated (NP) and single prehydrated (P) specimens permeated with 50 mM $CaCl_2$ solution.

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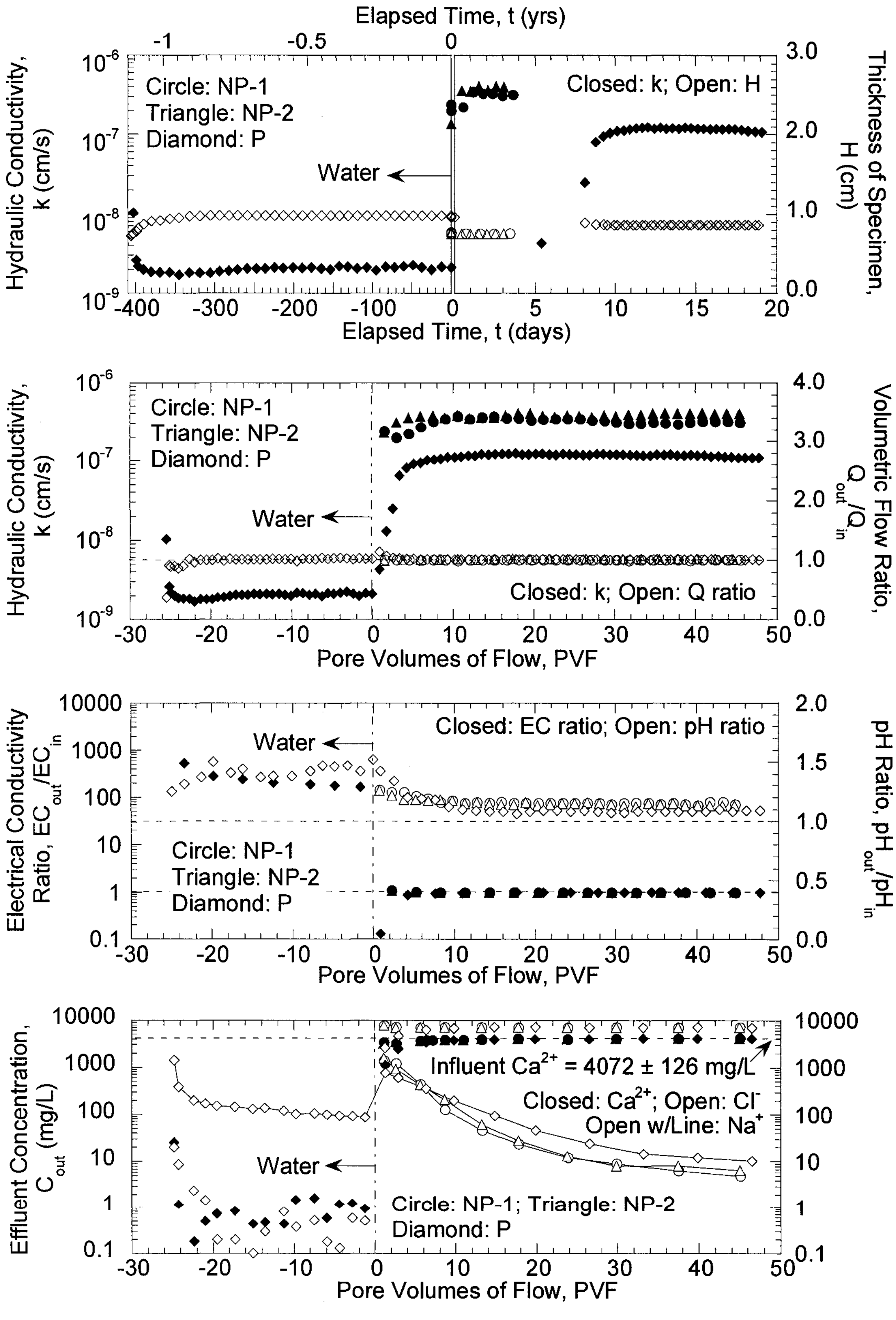

Fig. 3.6 – Test results for both duplicate non-prehydrated (NP) and single prehydrated (P) specimens permeated with 100 mM $CaCl_2$ solution.

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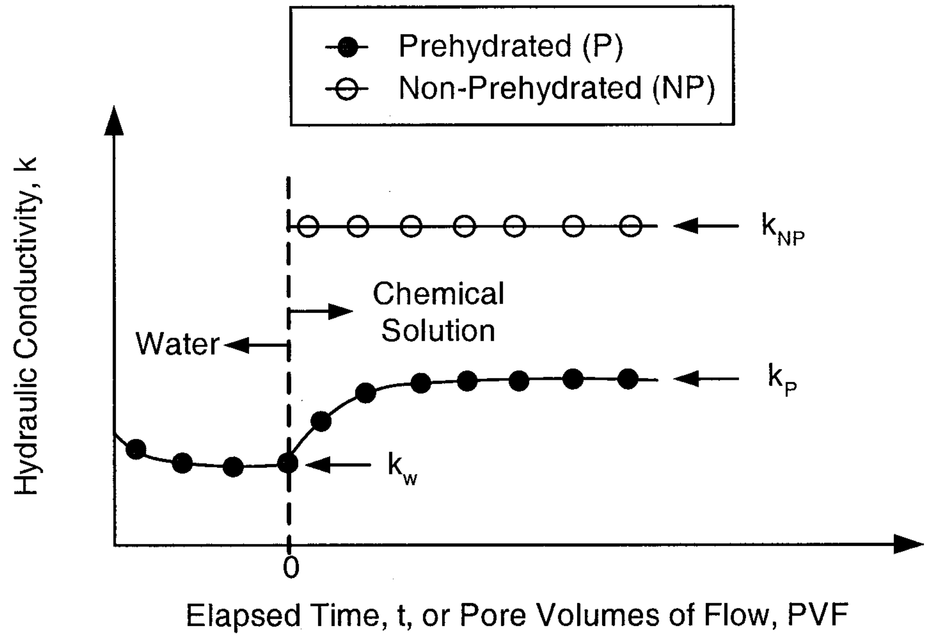

Fig. 3.7 – Schematic illustration of typical results obtained from hydraulic conductivity tests on both prehydrated and non-prehydrated specimens permeated with chemical solutions.

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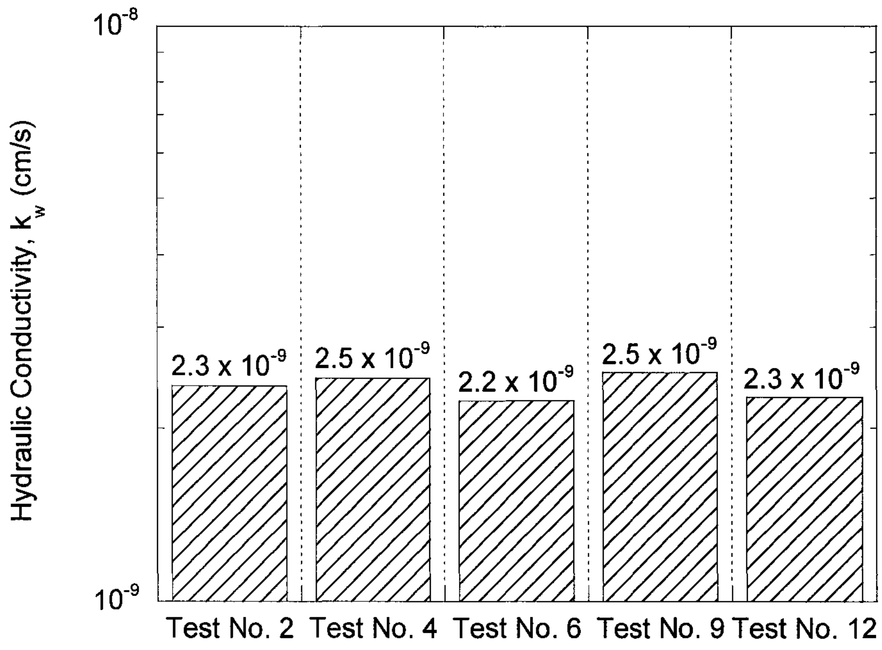

Fig. 3.8 – Hydraulic conductivity based on permeation with water prior to introducing $CaCl_2$ solutions for prehydrated specimens.

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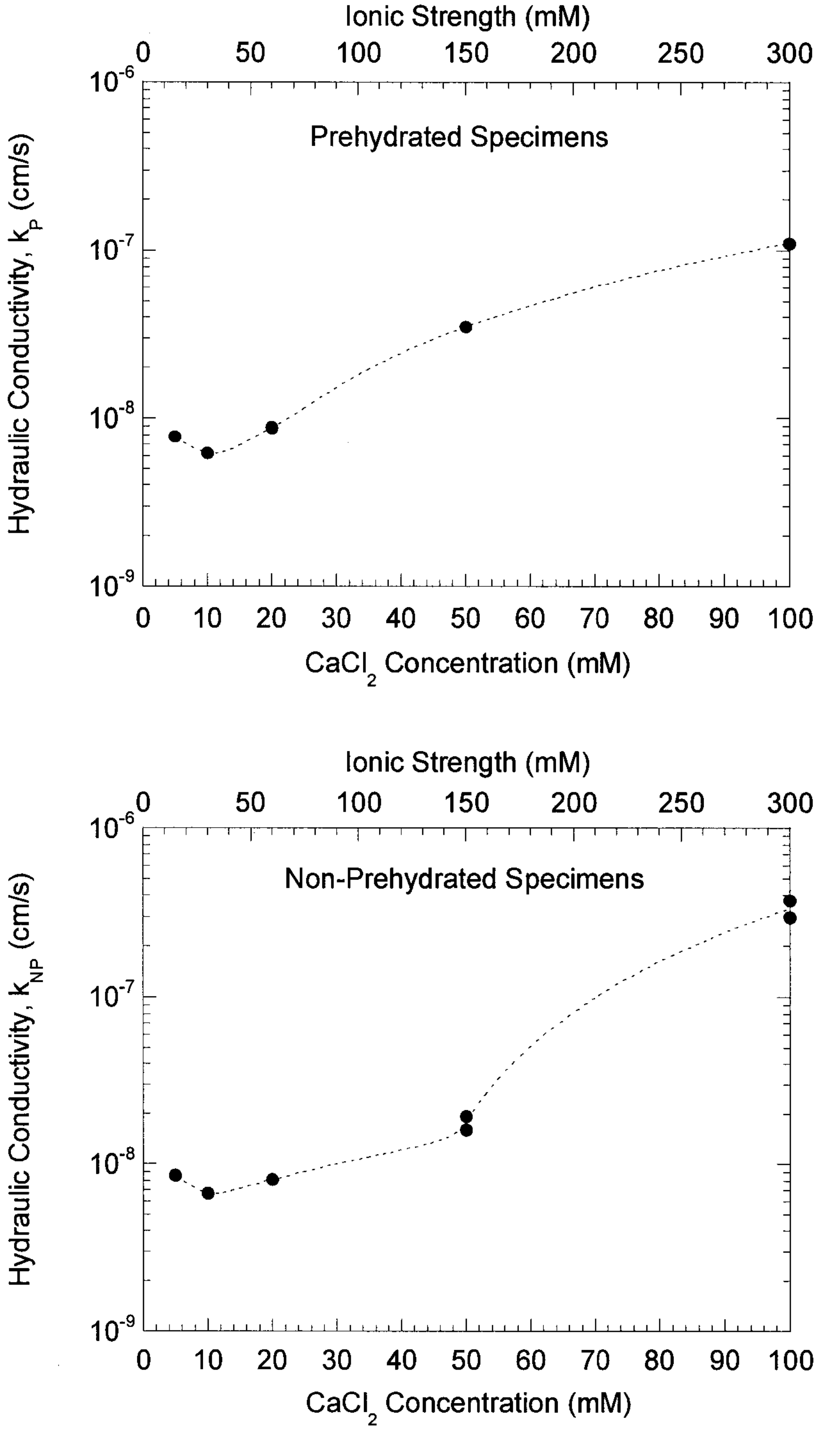

Fig. 3.9 – Hydraulic conductivity for both prehydrated (k_P) and non-prehydrated (k_{NP}) specimens as a function of influent $CaCl_2$ concentration.

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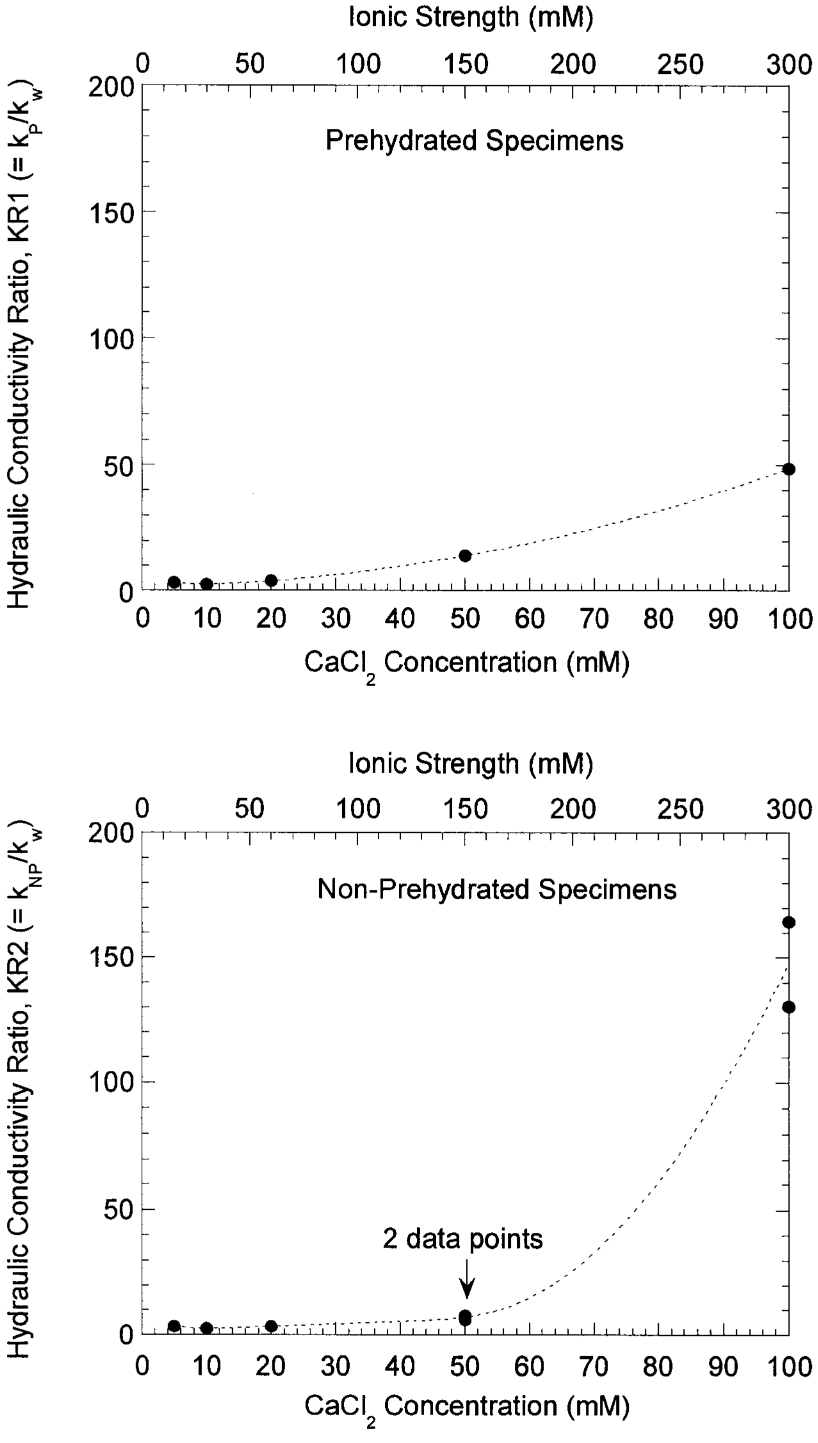

Fig. 3.10 – Hydraulic conductivity ratios relative to that based on permeation with water for both prehydrated (KR1) and non-prehydrated (KR2) specimens as a function of influent $CaCl_2$ concentration.

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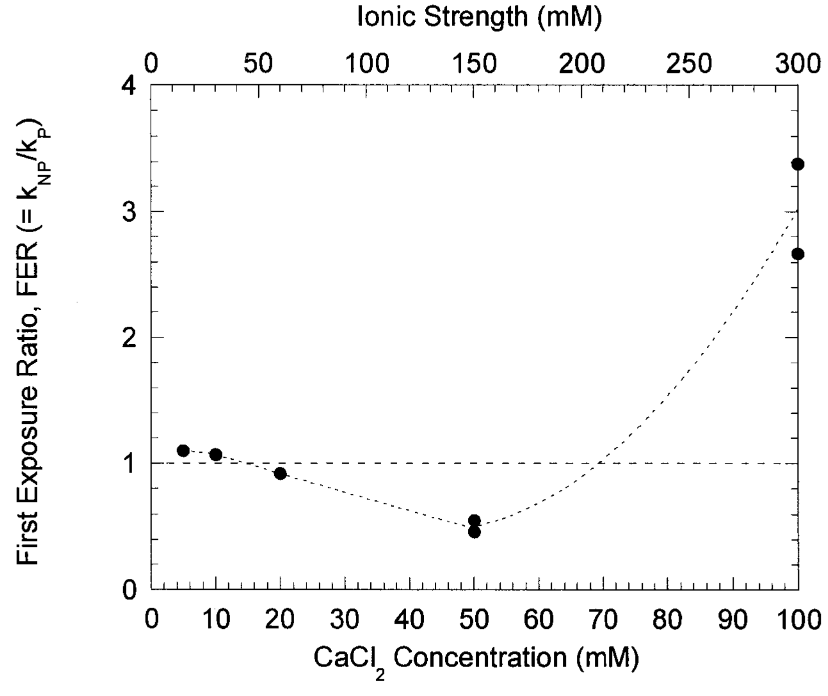

Fig. 3.11 – First exposure ratio (FER), i.e., ratio of hydraulic conductivity for non-prehydrated specimen (k_{NP}) to that for prehydrated specimen (k_P) as a function of influent $CaCl_2$ concentration.

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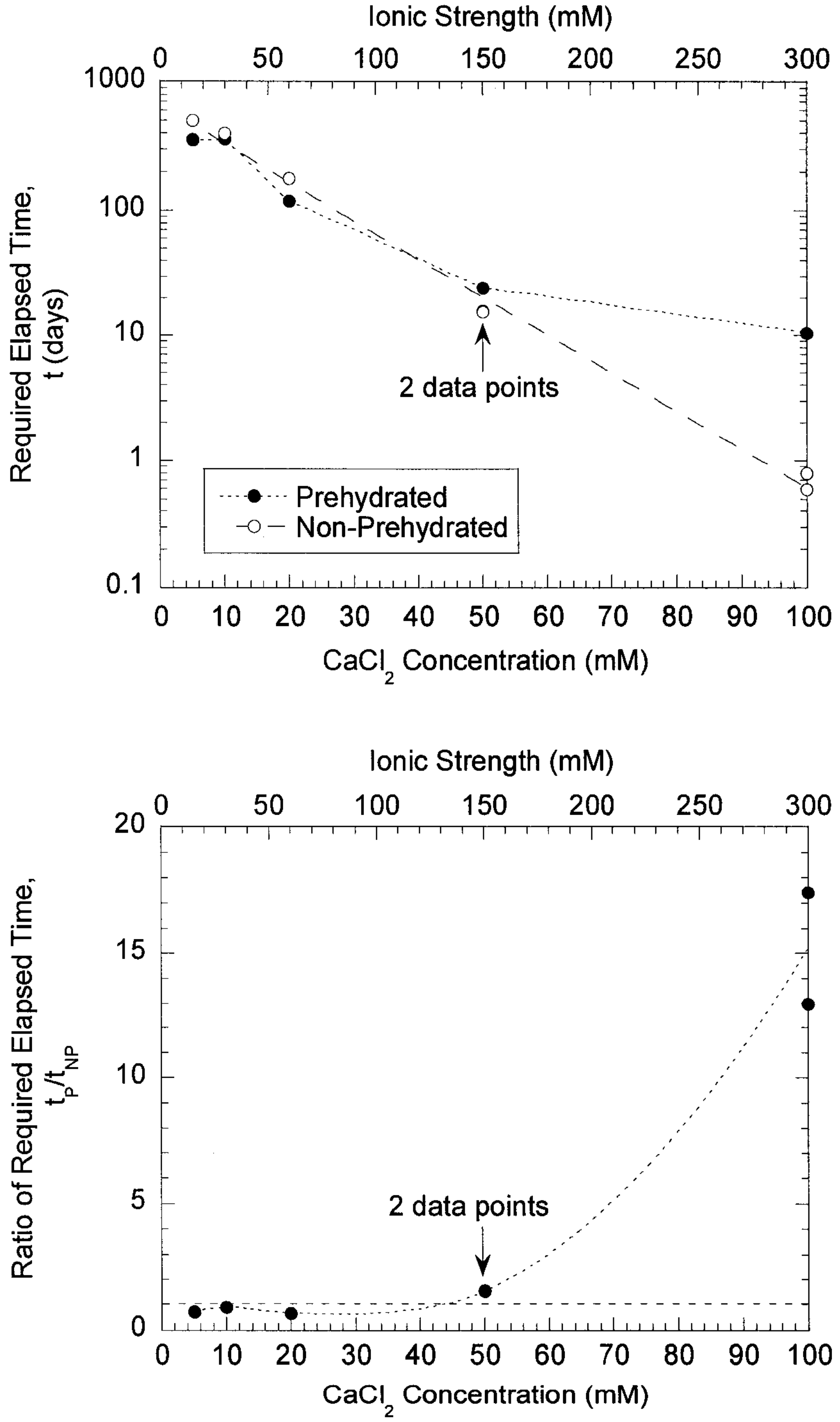

Fig. 3.12 – Elapsed time required to achieve chemical equilibrium for both prehydrated (t_P) and non-prehydrated (t_{NP}) specimens as a function of influent $CaCl_2$ concentration.

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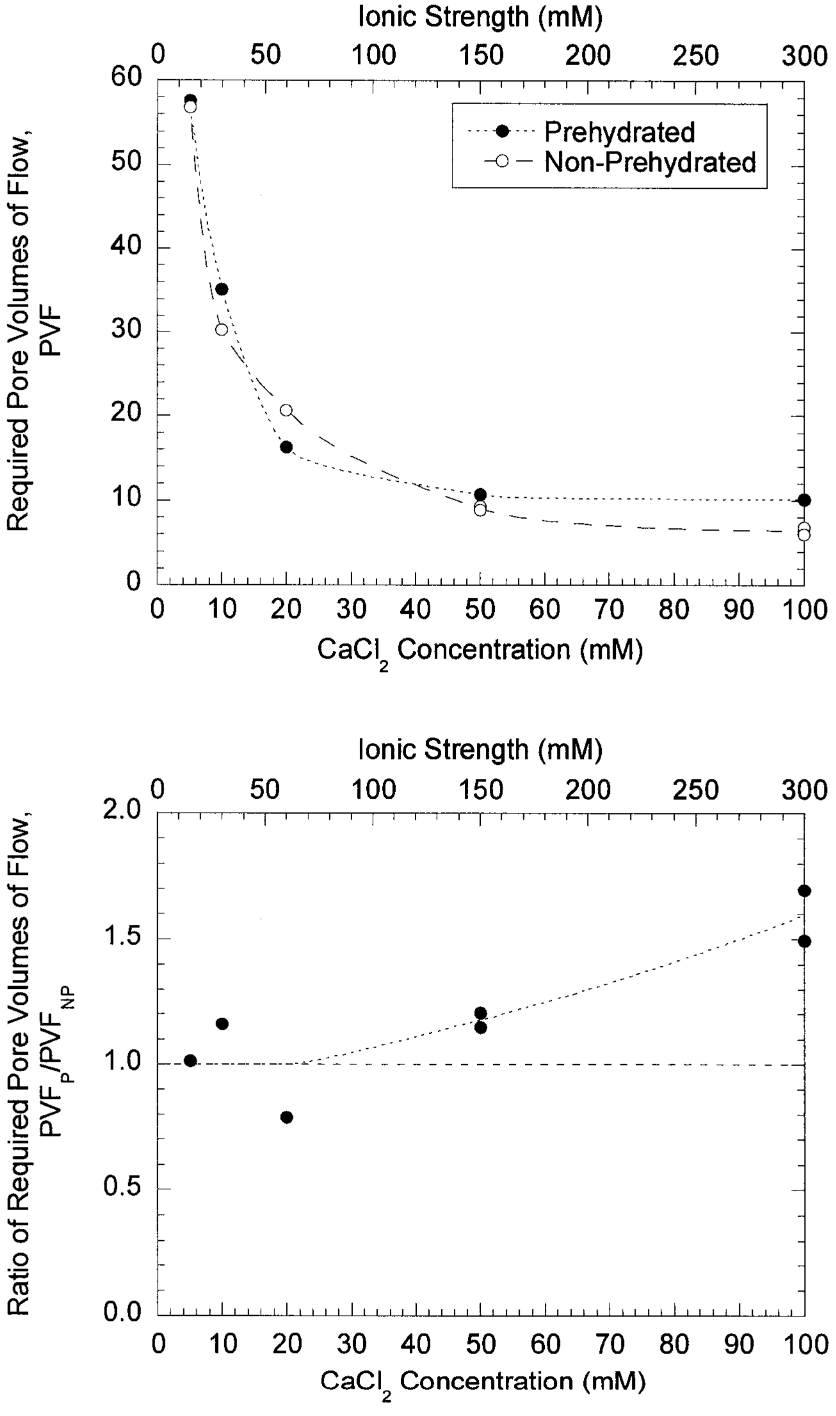

Fig. 3.13 – Pore volumes of flow required to achieve chemical equilibrium for both prehydrated (PVF_P) and non-prehydrated (PVF_{NP}) specimens as a function of influent $CaCl_2$ concentration.

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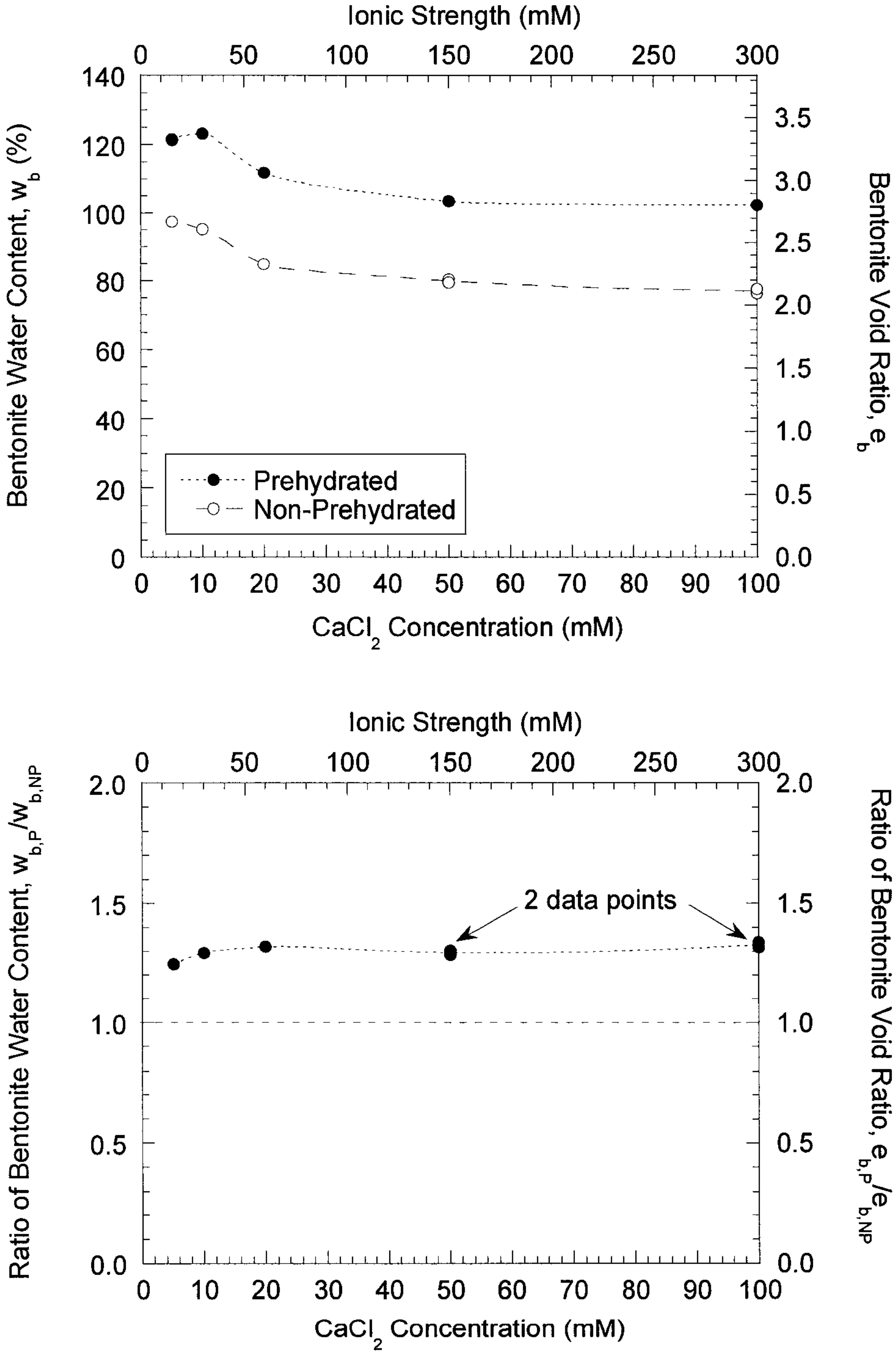

Fig. 3.14 – Final bentonite gravimetric water content and void ratio after permeation for both prehydrated ($w_{b,P}$ and $e_{b,P}$) and non-prehydrated ($w_{b,NP}$ and $e_{b,NP}$) specimens as a function of influent $CaCl_2$ concentration.

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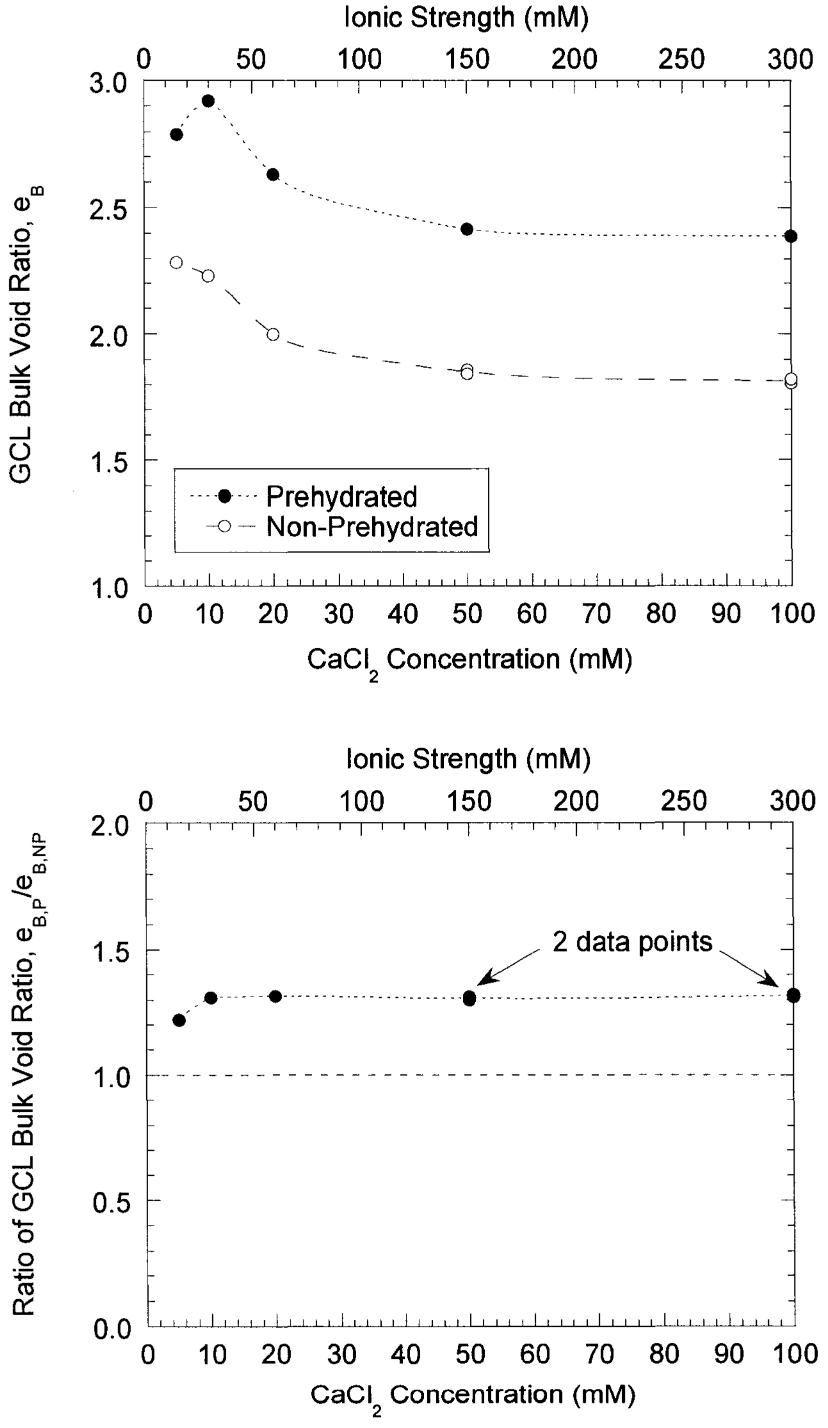

Fig. 3.15 – Final GCL bulk void ratio after permeation for both prehydrated ($e_{B,P}$) and non-prehydrated ($e_{B,NP}$) specimens as a function of influent $CaCl_2$ concentration.

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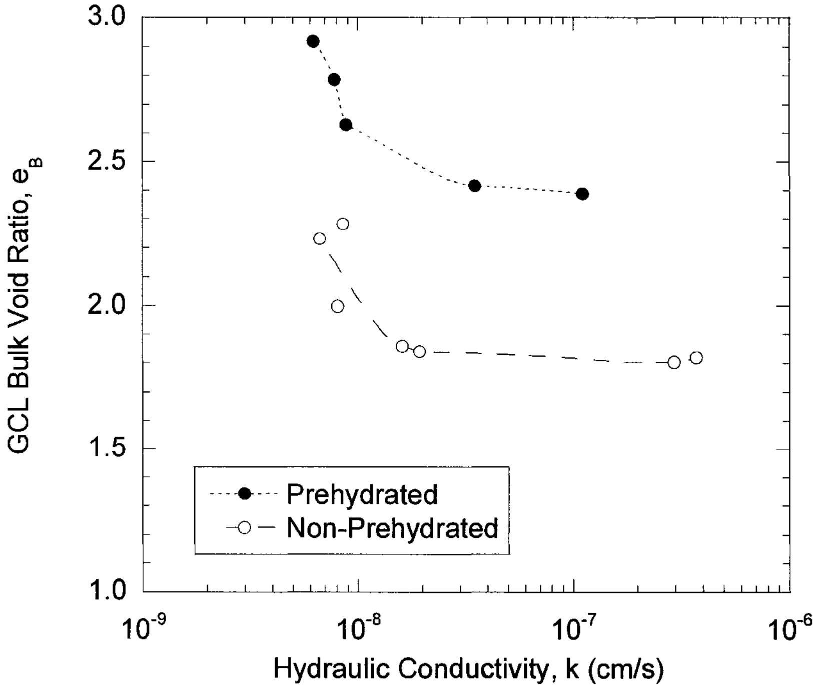

Fig. 3.16 – Final GCL bulk void ratio after permeation versus hydraulic conductivity for both prehydrated and non-prehydrated specimens based on permeation with 5 to 100 mM $CaCl_2$ solutions.

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CHAPTER 4

IMPACT OF BENTONITE QUALITY ON HYDRAULIC CONDUCTIVITY OF GEOSYNTHETIC CLAY LINERS

ABSTRACT: The difference in hydraulic conductivity of two geosynthetic clay liners (GCLs) containing different qualities of bentonite is evaluated based on permeation with water and $CaCl_2$ solutions. The GCL with the higher quality bentonite (GCL-HQB) is characterized by a greater content of sodium montmorillonite (86 % vs. 77 %), a higher plasticity index (548 % vs. 393 %), and a higher cation exchange capacity (93 meq/100 g vs. 64 meq/100 g) relative to the GCL with the lower quality bentonite (GCL-LQB). For tests using $CaCl_2$ solutions as permeant liquids, the tests are performed until chemical equilibrium between the influent and effluent has been established, resulting in test durations lasting from less than 1 day to more than 900 days. The hydraulic conductivity for GCL-HQB, k_{HQB}, is ~ 3X lower than the hydraulic conductivity for GCL-LQB, k_{LQB}, when both GCL specimens are permeated with water. However, GCL-HQB exhibits more significant alteration in hydraulic conductivity than GCL-LQB when permeated with $CaCl_2$ solutions. In fact, the ratio of two hydraulic conductivity values, i.e., k_{HQB}/k_{LQB}, ranges between 2.0 and 2.6 for the tests performed using 5, 10, and 20 mM $CaCl_2$ solutions as the permeant liquids, whereas the k_{HQB}/k_{LQB} values are ~ 230, ~ 100,

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and ~ 40 for the tests performed using 50, 100, and 500 mM $CaCl_2$ solutions as the permeant liquids, respectively.

Key Words: geosynthetic clay liners, montmorillonite, bentonite quality, hydraulic conductivity

4.1 INTRODUCTION

The quality of a bentonite is affected by several factors, including the mineralogical composition of the bentonite (e.g., amount of montmorillonite), the surface area of the bentonite (e.g., particle-size distribution of the bentonite), the surface charge deficiency of the bentonite (e.g., amount and type of isomorphic substitution), and the composition of the exchange complex (e.g., amount of exchangeable Na^+ relative to exchangeable Ca^{2+}) (e.g., Shackelford et al. 2000, Ashmawy et al. 2002). In general, the quality of the bentonite increases with increase in montmorillonite content, surface area (decrease in particle size), surface charge deficiency, and/or percentage of Na^+ on the exchange complex. The effect of these factors on the quality of the bentonite generally is indicated macroscopically by an increase in cation exchange capacity (CEC), an increase in plasticity, an increase in swell capacity in the presence of water, and a decrease in hydraulic conductivity based on permeation with water.

For example, isomorphic substitution in montmorillonite $[(OH)_4Si_8Al_4O_{20}\cdot nH_2O]$ typically results in replacement of a portion of the trivalent aluminum (Al^{3+}) in the aluminum octahedra with a divalent metal, such as magnesium (Mg^{2+}), resulting in a negative surface charge deficiency that must be balanced to satisfy electroneutrality by

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cations that are external to the crystalline structure (Mitchell 1993). The resulting surface charge deficiency of pure montmorillonite [$(OH)_4Si_8Al_4O_{20}\cdot nH_2O$] typically ranges from 0.5 equivalents per unit cell [i.e., $\{(OH)_4Si_8Al_{3.5}Mg_{0.5}O_{20}\cdot nH_2O\}^{0.5-}$] to 1.2 equivalents per unit cell [i.e., $\{(OH)_4Si_8Al_{2.8}Mg_{1.2}O_{20}\cdot nH_2O\}^{1.2-}$], with an average value of 0.66 equivalents per unit cell being common [i.e., $\{(OH)_4Si_8Al_{3.44}Mg_{0.66}O_{20}\cdot nH_2O\}^{0.66-}$]. All other factors being equal (e.g., particle size), this range in surface charge deficiency for pure montmorillonite with sodium (Na^+) as the only exchangeable (external) cation results in a CEC that theoretically ranges from 70 meq/100 g to 167 meq/100 g, with a common value of 92 meq/100 g. This theoretical range in CEC for pure montmorillonite is close to the reported measured range of 80 to 150 meq/100 g, with the difference likely resulting from impurities commonly found in natural montmorillonites (e.g., Mitchell 1993). Thus, all other factors being equal, the greater the amount of isomorphic substitution in the montmorillonite, the higher the CEC of the bentonite containing the montmorillonite and the higher the quality of the bentonite. Similarly, for the same amount of isomorphic substitution, the greater the sodium montmorillonite content in the bentonite, the higher the CEC and, therefore, the higher the quality of the bentonite.

For example, Haug and Boldt-Leppin (1994) reported that the hydraulic conductivity to water of a sand-bentonite mixture containing 8 % bentonite (dry weight) with a lower montmorillonite content (i.e. 76 %) was ~ 400X higher than hydraulic conductivity to water of a comparable mixture containing bentonite with a higher montmorillonite content (i.e., 95 %). Also, Abichou et al. (2002) found that a mixture of glass beads and 5 % bentonite (w/w) containing a 77 % montmorillonite content was able to achieve approximately the same hydraulic conductivity to water of 1 x 10^{-8} cm/s as a

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mixture of glass beads and 8 % bentonite but a montmorillonite content of only 59 %. Finally, Ashmawy et al. (2002) found that the hydraulic conductivity of bentonite specimens decreased from ~ 1 x 10^{-7} cm/s to ~ 1 x 10^{-8} cm/s based on permeation with water when the specimen being permeated was changed from one containing 49 % montmorillonite to one containing 91 % montmorillonite.

However, since bentonites are sensitive to chemical composition of the pore liquid that influences the thickness of the adsorbed layer, liquids that cause the adsorbed layer to collapse also cause the hydraulic conductivity to increase (Mesri and Olson 1971, Daniel et al. 1993, Gleason et al. 1997, James et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Daniel 2000, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001). Consequently, bentonites with higher montmorillonite contents are potentially more vulnerable to chemical attack than bentonites with lower montmorillonite contents.

For example, Stern and Shackelford (1998) permeated compacted sand-clay mixtures that contained sand mixed with 20 % of a clay admixture comprised of various percentages of two processed clay soils – bentonite and attapulgite clay – with both water and a 500 mM $CaCl_2$ solution. They found that the hydraulic conductivity of the mixture to water decreased from ~ 8.0 x 10^{-8} cm/s to ~ 2.6 x 10^{-8} cm/s as the amount of a bentonite containing 77 % montmorillonite in the mixture increased from 5 % to 10 %, respectively. However, they also found that the hydraulic conductivity of the mixture to the 500 mM $CaCl_2$ solution increased from ~ 1.5 x 10^{-6} cm/s to ~ 3.2 x 10^{-6} cm/s as the bentonite content in the mixture increased from 5 % to 10 %, respectively.

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On the other hand, Ashmawy et al. (2002) found the hydraulic conductivity of bentonite specimens to be insensitive to the montmorillonite content for their tests performed using bentonite specimens with a leachate containing a relatively high divalent cationic concentration (i.e., ~ 200 mM). However, this observation is based on the results of only two tests (two data points), and the influent and effluent were not analyzed to determine the extent of chemical equilibrium due to limitations in the equipment.

As a result of the aforementioned considerations, the objective of this study is to evaluate the difference in the hydraulic performance of two geosynthetic clay liners (GCLs) containing different qualities of bentonite with water and inorganic solutions with a wide range in calcium chloride ($CaCl_2$) concentrations. This objective is achieved by permeating specimens of both GCLs until chemical equilibrium between the influent and effluent is established. The results of this evaluation may have significant implications with respect to the use of GCLs containing bentonite with relatively high montmorillonite content to enhance hydraulic performance of GCLs used in waste containment applications.

4.2 MATERIALS AND METHODS

4.2.1 Geosynthetic Clay Liners

Two geosynthetic clay liners (GCLs) containing bentonites with different montmorillonite contents are used in this study. Both GCLs consist of a layer of granular sodium bentonite sandwiched between two polypropylene geotextiles held together by needle-punched fibers. Both GCLs are ~ 6-mm thick in the air-dried condition, and the average gravimetric water contents of both bentonites are ~ 4 %. The physical and

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chemical properties and the mineralogical compositions for bentonite portions of the two GCLs are given in Table 4.1.

Particle-size distributions of the bentonite portions of the two GCLs were determined using both mechanical sieve analyses of the air-dried bentonites and hydrometer analyses (ASTM D 421, D 422). The corresponding test results for both bentonites are shown in Fig. 4.1.

For simplicity, the GCL containing the bentonite with the higher montmorillonite content (i.e., 86 %), higher plasticity index (i.e., 548 %), and higher CEC (i.e., 93 meq/100 g) is referred to hereafter as the GCL with the higher quality bentonite (GCL-HQB), whereas the GCL containing the bentonite with the lower montmorillonite content (i.e., 77 %), lower plasticity index (i.e., 393 %), and lower CEC (i.e., 64 meq/100 g) is to referred hereafter as the GCL with the lower quality bentonite (GCL-LQB).

4.2.2 Permeant Liquids

The permeant liquids used in the experiment consist of tap water that is processed by passage through three Barnstead® ion exchange columns in series and chemical solutions containing 5, 10, 20, 50, 100, and 500 mM $CaCl_2$. The properties of the permeant liquids are given in Table 4.2. Calcium chloride was chosen primarily because previous studies involving permeation of bentonite-based hydraulic barrier materials (e.g., GCLs and sand-bentonite mixtures) with $CaCl_2$ solutions have shown significant effects of the solutions on the hydraulic conductivity of these materials (Alther et al. 1985, Daniel et al. 1993, Shackelford 1994, Imamura et al. 1996, Gleason et al. 1997, James et al. 1997, Melchior 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Quaranta et al.

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1997, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001, Shan and Lai 2002).

The chemical solutions were prepared by dissolving $CaCl_2$ (powdered, > 96 % pure, Sigma-Aldrich Co., St. Louis, MO) in the water. Each solution was mixed in a 20-L carboy, and pH, EC, and solute concentrations of the influent liquids were monitored with time using a pH meter (Accumet® AB15 meter, Fisher Scientific Co., Pittsburgh, PA), an EC probe (Accumet® AB30 meter, Fisher Scientific Co., Pittsburgh, PA), and an ion chromatograph (Dionex® 4000i IC Module, Dionex Co., Sunnyvale, CA) for chloride concentrations, and an inductively coupled plasma – atomic emission spectrometer (IRIS® Advantage/1000 ICAP Spectrometer, Thermo Jarrell Ash Co., Franklin, MA) for calcium concentrations, respectively.

4.2.3 Hydraulic Conductivity Tests

Specimens of the two GCLs with nominal diameters of 102 mm were permeated using the falling-head procedure and flexible-wall permeameters in accordance with ASTM D 5084. Although Petrov et al. (1997a) indicate that the type of permeameter is not particularly important when testing GCLs, the flexible-wall permeameter is the most reliable device for testing GCLs, and provides the greatest assurance among the different types of permeameters that sidewall leakage does not affect the test results (Lin and Benson 2000, Shackelford et al. 2000).

Specimens were trimmed and assembled in the permeameters using the procedure described by Daniel et al. (1997) to prevent the possibility of short-circuiting through the geotextiles at the edge of the GCL specimens due to loss of bentonite and pinching of the

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geotextiles. The specimens initially were exposed to a permeant liquid in the permeameter for at least 48 hrs without applying a hydraulic gradient. Backpressure was not used so that effluent liquids could be conveniently collected for pH, EC, and solute concentration measurements. The thicknesses of specimens were measured before, during, and after the hydraulic conductivity tests using a caliper, a cathetometer, and a ruler. The measured thickness at the start of permeation was used to estimate the pore volume for each specimen, whereas the final GCL bulk void ratio was estimated based on the description given by Petrov et al. (1997b).

All the specimens were permeated at an average effective stress of 23.5 kPa (3.4 psi) and at an average hydraulic gradient of 200. While this hydraulic gradient is higher than the maximum gradient (i.e., 30) stipulated in ASTM D 5084, hydraulic gradients ranging from 50 to 600 typically are used for measuring the hydraulic conductivity of GCLs (e.g., Shan and Daniel 1991, Daniel et al. 1993, Didier and Comeaga 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Shackelford et al. 2000). Results of these studies indicate that the hydraulic conductivity of GCLs is affected to a greater extent by average effective stress than by the magnitude of hydraulic gradient (Shackelford et al. 2000).

For all tests involving water as the permeant liquid, the tests were not terminated before the termination criteria specified in ASTM D 5084 were achieved. These termination criteria include: (1) at least four consecutive volumetric flow ratios of effluent relative to influent within 1.00 ± 0.25; and (2) at least four consecutive hydraulic conductivity (k) values within ± 25 % of the mean value for $k \geq 1 \times 10^{-8}$ cm/s or within ± 50 % of the mean value for $k < 1 \times 10^{-8}$ cm/s. However, the tests performed with water in

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this study continued for approximately 2 yrs to assess the potential change in hydraulic conductivity due to the prolonged test duration.

For all tests involving $CaCl_2$ solutions, the tests were continued until equilibrium in EC and solute concentrations between influent and effluent was established (e.g., Daniel 1994, Shackelford et al. 1999, 2000). Equilibrium in EC was considered established when the EC of the effluent was within ± 10 % of the influent EC in accordance with ASTM D 6766, and equilibrium in both chloride (Cl^-) and calcium (Ca^{2+}) was considered established when the solute concentrations in the effluent were within ± 10 % of those in the source solutions. However, although the EC and solute concentrations of the influent solutions remained relatively constant during permeation, the pH of all influent solutions decreased slowly over time. For example, the pH of the 10 mM $CaCl_2$ solution decreased from ~ 6.6 to ~ 5.7 over a period of 1.7 yrs. This decrease in pH is attributed to time-dependent dissolution of carbon dioxide (CO_2) from the atmosphere into the solutions. Although the limited variation (i.e., ~ 5.9 ± 0.4) in influent pH probably had little effect, if any, on the measured hydraulic conductivities relative to the effects caused by the $CaCl_2$ solutions (Shackelford 1994, Ruhl and Daniel 1997, Shackelford et al. 2000, Jo et al. 2001, Shan and Lai 2002), equilibrium based on pH was found to be not particularly applicable in this study because the pH ratio (i.e., pH_{out}/pH_{in}) never met the typical acceptable range (i.e., 1.00 ± 0.10) throughout the tests, except for the tests performed using the 500 mM $CaCl_2$ solution (see Figs. 4.3 to 4.8). As a result, pH equilibrium was not considered as a termination criterion in this study.

Because the tests using solutions containing relatively low $CaCl_2$ concentrations (i.e., 5, 10, and 20 mM) required more than 4 months to establish chemical equilibrium,

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these tests could not be duplicated due to the limited number of permeameters available for testing. However, the tests using relatively high $CaCl_2$ concentrations (i.e., 50, 100, and 500 mM) were duplicated because the test durations were relatively short (< 20 days) allowing for reuse of the test equipment in a timely manner. In addition, the tests performed with water also were not duplicated due to extensive testing times resulting from the relatively low hydraulic conductivities to water (i.e., $< 4 \times 10^{-9}$ cm/s) for both GCLs.

4.3 RESULTS

4.3.1 Results with Water

The results of the hydraulic conductivity tests for specimens of the two GCLs permeated with water are shown in Fig. 4.2. The hydraulic conductivity values for specimens of the GCL with the lower quality bentonite (GCL-LQB) initially decreased to approximately 2.1×10^{-9} after about 9 days (~ 0.9 pore volumes of flow, PVF) of permeation, and subsequently increased to ~ 2.4×10^{-9} cm/s when the termination requirements specified in ASTM D 5084 were achieved, corresponding to ~ 16 days (~ 1.3 PVF) of permeation. Thereafter, the hydraulic conductivity values eventually increased to ~ 3.3×10^{-9} cm/s after ~ 2 yrs (~ 43 PVF) of permeation. In contrast, the hydraulic conductivity values of the GCL with the higher quality bentonite (GCL-HQB) initially decreased to ~ 2.5×10^{-10} cm/s after ~ 80 days (~ 0.2 PVF) of permeation, and subsequently increased to ~ 7.0×10^{-10} cm/s when the termination requirements in ASTM D 5084 were met, corresponding to ~ 209 days (~ 3.0 PVF) of permeation. Thereafter, the hydraulic conductivity values finally increased to ~ 9.5×10^{-10} cm/s after ~ 2 yrs (~

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16 PVF) of permeation. In fact, the final hydraulic conductivity after ~ 2 yrs of permeation for specimens of both GCLs permeated with water was not significantly different (i.e., ~ 1.4X) to that based on the termination criteria in ASTM D 5084.

On the other hand, the effluent calcium (Ca^{2+}) and chloride (Cl^-) concentrations initially were ~ 80 mg/L and ~ 170 mg/L, respectively, for the specimens of both GCLs, and then decreased gradually over a period of ~ 2 yrs to less than 1.0 mg/L and 0.1 mg/L, respectively, whereas the effluent sodium (Na^+) concentrations initially were greater than 1500 mg/L for the specimens of both GCLs, and then decreased to ~ 56 mg/L for the specimen of GCL-LQB and ~ 23 mg/L for the specimen of GCL-HQB over the same time frame. This gradual decrease in effluent Na^+ concentrations can be attributed, in part, to rate-limited diffusive mass transport of soluble Na^+ from the interlayer region of the bentonite particles to the interparticle and interclod migration pathways resulting from the relatively slow flow rate for the tests performed with water (Coats and Smith 1964, van Genuchten and Wierenga 1976, Rao et al. 1980, Tang et al. 1981, van Eijkeren and Loch 1984, Parker and Valocchi 1986, Pusch 1999, Pusch and Schomburg 1999). This slow leaching process also is likely responsible for significantly high ratios of effluent to influent EC throughout the tests (i.e., $EC_{out}/EC_{in} > 60$) in addition to the relatively low influent EC for the deionized water (i.e., ~ 0.21 mS/m). The slight increases in hydraulic conductivity to water observed between the time corresponding to the termination criteria based on ASTM D 5084 and the actual termination of the tests may be correlated, in part, to the gradual leaching of Na^+ from the bentonite.

4.3.2 Results with 5, 10, and 20 mM $CaCl_2$ Solutions

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The results of the hydraulic conductivity tests for the specimens of both GCLs permeated with 5, 10, and 20 mM $CaCl_2$ solutions are shown in Figs. 4.3 to 4.5, respectively. The hydraulic conductivity values for specimens of GCL-LQB initially decreased to approximately 1.5 x 10^{-9} cm/s after ~ 1 month (< 5 PVF). However, the hydraulic conductivity values began to increase within 6 months (< 10 PVF). Finally, at chemical equilibrium, the hydraulic conductivity values had increased by approximately 5X to a value of ~ 7.8 x 10^{-9} cm/s regardless of the influent concentration, corresponding to ~ 1.4 yrs (~ 57 PVF) ~ 1.1 yrs (~ 31 PVF), and ~ 0.4 yr (~ 21 PVF) of permeation with 5, 10, and 20 mM $CaCl_2$ solutions, respectively. The effluent Na^+ concentrations still were greater than 6.0 mg/L at the end of the tests for specimens of GCL-LQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

Similarly, the hydraulic conductivity values for specimens of GCL-HQB initially decreased to less than 1.0 x 10^{-9} cm/s after ~ 2 months (< 5 PVF), and then the hydraulic conductivity values began to increase within 6 months (< 10 PVF). At chemical equilibrium, the hydraulic conductivity values had increased by more than one order of magnitude to a value of ~ 1.7 x 10^{-8} cm/s regardless of the influent concentration, after ~ 2.6 yrs (~ 58 PVF), ~ 1.4 yrs (~ 60 PVF), and ~ 0.4 yr (~ 22 PVF) of permeation with 5, 10, and 20 mM $CaCl_2$ solutions, respectively. At the end of the tests, the effluent Na^+ concentrations were ~ 2.0 mg/L for the specimens of GCL-HQB permeated with 5 and 10 mM $CaCl_2$ solutions, whereas the effluent Na^+ concentration was ~ 40 mg/L for the specimen of GCL-HQB permeated with the 20 mM $CaCl_2$ solution.

4.3.3 Results with 50, 100, and 500 mM $CaCl_2$ Solutions

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Results of the hydraulic conductivity tests for the specimens of both GCLs permeated with 50, 100, and 500 mM $CaCl_2$ solutions are shown in Figs. 4.6 to 4.8, respectively. For the duplicate specimens of GCL-LQB, the hydraulic conductivity values stabilized within 20 days (< 10 PVF) at ~ 1.8 x 10^{-8}, ~ 3.4 x 10^{-7}, and ~ 1.5 x 10^{-6} cm/s for the tests performed with 50, 100, and 500 mM $CaCl_2$ solutions, respectively. Within the same time frame, chemical equilibrium also was established for all of the specimens of GCL-LQB permeated with 50, 100, and 500 mM $CaCl_2$ solutions. These hydraulic conductivity values are ~ 2X, ~ 40X, and ~ 200X higher for specimens of GCL-LQB permeated with 50, 100, and 500 mM $CaCl_2$ solutions, respectively, than the relatively constant hydraulic conductivity value of ~ 7.8 x 10^{-9} cm/s for specimens permeated with the 5, 10, and 20 mM $CaCl_2$ solutions.

For the duplicate specimens of GCL-HQB permeated with 50, 100, and 500 mM $CaCl_2$ solutions, the hydraulic conductivity values stabilized within 3 hrs (< 20 PVF), due to the significantly high hydraulic conductivity values (i.e., > 1 x 10^{-6} cm/s) throughout the tests. In fact, the hydraulic conductivity values based on chemical equilibrium are ~ 4.1 x 10^{-6}, 3.5 x 10^{-5}, and 6.0 x 10^{-5} cm/s for specimens of GCL-HQB permeated with 50, 100, and 500 mM $CaCl_2$ solutions, respectively. These hydraulic conductivity values are more than two orders-of-magnitude higher than the relatively constant hydraulic conductivity value of ~ 1.7 x 10^{-8} cm/s for specimens of GCL-HQB permeated with the 5, 10, and 20 mM $CaCl_2$ solutions. The effluent Na^+ concentrations were ~ 10 mg/L at the end of all the tests performed using specimens of both GCLs with 50, 100, and 500 mM $CaCl_2$ solutions.

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4.4 DISCUSSION

4.4.1 Effect of Bentonite Quality on Hydraulic Conductivity

The hydraulic conductivity values based on the tests performed with water and $CaCl_2$ solutions are summarized in Table 4.3 and shown in Fig. 4.9 as a function of $CaCl_2$ concentration of the permeant liquid. Since the measured Ca^{2+} concentration for the water was below the method detection limit (MDL) of 0.02 mg/L for Ca^{2+} (EPA Method 200.7) based on 10 independent measurements (see Table 4.2), the MDL is used to represent the Ca^{2+} concentration for the water. The ratios of the hydraulic conductivity for the specimens of GCL-HQB relative to the specimens of GCL-LQB, or k_{HQB}/k_{LQB}, are also summarized in Table 4.3 and shown in Fig. 4.10 as a function of $CaCl_2$ concentration of the permeant liquid.

The hydraulic conductivity of GCL-HQB is ~ 3X lower than the hydraulic conductivity of GCL-LQB based on permeation with water. Since the swelling capacity of bentonite upon hydration with water increases with increase in the montmorillonite content of the bentonite (e.g., Grim 1953, Mitchell 1993, Stern and Shackelford 1998, Shackelford et al. 2000), a lower hydraulic conductivity based on permeation with water is expected for GCLs that contain bentonite with a greater montmorillonite content, provided the other GCL properties (e.g., bonding method and particle size of bentonite) are similar. In addition, when the permeant liquid was changed from water to the 5 mM $CaCl_2$ solution, the hydraulic conductivity for the specimen of GCL-LQB increases only by ~ 3.6X relative to that based on water permeation, whereas the hydraulic conductivity for the specimen of the GCL-HQB increases by ~ 24X. In fact, the hydraulic conductivity values for the tests performed with $CaCl_2$ solutions are always higher for the specimens

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of GCL-HQB relative to the specimens of GCL-LQB, which indicates that GCL-HQB was more susceptible to incompatibility in hydraulic conductivity than GCL-LQB for the tests performed using $CaCl_2$ solutions.

For example, the ratios of the hydraulic conductivity for the GCL-HQB relative to the hydraulic conductivity for the GCL-LQB (i.e., k_{HQB}/k_{LQB}) ranges from 2.0 to 2.6 when permeated with 5, 10, and 20 mM $CaCl_2$ solutions. However, as shown in Fig. 4.10, k_{HQB}/k_{LQB} is greater than 40 when permeated with 50, 100, and 500 mM $CaCl_2$ solutions. As shown in Fig. 4.9, the hydraulic conductivity for GCL-LQB increases by ~ 2.3X when the $CaCl_2$ concentration of the permeant liquid increases from 20 mM to 50 mM, whereas the hydraulic conductivity for GCL-HQB increases by ~ 230X, and the resulting k_{HQB}/k_{LQB} value is ~ 230. When the $CaCl_2$ concentration of the permeant liquid increases from 50 mM to 100 mM, the hydraulic conductivity of GCL-LQB increases by ~ 19X, whereas the hydraulic conductivity of GCL-HQB increases by ~ 8.4X, and the resulting k_{HQB}/k_{LQB} value is ~ 100. Similarly, but to a lesser extent, the hydraulic conductivity increases by ~ 1.7X and ~ 4.4X for GCL-LQB and GCL-HQB, respectively, when the $CaCl_2$ concentration of the permeant liquid increases from 100 mM to 500 mM, and the resulting k_{HQB}/k_{LQB} value is ~ 40. As a result, the most significant change in hydraulic conductivity likely occurs over a specific concentration range that can be different for GCLs containing different quality of bentonite (i.e., 50 to 100 mM for GCL-LQB vs. 20 to 50 mM for GCL-HQB). In general, the hydraulic conductivity increases as the $CaCl_2$ concentration of the permeant liquid increases for both GCLs; however, the resulting hydraulic conductivity is higher for the GCL-HQB than for the GCL-LQB.

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4.4.2 Effect of Bentonite Quality on Equilibrium Time

As shown in Fig. 4.11, establishment of chemical equilibrium between the influent and effluent required ~ 430 and ~ 120 more days of permeation for the specimens of GCL-HQB permeated with the 5 and 10 mM $CaCl_2$ solutions, respectively, than for the specimens of GCL-LQB permeated with the same solutions. However, similar elapsed times were required to establish chemical equilibrium for specimens of both GCLs when permeated with the 20 mM $CaCl_2$ solution (i.e., ~ 5 months). When permeated with 50, 100, and 500 mM $CaCl_2$ solutions, specimens of GCL-LQB required longer test durations (i.e., > 35X) than did specimens of GCL-HQB, i.e., since chemical equilibrium for specimens of GCL-HQB was achieved within a relatively short test duration (i.e., < ~ 5 hrs). In general, the elapsed time required to establish chemical equilibrium decreases with increasing $CaCl_2$ concentration of the permeant liquid for both GCL specimens.

Similarly, as shown in Fig. 4.12, the pore volumes of flow (PVF) required to achieve chemical equilibrium decreases as the $CaCl_2$ concentration of the permeant liquid increases. For example, specimens of both GCLs required ~ 60 PVF and ~ 21 PVF to establish chemical equilibrium for the tests performed with 5 and 20 mM $CaCl_2$ solutions, respectively. In general, unlike the elapse time to reach chemical equilibrium (see Fig. 4.11), the PVF required to reach chemical equilibrium seem to be less dependent on the quality of the bentonite for the GCLs used in this study (see Fig. 4.12). However, specimens of GCL-HQB required slightly more PVF to establish chemical equilibrium (i.e., 1 to 10 more) than did the specimens the GCL-LQB for all the tests with some exceptions. Since increases in hydraulic conductivity of bentonite can be attributed to

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interactions between the permeant liquid and the bentonite resulting from the exchange of divalent cations (e.g., Ca^{2+}) in the permeant liquid for monovalent cations, primarily Na^+, on the exchange complex of the bentonite (e.g., Shackelford 1994, Gleason et al. 1997, Ruhl and Daniel 1997, Stern and Shackelford 1998, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Melchior 2002), the PVF required to achieve chemical equilibrium between influent and effluent are likely to be greater for GCLs containing bentonite with relatively high montmorillonite contents (i.e., provided the amounts of bentonite mass used in GCLs are similar), due to the associated higher cation exchange capacity (CEC) of the GCL.

4.4.3 Effect of Bentonite Quality on Final Properties of Specimens

The final bentonite gravimetric water content (w_b), bentonite void ratio (e_b), and GCL bulk void ratio (e_B) for specimens of both GCLs after permeation are shown in Figs. 4.13 and 4.14. As shown in Figs. 4.13 and 4.14, w_b, e_b, and e_B for specimens of GCL-LQB based on permeation with water are higher than those for specimens of GCL-LQB (i.e., 175 % vs. 160 % for w_b, 4.8 vs. 4.4 for e_b, and 4.1 vs. 3.6 for e_B). The lower w_b, e_b, and e_B for specimens of GCL-HQB relative to those for specimens of GCL-LQB based on permeation with water are presumably due to the other differences in the properties of the GCLs (e.g., integrity of geotextiles and needle-punched fibers, mass and gradation of bentonite, etc). However, w_b, e_b, and e_B for specimens of GCL-HQB permeated with the $CaCl_2$ solutions tend to be higher than those for specimens of GCL-LQB, except for the tests using the 500 mM $CaCl_2$ solution. For example, the values for the ratios of w_b, e_b, and e_B for specimens of GCL-HQB relative to those for specimens of GCL-LQB, or

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$w_{B,HQB}/w_{B,LQB}$, $e_{b,HQB}/e_{b,LQB}$, and $e_{B,HQB}/e_{B,LQB}$, range from 1.02 to 1.26 for the tests performed using solutions with $CaCl_2$ concentrations ranging from 5 mM to 100 mM, whereas the values for $w_{B,HQB}/w_{B,LQB}$, $e_{b,HQB}/e_{b,LQB}$, and $e_{B,HQB}/e_{B,LQB}$ values are less than unity (i.e., ~ 0.94 to ~ 0.97) for the tests performed using the 500 mM $CaCl_2$ solution.

The hydraulic conductivity is compared with GCL bulk void ratio (e_B) in Fig. 4.15. For the tests performed with $CaCl_2$ solutions, the hydraulic conductivity value at a given e_B is always higher for GCL-HQB than GCL-LQB. In fact, the greatest decrease in e_B for the GCL-LQB and GCL-HQB of ~ 1.80 (by 44 %) and ~ 1.04 (by 29%), respectively, occurs when the influent $CaCl_2$ concentration increases from 0 (water) to 5 mM, whereas the hydraulic conductivity of GCL-LQB and GCL-HQB increases by ~ 3.6X and ~ 24X, respectively, for the same increase in the influent $CaCl_2$ concentration. In contrast, the greatest increase in hydraulic conductivity (i.e., ~ 19X) occurred for GCL-LQB when the influent $CaCl_2$ concentration increases from 50 mM to 100 mM, but this increase in hydraulic conductivity is accompanied by a slight decrease in e_B of ~ 0.04 (2 %). Also, the greatest increase in hydraulic conductivity (i.e., ~ 235X) occurred for GCL-HQB when the influent $CaCl_2$ concentration increases from 20 mM to 50 mM, and this increase in hydraulic conductivity is accompanied by a decrease in e_B of ~ 0.46 (19 %). In general, increases in hydraulic conductivity are accompanied with decreases in e_B for both GCL. However, the hydraulic conductivity at a given GCL bulk void ratio based on permeation with $CaCl_2$ solutions is always higher for the GCL-HQB than for the GCL-LQB.

4.5 CONCLUSIONS

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The difference between the hydraulic performance of two geosynthetic clay liners (GCLs) containing different qualities of bentonite is evaluated by permeation with water and $CaCl_2$ solutions. The GCL with the higher quality bentonite (GCL-HQB) is characterized by a greater content of sodium montmorillonite (86 % vs. 77 %), a higher plasticity index (548 % vs. 393 %), and a higher cation exchange capacity (64 meq/100 g vs. 93 meq/100 g) relative to the GCL with the lower quality bentonite (GCL-LQB). The hydraulic conductivity tests are performed using both GCLs until chemical equilibrium between influent and effluent in terms of solute concentrations (i.e., $C_{out}/C_{in} = 1.00 \pm 0.10$) and EC (i.e., $EC_{out}/EC_{in} = 1.00 \pm 0.10$) is established for the tests using the $CaCl_2$ solutions as permeant liquids. Based on permeation with water, the hydraulic conductivity to water of GCL-HQB is ~ 3X lower than the hydraulic conductivity of GCL-LQB. However, the hydraulic conductivities for the tests performed with $CaCl_2$ solutions are always higher for GCL-HQB than for GCL-LQB, indicating that GCL-HQB exhibits more significant alteration in hydraulic conductivity than does GCL-LQB. In fact, the ratios of the hydraulic conductivity of GCL-HQB relative to that of GCL-LQB (i.e., k_{HQB}/k_{LQB}) are between 2.0 and 2.6 when permeated with 5, 10, and 20 mM $CaCl_2$ solutions. On the other hand, the k_{HQB}/k_{LQB} values are ~ 230, ~ 100, and ~ 40 when permeated with 50, 100, and 500 mM $CaCl_2$ solutions, respectively. In general, the hydraulic conductivity increases as $CaCl_2$ concentration of the permeant liquid increases for both GCL specimens. However, the resulting values of hydraulic conductivity are higher for GCL-HQB than for GCL-LQB.

In terms of equilibrium time, for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, more time is required to achieve chemical equilibrium for GCL-HQB

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relative to GCL-LQB, whereas GCL-HQB requires less time to establish chemical equilibrium than the GCL-HQB for the tests performed with 50, 100, and 500 mM $CaCl_2$ solutions as permeant liquids. However, the PVF required to achieve chemical equilibrium are less dependent on the bentonite quality for the GCLs used in this study, even though GCL-HQB generally requires slightly more PVF than does GCL-LQB. On the other hand, for the specimens permeated with $CaCl_2$ solutions, the GCL bulk void ratio of GCL-HQB is always higher than that of GCL-LQB, except for the specimens permeated with the 500 mM $CaCl_2$ solution. In addition, the hydraulic conductivity at a given GCL bulk void ratio is always higher for GCL-HQB than for GCL-LQB based on permeation with $CaCl_2$ solutions.

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Table 4.1 – Properties of bentonites in two geosynthetic clay liners.

Property	Standard	Average Value [No. of Trials]	
		LQB[e]	HQB[e]
Specific Gravity	ASTM D 854[a]	2.74 [3]	2.78 [2]
Soil Classification:	ASTM D 2487		
Sieve Analysis (Air-Dried)		SP [3]	SP [1]
Hydrometer		CH [7]	CH [1]
Atterberg Limits (%):	ASTM D 4318	[1]	[1]
Liquid Limit, LL		430	589
Plasticity Index, PI		393	548
Swell Index (mL/2 g)	ASTM D 5890	27.5 [17]	30.0 [2]
Bentonite Mass (kg/m^2)	ASTM D 5993	5.1 [5]	4.6 [5]
Principal Minerals (%):	b	[3]	[2]
Montmorillonite		77.2	86.0
Cristobalite		10.3	4.5
Plagioclase Feldspar		5.1	2.5
Quartz		3.4	3.5
Others		4.0	5.5
Cation Exchange Capacity, CEC (meq/100 g)	c	63.9 [3]	93.4 [2]
Exchangeable Metals (meq/100 g):	c	[3]	[2]
Ca^{2+}		11.5	15.3
Mg^{2+}		3.7	7.0
Na^{+}		45.8	69.0
K^{+}		0.7	0.8
Sum		61.7	92.1
Soluble Metals (mg/kg):	c, d	[3]	[2]
Ca^{2+}		218	737
Mg^{2+}		24	160
Na^{+}		3365	7107
K^{+}		48	216
Saturated Soil Paste:	c	[3]	[3]
pH		8.9	8.8
EC[f] (mS/m)		305	233

[a] Using a magnetic stirring device for de-airing.

[b] Based on X-ray diffraction (XRD) analyses performed by Mineralogy Inc., Tulsa, OK and GeoServices Inc., Argyle, TX.

[c] Based on procedures described in Shackelford and Redmond (1995).

[d] Measured from a 1 g:20 mL clay-water extract.

[e] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite.

[f] Electrical conductivity at 25 °C.

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Table 4.2 – Properties of permeant liquids.

Permeant Liquid	Salt Concentration (mM)		Measured Solute Concentrations (mg/L)		Measured pH [No. of Trials]	Measured EC[c] (mS/m) [No. of Trials]
	Target	Measured [No. of Trials]	Calcium (Ca^{2+}) [No. of Trials]	Chloride (Cl^{-}) [No. of Trials]		
DIW[a]	0	< 0.0005[b] [10]	< 0.02[b] [10]	< 0.04[b] [10]	5.6 ± 0.5 [19]	0.21 ± 0.11 [19]
$CaCl_2$ (Sigma Co., 96 %)	5	5.1 ± 0.2 [14]	216 ± 10 [14]	377 ± 38 [14]	5.7 ± 0.5 [25]	123 ± 2.1 [25]
	10	10.1 ± 0.2 [13]	436 ± 30 [13]	756 ± 65 [13]	6.0 ± 0.3 [19]	234 ± 2.6 [19]
	20	20.1 ± 0.6 [13]	872 ± 77 [13]	1457 ± 110 [13]	6.1 ± 0.3 [17]	445 ± 7.3 [17]
	50	50.7 ± 1.4 [9]	2055 ± 63 [9]	3548 ± 69 [9]	5.7 ± 0.1 [18]	1041 ± 26 [18]
	100	100 ± 2.6 [6]	4072 ± 126 [6]	7030 ± 95 [6]	5.8 ± 0.1 [13]	1958 ± 48 [13]
	500	505 ± 10 [5]	20289 ± 474 [5]	35755 ± 710 [5]	6.5 ± 0.2 [12]	7693 ± 25 [12]

[a] Deionized water.

[b] Method detection limit (MDL).

[c] Electrical conductivity at 25 °C.

Table 4.3 – Summary of test results to evaluate effect of bentonite quality.[a]

Permeant Liquid	Test No.	GCL Type[b]	Chemical Equilibrium[c]		k Ratios[d]	
			k (cm/s)	PVF [t (days)]	k/k_w	k_{HQB}/k_{LQB}
Deionized Water	1	LQB	2.4×10^{-9}	1.3 [16]	1.0	0.30
	2	HQB	7.0×10^{-10}	3.0 [209]	1.0	
5 mM $CaCl_2$	3	LQB	8.6×10^{-9}	57 [502]	3.6	2.0
	4	HQB	1.7×10^{-8}	58 [934]	24	
10 mM $CaCl_2$	5	LQB	6.7×10^{-9}	30 [397]	2.8	2.6
	6	HQB	1.7×10^{-8}	60 [515]	25	
20 mM $CaCl_2$	7	LQB	8.1×10^{-9}	21 [164]	3.4	2.2
	8	HQB	1.8×10^{-8}	22 [154]	25	
50 mM $CaCl_2$	9	LQB	1.6×10^{-8}	9.3 [16]	6.9	233[e]
	10	LQB	1.9×10^{-8}	8.9 [15]	8.2	
	11	HQB	4.6×10^{-6}	18 [0.11]	6649	
	12	HQB	3.6×10^{-6}	17 [0.18]	5183	
100 mM $CaCl_2$	13	LQB	3.0×10^{-7}	6.8 [0.80]	126	104[e]
	14	LQB	3.7×10^{-7}	6.0 [0.59]	159	
	15	HQB	3.1×10^{-5}	4.6 [0.004]	43955	
	16	HQB	3.9×10^{-5}	11 [0.006]	55752	
500 mM $CaCl_2$	17	LQB	1.2×10^{-6}	1.7 [0.03]	491	41[e]
	18	LQB	1.8×10^{-6}	1.6 [0.02]	759	
	19	HQB	5.7×10^{-5}	1.5 [0.0006]	82023	
	20	HQB	6.2×10^{-5}	1.6 [0.0006]	88613	

[a] k = hydraulic conductivity; PVF = pore volumes of flow; t = elapsed time.

[b] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite.

[c] Values at chemical equilibrium in terms of both electrical conductivity (EC) and solute concentrations (i.e., $EC_{out}/EC_{in} = 1.00 \pm 0.10$ and $C_{out}/C_{in} = 1.00 \pm 0.10$) except for the tests performed with deionized water, in which the values are based on ASTM D 5890.

[d] k/k_w = ratio of k based on any solution to k based on water; k_{HQB}/k_{LQB} = ratio of k for GCL-HQB relative to k for GCL-LQB.

[e] Based on average values.

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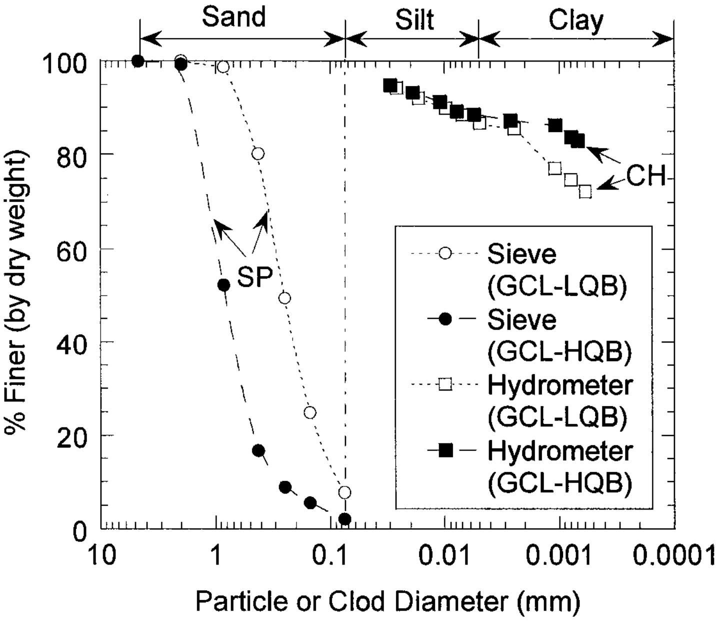

Fig. 4.1 – Particle-size distributions for either lower quality bentonite (LQB) or higher quality bentonite (HQB) taken from two GCLs based on mechanical sieve (dry) and hydrometer (wet) analyses.

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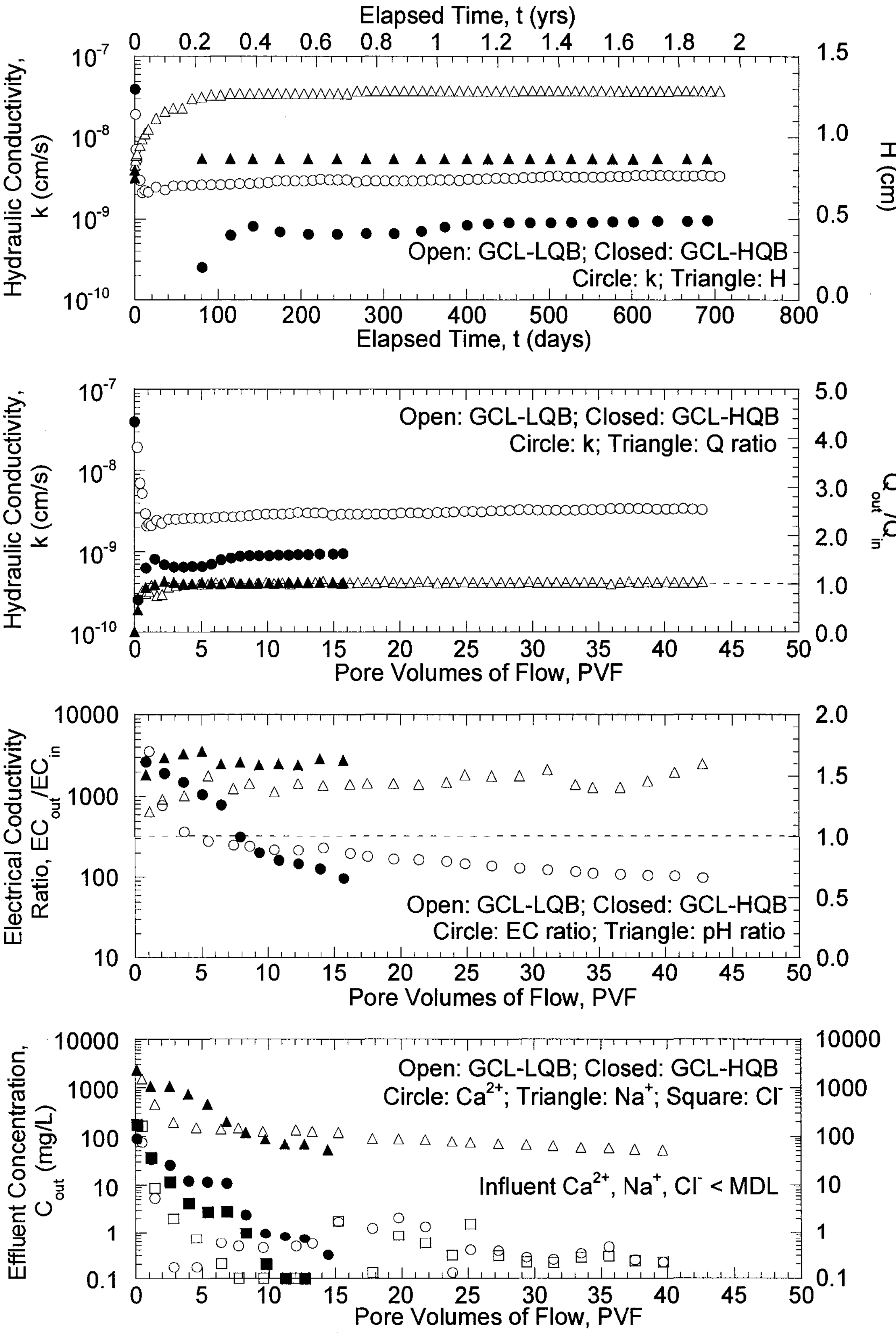

Fig. 4.2 – Test results for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) permeated with water (MDL = method detection limit; MDL for Ca^{2+}, Na^{+}, Cl^{-} = 0.02, 0.2, 0.04 mg/L).

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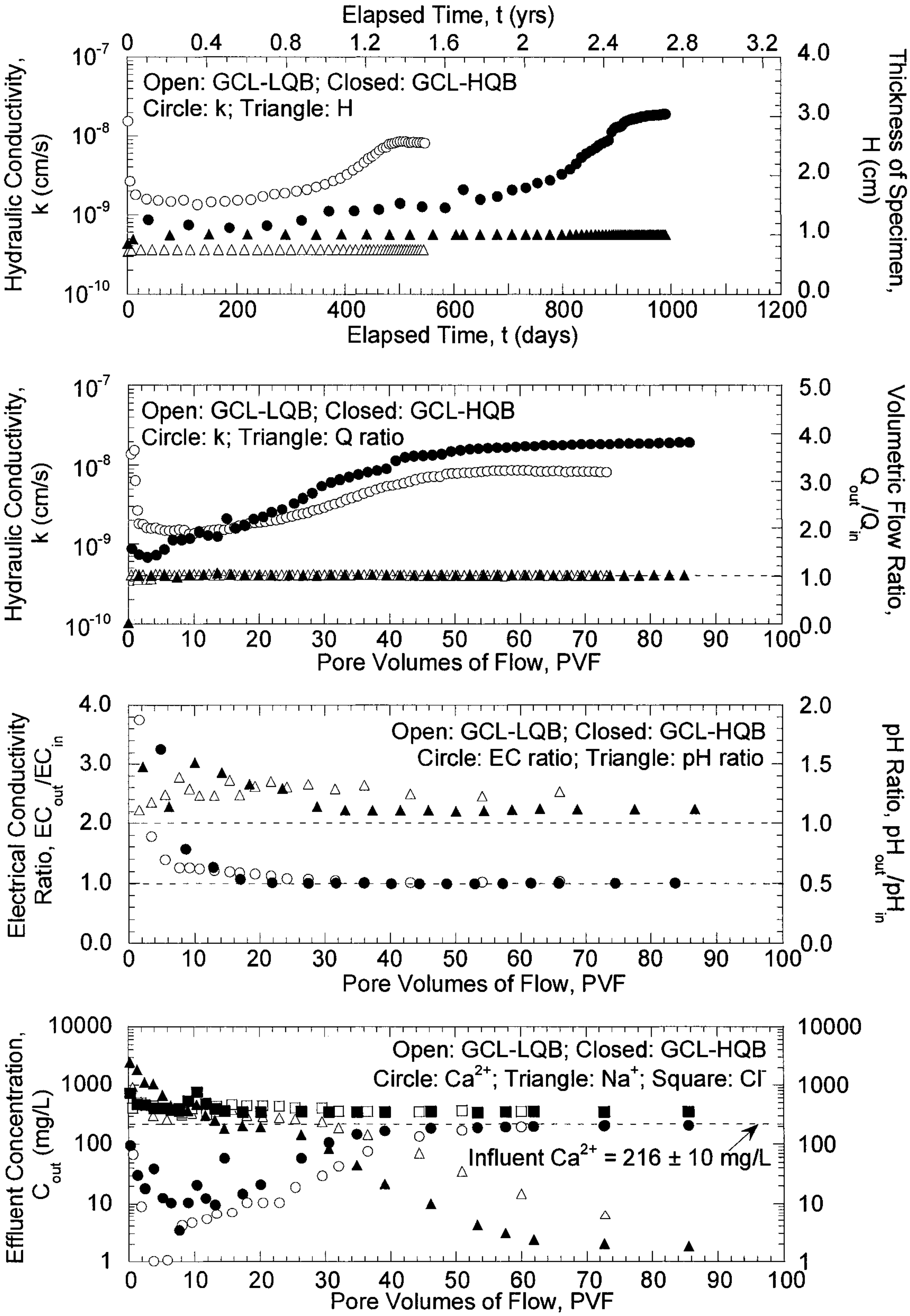

Fig. 4.3 – Test results for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) permeated with 5 mM $CaCl_2$ solution.

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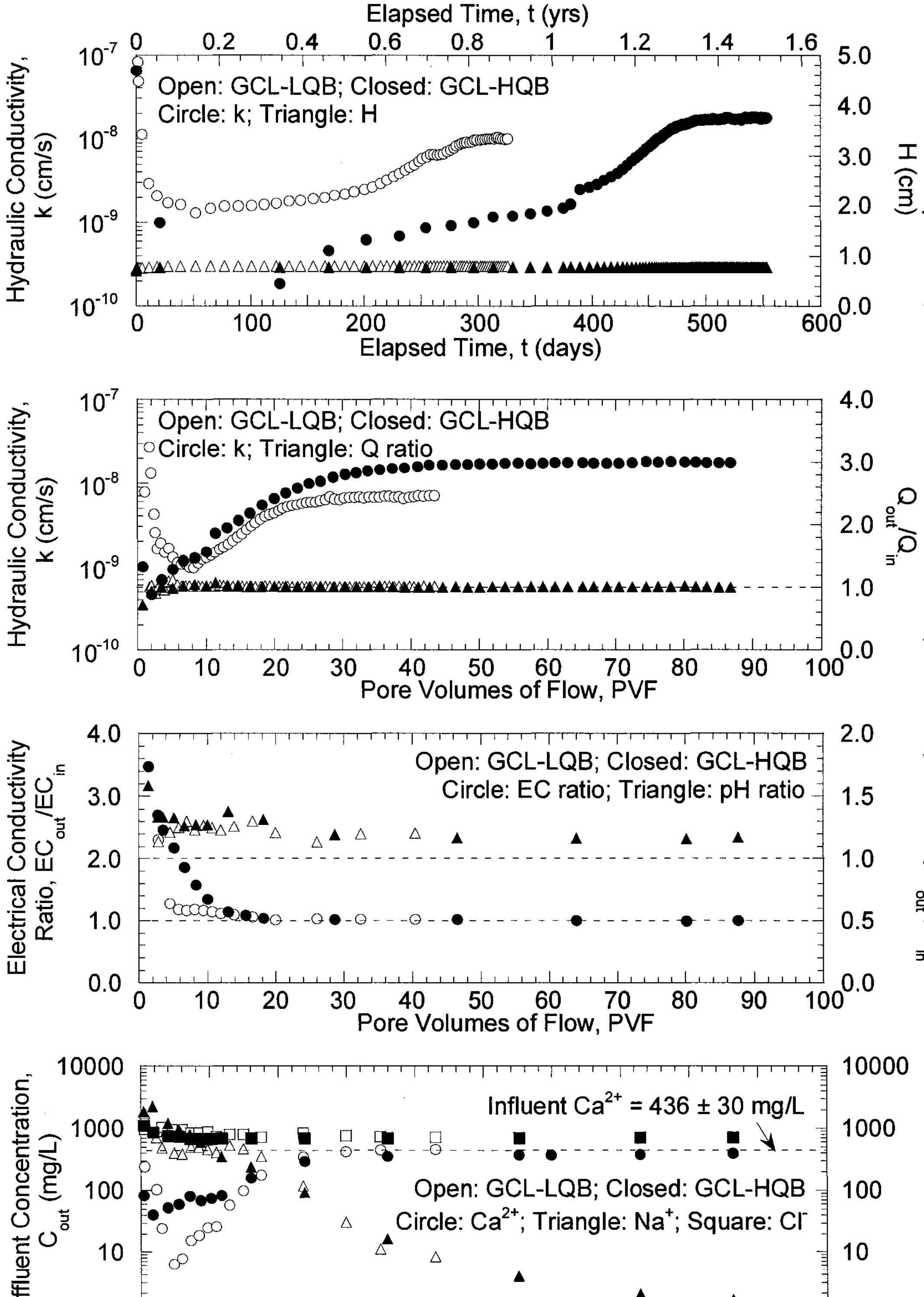

Fig. 4.4 – Test results for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) permeated with 10 mM $CaCl_2$ solution.

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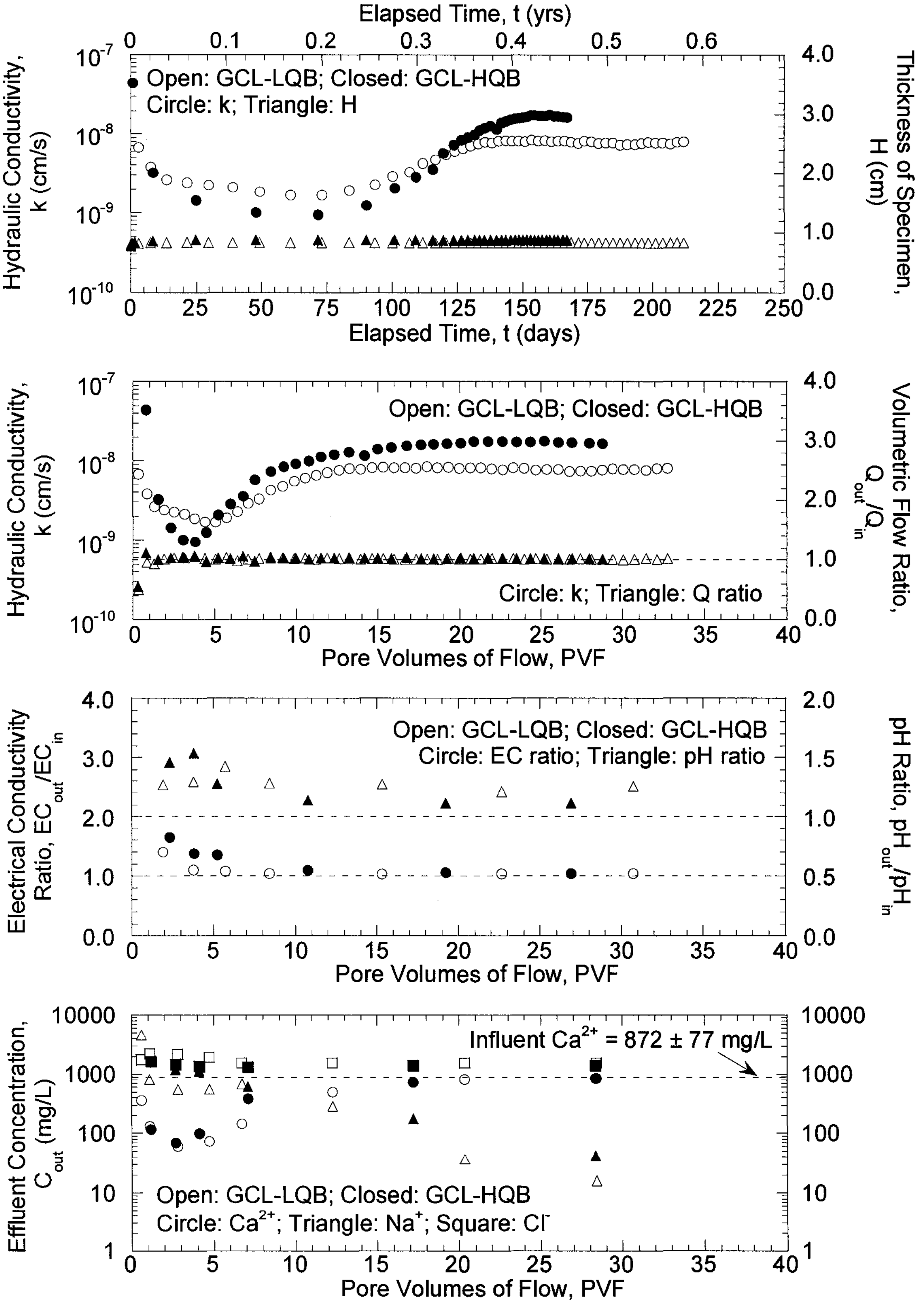

Fig. 4.5 – Test results for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) permeated with 20 mM $CaCl_2$ solution.

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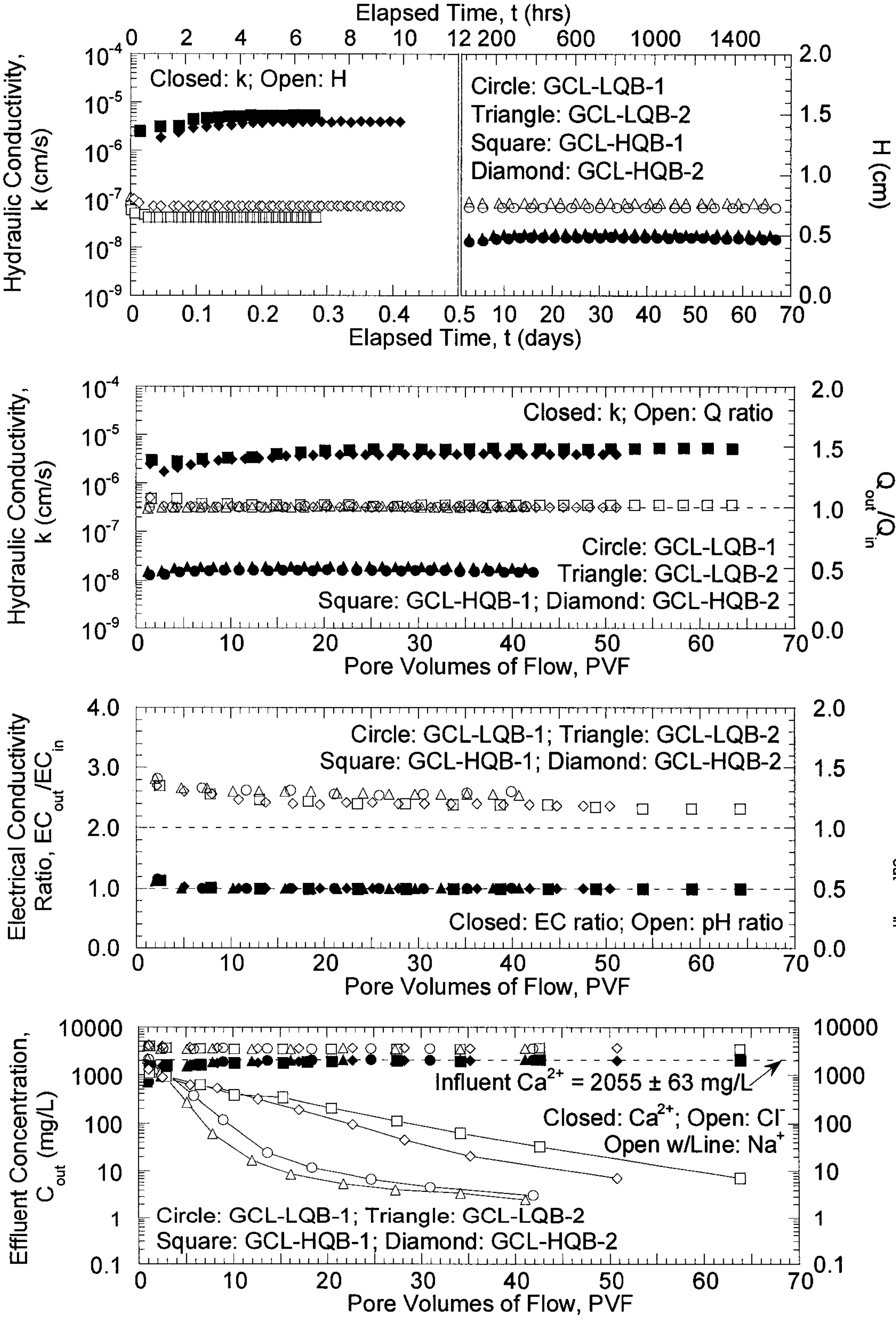

Fig. 4.6 – Test results for duplicate specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) permeated with 50 mM $CaCl_2$ solution.

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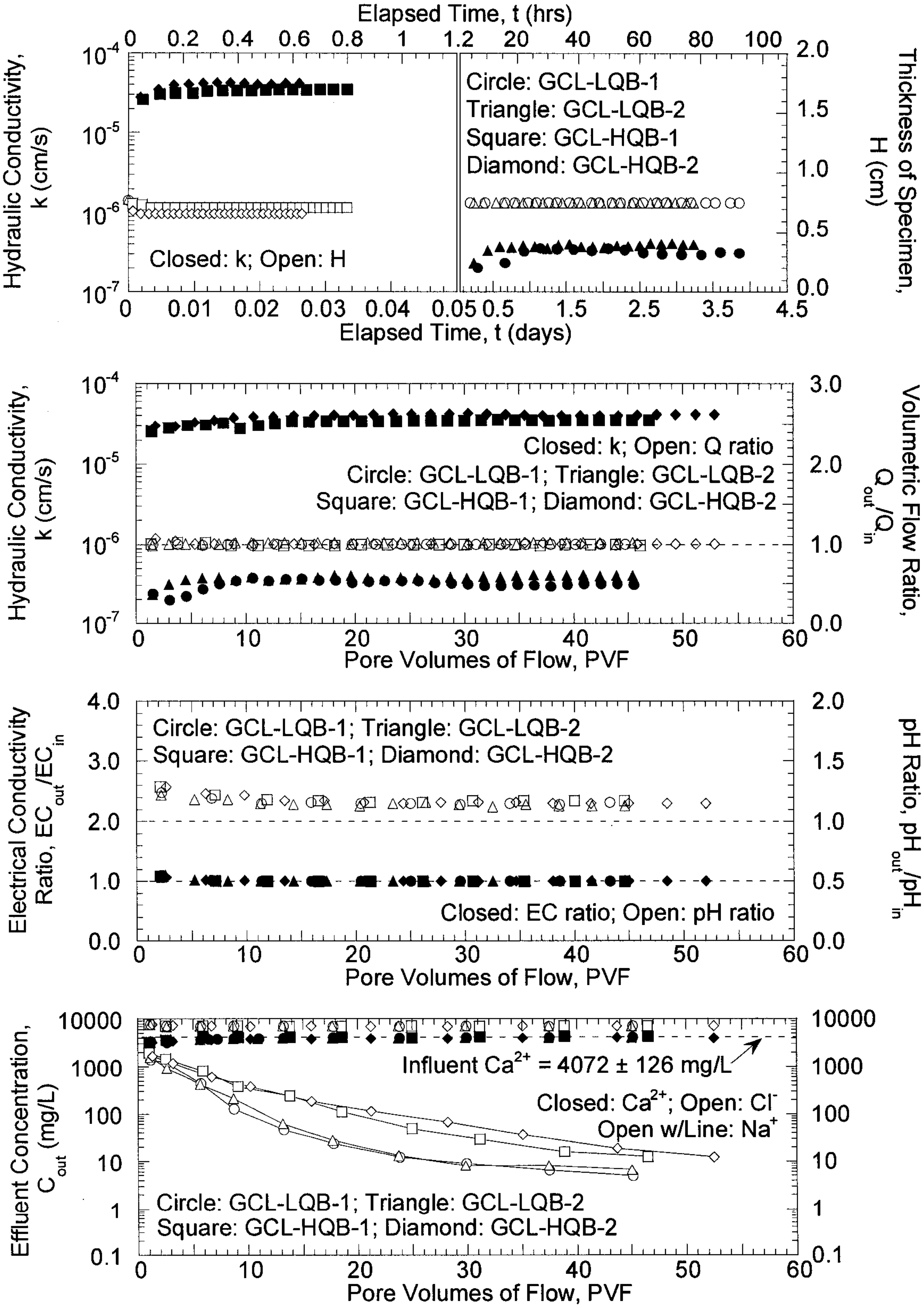

Fig. 4.7 – Test results for duplicate specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) permeated with 100 mM $CaCl_2$ solution.

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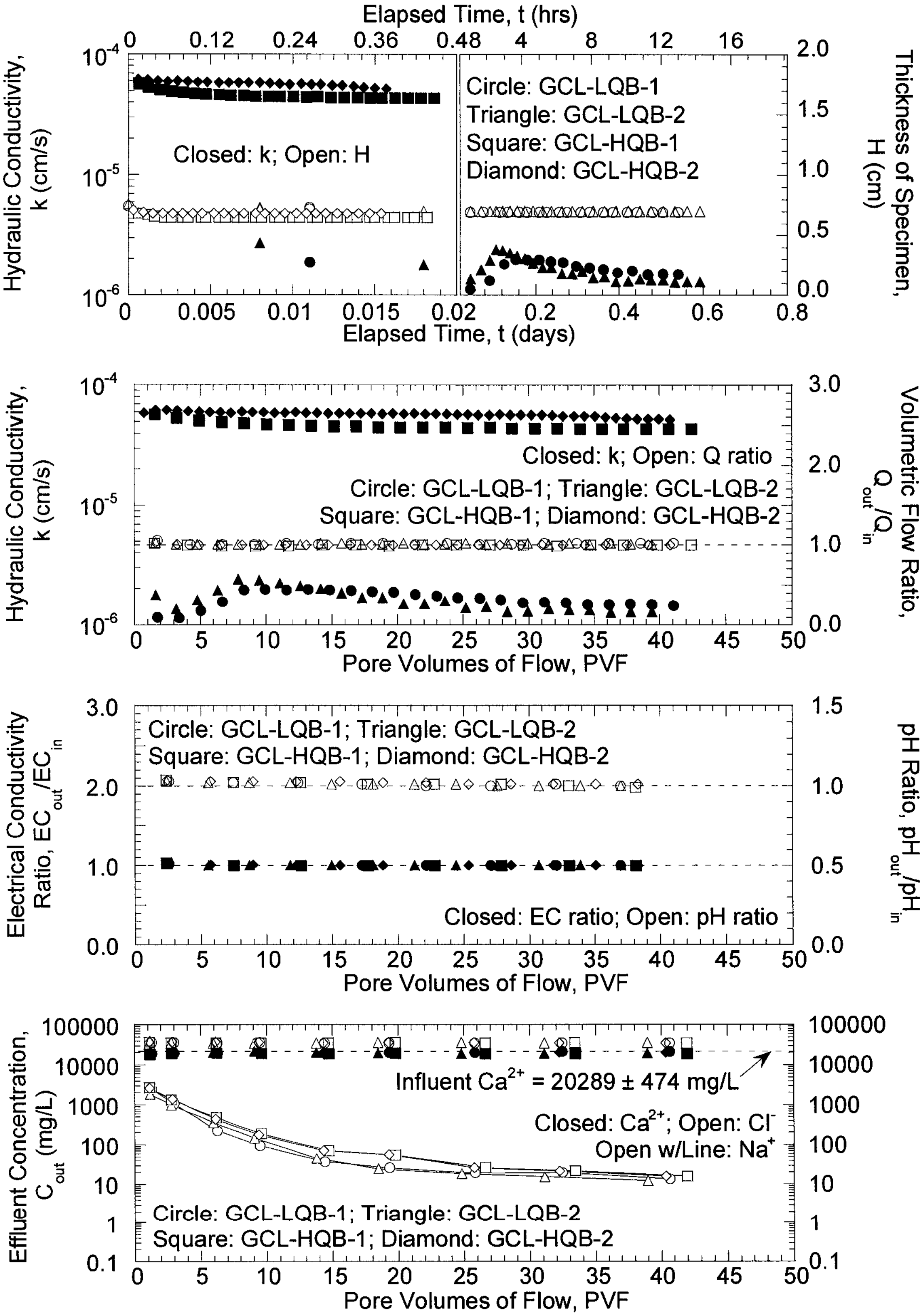

Fig. 4.8 – Test results for duplicate specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) permeated with 500 mM $CaCl_2$ solution.

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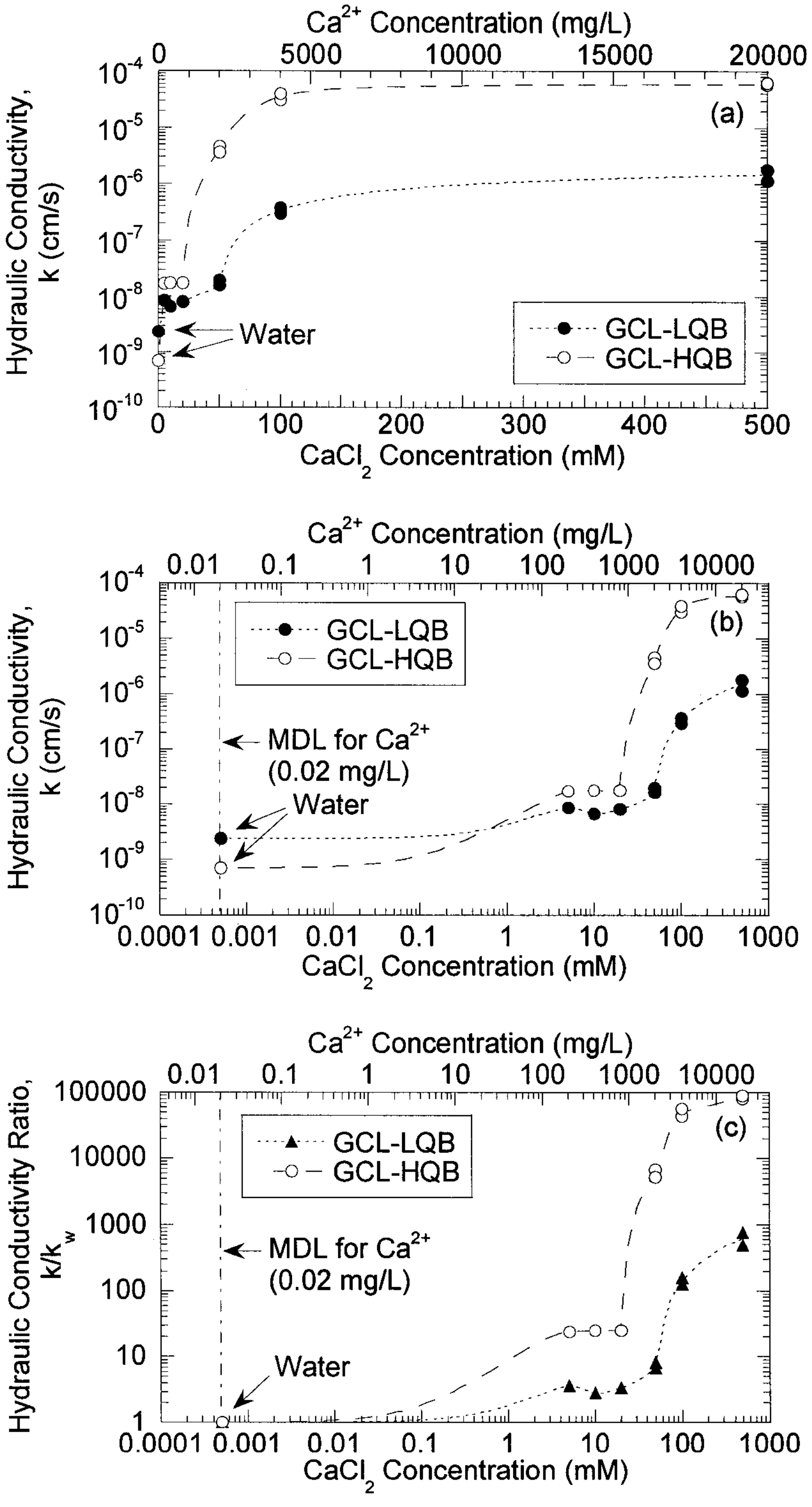

Fig. 4.9 – Results of hydraulic conductivity (k) tests for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB): (a) and (b) k values; and (c) ratio of k based on any solution to k based on water (MDL = method detection limit).

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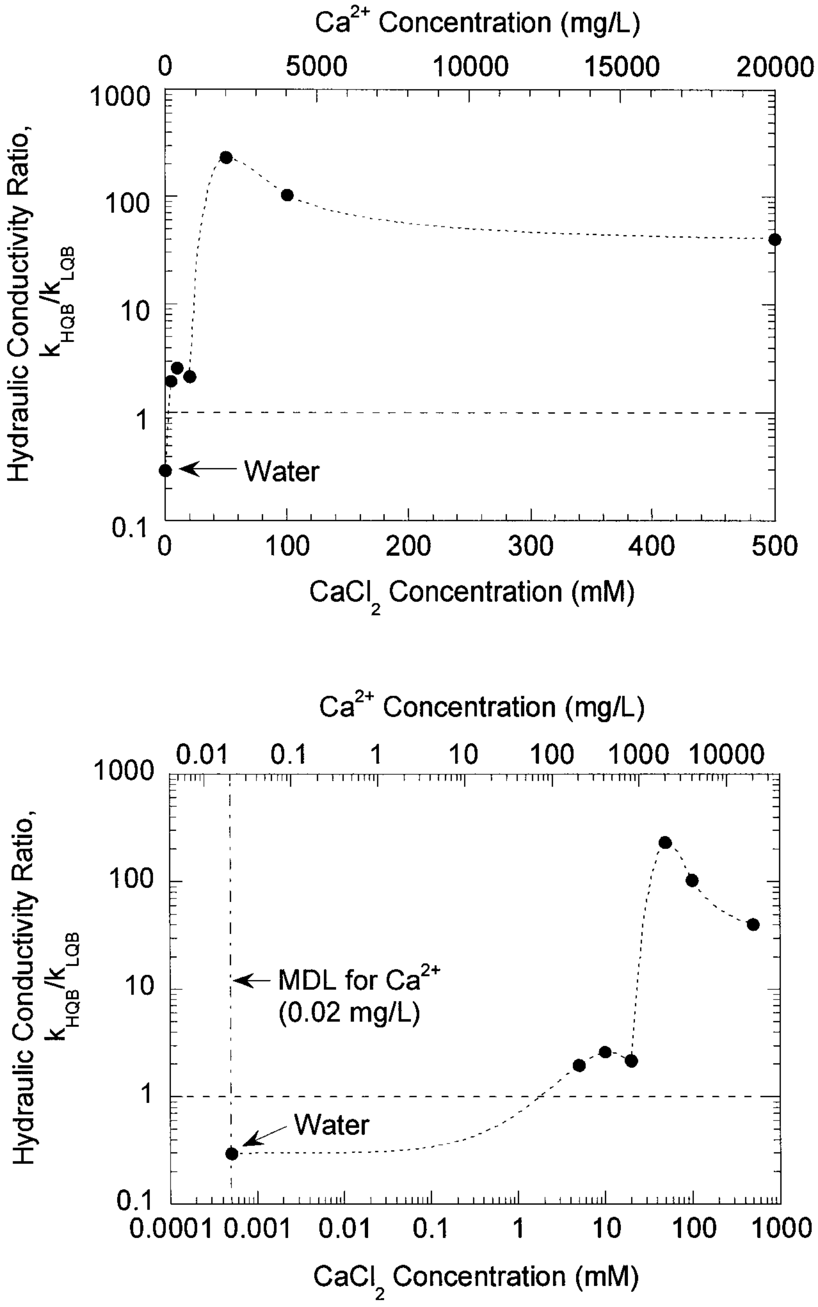

Fig. 4.10 – Ratio of hydraulic conductivity for GCL with higher quality bentonite (HQB) relative to that for GCL with lower quality bentonite (LQB) (MDL = method detection limit).

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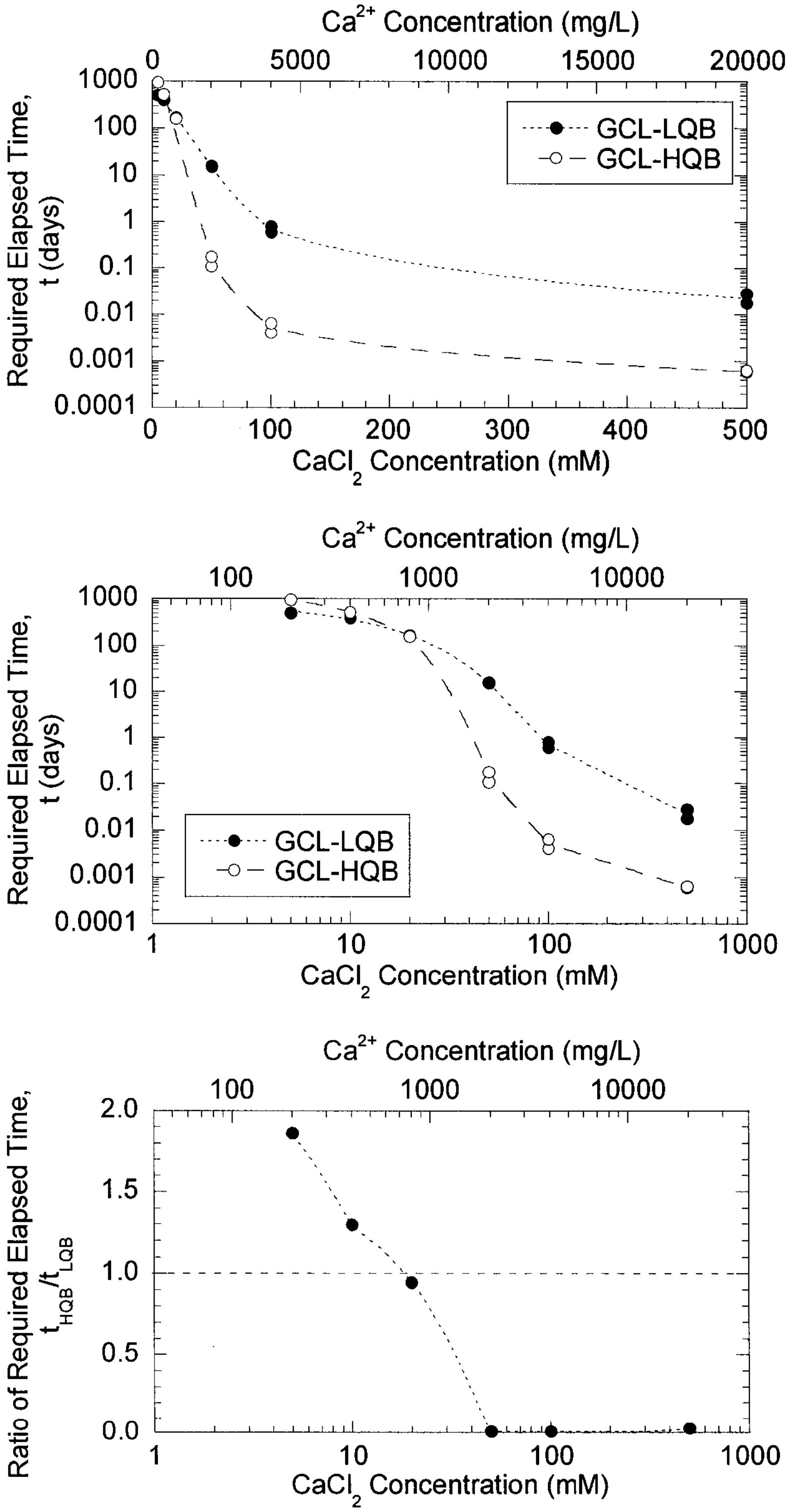

Fig. 4.11 – Elapsed time required to achieve chemical equilibrium for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB).

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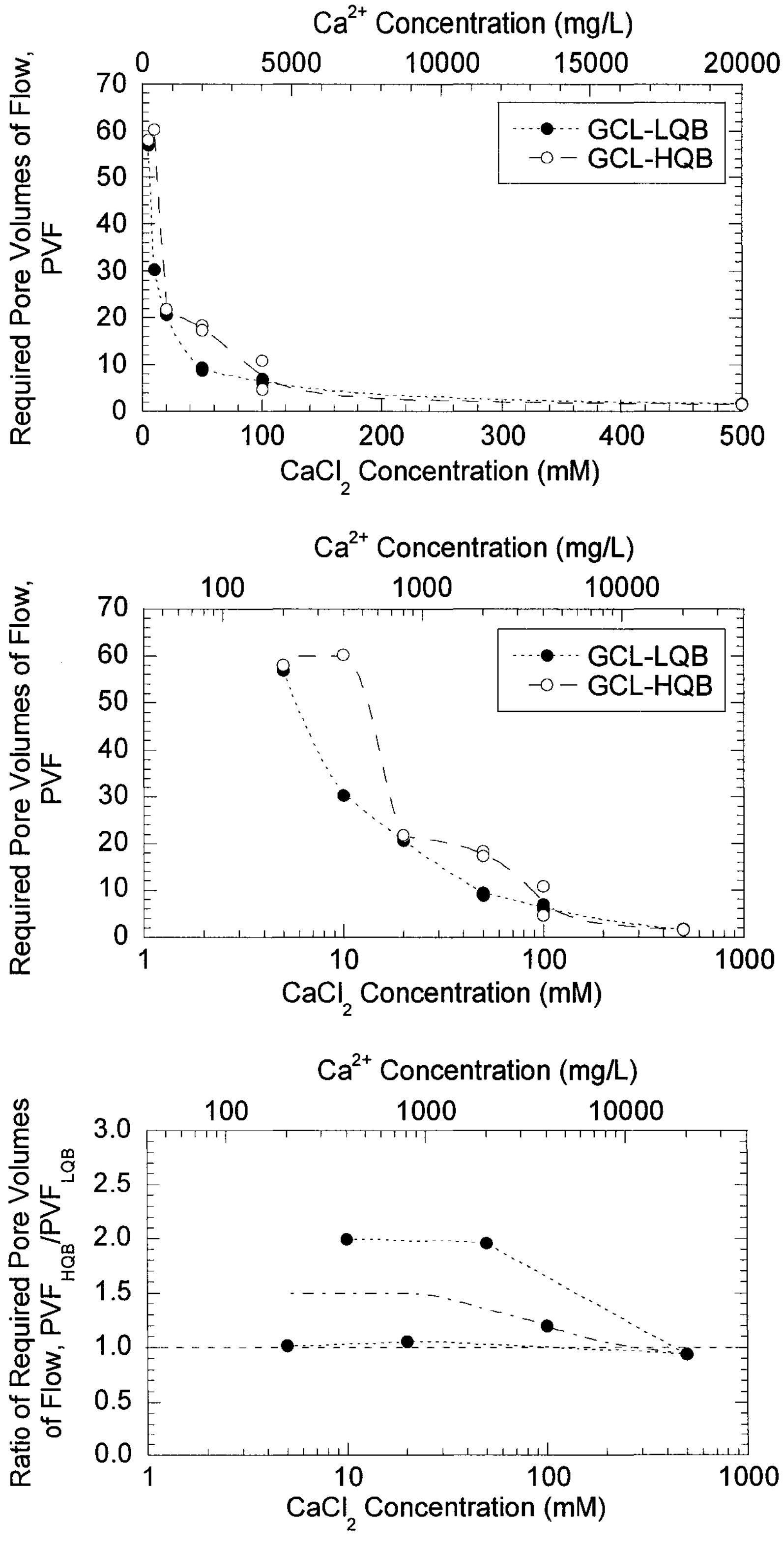

Fig. 4.12 – Pore volumes of flow required to achieve chemical equilibrium for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB).

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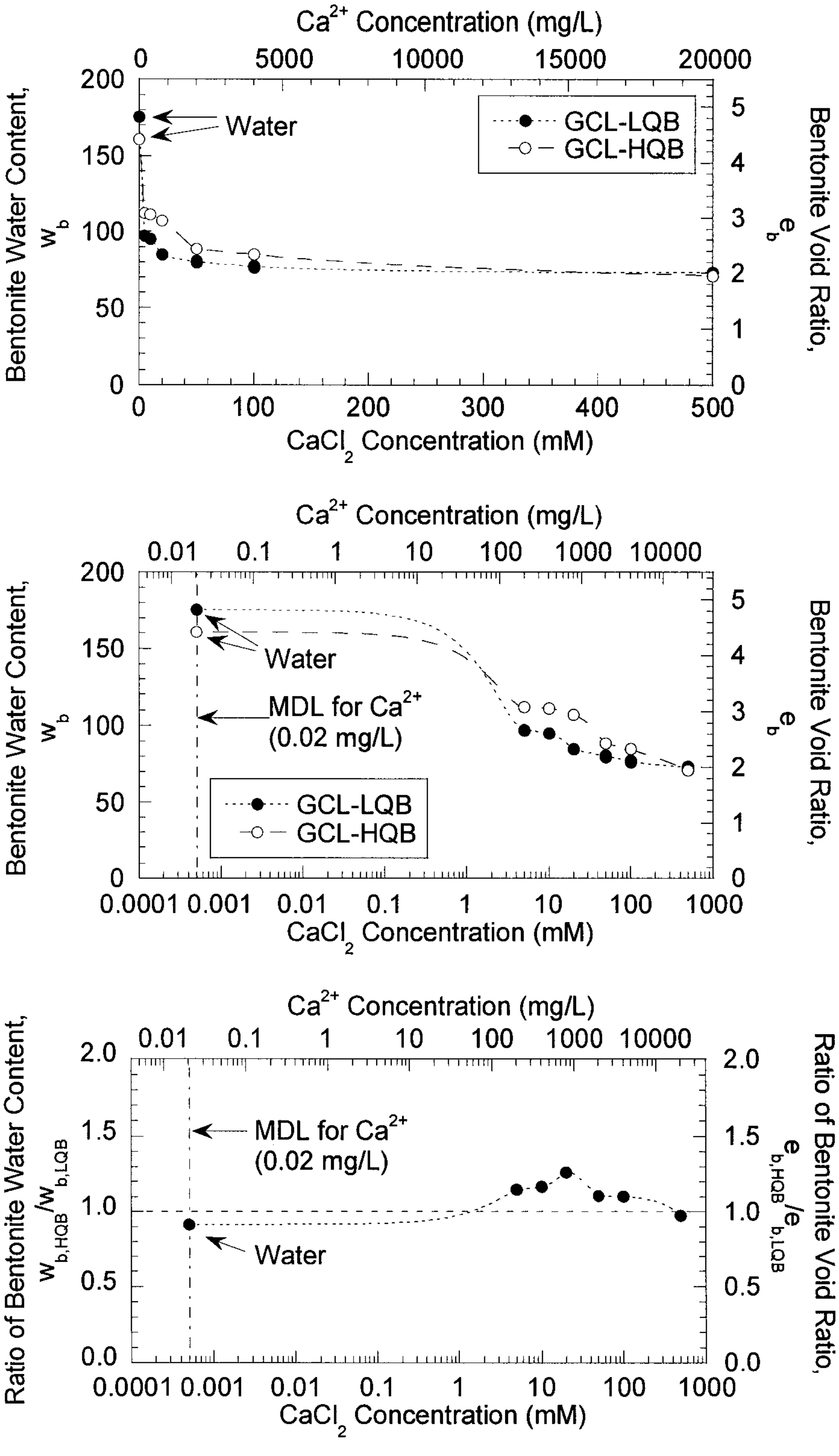

Fig. 4.13 – Final bentonite gravimetric water content and void ratio after permeation for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) (MDL = method detection limit).

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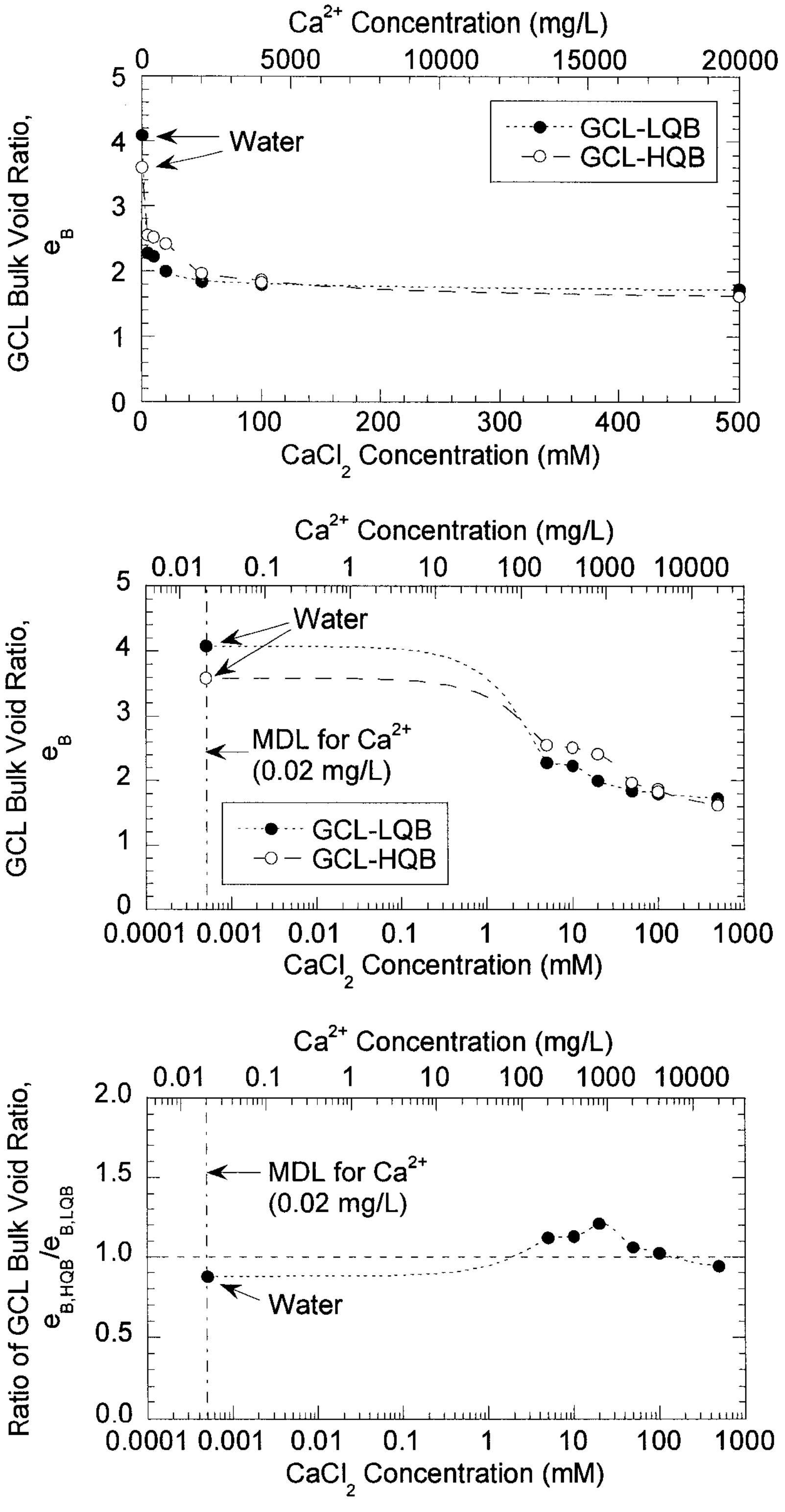

Fig. 4.14 – Final GCL bulk void ratio after permeation for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB) (MDL = method detection limit).

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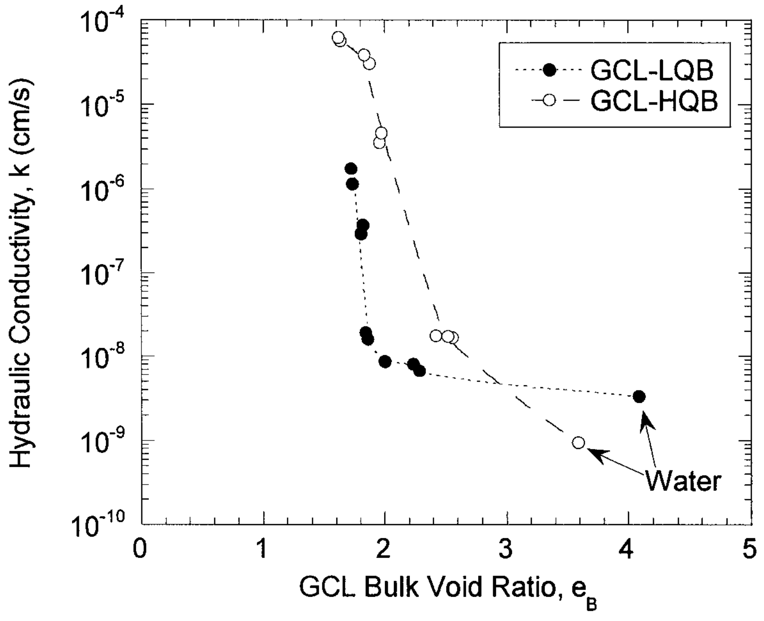

Fig. 4.15 – Final GCL bulk void ratio after permeation versus hydraulic conductivity for specimens of two GCLs with either lower quality bentonite (LQB) or higher quality bentonite (HQB).

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CHAPTER 5

SOLUTION RETENTION CAPACITY AS AN ALTERNATIVE TO THE SWELL INDEX TEST FOR BENTONITE

ABSTRACT: An alternative to the swell index approach (ASTM D 5890) for bentonite referred to as the solution retention capacity (SRC) approach is developed and evaluated. The SRC values for two sodium bentonites measured using deionized water and chemical solutions containing calcium chloride ($CaCl_2$) at concentrations ranging from 5 mM to 500 mM are compared with the swell index values for both bentonites and the same test liquids. In general, both swell index and SRC decrease with increase in $CaCl_2$ concentration due to a decrease in the thickness of adsorbed layer of the bentonite particles. However, the SRC approach has several advantages relative to the swell index approach, including a shorter testing time, minimal potential for bentonite loss and entrapped air bubbles, and greater measurement accuracy. Also, the SRC approach uses only mechanical devices that require less operator judgment resulting in the potential for relatively less operator error. The strong correlation between the SRC and swell index suggests that the SRC approach may be used as an alternative to the swell index approach for qualitatively assessing the potential impact of inorganic salt solutions on the hydraulic conductivity of bentonite-based materials, such as geosynthetic clay liners.

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Key Words: bentonite, geosynthetic clay liners, hydraulic conductivity, swell index

5.1 INTRODUCTION

The high swelling potential of montmorillonite is attributed to adsorption of hydrated cations and water molecules, resulting in strong repulsive forces and interlayer expansion in the presence of electrolyte solutions (Norrish 1954, Mitchell 1993, Shackelford et al. 2000). In the presence of water, sodium montmorillonite can swell to as much as 20 times its own volume (Norrish 1954). The primary factors contributing to the high swelling potential of montmorillonite relative to other clay minerals, such as illite and kaolinite, include a relatively high specific surface (i.e., 100 to 800 m^2/g) and a relatively high net negative charge as reflected by relatively high cation exchange capacities typically ranging from 80 meq/100 g to 150 meq/100 g (Grim 1953, Norrish and Quirk 1954, Mitchell 1993). Since montmorillonite also is the primary mineral in most bentonites (typically 60 % to 90 %), bentonites generally exhibit the same swelling characteristic as montmorillonite. In fact, the low hydraulic conductivity values to water typically measured for sodium bentonites (i.e., 10^{-9} to 10^{-8} cm/s) are attributed to the relatively high swelling potential of the bentonite in the presence of water (Mitchell 1993, Shackelford et al. 2000).

Two methods have been used to determine the swelling behavior of bentonite, i.e., Geosynthetic Research Institute (GRI) GCL-1 (*Free Swell of the Clay Component of Geosynthetic Clay Liners*) (e.g., Narejo and Memon 1995, Lin and Benson 2000) and ASTM D 5890 (*Standard Test Method for Swell Index of Clay Mineral Component of Geosynthetic Clay Liners*) (e.g., Didier and Comeaga 1997, Ruhl and Daniel 1997,

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Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Ashmawy et al 2002, Shan and Lai 2002). The primary differences between these two approaches are the method of hydration (i.e., under a 0.7-kPa confinement for GRI GCL-1 vs. self-weight sedimentation for ASTM D 5890) and the longer equilibrium time required for GRI GCL-1 (i.e., > 400 hrs vs. < 24 hrs) relative to that required for ASTM D 5890 (Lin and Benson 2000, Shackelford et al. 2000, Jo et al. 2001). However, only the approach specified in ASTM D 5890 (i.e., swell index test) is currently accepted as a standard by the industry (Shackelford et al. 2000).

Several studies have shown that the swelling behavior of bentonite is directly correlated with the hydraulic conductivity of bentonite-based GCLs (Egloffstein 1995, Didier and Comeaga 1997, Ruhl and Daniel 1997, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Kashir and Yanful 2001, Ashmawy et al. 2002, Shan and Lai 2002). For example, Shackelford et al. (2000) and Jo et al. (2001) correlate the results of swell index tests on sodium bentonite from a GCL using solutions with various concentrations of several inorganic compounds (e.g., NaCl, $CaCl_2$, and $LaCl_3$) with the hydraulic conductivity of the GCL permeated with the same test solutions. Their results show that a decrease in swell index with increasing electrolyte concentration and/or cation valence is correlated with an increase in hydraulic conductivity of the GCL with increasing electrolyte concentration and/or cation valence. The observed effects are consistent with changes in the thickness of adsorbed layer such that an increase in cationic valence and/or electrolyte concentration reduces the swell index of sodium bentonite. Thus, the results of swell index tests may provide a qualitative indication of the expected hydraulic behavior of bentonite-based materials, thereby providing a relatively simple, rapid, and

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inexpensive method for assessing the compatibility between the bentonite and the permeant liquid (Ruhl and Daniel 1997, Didier and Comeaga 1997, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Ashmawy et al 2002, Shan and Lai 2002). However, the measurement of swell index can be affected by several factors, including inconsistency in the hydration procedure, failure to spread the clay evenly, and friction between the bentonite and the graduated cylinder (Shackelford et al. 2000). In addition to these factors, the procedure for the swell index test is tedious and time-consuming.

As a result, a new approach, referred to as the "solution retention capacity (SRC)", is proposed herein as a potentially less tedious and quicker alternative to the swell index approach for bentonite. The development of the SRC approach is described in this chapter, and the results of SRC tests, using water and solutions containing a range of $CaCl_2$ concentrations with sodium bentonites from two GCLs, are compared with the results of swell index tests for the same bentonites using the same solutions. In addition, several advantages of the SRC approach relative to the swell index testing are discussed.

5.2 MATERIALS AND METHODS

5.2.1 Bentonites

Two granular sodium bentonites were taken from two commercially available geosynthetic clay liners (GCLs). The average gravimetric water content was 4 % in an air-dried condition for both bentonite samples. The physical and chemical properties and the mineralogical compositions for the two bentonites are given in Table 5.1. As shown in Table 5.1, the montmorillonite content for the lower quality bentonite (LQB) is lower than that for the higher quality bentonite (HQB) by ~ 9 % (i.e., 77 % vs. 86 %), resulting

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in a lower cation exchange capacity (i.e., 64 meq/100 g vs. 93 meq/100 g) as well as a lower plasticity index (i.e., 393 % vs. 548 %). Both bentonites have aggregate-size distributions similar to sands (i.e., classified as SP per Unified Soil Classification System [USCS]; ASTM D 2487) based on the mechanical sieve analyses performed on the air-dried samples (ASTM D 421, D 422). However, the bentonites from both GCLs are classified as high-plasticity clays (CH) based on the wet analysis.

5.2.2 Testing Liquids

The liquids used in this study consist of tap water that is processed to remove ions by passage through three Barnstead® ion exchange columns in series (electrical conductivity, EC, at 25 °C ~ 0.2 mS/m, pH ~ 5.6) and inorganic chemical solutions containing a range in calcium chloride ($CaCl_2$) concentrations. The processed tap water classifies as Type IV deionized water (DIW) according to ASTM D 1193. The $CaCl_2$ solutions were prepared by dissolving $CaCl_2$ (powdered, > 96 % pure, Sigma-Aldrich Co., St. Louis, MO) in the DIW at concentrations of 5, 10, 20, 50, 100, and 500 mM. The solute concentrations of the testing liquids were measured using an ion chromatograph (Dionex® 4000i IC Module, Dionex Co., Sunnyvale, CA) for chloride (Cl^-) concentrations and an inductively coupled plasma – atomic emission spectrometer (IRIS® Advantage/1000 ICAP Spectrometer, Thermo Jarrell Ash Co., Franklin, MA) for calcium (Ca^{2+}) concentrations, respectively. The measured solute concentrations for the DIW and $CaCl_2$ solutions are given in Table 5.2. For the DIW, the measured solute concentrations were below the method detection limits (MDLs) of 0.02 mg/L for Ca^{2+} (EPA Method 200.7) and 0.04 mg/L for Cl^- (EPA Method 300.0).

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5.2.3 Swell Index Testing

Materials and Equipment. The primary materials and equipment used to conduct the swell index tests according to ASTM D 5890 are shown in Fig. 5.1a. These materials and equipment include:

- a No. 200 (0.075-mm) U.S. Standard Sieve;
- a mortar and pestle;
- a clean 100-mL graduated cylinder;
- a stainless-steel laboratory scoop; and
- a disposable syringe.

Procedure. Swell index tests were conducted following the procedures described in ASTM D 5890 using both the DIW and $CaCl_2$ solutions. Samples of each bentonite (i.e., LQB or HQB) were prepared by passing the bentonite through the No. 200 U.S. Standard Sieve using the mortar and pestle. First, approximately 90 mL of each testing liquid (i.e., either DIW or one of $CaCl_2$ solutions) was added to the 100-mL graduated cylinder. Then, 2.0 g of oven-dried bentonite taken from the pulverized and sieved bentonite samples were dusted over the entire surface of the testing liquid in the graduated cylinder in increments of less than 0.1 g. Each increment of bentonite was added by tapping the bentonite out of the scoop over a period of approximately 30 seconds, and a standing period after the addition of each increment was a minimum of 10 minutes as required by ASTM D 5890. These requirements result in a minimum duration of 210 minutes (3.5 hrs). However, this minimum duration does not take into account the possibility of longer

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standing periods of > 10 minutes (e.g., due to convenience) or the use of bentonite increments that typically are much less than 0.1 g. As a result, the average time required to add 2.0 g of bentonite in this study was approximately 6 hrs. After the entire bentonite specimen was added, the syringe filled with the same testing liquid was used to rinse any particles adhering to the sides of the cylinder and to fill the cylinder to the 100-mL mark. After 2 hrs, entrapped air bubbles and/or water separation in the sediment, if any, were removed by tipping and rolling the cylinder as per ASTM D 5890. The swell volume of the bentonite in mL/2 g then was measured after an elapsed time of 16 hrs, which is the minimum hydration period required by ASTM D 5890.

5.2.4 Solution Retention Capacity Testing

Materials and Equipment. The primary materials and equipment required for the solution retention capacity (SRC) approach are shown in Fig. 5.1b. These materials and equipment include:

- a clean 50-mL centrifuge tube (polypropylene, capacity of 6000 *g*, Fisher-Scientific Co., Pittsburgh, PA);
- a vortex mixer (Touch Mixer Model 231, Fisher Scientific Co., Pittsburgh, PA);
- a centrifuge (IEC Centra-CL2, Fisher Scientific Co., Pittsburgh, PA); and
- a laboratory mass balance.

Procedure. The SRC represents the volume of a testing liquid retained per 1.0 g of bentonite after centrifugation, which is related to the thickness of adsorbed layer of the bentonite. The SRC tests were conducted using the same liquids and bentonite samples

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used in the swell index tests. In addition, a soil-to-liquid ratio of 1 g/50 mL was used in the SRC tests to be consistent with the soil-to-liquid ratio in the swell index test, which is approximately the same (i.e., 2 g/(100 mL – V_s) ≅ 1 g/50 mL, where V_s = the volume occupied by 2.0 g of bentonite, or ≅ 0.75 mL).

The first step in the SRC approach is to measure the mass of the 50-mL centrifuge tube (M_{tube}). After this measurement, 1.0 g of oven-dried bentonite (M_b) taken from the pulverized and sieved bentonite samples is placed into the tube followed by 50 mL (V_{sol}) of a testing liquid (i.e., either DIW or one of $CaCl_2$ solutions). The centrifuge tube then is shaken vigorously on the vortex mixer for 30 seconds, and then the shaken tube is allowed to stand for at least 16 hrs without operator intervention. After the standing period, the tube is re-shaken using the vortex mixer for 30 seconds. The sample tube then is centrifuged for 30 minutes at 5000 rpm (i.e., acceleration = 2750 *g*). After centrifuging, the supernatant is decanted by tilting the tube, and the total mass of the tube with the remaining plug of hydrated bentonite (M_f) is measured.

For the tests performed with the DIW, the supernatant decanted after centrifugation (i.e., 30 min @ 2750 *g*) was found to contain a visible amount of a gel-like substance. In addition, either suspended particles and/or a fraction of sediment can be lost during the decanting process for the tests performed with $CaCl_2$ solutions. As a result of these considerations, the SRC is defined as follows:

$$\mathrm{SRC} = \left(\frac{M_b}{M_b - M_{b,lost}}\right)\left[\frac{M_f - M_{tube} - \left(M_b - M_{b,lost}\right)}{\rho_{sol}}\right] \tag{5.1}$$

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where SRC = the solution retention capacity per 1.0 g of bentonite in [mL/1 g], ρ_{sol} = the density of the solution (or water) in [g/mL] (see Table 5.2), and $M_{b,lost}$ = the mass of bentonite lost during decanting process. The mass of the bentonite lost ($M_{b,lost}$) can be estimated by measuring the oven-dried mass of the decanted supernatant (M_{dried}) as follows:

$$M_{b,lost} = \left(\frac{\rho_{sol}}{\rho_{sol} - C_s}\right)\left\{M_{dried} - C_s\left[V_{sol} - \left(\frac{M_f - M_{tube} - M_b}{\rho_{sol}}\right)\right]\right\} \tag{5.2}$$

where C_S = the salt concentration of the test liquid in [g/mL] (see Table 5.2).

As shown in Table 5.2, the densities of the test liquids range from 0.997 g/mL (DIW) to 1.027 g/mL (500 mM $CaCl_2$ solution) at the standard state (i.e., 25 °C and 101.325 kPa). Due to this narrow range of densities, the density of solution can be approximated as the density of water (ρ_w) at 4 °C and 101.325 kPa (i.e., $\rho_w = 1.000$ g/mL) with an error of < 3 % (Lide 1991). Thus, the SRC can be written more conveniently as follows:

$$SRC \cong \left(\frac{M_b}{M_b - M_{b,lost}}\right)\left[\frac{M_f - M_{tube} - \left(M_b - M_{b,lost}\right)}{\rho_w}\right] \tag{5.3}$$

The procedure described above does not take into account the change in chemical composition of the bulk solution due to dissolution of the soluble salts originally in the bentonite (see Table 5.1) and/or chemical interaction between the bentonite and the test

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solution. Consequently, the mass of the bentonite lost ($M_{b,lost}$) for the tests performed using DIW as the test liquid is assumed to be equal to the oven-dried mass of the decanted supernatant (M_{dried}), i.e., since the salt concentration for DIW is essentially zero (i.e., $C_s = 0$). Also, the oven-dried mass of the decanted supernatant (M_{dried}) for the tests performed with $CaCl_2$ solutions is assumed to be equal to the bentonite lost during decanting process and the dissolved salts ($CaCl_2$) corresponding to the concentration of the test solution.

The SRC approach as described above has several advantages over the swell index approach, including a shorter testing time (i.e., < 1 hr vs. > 3.5 hrs), minimal potential for loss of bentonite and entrapment of air bubbles, and greater measurement accuracy (i.e., ± 0.01 g for a typical mass balance vs. ± 1.0 mL for a typical 100-mL graduated cylinder). In addition, the SRC approach is potentially less affected by operator error than the swell index approach, because the SRC tests are performed using only mechanical devices that require less operator judgment.

5.3 RESULTS AND DISCUSSION

5.3.1 Swell Index

The results of the swell index tests based on a 16-hr hydration period are shown in Fig. 5.2. Since the measured calcium (Ca^{2+}) concentration for the deionized water (DIW) is below the method detection limit (MDL) of 0.02 mg/L for Ca^{2+} based on 10 independent measurements (see Table 5.2), the MDL is used to represent the Ca^{2+} concentration for the DIW.

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As shown in Fig. 5.2, the swell index value for the lower quality bentonite (LQB) decreases from approximately 27.5 mL/2 g when the DIW is used as the testing liquid to ~ 7.5 mL/2 g when the 500 mM $CaCl_2$ solution is used as the testing liquid. Similarly, the swell index value for the higher quality bentonite (HQB) decreases from approximately 30.0 mL/2 g when the DIW is used as the testing liquid to ~ 7.5 mL/2 g when the 500 mM $CaCl_2$ solution is used as the testing liquid. This decrease in swell index with increasing $CaCl_2$ concentration is consistent with the individual granules of the bentonite becoming smaller due to the compression of the interlayer region induced by the elevated Ca^{2+} concentration in the bulk solution (Sposito 1981, McBride 1994, Shackelford et al. 2000, Jo et al. 2001).

In addition, the swell index based on the DIW is greater by about 2.5 mL/2 g for the HQB relative to the LQB. This difference can be attributed to the higher montmorillonite content of the HQB (see Table 5.1). Also, the swell index for the HQB is greater than that for the LQB by from 3 % to 11 % for the tests performed with solutions containing $CaCl_2$ concentrations $\leq$ 50 mM, with the magnitude in this difference decreasing with increasing $CaCl_2$ concentration. However, the ratio of the swell index of the HQB relative to that of the LQB, or SI_{HQB}/SI_{LQB}, is slightly less than unity (i.e., ~ 0.98) for 100 and 500 mM $CaCl_2$ solutions, indicating that these relatively strong $CaCl_2$ solutions cause more significant alteration in swelling for the higher quality bentonite (HQB) relative to the lower quality bentonite (LQB).

The values for the ratio of the swell index based on either water (DIW) or one of $CaCl_2$ solutions to that based on water, or SI/SI_w, are shown in Fig. 5.3. For both bentonites, the swell indexes based on hydration with the 5 mM $CaCl_2$ solution are

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comparable, albeit slightly lower (< 2 %), to those based on the DIW, whereas a further increase in the $CaCl_2$ concentration of the testing liquids results in a relatively significant decrease (i.e., from 30 % to 75 %) in SI/SI_w. However, the change in the SI/SI_w is greater for the HQB relative to the LQB, indicating that the swelling of the HQB is affected to a greater extent than that of the LQB as the concentration of $CaCl_2$ in the testing liquid increases.

5.3.2 Solution Retention Capacity

The results of the solution retention capacity (SRC) tests performed on the two bentonites with the DIW and $CaCl_2$ solutions are shown in Figs. 5.4 and 5.5. For the tests performed with $CaCl_2$ solutions, no loss of bentonite was observed during decanting process (i.e., $M_{b,lost} = 0$), allowing calculation of the SRC with the following reduced form of Eq. 5.3:

$$\mathrm{SRC} \cong \frac{M_f - M_{tube} - M_b}{\rho_w} \tag{5.4}$$

As shown in Fig. 5.4, the SRC values for the lower quality bentonite (LQB) decreased from ~ 5.7 mL/1 g to ~ 1.8 mL/1 g with increase in $CaCl_2$ concentration in the testing liquid from 0 (DIW) to 500 mM. Similarly, the SRC values for the higher quality bentonite (HQB) decreased from ~ 7.2 mL/1 g to ~ 1.7 mL/1 g with increase in $CaCl_2$ concentration in the testing liquid from 0 (DIW) to 500 mM. In fact, the SRC values for the HQB are greater than those for the LQB by approximately 1.4 mL/ g for the tests performed with the DIW and 5 mM $CaCl_2$ solution. Similarly, but to a lesser extent, the

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SRC values for the HQB are about 11 % higher than the SRC values for the LQB based on the tests performed with the 10 mM $CaCl_2$ solution. However, the SRC ratio based on two bentonites (i.e., SRC_{HQB}/SRC_{LQB}) was slightly less than unity (i.e., 0.96 to 0.98) for the solutions with $CaCl_2$ concentrations ranging from 20 mM to 500 mM. These results are similar to the results of swell index tests such that the relatively strong (i.e., 100 and 500 mM) $CaCl_2$ solutions result in more significant decreases in the thickness of adsorbed layer of the HQB relative to the LQB.

On the other hand, the values for the ratio of the SRC based on either water (DIW) or one of $CaCl_2$ solutions to that based on water, or SRC/SRC_w, decreased significantly from unity to between 0.51 and 0.58 with increase in $CaCl_2$ concentration in the testing liquid from 0 (DIW) to 5 mM. Thereafter, the SRC/SRC_w values continued to decrease with a further increase in $CaCl_2$ concentration, but to a lesser extent. However, the SRC/SRC_w value for the HQB is always slightly lower than that for the LQB by 0.05 to 0.09 based on the tests performed with $CaCl_2$ solutions, except for the tests performed with the 5 mM $CaCl_2$ solution. In fact, the SRC/SRC_w for the HQB is slightly higher (i.e., by ~ 0.09) than that for the LQB for the tests performed with the 5 mM $CaCl_2$ solution. Therefore, the 5 mM $CaCl_2$ concentration probably was not sufficiently strong to result in a significant decrease in the thickness of adsorbed layer of the higher quality bentonite (HQB) relative to the lower quality bentonite (LQB). In general, the greater change observed in the SRC/SRC_w with increasing $CaCl_2$ concentration for the HQB relative to the LQB is similar to the trends for the swell index tests, such that that the thickness of adsorbed layer of the HQB is affected to a greater extent than that for the LQB as the concentration of $CaCl_2$ in the testing liquid increases.

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5.3.3 Swell Index versus Solution Retention Capacity

The SRC and swell index values are plotted as a function of $CaCl_2$ concentration of the testing liquids in Fig. 5.6. For both LQB and HQB, the swell index values for the tests performed with the DIW are comparable to the swell index values for the tests performed with the 5 mM $CaCl_2$ solution, whereas the SRC values for the tests performed with the DIW are approximately two times greater than the SRC values for the tests performed with the 5 mM $CaCl_2$ solution. This significant difference between swell index and SRC based on the tests performed with the DIW and 5 mM $CaCl_2$ solution likely is due to the difference in the testing procedure, i.e., self-weight sedimentation at the acceleration of gravity (i.e., 1 *g*) for the swell index testing versus centrifugation at an acceleration of 2750 *g* for the SRC testing. However, when the tests are performed with $CaCl_2$ solutions, the trends in both the SRC and swell index with $CaCl_2$ concentration are in close agreement for both bentonites, as shown in Fig. 5.6. A linear regression on SRC-versus-swell index plot as shown in Fig. 5.7 results in the coefficient of determination (r^2) close to unity (i.e., 0.958 and 0.970 for LQB and HQB, respectively), supporting a strong correlation between swell index and SRC, particularly in the case where the testing liquid is a $CaCl_2$ solution as opposed to DIW. The strong correlation between the SRC and swell index suggests that the SRC approach may be used as an alternative to the swell index approach when assessing qualitatively the potential impact of inorganic salt solutions on the hydraulic conductivity of bentonite-based materials, such as geosynthetic clay liners.

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5.4 CONCLUSIONS

A "solution retention capacity (SRC)" approach was developed and evaluated as an alternative to the swell index (SI) approach (ASTM D 5890) for the bentonite. Both SI and SRC tests were performed on samples from two different bentonites using deionized water (DIW) and chemical solutions containing 5 mM to 500 mM $CaCl_2$. The results show a decrease in both SI and SRC with increasing $CaCl_2$ concentration of the testing liquids. This decrease in both SI and SRC is consistent with the individual granules of the bentonite becoming smaller with increasing $CaCl_2$ concentration due to the compression in the thickness of adsorbed layer of the bentonite. Also, the relatively strong (i.e., 100 and 500 mM) $CaCl_2$ solutions can cause more significant decrease in the thickness of adsorbed layer of the higher quality bentonite than the lower quality bentonite. On the other hand, the SI values for the tests performed with the DIW are equivalent to the SI values for the tests performed with the 5 mM $CaCl_2$ solution, whereas the SRC values for the tests performed with the DIW are approximately two times greater than the SRC values for the tests performed with the 5 mM $CaCl_2$ solution. However, when the tests are performed with $CaCl_2$ solutions, the trend in SRC with increasing $CaCl_2$ concentration is in good agreement with that for the SI.

The proposed SRC approach has several advantages over the SI approach, including a shorter testing time (i.e., < 1 hr vs. > 3.5 hrs), minimal potential for bentonite loss and entrapped air bubbles, and greater measurement accuracy (i.e., ± 0.01 g vs. ± 1.0 mL). In addition, the SRC approach is less susceptible to operator error than the SI approach, because the SRC tests are performed using only mechanical devices that require less operator judgment. Therefore, on the basis of these advantages and the strong

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correlation between SRC and SI, the SRC approach may be a more useful alternative to the SI approach in terms of evaluating the potential impact of inorganic salt solutions on the behavior of bentonite.

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Table 5.1 – Properties of two bentonites used in this study.

Property	Standard	Average Value or Type [Number of Trials]	
		LQB[e]	HQB[e]
Specific Gravity	ASTM D 854[a]	2.74 [3]	2.78 [2]
Soil Classification:	ASTM D 2487		
Sieve Analysis (Air-Dried)		SP [3]	SP [1]
Hydrometer		CH [7]	CH [1]
Atterberg Limits (%):	ASTM D 4318	[1]	[1]
Liquid Limit, LL		430	589
Plasticity Index, PI		393	548
Principal Minerals (%):	b	[3]	[2]
Montmorillonite		77.2	86.0
Cristobalite		10.3	4.5
Plagioclase Feldspar		5.1	2.5
Quartz		3.4	3.5
Others		4.0	3.5
Cation Exchange Capacity, CEC (meq/100 g)	c	63.9 [3]	93.4 [2]
Exchangeable Metals (meq/100 g):	c	[3]	[2]
Ca^{2+}		11.5	15.3
Mg^{2+}		3.7	7.0
Na^{+}		45.8	69.0
K^{+}		0.7	0.8
Sum		61.7	92.1
Soluble Metals (mg/kg):	c, d	[3]	[2]
Ca^{2+}		218	737
Mg^{2+}		24	160
Na^{+}		3365	7107
K^{+}		48	216

[a] Using a magnetic stirring device for de-airing.

[b] Based on X-ray diffraction (XRD) analyses performed by Mineralogy Inc., Tulsa, OK and GeoServices Inc., Argyle, TX.

[c] Based on procedures described in Shackelford and Redmond (1995).

[d] Measured from a 1 g:20 mL clay-water extract.

[e] LQB = lower quality bentonite; HQB = higher quality bentonite.

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Table 5.2 - Properties of liquids used in this study.

Liquid	Target Concentration (mM)	Number of Analyses	Measured Salt Concentration, C_s		Measured Solute Concentrations (mg/L)		Density[a], ρ_{sol} (g/mL)
			(mM)	(g/L)	Calcium (Ca^{2+})	Chloride (Cl^-)	
DIW[b]	0	10	< 0.0005[c]	0.000	< 0.02[c]	< 0.04[c]	0.9970
$CaCl_2$ (Sigma Co., 96 %)	5	14	5.1 ± 0.2	0.566	216 ± 10	377 ± 38	0.9974
	10	13	10.1 ± 0.2	1.12	436 ± 30	756 ± 65	0.9976
	20	13	20.1 ± 0.6	2.23	872 ± 77	1457 ± 110	0.9982
	50	9	50.7 ± 1.4	5.63	2055 ± 63	3548 ± 69	1.0001
	100	6	100 ± 2.6	11.1	4072 ± 126	7030 ± 95	1.0030
	500	5	505 ± 10	56.0	20289 ± 474	35755 ± 710	1.0271

[a] Calculated value at the standard state, i.e., 25 °C and 101.325 kPa (Lide 1991).

[b] Deionized water.

[c] Method detection limits (MDLs).

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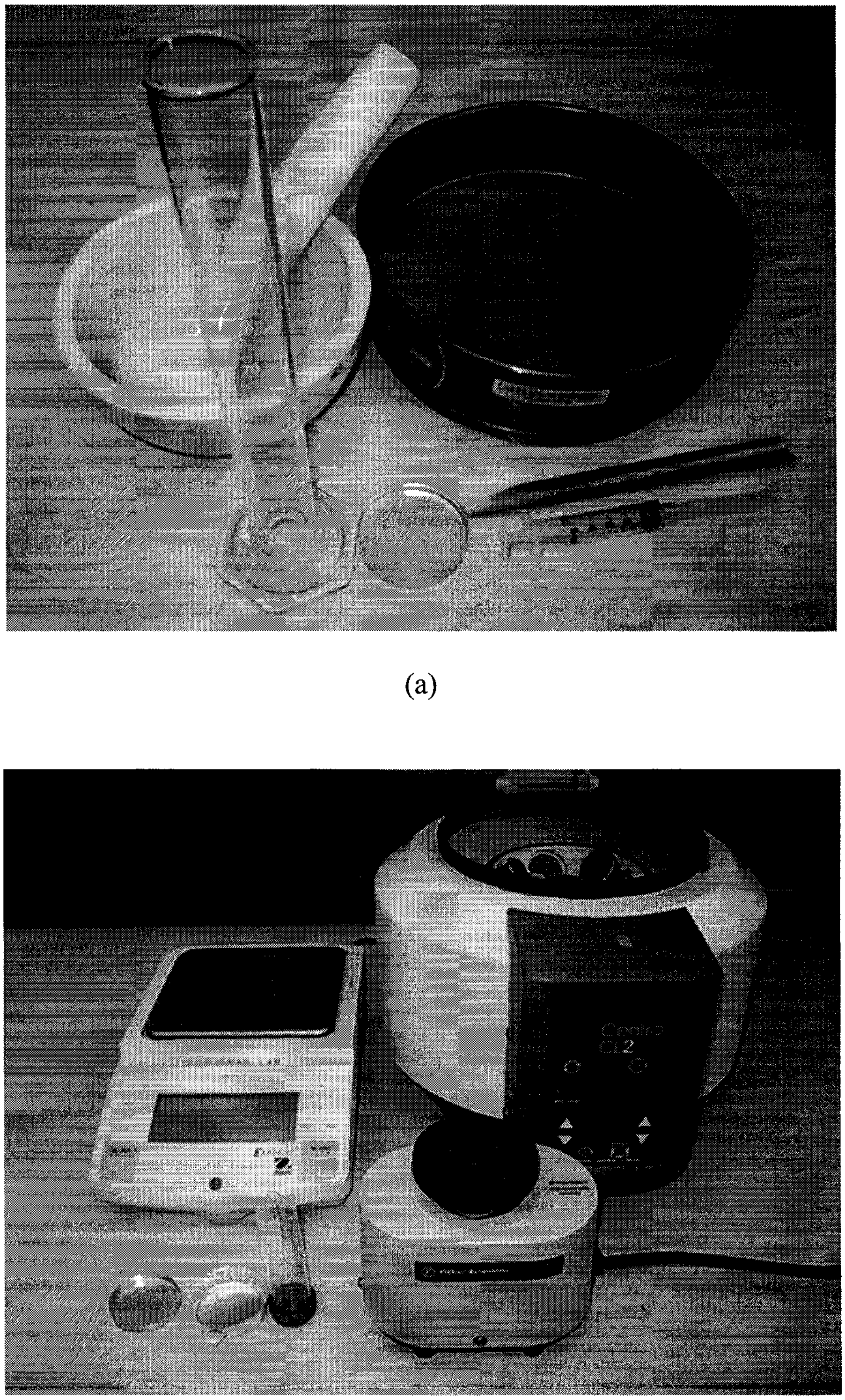

(a)

(b)

Fig. 5.1 – Pictorial view of testing apparatus: (a) swell index tests; and (b) solution retention capacity tests.

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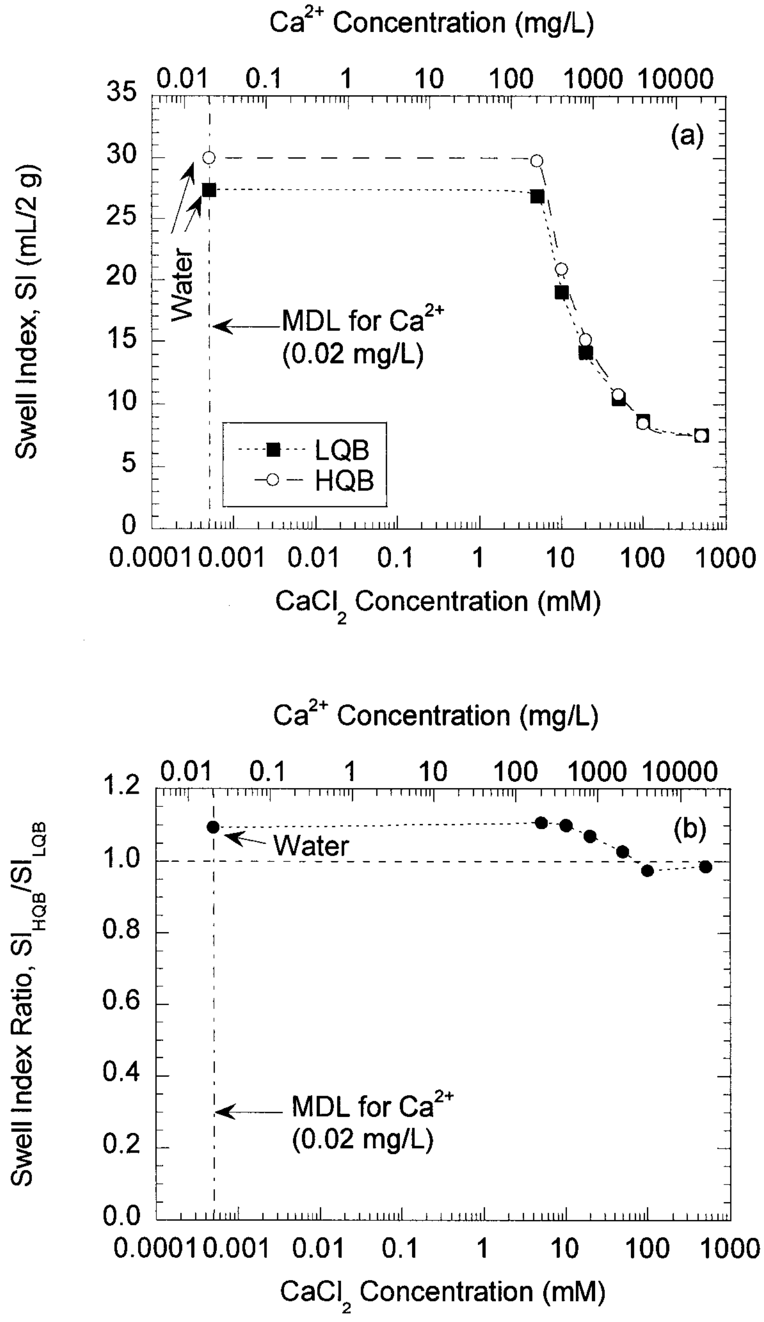

Fig. 5.2 – Results of swell index (SI) tests performed with water and $CaCl_2$ solutions: (a) SI values; and (b) ratio of SI for higher quality bentonite (HQB) to SI for lower quality bentonite (LQB) (MDL = method detection limit).

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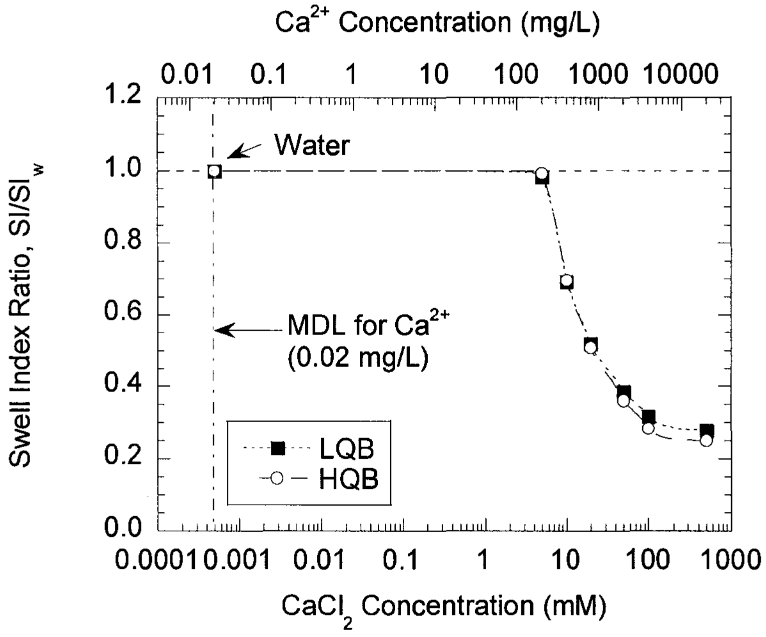

Fig. 5.3 – Ratio of swell index (SI) based on either water or one of $CaCl_2$ solutions to SI based on water (LQB = lower quality bentonite; HQB = higher quality bentonite; MDL = method detection limit).

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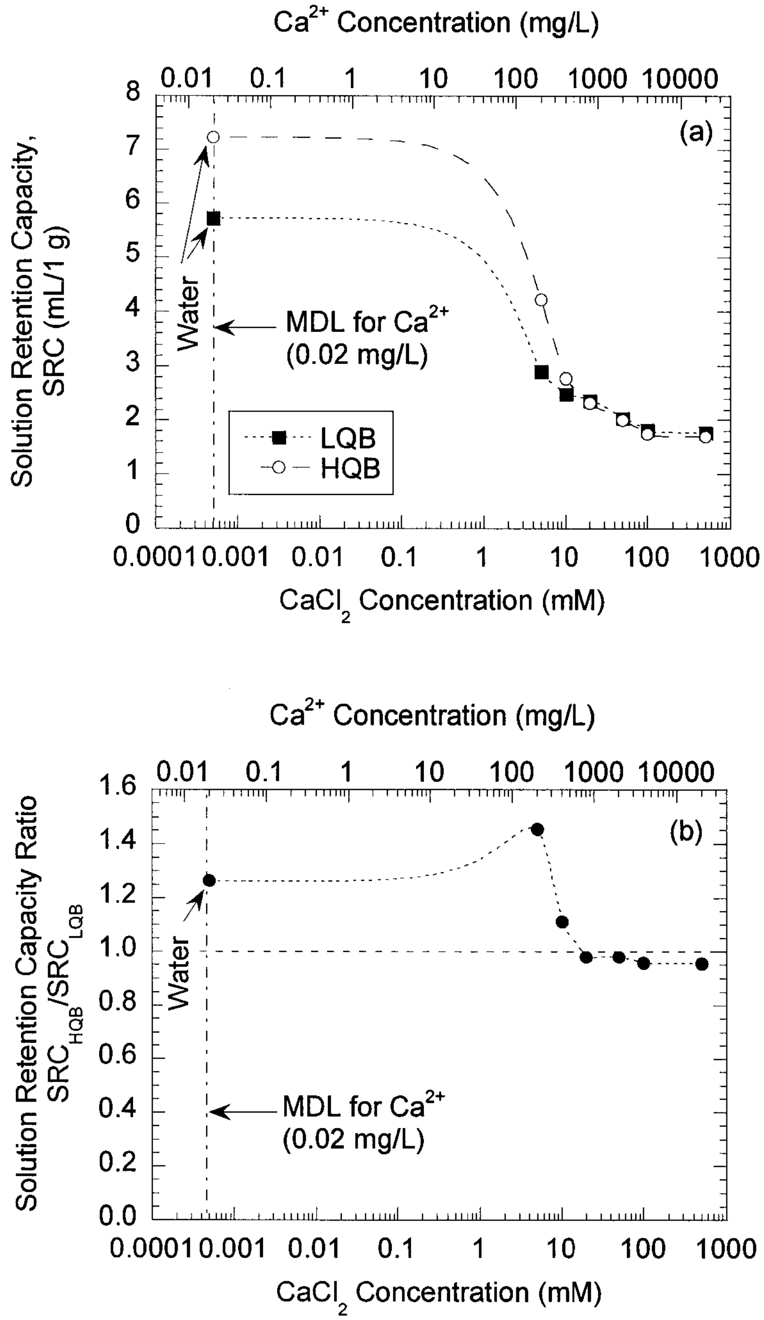

Fig. 5.4 – Results of solution retention capacity (SRC) tests performed with water and $CaCl_2$ solutions: (a) SRC values; and (b) ratio of SRC for higher quality bentonite (HQB) to SRC for lower quality bentonite (LQB) (MDL = method detection limit)

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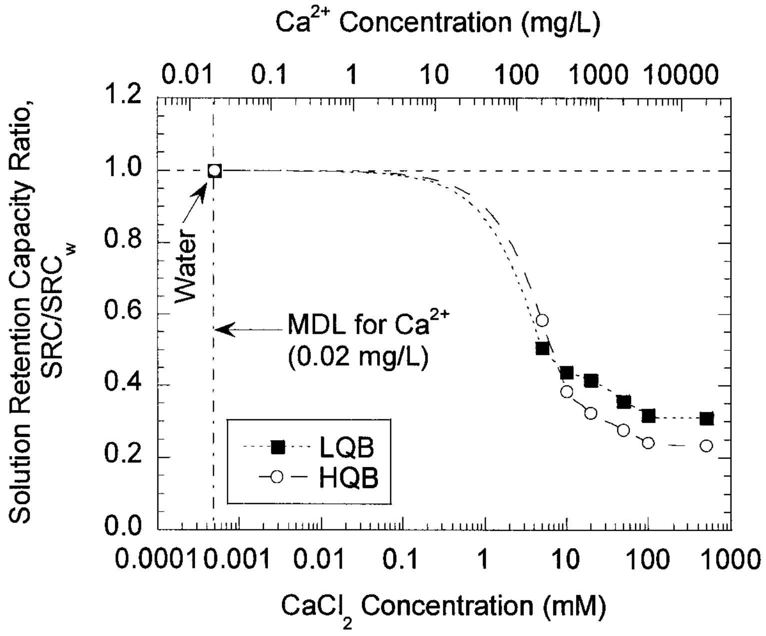

Fig. 5.5 – Ratio of solution retention capacity (SRC) based on either water or one of $CaCl_2$ solutions to SRC based on water (LQB = lower quality bentonite; HQB = higher quality bentonite; MDL = method detection limit).

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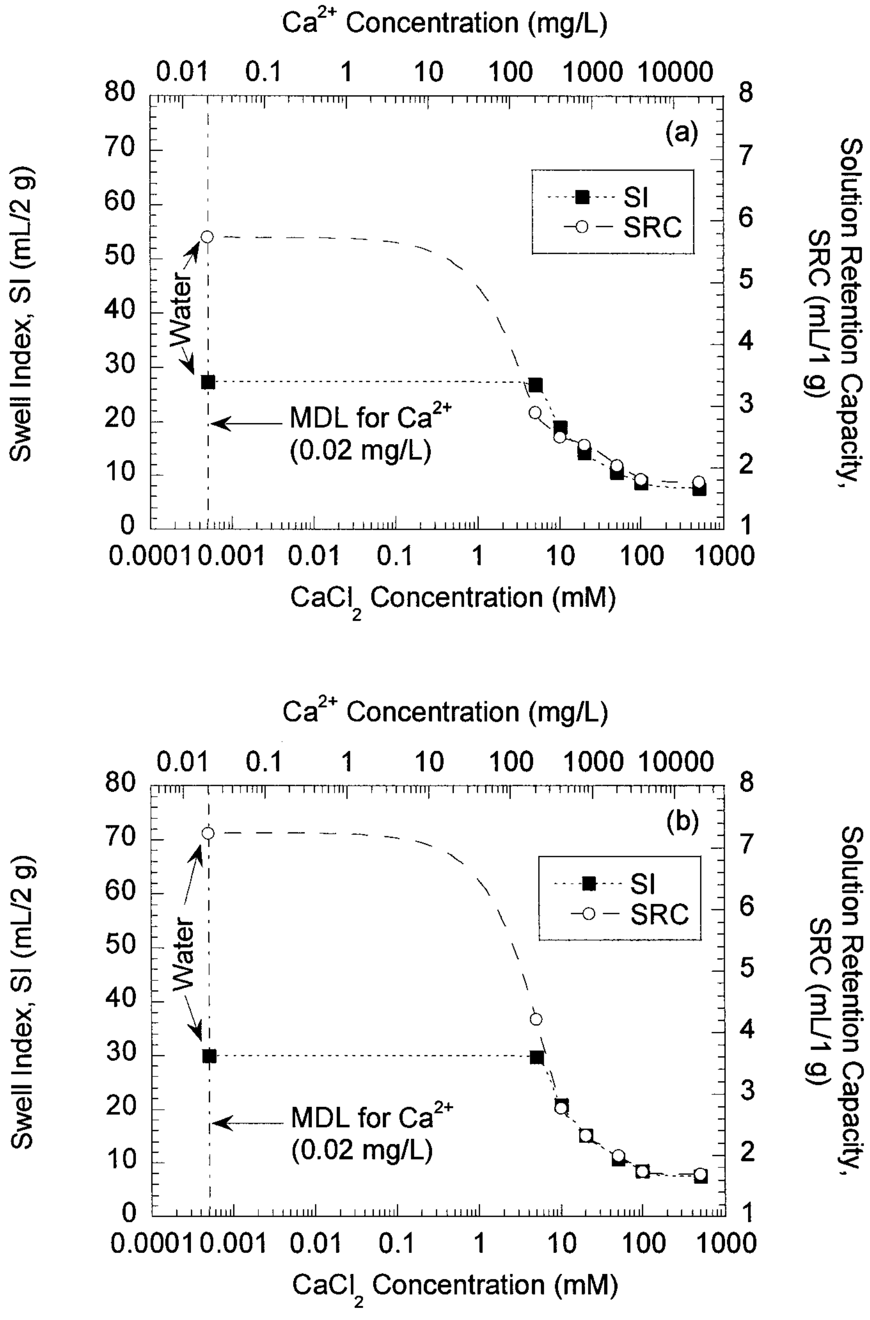

Fig. 5.6 – Comparison between swell index (SI) and solution retention capacity (SRC) based on the tests performed with water and $CaCl_2$ solutions: (a) lower quality bentonite (LQB); and (b) higher quality bentonite (HQB) (MDL = method detection limit).

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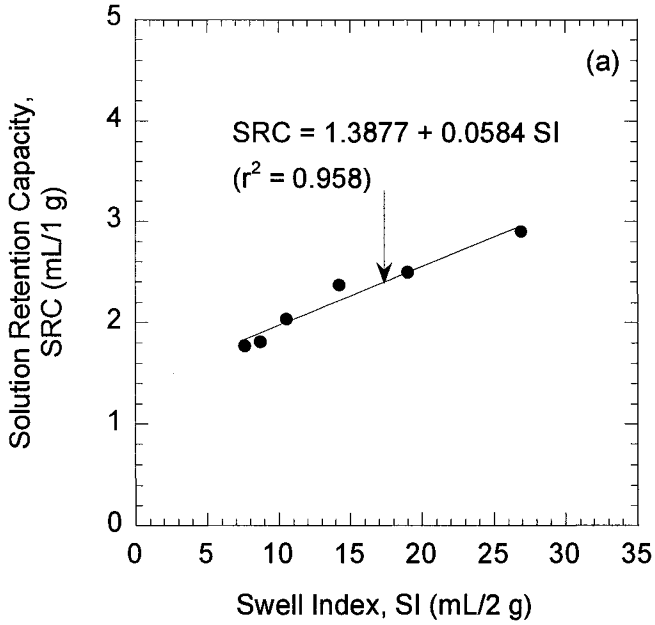

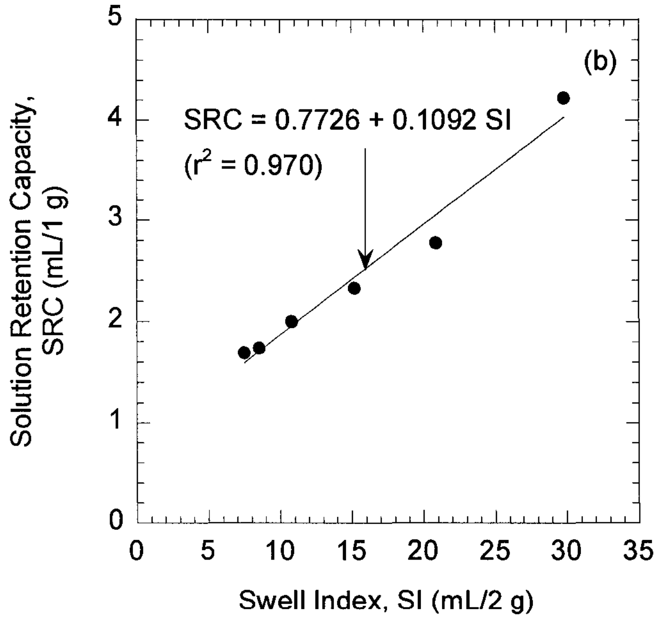

Fig. 5.7 – Correlation between swell index (SI) and solution retention capacity (SRC) based on the tests performed with only $CaCl_2$ solutions: (a) lower quality bentonite (LQB); and (b) higher quality bentonite (HQB).

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CHAPTER 6

CORRELATING INDEX PROPERTIES AND HYDRAULIC CONDUCTIVITY OF GOESYNTHETIC CLAY LINERS

ABSTRACT: The results of four index properties, including the liquid limit (LL), sedimentation volume (SV), swell index (SI), and solution retention capacity (SRC), for two sodium bentonites from geosynthetic clay liners (GCLs) using both water and calcium chloride ($CaCl_2$) solutions are correlated with the hydraulic conductivity (k) of the same GCLs permeated with the same solutions. For the GCL with the lower quality bentonite, 10-fold and 100-fold increases in k based on permeation with $CaCl_2$ solutions relative to water correlate with ≥ 39 % and ≥ 48 % decreases in any index property, respectively, for the same $CaCl_2$ solutions relative to water. However, for the GCL with the higher quality bentonite, LL, SV, and SI decrease by ≤ 3 % when the same $CaCl_2$ solution that results in a 10-fold increase in k relative to water is used, whereas the $CaCl_2$ solution that causes a 100-fold increase in k also causes a ≥ 31 % decrease in any index property. Thus, the correlation between a change in index property and a change in k is a function of the magnitude of the change in k being considered (i.e., 10-fold or 100-fold), the index property, and the bentonite quality. Consequently, compatibility in the index property of bentonites from GCLs does not always correlate well with compatibility in the hydraulic performance of the GCLs.

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Key Words: bentonite, geosynthetic clay liners, hydraulic conductivities, index properties, compatibility

6.1 INTRODUCTION

The hydraulic performance of soil barriers (e.g., compacted clay liners, geosynthetic clay liners, and soil-bentonite vertical cutoff walls) used to contain potentially hazardous liquids (e.g., landfill leachate and polluted ground water) depends primarily on the hydraulic conductivity of the barrier to the liquid being contained. As a result, hydraulic conductivity testing of the soil barrier material using the actual liquid to be contained (or a suitable representative of the actual liquid) as the permeant liquid may be inevitable to evaluate the hydraulic performance of the soil barrier. These tests often are referred to as compatibility tests, because the primary objective of the test is to determine whether or not the barrier soil is compatible with the permeating liquid with respect to the hydraulic conductivity of the soil (Shackelford 1994, Shackelford et al. 2000). In some cases, interactions between the constituents in the permeating liquid (e.g., solutes) and the soil can result in significant increases (> 10X) in the hydraulic conductivity of the soil relative to that based on water (Daniel et al. 1993, Immamura et al. 1996, Gleason et al. 1997, James et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001).

Several investigators have noted the need to perform compatibility tests until complete chemical equilibrium between the effluent and influent has been established in

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order to ensure that all possible interactions between the permeating liquid and the soil have occurred (e.g., Bowders and Daniel 1987, Daniel 1994, Shackelford 1994, Shackelford et al 2000). Unfortunately, due to the low hydraulic conductivity typically required for barrier soils (i.e., ≤ 10^{-7} cm/s), the test durations required to achieve chemical equilibrium may result in several months or even years, depending on the hydraulic gradient (e.g., Dobras and Elzea 1993, Daniel 1994, Imamura et al. 1996, James et al. 1997, Shackelford et al. 2000, Egloffstein 2001, Melchior 2002). Therefore, compatibility testing often is considered prohibitive from the standpoint of the timeliness typically imperative in engineering practice. As a result, an alternative approach has been proposed whereby changes in the index properties of the barrier soil (e.g., Atterberg limits, particle size, etc.) in the presence of the containment liquids relative to water are used as a qualitative, yet more rapid, indicators of the potential for incompatibility with respect to hydraulic conductivity (Dunn and Mitchell 1984, Bowders 1985, Bowders et al. 1986, Bowders and Daniel 1987, Daniel et al. 1988, Acar and Olivieri 1989, Shackelford 1994, Narejo and Memon 1995, Shackelford et al. 2000, Jo et al. 2001).

For example, the results of liquid limit tests based on non-standard liquids (i.e., liquids other than water) relative to those based on water have been used to provide a qualitative indication of the potential effect of the liquid on the hydraulic conductivity of the soil (Bowders et al. 1986, Sridharan et al. 1986, Daniel et al. 1988, Acar and Olivieri 1989, Shackelford 1994, Gleason et al. 1997, Petrov and Rowe 1997, Lin and Benson 2000, Sridharan and Prakash 2000). In general, the results of these studies show that an increase in cationic valence and/or electrolyte concentration (e.g., inorganic liquids) or a decrease in dielectric constant (e.g., organic liquids) reduces the liquid limit and increases

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the hydraulic conductivity of the soils, with greater effects being discerned for soils containing higher activity clays, such as bentonite.

For example, Petrov and Rowe (1997) showed that the liquid limit of bentonite decreased from 530 % to 96 % as the sodium chloride (NaCl) concentration of the testing solutions changed from 0 (i.e., water) to 2.0 M, whereas the hydraulic conductivity values increased from ~ 10^{-9} cm/s to ~ 10^{-6} cm/s for the same range in NaCl concentrations. Thus, a relatively high activity clay that suffers a decrease in the liquid limit in the presence of a non-standard liquid relative to that measured using water also likely would shrink upon permeation with the liquid resulting in a concomitant increase in hydraulic conductivity (Bowders et al. 1986, Shackelford 1994).

In some cases, sedimentation tests have been performed to discern the effects of non-standard liquids on the sedimentation rate of clayey soils as an indirect indication of the potential for the non-standard liquid to adversely affect the hydraulic conductivity of the soil (Dunn and Mitchell 1984, Bowders 1985, Bowders et al. 1986, Bowders and Daniel 1987, Ryan 1987, Shackelford 1994). These tests typically are similar to hydrometer tests (i.e., ASTM D 422), except the non-standard liquid is used instead of water, with or without a dispersing agent. Also, the settling behavior typically is determined either by measuring the particle-size distribution using a hydrometer (e.g., Dunn and Mitchell 1984), or by measuring the sedimentation volume as a function of time (e.g., Bowders 1985, Bowders et al. 1986, Bowders and Daniel 1987, Shackelford 1994). Measurement of the sedimentation volume is more common in the case of high swelling soils, such as bentonite, because the extensive swelling of these soils inhibits the displacement of the suspension by the hydrometer (Shackelford 1994).

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For example, Dunn and Mitchell (1984) performed hydrometer tests as well as hydraulic conductivity tests on two silty clay soils using both water and a synthetic acidic lead-zinc tailings leachate, and found that the waste leachate caused larger particle sizes, presumably due to flocculation, relative to those based on water as well as significant increases (> 10X) in the hydraulic conductivity of the two soils relative to permeation with water. Similarly, Bowders et al. (1986) found that an increase in methanol concentration of testing solutions also caused more rapid settling of both kaolinite and illite-chlorite soils relative to that observed using water, as well as increases in the hydraulic conductivity of the two soils at relatively high concentrations (≥ 80 % by volume). Similar results were reported by Ryan (1987), who measured the settlement of particles of two bentonites being considered for use in a soil-bentonite vertical cutoff wall using both water and a waste leachate containing several organic solvents. Ryan (1987) concluded that an increase in particle size or an increased rate of settling was consistent with the existence of a flocculated fabric corresponding to the potential for a higher hydraulic conductivity upon permeation with the waste leachate relative to permeation with water.

Several studies also have shown that the swell index of bentonite is directly correlated with the hydraulic behavior of bentonite-based GCLs (Didier and Comeaga 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Shan and Lai 2002). For example, Shackelford et al. (2000) and Jo et al. (2001) show that the results of swell index tests on sodium bentonite from a GCL using solutions with various concentrations of several inorganic compounds (e.g., NaCl, $CaCl_2$, and $LaCl_3$) are consistent with changes in the thickness of the adsorbed layer of

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cations such that an increase in cationic valence and/or electrolyte concentration reduces the swell index of sodium bentonite. They also showed that the hydraulic conductivity of the same GCL increased upon permeation with stronger electrolyte solutions (i.e., higher cationic valence and/or electrolyte concentration). A comparison of these results led to the conclusion that a decrease in swell index is correlated with an increase in hydraulic conductivity, with greater decreases in swell index correlated with greater increases in hydraulic conductivity.

Based on the aforementioned studies, the results of index tests may provide a qualitative indication of the expected hydraulic behavior of clay barrier materials, thereby providing a relatively simple, rapid, and inexpensive method for assessing the potential use of a variety of materials. As a result, the objective of this study is to evaluate the use of modified index properties (i.e., index properties based on use of testing liquids other than water) as indirect indicators of the long-term hydraulic compatibility of GCLs in the presence of inorganic solutions containing a range of calcium chloride ($CaCl_2$) concentrations. This objective is achieved by comparing the results of several index property measurements, including the liquid limit, sedimentation volume, swell index, and "solution retention capacity (SRC)" (see Chapter 5), using solutions containing a range of $CaCl_2$ concentrations with the sodium bentonite taken from two GCLs, with measured hydraulic conductivities of the same GCLs permeated with the same solutions. In addition, the comparison between swell indexes and hydraulic conductivities for one GCL is extended to the results of tests conducted collaboratively by Colorado State University (CSU) and the University of Wisconsin - Madison (UW).

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6.2 MATERIALS AND METHODS

6.2.1 Geosynthetic Clay Liners

Two geosynthetic clay liners (GCLs) containing bentonite with different montmorillonite contents were used in this study. Both GCLs consist of a thin layer of granular sodium bentonite sandwiched between two polypropylene geotextiles held together by needle-punched fibers. Both GCLs are ~ 6-mm thick in the air-dried condition, and the average gravimetric water contents of bentonites are ~ 4 %. The physical and chemical properties and the mineralogical compositions for the bentonite portions of two GCLs are given in Table 6.1. The GCL with the higher quality bentonite (GCL-HQB) is characterized by a greater content of sodium montmorillonite (86 % vs. 77 %), a higher plasticity index (548 % vs. 393 %), and a greater cation exchange capacity (93 meq/100 g vs. 64 meq/100 g) relative to the GCL with the lower quality bentonite (GCL-LQB). The tests at UW were performed using only GCL-LQB, whereas the tests at CSU were performed using both GCLs.

Particle-size distributions of the bentonite portions of the two GCLs were determined using both mechanical sieve analysis of the air-dried bentonite and hydrometer analysis (ASTM D 421, D 422). The corresponding test results for both GCLs are shown in Fig. 6.1. The granular nature of the bentonite for both GCLs is evident by the difference in the particle-size distributions based on the dry and wet procedures, as well as the difference in the resulting classifications (Unified Soil Classification System; ASTM D 2487) for the two bentonites.

6.2.2 Testing Liquids

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The liquids used in the experiment consist of deionized water (DIW) and calcium chloride ($CaCl_2$) solutions. The $CaCl_2$ solutions were chosen because previous studies pertaining to the measurement of the hydraulic conductivity and/or index properties of bentonite-based hydraulic barrier materials (e.g., GCLs and sand-bentonite mixtures) with $CaCl_2$ solutions have shown significant effects of the solutions on the hydraulic conductivity and swelling of the materials (Alther et al. 1985, Daniel et al. 1993, Shackelford 1994, Gleason et al. 1997, James et al. 1997, Melchior 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001, Shan and Lai 2002).

The $CaCl_2$ solutions were prepared by dissolving $CaCl_2$ (powdered, > 96 % pure, Sigma-Aldrich Co., St. Louis, MO) in the DIW at concentrations ranging from 5 mM to 500 mM. The resulting properties of the DIW and $CaCl_2$ solutions are given in Table 6.2. The properties of the testing liquids used at UW were found to be similar to those used at CSU with a subtle difference in type of DIW. In fact, the DIW used at UW (electrical conductivity, EC, at 25 °C $\cong$ 0.04 mS/m) classifies as Type II per ASTM D 1193 (EC $\leq$ 0.1 mS/m), whereas the DIW used at CSU (EC $\cong$ 0.21 mS/m) classifies as Type IV (EC $\leq$ 0.5 mS/m). However, since the measured calcium (Ca^{2+}) concentration is below the method detection limit (MDL) of 0.02 mg/L for both DIWs (EPA Method 200.7), this subtle difference in type of DIW is likely to have little, if any, effect on the measured index property or hydraulic conductivity.

6.2.3 Hydraulic Conductivity Testing

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Specimens of the two GCLs (i.e., GCL-LQB and GCL-HQB) with nominal diameters of 102 mm were permeated with DIW and solutions containing 5, 10, 20, 50, 100, and 500 mM $CaCl_2$. The specimens were permeated using the falling-head procedure with flexible-wall permeameters in accordance with ASTM D 5084. Specimens were trimmed and assembled in the permeameters using the procedure described by Daniel et al. (1997) to prevent the possibility of short-circuiting through the geotextiles at the edge of the GCL specimens due to loss of bentonite and pinching of the geotextiles. Backpressure was not used so that effluent liquids could be conveniently collected for EC and solute concentration measurements. The thicknesses of specimens were measured before, during, and after the hydraulic conductivity tests using a caliper, a cathetometer, and a ruler. The water contents of the specimens were measured after termination of the tests.

For all tests involving DIW as the permeant liquid, the tests were not terminated before the termination criteria specified in ASTM D 5084 were achieved, whereas for all tests involving $CaCl_2$ solutions, the tests were continued until chemical equilibrium between influent and effluent was established (e.g., Daniel 1994, Shackelford et al. 1999, 2000). Chemical equilibrium was considered to be established when the EC of the effluent was within ± 10 % of the influent EC in accordance with ASTM D 6766, and the concentrations of both chloride (Cl^-) and calcium (Ca^{2+}) in the effluent were within ± 10 % of those in the source solutions. The same methods were used at CSU and UW except for slight differences in the average effective stress (23.5 kPa at CSU vs. 16.2 kPa at UW) and the average hydraulic gradient (200 at CSU vs. 130 at UW). While these hydraulic gradients are higher than the maximum gradient (i.e., 30) stipulated in ASTM

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D 5084, hydraulic gradients ranging from 50 to 600 typically are used for measuring the hydraulic conductivity of GCLs (e.g., Shan and Daniel 1991, Daniel et al. 1993, Didier and Comeaga 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Shackelford et al. 2000). As shown by Shackelford et al. (2000), the hydraulic conductivity of GCLs is affected to a greater extent by average effective stress than by the magnitude of hydraulic gradient.

6.2.4 Index Property Testing

6.2.4.1 Liquid Limit Testing

Liquid limit tests for the bentonites taken from the two GCLs were conducted only at CSU following Method A (i.e., multipoint test) specified in ASTM 4318 using both DIW and solutions with $CaCl_2$ concentrations ranging from 5 mM to 500 mM. Specimens were prepared by mixing air-dried bentonite with each testing liquid thoroughly for more than 30 minutes. The prepared specimens were placed in double, plastic sealable bags, and then were stored in a humidity-controlled chamber (i.e., relative humidity [RH] = 90 ± 5 % and temperature = 20 ± 1 °C) for at least 16 hrs prior to testing. After the standing period, the stored specimen was remixed thoroughly for at least 15 minutes to perform the first trial. A minimum of six trials was performed for each testing liquid to produce successive numbers of blows between 15 and 35.

6.2.4.2 Hydrometer and Sedimentation Testing

Hydrometer tests were conducted only at CSU following the methods in ASTM D 422 using both DIW and $CaCl_2$ solutions with air-dried bentonite taken from the two

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GCLs. Due to the high swelling potential of bentonite, the mass of air-dried bentonite used for hydrometer testing was approximately 30 g, which is less than the mass of soil samples required by ASTM D 422 (i.e., ~ 50 g). Nonetheless, for the tests performed with 50, 100, and 500 mM $CaCl_2$ solutions, the bentonite particles settled out of suspension too fast to perform hydrometer tests even with the aid of a dispersant (i.e., 5 g of sodium hexametaphosphate [$(NaPO_3)_6$] per 1000-mL suspension). In addition, since a typical soil hydrometer (i.e., 151H or 152H) is designed to measure up to ~ 50 g of suspended soil particles in a 1000-mL suspension when using DIW as the testing liquid, the mass of suspended particles measured by the typical soil hydrometer for testing liquids other than DIW (e.g., $CaCl_2$ solution) is less than its capacity of 50 g/L due to dissolved salts (e.g., $CaCl_2$) corresponding to the concentration of the testing liquid. As a result, a special hydrometer would be required particularly for the tests using solutions containing a considerable amount of dissolved salts (e.g., 55.5 g/L for 500 mM $CaCl_2$).

Therefore, the time rate of sedimentation volume was measured *in lieu* of the standard hydrometer test. The testing procedures for measuring sedimentation volume were similar to those for the hydrometer testing except the dispersing agent was not used to accelerate the settling of bentonite particles. Sedimentation tests were conducted for the bentonites from both GCLs using both DIW and $CaCl_2$ solutions with concentrations ranging from 5 mM to 500 mM with 30 g of air-dried bentonite. The bentonite specimens were mixed with a mechanical mixer (Model 936, Hamilton Beach/Proctor-Silex, Inc., Washington, NC) with each testing liquid for ~ 1 minute. The suspension in a 1000-mL sedimentation cylinder was allowed to stand for at least 16 hrs before the start of the sedimentation test. After the standing period, the suspension was shaken for 1 minute per

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ASTM D 422, and the volume of sedimentation per 30 g of air-dried bentonite (in mL/30 g) then was estimated based on calibration of sedimentation cylinder by measuring the depositional height at the elapsed time of 24 hrs. The maximum sedimentation volume was limited to the volume of the suspension in the sedimentation cylinder (i.e., 1000 mL).

6.2.4.3 Swell Index Testing

Swell index tests were performed following the methods in ASTM D 5890 using both DIW and solutions with $CaCl_2$ concentrations ranging from 5 mM to 500 mM. Swell index tests performed at CSU were based on the bentonites from both GCLs, whereas the tests performed at UW were based only on the lower quality bentonite from the GCL-LQB. The bentonite samples were prepared by passing the bentonite through a No. 200 U.S. Standard Sieve using a mortar and pestle. First, approximately 90 mL of each testing liquid were added to a clean 100-mL graduated cylinder. Then, 2.0 g of oven-dried bentonite were dusted over the entire surface of the testing liquid in the graduated cylinder in less than 0.1-g increments. Each increment of bentonite was added over a period of ~ 30 seconds with a minimum standing period of 10 minutes after the addition of each increment. The resulting average time required to add 2.0 g of bentonite in this study was ~ 6 hrs. After the entire bentonite specimen was added, the same testing liquid was used to rinse any particles adhering to the sides of the cylinder and to fill the cylinder to the 100-mL mark. The swell volume of bentonite per 2.0 g of bentonite (in mL/2 g) then was measured after an elapsed time of 16 hrs, i.e., the minimum hydration period required by ASTM D 5890.

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6.2.4.4 Solution Retention Capacity Testing

Solution retention capacity (SRC) tests were conducted only at CSU using the bentonite taken from both GCLs with both DIW and solutions containing from 5 mM to 500 mM $CaCl_2$. The SRC is an index of the volume of testing liquid retained per 1.0 g of oven-dried and pulverized bentonite after centrifugation, which is related to the thickness of adsorbed layer of the bentonite. Since the SRC procedure is described in detail in Chapter 5, only a brief description of the testing procedure is discussed here.

The bentonite samples were prepared using the same procedure as for swell index testing. One gram of oven-dried and pulverized bentonite was placed into a clean centrifuge tube followed by 50 mL of a testing liquid. The centrifuge tube then was shaken for 30 seconds. After a 16-hr standing period, the tube was re-shaken for 30 seconds. After centrifuging (i.e., 30 min @ 2750 *g*) and decanting the supernatant, the SRC in mL/1 g (i.e., the volume of the testing liquid retained per 1 g of bentonite) was calculated based on the measured mass of the tube with hydrated bentonite. If some of the bentonite was lost during the decanting process, the SRC was corrected for the loss of bentonite by measuring the oven-dried mass of the decanted supernatant.

6.3 RESULTS

6.3.1 Hydraulic Conductivity Tests

6.3.1.1 Hydraulic Conductivity

The results of the hydraulic conductivity tests conducted on the two GCLs with the lower quality bentonite (GCL-LQB) and higher quality bentonite (GCL-HQB) are shown in Fig. 6.2, and summarized in Table 6.3. Since the measured Ca^{2+} concentrations

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for both DIWs used at the University of Wisconsin (UW) and Colorado State University (CSU) were below the MDL of 0.02 mg/L for Ca^{2+}, the MDL is used to represent the Ca^{2+} concentration for the DIWs at both laboratories.

For the GCL-LQB, the hydraulic conductivity measured at CSU (i.e., k_{CSU}) is close to the hydraulic conductivity measured at UW (i.e., k_{UW}) when permeated with water (DIW) (i.e., 2.3×10^{-9} cm/s at CSU vs. 1.7×10^{-9} cm/s at UW). Similarly, the k_{CSU} values are similar, but slightly lower ($\leq 3.3X$), to the k_{UW} values for all of the specimens permeated with $CaCl_2$ solutions except for the specimens permeated with the 50 mM $CaCl_2$ solution, where the k_{CSU} value is ~ 90X lower than the k_{UW} value. Except for the specimens permeated with the 50 mM $CaCl_2$ solution, the difference between k_{CSU} and k_{UW} likely is due, in part, to the difference in average applied effective stress, which was slightly greater at CSU relative to UW (i.e., 23.5 kPa at CSU vs. 16.2 kPa at UW).

As expected, the ratio of the hydraulic conductivity based on either water or one of the $CaCl_2$ solutions to that based on the water, or k/k_w, increases as the $CaCl_2$ concentration increases for the GCL-LQB at both laboratories. In fact, the k/k_w values at UW are higher, but at most 5X, than the k/k_w values at CSU except for the specimens permeated with the 50 mM $CaCl_2$ solution, where k/k_w at UW is approximately two orders-of-magnitude higher than k/k_w at CSU. In addition to the difference in applied effective stress, the slightly lower k_w at UW (i.e., 1.7×10^{-9} cm/s vs. 2.3×10^{-9} cm/s) contributes to the higher k/k_w values at UW. Nevertheless, the overall trends in hydraulic conductivity as a function of influent $CaCl_2$ concentration are similar between two laboratories.

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For the tests conducted at CSU using both GCLs, the hydraulic conductivity for GCL-LQB is ~ 3X higher than the hydraulic conductivity for GCL-HQB based on permeation with water. However, the hydraulic conductivity values for the specimens permeated with $CaCl_2$ solutions are always lower for GCL-LQB relative to GCL-HQB. In fact, the values of the ratio of the hydraulic conductivity for GCL-HQB to the hydraulic conductivity for GCL-LQB, or k_{HQB}/k_{LQB}, are ~ 2.0, regardless of the concentration, for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In addition, the k_{HQB}/k_{LQB} values are ~ 230, ~ 100, and ~ 40 for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, respectively. Thus, for the tests performed using $CaCl_2$ solutions as permeant liquids, the GCL with the higher quality bentonite exhibits more significant alteration in hydraulic conductivity than does the GCL with the lower quality bentonite.

The values of the ratio of the hydraulic conductivity for the GCL-HQB based on either water or one of the $CaCl_2$ solutions to that based on water, or $k_{HQB}/k_{w,HQB}$, are all ~ 6.5X higher than the values of the ratio of the hydraulic conductivity for the GCL-LQB based on either water or one of $CaCl_2$ solutions to that based on the water, or, $k_{LQB}/k_{w,LQB}$, for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. However, for the specimens permeated with 50, 100, and 500 mM $CaCl_2$ solutions, $k_{HQB}/k_{w,HQB}$ is at least two orders-of-magnitude higher than $k_{LQB}/k_{w,LQB}$. In general, the hydraulic conductivity increases as $CaCl_2$ concentration of the permeant liquid increases for both GCLs, but the resulting values of hydraulic conductivity are higher for GCL-HQB than GCL-LQB. In addition, the lower $k_{w,HQB}$ value (i.e., ~ 7.0 x 10^{-10} cm/s vs. ~ 2.3 x 10^{-9} cm/s) also

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contributes to higher values of $k_{HQB}/k_{w,HQB}$ for GCL-HQB relative to $k_{LQB}/k_{w,LQB}$ for GCL-LQB.

6.3.1.2 Final Properties of Specimens

Bentonite gravimetric water content (w_b), bentonite void ratio (e_b), and GCL bulk void ratio (e_B) of the GCL specimens after permeation based on the results from both laboratories are shown in Figs. 6.3 and 6.4. For the GCL-LQB specimens tested at CSU, w_b decreased from ~ 189 % to ~ 73 % as the influent $CaCl_2$ concentration increased from 0 (DIW) to 500 mM, while w_b for the same GCL specimens tested at UW decreased from ~ 344 % to ~ 77 % for the same range in influent $CaCl_2$ concentrations. The significant difference in w_b (i.e., 189 % vs. 344 %) for the GCL-LQB specimens permeated with water between the two laboratories may be due, in part, to the difference in applied effective stress. However, w_b for specimens of GCL-LQB permeated with all $CaCl_2$ solutions tends to be higher by 1.06X to 1.21X at UW relative to CSU. Similarly, for the tests performed with all $CaCl_2$ solutions, e_B for specimens of GCL-LQB tested at UW (i.e., $e_{B,UW}$) is higher than the e_B for specimens of GCL-LQB tested at CSU (i.e., $e_{B,CSU}$) by a factor ranging from 1.03 to 1.39, whereas $e_{B,UW}/e_{B,CSU}$ is ~ 1.70 for the tests based on water. Although w_b, e_b, and e_B for the specimens tested at UW tend to be higher that those for the specimens tested at CSU due to the lower applied effective stress, the trends in w_b, e_b, and e_B with influent $CaCl_2$ concentration for the specimens of GCL-LQB tested at both laboratories are the same.

As shown in Figs. 6.3 and 6.4, for the tests conducted at CSU using both GCLs, w_b, e_b, and e_B for specimens of GCL-LQB are higher than those for specimens of GCL-

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LQB based on permeation with water (i.e., 189 % vs. 160 % for w_b, 5.2 vs. 4.2 for e_b, 4.7 vs. 3.6 for e_B). The lower w_b, e_b, and e_B for specimens of GCL-HQB relative to those for specimens of GCL-LQB based on permeation with water are presumably due to the other differences in the properties of the GCLs (e.g., integrity of geotextiles and needle-punched fibers, mass and gradation of bentonite, etc). However, w_b, e_b, and e_B for specimens of GCL-HQB permeated with the $CaCl_2$ solutions tend to be higher than those for specimens of GCL-LQB, except for the specimens permeated with the 500 mM $CaCl_2$ solution. For example, the values for the ratios of w_b, e_b, and e_B for specimens of GCL-HQB relative to those for specimens of GCL-LQB, or $w_{B,HQB}/w_{B,LQB}$, $e_{b,HQB}/e_{b,LQB}$, and $e_{B,HQB}/e_{B,LQB}$, range from 1.02 to 1.26 for the specimens permeated with the solutions containing from 5 mM to 100 mM $CaCl_2$, whereas the values for $w_{B,HQB}/w_{B,LQB}$, $e_{b,HQB}/e_{b,LQB}$, and $e_{B,HQB}/e_{B,LQB}$ are less than unity (i.e., ~ 0.94 to 0.97) for the specimens permeated with the 500 mM $CaCl_2$ solution.

6.3.2 Index Property Tests

6.3.2.1 Liquid Limit

The results of the liquid limit (LL) tests performed using the bentonite from both GCLs are shown in Fig. 6.5. As expected, the LL of the bentonite decreases as the $CaCl_2$ concentration of the testing liquid increases. In fact, as the $CaCl_2$ concentration in the hydrating liquid increased from 0 (DIW) to 500 mM, the LL for the bentonite from GCL-LQB decreases from ~ 430 % to ~ 106 %, whereas the LL for the bentonite from GCL-HQB decreases from ~ 589 % to ~ 102 %. The decrease in LL with increase in $CaCl_2$ concentration can be attributed to a decrease in the thickness of the adsorbed layer of the

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bentonite particles (Gleason et al. 1997, Petrov and Rowe 1997, Lin and Benson 2000, Sridharan and Prakash 2000).

For the tests performed with water, the value for the ratio of the LL for the bentonite from GCL-HQB to the LL for the bentonite from GCL-LQB, or LL_{HQB}/LL_{LQB}, is approximately 1.4. Similarly, the LL_{HQB}/LL_{LQB} values are ~ 1.5 for the tests performed with 5, 10, and 20 mM $CaCl_2$ solutions. However, a further increase in $CaCl_2$ concentration beyond 20 mM results in a further decrease in the LL_{HQB}/LL_{LQB} value. For example, the LL_{HQB}/LL_{LQB} values are approximately 1.4, 1.1, and 1.0 for the tests performed with 50, 100, and 500 mM $CaCl_2$ solutions, respectively. In general, the change in LL is greater for the bentonite from GCL-HQB relative to the bentonite from GCL-LQB, indicating that the higher quality bentonite tends to be affected to a greater extent as the concentration of $CaCl_2$ increases than does the lower quality bentonite.

On the other hand, the values for the ratio of the LL based on any testing liquid to that based on water, or LL/LL_w, decrease as the $CaCl_2$ concentration in the testing liquid increases, regardless of the bentonite. In fact, the LL/LL_w values for the bentonite from GCL-HQB are slightly higher (i.e., by < 0.08) than those for the bentonite from GCL-LQB for the tests performed with 5, 10, and 20 mM $CaCl_2$ solutions, whereas the LL/LL_w values for the bentonite from GCL-HQB are slightly lower (i.e., by < 0.07) than those for the bentonite from the GCL-LQB for the tests performed with 50, 100, and 500 mM $CaCl_2$ solutions. However, as shown in Fig. 6.5c, the overall trend in the LL/LL_w as a function of the $CaCl_2$ concentration in the testing liquid is unique for each bentonite.

6.3.2.2 Sedimentation Volume

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The results of the sedimentation volume (SV) tests performed using the bentonites from both GCLs are shown in Fig. 6.6. For the tests performed with water, the SV values for the bentonites from both GCLs is limited to the volume of the suspension in the sedimentation cylinder (i.e., 1000 mL/30 g) throughout the 24-hr test period. In addition, for the tests performed with the 5 mM $CaCl_2$ solution, the SV value for the bentonite from GCL-LQB is approximately 862 mL/30 g, whereas the SV value for the bentonite from GCL-HQB is 1000 mL/30 g (i.e., volume of the suspension). These high SV values indicate that the $CaCl_2$ concentration of 5 mM probably is not sufficiently high for the given mass of air-dried bentonite to result in significant flocculation of particles, particularly for the higher quality bentonite from GCL-HQB. Nonetheless, as the $CaCl_2$ concentration for the hydrating liquid increases from 0 (DIW) to 500 mM, the SV values for the bentonite decrease from 1000 mL/30 g to ~ 168 mL/30 g and from 1000 mL/30 g to ~ 117 mL/30 g for the bentonites from GCL-LQB and GCL-HQB, respectively.

In general, the SV based on hydration with a solution containing a lower $CaCl_2$ concentration is consistently lower than the SV based on hydration with a solution containing a higher $CaCl_2$ concentration. Shackelford (1994) reported similar results for tests performed using sodium bentonite specimens and solutions containing sodium chloride (NaCl) at concentrations of 10, 100, and 1000 mM. The decrease in SV with increase in $CaCl_2$ concentration results from flocculation of particles and a more rapid settling of the flocs.

As shown in Fig. 6.6b, the values of the ratio of the SV for the bentonite from GCL-HQB to the SV for the bentonite from GCL-LQB, or SV_{HQB}/SV_{LQB}, are less than unity (i.e., ~ 0.55 to ~ 0.76) for all of the tests performed with $CaCl_2$ solutions, i.e.,

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except for the tests performed with the 5 mM $CaCl_2$ solution, in which case the resulting SV_{HQB}/SV_{LQB} value is approximately 1.16. In general, the SV values tend to be greater for the lower quality bentonite than the higher quality bentonite.

As expected, the values for the ratio of the SV based on any testing liquid to that based on water, or SV/SV_w, decrease as the $CaCl_2$ concentration in the testing liquid increases for the bentonites from both GCLs, i.e., except for the test performed using the bentonite from GCL-HQB with the 5 mM $CaCl_2$ solution, in which the SV value is 1000 mL/30 g. In fact, the SV/SV_w values for the bentonite from GCL-LQB are higher (i.e., by ~ 0.05 to 0.38) than those for the bentonite from GCL-HQB for the tests performed with $CaCl_2$ solutions, i.e., except for the tests performed with the 5 mM $CaCl_2$ solution, in which the SV/SV_w values are 1.0 and ~ 0.86 for the bentonites from GCL-LQB and GCL-HQB, respectively.

6.3.2.3 Swell Index

The results of the swell index (SI) tests conducted using the bentonites from both GCLs are shown in Fig. 6.7. For the bentonite from GCL-LQB, the SI measured at CSU decreased from ~ 27.5 mL/2 g to ~ 7.5 mL/2 g as the $CaCl_2$ concentration in the testing liquid increased from 0 (DIW) to 500 mM, whereas the SI measured at UW decreased from ~ 26.0 mL/2 g to ~ 8.0 mL/2 g for the same range in $CaCl_2$ concentrations. In fact, the SI values between the two laboratories are very close (i.e., < 13 % difference), except for the tests performed with the 5 mM $CaCl_2$ solution (~ 34 % higher at CSU). Nonetheless, the overall trends in the SI values with the $CaCl_2$ concentration of the hydrating liquids are similar for the results from the two laboratories, and indicate the SI

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decreases with increasing $CaCl_2$ concentration of the testing liquid. This decrease in the SI with increasing $CaCl_2$ concentration is consistent with the individual granules of the bentonite becoming smaller due to the compression of the interlayer region induced by the elevated calcium concentration in the bulk solution (Sposito 1981, McBride 1994, Shackelford et al. 2000, Jo et al. 2001).

Similarly, the SI for the bentonite from GCL-HQB decreased from ~ 30.0 mL/2 g to ~ 7.5 mL/2 g with increase in $CaCl_2$ concentration from 0 (DIW) to 500 mM. For the tests performed at CSU, the values for the ratio of SI for the bentonite from GCL-HQB to SI for the bentonite from GCL-LQB, or SI_{HQB}/SI_{LQB}, are slightly above unity (i.e., 1.02 to 1.11) for the tests performed with water and $\leq$ 50 mM $CaCl_2$ solutions. However, further increases in the $CaCl_2$ concentration of the testing liquids result in concomitant decreases in the SI_{HQB}/SI_{LQB} values (i.e., ~ 0.98) for the tests performed with 100 and 500 mM $CaCl_2$ solutions. On the other hand, the values for the ratio of the SI based on any testing liquid to that based on water, or SI/SI_w, decrease as the $CaCl_2$ concentration in the testing liquid increases for the bentonite from both GCLs. As shown in Fig. 6.7c, the overall trends in the SI/SI_w values as a function of the $CaCl_2$ concentration of the testing liquids are similar for the bentonites from both GCLs.

6.3.2.4 Solution Retention Capacity

The results of the solution retention capacity (SRC) tests performed using the bentonites taken from both GCLs are shown in Fig. 6.8. The SRC for the bentonite from GCL-LQB decreased from ~ 5.7 mL/1 g to ~ 1.8 mL/1 g with increase in $CaCl_2$ concentration in the testing liquid from 0 (DIW) to 500 mM. Similarly, the SRC for the

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bentonite from GCL-HQB decreased from ~ 7.2 mL/1 g to ~ 1.7 mL/1 g with increase in $CaCl_2$ concentration in the testing liquid from 0 (DIW) to 500 mM.

As shown in Fig. 6.8, the SRC for the bentonite from GCL-HQB is greater by approximately 1.4 mL/1 g than that for the bentonite from GCL-LQB for the tests performed with both water and 5 mM $CaCl_2$ solution. Similarly, but to a lesser extent, the SRC for the bentonite from GCL-HQB is about 11 % (= 0.28 mL/1 g) higher than the SRC for the bentonite from GCL-LQB based on the tests performed with the 10 mM $CaCl_2$ solution. However, the value for the ratio of the SRC for the bentonite from GCL-HQB to that for the bentonite from GCL-LQB, or SRC_{HQB}/SRC_{LQB}, is slightly less than unity (i.e., 0.96 to 0.98) for the solutions with $CaCl_2$ concentrations ranging from 20 mM to 500 mM. These results are similar to the results of swell index tests in that the relatively strong $CaCl_2$ solutions result in more significant decrease in the thickness of adsorbed layer of the higher quality bentonite relative to the lower quality bentonite.

On the other hand, the values for the ratio of the SRC based on any testing liquid to that based on water, or SRC/SRC_w, decrease significantly from unity to between 0.5 and 0.6 with increase in $CaCl_2$ concentration in the testing liquid from 0 (DIW) to 5 mM. Also, the SRC/SRC_w values decrease, but to a lesser extent, with increasing $CaCl_2$ concentration. However, except for the tests performed with the 5 mM $CaCl_2$ solution, the SRC/SRC_w for the bentonite from GCL-HQB is always slightly less (i.e., by ~ 0.05 to 0.09) than that for the bentonite from GCL-LQB for the tests performed with the $CaCl_2$ solutions. In fact, the SRC/SRC_w for the bentonite from GCL-HQB is slightly higher (i.e., by ~ 0.08) than that for the bentonite from GCL-LQB for the tests performed with the 5 mM $CaCl_2$ solution. Therefore, the 5 mM $CaCl_2$ solution was not sufficiently strong to

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result in a significant alteration in the thickness of adsorbed layer of the higher quality bentonite relative to the lower quality bentonite.

6.4 DISCUSSION

6.4.1 Index Property versus Hydraulic Conductivity

The index properties, such as liquid limits (LLs), sedimentation volumes (SVs), swell indexes (SIs), and solution retention capacities (SRCs), are compared with the hydraulic conductivity (k) values for both GCLs in Figs. 6.9 to 6.12, respectively. In addition, the values for the ratio of an index property based on any liquid to the same index property based on water (index/index$_w$) corresponding to three different k criteria, viz., k = 10^{-7} cm/s (regulatory limit specified in 40CFR258.40, Code of Federal Regulations), and increases in k relative to water of 10X (i.e., $k/k_w = 10$) and 100X (i.e., $k/k_w = 100$), are summarized in Table 6.4 and shown in Figs. 6.13 and 6.14. The values for index property ratio in Table 6.4 and Figs. 6.13 and 6.14 are interpolated between two actual values (see Figs. 6.9 to 6.12).

As shown in Figs. 6.9 to 6.12, the magnitude of the change in the index property is shown to be a function of the type of index property as well as the quality of bentonite in the GCLs. For example, as shown in Fig. 6.9, the k value for GCL-LQB increases by 10X (i.e., $k/k_w = 10$) for a decrease in LL of ~ 55 % and by 100X (i.e., $k/k_w = 100$) for a decrease in LL of ~ 65 %, whereas the k value for GCL-HQB increases by 10X for a slight decrease in LL of ~ 3 % and by 100X for a decrease in LL of ~ 31 %. As shown in Fig. 6.10, the k value for GCL-LQB increases by 10X for a decrease in SV of ~ 80 % and by 100X for a decrease in SV of ~ 82 %, whereas the k value for GCL-HQB increases by

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10X for no change in SV and by 100X for a decrease in SV of ~ 73 %. Overall, all of the index/index$_w$ values corresponding to $k/k_w = 10$ are ≤ ~ 0.61 regardless of index property for GCL-LQB, as shown Figs. 6.13 and 6.14. However, the index/index$_w$ values corresponding to $k/k_w = 10$ are all ≥ ~ 0.97 for all index properties for GCL-HQB except SRC, in which case the SRC/SRC$_w$ value is ~ 0.71. Therefore, compatibility in index property does not always correlate well with compatibility in k.

This lack of strong correlation between index property and k may be due to the differences in the procedures for determining the index property and k. For example, the bentonite in the GCL specimens tested for k is continuously subjected to fresh influent until permeation is terminated, whereas the volume of the testing liquid required for measurement of the index property is fixed (e.g., ~ 50 mL per 1.0 g of bentonite for SI). As a result, the bentonite in the k tests is exposed to a significantly greater mass of Ca^{2+} than is the bentonite in the index property tests. Furthermore, k can be affected significantly by factors that are not relevant for index property testing, such as the state of stress during hydration and permeation (e.g., Fernandez and Quigley 1991, Shackelford et al. 2000). However, such change in k (i.e., $k/k_w = 10$) results in the k value of still below than the regulatory limit (i.e., 10^{-7} cm/s), regardless of the applied effective stress and the quality of bentonite in this study (see Figs. 6.9 to 6.12).

As shown in Figs. 6.13 and 6.14, all of the index/index$_w$ values corresponding to $k = 10^{-7}$ cm/s are ≤ ~ 0.54 for GCL-LQB and ≤ ~ 0.67 for GCL-HQB, regardless of index property. Similarly, all of the index/index$_w$ values corresponding to $k/k_w = 100$ are ≤ ~ 0.52 for GCL-LQB and ≤ ~ 0.69 for GCL-HQB. Since the resulting k value corresponding to the $k/k_w = 100$ is close to 10^{-7} cm/s (i.e., 2.3X for GCL-LQB at CSU,

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1.7X for GCL-LQB at UW, and 0.7X for GCL-HQB at CSU) in this study, the index/index$_w$ values corresponding to $k/k_w = 100$ are also very close (i.e., by 0.03 at most) to those corresponding to $k = 10^{-7}$ cm/s. As a result, depending on the magnitude of the change in k, the changes in the index properties can provide a qualitative indication of the relative impact of the $CaCl_2$ solutions on the hydraulic performance of GCLs. However, a quantitative indication can only be ascertained by performing the compatibility tests (e.g., Petrov and Rowe 1997, Shackelford et al. 2000).

Finally, the changes in k corresponding to $k/k_w = 10$ and 100 for GCL-LQB do not occur until the influent $CaCl_2$ concentration exceeds 50 mM at the effective stress of 23.5 kPa, whereas the same changes in k (i.e., $k/k_w = 10$ and 100) for GCL-LQB at the lower effective stress of 16.2 kPa occur when the influent $CaCl_2$ concentration exceeds only 20 mM (see Fig. 6.2). For the cases of GCL-HQB at the effective stress of 23.5 kPa, the change in k corresponding to $k/k_w = 10$ occurs even for the lowest influent $CaCl_2$ concentration (i.e., 5 mM), whereas the change in k corresponding to $k/k_w = 100$ only occurs when the influent $CaCl_2$ concentration exceeds 20 mM (see Fig. 6.2). Thus, the change in k is dependent on the quality of bentonite used in the GCLs as well as the applied effective stress.

6.4.2 Index Property versus Final Properties of Specimens

The index properties, including liquid limits (LLs), sedimentation volumes (SVs), swell indexes (SIs), and solution retention capacities (SRCs), are compared with the bentonite water content (w_b), bentonite void ratio (e_b), and GCL bulk void ratio (e_B) after permeation for the GCL specimens in Figs. 6.15 to 6.18, respectively. For example, as

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shown in Fig. 6.15, w_b, e_b, and e_B of GCL specimens decrease as LL/LL_w decreases for both GCLs (i.e., GCL-LQB and GCL-HQB). Also, w_b, e_b, and e_B tend to decrease as SV/SV_w decreases for the bentonites from both GCLs, as shown in Fig. 6.16. In addition, as shown in Fig. 6.17, w_b, e_b, and e_B also decrease as SI/SI_w decreases for both GCLs based on the tests performed at both CSU and UW. The difference in applied effective stress probably contributes, in part, to the difference in the results from the two laboratories, whereas the difference in the results for the two GCLs at CSU is probably due to the differences in the property of the GCLs (e.g., bentonite, geotextiles, and needle-punched fibers, etc). Finally, as shown in Fig. 6.18, w_b, e_b, and e_B tend to decrease as SRC/SRC_w decreases for both GCLs. In general, w_b, e_b, and e_B tend to decrease as the index properties decrease, regardless of the quality of bentonite or the index property, although the magnitudes of the decreases in each index property are not the same.

6.5 CONCLUSIONS

The effect of chemical solutions containing a range of $CaCl_2$ concentrations on several index properties (viz., liquid limit, sedimentation volume, swell index, and solution retention capacity) for two sodium bentonites taken from different GCLs is correlated with the effect of the same chemical solutions used as permeant liquids on the hydraulic conductivity of the two GCLs. In general, an increase in $CaCl_2$ concentration of the testing liquid results in a decrease in the index property for the bentonites, regardless of the index property or bentonite.

For the GCL with the lower quality bentonite (GCL-LQB), an increase in hydraulic conductivity by 10X relative to that based on permeation with water correlates

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with a significant decrease in index property by a minimum of 39 %. However, for the GCL with the higher quality bentonite (GCL-HQB), an increase in hydraulic conductivity by 10X only results in a slight decrease in index property by a maximum of 3 % except SRC, in which case a decrease in SRC is ~ 29 %. Therefore, compatibility in index property does not always correlate well with compatibility in hydraulic conductivity. However, such increase in hydraulic conductivity (i.e., 10X) in this study results in the k value of still below than the regulatory limit (i.e., 10^{-7} cm/s).

On the other hand, an increase in hydraulic conductivity by 100X relative to that based on permeation with water correlates with a significant decrease in index property by a minimum of 48 % for GCL-LQB and by a minimum of 31 % for GCL-HQB. As a result, depending on the magnitude of the change in hydraulic conductivity, the changes in the index properties can provide a qualitative indication of the relative impact of the $CaCl_2$ solutions on the hydraulic performance of GCLs. However, the magnitude of the change in the index property is shown to be a function of the type of index property as well as the quality of bentonite in the GCLs. The resulting hydraulic conductivity value corresponding to an increase by 100X in this study is close to the regulatory limit (i.e., 10^{-7} cm/s).

Finally, these changes in hydraulic conductivity (i.e., 10X and 100X) for GCL-LQB do not occur until the influent $CaCl_2$ concentration exceeds 50 mM at the effective stress of 23.5 kPa, whereas the same changes in hydraulic conductivity (i.e., 10X and 100X) for GCL-LQB at the lower effective stress of 16.2 kPa occur when the influent $CaCl_2$ concentration exceeds only 20 mM. For GCL-HQB at the effective stress of 23.5 kPa, the change in hydraulic conductivity by 10X occurs even for the lowest influent

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$CaCl_2$ concentration (i.e., 5 mM), whereas the change in hydraulic conductivity by 100X occurs when the influent $CaCl_2$ concentration exceeds 20 mM. Thus, the change in hydraulic conductivity is dependent on the quality of bentonite used in the GCLs as well as the applied effective stress.

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Table 6.1 – Properties of bentonites in two geosynthetic clay liners.

Property	Standard	Average Value or Type [No. of Trials]	
		LQB[d]	HQB[d]
Specific Gravity	ASTM D 854[a]	2.74 [3]	2.78 [2]
Soil Classification:	ASTM D 2487		
Sieve Analysis (Air-Dried)		SP [3]	SP [1]
Hydrometer		CH [7]	CH [1]
Atterberg Limits (%):	ASTM D 4318	[1]	[1]
Liquid Limit, LL		430	589
Plasticity Index, PI		393	548
Bentonite Mass (kg/m^2)	ASTM D 5993	5.1 [5]	4.6 [5]
Principal Minerals (%):	b	[3]	[2]
Montmorillonite		77.2	86.0
Cristobalite		10.3	4.5
Plagioclase Feldspar		5.1	2.5
Quartz		3.4	3.5
Others		4.0	5.5
Cation Exchange Capacity, CEC (meq/100 g)	c	63.9 [3]	93.4 [2]
Exchangeable Cations (meq/100 g):	c	[3]	[2]
Ca^{2+}		11.5	15.3
Mg^{2+}		3.7	7.0
Na^{+}		45.8	69.0
K^{+}		0.7	0.8
Sum		61.7	92.1

[a] Using a magnetic stirring device for de-airing.

[b] Based on X-ray diffraction (XRD) analyses performed by Mineralogy Inc., Tulsa, OK and GeoServices Inc., Argyle, TX.

[c] Based on procedures described in Shackelford and Redmond (1995).

[d] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite.

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Table 6.2 – Properties of liquids used in this study.

Liquid	Salt Concentration (mM)			Measured Solute Concentrations (mg/L)				Measured pH		Measured Electrical Conductivity, EC @ 25°C (mS/m)	
	Target	Measured		Calcium (Ca^{2+})		Chloride (Cl^{-})					
		Concentration	No.	Concentration	No.	Concentration	No.	pH	No.	EC	No.
DIW[a]	0	< 0.0005[b]	10	< 0.02[b]	10	< 0.04[b]	10	5.6 ± 0.5	19	0.21 ± 0.11 (CSU)[c] 0.04 ± 0.00 (UW)[c]	19
$CaCl_2$ (Sigma Co., 96 %)	5	5.1 ± 0.2	14	216 ± 10	14	377 ± 38	14	5.7 ± 0.5	25	123 ± 2.1	25
	10	10.1 ± 0.2	13	436 ± 30	13	756 ± 65	13	6.0 ± 0.3	19	234 ± 2.6	19
	20	20.1 ± 0.6	13	872 ± 77	13	1457 ± 110	13	6.1 ± 0.3	17	445 ± 7.3	17
	50	50.7 ± 1.4	9	2055 ± 63	9	3548 ± 69	9	5.7 ± 0.1	18	1041 ± 26	18
	100	100 ± 2.6	6	4072 ± 126	6	7030 ± 95	6	5.8 ± 0.1	13	1958 ± 48	13
	500	505 ± 10	5	20289 ± 474	5	35755 ± 710	5	6.5 ± 0.2	12	7693 ± 25	12

[a] Deionized water.

[b] Method detection limit (MDL).

[c] CSU = Colorado State University; UW = University of Wisconsin - Madison.

Table 6.3 – Summary of results for hydraulic conductivity (k) tests.

Permeant Liquid	Laboratory[a]	No. of Tests	GCL Type[b]	Effective Stress (kPa)	Average k (cm/s)[c]	k Ratios[d]		
						k/k_w	k_{UW}/k_{CSU}	k_{HQB}/k_{LQB}
De-ionized Water	UW	1	LQB	16.2	1.7 x 10^{-9}	1.0	0.74	0.30
	CSU	2	LQB	23.5	2.3 x 10^{-9}	1.0		
	CSU	1	HQB	23.5	7.0 x 10^{-10}	1.0		
5 mM $CaCl_2$	UW	3	LQB	16.2	1.5 x 10^{-8}	8.6	1.7	1.9
	CSU	2	LQB	23.5	8.6 x 10^{-9}	3.7		
	CSU	1	HQB	23.5	1.7 x 10^{-8}	24		
10 mM $CaCl_2$	UW	2	LQB	16.2	1.7 x 10^{-8}	9.7	2.0	2.1
	CSU	2	LQB	23.5	8.2 x 10^{-9}	3.5		
	CSU	1	HQB	23.5	1.7 x 10^{-8}	25		
20 mM $CaCl_2$	UW	2	LQB	16.2	1.6 x 10^{-8}	9.1	1.8	2.0
	CSU	2	LQB	23.5	8.8 x 10^{-9}	3.8		
	CSU	1	HQB	23.5	1.8 x 10^{-8}	25		
50 mM $CaCl_2$	UW	1	LQB	16.2	1.6 x 10^{-6}	941	90	233
	CSU	2	LQB	23.5	1.8 x 10^{-8}	7.7		
	CSU	2	HQB	23.5	4.1 x 10^{-6}	5916		
100 mM $CaCl_2$	UW	1	LQB	16.2	1.1 x 10^{-6}	647	3.3	104
	CSU	2	LQB	23.5	3.4 x 10^{-7}	146		
	CSU	2	HQB	23.5	3.5 x 10^{-5}	49854		
500 mM $CaCl_2$	UW	1	LQB	16.2	1.9 x 10^{-6}	1118	1.3	41
	CSU	2	LQB	23.5	1.5 x 10^{-6}	639		
	CSU	2	HQB	23.5	6.0 x 10^{-5}	85318		

[a] CSU = Colorado State University; UW = University of Wisconsin - Madison.

[b] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite.

[c] Values at chemical equilibrium in terms of both electrical conductivity (EC) and solute concentrations (i.e., $EC_{out}/EC_{in} = 1.00 \pm 0.10$ and $C_{out}/C_{in} = 1.00 \pm 0.10$) except for the tests performed with deionized water, in which the values are based on ASTM D 5890.

[d] k/k_w = ratio of k based on any testing liquid to k based on water; k_{UW}/k_{CSU} = ratio of k at UW to k at CSU; k_{HQB}/k_{LQB} = ratio of k of GCL-HQB at CSU to k of GCL-LQB at CSU.

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Table 6.4 – Summary of index property ratios corresponding to three hydraulic conductivity criteria.

Criterion[a]	Laboratory[b]	Index Property Ratio[c]	GCL Type[d]	
			LQB	HQB
(1) $k = 10^{-7}$ cm/s	CSU	LL/LL_w	0.38	0.67
	CSU	SV/SV_w	0.19	0.25
	CSU	SI/SI_w	0.34	0.46
	UW		0.54	-
	CSU	SRC/SRC_w	0.33	0.31
(2) $k/k_w = 10$	CSU	LL/LL_w	0.45	0.97
	CSU	SV/SV_w	0.20	1.0
	CSU	SI/SI_w	0.38	1.0
	UW		0.61	-
	CSU	SRC/SRC_w	0.35	0.71
(3) $k/k_w = 100$	CSU	LL/LL_w	0.35	0.69
	CSU	SV/SV_w	0.18	0.27
	CSU	SI/SI_w	0.32	0.47
	UW		0.52	-
	CSU	SRC/SRC_w	0.32	0.31

Note: All values are interpolated based on two actual values of index property ratio.

[a] k/k_w = ratio of k based on any testing liquid to k based on water.

[b] CSU = Colorado State University; UW = University of Wisconsin - Madison.

[c] LL = liquid limit; SV = sedimentation volume; SI = swell index; SRC = solution retention capacity; ratio = index property based on any testing liquid to index property based on water.

[d] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite.

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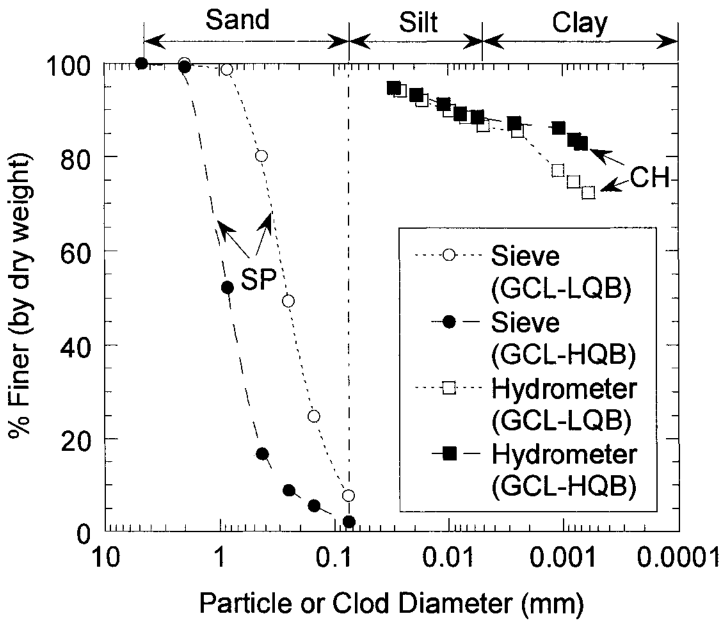

Fig. 6.1 – Particle-size distributions for the bentonites taken from two GCLs based on mechanical sieve (dry) and hydrometer (wet) analyses.

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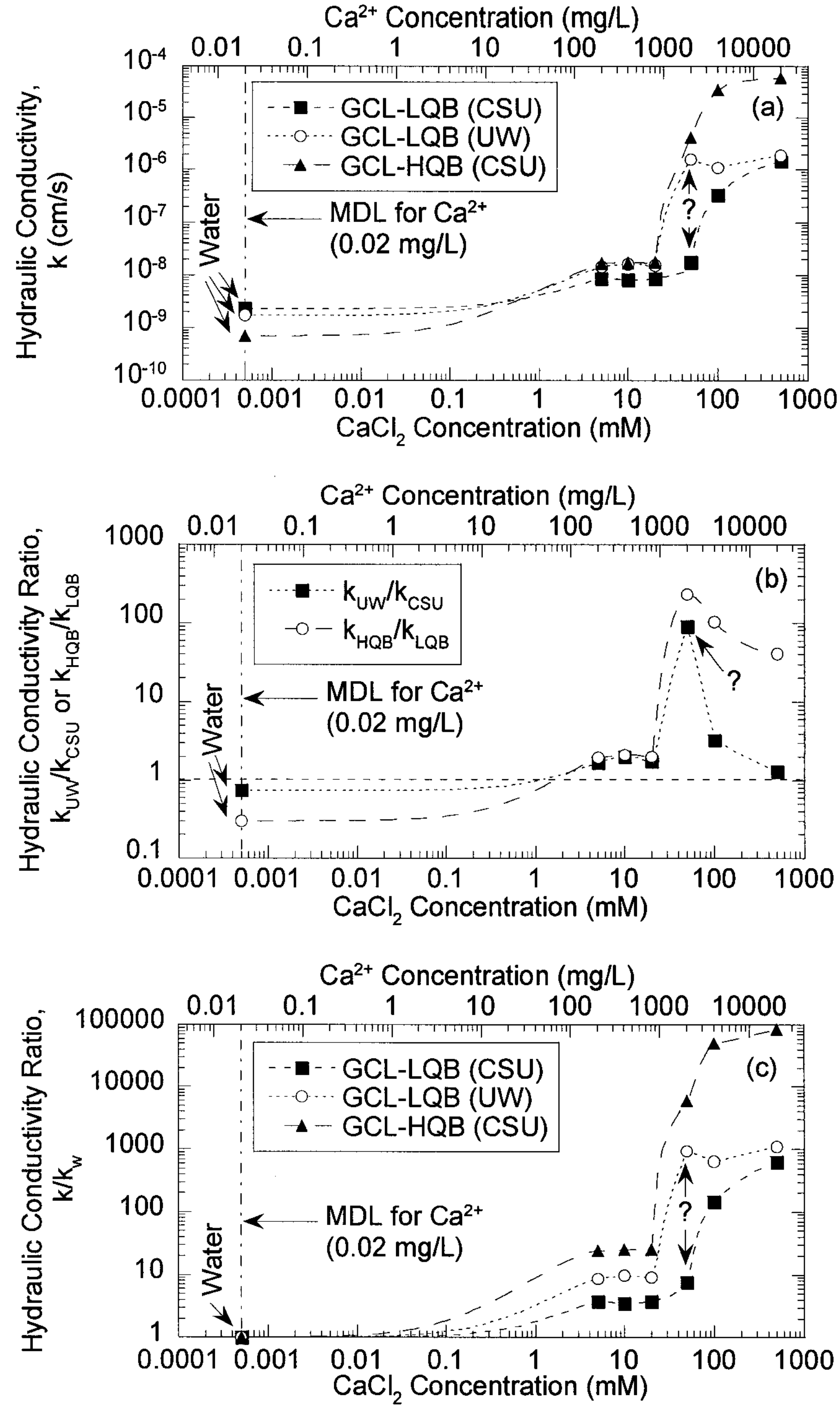

Fig. 6.2 – Results of hydraulic conductivity (k) tests performed with water and $CaCl_2$ solutions: (a) k; (b) ratio of k for GCL-LQB at UW to k for GCL-LQB at CSU or k for GCL-HQB at CSU to k for GCL-LQB at CSU; and (c) ratio of k based on any testing liquid to k based on water (CSU = Colorado State University; UW = University of Wisconsin - Madison; MDL = method detection limit).

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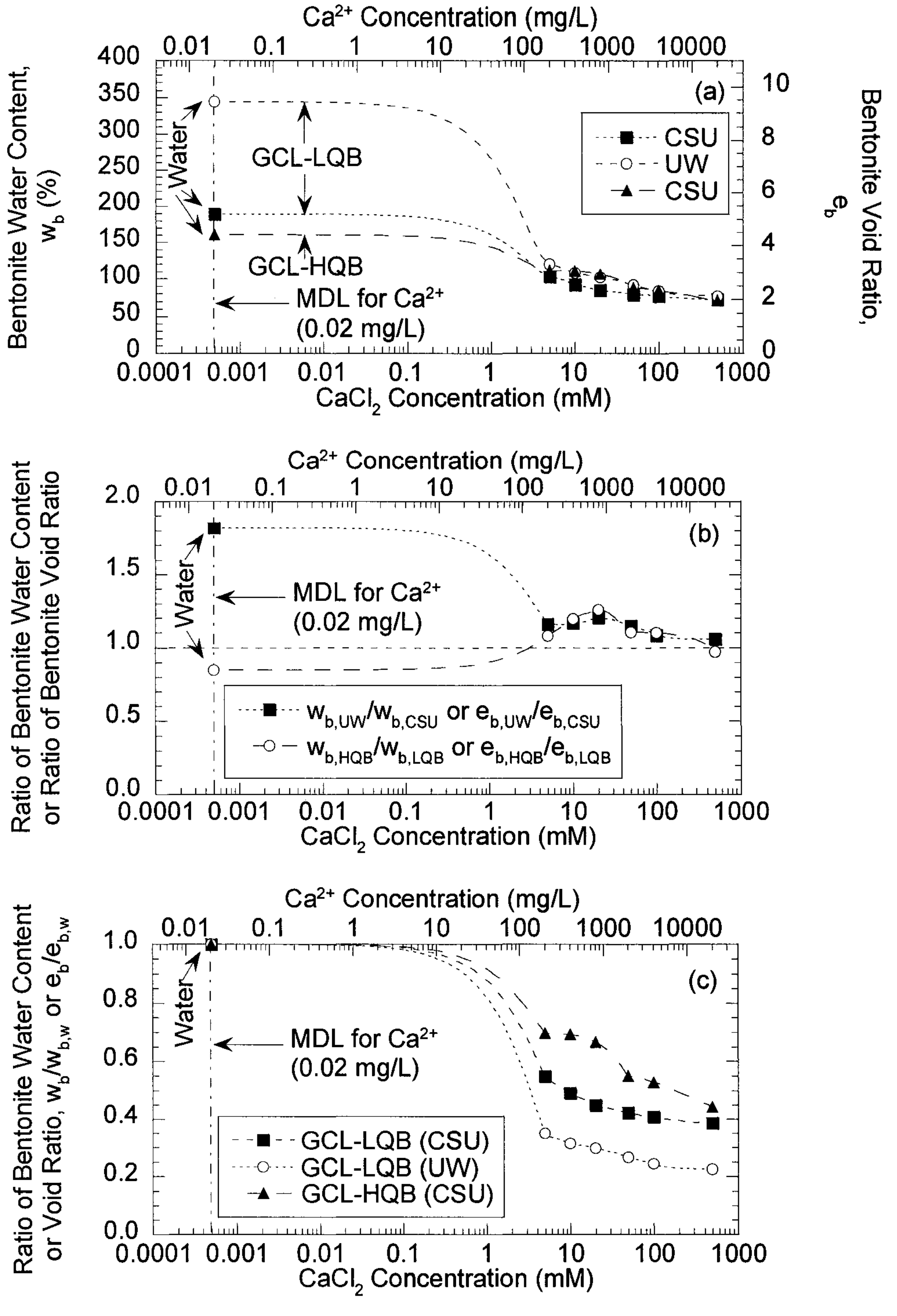

Fig. 6.3 – Final bentonite gravimetric water content (w_b) and void ratio (e_b) after permeation: (a) w_b or e_b; (b) ratio of w_b or e_b for GCL-LQB at UW to w_b or e_b for GCL-LQB at CSU or w_b or e_b for GCL-HQB to w_b or e_b for GCL-LQB at CSU; and (c) ratio of w_b or e_b based on permeation with any testing liquid to w_b or e_b based on permeation with water (CSU = Colorado State University; UW = University of Wisconsin - Madison; MDL = method detection limit).

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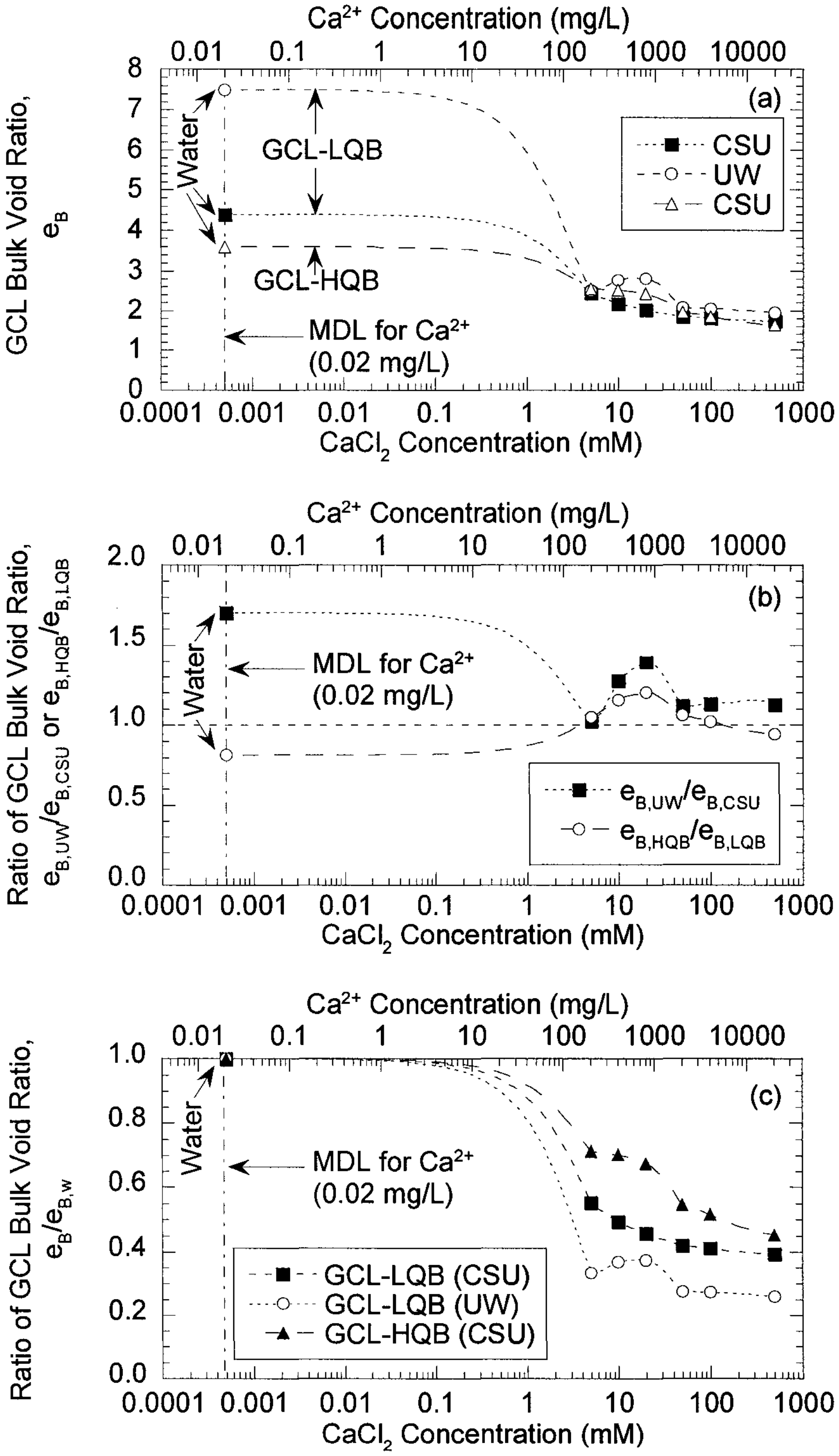

Fig. 6.4 – Final GCL bulk void ratio (e_B) after permeation: (a) e_B; (b) ratio of e_B for GCL-LQB at UW to e_B for GCL-LQB at CSU or e_B for GCL-HQB at CSU to e_B for GCL-LQB at CSU; and (c) ratio of e_B based on permeation with any testing liquid to e_B based on permeation with water (CSU = Colorado State University; UW = University of Wisconsin - Madison; MDL = method detection limit).

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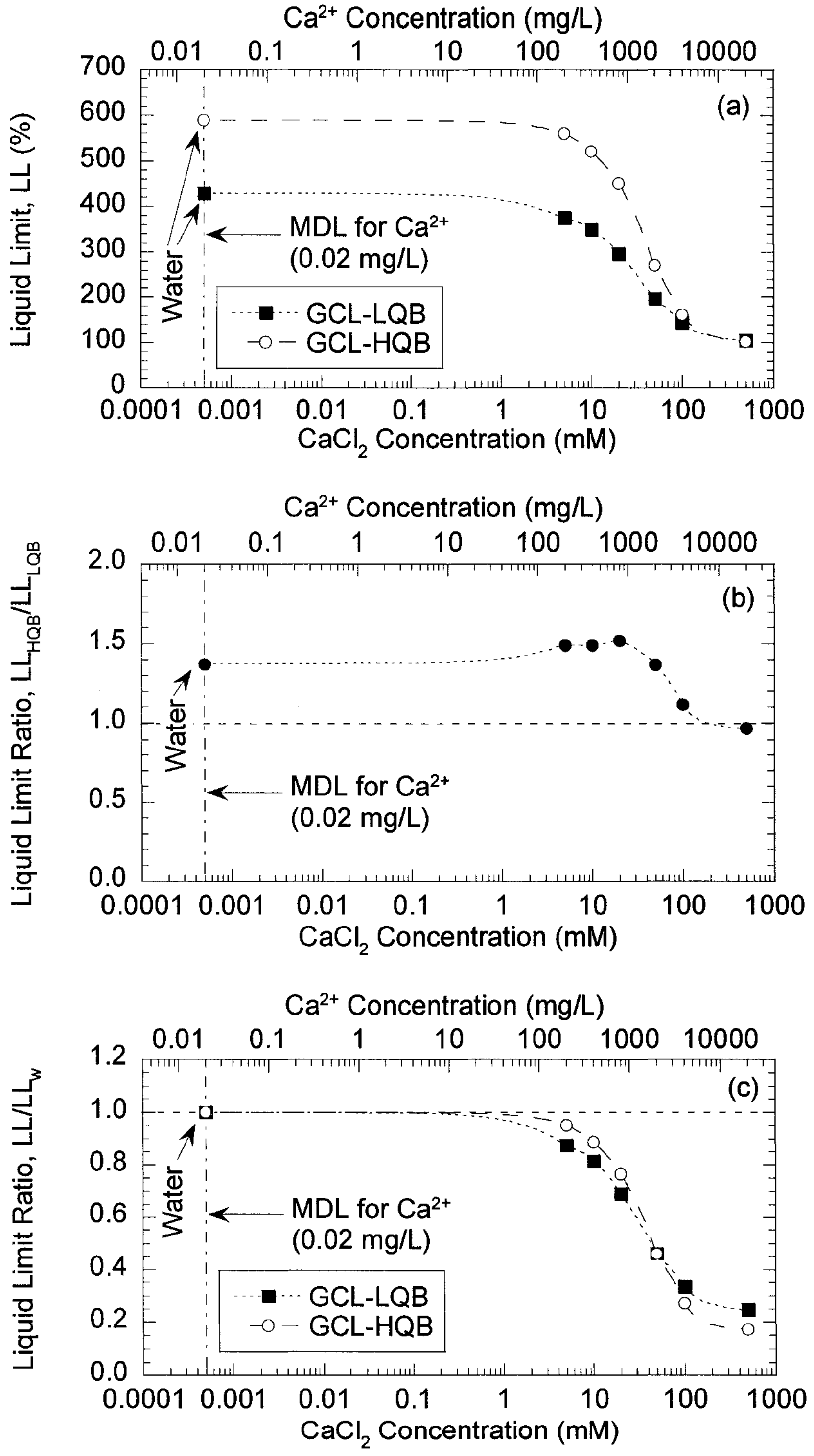

Fig. 6.5 – Results of liquid limit (LL) tests performed on the bentonites taken from two GCLs with water and $CaCl_2$ solutions: (a) LL; (b) ratio of LL for GCL-HQB to LL for GCL-LQB; and (c) LL based on any testing liquid to LL based on water (MDL = method detection limit).

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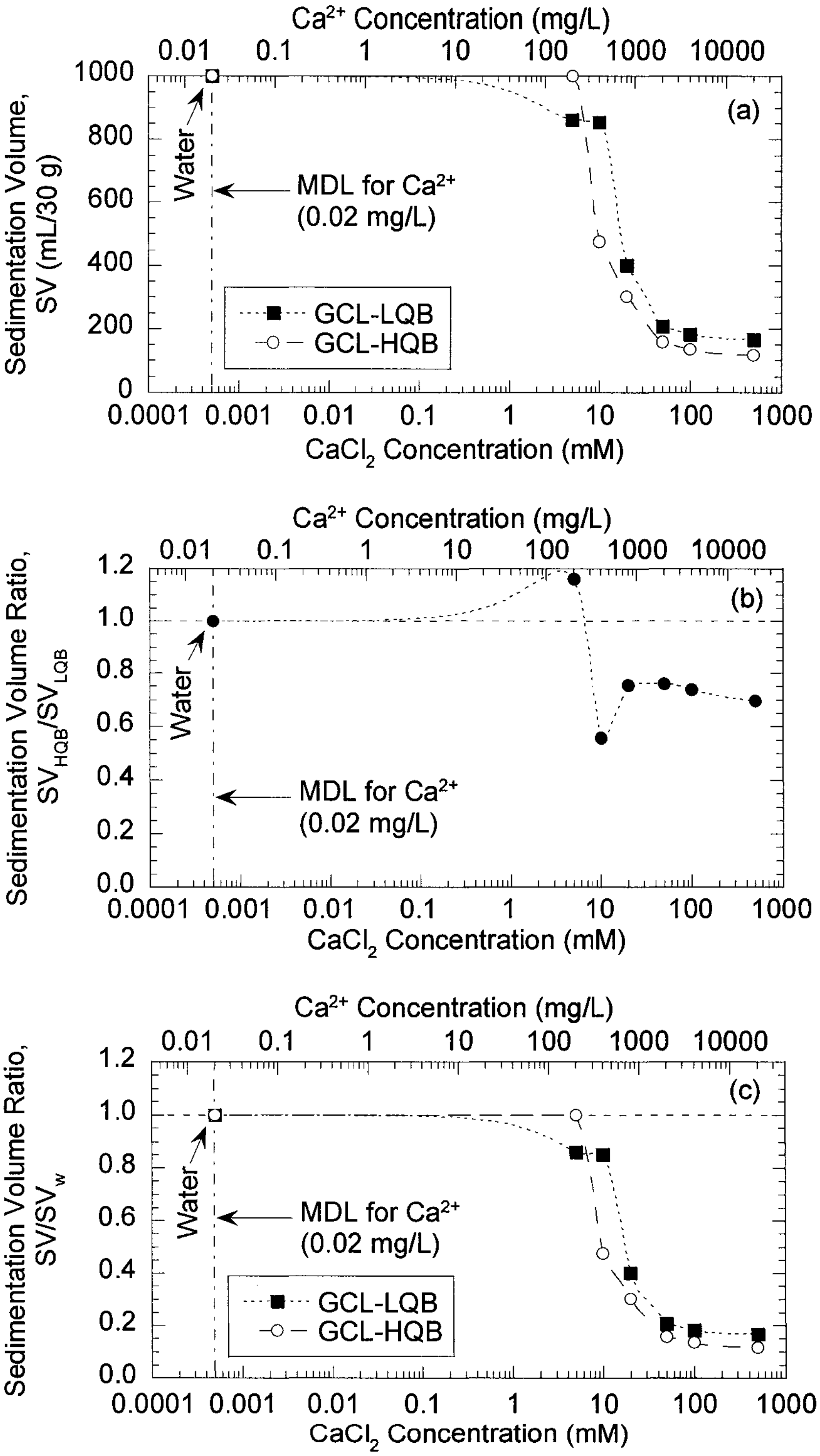

Fig. 6.6 – Results of sedimentation volume (SV) tests performed on the bentonites taken from two GCLs with water and CaCl$_2$ solutions: (a) SV; (b) ratio of SV for GCL-HQB to SV for GCL-LQB; and (c) SV based on any testing liquid to SV based on water (MDL = method detection limit).

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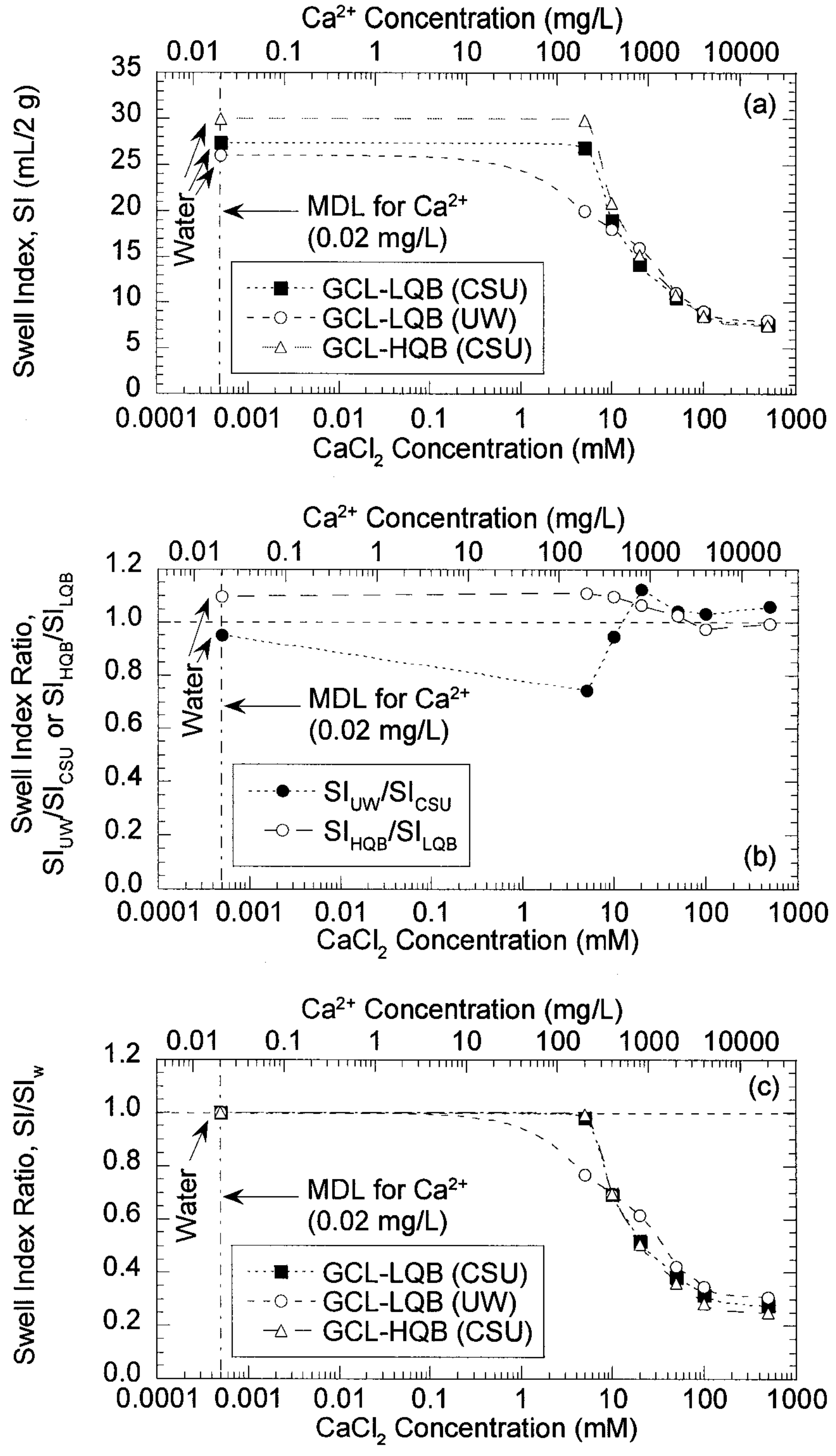

Fig. 6.7 – Results of swell index (SI) tests performed on the bentonites taken from two GCLs with water and $CaCl_2$ solutions: (a) SI; (b) ratio of SI for GCL-LQB at UW to SI for GCL-LQB at CSU or SI for GCL-HQB at CSU to SI for GCL-LQB at CSU; and (c) SI based on any testing liquid to SI based on water (CSU = Colorado State University; UW = University of Wisconsin - Madison; MDL = method detection limit).

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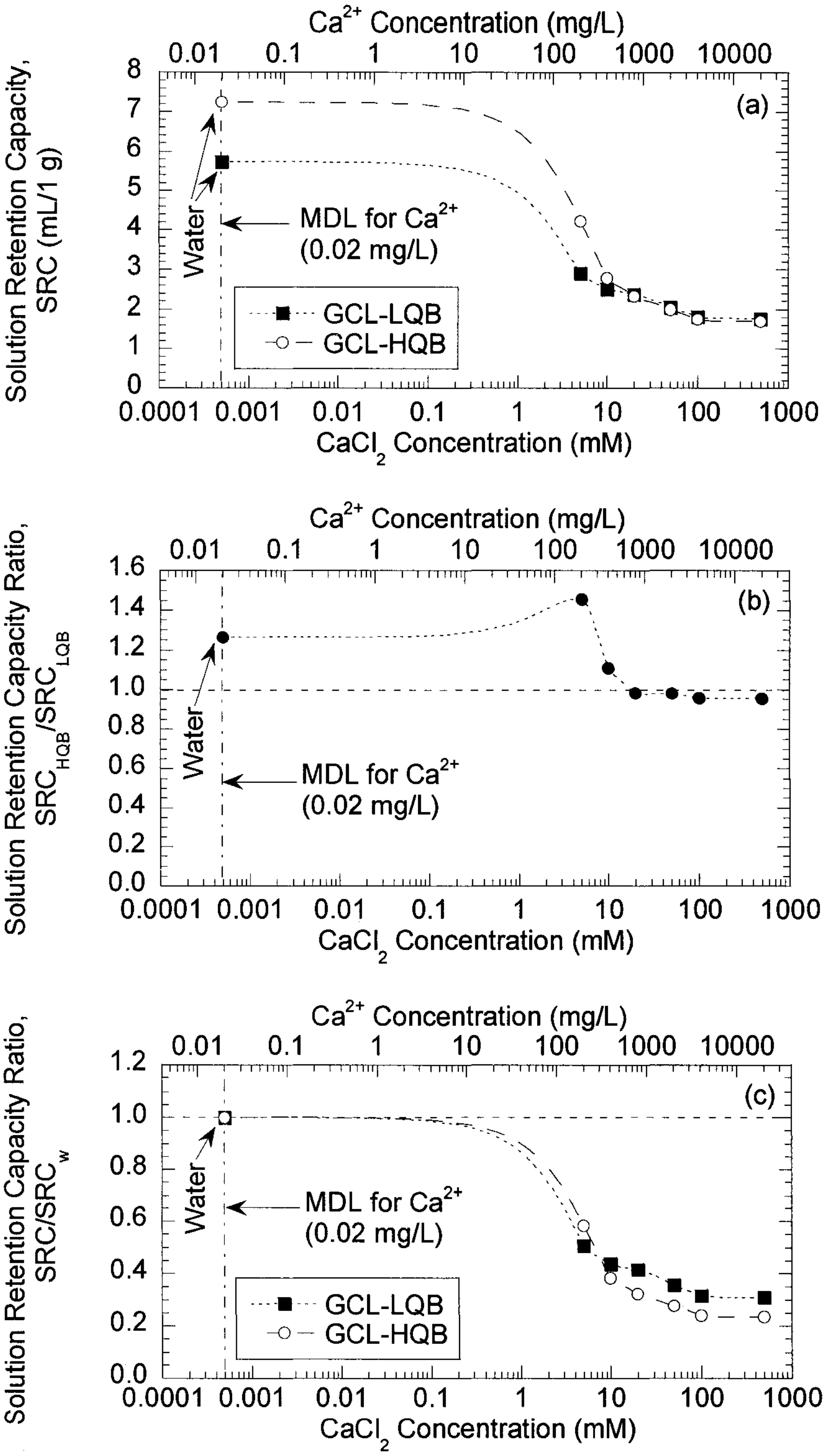

Fig. 6.8 – Results of solution retention capacity (SRC) tests performed on the bentonites taken from two GCLs with water and $CaCl_2$ solutions: (a) SRC; (b) ratio of SRC for GCL-HQB to SRC for GCL-LQB; and (c) SRC based on any testing liquid to SRC based on water (MDL = method detection limit).

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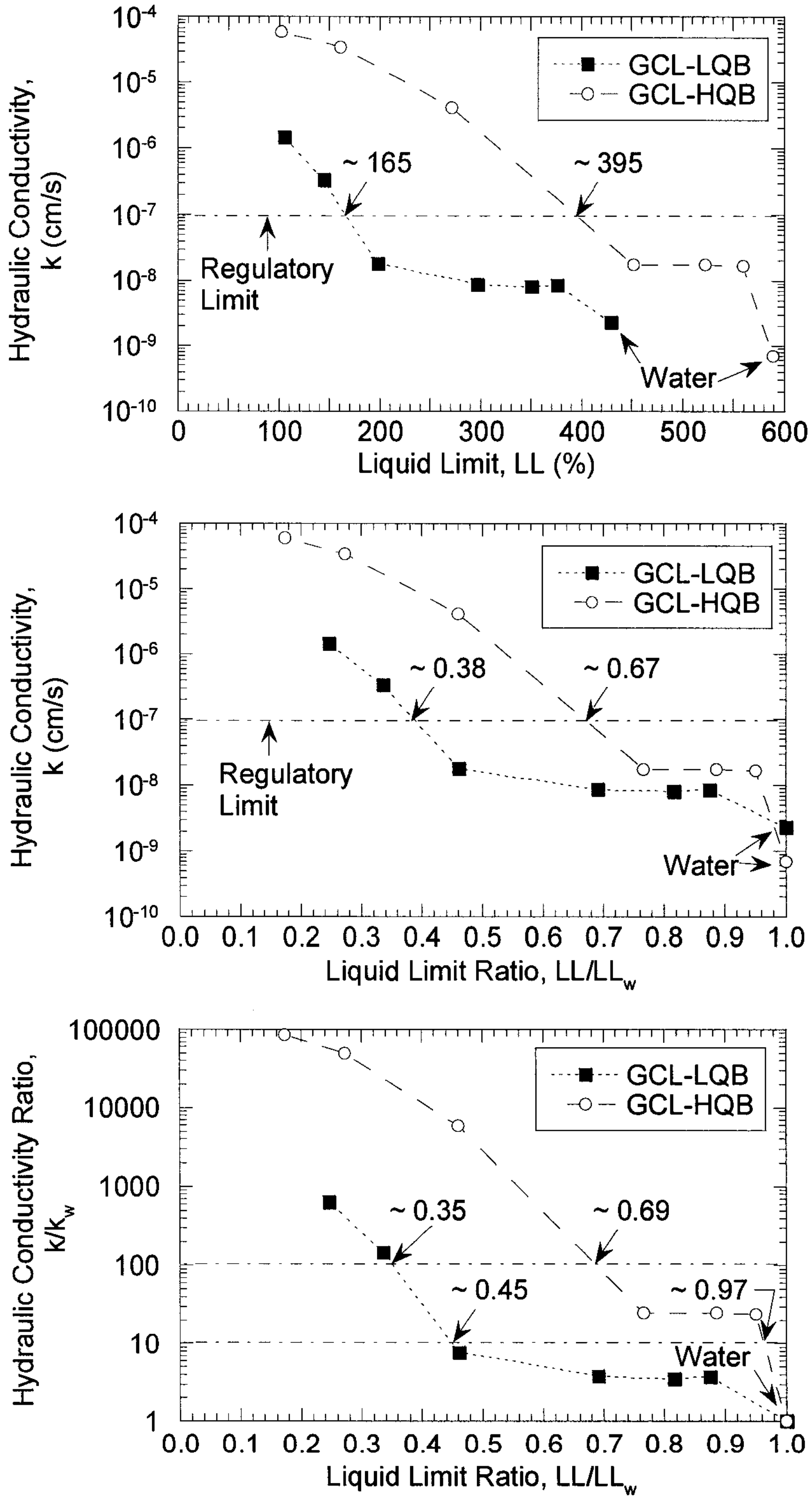

Fig. 6.9 – Comparison between liquid limit and hydraulic conductivity based on the tests performed using two GCLs (ratio = property based on any testing liquid to property based on water).

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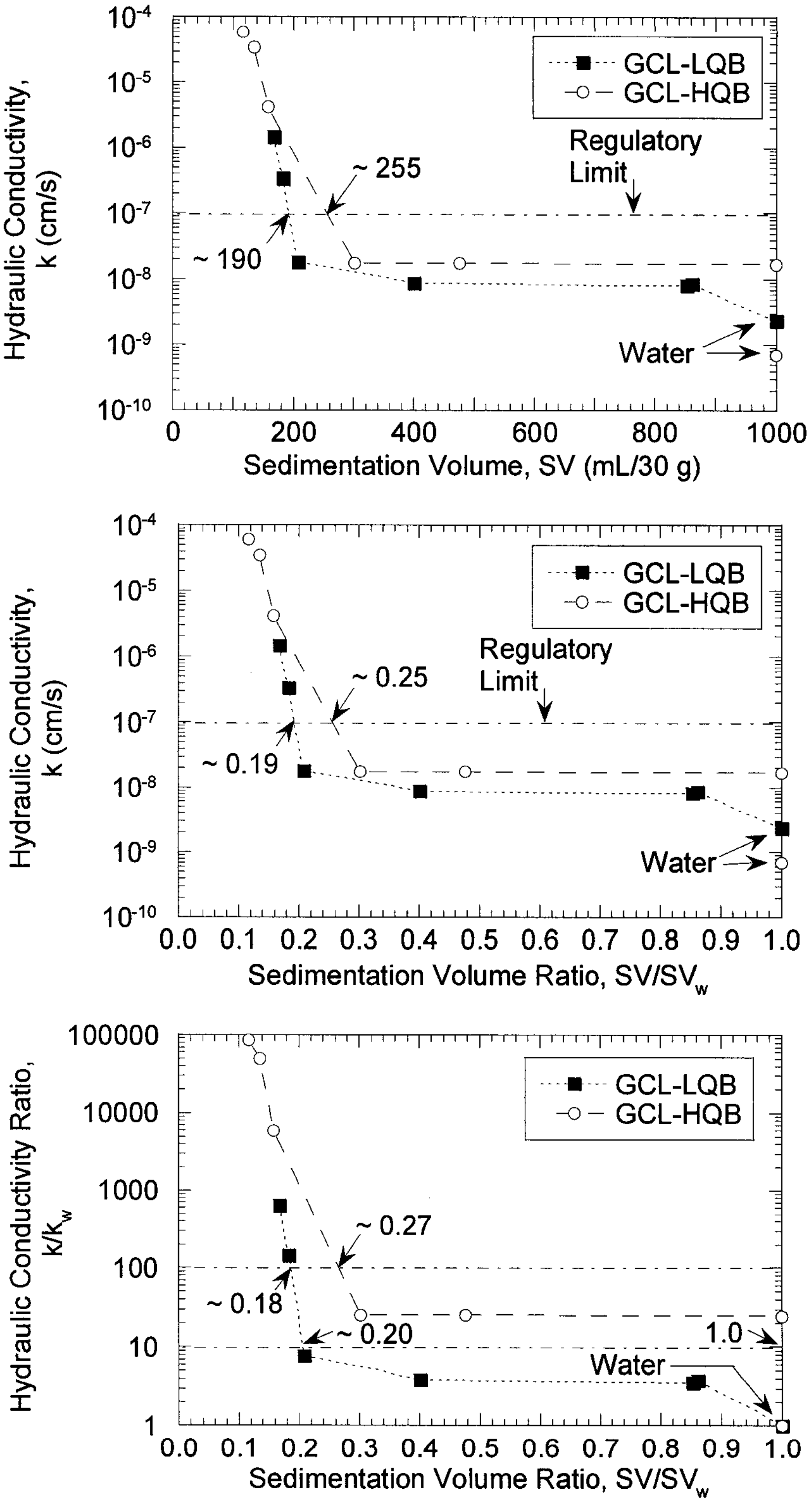

Fig. 6.10 – Comparison between sedimentation volume and hydraulic conductivity based on the tests performed using two GCLs (ratio = property based on any testing liquid to property based on water).

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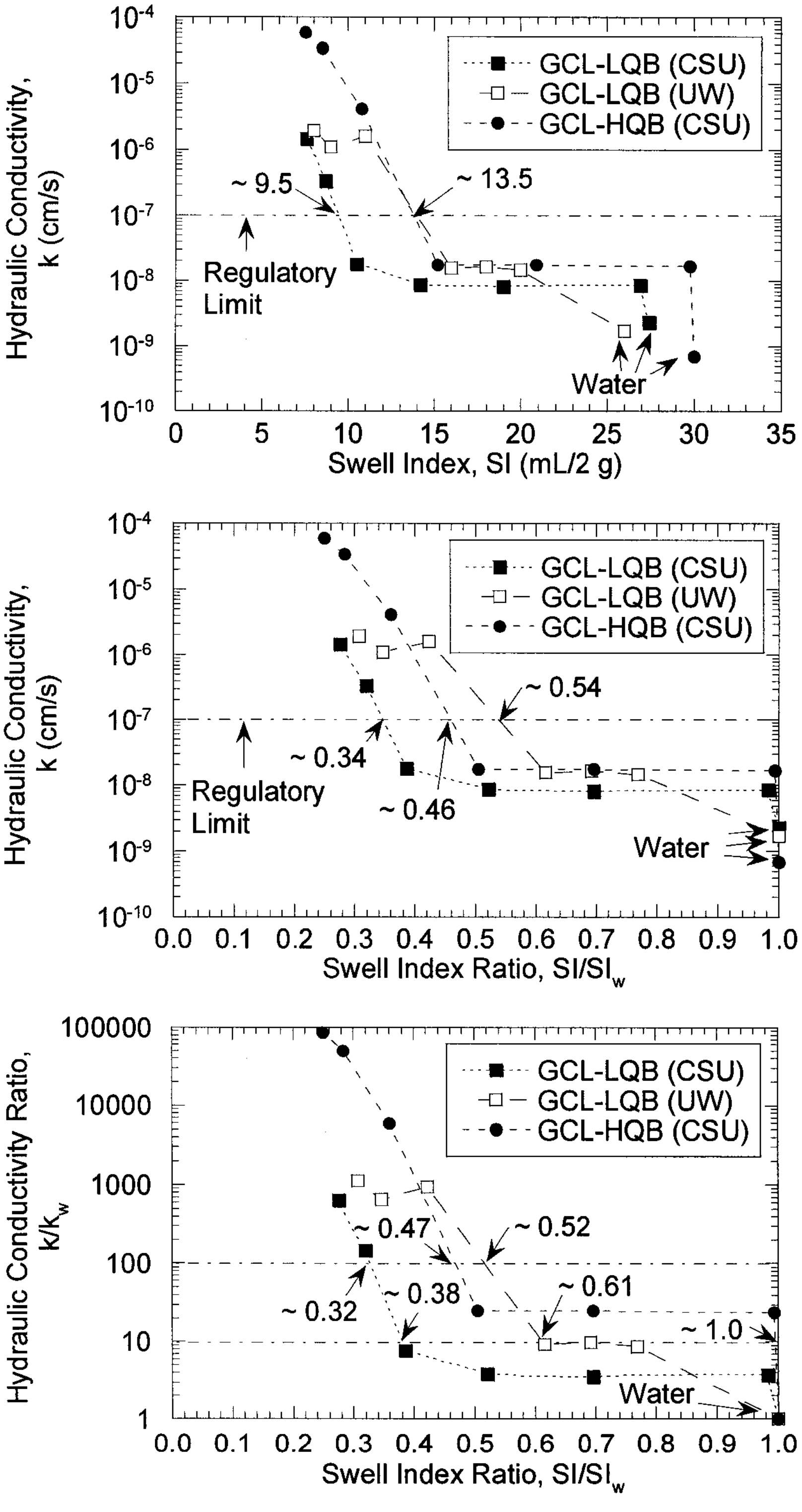

Fig. 6.11 – Comparison between swell index and hydraulic conductivity based on the tests performed using two GCLs at either Colorado State University (CSU) or University Wisconsin - Madison (UW) (ratio = property based on any testing liquid to property based on water).

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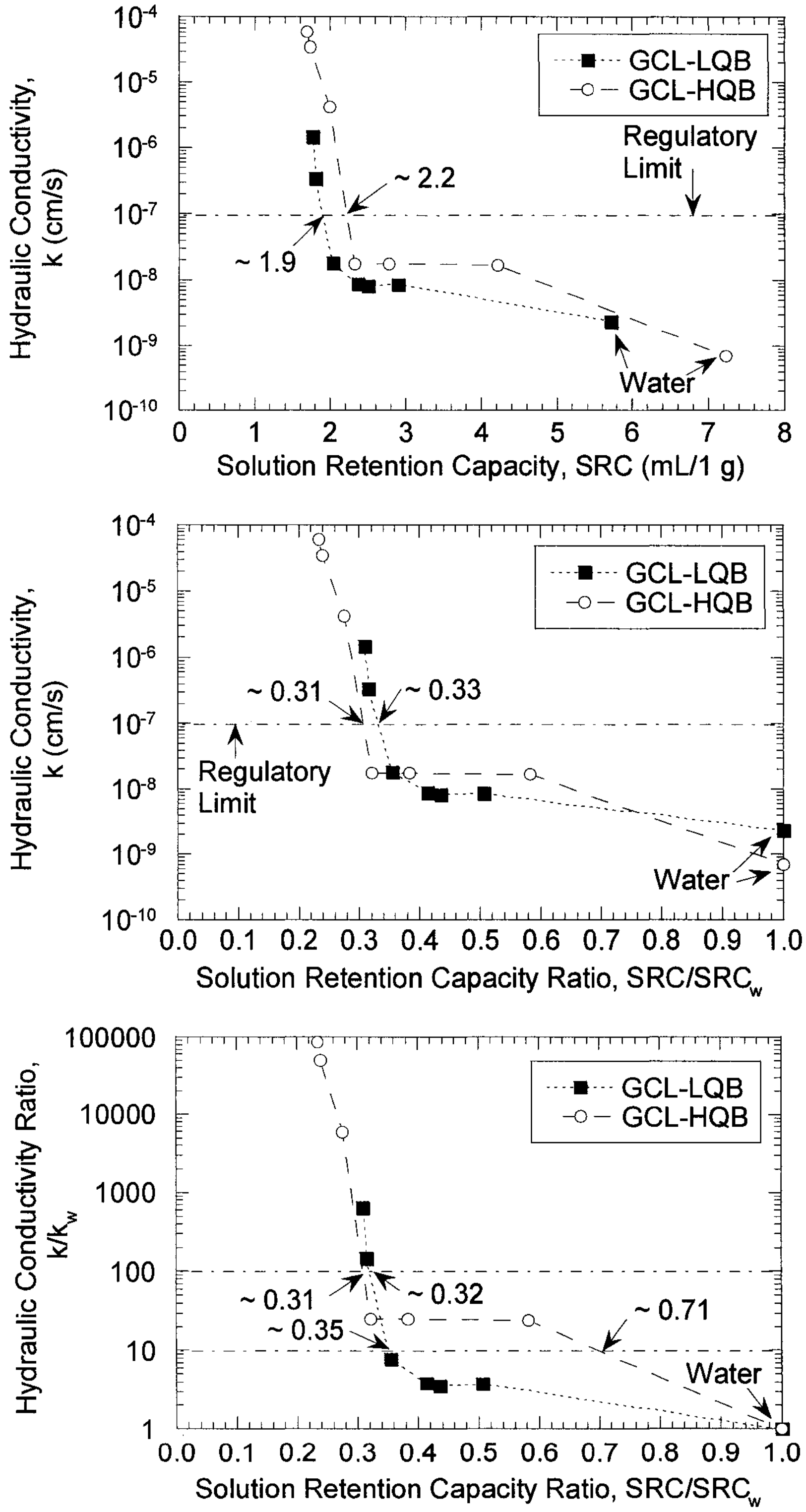

Fig. 6.12 – Comparison between solution retention capacity and hydraulic conductivity based on the tests performed using two GCLs (ratio = property based on any testing liquid to property based on water).

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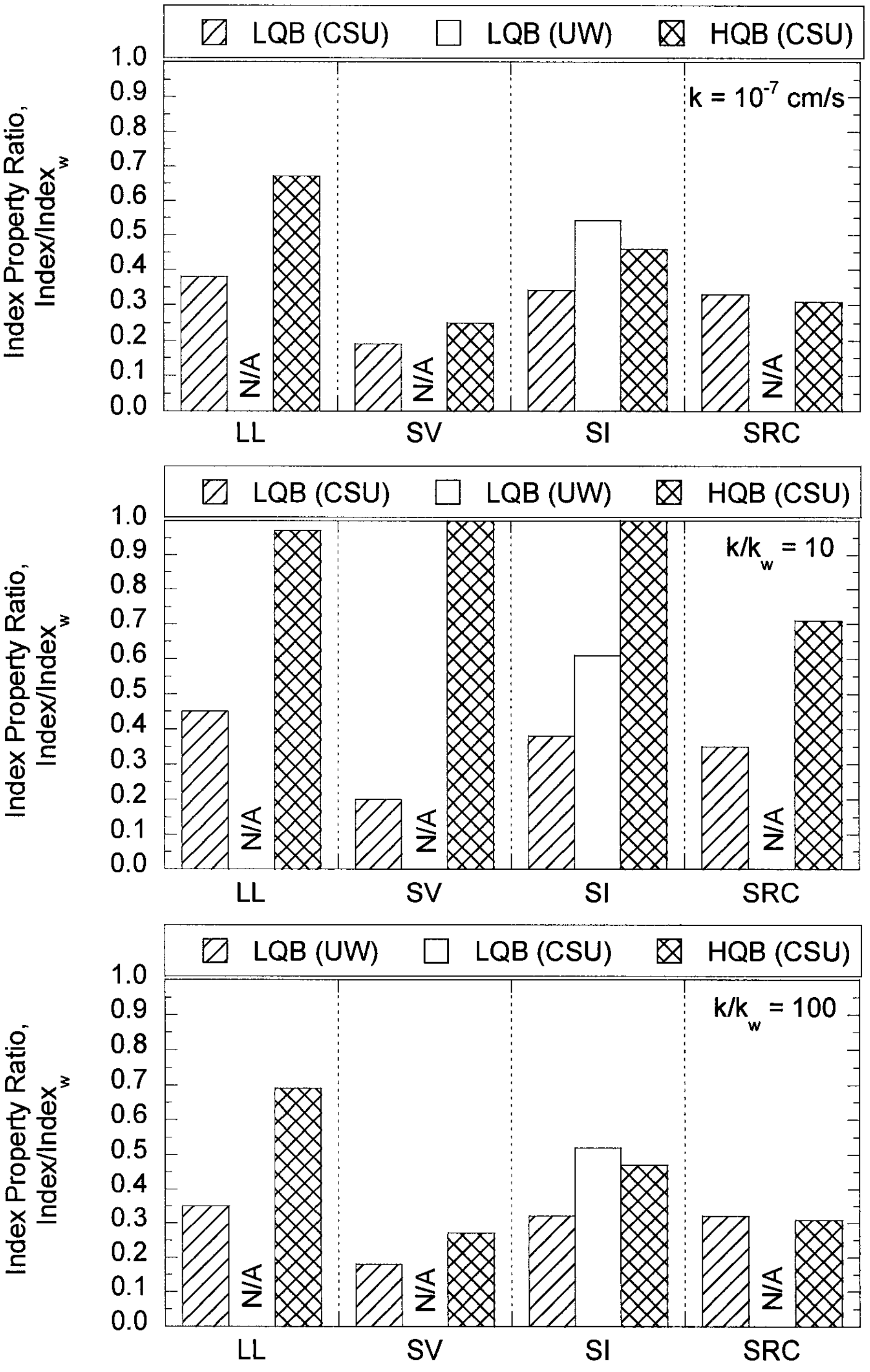

Fig. 6.13 – Ratio of index property based on any testing liquid to index property based on water corresponding to three hydraulic conductivity criteria (LQB or HQB = lower or higher quality bentonite; CSU = Colorado State University; UW = University of Wisconsin - Madison; LL = liquid limit; SV = sedimentation volume; SI = swell index; SRC = solution retention capacity; N/A = not applicable).

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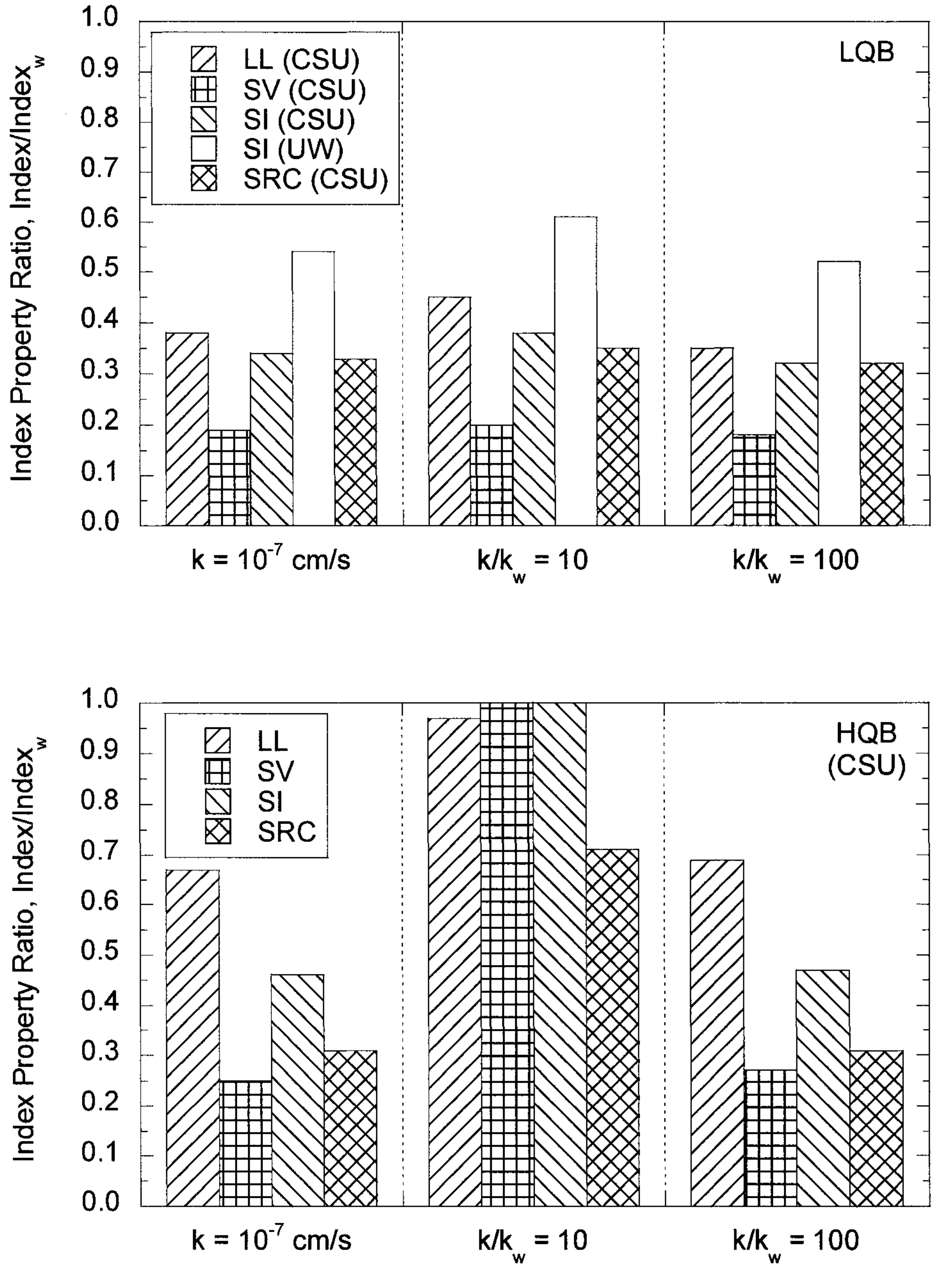

Fig. 6.14 – Ratio of index property based on any testing liquid to index property based on water corresponding to three hydraulic conductivity criteria (LQB or HQB = lower or higher quality bentonite; CSU = Colorado State University; UW = University of Wisconsin - Madison; LL = liquid limit; SV = sedimentation volume; SI = swell index; SRC = solution retention capacity).

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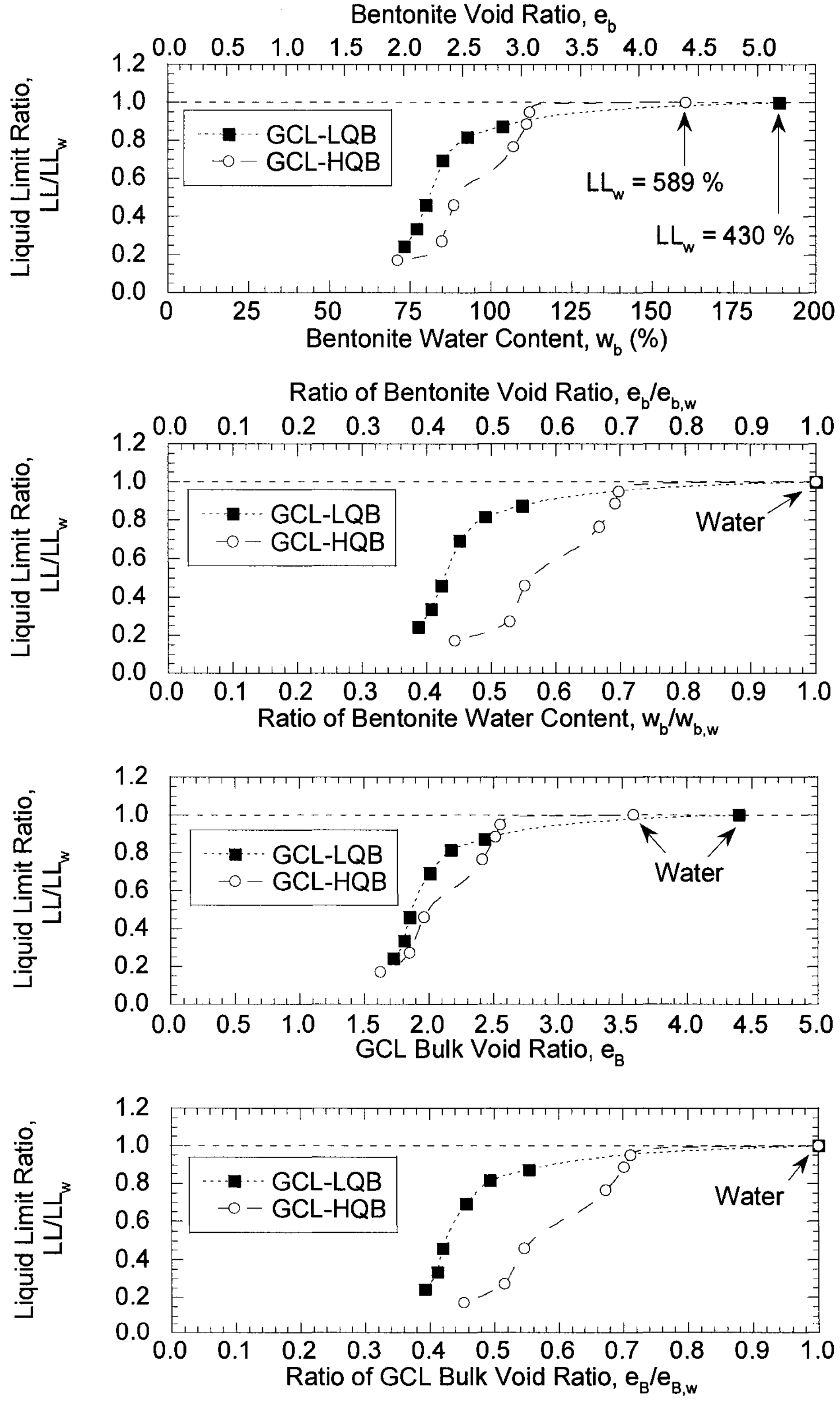

Fig. 6.15 – Comparison between liquid limit and final properties of specimen after permeation based on the tests performed using two GCLs (ratio = property based on any testing liquid to property based on water).

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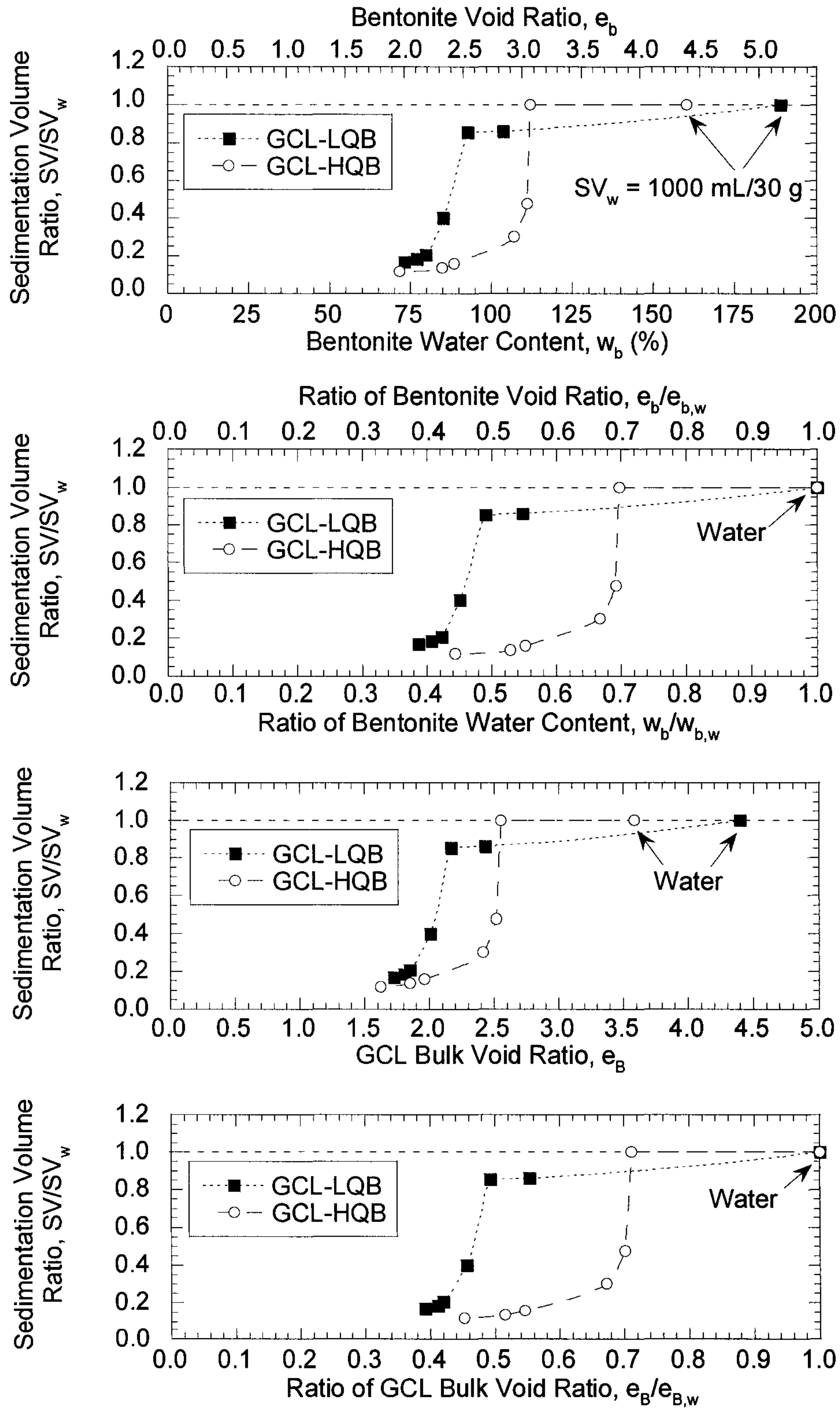

Fig. 6.16 – Comparison between sedimentation volume and final properties of specimen after permeation based on the tests performed using two GCLs (ratio = property based on any testing liquid to property based on water).

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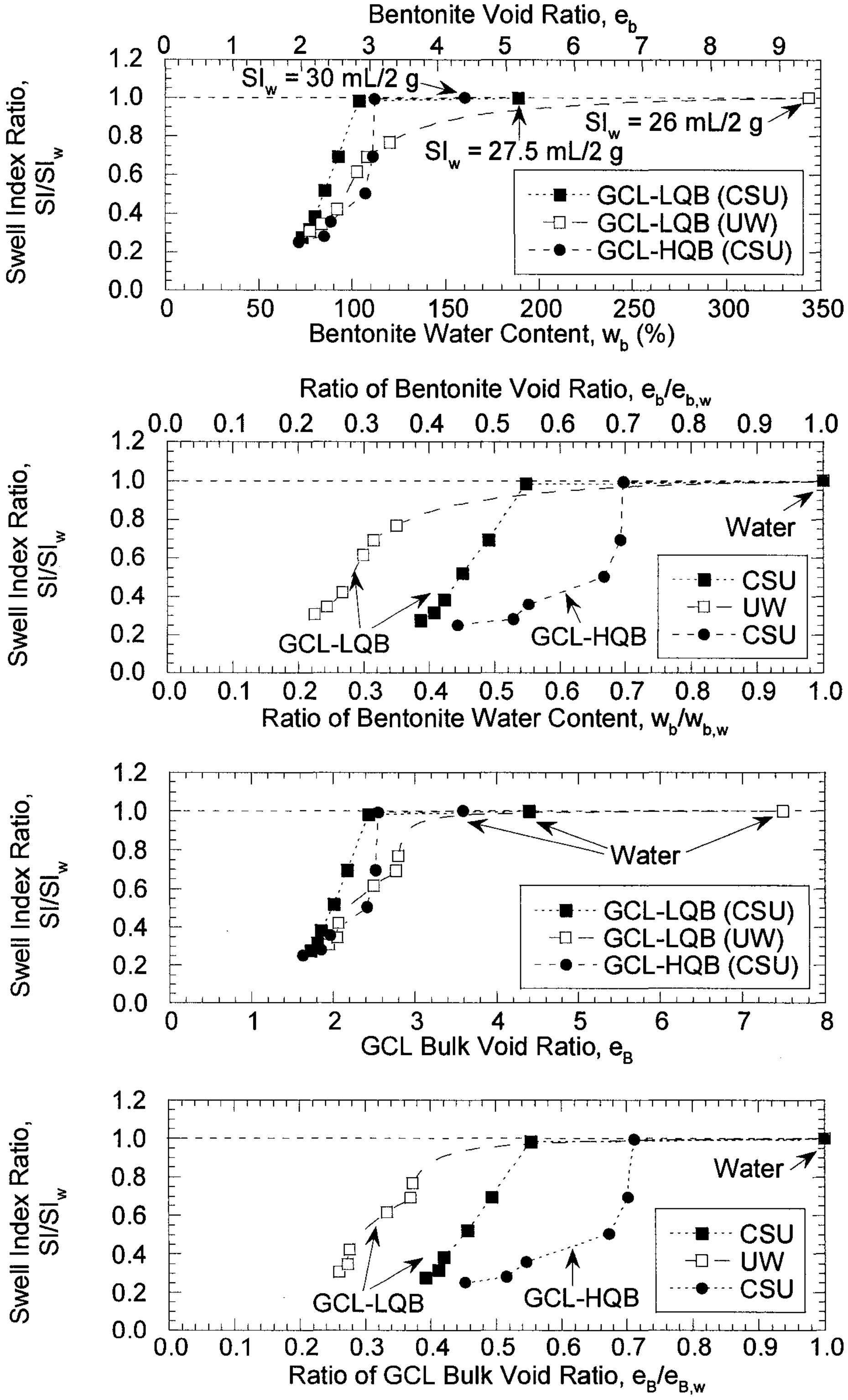

Fig. 6.17 – Comparison between swell index and final properties of specimen after permeation based on the tests performed using two GCLs (CSU = Colorado State University; UW = University of Wisconsin - Madison; ratio = property based on any testing liquid to property based on water).

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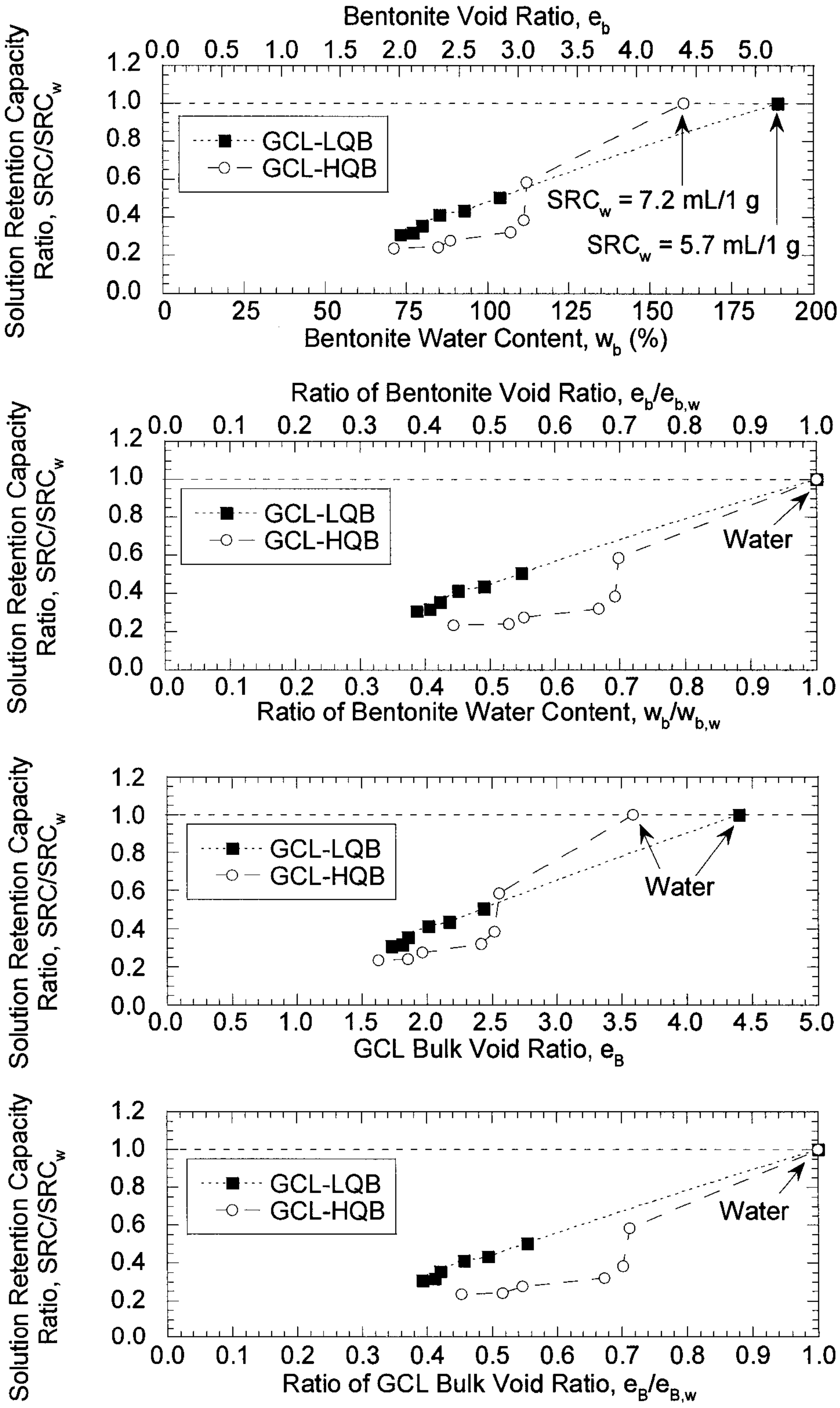

Fig. 6.18 – Comparison between solution retention capacity and final properties of specimen after permeation based using the tests performed on two GCLs (ratio = property based on any testing liquid to property based on water).

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CHAPTER 7

THE DESTRUCTIVE ROLE OF DIFFUSION ON MEMBRANE BEHAVIOR OF A GEOSYNTHETIC CLAY LINER

ABSTRACT: The results of a combined chemico-osmotic/diffusion experiment conducted on a geosynthetic clay liner (GCL) containing sodium bentonite illustrate the destructive role of diffusion on the ability of the GCL to act as a semipermeable membrane. The experiment is conducted by maintaining a concentration difference of 5 mM $CaCl_2$ across the GCL specimen while preventing the flow of solution through the specimen. A time-dependent membrane efficiency is derived from measured pressure differences induced across the specimen in response to the applied concentration difference. The diffusive mass fluxes of the solutes (Cl^- and Ca^{2+}) through the specimen also are measured simultaneously. An initial increase in induced pressure difference across the specimen to a peak value of 19.3 kPa is observed, followed by a gradual decrease to zero. The decrease in induced pressure difference is consistent with compression of adsorbed layers between clay particles and particle clusters due to diffusion of Ca^{2+}, resulting in concomitant increase in pore sizes and decrease in the observed membrane behavior. The time required for effective destruction of the initially observed semipermeable membrane behavior correlates well with the time required to

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achieve steady-state Ca^{2+} diffusion. The results have important implications with respect to the ability of clays to sustain membrane behavior.

Key Words: chemico-osmotic efficiency, clay membrane, adsorbed layer, diffusion, membrane behavior, reflection coefficient, solute restriction

7.1 INTRODUCTION

Solute restriction resulting from the existence of membrane behavior in clays has been shown to influence volume change behavior, cause apparent deviations from Darcy's law in hydraulic conductivity testing, generate anomalous pore-water pressures in low-permeability geologic formations, and affect the rate of solute migration through low-permeability clays (Malusis and Shackelford 2002a). Restricted solute migration resulting from membrane behavior also is currently being considered in the context of clay containment barriers for geoenvironmental applications, such as aquitards and engineered clay liners for containment of disposed waste, and vertical cutoff walls (e.g., soil-bentonite walls) for *in situ* containment of contaminated ground water (e.g., Keijzer and Loch 2001, Malusis et al. 2001a, Shackelford et al. 2001). In such cases, the existence of membrane behavior may be important in terms of evaluating the hydraulic and contaminant transport performance of the containment barrier, since the primary objective of the barrier is to maintain a contaminant concentration at the outer boundary of the barrier that is lower than the source concentration of the same contaminant. For example, in the case where the clay containment barrier acts as a semipermeable membrane, both chemico-osmotic counter flow and contaminant (solute) restriction

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would act to reduce the outward contaminant flux (Malusis et al. 2001a, Shackelford et al. 2001). Thus, a clay containment barrier that behaves as a semipermeable membrane is expected to perform better than one that does not exhibit membrane behavior.

In the case of electrolyte solutions, membrane behavior in clays generally is attributed to electrostatic repulsion of the ions by electric fields associated with the adsorbed layers of adjacent clay particles (e.g., Hanshaw and Coplen 1973, Fritz 1986). Thus, the factors that tend to cause an increase in the thickness of adsorbed layers (i.e., at constant porosity), such as decreasing ion concentration and/or decreasing ion valence, also tend to enhance the membrane efficiency of clays that behave as semipermeable membranes (see Kemper and Rollins 1966, Kemper and Quirk 1972). However, an increasing ion concentration and/or ion valence also may result in a reduction in membrane efficiency.

For example, Barbour (1986) and Barbour and Fredlund (1989) attributed expulsion of pore water from specimens in chemico-osmotic consolidation tests due to diffusion of high-concentration salts into the soil specimen and subsequent "collapse" of the adsorbed layers. Whitworth and Fritz (1994) correlated reductions in membrane efficiency of compacted smectitic membranes during forced passage of a 10 mM NaCl solution through the membranes to compression of adsorbed layers reflected by changes in the permeability of the membranes.

Malusis et al. (2001b) and Malusis and Shackelford (2002a) observed partial time-dependent decreases in membrane efficiency for thin specimens (8-13 mm) of a geosynthetic clay liner (GCL) containing sodium bentonite subjected to differences in potassium chloride (KCl) concentrations. For example, the induced pressure difference

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for a test with a concentration difference of 47 mM KCl increased to approximately 40 kPa after approximately three days, but subsequently decreased before reaching a steady value of 32 kPa. This time-dependent decrease in membrane efficiency tended to increase with increasing KCl concentration, and/or increasing specimen porosity (Malusis and Shackelford 2002a). Malusis et al. (2001b) and Malusis and Shackelford (2002a) concluded that the observed behavior was consistent with expected behavior based on compression of adsorbed layers resulting from increases in KCl concentrations due to solute diffusion in their closed-system (no-flow) testing apparatus.

However, apparent reductions in membrane efficiency have not always been attributed to collapse of adsorbed layers due to increased solute concentrations within the clay membrane. For example, Keijzer et al. (1997, 1999) attributed changes in induced chemico-osmotic pressures across compacted sodium bentonite specimens located between fresh- and salt-water reservoirs to time-dependent changes in the boundary salt concentrations, resulting in a time-dependent decrease in the concentration gradient across the specimen. These boundary concentration changes were attributed to the net migration of water in a direction of decreasing concentration gradient due to the process of diffusion-osmosis (Olsen et al. 1990). As a result, Keijzer et al. (1997, 1999) concluded that the decrease in observed pressure difference did not necessarily correlate with a decrease in membrane efficiency of the specimens.

The results of the aforementioned studies suggest that migrating solutes may adversely affect the efficiency of clay membranes. However, these previous studies were not performed with the specific purpose of evaluating the potential effect of diffusion on clay membrane efficiency. In addition, differences among the studies in terms of testing

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objectives (e.g., consolidation vs. membrane efficiency) and testing approaches (e.g., open systems vs. closed systems, constant vs. time-dependent boundary conditions) have precluded any consensus with respect to the potential effect of diffusion of invading solutes on clay membrane efficiency. As a result, the objective of this study is to illustrate a direct correlation between diffusion of invading solutes and the destruction of the efficiency of a semipermeable clay membrane. This objective is achieved using a unique testing apparatus that maintains constant boundary concentrations while preventing solution flow through the specimen, thereby eliminating the potential effects of changes in boundary concentrations and transport processes other than diffusion (e.g., chemico-osmosis, diffusion-osmosis) from consideration. The results of this evaluation may have significant ramifications with respect to use and performance of clay membranes as barriers for geoenvironmental containment applications.

7.2 MATERIALS AND METHODS

7.2.1 Materials

The geosynthetic clay liner (GCL) used in this study consists of a layer of granular sodium bentonite sandwiched between woven and non-woven polypropylene geotextiles held together by needle-punched fibers. A schematic cross-section of this GCL is shown in Fig. 7.1. The GCL is approximately 6-mm thick in an air-dried condition, but quickly swells to a thickness typically ranging from 10 mm to 15 mm upon exposure to water when unconfined. The bentonite content of the GCL measured in accordance with ASTM D 5993 is 5.1 kg/m^2. The mineralogy, exchangeable metals, and

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cation exchange capacity (CEC) for the bentonite portion of the GCL are given in Table 7.1.

Although the GCL used in this study does not come from the same manufacturer as the GCL used by Malusis et al. (2001b) and Malusis and Shackelford (2002a,b), the components of the GCL and the mineralogical composition of the bentonite in the two GCLs are very similar. This similarity was considered important because the GCL used by Malusis et al. (2001b) and Malusis and Shackelford (2002a,b) was shown to behave as a semipermeable membrane in the presence of KCl solutions ranging from 3.9 mM to 47 mM for specimen thicknesses ranging from 8 mm to 13 mm, with greater membrane efficiencies associated with lower KCl concentrations and/or thinner GCL specimens. As a result, the GCL used in this study was expected to exhibit semipermeable membrane behavior, i.e., provided the boundary salt concentration was suitably low and the specimen was suitably thin.

The liquids used in the experiment consist of tap water that is processed to remove ions by passage through three Barnstead® ion exchange columns in series (electrical conductivity, EC, at 25 °C ~ 0.2 mS/m, pH ~ 5.6), and a 5 mM calcium chloride ($CaCl_2$) solution (EC ~ 121 mS/m, pH ~ 5.6) prepared by dissolving $CaCl_2$ (powdered, > 96 % pure, Sigma-Aldrich Co., St. Louis, MO) in the water. The processed tap water classifies as Type IV deionized water (DIW) as per ASTM D 1193. The $CaCl_2$ was selected for use in this study to determine if the GCL would exhibit membrane behavior when exposed to the divalent calcium cation, as opposed to the previous studies that used the monovalent potassium cation, and the 5 mM concentration was thought to be sufficiently low to enhance the possibility of observing membrane behavior.

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7.2.2 Testing Apparatus

The testing apparatus and testing procedures are the same as described by Malusis et al. (2001b), and Malusis and Shackelford (2002a,b); therefore, only a relatively brief description is provided here. A schematic illustration of the testing apparatus is shown in Fig. 7.2.

The testing cell consists of a rigid acrylic cylinder, top piston, and base pedestal. The top piston is locked in place to prevent soil expansion and to control the thickness (porosity) of the soil specimen. Solutions containing initial concentrations of a given electrolyte (designated as C_{ot} and C_{ob} in Fig. 7.2) are expelled from each of the two actuators (syringes) at the same, constant rate via the plunger that is attached to a flow-pump drive (not shown), and subsequently are infused through the porous stones across the top and bottom boundaries of the specimen. Circulation outflow from these boundaries is simultaneously collected through the opposite end of the actuator at the same rate in order to maintain a constant volume inside the testing cell (i.e., $\Delta V_{cell} = 0$) and prevent liquid flux through the specimen. Under these conditions, the chemico-osmotic efficiency coefficient, ω, also commonly known as the reflection coefficient, σ, is defined as follows (Staverman 1952, Katchalsky and Curran 1965, Groenevelt and Elrick 1976, van Oort et al. 1996, Malusis et al. 2001b):

$$\omega = \frac{\Delta P}{\Delta \pi} \tag{7.1}$$

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where ΔP = the measured pressure difference induced across the specimen as a result of prohibiting chemico-osmotic flux of solution, and $\Delta\pi$ = the theoretical chemico-osmotic pressure difference across an "ideal" semipermeable membrane (i.e., $\omega = 1$) subjected to an applied difference in solute concentration (e.g., Olsen et al. 1990).

The value for $\Delta\pi$ in Eq. 7.1 is calculated based on the salt concentrations at the specimen boundaries in accordance with the van't Hoff expression as follows (Malusis et al. 2001b, Malusis and Shackelford 2002a):

$$\Delta\pi = RT\sum_{i=1}^{N}\left(C_{ob,i} - C_{ot,i}\right) \qquad (7.2)$$

where R = the universal gas constant [8.314 $J \cdot mol^{-1} \cdot K^{-1}$], T = the absolute temperature [K], $C_{ob,i}$ = the initial concentration of solute species i at the bottom of the specimen [$mol \cdot L^{-3}$], $C_{ot,i}$ = the initial concentration of solute species i at the top of the specimen [$mol \cdot L^{-3}$], and N = the total number of solute species. For simple salt solutions, such as $CaCl_2$, Eq. 7.2 may be written more conveniently as follows:

$$\Delta\pi = \nu RT\Delta C \qquad (7.3)$$

where ν = the number of ions per molecule of the salt, and ΔC (= $C_{ob} - C_{ot}$) = the salt concentration gradient. The induced pressure difference, ΔP, in Eq. 7.1 is measured using a differential pressure transducer that is located as shown in Fig. 7.2. Typical trends in the induced pressure difference as a function of time based on the data reported by Malusis et

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al. (2001b) and Malusis and Shackelford (2002a) are illustrated schematically in Fig. 7.3a. The observed effect of increasing solute concentration difference on the post-peak pressure difference previously described also is illustrated in Fig. 7.3a.

The differences in solute (Cl^- and Ca^{2+}) concentrations between the top and bottom boundaries of the specimen also cause solute diffusion from the higher concentration boundary (top) to the lower concentration boundary (bottom), such that a steady-state solute flux through the bottom of the specimen is eventually established and maintained. This scenario commonly is referred to as the steady-state approach for diffusion testing (Shackelford 1991).

In the steady-state approach, the measured concentrations for a given solute in the circulation outflow (i.e., from the base pedestal) typically are converted to cumulative mass per unit area, Q_t, using the following expression (Malusis et al. 2001b):

$$Q_t = \frac{1}{A}\sum_{i=1}^{N_s} \Delta m_i = \frac{1}{A}\sum_{i=1}^{N_s} C_{b,i}\Delta V_i \tag{7.4}$$

where A = the cross-sectional area of the specimen, Δm_i = the incremental mass of the solute species collected over a time increment (Δt), $C_{b,i}$ = the concentration of the solute species in the incremental volume, ΔV_i, of circulation outflow from the base pedestal corresponding to the same Δt, and N_s = the number of incremental samples corresponding to the total elapsed time, t. The results are plotted in terms of Q_t versus t, as illustrated schematically in Fig. 7.3b. The curved portion of the example plot in Fig. 7.3b represents

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transient diffusion, while the linear portion of the data in Fig. 7.3b corresponding to the constant slope, $\Delta Q_t / \Delta t$, represents steady-state diffusion.

Two characteristic times also are associated with the plot in Fig. 7.3b. First, the time corresponding to the intersection of the extension of the steady-state slope to the x-axis is referred to as the time lag, t_L (Shackelford 1991). The value of t_L can be used to determine the retardation factor, R_d, that reflects the adsorption behavior of the solute during transient diffusion (see Malusis et al. 2001b). Second, the time corresponding to the intersection of the initial curved portion of the example plot shown in Fig. 7.3b, representing the transient diffusion stage, and the linear portion of the example plot, representing steady-state diffusion, is the time required to achieve steady-state diffusion, t_{ss} Note that t_{ss} is always greater than t_L, and that t_{ss} typically is not evaluated when steady-state diffusion tests are performed.

The effective diffusion coefficient, D^*, of the given solute species is determined from the slope of the steady-state portion of the response, $\Delta Q_t/\Delta t$, in accordance with the following expression:

$$D^* = -\left(\frac{\Delta Q_t}{\Delta t}\right)\left(\frac{L}{n\Delta C}\right) \tag{7.5}$$

where n = the specimen porosity, D^* = the effective diffusion coefficient, and L = the specimen thickness. As noted by Malusis and Shackelford (2002b), the value of D^* determined according to Eq. 7.5 is a coupled effective diffusion coefficient that includes a coupling term associated with the prevention of solution flow in accordance with the

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principles of irreversible thermodynamics. In the limit, as the membrane efficiency of a clay approaches zero, the coupled effective diffusion coefficient given by Eq. 7.5 converges to the true effective diffusion coefficient represented by Fick's first law for diffusion in soil as defined by Shackelford and Daniel (1991).

7.2.3 Specimen Assembly and Disassembly

A circular specimen of the GCL with a nominal diameter of 71 mm was cut from a larger GCL sheet, and placed on the base pedestal inside the testing cell. The cylinder then was filled with DIW to submerge the specimen, and the top piston was lowered into the cylinder to compress the GCL to a thickness of approximately 5 mm to enhance the potential for membrane behavior. After completion of compression, the top piston was locked in place to prevent further volume expansion of the specimen during the test due to swelling of the bentonite.

The initial concentrations of the soluble metals in the pore water of the specimen based on the measured soluble metals concentrations shown in Table 7.1, the assumption of 100 percent saturation, and a measured porosity of the specimen of 0.718, were approximately 161 mM for Na^+, 6.0 mM for Ca^{2+}, 1.3 mM for K^+, and 1.1 mM for Mg^{2+}. Since the sum of these metals concentrations far exceeds the concentration of the source solution (i.e., 5 mM $CaCl_2$), the specimen was permeated under backpressure with DIW before testing to saturate the specimen and to enhance the potential for membrane behavior by removing soluble salts. This permeation was continued until the electrical conductivity, EC, of the effluent from the specimen was approximately 50 percent of the measured EC for the 5 mM $CaCl_2$ source solution of 121 mS/m, as shown in Fig. 7.4.

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After permeation, the DIW was circulated at the top and bottom boundaries of the specimen for approximately five days to establish a steady baseline differential pressure (see Malusis et al. 2001b). The chemico-osmotic/diffusion portion of the experiment then was initiated by circulating the 5 mM $CaCl_2$ solution in the top piston (i.e., $C_{ot} > 0$) while continuing circulation of DIW in the base pedestal. Thus, in this study, the initial concentration of solute in the base pedestal was maintained at zero (i.e., $C_{ob} = 0$).

The circulation outflow from the bottom of the specimen also was collected and subsequently analyzed for electrical conductivity (EC), chloride (Cl^-) concentrations using ion chromatography, and calcium (Ca^{2+}) concentrations using inductively coupled plasma (detection via atomic emission spectrometry). At the end of the experiment, which lasted approximately 75 days, the cell was disassembled, and the final thickness and porosity of the specimen were measured.

7.3 RESULTS AND DISCUSSION

7.3.1 Electrical Conductivities

The electrical conductivities measured in the circulation outflows from the top and bottom boundaries during the chemico-osmotic/diffusion stage of the experiment are shown in Fig. 7.5. The electrical conductivity in the circulation outflow from the top boundary of the specimen, EC_{top}, was maintained relatively constant at a value of slightly greater than 100 mS/m. However, the electrical conductivity of the circulation outflow from the bottom boundary, $EC_{botttom}$, gradually increases from about 4 mS/m immediately after the start of the chemico-osmotic/diffusion stage to about 20 mS/m at about 30 to 35 days after the start of the chemico-osmotic stage. These measured EC values reflect the

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boundary conditions imposed in the experiment. For example, the lower EC_{top} relative to the source solution (i.e., $EC_{top} < 121$ mS/m) is consistent with the loss of solute mass from the source solution due to diffusion into the specimen, whereas the eventual increase in EC_{bottom} with time is consistent with the gain of solute mass in the bottom circulation outflow due to diffusion through the specimen. The establishment of steady EC_{bottom} values of approximately 20 mS/m about 30 to 35 days after the start chemico-osmotic stage of the experiment is consistent with the establishment of steady-state diffusion of $CaCl_2$ through the specimen.

7.3.2 Membrane Efficiency

The induced pressure difference, $-\Delta P$ (> 0), across the GCL specimen and the corresponding membrane efficiency in the form of the chemico-osmotic efficiency coefficient, ω, are plotted versus time in Fig. 7.6 (Note: values of ΔP and $\Delta\pi$ are < 0 because pressure increases in the negative x direction, or upward; see Fig. 7.2). The values of ω in Fig. 7.6 were calculated using Eq. 7.1, the measured induced pressure differences, and a chemico-osmotic pressure, $\Delta\pi$, of $-$ 36.9 kPa in accordance with Eq. 7.3 using $\nu = 3$ for $CaCl_2$ and $\Delta C = -$ 0.005 M $CaCl_2$.

A slight induced pressure difference was observed during the initial 5-day stage where DIW was circulated through both porous stones such that a concentration gradient was not applied across the specimen. This pressure difference has been attributed, in part, to slightly different hydraulic resistances of the two porous stones such that the head losses in each stone are not exactly the same, typically resulting in a slight recorded pressure difference across the specimen (Malusis et al. 2001b, Malusis and Shackelford

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2002a). However, the induced pressure difference at the end of this 5-day flushing stage was negligible, as shown in Fig. 7.6.

Immediately after replacing the DIW circulating across the top of the specimen with the 5 mM $CaCl_2$ solution (i.e., at $t = 0$), the induced pressure difference increases immediately and continues to increase gradually to a maximum value of approximately 19.3 kPa after 9 days corresponding to a maximum chemico-osmotic efficiency coefficient, ω_{max}, of 0.52 or membrane efficiency of 52 percent. Thereafter, the induced pressure difference and corresponding membrane efficiency gradually decrease such that the observed membrane behavior is effectively destroyed after 35 days.

Short circuiting of the specimen, for example, in terms of side-wall leakage (see Shackelford 1994), is not likely in this experiment for the following reasons: (1) solution flow through the specimen, which is a prerequisite in most studies showing side-wall leakage, was prevented during the chemico-osmotic stage of the experiment; (2) the electrolyte concentration (5 mM $CaCl_2$) used in the experiment is low, and certainly lower than the vast majority of cases in which side-wall leakage has been reported; (3) the swelling pressure of the specimen likely was sufficiently high to prevent shrinkage, and no physical evidence of shrinkage after breakdown of the test apparatus was observed; and (4) a much more rapid diminishing of the induced chemico-osmotic pressure difference than was observed would be expected had specimen shrinkage, if any, been significant. Instead, the gradual post-peak decrease in $-\Delta P$ with time shown in Fig. 7.6 suggests that the response of the specimen to the imposed boundary conditions is due to a naturally occurring, physico-chemical process, such as collapse of the adsorbed layers due to an increase in the Ca^{2+} concentration in the pore water of the specimen,

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which is consistent with previous conclusions (Barbour 1986, Barbour and Fredlund 1989, Whitworth and Fritz 1994, Malusis et al. 2001b, Malusis and Shackelford 2002a). However, unlike previous studies whereby an increase in salt concentration in the pore water of the specimen resulted in only a partial reduction in the observed membrane efficiency during the test, the divalent calcium concentration (5 mM Ca^{2+}) used in this study apparently was sufficiently strong to completely destroy the tendency of the GCL specimen to behave as a semipermeable membrane. Since the migration of Ca^{2+} is due solely to diffusion, the time required for complete destruction of the observed membrane behavior should be reasonably correlated with the time required to reach steady-state diffusion of the Ca^{2+}.

7.3.3 Solute Diffusion

The measured chloride (Cl^-) and calcium (Ca^{2+}) concentrations in the circulating liquid exiting the base pedestal are plotted versus time in Fig. 7.7. The corresponding values of cumulative mass per unit area, Q_t, based on the Cl^- and Ca^{2+} concentrations calculated in accordance with Eq. 7.4 are plotted versus time in Fig. 7.8.

The scatter in the measured Cl^- concentration data masks somewhat the existence of steady-state conditions with respect to diffusion of the Cl^-, and the Ca^{2+} concentration data appear to be increasing, albeit slightly, even after 68 days of monitoring, suggesting that steady-state diffusion of Ca^{2+} was approached, but not necessarily established. As a result, the time required to reach steady-state diffusion was evaluated in a more systematic manner by performing sequential linear regression analyses on an increasing number of Q_t-versus-t data, starting from an analysis performed using only the last two

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data points, followed by subsequent linear regression analyses on an increasing number of data (i.e., adding one additional data for each subsequent analysis) until all of the data were used in an analysis. Therefore, since 67 samples were collected during the test at a rate of one per day, a total of 66 linear regression analyses were performed for each solute.

The coefficient of determination, r^2, resulting from each regression analysis is plotted as a function of the number of data used in the analysis for both Cl^- and Ca^{2+} in Fig. 7.9. The number of data corresponding to the location where r^2 starts to deviate significantly from unity is taken as the transition from a non-linear to linear slope in the Q_t-versus-t data corresponding to the transition from the transient portion of the data to the steady-state portion of the data. Accordingly, the times corresponding to the earliest data used in each regression analysis also are plotted versus the corresponding r^2 values in Fig. 7.9.

As shown in Fig. 7.9, the r^2 values based on the regression analyses using the Q_t-versus-t data for Cl^- decrease dramatically when more than 48 data are used in the analysis. Thus, the elapsed time associated with the earliest of the 48 data points used in the analysis represents the time at which steady-state diffusion of Cl^- is established; i.e., t_{ss} is 20 days for Cl^-. Although this distinction is not quite as evident in the results based on the Q_t-versus-t data for Ca^{2+}, the use of 33 ± 2 data corresponding to t_{ss} of 35 ± 2 days appears reasonable for Ca^{2+}.

The time lag, t_L, and slope of the steady-state portion of the data for each solute shown in Fig. 7.8 are based on the results of the linear regression analyses using 48 Q_t-versus-t data for Cl^- and 33 Q_t-versus-t data for Ca^{2+}. The higher t_L of 694 hrs (28.9 days)

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for Ca^{2+} relative to the t_L of 285 hours (11.9 days) for Cl^- is attributed to the tendency for cation exchange associated with the divalent calcium cation (e.g., Malusis et al. 2001b).

At steady state, electroneutrality requires that the charge flux of the Cl^- has the same magnitude as the charge flux of the Ca^{2+}. This requirement may be written as follows:

$$J_{Cl^-}\left|z_{Cl^-}\right| = J_{Ca^{2+}}\left|z_{Ca^{2+}}\right| \tag{7.6}$$

where J_{Cl^-} and $J_{Ca^{2+}}$ = the steady-state diffusive molar fluxes of Cl^- and Ca^{2+}, and z_{Cl^-} and $z_{Ca^{2+}}$ = the charges of Cl^- and Ca^{2+} (i.e., –1 and +2, respectively). Therefore, the steady-state diffusive molar flux of Cl^- theoretically should be twice the magnitude of the steady-state diffusive molar flux of Ca^{2+}. In terms of mass fluxes, this ratio must be multiplied by the ratio of the atomic weight of Ca^{2+} (40.08) to the atomic weight of Cl^- (35.453). Therefore, the magnitude of the steady-state diffusive mass flux of Cl^- theoretically should be 2.26 [= 2 x (40.08/35.453)] times the magnitude of the steady-state diffusive mass flux of Ca^{2+}. Based on the results shown in Fig. 7.8, the observed ratio of the steady-state diffusive mass flux of Cl^- to the steady-state diffusive mass flux of Ca^{2+} in this study is 2.11 (= 21.8/10.3), which is sufficiently close to the theoretical value of 2.26 to suggest that steady-state diffusion of Ca^{2+} had essentially been established.

Finally, the effective diffusion coefficients, D^*, for Cl^- and Ca^{2+} calculated in accordance with Eq. 7.5 using a measured porosity (n) of 0.718 and an averaged measured thickness (L) of 5.6 mm are 1.21×10^{-10} m^2/s and 1.10×10^{-10} m^2/s,

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respectively. The closeness in these D^* values also is consistent with the electroneutrality constraint that requires the two D^* values to be the same at steady-state diffusion.

7.3.4 Conceptual Explanation

The t_{ss} of 35 ± 2 days for Ca^{2+} is identical to the time required for effective destruction of the observed membrane behavior, as indicated in Fig. 7.6. Thus, the correlation between the times required for effective destruction of the membrane behavior and the establishment of steady-state diffusion of the Ca^{2+} is excellent. Therefore, the results of this study provide the first direct evidence that complete destruction of clay membrane behavior can be caused by diffusion of the principal salt cation (i.e., Ca^{2+}). However, because clay membranes by definition restrict solute migration, the question as to how this migration can occur is raised.

A conceptual explanation for the observed correlation between calcium diffusion and the destruction of the observed membrane behavior of the GCL can be formulated on the basis of the clay structure models described by Pusch (1999) and Pusch and Schomburg (1999). In these models, the bentonite consists of an intermingled structure of both unit particles and particle clusters, with the primary pores located between the unit particles and the clusters. At the measured porosity of the specimen of 0.718, interlayer spacing of the particles will be controlled by surface hydration rather than by the adsorbed layer interactions, such that the interlayer spacing of the unit particles likely will not have been affected much by the exchangeable cation (e.g., van Olphen 1977). However, adsorbed layers likely will have extended into the voids between both unit particles and particle clusters, thereby restricting the diffusive migration of the ions. In

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this case, the destruction of the observed membrane behavior can be explained in terms of decreasing adsorbed layer thickness between unit particles and particle clusters with increasing pore concentration due to ion diffusion, resulting in a gradual destruction of the observed membrane behavior.

7.4 CONCLUSIONS

The results of a combined chemico-osmotic/diffusion experiment conducted on a geosynthetic clay liner (GCL) containing sodium bentonite and exposed to a constant concentration difference of 5 mM $CaCl_2$ show an initial increase in induced pressure difference across the specimen to a maximum value of 19.3 kPa corresponding to a maximum membrane efficiency of 52 percent after 9 days of testing. This initially observed membrane behavior is followed by a gradual decrease in induced pressure difference to almost zero (0.6 kPa) corresponding to a membrane efficiency of only 1.6 percent after 35 days of testing, and subsequently to zero after 48 days of testing. The effective destruction of the initially observed semipermeable membrane behavior after 35 days of testing correlates well with the time of 35 ± 2 days required to essentially achieve steady-state Ca^{2+} diffusion. This correlation suggests that the decrease in induced pressure difference is consistent with compression of adsorbed layers between clay particles and particle clusters due to diffusion of Ca^{2+}, resulting in concomitant increase in pore sizes and decrease in the membrane efficiency. The results illustrate the potentially destructive role of diffusion of invading salt cations on the membrane behavior of clays, and are particularly relevant with respect to the ability of clays to sustain membrane behavior.

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Table 7.1 – Properties of bentonite in a geosynthetic clay liner.

Property	Standard	No. of Trials	Average Value [Max, Min]
Principal Minerals (%):	a	3	
Montmorillonite			77.2 [79.6, 74.0]
Cristobalite			10.3 [15.0, 6.8]
Plagioclase Feldspar			5.1 [7.4, 4.0]
Quartz			3.4 [4.0, 3.0]
Others			4.0 [6.0, 2.9]
Cation Exchange Capacity, CEC (meq/100 g)	b	3	63.9 [73.5, 53.1]
Exchangeable Metals (meq/100 g):	b	3	
Ca^{2+}			11.5 [15.7, 6.9]
Mg^{2+}			3.7 [4.8, 2.2]
Na^{+}			45.8 [56.1, 40.0]
K^{+}			0.7 [0.8, 0.6]
Sum			61.7 [72.7, 51.2]
Soluble Metals (mg/kg):	b, c	3	
Ca^{2+}			218 [241, 174]
Mg^{2+}			24 [29, 14]
Na^{+}			3365 [3766, 3451]
K^{+}			48 [52, 43]
Saturated Soil Paste:	b	3	
pH			8.9 [8.9, 8.8]
EC[d] (mS/m)			305 [315, 290]

[a] Based on X-ray diffraction (XRD) analyses performed by Mineralogy Inc., Tulsa, OK and GeoServices Inc., Argyle, TX.

[b] Based on procedures described in Shackelford and Redmond (1995).

[c] Measured from a 1 g:20 mL clay-water extract.

[d] Electrical conductivity at 25 °C.

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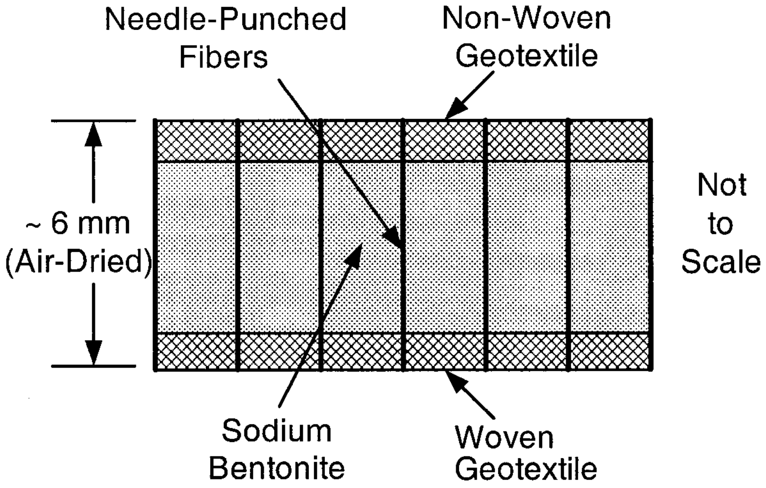

Fig. 7.1 – Schematic cross-section of geosynthetic clay liner (GCL) used in this study.

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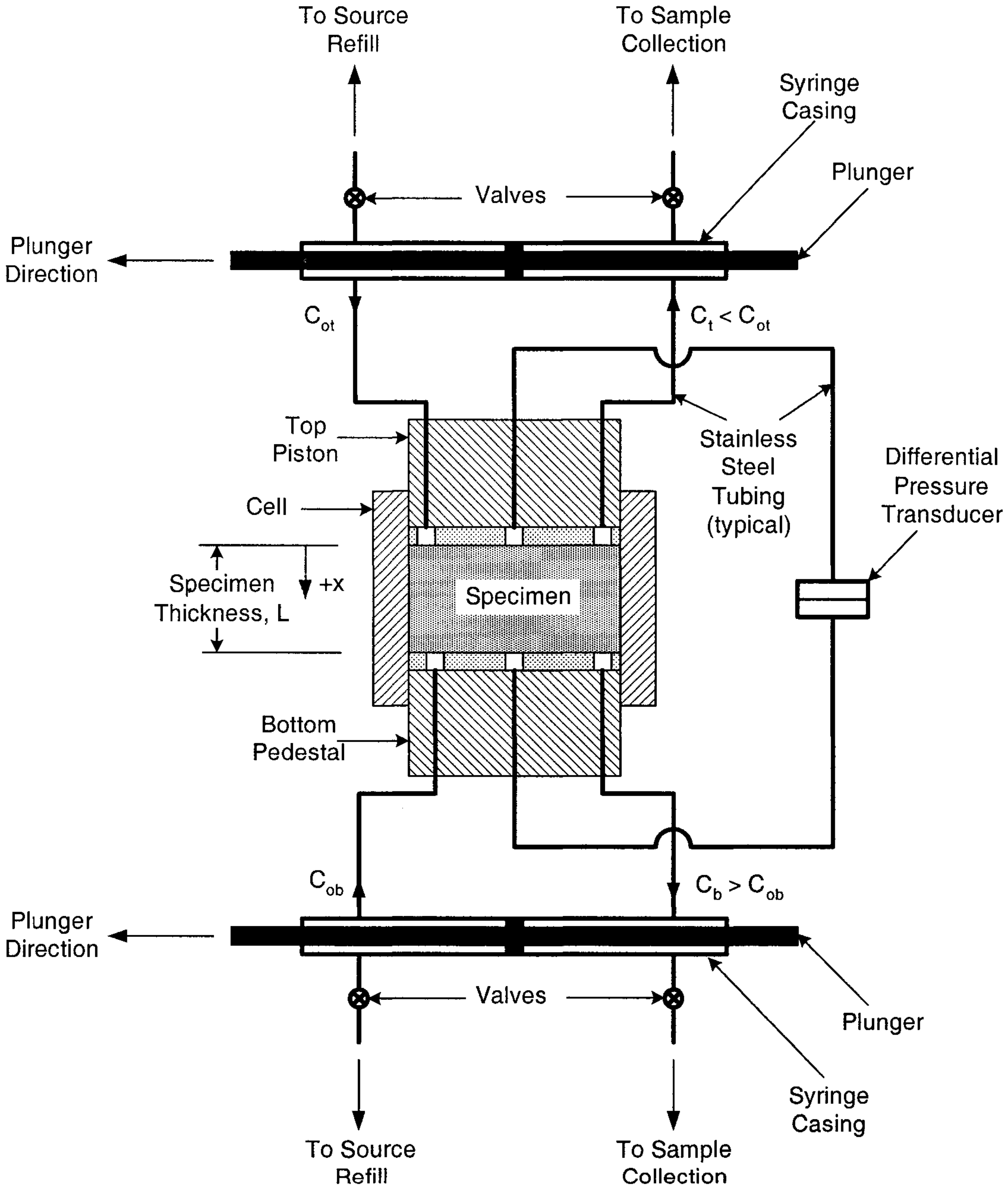

Fig. 7.2 – Schematic cross-section of test cell (re-drawn after Malusis and Shackelford 2002a).

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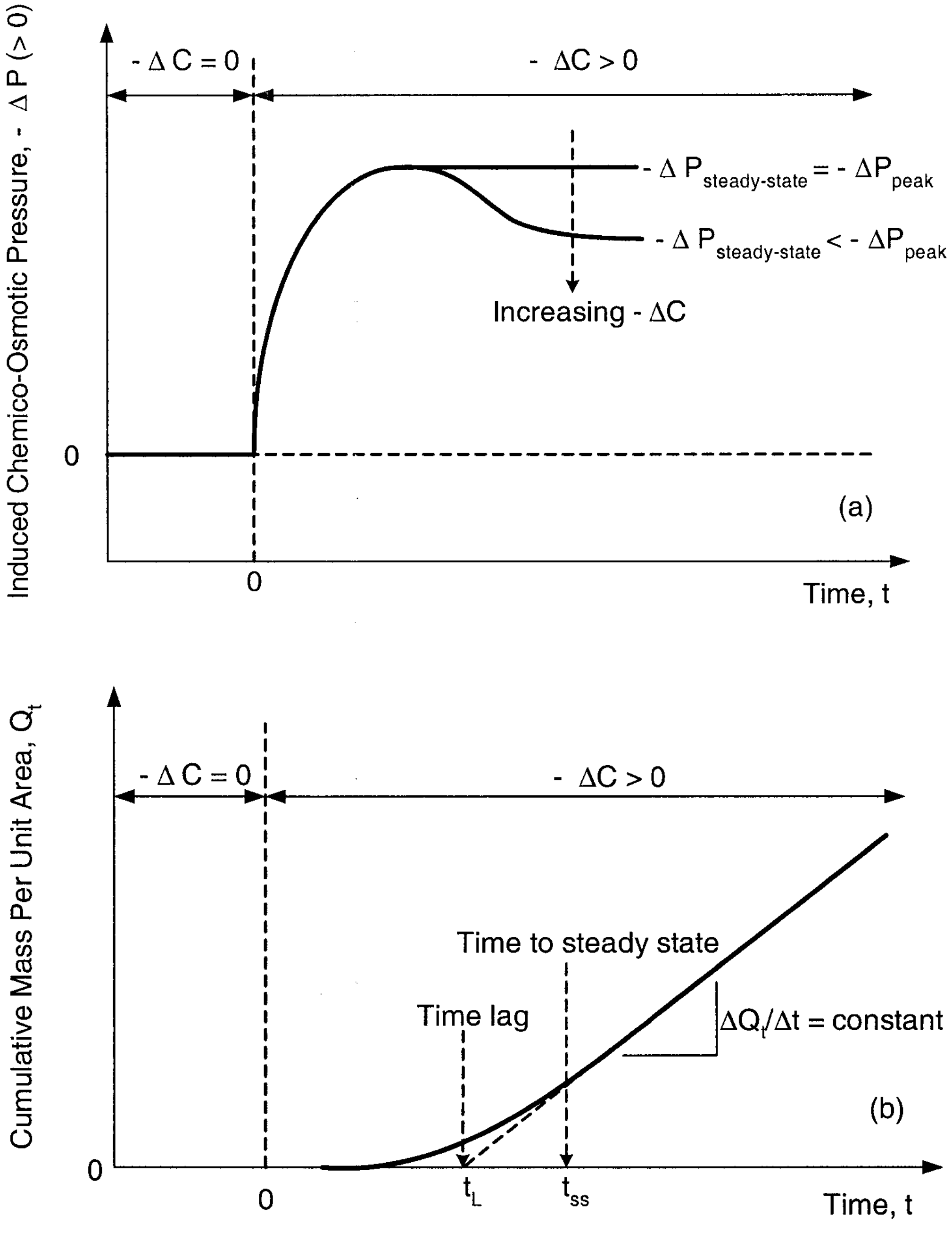

Fig. 7.3 – Schematic illustration of typical results obtained from combined chemico-osmotic/diffusion experiments: (a) trends in induced chemico-osmotic pressure observed for clay membranes; and (b) trends in cumulative solute mass through specimen due to diffusion.

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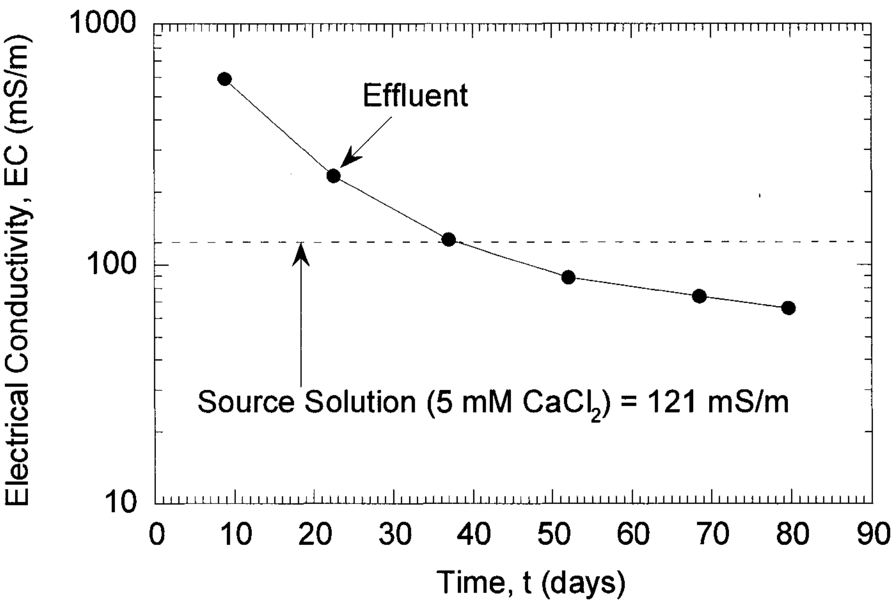

Fig. 7.4 – Electrical conductivity of effluent from specimen resulting from permeating specimen with deionized water prior to the chemico-osmotic stage of the experiment.

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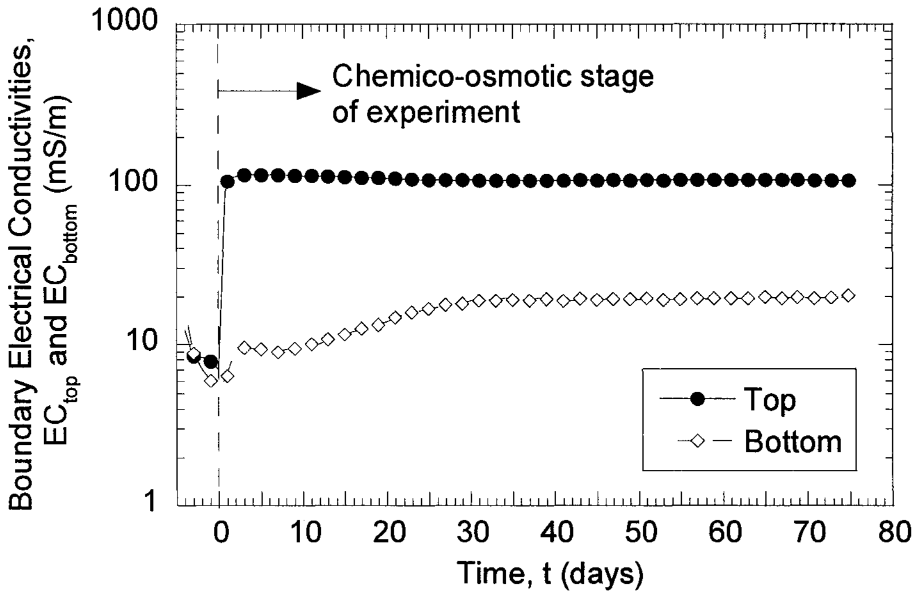

Fig. 7.5 – Electrical conductivities of circulation outflows from top and bottom boundaries of specimen during chemico-osmotic stage of experiment.

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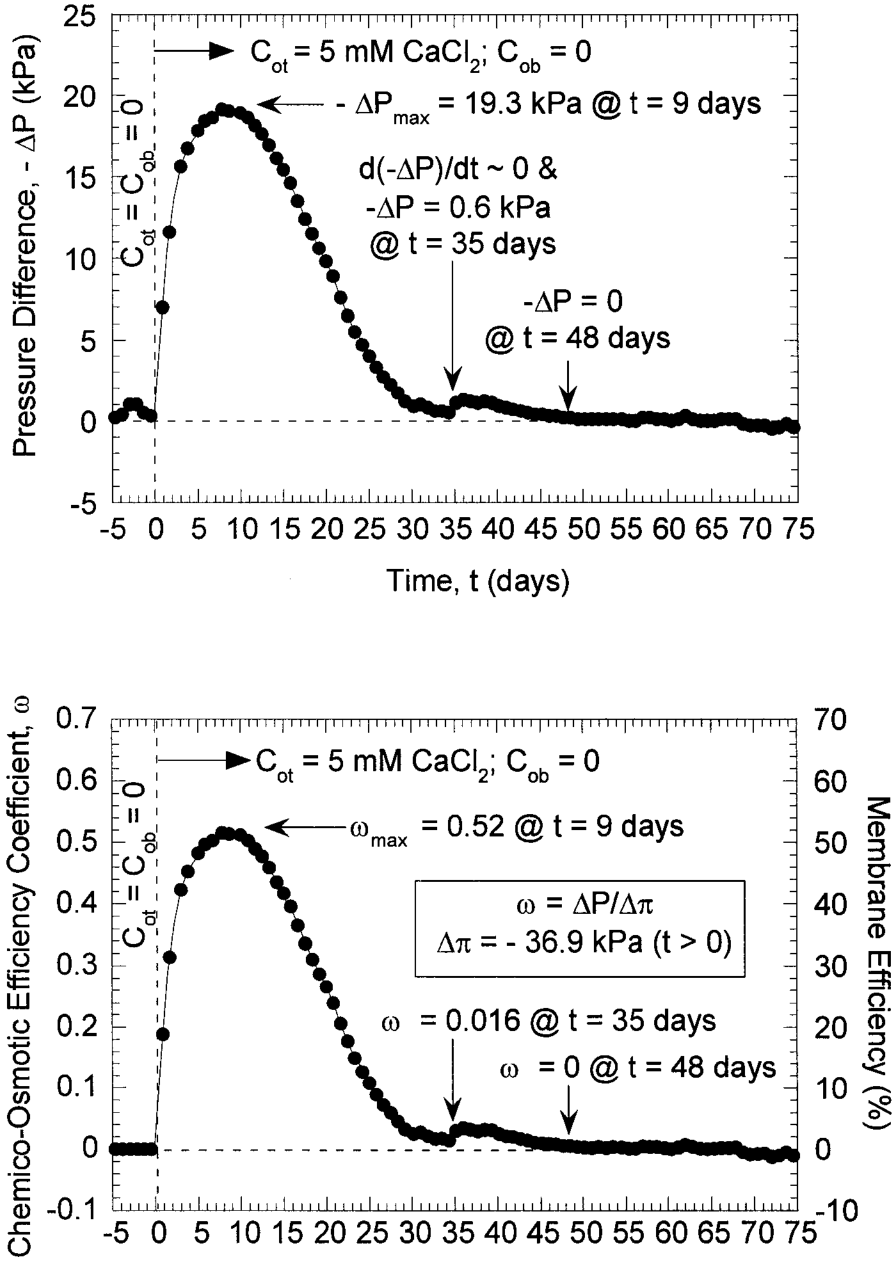

Fig. 7.6 – Measured induced chemico-osmotic pressure difference and calculated chemico-osmotic efficiency as a function of time.

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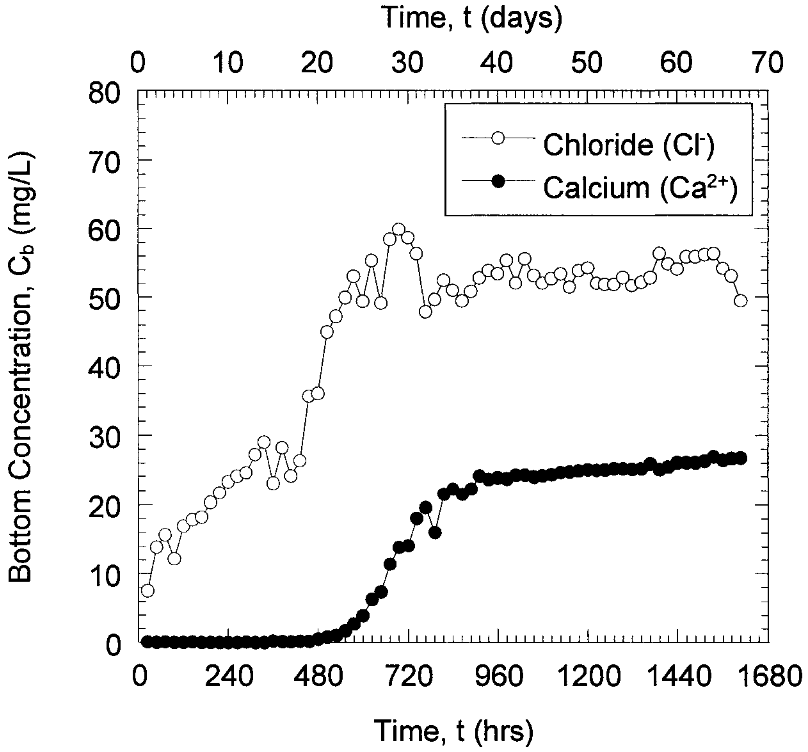

Fig. 7.7 – Measured chloride and calcium concentrations exiting the base pedestal of the test cell due to diffusion.

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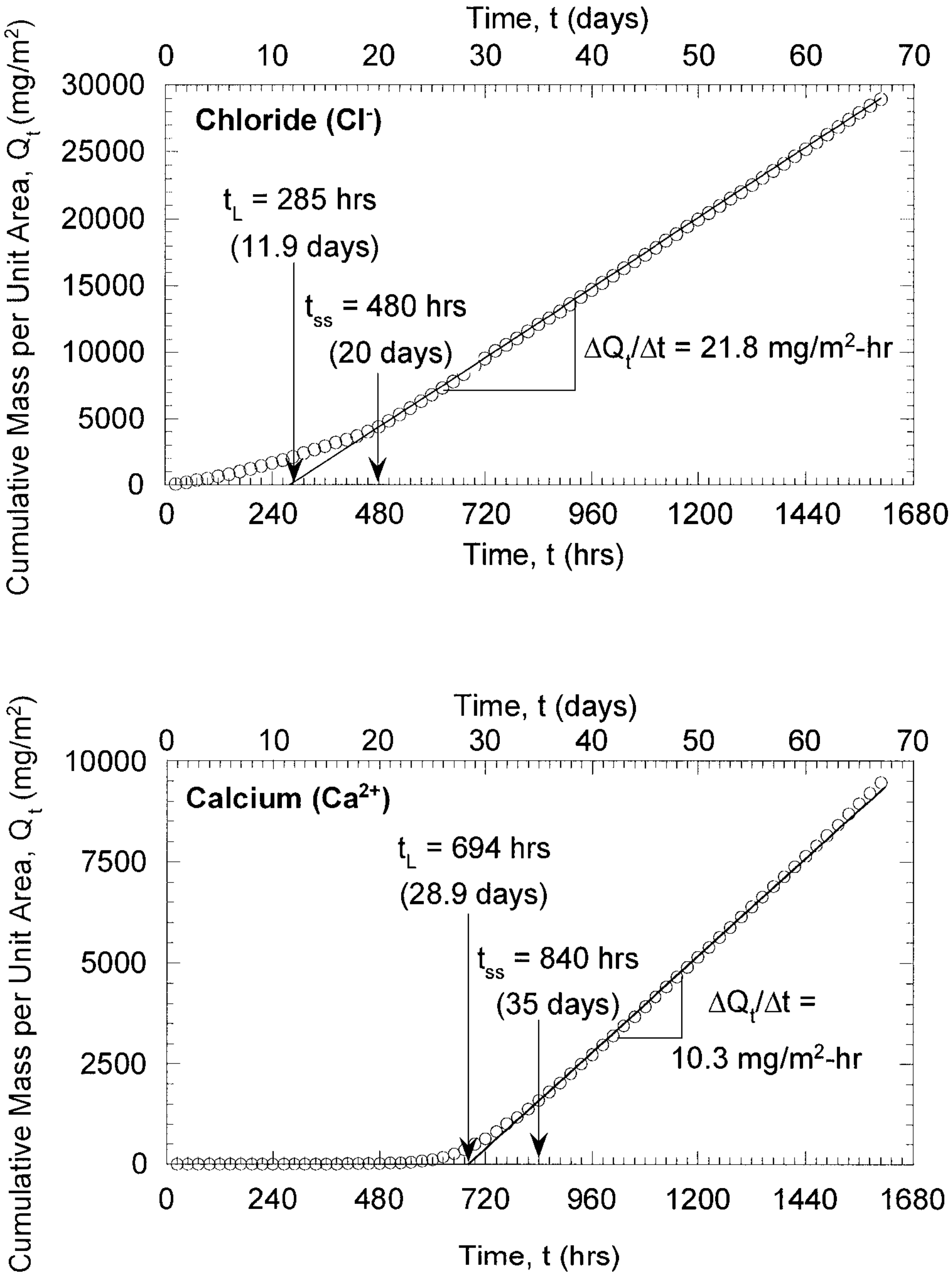

Fig. 7.8 – Cumulative mass data based on measured bottom concentrations (t_L = time lag; t_{ss} = time to steady-state diffusion).

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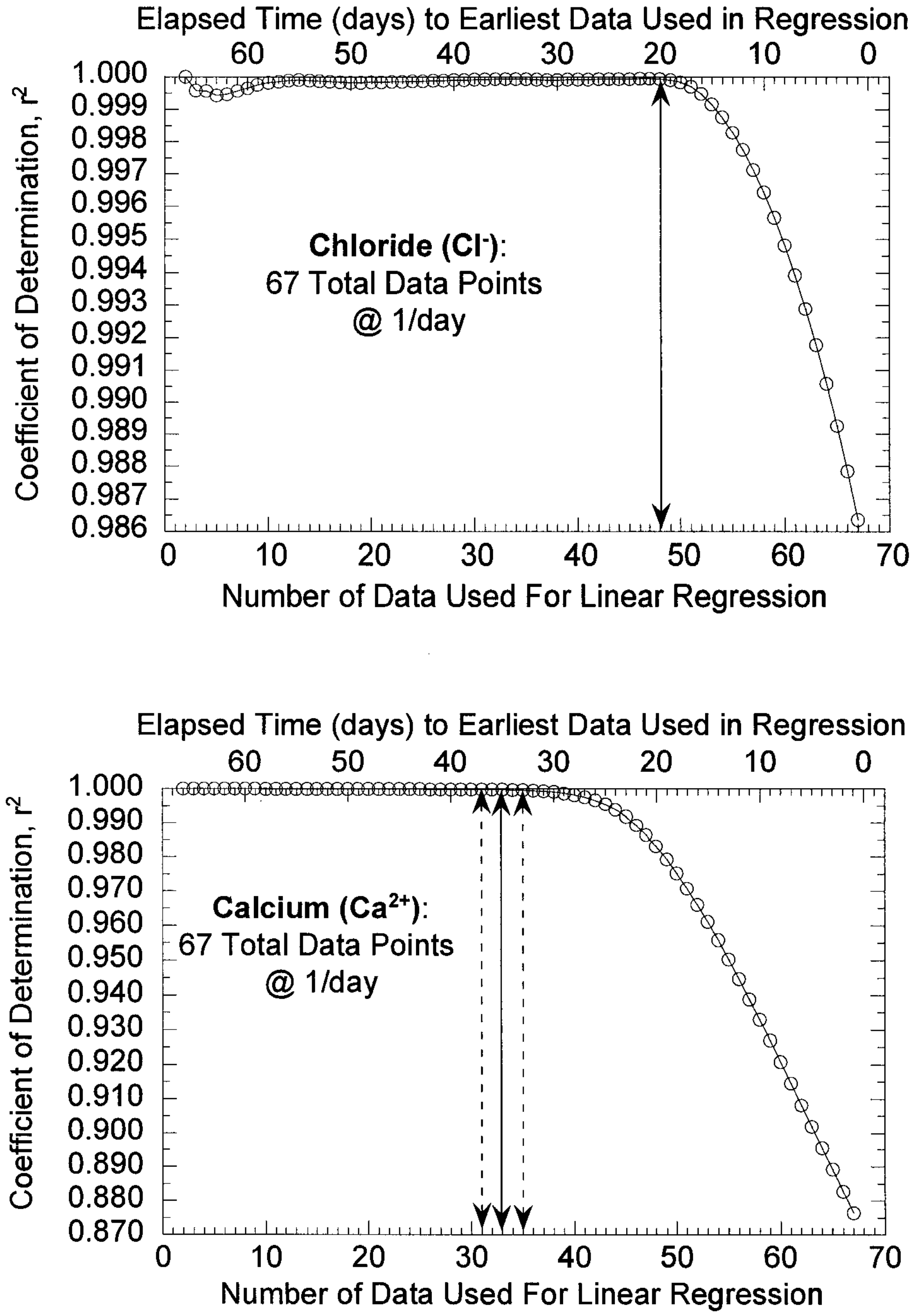

Fig. 7.9 – Coefficients of determination from multiple linear regression analyses performed on measured cumulative mass data as a function of number of data used for linear regression and the elapsed time to the earliest data used in the regression.

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CHAPTER 8

DEPENDENCY OF COMPATIBILITY TERMINATION CRITERIA ON PREHYDRATION AND BENTONITE QUALITY FOR GCLs

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ABSTRACT: The dependency of criteria used to terminate compatibility tests on the prehydration and quality of bentonite in geosynthetic clay liners (GCLs) is evaluated based on permeation with calcium chloride ($CaCl_2$) solutions. The evaluation includes both physical termination criteria (i.e., volumetric flow ratio and steady hydraulic conductivity per ASTM D 5084, $\geq$ 2 pore volumes of flow, constant thickness of specimen) and chemical termination criteria requiring equilibrium between influent and effluent chemistry (viz., electrical conductivity, pH, and Ca^{2+} and Cl^- concentrations). For specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, only the criterion based on chemical equilibrium in Ca^{2+} correlates well with equilibrium in hydraulic conductivity, regardless of prehydration or quality of bentonite. However, all of the termination criteria, except some physical criteria (i.e., volumetric flow ratio and 2 pore volumes of flow) for the prehydrated specimens, correlate well with equilibrium in hydraulic conductivity regardless of prehydration or quality of bentonite when permeated with 50 and 100 mM $CaCl_2$ solutions. The results illustrate the uniqueness of the termination criterion based on solute equilibrium between the effluent and influent with respect to both prehydration and quality of bentonite in the GCL.

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Key Words: bentonite quality, chemical equilibrium, compatibility, geosynthetic clay liners, hydraulic conductivity, prehydration, termination criteria

8.1 INTRODUCTION

The hydraulic conductivity of geosynthetic clay liners (GCLs) based on permeation with chemical solutions can be significantly higher than that based on permeation with water due to chemical interactions between the solutions and the bentonite (Daniel et al. 1993, Gleason et al. 1997, James et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001). The potential effect of a non-standard permeant liquid (i.e., liquid other than water) on the hydraulic conductivity of a clay barrier usually is assessed by permeating the clay barrier material with the actual liquid to be contained or, in the absence of the actual liquid, a simulated liquid with characteristics similar to those expected for the actual liquid. Since the primary objective of the test is to determine if the barrier material (e.g., bentonite in GCLs) and the permeant liquid are compatible, such that no significant change in hydraulic conductivity occurs, this type of test often is referred to as a compatibility test (Shackelford 1994, Shackelford et al. 2000).

In cases where GCLs have been permeated with solutions containing relatively low concentrations of polyvalent cations (i.e., < 50 mM), the GCLs typically have exhibited compatibility over relatively short durations (≤ 0.5 yr), but incompatibility after longer durations of permeation (> 1 yr) (e.g., Dobras and Elzea 1993, Didier and

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Comeaga 1997, James et al. 1997, Petrov and Rowe 1997, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001, Melchior 2002). This apparent time-dependent compatibility of GCLs implies that the potential chemical interactions between the solutions and bentonites in the GCLs may not be complete within relatively short test durations when solutions containing polyvalent cations at relatively low concentrations (< 50 mM) are used as permeant liquids (Shackelford et al. 2000). For relatively high concentrations of polyvalent cations (i.e., ≥ 50 mM), several studies have shown significant increases in the hydraulic conductivity (> 10X) of GCLs over short test durations (Ruhl and Daniel 1997, Kolstad 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001).

On the other hand, several investigators have reported that prehydration of bentonite mixtures and/or GCLs with water prior to permeation with actual permeant liquids can have a significant effect on hydraulic conductivity (e.g., Shan and Daniel 1991, Daniel et al. 1993, Shackelford 1994, Didier and Comeaga 1997, Gleason et al. 1997, Petrov and Rowe 1997, Petrov et al. 1997a, Quaranta et al. 1997, Ruhl and Daniel 1997, Stern and Shackelford 1998, Lin and Benson 2000, Shackelford et al. 2000, Vasko et al. 2001, Shan and Lai 2002). For example, the hydraulic conductivity of GCLs permeated directly with chemical solutions typically has been found to be significantly higher (i.e., > 10X) than the hydraulic conductivity of the same GCLs permeated with the same chemical solutions but after prehydration with water.

In addition, soil mixtures such as sand-bentonite mixtures that contain greater amounts of bentonite are potentially more vulnerable to chemical attack and incompatibility than the mixtures with less amounts of bentonite (e.g., Stern and

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Shackelford 1998). Consequently, similar results for GCLs are expected such that the higher the quality of the bentonite (e.g., the higher the montmorillonite content) used in the GCL, the more vulnerable the GCL to chemical attack and, therefore, incompatibility, i.e., provided all other GCL properties (e.g., bentonite dosage) are the same (e.g., Shackelford et al. 2000).

As a result of the aforementioned considerations, the objective of this study is to evaluate the potential dependency of criteria commonly used to terminate laboratory compatibility tests on the prehydration and quality of bentonite for GCLs permeated with $CaCl_2$ solutions. In order to achieve this objective, hydraulic conductivity tests are performed on both non-prehydrated and prehydrated specimens of a single GCL containing relatively low quality bentonite as well as non-prehydrated specimens of a different GCL containing relatively high quality bentonite. The tests are conducted until complete chemical equilibrium between the influent and effluent is established, which in some cases required in excess of 2 yrs of permeation. The results of this study should improve our understanding of appropriate termination criteria to be used for compatibility testing of GCLs.

8.2 MATERIALS AND METHODS

8.2.1 Geosynthetic Clay Liners

Two geosynthetic clay liners (GCLs) containing bentonite with different montmorillonite contents were used in this study. Both GCLs consist of a thin layer of granular sodium bentonite sandwiched between two polypropylene geotextiles held together by needle-punched fibers. Both GCLs are ~ 6-mm thick in the air-dried

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condition, and the average gravimetric water contents of bentonites are ~ 4 %. The physical and chemical properties and the mineralogical compositions for the bentonite portions of the two GCLs are given in Table 8.1. The GCL with the higher quality bentonite (GCL-HQB) is characterized by a greater content of sodium montmorillonite (86 % vs. 77 %), a higher plasticity index (548 % vs. 393 %), and a higher cation exchange capacity (93 meq/100 g vs. 64 meq/100 g), i.e., relative to the GCL with the lower quality bentonite (GCL-LQB).

Particle-size distributions of the bentonite portions of the two GCLs were determined using both mechanical sieve analysis of the air-dried bentonite and hydrometer analysis (ASTM D 421, D 422). For both GCLs, the air-dried bentonite consists of more than 90 % (w/w) sand-sized granules (75 to 2000 μm) based on mechanical sieve analyses, whereas approximately 90 % of particles are clay sized (< 5 μm) based on the hydrometer analysis. Consequently, the bentonites from both GCLs are classified as high-plasticity clays (CH) according to the Unified Soil Classification System (ASTM D 2487) based on the wet analysis, whereas the results from the mechanical analysis indicate that the air-dried bentonites actually consist of assemblages or granules (i.e., clods) of individual clay particles and, therefore, are classified as poorly graded sand (SP). Shackelford et al. (2000) note that GCLs containing granular bentonite may have significantly higher hydraulic conductivities relative to GCLs containing powdered bentonite upon direct permeation with non-standard liquids (i.e., liquids other than water).

8.2.2 Permeant Liquids

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The permeant liquids used in the experiment consist of tap water that is processed by passage through three ion exchange columns (Barnstead®) in series (pH ~ 5.6, electrical conductivity, EC, at 25 °C ~ 0.2 mS/m) and solutions containing concentrations of calcium chloride ($CaCl_2$) ranging from 5 mM to 500 mM. The processed tap water classifies as Type IV deionized water (DIW) as per ASTM D 1193. Calcium chloride was chosen primarily because previous studies involving permeation of bentonite-based hydraulic barrier materials (e.g., GCLs, sand-bentonite mixtures) with $CaCl_2$ solutions have shown significant effects of the solutions on the hydraulic conductivity of these materials (Alther et al. 1985, Daniel et al. 1993, Shackelford 1994, Imamura et al. 1996, Gleason et al. 1997, James et al. 1997, Melchior 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Ruhl and Daniel 1997, Kolstad 2000, Lin and Benson 2000, Shackelford et al. 2000, Egloffstein 2001, Jo et al. 2001, Vasko et al. 2001, Shan and Lai 2002).

The $CaCl_2$ solutions were prepared by dissolving $CaCl_2$ (powdered, > 96 % pure, Sigma-Aldrich Co., St. Louis, MO) in the DIW. Each solution was mixed in a 20-L carboy, and pH, EC, and solute concentrations of the permeant liquids were monitored with time using a pH meter (Accumet® AB15 meter, Fisher Scientific Co., Pittsburgh, PA), an EC probe (Accumet® AB30 meter, Fisher Scientific Co., Pittsburgh, PA), an ion chromatograph (Dionex® 4000i IC Module, Dionex Co., Sunnyvale, CA) for chloride (Cl^-) concentrations, and an inductively coupled plasma – atomic emission spectrometer (IRIS® Advantage/1000 ICAP Spectrometer, Thermo Jarrell Ash Co., Franklin, MA) for calcium (Ca^{2+}) concentrations, respectively. The measured properties of the permeant liquids are given in Table 8.2. As expected, the measured solute concentrations for the

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DIW were below the method detection limits (MDLs) of 0.02 mg/L for Ca^{2+} (EPA Method 200.7) and 0.04 mg/L for Cl^- (EPA Method 300.0).

The EC and solute concentrations of the permeant liquids remained relatively constant, whereas the pH of each solution slowly decreased over time (e.g., from 6.3 to 5.9 for 20 mM $CaCl_2$ solution over 1.5 yrs). The decrease in pH is probably due to time-dependent dissolution of carbon dioxide (CO_2) from the atmosphere into the solutions. Nevertheless, any effect of decreasing source solution pH on the measured hydraulic conductivity likely was negligible relative to the effects caused by the various $CaCl_2$ solutions, because the range of measured pH (i.e., 5.0 to 7.0) was relatively narrow and close to neutral pH (Shackelford 1994, Jo et al. 2001, Shan and Lai 2002).

8.2.3 Hydraulic Conductivity Tests

Specimens of the two GCLs with nominal diameters of 102 mm were permeated using the falling-head procedure and flexible-wall permeameters in accordance with ASTM D 5084. Hydraulic conductivity tests are performed on both non-prehydrated and prehydrated specimens of the GCL with the lower bentonite quality (i.e., GCL-LQB), as well as non-prehydrated specimens for the GCL with the higher bentonite quality (i.e., GCL-HQB). Prehydration was achieved by permeating the GCL specimens with deionized water. Specimens were trimmed and assembled in the permeameters using the method described by Daniel et al. (1997) to prevent the possibility of short-circuiting through the geotextiles at the edge of the GCL specimens due to loss of bentonite and pinching of the geotextiles. Backpressure was not used so that effluent liquids could be conveniently collected for pH, EC, and solute concentration measurements. The

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thicknesses of specimens were measured before, during, and after the hydraulic conductivity tests using a caliper, a cathetometer, and a ruler.

All the specimens were permeated at an average effective stress of ~ 23.5 kPa (3.4 psi) and at an average hydraulic gradient of ~ 200. While this hydraulic gradient is higher than the maximum gradient (i.e., 30) stipulated in ASTM D 5084, hydraulic gradients ranging from 50 to 600 typically are used for measuring the hydraulic conductivity of GCLs (e.g., Shan and Daniel 1991, Daniel et al. 1993, Didier and Comeaga 1997, Petrov and Rowe 1997, Petrov et al. 1997a,b, Quaranta et al. 1997, Ruhl and Daniel 1997, Lin and Benson 2000, Shackelford et al. 2000). Results of these studies indicate that the hydraulic conductivity of GCLs is affected to a greater extent by average effective stress than by the magnitude of hydraulic gradient (Shackelford et al. 2000).

Hydraulic conductivity tests performed on non-prehydrated specimens using solutions with relatively high $CaCl_2$ concentrations (i.e., 50 and 100 mM) were duplicated because the test durations were relatively short, allowing for the re-use of the permeameters. However, because the durations for the tests using solutions containing relatively low $CaCl_2$ concentrations (i.e., 5, 10, and 20 mM) required more than 4 months to establish chemical equilibrium, these tests could not be duplicated due to the limited number of permeameters available for testing.

Two categories of common termination criteria used for compatibility tests were considered in this study (e.g., Shackelford et al. 2000). The first category is referred to as physical termination criteria, and includes the following criteria: (1) at least four consecutive values for the ratio of the volumetric outflow to the volumetric inflow within the range of 1.00 ± 0.25 (e.g., ASTM D 5084); (2) at least four consecutive hydraulic

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conductivity (k) values within ± 25 % of the mean value for $k \geq 1 \times 10^{-8}$ cm/s or within ± 50 % for $k < 1 \times 10^{-8}$ cm/s (e.g., ASTM D 5084); (3) a minimum of two pore volumes of flow (PVF) through the specimen (e.g., Bowders et al. 1986, Daniel 1994, Shackelford et al. 2000, ASTM D 6766); and (4) a constant thickness of the specimen (e.g., Petrov et al. 1997a). The second category of termination criteria relates to the need to establish chemical equilibrium between the effluent and influent (e.g., Bowders et al. 1986, Bowders and Daniel 1987, Bowders 1988, Daniel 1994, Shackelford 1994, Shackelford et al. 2000). This category, referred to as chemical termination criteria, includes the following criteria: (1) the ratio of effluent pH and EC relative to influent pH and EC within 1.00 ± 0.10 (e.g., Shackelford et al. 2000, ASTM D 6766); and (2) the ratio of effluent solute concentration to influent solute concentration within 1.00 ± 0.10 (e.g., Shackelford et al. 2000).

8.3 RESULTS

8.3.1 Results for Non-Prehydrated GCL-LQB Specimens

Results of the hydraulic conductivity tests performed on the non-prehydrated specimens of the GCL with the lower quality bentonite (i.e., GCL-LQB) are shown in Figs. 8.1 and 8.2. The hydraulic conductivity values for the specimens permeated with 5, 10, and to 20 mM $CaCl_2$ solutions initially decreased to ~ 10^{-9} cm/s after ~ 1 month (< 5 PVF), and then began to increase after ~ 3 to 6 months (< 10 PVF). Thereafter, the hydraulic conductivity values increased from approximately 5X to 10X to a value of ~ 8.2×10^{-9} cm/s regardless of the influent concentration at times corresponding to ~ 1.4

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yrs (~ 54 PVF), ~ 1.0 yr (~ 26 PVF), and ~ 0.4 yr (~ 18 PVF) for the non-prehydrated specimens of GCL-LQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively.

The results for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions are shown in Fig. 8.2. The hydraulic conductivity values stabilized within 5 days (~ 10 PVF), and were always greater than 1.3×10^{-8} and 1.3×10^{-7} cm/s for the non-prehydrated specimens of GCL-LQB permeated with 50 and 100 mM $CaCl_2$ solutions, respectively. In fact, the final hydraulic conductivity values at the end of the tests were approximately 1.6×10^{-8} and 3.6×10^{-7} cm/s for the non-prehydrated specimens of GCL-LQB permeated with 50 and 100 mM $CaCl_2$ solutions, respectively. These values are approximately 2X and 40X higher, respectively, than the hydraulic conductivity of ~ 8.2×10^{-9} cm/s for the non-prehydrated specimens of GCL-LQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

8.3.2 Results for Prehydrated GCL-LQB Specimens

The results of the hydraulic conductivity tests performed on the prehydrated specimens of the GCL with the lower quality bentonite (i.e., GCL-LQB) are shown in Figs. 8.3 and 8.4. The hydraulic conductivity values at the end of prehydration (i.e., permeation with water) were approximately 2.4×10^{-9} cm/s and in close agreement (i.e., ≤ 5 % difference) for all five specimens which confirms reproducibility in the case of water permeation. Daniel et al. (1997) also reported similar results based on round-robin tests (i.e., 18 different laboratories) performed with water on a single type and make of GCL.

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On the other hand, the electrical conductivity (EC) of effluent, EC_{out}, was higher than 30 mS/m throughout the prehydration period even though the EC of the influent (i.e., deionized water), EC_{in}, was significantly lower (i.e., ~ 0.2 mS/m). As a result, the ratio of effluent to influent EC remained significantly high (i.e., $EC_{out}/EC_{in} > 100$). However, the effluent calcium (Ca^{2+}) concentrations during the prehydration period initially were > 25 mg/L, and then decreased gradually to less than 1.0 mg/L (see Figs. 8.3 and 8.4). Thus, the relatively high EC values of effluent even after ~ 20 PVF of permeation with water are likely due to slow leaching of soluble salts other than Ca^{2+} (e.g., Na^+) from the interlayer region of the bentonite particles to the interparticle and interclod migration pathways through rate-limited diffusive mass transport (Coats and Smith 1964, van Genuchten and Wierenga 1976, Pusch 1999, Pusch and Schomburg 1999).

After switching the influent from water to the solutions containing 5, 10, and 20 mM $CaCl_2$, the hydraulic conductivity values began to increase within 3 months (~ 10 PVF), whereas the thickness of specimens remained constant, as shown in Fig. 8.3. Finally, the hydraulic conductivity values increased by ~ 3.5X to a value of ~ 7.8×10^{-9} cm/s regardless of the influent concentration after ~ 0.8 yr (~ 42 PVF), ~ 0.7 yr (~ 20 PVF), and ~ 0.3 yr (~ 10 PVF) for the prehydrated specimens of GCL-LQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively.

As shown in Fig. 8.4, the hydraulic conductivity values immediately began to increase upon switching the influent from water to the solutions containing 50 and 100 mM $CaCl_2$, and then increased by approximately 7X and 160 X after about 25 days (~ 11 PVF) and 11 days (~ 14 PVF), respectively. The hydraulic conductivity values eventually stabilized at approximately 3.5×10^{-8} cm/s and 1.2×10^{-7} cm/s for the prehydrated

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specimens of GCL-LQB permeated with 50 and 100 mM $CaCl_2$ solutions, respectively. These values are approximately 4.5X and 16X higher, respectively, than the hydraulic conductivity of ~ 7.8 x 10^{-9} cm/s for the prehydrated specimens of GCL-LQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In contrast, the thickness of prehydrated specimens of GCL-LQB permeated with 50 and 100 mM $CaCl_2$ solutions eventually decreased by approximately 15 % relative to the thickness at the end of prehydration with water.

8.3.3 Results for Non-Prehydrated GCL-HQB Specimens

The results of the hydraulic conductivity tests performed on the non-prehydrated specimens of the GCL with the higher quality bentonite (i.e., GCL-HQB) are shown in Figs. 8.5 and 8.6. The hydraulic conductivity values for the non-prehydrated specimens of GCL-HQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions initially decreased to less than 1.0 x 10^{-9} cm/s after about 2 months (< 5 PVF), and then began to increase within 6 months (< 10 PVF). Thereafter, the hydraulic conductivity values increased by more than one order of magnitude after ~ 2.6 yrs (~ 73 PVF), ~ 1.4 yrs (~ 51 PVF), and ~ 0.4 yr (~ 19 PVF) for the non-prehydrated specimens of GCL-HQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions, respectively. Overall, the hydraulic conductivity values were approximately 1.7 x 10^{-8} cm/s regardless of concentration for the non-prehydrated specimens of GCL-HQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

As shown in Fig. 8.6 for the duplicate non-prehydrated specimens of GCL-HQB permeated with 50 and 100 mM $CaCl_2$ solutions, the hydraulic conductivity values stabilized within 3 hrs (~ 20 PVF) at ~ 4.1 x 10^{-6} cm/s and ~ 3.5 x 10^{-5} cm/s, respectively.

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These hydraulic conductivity values are more than two orders-of-magnitude higher than the hydraulic conductivity of ~ 1.7 x 10^{-8} cm/s for the non-prehydrated specimens of GCL-HQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

8.4 DISCUSSION

8.4.1 Inadequacy of pH Equilibrium

As shown in Figs. 8.1 to 8.6, the termination criterion based on pH equilibrium was found not to be applicable in this study, because the pH ratio (i.e., pH_{out}/pH_{in}) never reached the acceptable range (i.e., 1.00 ± 0.10) for all of the tests, except for one test performed on the prehydrated specimen with the 100 mM $CaCl_2$ solution. The increased effluent pH relative to the influent pH (i.e., $pH_{out}/pH_{in} > 1.10$) is due, in part, to the buffering capacity of bentonite as well as the decrease in the influent pH due to time-dependent dissolution of carbon dioxide (CO_2). In addition, if the liquid accumulated in the effluent reservoir is open to the atmosphere, then the release of aqueous-phase carbon dioxide ($CO_{2(aq)}$) into the atmosphere will result in a continual increase in the effluent pH with time (Shackelford 1994). Also, in closed systems such as the flexible-wall apparatus used in this study, the concentration of the $CO_{2(aq)}$, in the pore liquid of a soil likely increases due to respiration by microorganisms under anaerobic conditions (Shackelford 1994). As a result, a pH increase in the effluent is expected due to release of $CO_{2(aq)}$ as equilibrium with the atmosphere is established.

8.4.2 Equilibrium in Hydraulic Conductivity

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In general, all of the hydraulic conductivity values for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions increased by ~ 3.5X to ~ 20X after > ~ 10 PVF (~ 0.3 yr) of permeation depending on prehydration condition and quality of bentonite in the GCLs, and then appear to stabilize. To determine equilibrium in hydraulic conductivity, the slope of hydraulic conductivity versus number of PVF was analyzed statistically using linear regression based on the t-test at a 5 % significance level as described in Peirce and Witter (1986). The statistically zero slope of hydraulic conductivity was evaluated through analyzing the slope of five successive hydraulic conductivity values in series.

However, all of the hydraulic conductivity values for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions initially appear to stabilize within 10 PVF, and then begin to increase (see Figs. 8.1, 8.3, 8.5). As a result, the achievement of statistically zero slope in hydraulic conductivity (hereafter referred to as "zero slope") was considered valid only after the initial stage of the compatibility tests, particularly for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. Even though the statistical approach is useful to determine the establishment of equilibrium in hydraulic conductivity, the statistical approach is meaningful only in conjunction with knowledge of the mechanisms involved in the compatibility tests (e.g., see Bowders 1988).

8.4.3 Effect of Prehydration on Termination Criteria

The test results based on the physical termination criteria, including volumetric flow ratio and steady hydraulic conductivity per ASTM D 5084, 2 PVF, and constant thickness of specimen, as well as the chemical termination criteria, including electrical

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conductivity (EC) and solute (i.e., Cl^- and Ca^{2+}) concentration equilibrium, are summarized in Tables 8.3 and 8.4, respectively. In addition, the hydraulic conductivity values based on each physical termination criterion are compared with those at the zero slope (or $k_{\Delta k\sim 0}$) for both non-prehydrated and prehydrated specimens of the GCL with the lower quality bentonite (i.e., GCL-LQB) in Fig. 8.7.

The hydraulic conductivity values based on the volumetric flow ratio per ASTM D 5084 (i.e., k_Q) are always from ~ 2X to ~ 7X lower than the $k_{\Delta k\sim 0}$ values regardless of prehydration for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In the case of the termination criterion based on the steady hydraulic conductivity per ASTM D 5084 (i.e., k_k), the hydraulic conductivity ratios (i.e., $k_k/k_{\Delta k\sim 0}$) for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions are always less than 0.5 regardless of prehydration. Similarly, the hydraulic conductivity ratios based on 2 PVF (i.e., $k_{2PVF}/k_{\Delta k\sim 0}$) are between ~ 0.1 and ~ 0.5 except for one test performed with the 10 mM $CaCl_2$ solution. In addition, the hydraulic conductivity values based on the constant thickness of specimens (i.e., k_H) are from ~ 2X to ~ 5X lower than the $k_{\Delta k\sim 0}$ values. Thus, none of physical termination criteria appears to be adequate regardless of prehydration for the specimens of GCL-LQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

For the specimens permeated with 50 and 100 mM $CaCl_2$ solutions, the hydraulic conductivity values based on all of the physical termination criteria are not significantly lower (i.e., $\leq$ 31 %) than the $k_{\Delta k\sim 0}$ values regardless of prehydration. However, the hydraulic conductivity values based on one single physical criterion (e.g., 2 PVF) for the prehydrated specimens are as much as ~ 5X lower than the $k_{\Delta k\sim 0}$ values, whereas the hydraulic conductivity values based on any one of the physical criteria for the non-

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prehydrated specimens are not significantly lower (i.e., < 45 %) than the $k_{\Delta k\sim 0}$ values (see Fig. 8.7). Thus, any physical termination criterion appears to be adequate for the non-prehydrated specimens permeated with the 50 and 100 mM $CaCl_2$ solutions, whereas all of the physical termination criteria should be met for the prehydrated specimens to ensure equilibrium in hydraulic conductivity. This difference results from the need to displace the initial pore liquid (i.e., water) with the $CaCl_2$ solution for the prehydrated specimens and the subsequent chemical interactions that occur between the solution and the bentonite in the specimens. In fact, as shown in Fig. 8.7, the termination criterion based on the steady hydraulic conductivity per ASTM D 5084 tends to be the most appropriate in this study among the physical termination criteria for the prehydrated specimens of the GCL-LQB permeated with the 50 and 100 mM $CaCl_2$ solutions.

The hydraulic conductivity values based on the chemical termination criteria are compared with the $k_{\Delta k\sim 0}$ values for both non-prehydrated and prehydrated specimens of GCL-LQB in Fig. 8.8. Two limiting tolerances on EC equilibrium were considered to evaluate the effect of a more restrictive tolerance of $EC_{out}/EC_{in} = 1.00 \pm 0.05$ relative to the more commonly imposed tolerance of $EC_{out}/EC_{in} = 1.00 \pm 0.10$ (e.g., ASTM D 6766).

As shown in Fig. 8.8, the hydraulic conductivity values based on either EC tolerance generally are always lower than the $k_{\Delta k\sim 0}$ values regardless of prehydration for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In fact, the hydraulic conductivity ratios based on the EC ratio of 1.00 ± 0.10 (i.e., $k_{EC0.1}/k_{\Delta k\sim 0}$) are approximately 0.2 for the non-prehydrated specimens and ~ 0.4 for the prehydrated specimens, whereas the hydraulic conductivity ratios based on the EC ratio of 1.00 ± 0.05 (i.e., $k_{EC0.05}/k_{\Delta k\sim 0}$) are about 0.5 for both non-prehydrated and prehydrated specimens. On

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the other hand, for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions, the hydraulic conductivity values based on both ranges of the EC ratio are close to the $k_{\Delta k\sim0}$ values (i.e., $0.78 \leq k_{EC0.1}/k_{\Delta k\sim0} \leq 0.88$ and $0.91 \leq k_{EC0.05}/k_{\Delta k\sim0} \leq 0.96$), except for one of the duplicate non-prehydrated specimens permeated with the 100 mM $CaCl_2$ solution, where the $k_{EC0.1}/k_{\Delta k\sim0}$ and $k_{EC0.05}/k_{\Delta k\sim0}$ values are 0.58 and 0.62, respectively. Thus, establishment of equilibrium in EC between effluent and influent is not sufficient to ensure equilibrium in hydraulic conductivity for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions regardless of prehydration, whereas the establishment of EC equilibrium tends to ensure hydraulic conductivity equilibrium for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions.

As shown in Fig. 8.8, the hydraulic conductivity values based on equilibrium in chloride (i.e., $C_{Cl,out}/C_{Cl,in} = 1.00 \pm 0.10$) are always less than the $k_{\Delta k\sim0}$ values for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In fact, the hydraulic conductivity ratios (i.e., $k_{Cl0.1}/k_{\Delta k\sim0}$) based on the chloride (Cl^-) concentration equilibrium are ~ 0.2 for the non-prehydrated specimens and ~ 0.4 for the prehydrated specimens. Thus, Cl^- equilibrium is not sufficient to ensure the achievement of equilibrium in hydraulic conductivity for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, regardless of prehydration. However, as shown in Fig. 8.8, the hydraulic conductivity at zero slope (or $k_{\Delta k\sim0}$) and hydraulic conductivity based on Ca^{2+} concentration equilibrium are very close (i.e., $0.94 \leq k_{Ca0.1}/k_{\Delta k\sim0} \leq 1.04$), supporting the applicability of salt cation concentration equilibrium as a necessary termination criterion for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, regardless of prehydration. For the specimens permeated with the 50 and 100 mM $CaCl_2$ solutions, the

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hydraulic conductivity values based on either Cl^- or Ca^{2+} concentration equilibrium are not significantly different than the $k_{\Delta k\sim 0}$ values (i.e., $0.59 \leq k_{Cl0.1}/k_{\Delta k\sim 0} \leq 0.91$ and $0.87 \leq k_{Ca0.1}/k_{\Delta k\sim 0} \leq 1.06$).

The elapsed time and PVF required to reach each termination criterion are compared with those at the zero slope in Figs. 8.9 to 8.12. For example, the elapsed time required to achieve steady hydraulic conductivity per ASTM D 5084 was ~ 2X to ~ 20X lower than the elapsed time required to achieve $k_{\Delta k\sim 0}$ for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. Similarly, the required PVF based on the same criterion was still less than 5 PVF for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In other words, significantly more PVF (i.e., ~ 10 to 73 more) are required to achieve $k_{\Delta k\sim 0}$ than are required to meet the physical termination criteria. In fact, the overall physical termination criteria required ~ 3 PVF, representing ~ 40 days of permeation, for both non-prehydrated and prehydrated specimens of GCL-LQB permeated with 5, 10, and 20 mM $CaCl_2$ solutions, whereas ≥ 18 PVF for the non-prehydrated specimens and a minimum of 10 PVF for the prehydrated specimens are required to achieve the $k_{\Delta k\sim 0}$. For the specimens permeated with 50 and 100 mM $CaCl_2$ solutions, the elapsed time and PVF required to achieve each criterion as well as $k_{\Delta k\sim 0}$ generally are greater for the prehydrated specimens than for the non-prehydrated specimens.

8.4.4 Effect of Bentonite Quality on Termination Criteria

The hydraulic conductivity values based on each physical termination criterion are compared with the $k_{\Delta k\sim 0}$ values for the non-prehydrated specimens of the two GCLs

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with the lower quality bentonite (i.e., GCL-LQB) and the higher quality bentonite (i.e., GCL-HQB) in Fig. 8.13. The hydraulic conductivity values based on the volumetric flow ratio per ASTM D 5084 (k_Q) are always lower than $k_{\Delta k\sim0}$ by a factor of ~ 2.7X to ~ 6.7X for the GCL-LQB and by a factor of ~ 17X to ~ 25X for the GCL-HQB. Thus, this termination criterion is inadequate in representing $k_{\Delta k\sim0}$ regardless of bentonite quality for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. For these tests, the elapsed time and PVF required to achieve $k_{\Delta k\sim0}$ are significantly greater (i.e., > 3 months and > 14 PVF) than those needed to meet the requirement for the volumetric flow ratio, regardless of the quality of bentonite used in the GCLs, as shown in Figs. 8.15 and 8.17, respectively. In the case of the termination criterion based on the steady hydraulic conductivity per ASTM D 5084, the hydraulic conductivity ratios (i.e., $k_k/k_{\Delta k\sim0}$) for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions are always less than 0.3 for the GCL-LQB and less than 0.1 for the GCL-HQB, also indicating the inadequacy of this termination criterion regardless of bentonite quality.

Similarly, the hydraulic conductivity ratios based on the minimum requirement of 2 PVF (i.e., $k_{2PVF}/k_{\Delta k\sim0}$) are ~ 0.2 for the GCL-LQB and ~ 0.05 for the GCL-HQB except for the specimen of GCL-LQB permeated with 10 mM $CaCl_2$ solution, in which the $k_{2PVF}/k_{\Delta k\sim0}$ value is ~ 1.9 due to relatively high hydraulic conductivity values at the beginning of the test. Thus, the termination criterion for steady hydraulic conductivity based on ASTM D 5084 is insufficient for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions regardless of bentonite quality. In addition, the hydraulic conductivity values based on the constant thickness of specimens (i.e., k_H) are from ~ 4X to ~ 5X for the GCL-LQB and from ~ 11X to ~ 25X for the GCL-HQB lower than the

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$k_{\Delta k\sim0}$ values. Thus, this termination criterion also is not applicable for the tests on both GCL specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

Thus, the physical termination criteria evaluated in this study are not particularly applicable in terms of their ability to achieve equilibrium in hydraulic conductivity for the specimens of both GCLs (i.e., GCL-LQB and GCL-HQB) permeated with 5, 10, and 20 mM $CaCl_2$ solutions. For the specimens permeated with 50 and 100 mM $CaCl_2$ solutions, the hydraulic conductivity values based on overall physical termination criteria are not significantly different (i.e., < 50 %) to the $k_{\Delta k\sim0}$ values regardless of quality of bentonite used in the GCLs. Thus, any physical termination criterion appears to be adequate for both GCLs. As shown in Figs. 8.15 and 8.17, the elapsed times and PVF for the GCL-HQB required to meet the physical termination criteria generally are greater than those for the GCL-LQB for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, whereas the elapsed times and PVF required for the GCL-HQB specimens generally are lower than those for the GCL-LQB specimens when the specimens are permeated with 50 and 100 mM $CaCl_2$ solutions.

The hydraulic conductivity values based on the chemical termination criteria are compared with the $k_{\Delta k\sim0}$ values for non-prehydrated specimens of both GCLs (i.e., GCL-LQB and GCL-HQB) in Fig. 8.14. The hydraulic conductivity values based on either tolerance for the EC ratio criteria (i.e., $EC_{out}/EC_{in} = 1.00 \pm 0.10$ or 1.00 ± 0.05) are always less than the $k_{\Delta k\sim0}$ values regardless of bentonite quality for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In fact, the hydraulic conductivity ratios based on the EC ratio of 1.00 ± 0.10 (i.e., $k_{EC0.1}/k_{\Delta k\sim0}$) range from ~ 0.2 to ~ 0.3 for the GCL-LQB and from ~ 0.1 to ~ 0.2 for the GCL-HQB, except for the GCL-HQB

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permeated with the 20 mM $CaCl_2$ solution, where the $k_{EC0.1}/k_{\Delta k\sim0}$ value is about 0.6. Similarly, the hydraulic conductivity ratios based on the EC ratio of 1.00 ± 0.05 (i.e., $k_{EC0.05}/k_{\Delta k\sim0}$) range from ~ 0.4 to ~ 0.6 for the GCL-LQB and from ~ 0.1 to ~ 0.3 for the GCL-HQB, except for the GCL-HQB permeated with the 20 mM $CaCl_2$ solution, where the $k_{EC0.1}/k_{\Delta k\sim0}$ value is ~ 1.0. Thus, equilibrium between effluent and influent EC apparently is a necessary, but not a sufficient, condition to ensure equilibrium in hydraulic conductivity regardless of bentonite quality for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. On the other hand, for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions, the hydraulic conductivity values based on either tolerance of the EC ratio are not significantly lower (i.e., $\leq$ 50 %) than the $k_{\Delta k\sim0}$ values for both GCLs. Therefore, the EC criteria apparently are more appropriate in terms of providing a true measure of $k_{\Delta k\sim0}$ for the specimens of both GCLs permeated with 50 and 100 mM $CaCl_2$ solutions.

Similarly, the hydraulic conductivity ratios based on the Cl^- concentration equilibrium requiring $C_{Cl,out}/C_{Cl,in} = 1.00 \pm 0.10$ (i.e., $k_{Cl0.1}/k_{\Delta k\sim0}$) are less than 0.3 for the GCL-LQB and less than 0.1 for the GCL-HQB, which also indicates its insufficiency as a termination criterion, for the specimens of both GCLs permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In fact, as shown in Fig. 8.14, $k_{\Delta k\sim0}$ for both GCLs was only established when the Ca^{2+} concentrations in the effluent and influent were similar (i.e., $C_{Ca,out}/C_{Ca,in} = 1.00 \pm 0.10$). Thus, regardless of the quality of bentonite used in the GCLs, the chemical termination criterion based on Ca^{2+} concentration equilibrium is both necessary and sufficient to ensure the establishment of equilibrium in hydraulic conductivity based on the results for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. As

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shown in Fig. 8.14, the hydraulic conductivity values based on either Cl^- or Ca^{2+} concentration equilibrium are not significantly lower than the $k_{\Delta k\sim 0}$ values (i.e., ≤ 50 %) for the specimens of both GCLs permeated with 50 and 100 mM $CaCl_2$ solutions.

As shown in Figs. 8.16 and 8.18, the elapsed times and PVF based on the chemical termination criteria generally are greater for the GCL-HQB than for the GCL-LQB for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In contrast, the elapsed times and PVF generally are lower for the GCL-HQB than for the GCL-LQB for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions.

8.5 SUMMARY AND CONCLUSIONS

Hydraulic conductivity tests are performed on two geosynthetic clay liners (GCLs) containing different qualities of bentonite with or without prehydration to evaluate adequacy of a wide range of termination criteria commonly used in compatibility testing of GCLs with respect to prehydration and quality of bentonite by permeating the GCL specimens with calcium chloride ($CaCl_2$) solutions until complete chemical equilibrium between the influent and effluent is established. None of the physical termination criteria (i.e., volumetric flow ratio and steady hydraulic conductivity per ASTM D 5084, 2 pore volumes of flow, constant thickness of specimen) was found to be adequate for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions regardless of prehydration or quality of bentonite because the equilibrium in hydraulic conductivity had not been established at the times corresponding to those criteria. On the other hand, the overall physical termination criteria tend to ensure equilibrium in

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hydraulic conductivity regardless of prehydration or quality of bentonite for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions.

In terms of chemical termination criterion, the pH ratio (i.e., pH_{out}/pH_{in}) was never within the acceptable range (i.e., 1.00 ± 0.10) throughout any of the tests performed in this study, except for one prehydrated GCL specimen permeated with a 100 mM $CaCl_2$ solution. Furthermore, the hydraulic conductivity values based on electrical conductivity (EC) equilibrium are always from ~ 2X to ~ 10X lower than the hydraulic conductivity values at the statistically zero slope (or $k_{\Delta k\sim 0}$), regardless of prehydration or quality of bentonite for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, except for one specimen permeated with the 20 mM $CaCl_2$ solution. Thus, the EC equilibrium is a necessary, but not sufficient, condition to ensure equilibrium in hydraulic conductivity particularly for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. In fact, equilibrium in hydraulic conductivity was not established until the Ca^{2+} concentrations in the effluent and influent were similar (i.e., $C_{Ca,out}/C_{Ca,in} = 1.00 \pm 0.10$), regardless of prehydration or quality of bentonite. On the other hand, any chemical termination criterion tends to ensure equilibrium in hydraulic conductivity regardless of prehydration or quality of bentonite for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions. Thus, the termination criteria based on equilibrium in effluent and influent calcium concentration is unique so that this criteria can be used to represent the equilibrium hydraulic conductivity based on a statistically zero slope (or $k_{\Delta k\sim 0}$), regardless of $CaCl_2$ concentration, prehydration of the GCL, or quality of the bentonite in the GCL.

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Table 8.1 – Properties of bentonites in two geosynthetic clay liners.

Property	Standard	Average Value [No. of Trials]	
		LQB[e]	HQB[e]
Specific Gravity	ASTM D 854[a]	2.74 [3]	2.78 [2]
Soil Classification:	ASTM D 2487		
Sieve Analysis (Air-Dried)		SP [3]	SP [1]
Hydrometer		CH [7]	CH [1]
Atterberg Limits (%):	ASTM D 4318	[1]	[1]
Liquid Limit, LL		430	589
Plasticity Index, PI		393	548
Swell Index (mL/2 g)	ASTM D 5890	27.5 [17]	30.0 [2]
Bentonite Mass (kg/m^2)	ASTM D 5993	5.1 [5]	4.6 [5]
Principal Minerals (%):	b	[3]	[2]
Montmorillonite		77.2	86.0
Cristobalite		10.3	4.5
Plagioclase Feldspar		5.1	2.5
Quartz		3.4	3.5
Others		4.0	5.5
Cation Exchange Capacity, CEC (meq/100 g)	c	63.9 [3]	93.4 [2]
Exchangeable Metals (meq/100 g):	c	[3]	[2]
Ca^{2+}		11.5	15.3
Mg^{2+}		3.7	7.0
Na^{+}		45.8	69.0
K^{+}		0.7	0.8
Sum		61.7	92.1
Soluble Metals (mg/kg):	c, d	[3]	[2]
Ca^{2+}		218	737
Mg^{2+}		24	160
Na^{+}		3365	7107
K^{+}		48	216
Saturated Soil Paste:	c	[3]	[3]
pH		8.9	8.8
EC[f] (mS/m)		305	233

[a] Using a magnetic stirring device for de-airing.

[b] Based on X-ray diffraction (XRD) analyses performed by Mineralogy Inc., Tulsa, OK and GeoServices Inc., Argyle, TX.

[c] Based on procedures described in Shackelford and Redmond (1995).

[d] Measured from a 1 g:20 mL clay-water extract.

[e] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite.

[f] Electrical conductivity at 25 °C.

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Table 8.2 – Properties of permeant liquids.

Permeant Liquid	Salt Concentration (mM)		Measured Solute Concentrations (mg/L)		Measured pH [No. of Trials]	Measured EC[c] (mS/m) [No. of Trials]
	Target	Measured [No. of Trials]	Calcium (Ca^{2+}) [No. of Trials]	Chloride (Cl^-) [No. of Trials]		
DIW[a]	0	< 0.0005[b] [10]	< 0.02[b] [10]	< 0.04[b] [10]	5.6 ± 0.5 [19]	0.21 ± 0.11 [19]
$CaCl_2$ (Sigma Co., 96 %)	5	5.1 ± 0.2 [14]	216 ± 10 [14]	377 ± 38 [14]	5.7 ± 0.5 [25]	123 ± 2.1 [25]
	10	10.1 ± 0.2 [13]	436 ± 30 [13]	756 ± 65 [13]	6.0 ± 0.3 [19]	234 ± 2.6 [19]
	20	20.1 ± 0.6 [13]	872 ± 77 [13]	1457 ± 110 [13]	6.1 ± 0.3 [17]	445 ± 7.3 [17]
	50	50.7 ± 1.4 [9]	2055 ± 63 [9]	3548 ± 69 [9]	5.7 ± 0.1 [18]	1041 ± 26 [18]
	100	100 ± 2.6 [6]	4072 ± 126 [6]	7030 ± 95 [6]	5.8 ± 0.1 [13]	1958 ± 48 [13]

[a] Deionized water.
[b] Method detection limit (MDL).
[c] Electrical conductivity at 25 °C.

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Table 8.3 – Summary for results of hydraulic conductivity tests based on physical termination criteria.[a]

Per-meant Liquid	Test No.	GCL Type[b]	Pre-hydra-tion	Slope of k ~ 0[c]		Physical Termination Criteria							
						ASTM D 5084				2 PVF		Constant Thickness	
						Q Ratio		Steady k					
				$PVF_{\Delta k\sim 0}$ $[t_{\Delta k\sim 0}]$*	$k_{\Delta k\sim 0}$ (cm/s)	PVF_Q $[t_Q]$*	$k_Q/k_{\Delta k\sim 0}$	PVF_k $[t_k]$*	$k_k/k_{\Delta k\sim 0}$	$[t_{2PVF}]$*	$k_{2PVF}/k_{\Delta k\sim 0}$	PVF_H $[t_H]$*	$k_H/k_{\Delta k\sim 0}$
5 mM $CaCl_2$	1	LQB	No	54 [494]	8.3×10^{-9}	1.5 [5.5]	0.32	2.8 [25]	0.24	[15]	0.21	2.2 [15]	0.21
	2	LQB	Yes	42 [306]	8.0×10^{-9}	3.4 [40]	0.29	3.4 [40]	0.27	[31]	0.28	0.84 [11]	0.26
	3	HQB	No	68 [955]	1.8×10^{-8}	2.9 [187]	0.04	2.2 [150]	0.04	[150]	0.04	1.6 [112]	0.04
10 mM $CaCl_2$	4	LQB	No	26 [376]	6.8×10^{-9}	2.6 [8.6]	0.37	3.9 [36]	0.28	[2.5]	1.92	3.4 [23]	0.28
	5	LQB	Yes	20 [246]	6.1×10^{-9}	3.0 [47]	0.48	3.0 [47]	0.48	[36]	0.46	0.74 [13]	0.40
	6	HQB	No	51 [502]	1.7×10^{-8}	3.6 [231]	0.04	4.4 [254]	0.04	[169]	0.03	0.75 [21]	0.06
20 mM $CaCl_2$	7	LQB	No	18 [147]	9.5×10^{-9}	3.2 [47]	0.15	3.9 [59]	0.16	[34]	0.14	1.1 [9.6]	0.28
	8	LQB	Yes	10 [92]	9.3×10^{-9}	2.5 [41]	0.37	2.5 [41]	0.37	[41]	0.37	0.62 [14]	0.21
	9	HQB	No	19 [150]	1.7×10^{-8}	3.1 [48]	0.06	4.5 [90]	0.07	[25]	0.09	2.0 [25]	0.09
50 mM $CaCl_2$	10	LQB	No	7.0 [12]	1.6×10^{-8}	3.0 [5.6]	0.85	3.0 [5.6]	0.85	[4.2]	0.80	1.5 [2.7]	0.83
	11	LQB	No	4.8 [8.9]	1.8×10^{-8}	2.7 [5.5]	0.86	2.7 [5.5]	0.86	[4.2]	0.81	1.3 [2.6]	0.83
	12	LQB	Yes	11 [25]	3.5×10^{-8}	3.0 [15]	0.43	6.5 [20]	0.88	[15]	0.43	6.5 [20]	0.88
	13	HQB	No	24 [0.13]	4.8×10^{-6}	3.4 [0.021]	0.53	4.3 [0.027]	0.57	[0.014]	0.54	5.3 [0.033]	0.62
	14	HQB	No	18 [0.18]	3.7×10^{-6}	2.9 [0.035]	0.46	3.6 [0.046]	0.54	[0.024]	0.52	2.9 [0.035]	0.46
100 mM $CaCl_2$	15	LQB	No	9.1 [0.98]	3.4×10^{-7}	3.0 [0.39]	0.58	3.0 [0.39]	0.58	[0.29]	0.59	1.5 [0.19]	0.69
	16	LQB	No	5.3 [0.54]	3.5×10^{-7}	3.0 [0.37]	0.89	3.7 [0.43]	0.83	[0.31]	0.82	0.75 [0.15]	0.38
	17	LQB	Yes	14 [11]	1.2×10^{-7}	3.4 [8.5]	0.54	6.8 [9.5]	0.72	[8.1]	0.21	6.8 [9.5]	0.84
	18	HQB	No	19 [0.015]	3.4×10^{-5}	2.9 [0.003]	0.84	2.9 [0.003]	0.84	[0.002]	0.76	4.6 [0.004]	0.89
	19	HQB	No	22 [0.012]	4.2×10^{-5}	3.6 [0.002]	0.71	3.6 [0.002]	0.71	[0.002]	0.67	2.7 [0.002]	0.67

[a] k = hydraulic conductivity; Q = volumetric flow rate; PVF = pore volumes of flow. [b] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite. [c] When the slope of k vs. number of PVF is statistically zero (Peirce & Witter 1986). * Elapsed time [days].

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Table 8.4 – Summary for results of hydraulic conductivity tests based on chemical termination criteria.[a]

Permeant Liquid	Test No.	GCL Type[b]	Pre-hydration	$k_{\Delta k\sim0}$[c] (cm/s)	Chemical Termination Criteria							
					EC Ratio[d]				C_{Cl} Ratio[d] (1.00 ± 0.10)		C_{Ca} Ratio[d] (1.00 ± 0.10)	
					(1.00 ± 0.10)		(1.00 ± 0.05)					
					$PVF_{EC0.1}$ [$t_{EC0.1}$]*	$k_{EC0.1}/k_{\Delta k\sim0}$	$PVF_{EC0.05}$ [$t_{EC0.05}$]*	$k_{EC0.05}/k_{\Delta k\sim0}$	$PVF_{Cl0.1}$ [$t_{Cl0.1}$]*	$k_{Cl0.1}/k_{\Delta k\sim0}$	$PVF_{Ca0.1}$ [$t_{Ca0.1}$]*	$k_{Ca0.1}/k_{\Delta k\sim0}$
5 mM $CaCl_2$	1	LQB	No	8.3×10^{-9}	24 [338]	0.26	32 [403]	0.39	6.3 [80]	0.18	57 [502]	1.04
	2	LQB	Yes	8.0×10^{-9}	4.2 [51]	0.28	16 [174]	0.34	2.5 [31]	0.28	58 [358]	0.98
	3	HQB	No	1.8×10^{-8}	16 [632]	0.10	20 [721]	0.11	4.2 [256]	0.04	58 [934]	0.93
10 mM $CaCl_2$	4	LQB	No	6.8×10^{-9}	14 [280]	0.30	20 [341]	0.64	11 [234]	0.22	30 [397]	0.98
	5	LQB	Yes	6.1×10^{-9}	3.0 [47]	0.48	3.8 [60]	0.43	3.0 [47]	0.48	35 [360]	1.02
	6	HQB	No	1.7×10^{-8}	16 [422]	0.23	18 [435]	0.32	4.4 [254]	0.05	60 [515]	1.02
20 mM $CaCl_2$	7	LQB	No	9.5×10^{-9}	4.6 [70]	0.17	12 [127]	0.61	1.8 [21]	0.17	31 [178]	0.99
	8	LQB	Yes	9.3×10^{-9}	3.2 [49]	0.43	4.5 [60]	0.55	1.9 [34]	0.31	16 [120]	0.94
	9	HQB	No	1.7×10^{-8}	11 [131]	0.59	27 [164]	1.03	3.1 [48]	0.06	22 [154]	1.07
50 mM $CaCl_2$	10	LQB	No	1.6×10^{-8}	3.0 [5.6]	0.85	3.8 [7.0]	0.91	2.2 [4.2]	0.80	9.3 [16]	1.03
	11	LQB	No	1.8×10^{-8}	2.7 [5.5]	0.86	3.4 [6.6]	0.91	2.0 [4.2]	0.81	8.9 [15]	1.06
	12	LQB	Yes	3.5×10^{-8}	6.5 [20]	0.88	7.9 [21]	0.96	7.2 [21]	0.91	11 [24]	0.99
	13	HQB	No	4.8×10^{-6}	4.3 [0.027]	0.59	6.1 [0.039]	0.63	2.5 [0.014]	0.54	18 [0.11]	0.97
	14	HQB	No	3.7×10^{-6}	3.6 [0.046]	0.50	5.1 [0.065]	0.61	3.6 [0.046]	0.50	17 [0.18]	0.98
100 mM $CaCl_2$	15	LQB	No	3.4×10^{-7}	3.0 [0.39]	0.58	3.8 [0.48]	0.62	2.3 [0.29]	0.59	6.8 [0.80]	0.87
	16	LQB	No	3.5×10^{-7}	2.2 [0.31]	0.82	3.7 [0.43]	0.96	1.5 [0.24]	0.65	6.0 [0.59]	1.07
	17	LQB	Yes	1.2×10^{-7}	5.9 [9.3]	0.78	9.3 [10]	0.91	7.6 [9.7]	0.86	10 [10]	0.92
	18	HQB	No	3.4×10^{-5}	2.1 [0.002]	0.76	3.8 [0.003]	0.88	1.4 [0.001]	0.76	4.6 [0.004]	0.89
	19	HQB	No	4.2×10^{-5}	2.7 [0.002]	0.67	4.5 [0.003]	0.73	1.8 [0.001]	0.73	11 [0.006]	0.93

[a] k = hydraulic conductivity; PVF = pore volumes of flow. [b] LQB = GCL with lower quality bentonite; HQB = GCL with higher quality bentonite. [c] When the slope of k vs. number of PVF is statistically zero (Peirce & Witter 1986). [d] EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium; ratio = effluent relative to influent. * Elapsed time [days].

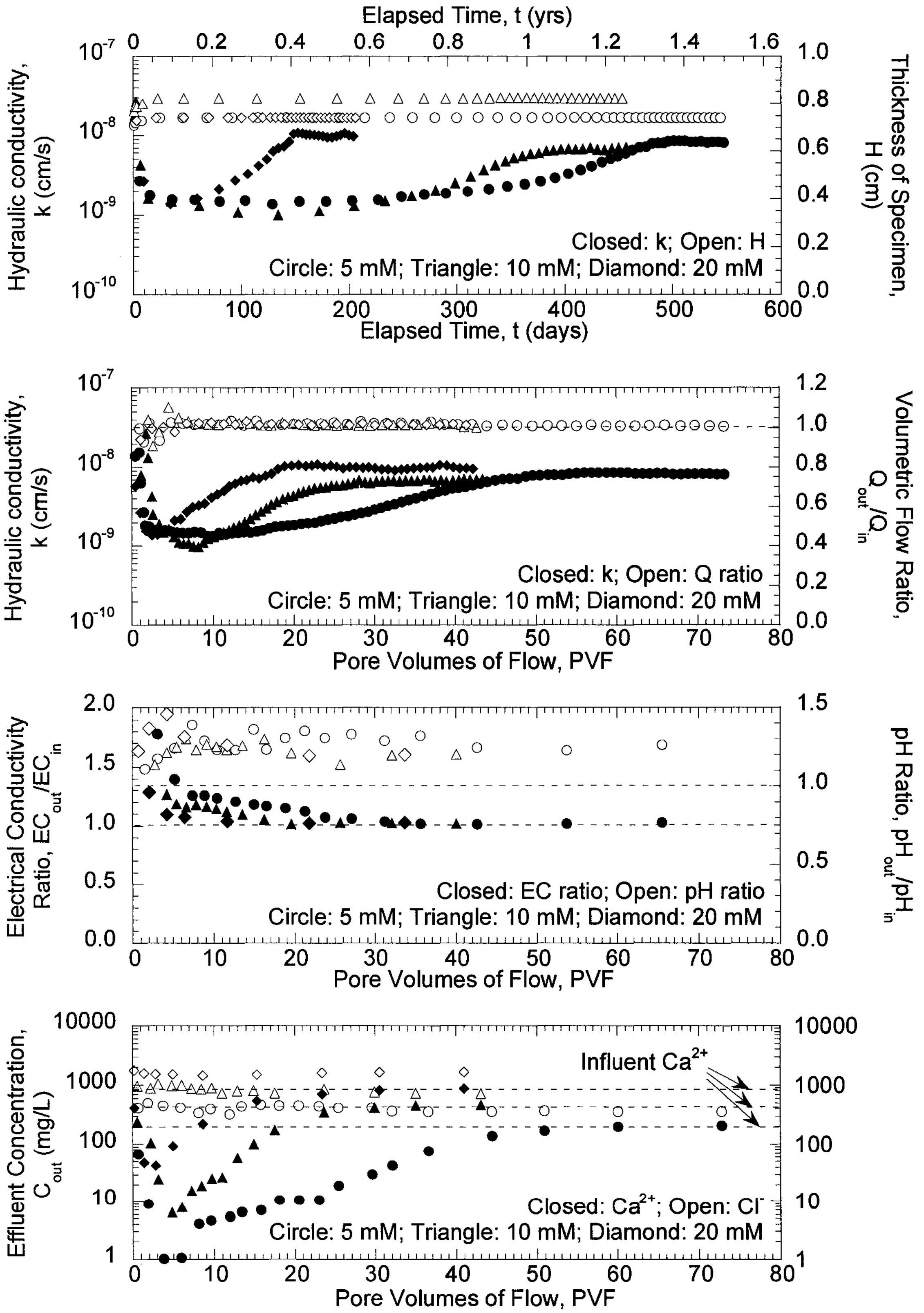

Fig. 8.1 – Test results for non-prehydrated specimens of GCL with lower quality bentonite permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

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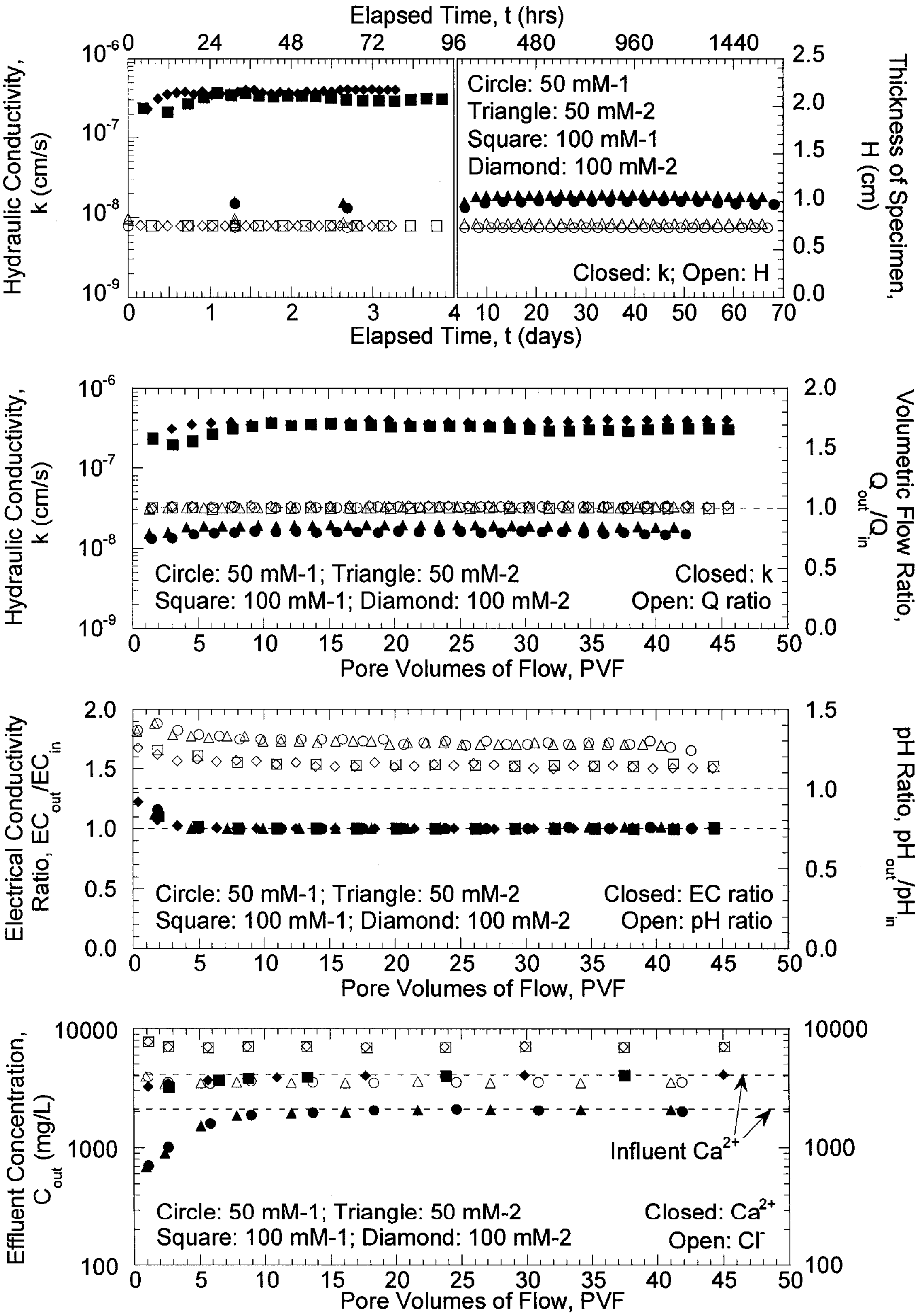

Fig. 8.2 – Test results for non-prehydrated duplicate specimens of GCL with lower quality bentonite permeated with 50 and 100 mM $CaCl_2$ solutions.

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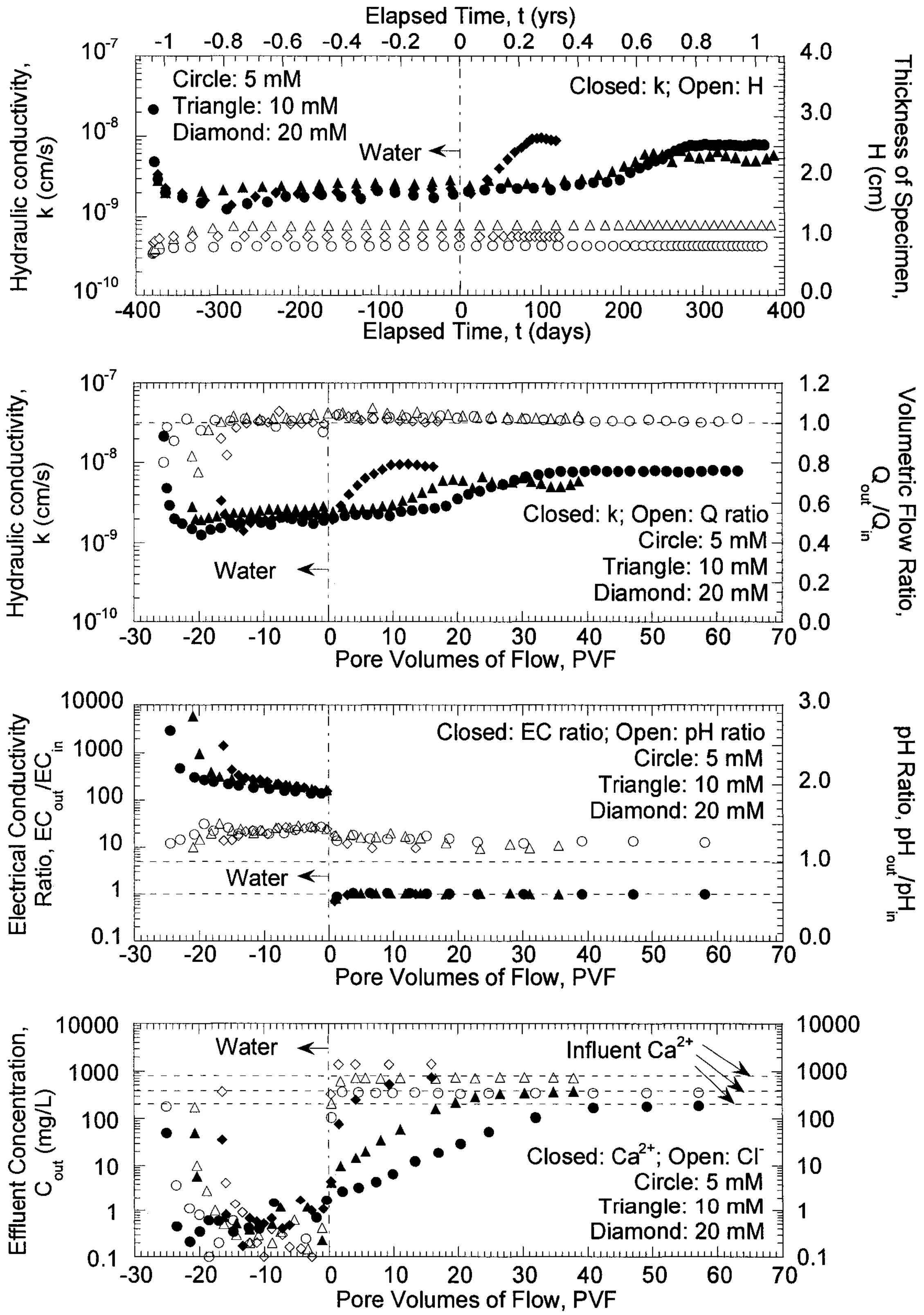

Fig. 8.3 – Test results for prehydrated specimens of GCL with lower quality bentonite permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

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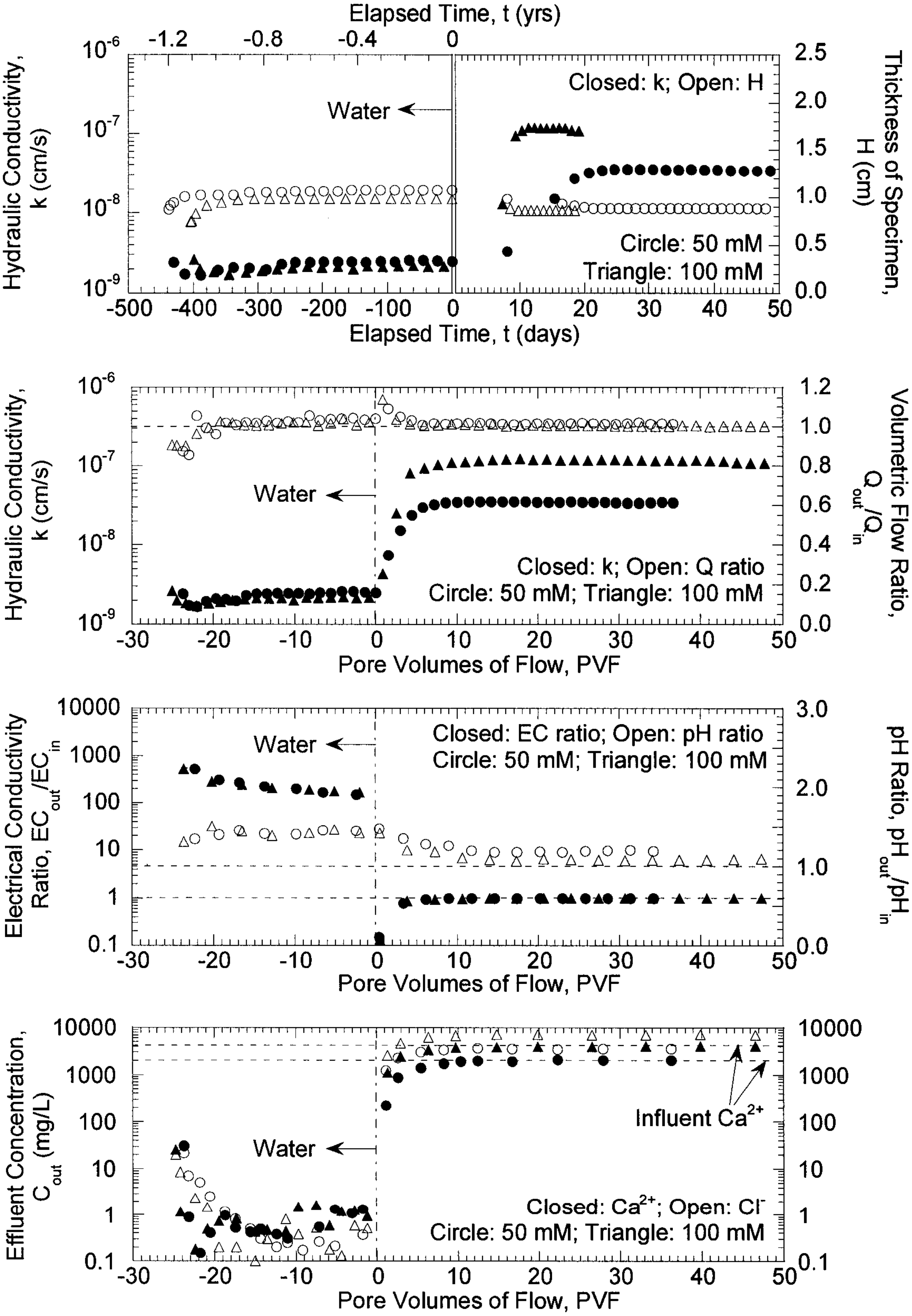

Fig. 8.4 – Test results for prehydrated specimens of GCL with lower quality bentonite permeated with 50 and 100 mM $CaCl_2$ solutions.

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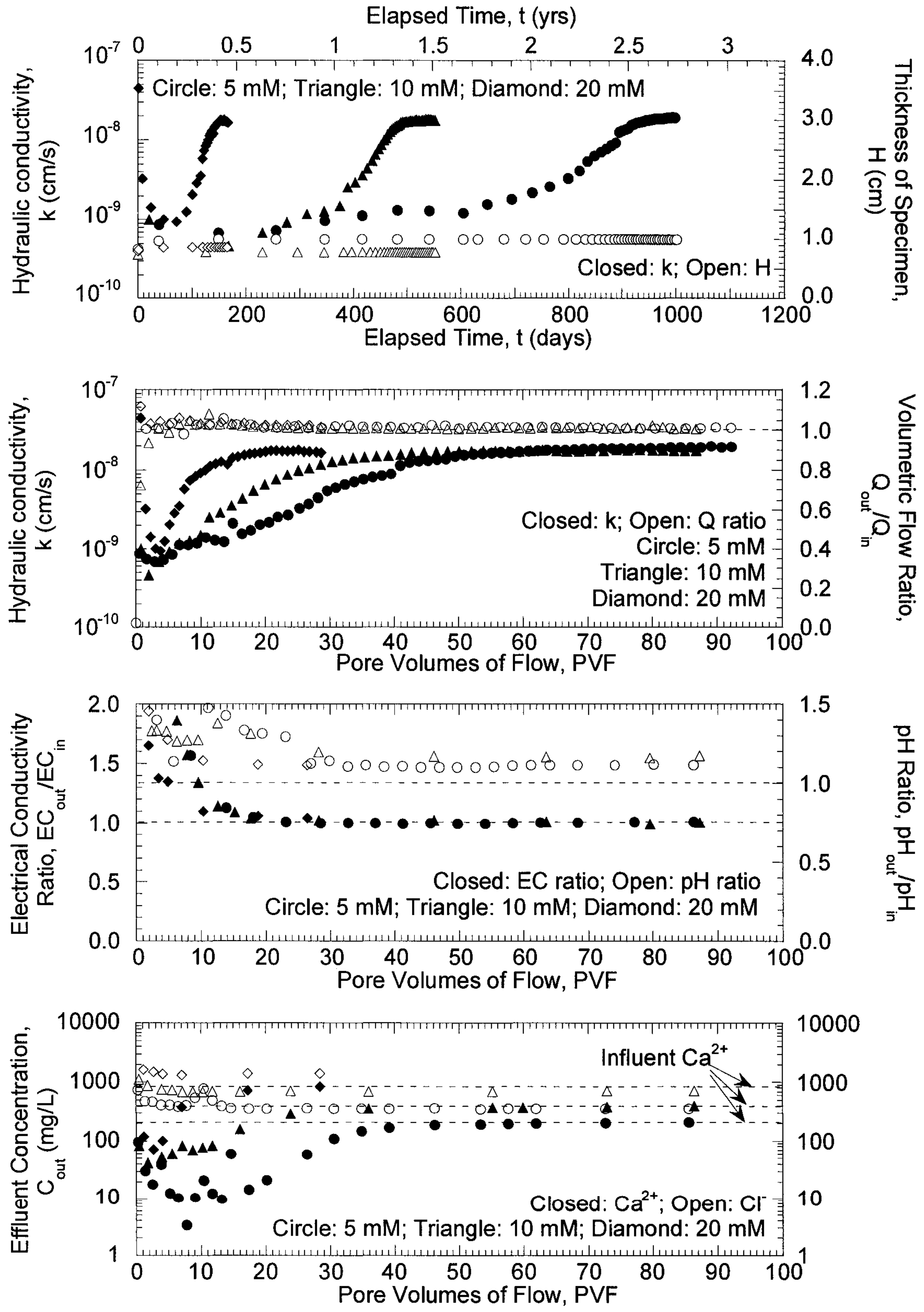

Fig. 8.5 – Test results for non-prehydrated specimens of GCL with higher quality bentonite permeated with 5, 10, and 20 mM $CaCl_2$ solutions.

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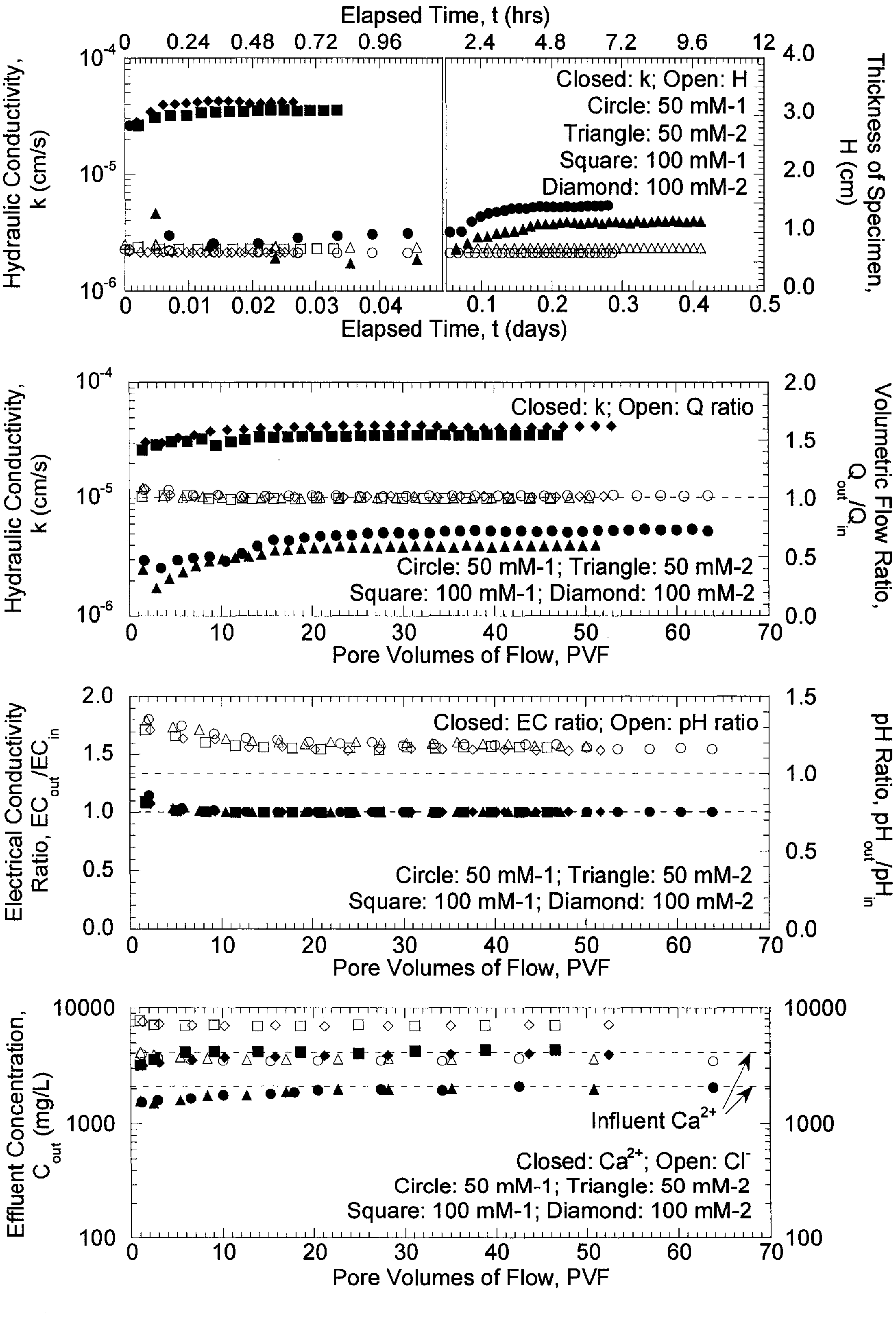

Fig. 8.6 – Test results for non-prehydrated duplicate specimens of GCL with higher quality bentonite permeated with 50 and 100 mM $CaCl_2$ solutions.

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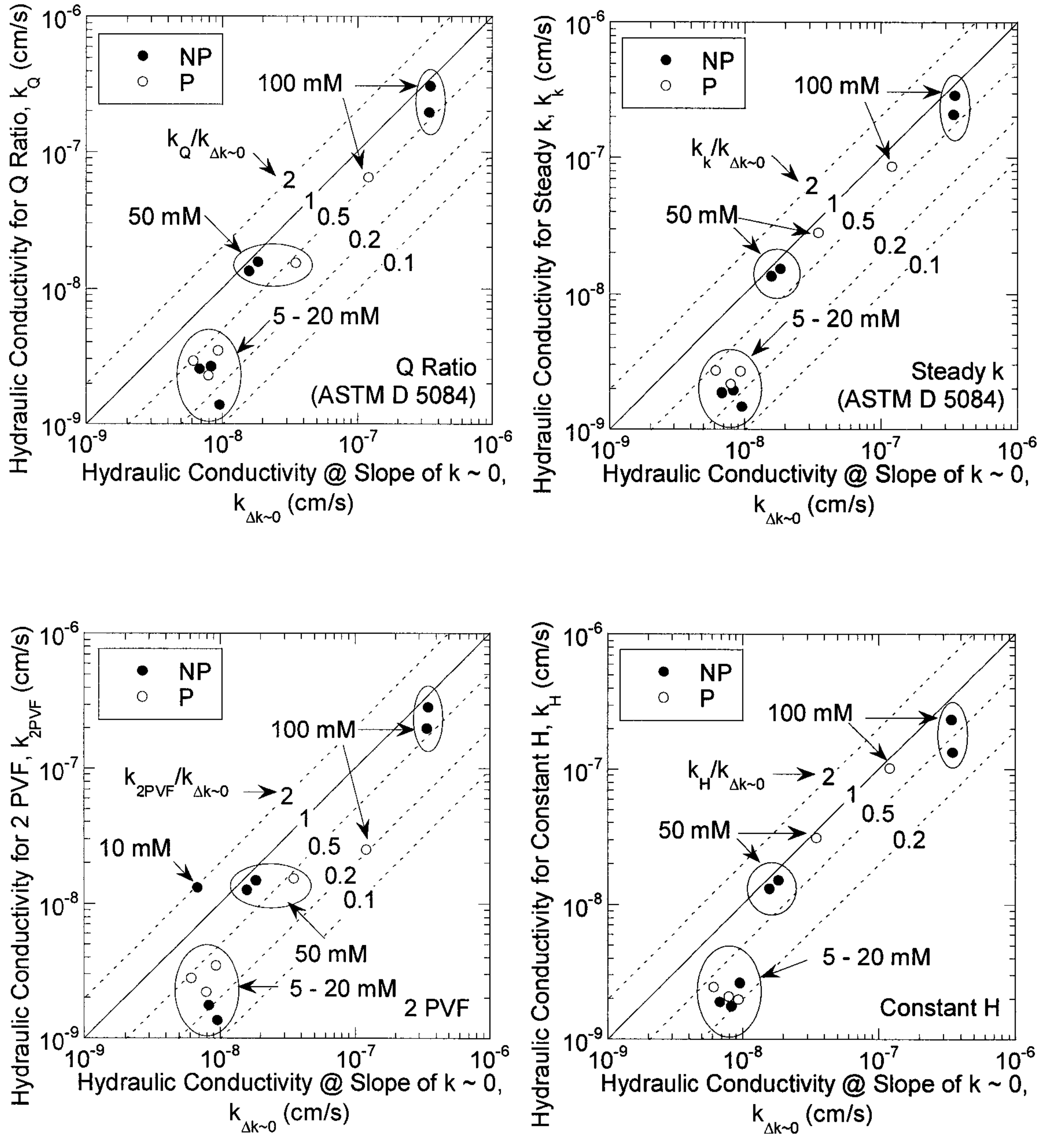

Fig. 8.7 – Hydraulic conductivity for physical termination criteria versus hydraulic conductivity at the slope of k ~ 0 for both non-prehydrated (NP) and prehydrated (P) specimens of GCL with lower quality bentonite (Q = volumetric flow rate; PVF = pore volumes of flow; H = thickness of specimen).

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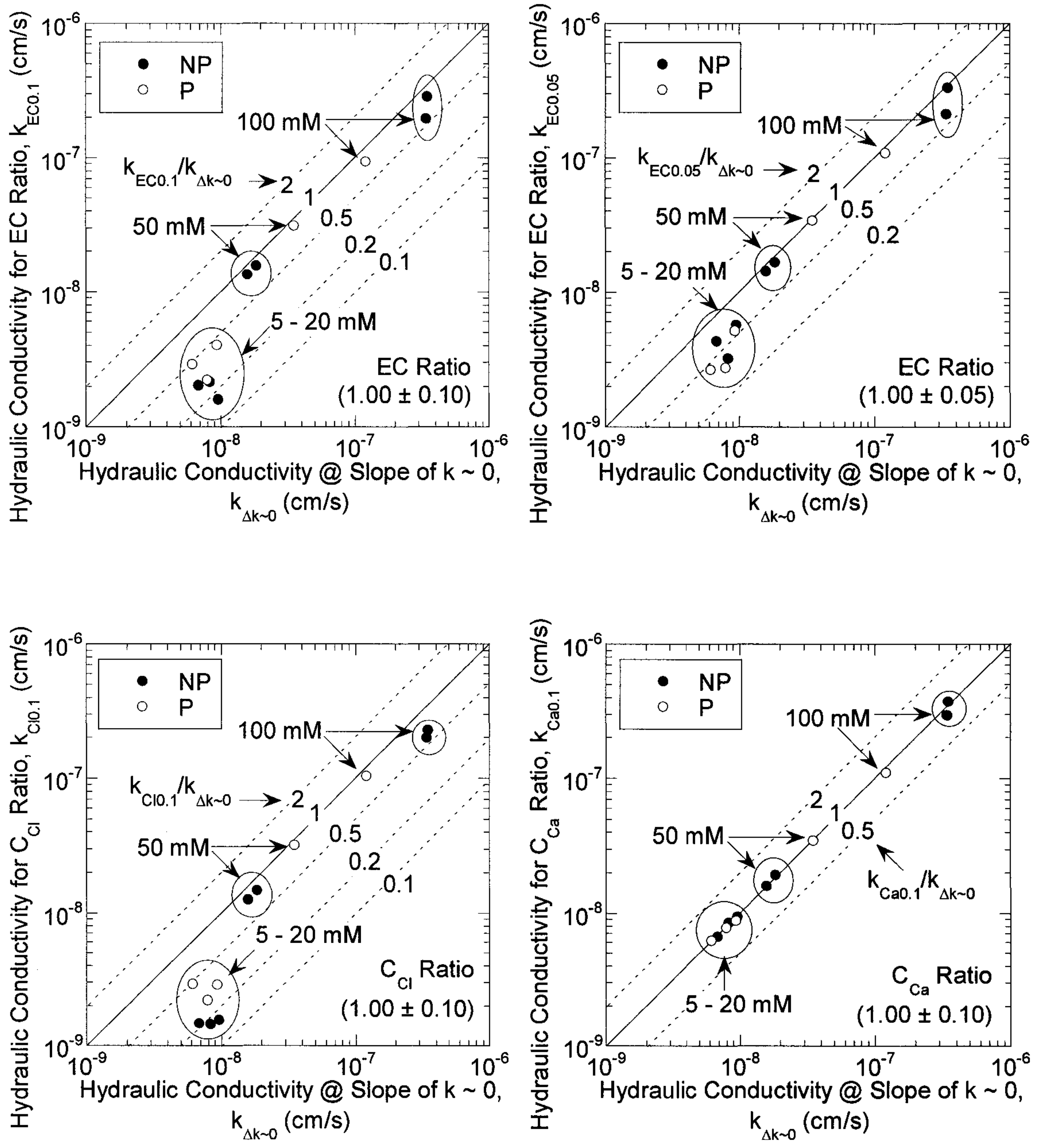

Fig. 8.8 – Hydraulic conductivity for chemical termination criteria versus hydraulic conductivity at the slope of k ~ 0 for both non-prehydrated (NP) and prehydrated (P) specimens of GCL with lower quality bentonite (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium).

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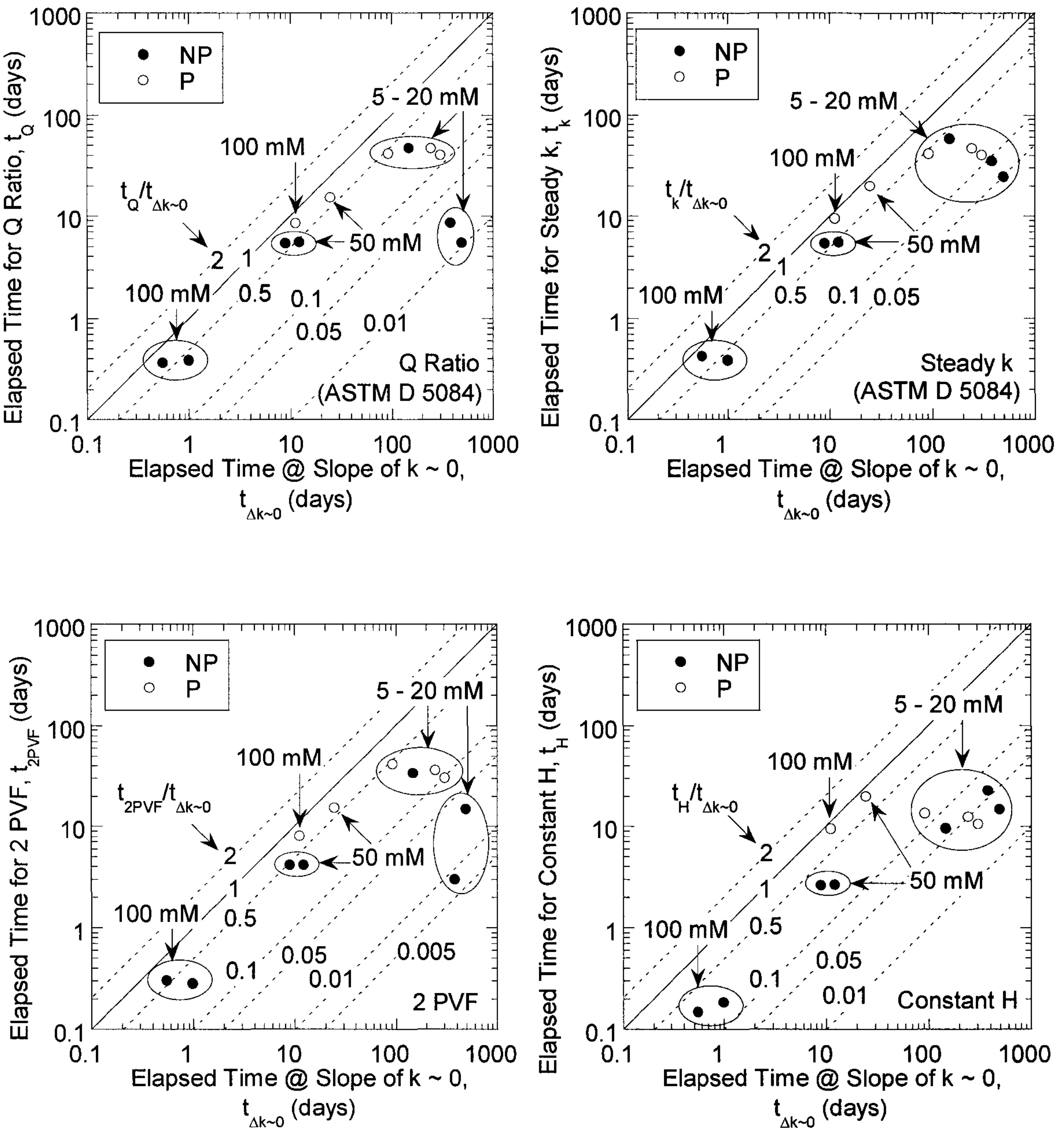

Fig. 8.9 – Elapsed time for physical termination criteria versus elapsed time at the slope of hydraulic conductivity ~ 0 for both non-prehydrated (NP) and prehydrated (P) specimens of GCL with lower quality bentonite (Q = volumetric flow rate; PVF = pore volumes of flow; H = thickness of specimen).

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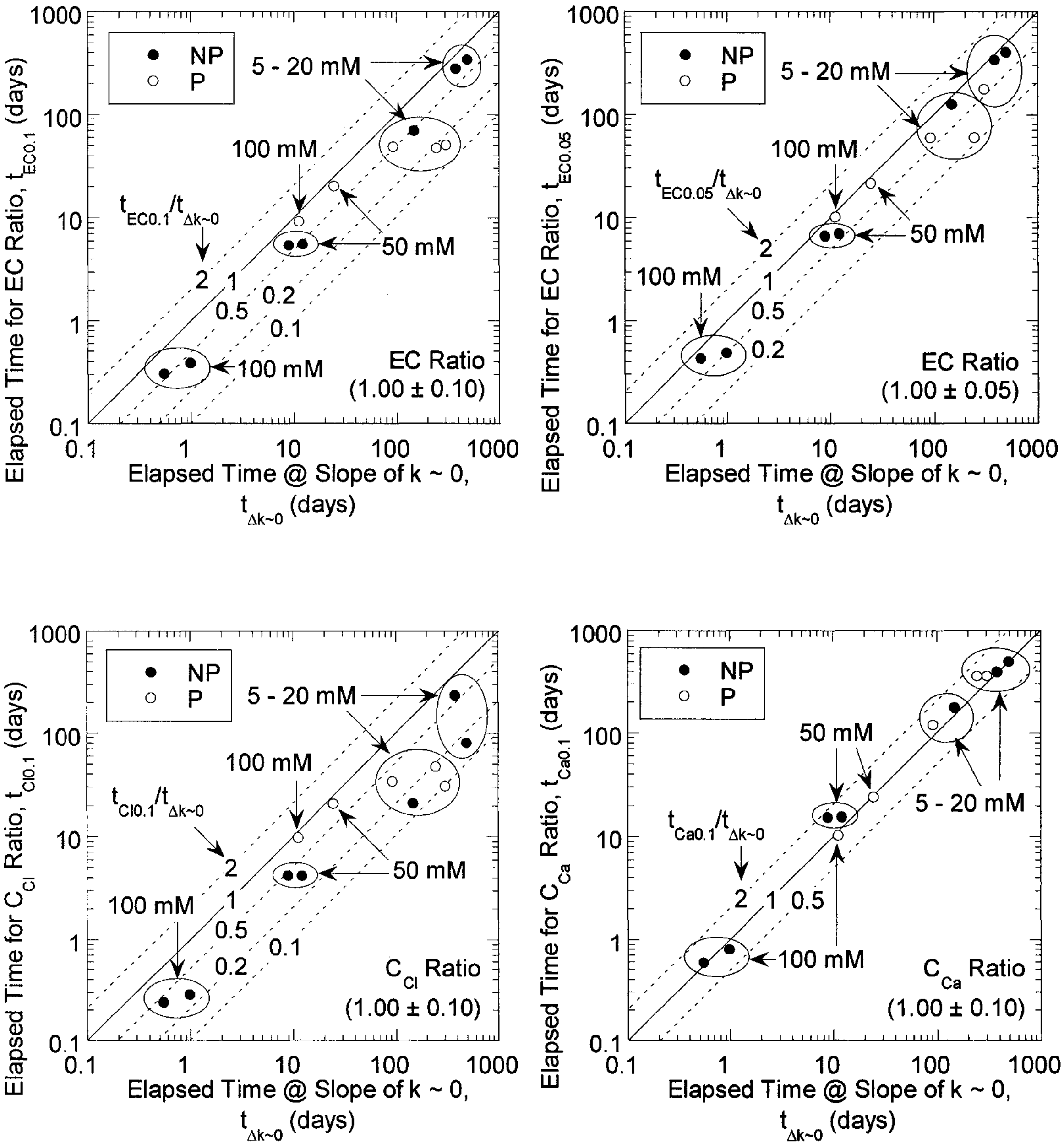

Fig. 8.10 – Elapsed time for chemical termination criteria versus elapsed time at the slope of hydraulic conductivity ~ 0 for both non-prehydrated (NP) and prehydrated (P) specimens of GCL with lower quality bentonite (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium).

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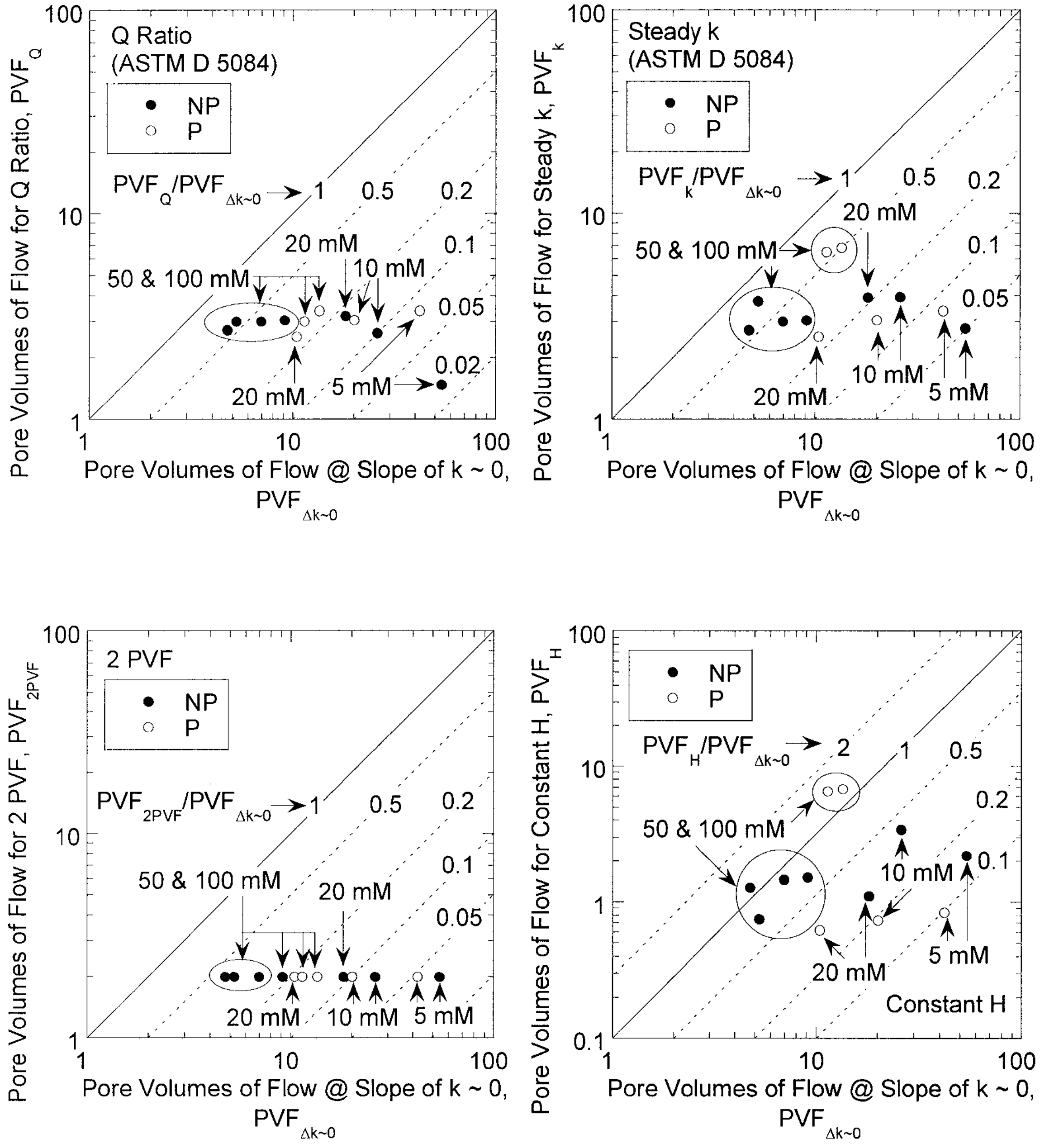

Fig. 8.11 – Pore volumes of flow (PVF) for physical termination criteria versus PVF at the slope of hydraulic conductivity ~ 0 for both non-prehydrated (NP) and prehydrated (P) specimens of GCL with lower quality bentonite (Q = volumetric flow rate; H = thickness of specimen).

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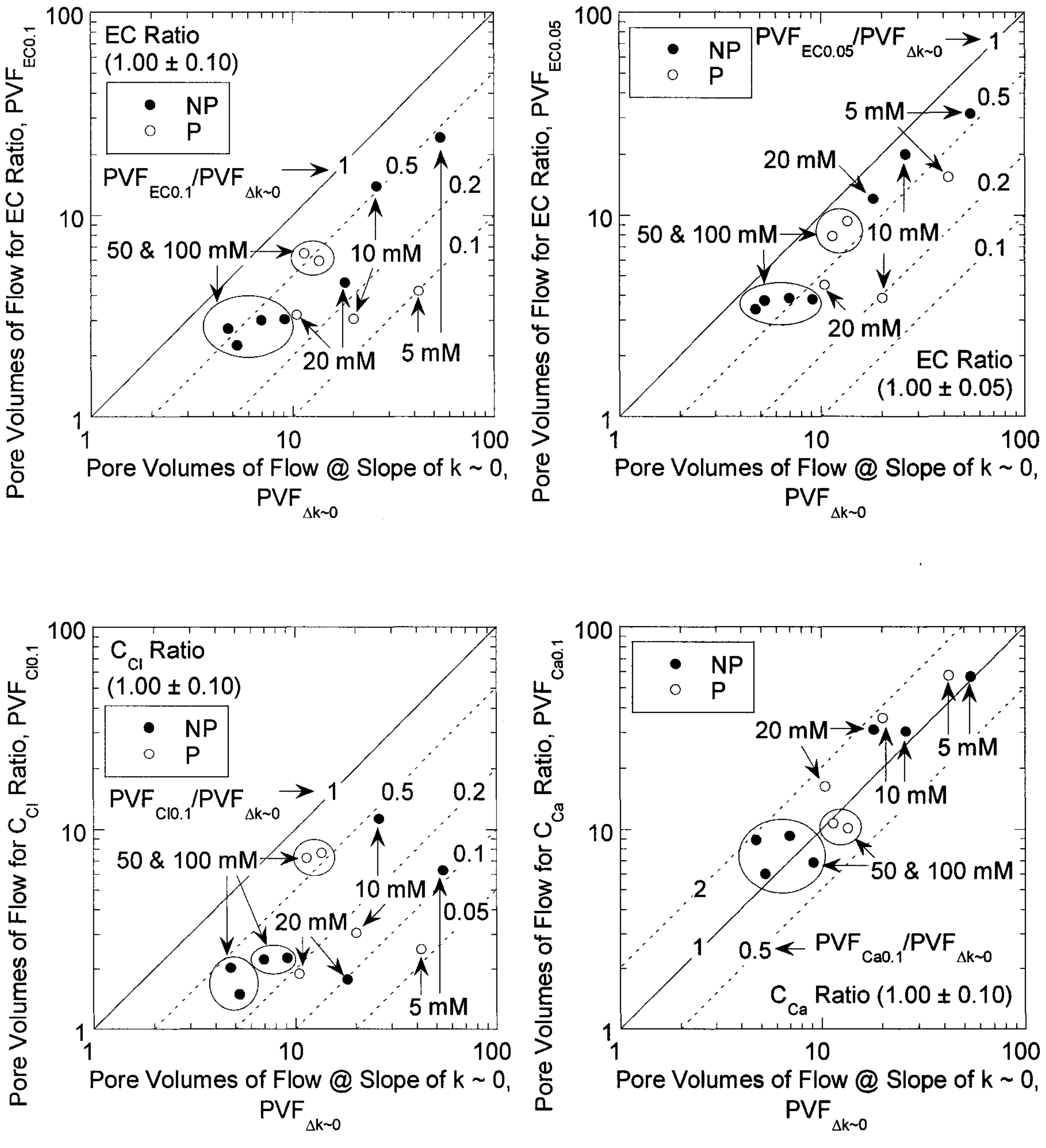

Fig. 8.12 – Pore volumes of flow (PVF) for chemical termination criteria versus PVF at the slope of hydraulic conductivity ~ 0 for both non-prehydrated (NP) and prehydrated (P) specimens of GCL with lower quality bentonite (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium).

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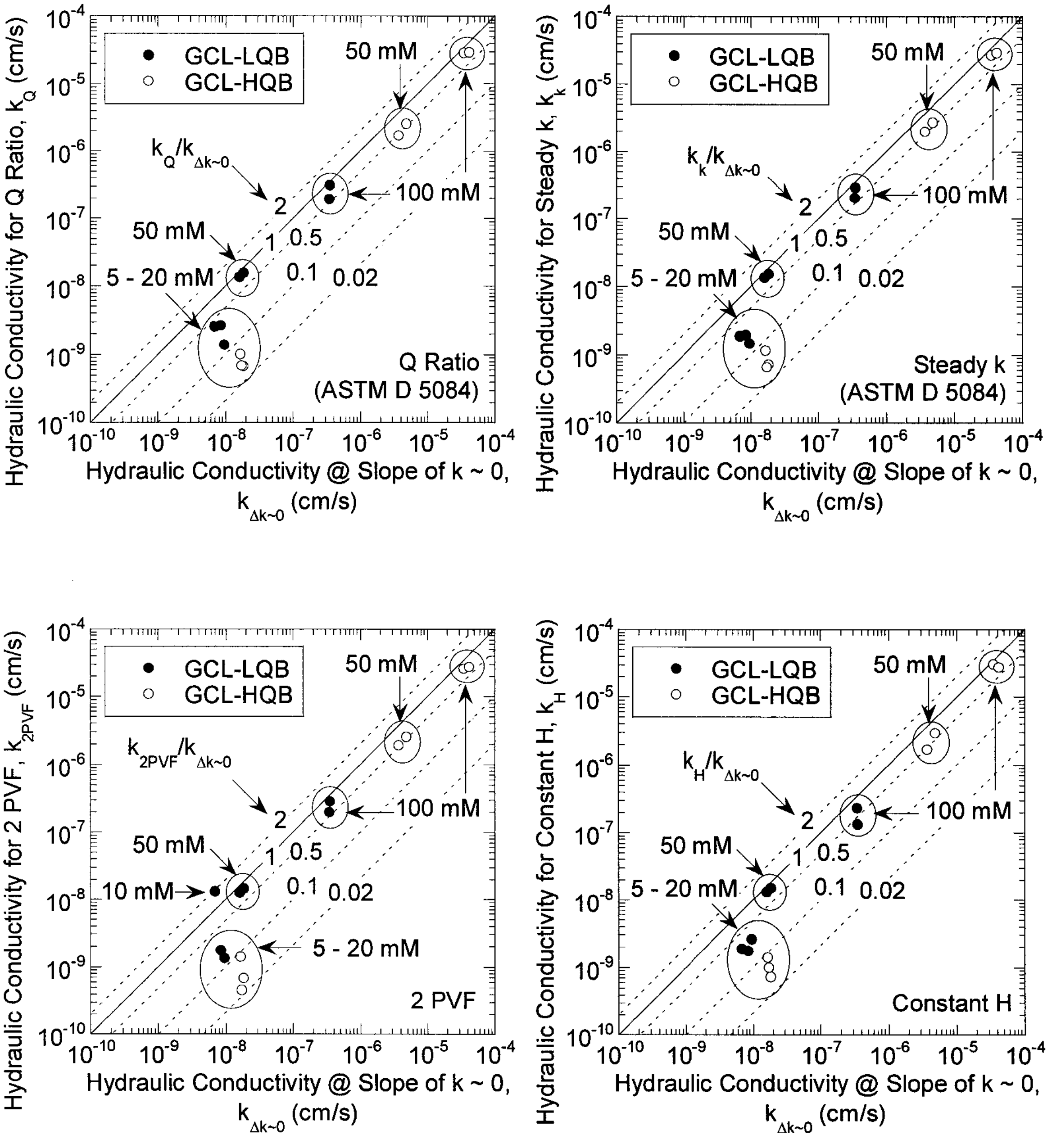

Fig. 8.13 – Hydraulic conductivity for physical termination criteria versus hydraulic conductivity at the slope of k ~ 0 for non-prehydrated specimens of GCL with either lower quality bentonite (GCL-LQB) or higher quality bentonite (GCL-HQB) (Q = volumetric flow rate; PVF = pore volumes of flow; H = thickness of specimen).

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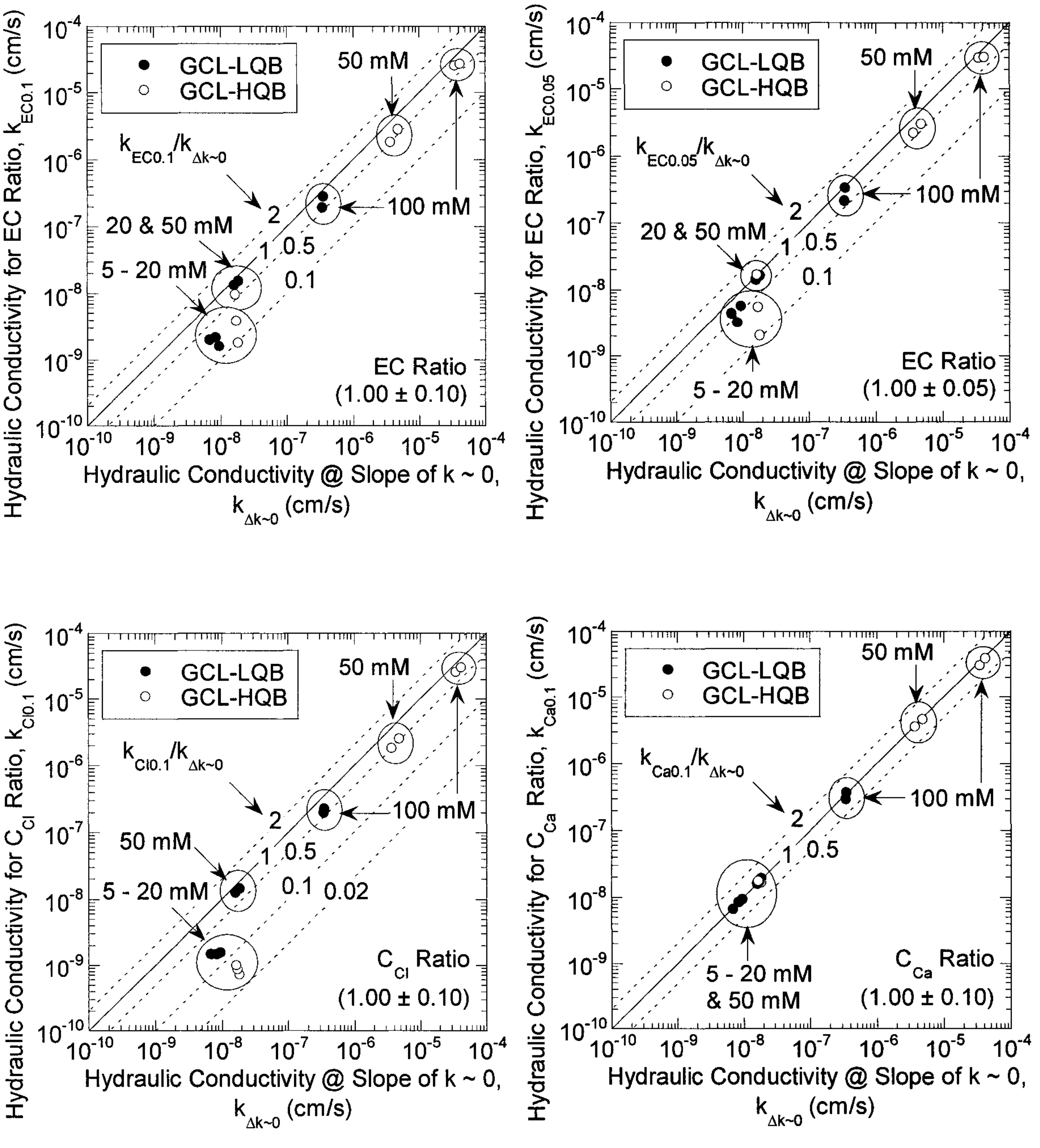

Fig. 8.14 – Hydraulic conductivity for chemical termination criteria versus hydraulic conductivity at the slope of k ~ 0 for non-prehydrated specimens of GCL with either lower quality bentonite (GCL-LQB) or higher quality bentonite (GCL-HQB) (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium).

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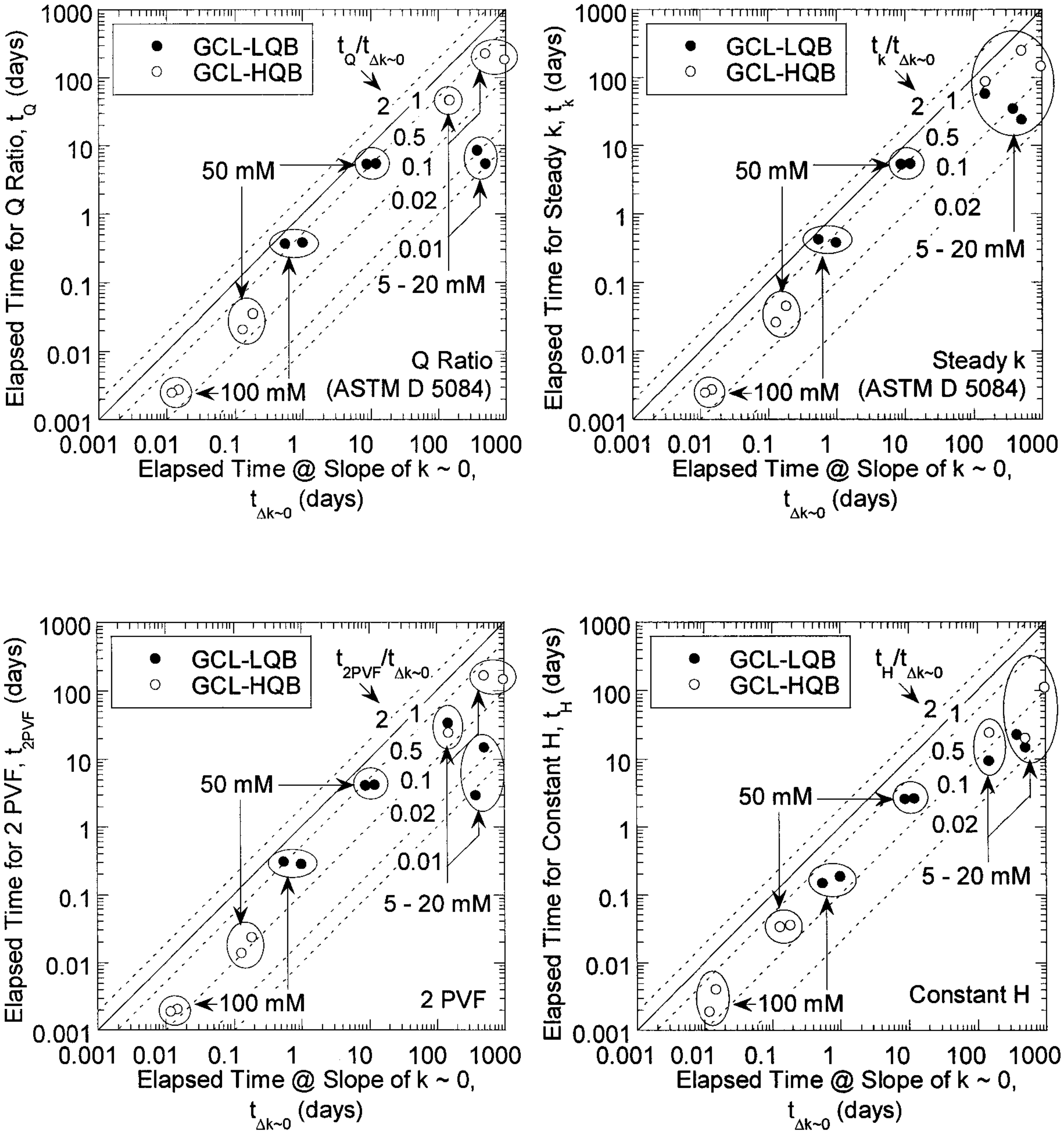

Fig. 8.15 – Elapsed time for physical termination criteria versus elapsed time at the slope of hydraulic conductivity ~ 0 for non-prehydrated specimens of GCL with either lower quality bentonite (GCL-LQB) or higher quality bentonite (GCL-HQB) (Q = volumetric flow rate; PVF = pore volumes of flow; H = thickness of specimen).

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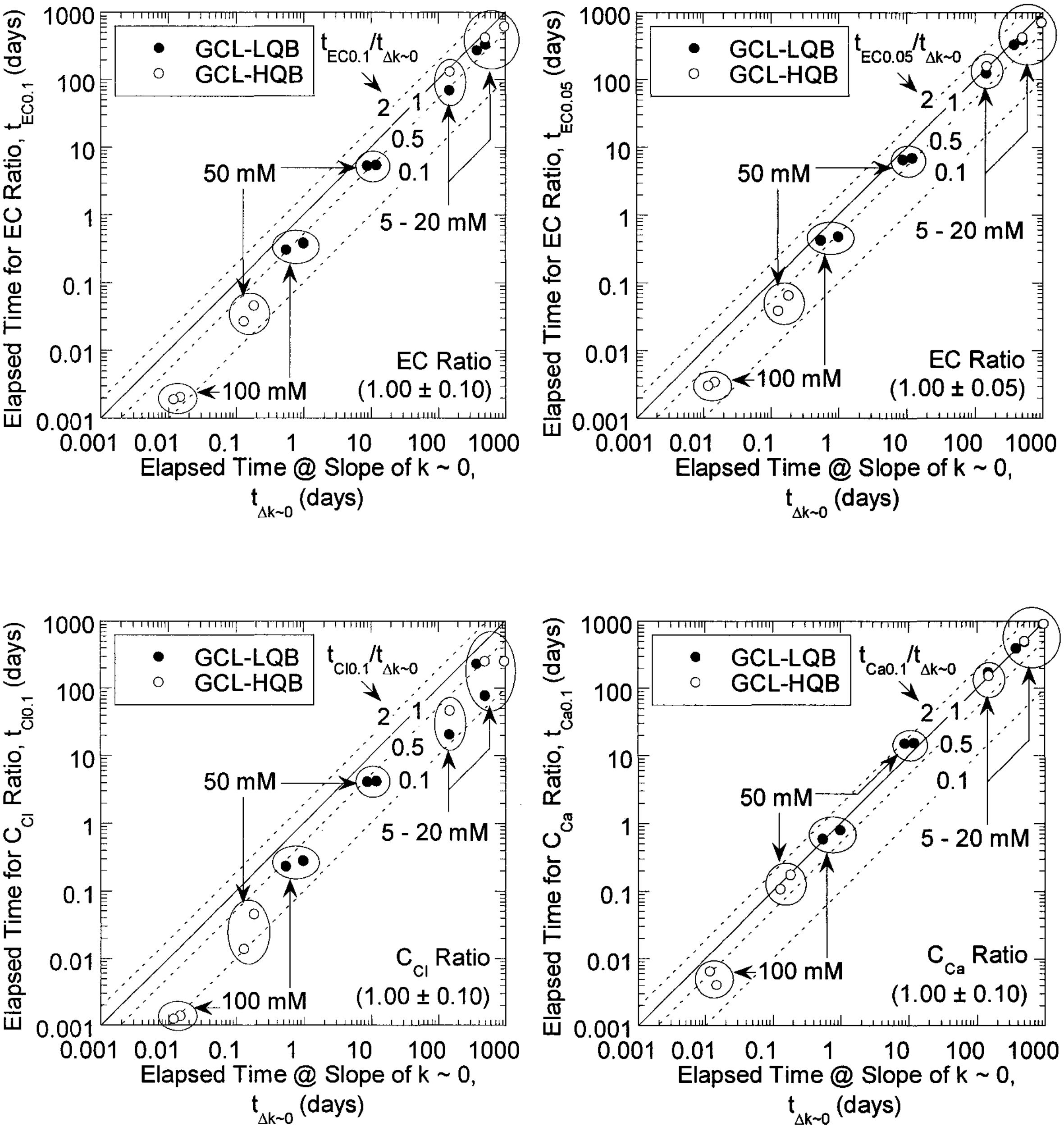

Fig. 8.16 – Elapsed time for chemical termination criteria versus elapsed time at the slope of hydraulic conductivity ~ 0 for non-prehydrated specimens of GCL with either lower quality bentonite (GCL-LQB) or higher quality bentonite (GCL-HQB) (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium).

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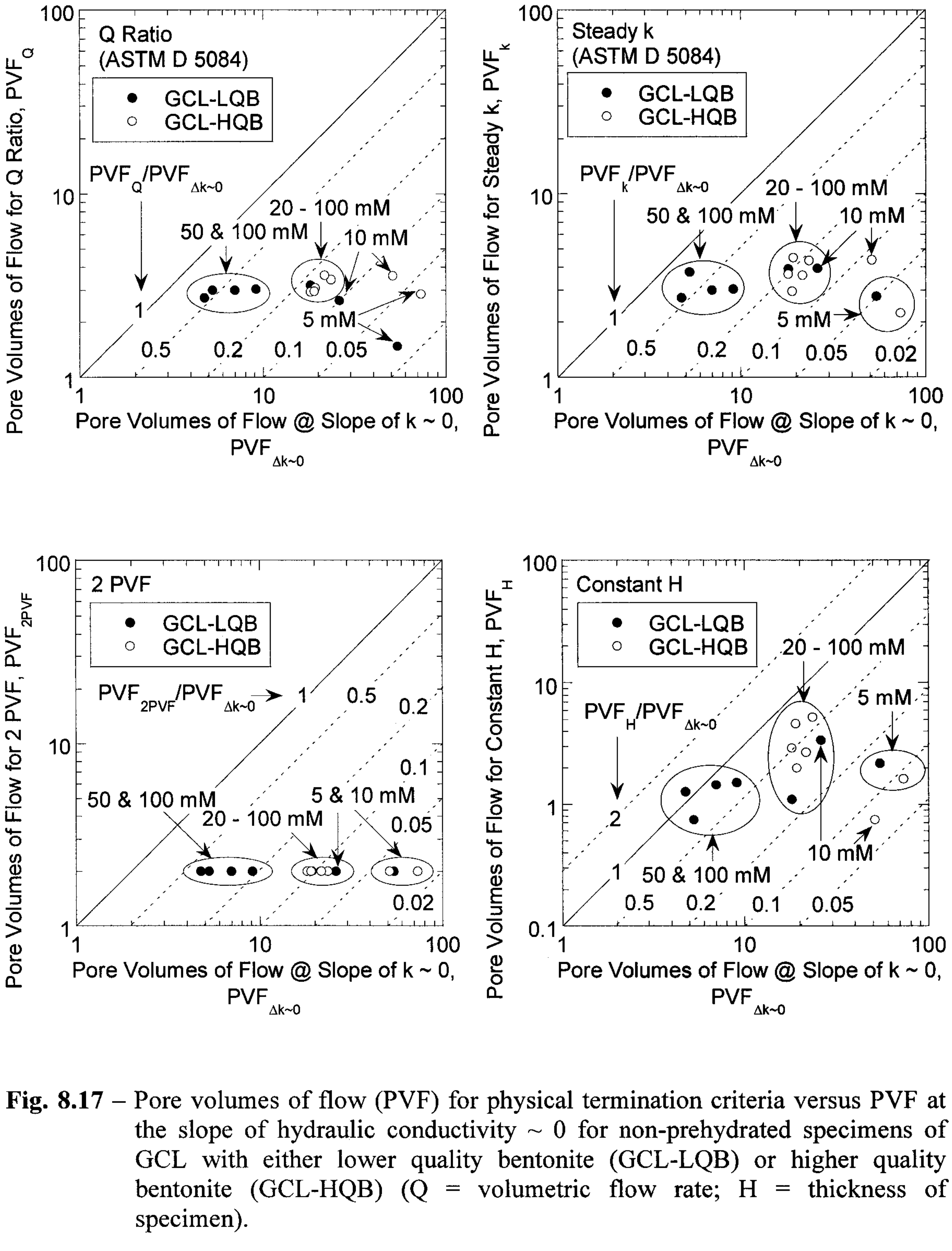

Fig. 8.17 – Pore volumes of flow (PVF) for physical termination criteria versus PVF at the slope of hydraulic conductivity ~ 0 for non-prehydrated specimens of GCL with either lower quality bentonite (GCL-LQB) or higher quality bentonite (GCL-HQB) (Q = volumetric flow rate; H = thickness of specimen).

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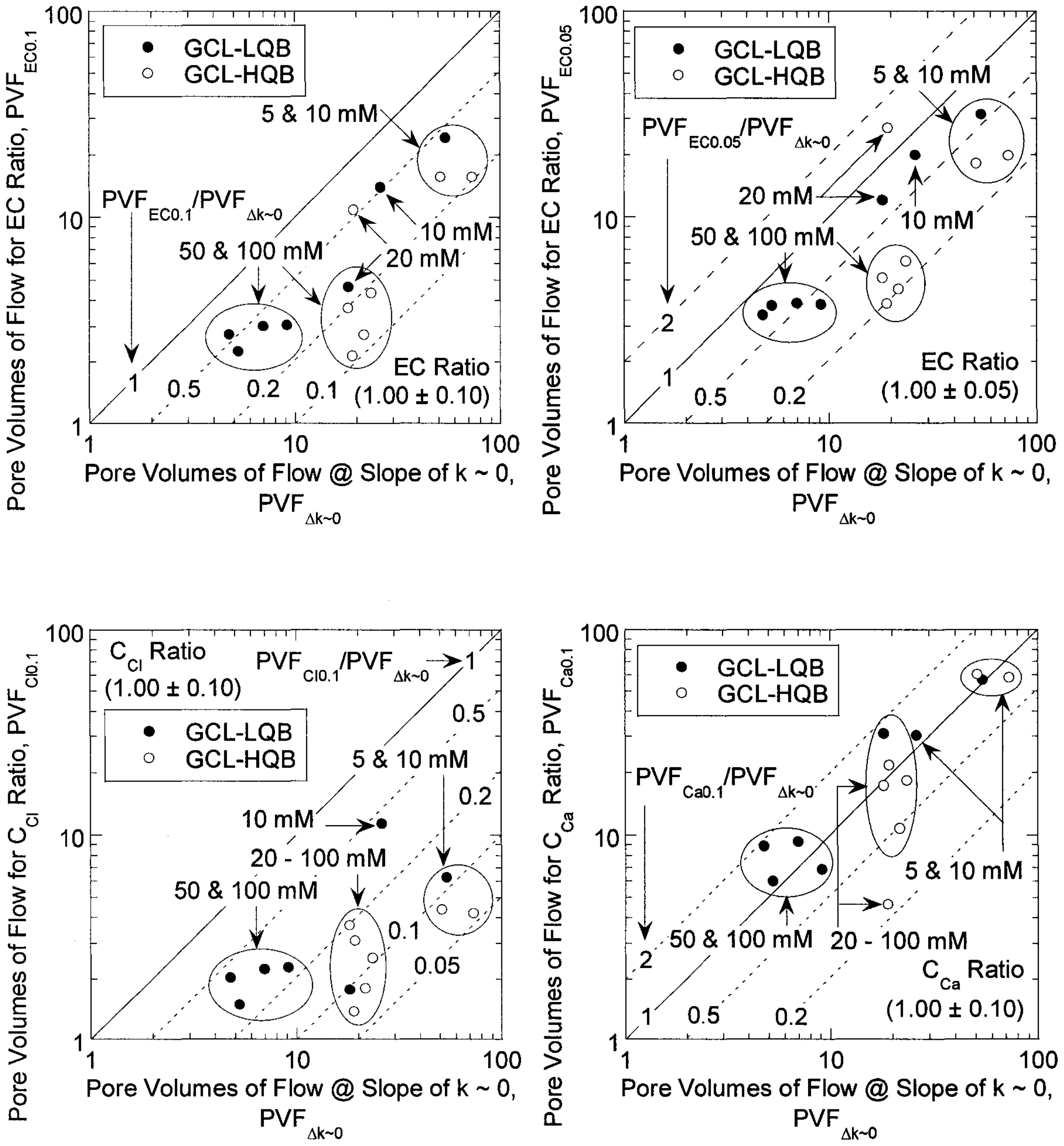

Fig. 8.18 – Pore volumes of flow (PVF) for chemical termination criteria versus PVF at the slope of hydraulic conductivity ~ 0 for non-prehydrated specimens of GCL with either lower quality bentonite (GCL-LQB) or higher quality bentonite (GCL-HQB) (EC = electrical conductivity; C_{Cl} or C_{Ca} = concentration of chloride or calcium).

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CHAPTER 9

SUMMARY AND CONCLUSIONS

9.1 SUMMARY

The long-term hydraulic performance of two geosynthetic clay liners (GCLs) was evaluated by permeation with water and inorganic salt solutions containing from 5 mM to 500 mM calcium chloride ($CaCl_2$). Both GCLs consist of a layer of granular sodium bentonite sandwiched between two polypropylene geotextiles held together by needle-punched fibers. However, one GCL contains a higher quality bentonite (GCL-HQB) that is characterized by a greater content of sodium montmorillonite (86 % vs. 77 %), a higher plasticity index (548 % vs. 393 %), and a higher cation exchange capacity (93 meq/100 g vs. 64 meq/100 g) relative to the other GCL with a lower quality bentonite (GCL-LQB). All tests were conducted until equilibrium between the effluent and influent electrical conductivity (EC) and solute concentrations was established, resulting in tests durations ranging from less than 1 day to more than 900 days, with longer test durations associated with lower $CaCl_2$ concentrations of the permeant liquids.

The results were evaluated in terms of criteria commonly used to terminate hydraulic conductivity tests involving non-standard permeant liquids (i.e., liquids other than water). The termination criteria considered in this study included both physical termination criteria, i.e., volumetric flow ratio and steady hydraulic conductivity per

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ASTM D 5084, two pore volumes of flow, and constant thickness of specimen, as well as chemical termination criteria, i.e., pH, EC and solute (i.e., Cl^- and Ca^{2+}) concentration equilibrium. The evaluation was extended to potential effects of quality of bentonite and prehydration on the hydraulic conductivities as well as the termination criteria.

In addition, a new index property, referred to as the solution retention capacity (SRC), was developed and evaluated as an alternative to the use of the swell index approach for providing a qualitative indication of the relative impact of $CaCl_2$ solutions on the hydraulic performance of the GCLs. The results of four index properties, including the liquid limit, sedimentation volume, swell index, and SRC, of the bentonites taken from both GCLs using both water and $CaCl_2$ solutions were compared with the hydraulic conductivity values of the same GCLs permeated with the same solutions to evaluate the potential correlation between index properties of the bentonite and hydraulic conductivity of the GCLs.

Also, the potential effect of Ca^{2+} diffusion on the semipermeable membrane behavior was evaluated on the basis of a combined chemico-osmotic/diffusion test performed on a specimen of GCL-LQB. The test was conducted by continuously replenishing the top and bottom boundaries of the specimen with water and a 5 mM $CaCl_2$ solution to establish and maintain a constant concentration difference of 5 mM $CaCl_2$ across the specimen while preventing the flow of solution through the specimen.

9.2 CONCLUSIONS

First, for non-prehydrated specimens of GCL-LQB, hydraulic conductivity values for specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions were comparable with

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those for specimens permeated with water (~ 10^{-9} cm/s) during short test durations (< 3 to 6 months), and then increased to a similar value of ~ 8.5×10^{-9} cm/s regardless of the influent concentration after 0.4 yr to 1.6 yrs of permeation. In contrast, hydraulic conductivity values for specimens of GCL-LQB permeated with 50, 100, and 500 mM $CaCl_2$ solutions were about 2X, 40X, and 200X higher, respectively, than the hydraulic conductivity of ~ 8.5×10^{-9} cm/s for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. All of the physical termination criteria as well as pH and EC equilibrium were found to be inapplicable, particularly for the specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions. For these specimens, equilibrium in hydraulic conductivity was not established until equilibrium in the Ca^{2+} concentrations between the effluent and influent was achieved.

Second, the effect of prehydration was evaluated based on the hydraulic conductivity tests performed using both non-prehydrated and prehydrated specimens of GCL-LQB with solutions containing 5, 10, 20, 50, and 100 mM $CaCl_2$. The results indicated that prehydration had little, if any, effect on hydraulic conductivity of GCL-LQB for specimens permeated with solutions containing 5 to 50 mM $CaCl_2$. For both non-prehydrated and prehydrated specimens permeated with a 100 mM $CaCl_2$ solution, the hydraulic conductivity of the non-prehydrated specimen was ~ 3X higher than the hydraulic conductivity of the prehydrated specimen, indicating that prehydration was a more significant factor in terms of the hydraulic conductivity of GCL-LQB permeated with the 100 mM $CaCl_2$ solution. The results represent the first evidence that the previously reported prehydration effect based on fully prehydrated specimens is

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concentration dependent, and may be insignificant when the permeant liquid contains relatively low concentrations of inorganic solutes.

Third, in terms of the effect of bentonite quality on the hydraulic performance of GCLs, the GCL containing the higher quality bentonite (GCL-HQB) was found to be more susceptible to incompatibility in hydraulic conductivity than the GCL with the lower quality bentonite (GCL-LQB) when permeated with $CaCl_2$ solutions. The hydraulic conductivity for GCL-HQB was ~ 3X lower than the hydraulic conductivity for GCL-LQB when both GCL specimens were permeated with water. However, for the tests performed using 5, 10, and 20 mM $CaCl_2$ solutions as the permeant liquids, the hydraulic conductivity for GCL-HQB was ~ 2.3X higher than the hydraulic conductivity for GCL-LQB, regardless of the concentration. Furthermore, the hydraulic conductivities for GCL-HQB were about 230X, 100X, and 40X higher than the hydraulic conductivities for GCL-LQB for the tests performed using 50, 100, and 500 mM $CaCl_2$ solutions as the permeant liquids, respectively.

Fourth, the solution retention capacity (SRC) values for the two bentonites taken from GCL-LQB and GCL-HQB measured using water and solutions containing from 5 mM to 500 mM $CaCl_2$ were compared with the swell index values for both bentonites using the same testing liquids. In general, both swell index and SRC decreased with increase in $CaCl_2$ concentration due to a decrease in the thickness of adsorbed layer of the bentonite particles. However, the SRC approach was shown to have several advantages relative to the swell index approach, including a shorter testing time, minimal potential for bentonite loss and entrapped air bubbles, greater measurement accuracy, and less operator error. The strong correlation between the SRC and swell index suggests that the

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SRC approach may be used as an alternative to the swell index approach for qualitatively assessing the potential impact of inorganic salt solutions on the hydraulic conductivity of the GCLs.

Fifth, the results of four index properties, including the liquid limit (LL), sedimentation volume (SV), swell index (SI), and solution retention capacity (SRC), for the bentonites from both GCLs using both water and $CaCl_2$ solutions containing from 5 mM to 500 mM $CaCl_2$ were correlated with the hydraulic conductivity (k) of the same GCLs permeated with the same solutions. For GCL-LQB, 10X and 100X increases in k based on permeation with $CaCl_2$ solutions relative to water correlated with $\geq$ 39 % and $\geq$ 48 % decreases in any index property, respectively, for the same $CaCl_2$ solutions relative to water. However, for GCL-HQB, LL, SV, and SI decreased by $\leq$ 3 % when the same $CaCl_2$ solution that results in a 10X increase in k relative to water was used, whereas the $CaCl_2$ solution that caused a 100X increase in k also caused a $\geq$ 31 % decrease in any index property. Thus, the correlation between a change in index property and a change in k was a function of the magnitude of the change in k being considered (i.e., 10X and 100X), the index property, and the bentonite quality. Consequently, compatibility in the index property of bentonites taken from GCLs does not always correlate well with compatibility in the hydraulic performance of the GCLs.

Sixth, the results of a combined chemico-osmotic/diffusion experiment conducted on GCL-LQB illustrated the destructive role of diffusion on the ability of the GCL to act as a semipermeable membrane. A time-dependent membrane efficiency was derived from measured pressure differences induced across the specimen in response to the applied concentration difference (i.e., 5 mM $CaCl_2$). An initial increase in induced pressure

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difference across the specimen to a peak value of 19.3 kPa was observed, followed by a gradual decrease to zero. The decrease in induced pressure difference is consistent with compression of adsorbed layers between clay particles and particle clusters due to diffusion of Ca^{2+}, resulting in concomitant increase in pore sizes and decrease in the observed membrane behavior. The time required for effective destruction of the initially observed semipermeable membrane behavior correlated well with the time required to achieve steady-state Ca^{2+} diffusion. The results have important implications with respect to the ability of GCLs to sustain membrane behavior.

Finally, the potential dependency of the termination criteria on the prehydration and quality of bentonite of GCLs was evaluated based on the tests performed using solutions containing from 5 mM to 100 mM $CaCl_2$ as permeant liquids. For specimens permeated with 5, 10, and 20 mM $CaCl_2$ solutions, only the termination criterion based on equilibrium between influent and effluent Ca^{2+} resulted in equilibrium in hydraulic conductivity, regardless of prehydration or quality of bentonite. However, for the specimens permeated with 50 and 100 mM $CaCl_2$ solutions, all of the termination criteria, except some physical criteria (i.e., volumetric flow ratio and two pore volumes of flow) for the prehydrated specimens, tended to ensure equilibrium in hydraulic conductivity, regardless of prehydration or quality of bentonite. The results illustrate the uniqueness of the termination criterion based on solute equilibrium between the effluent and influent with respect to both prehydration and quality of bentonite in the GCL.

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APPENDIX A

PROPERTIES FOR TESTING LIQUIDS AND METHOD DETECTION LIMITS

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Table A.1 – pH and Electrical Conductivity of Testing Liquids.

pH & Electrical Condutivity (EC) for Testing Liquids													
Deionized Water							5 mM $CaCl_2$						
Date	Δt	$\Sigma \Delta t$	pH_{in}	EC_{in}		Comment	Date	Δt	$\Sigma \Delta t$	pH_{in}	EC_{in}		Comment
	(days)			(mS/m)	(dS/m)			(days)			(mS/m)	(dS/m)	
3/19/2000	0	0				New	3/19/2000	0	0				New
3/20/2000	1	1	6.50	0.20	0.0020		3/20/2000	1	1	6.87	122.4	1.224	
5/4/2000	45	46	6.48	0.26	0.0026		5/4/2000	45	46	6.85	122.6	1.226	
7/9/2000	66	112	6.35	0.30	0.0030		7/9/2000	66	112	6.61	122.5	1.225	
10/20/2000	103	215	6.19	0.40	0.0040		10/20/2000	103	215	6.35	121.9	1.219	
1/3/2001	75	290	6.01	0.36	0.0036		1/3/2001	75	290	6.12	122.0	1.220	
5/30/2001	147	437	5.74	0.23	0.0023		5/30/2001	147	437	5.87	122.2	1.222	
9/13/2001	106	543	5.55	0.25	0.0025		9/13/2001	106	543	5.66	121.9	1.219	
10/14/2001	31	574	5.95	0.24	0.0024	New	10/14/2001	31	574	5.68	121.2	1.212	
12/16/2001	63	637	5.74	0.29	0.0029		12/16/2001	63	637	5.65	122.2	1.222	
1/11/2002	26	663	5.42	0.44	0.0044		1/11/2002	26	663	5.61	121.4	1.214	New
2/28/2002	48	711	5.34	0.12	0.0012		2/28/2002	48	711	5.67	120.2	1.202	
4/1/2002	32	743	5.24	0.09	0.0009		4/1/2002	32	743	5.60	121.8	1.218	
5/12/2002	41	784	5.22	0.11	0.0011		5/12/2002	41	784	5.65	120.5	1.205	
6/20/2002	39	823	5.20	0.15	0.0015		6/20/2002	39	823	5.53	121.7	1.217	
7/30/2002	40	863	5.09	0.11	0.0011		7/30/2002	40	863	5.39	117.7	1.177	New
9/4/2002	36	899	5.20	0.12	0.0012		9/4/2002	36	899	5.41	123.3	1.233	
10/14/2002	40	939	5.29	0.13	0.0013		10/14/2002	40	939	5.40	125.9	1.259	
12/13/2002	60	999	5.01	0.34	0.0034	New	12/13/2002	60	999	5.37	124.9	1.249	
3/5/2003	82	1081	4.93	0.20	0.0020		3/5/2003	82	1081	5.37	120.8	1.208	
3/18/2003	13	1094					3/18/2003	13	1094	5.39	124.3	1.243	
4/6/2003	19	1113					4/6/2003	19	1113	5.58	126.2	1.262	
4/28/2003	22	1135					4/28/2003	22	1135	5.42	125.0	1.250	New
5/9/2003	11	1146					5/9/2003	11	1146	5.38	125.0	1.250	
5/23/2003	14	1160					5/23/2003	14	1160	5.26	125.9	1.259	
6/24/2003	32	1192					6/24/2003	32	1192	5.06	121.0	1.210	
Minimum			4.93	0.09	0.0009		Minimum			5.06	117.7	1.177	
Maximum			6.5	0.44	0.0044		Maximum			6.87	126.2	1.262	
Average			5.60	0.23	0.0023		Average			5.71	122.58	1.23	
SD			0.510	0.106	0.001		SD			0.482	2.056	0.021	

10 mM $CaCl_2$							20 mM $CaCl_2$						
Date	Δt	$\Sigma \Delta t$	pH_{in}	EC_{in}		Comment	Date	Δt	$\Sigma \Delta t$	pH_{in}	EC_{in}		Comment
	(days)			(mS/m)	(dS/m)			(days)			(mS/m)	(dS/m)	
3/19/2000	0	0				New	3/19/2000	0	0				New
3/20/2000	1	1	6.64	234	2.34		3/20/2000	1	1	6.25	444	4.44	
5/4/2000	45	46	6.66	234	2.34		5/4/2000	45	46	6.28	444	4.44	
7/9/2000	66	112	6.41	234	2.34		7/9/2000	66	112	6.16	444	4.44	
10/20/2000	103	215	6.23	234	2.34		10/20/2000	103	215	6.07	445	4.45	
1/3/2001	75	290	6.12	235	2.35		1/3/2001	75	290	6.02	445	4.45	
5/30/2001	147	437	6.06	235	2.35		5/30/2001	147	437	5.97	446	4.46	
9/13/2001	106	543	5.74	235	2.35		9/13/2001	106	543	5.88	447	4.47	
10/14/2001	31	574	5.73	234	2.34		10/14/2001	31	574	6.30	446	4.46	New
12/16/2001	63	637	5.74	235	2.35		12/16/2001	63	637	6.29	449	4.49	
1/11/2002	26	663	6.08	234	2.34	New	1/11/2002	26	663	6.27	458	4.58	
2/28/2002	48	711	6.22	231	2.31		2/28/2002	48	711	6.32	442	4.42	
4/1/2002	32	743	6.10	232	2.32		4/1/2002	32	743	6.23	459	4.59	
5/12/2002	41	784	6.16	232	2.32		5/12/2002	41	784	6.34	443	4.43	
6/20/2002	39	823	6.03	231	2.31		6/20/2002	39	823	5.73	431	4.31	New
7/30/2002	40	863	5.60	228	2.28	New	7/30/2002	40	863	5.68	433	4.33	
9/4/2002	36	899	5.55	237	2.37		9/4/2002	36	899	5.69	445	4.45	
10/14/2002	40	939	5.57	240	2.40		10/14/2002	40	939	5.66	451	4.51	
12/13/2002	60	999	5.57	234	2.34		12/13/2002	60	999	5.59	449	4.49	
3/5/2003	82	1081	5.48	230	2.30		3/5/2003	82	1081	5.52	432	4.32	
Minimum			5.48	228	2.28		Minimum			5.52	431	4.31	
Maximum			6.66	240	2.4		Maximum			6.34	459	4.59	
Average			5.98	233.63	2.34		Average			6.01	444.89	4.45	
SD			0.364	2.629	0.026		SD			0.287	7.317	0.073	

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50 mM $CaCl_2$						
Date	Δt	Σ Δt	pH_{in}	EC_{in}		Comment
	(days)			(mS/m)	(dS/m)	
2/27/2002	0	0				New
2/28/2002	1	1	5.86	1027	10.27	
4/1/2002	32	33	5.92	1033	10.33	
5/12/2002	41	74	5.89	1033	10.33	
6/20/2002	39	113	5.69	1038	10.38	
7/10/2002	20	133	5.84	1042	10.42	
7/24/2002	14	147	5.48	1036	10.36	
9/4/2002	42	189	5.61	1112	11.12	
10/14/2002	40	229	5.60	1101	11.01	
12/13/2002	60	289	5.50	1068	10.68	New
3/5/2003	82	371	5.53	1027	10.27	
3/16/2003	11	382	5.58	1030	10.3	
3/18/2003	2	384	5.58	1027	10.27	
4/6/2003	19	403	5.60	1020	10.2	
4/26/2003	20	423	5.77	1031	10.31	New
5/9/2003	13	436	5.79	1027	10.27	
5/23/2003	14	450	5.66	1031	10.31	
6/5/2003	13	463	5.74	1029	10.29	
6/24/2003	19	482	5.61	1027	10.27	
Minimum			5.48	1020	10.2	
Maximum			5.92	1112	11.12	
Average			5.68	1041.06	10.41	
SD			0.138	25.917	0.259	

100 mM $CaCl_2$						
Date	Δt	Σ Δt	pH_{in}	EC_{in}		Comment
	(days)			(mS/m)	(dS/m)	
6/28/2002	0	0				New
7/10/2002	12	12	5.88	1973	19.73	
7/24/2002	14	26	5.79	1960	19.6	
9/4/2002	42	68	5.95	2030	20.3	
10/14/2002	40	108	5.85	2040	20.4	
12/13/2002	60	168	5.69	1946	19.46	
3/5/2003	82	250	5.63	2040	20.4	
3/13/2003	8	258	5.71	1923	19.23	
3/16/2003	3	261	5.70	1918	19.18	
3/18/2003	2	263	5.70	1917	19.17	
4/6/2003	19	282	5.71	1913	19.13	
4/26/2003	20	302	6.04	1934	19.34	New
5/9/2003	13	315	6.02	1926	19.26	
5/23/2003	14	329	5.88	1935	19.35	
Minimum			5.630	1913.000	19.130	
Maximum			6.040	2040.000	20.400	
Average			5.81	1958.08	19.58	
SD			0.135	48.015	0.480	

500 mM $CaCl_2$						
Date	Δt	Σ Δt	pH_{in}	EC_{in}		Comment
	(days)			(mS/m)	(dS/m)	
3/1/2003	0	0				New
3/5/2003	4	4	6.33	7730	77.3	
3/13/2003	8	12	6.25	7740	77.4	
3/16/2003	3	15	6.30	7680	76.8	
3/18/2003	2	17	6.31	7690	76.9	
3/29/2003	11	28	6.22	7690	76.9	
4/6/2003	8	36	6.25	7670	76.7	
4/21/2003	15	51	6.18	7680	76.8	
4/28/2003	7	58	6.75	7670	76.7	New
5/5/2003	7	65	6.72	7670	76.7	
5/23/2003	18	83	6.71	7720	77.2	
6/5/2003	13	96	6.69	7670	76.7	
6/24/2003	19	115	6.70	7700	77	
Minimum			6.18	7670.00	76.70	
Maximum			6.75	7740.00	77.40	
Average			6.45	7692.50	76.93	
SD			0.236	24.909	0.249	

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Table A.2 – Solute Concentrations of Testing Liquids.

Solute Concentrations for Testing Liquids								
5 mM $CaCl_2$								
Date	Δt	Σ Δt	(mg/L)	(mM)	(mg/L)	(mM)	(mM)$_{CaCl2}$	Comment
	(days)		Ca		Cl			
10/1/2000	196	196	223.0	5.564	357	10.07	5.035	
11/1/2000	31	227	240.0	5.988	366	10.32	5.162	
12/1/2000	30	257	222.0	5.539	350	9.872	4.936	
1/13/2001	43	300	219.4	5.474	440	12.41	6.205	
3/25/2001	71	371	221.9	5.535	442	12.47	6.234	
5/23/2001	59	430	218.2	5.444	456	12.86	6.431	
10/14/2001	144	574	209.0	5.214	365	10.30	5.148	
1/21/2002	99	673	209.9	5.237	363	10.23	5.116	
4/20/2002	89	762	203.4	5.076	353	9.968	4.984	
5/31/2002	41	803	210.2	5.245	370	10.44	5.218	
7/1/2002	31	834	207.5	5.177	362	10.20	5.099	
8/6/2002	36	870	205.3	5.123	356	10.03	5.015	
10/2/2002	57	927	212.9	5.312	344	9.69	4.847	
4/28/2003	208	1135	220.1	5.492	352	9.93	4.965	
Average			215.9	5.387	376.8	10.63	5.314	
SD			9.62	0.24	38.30	1.08	0.54	
10 mM $CaCl_2$								
Date	Δt	Σ Δt	(mg/L)	(mM)	(mg/L)	(mM)	(mM)$_{CaCl2}$	Comment
	(days)		Ca		Cl			
10/1/2000	36800	36800	464.0	11.58	730	20.59	10.30	
11/1/2000	31	36831	467.0	11.65	764	21.55	10.77	
12/1/2000	30	36861	464.0	11.58	709	20.00	10.00	
1/13/2001	43	36904	469.9	11.72	892	25.16	12.58	
3/25/2001	71	36975	464.8	11.60	801	22.59	11.30	
5/23/2001	59	37034	473.3	11.81	858	24.20	12.10	
10/14/2001	144	37178	423.1	10.56	722	20.38	10.19	
1/21/2002	99	37277	416.1	10.38	706	19.90	9.95	
4/20/2002	89	37366	403.8	10.07	703	19.83	9.91	
5/31/2002	41	37407	414.4	10.34	712	20.10	10.05	
7/1/2002	31	37438	411.8	10.27	704	19.86	9.93	
8/6/2002	36	37474	405.2	10.11	702	19.79	9.90	
10/2/2002	57	37531	395.7	9.87	691	19.50	9.75	
Average			436.4	10.888	745.8	21.04	10.518	
SD			30.45	0.76	64.98	1.83	0.92	
20 mM $CaCl_2$								
Date	Δt	Σ Δt	(mg/L)	(mM)	(mg/L)	(mM)	(mM)$_{CaCl2}$	Comment
	(days)		Ca		Cl			
10/1/2000	36800	36800	979.0	24.427	1393	39.29	19.65	
11/1/2000	31	36831	999.0	24.926	1395	39.35	19.67	
12/1/2000	30	36861	994.0	24.802	1405	39.63	19.82	
1/13/2001	43	36904	893.4	22.292	1521	42.90	21.45	
3/25/2001	71	36975	877.4	21.892	1617	45.61	22.81	
5/23/2001	59	37034	898.2	22.411	1743	49.16	24.58	
10/14/2001	144	37178	849.1	21.186	1456	41.07	20.54	
1/21/2002	99	37277	835.4	20.844	1440	40.63	20.32	
4/20/2002	89	37366	813.6	20.300	1410	39.77	19.89	
5/31/2002	41	37407	819.3	20.443	1419	40.04	20.02	
7/1/2002	31	37438	805.5	20.098	1388	39.15	19.57	
8/6/2002	36	37474	804.4	20.071	1387	39.12	19.56	
10/2/2002	57	37531	772.2	19.267	1365	38.50	19.25	
Average			872.3	21.766	1456.9	41.09	20.547	
SD			76.72	1.91	109.62	3.09	1.55	

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50 mM CaCl$_2$

Date	Δt	$\Sigma\ \Delta t$	(mg/L)	(mM)	(mg/L)	(mM)	(mM)$_{CaCl2}$	Comment
	(days)		Ca		Cl			
4/20/2002	52	52	2022	50.45	3469	97.86	48.93	
5/31/2002	41	93	2008	50.09	3649	102.9	51.46	
7/1/2002	31	124	2032	50.70	3564	100.5	50.27	
8/6/2002	36	160	1950	48.65	3438	96.98	48.49	
10/2/2002	57	217	2140	53.38	3512	99.06	49.53	
3/11/2003	160	377	2032	50.70	3568	100.64	50.32	
4/9/2003	29	406	2075	51.77	3520	99.28	49.64	
4/28/2003	19	425	2131	53.17	3616	102.00	51.00	
5/25/2003	27	452	2108	52.60	3595	101.40	50.70	
Average			2055.2	51.3	3548.0	100.1	50.0	
SD			62.85	1.57	68.91	1.94	0.97	

100 mM CaCl$_2$

Date	Δt	$\Sigma\ \Delta t$	(mg/L)	(mM)	(mg/L)	(mM)	(mM)$_{CaCl2}$	Comment
	(days)		Ca		Cl			
8/6/2002	39	39	3905	97.44	6966	196.5	98.25	
10/2/2002	57	96	4276	106.69	7161	202.0	100.99	
3/11/2003	160	256	4099	102.28	6927	195.4	97.69	
4/9/2003	29	285	3983	99.38	6960	196.3	98.16	
4/28/2003	19	304	4106	102.45	7046	198.7	99.37	
5/25/2003	27	331	4061	101.33	7121	200.9	100.43	
Average			4072	101.59	7030	198.30	99.15	
SD			126.04	3.14	95.09	2.68	1.34	

500 mM CaCl$_2$

Date	Δt	$\Sigma\ \Delta t$	(mg/L)	(mM)	(mg/L)	(mM)	(mM)$_{CaCl2}$	Comment
	(days)		Ca		Cl			
7/1/2002	11	11	19504	486.7	34619	976.5	488.2	
3/11/2003	10	21	20312	506.8	35939	1013.7	506.9	
4/9/2003	29	50	20780	518.5	35936	1013.6	506.8	
4/28/2003	19	69	20384	508.6	36567	1031.4	515.7	
5/25/2003	27	96	20464	510.6	35714	1007.4	503.7	
Average			20289	506.23	35755	1008.53	504.26	
SD			473.68	11.82	710.27	20.03	10.02	

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Table A.3 – Method Detection Limit for Calcium, Sodium, and Chloride.

Method Detection Limit (MDL) Determination

MDL for Calcium (EPA Method 200.7)			MDL for Sodium (EPA Method 200.7)		
Standard Conc (ppm)	Sample No.	Intensity Ratio (IR)	Standard Conc (ppm)	Sample No.	Intensity Ratio (IR)
0	Ca0	0.63453	0	Na0	-2.147
1	Ca1	10.2575	1	Na1	-1.133
2	Ca2	19.1659	2	Na2	-0.0055
3	Ca3	30.9463	3	Na3	1.019
Standard Conc (ppm)	Sample No.	Conc (ppm)	Standard Conc (ppm)	Sample No.	Conc (ppm)
0.5	MDLP50-1	0.4523	0.5	MDLP50-1	0.5711
0.5	MDLP50-2	0.4436	0.5	MDLP50-2	0.585
0.5	MDLP50-3	0.4418	0.5	MDLP50-3	0.4169
0.5	MDLP50-4	0.4455	0.5	MDLP50-4	0.5162
0.5	MDLP50-5	0.4559	0.5	MDLP50-5	0.4232
0.5	MDLP50-6	0.4474	0.5	MDLP50-6	0.5252
0.5	MDLP50-7	0.4462	0.5	MDLP50-7	0.4859
	Mean =	0.4475		Mean =	0.5034
	SD =	0.0049		SD =	0.0660
	$t_{6,\alpha=0.01}$ =	3.143		$t_{6,\alpha=0.01}$ =	3.143
	MDL (ppm) =	0.02		MDL (ppm) =	0.2

MDL for Chloride (EPA Method 300.0)

Standard Conc (ppm)	Sample No.	Area of Spectrum (A)
0	Cl0	171
1	Cl1	14075
2	Cl2	28289
3	Cl3	43725

Standard Conc (ppm)	Sample No.	Conc (ppm)
0.5	MDLP50-1	0.479612018
0.5	MDLP50-2	0.487955265
0.5	MDLP50-3	0.515974669
0.5	MDLP50-4	0.50130446
0.5	MDLP50-5	0.489554387
0.5	MDLP50-6	0.479542491
0.5	MDLP50-7	0.502416893
	Mean =	0.49376574
	SD =	0.013410425
	$t_{6,\alpha=0.01}$ =	3.143
	MDL (ppm) =	0.04

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APPENDIX B

EVAPORATION AND TEMPERATURE MEASUREMENTS

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Table B.1 – Evaporation and Temperature Measurements.

Measurement of Evaporation Rate for Influent Burette and Effluent Cylinder

Date &Time	Δt	Σ Δt	Buret					Cylinder				
			Read	ΔRead	Σ Δ	ER	Avg ER	Read	ΔRead	Σ Δ	ER	Avg ER
	(days)	(days)				(mL/d)	(mL/d)				(mL/d)	(mL/d)
4/2/2000 20:05	0.00	0.00	2.60					96.7				
4/3/2000 19:50	0.99	0.99	2.75	0.15	0.15	0.152	0.152	96.7	0.0	0.0	0.000	0.000
4/4/2000 12:40	0.70	1.69	2.85	0.10	0.25	0.143	0.148	96.7	0.0	0.0	0.000	0.000
4/5/2000 20:20	1.32	3.01	3.10	0.25	0.50	0.189	0.166	96.6	0.1	0.1	0.076	0.033
4/9/2000 8:12	3.49	6.50	3.49	0.39	0.89	0.112	0.137	96.5	0.1	0.2	0.029	0.031
4/11/2000 10:17	2.09	8.59	3.75	0.26	1.15	0.125	0.134	96.5	0.0	0.2	0.000	0.023
4/15/2000 8:08	3.91	12.50	4.20	0.45	1.60	0.115	0.128	96.4	0.1	0.3	0.026	0.024
4/16/2000 18:10	1.42	13.92	4.39	0.19	1.79	0.134	0.129	96.4	0.0	0.3	0.000	0.022
4/18/2000 18:50	2.03	15.95	4.60	0.21	2.00	0.104	0.125	96.3	0.1	0.4	0.049	0.025
4/22/2000 15:50	3.88	19.82	5.10	0.50	2.50	0.129	0.126	96.0	0.3	0.7	0.077	0.035
4/28/2000 12:30	5.86	25.68	5.73	0.63	3.13	0.107	0.122	95.9	0.1	0.8	0.017	0.031
4/29/2000 15:52	1.14	26.82	5.87	0.14	3.27	0.123	0.122	95.9	0.0	0.8	0.000	0.030
5/2/2000 5:12	2.56	29.38	6.13	0.26	3.53	0.102	0.120	95.7	0.2	1.0	0.078	0.034
5/3/2000 10:11	1.21	30.59	6.27	0.14	3.67	0.116	0.120	95.6	0.1	1.1	0.083	0.036
5/4/2000 22:05	1.50	32.08	6.40	0.13	3.80	0.087	0.118	95.6	0.0	1.1	0.000	0.034
5/8/2000 8:27	3.43	35.52	6.70	0.30	4.10	0.087	0.115	95.5	0.1	1.2	0.029	0.034
5/9/2000 10:35	1.09	36.60	6.81	0.11	4.21	0.101	0.115	95.4	0.1	1.3	0.092	0.036
5/11/2000 15:00	2.18	38.79	7.01	0.20	4.41	0.092	0.114	95.3	0.1	1.4	0.046	0.036
5/14/2000 9:15	2.76	41.55	7.33	0.32	4.73	0.116	0.114	95.2	0.1	1.5	0.036	0.036
5/19/2000 17:40	5.35	46.90	7.89	0.56	5.29	0.105	0.113	95.0	0.2	1.7	0.037	0.036
5/20/2000 9:55	0.68	47.58	7.94	0.05	5.34	0.074	0.112	95.0	0.0	1.7	0.000	0.036
5/21/2000 6:42	0.87	48.44	8.02	0.08	5.42	0.092	0.112	95.0	0.0	1.7	0.000	0.035
5/22/2000 9:53	1.13	49.58	8.11	0.09	5.51	0.079	0.111	94.9	0.1	1.8	0.088	0.036
5/23/2000 11:44	1.08	50.65	8.21	0.10	5.61	0.093	0.111	94.9	0.0	1.8	0.000	0.036
5/25/2000 10:45	1.96	52.61	8.40	0.19	5.80	0.097	0.110	94.8	0.1	1.9	0.051	0.036
5/29/2000 12:40	4.08	56.69	8.82	0.42	6.22	0.103	0.110	94.7	0.1	2.0	0.025	0.035
5/30/2000 10:15	0.90	57.59	8.90	0.08	6.30	0.089	0.109	94.7	0.0	2.0	0.000	0.035
6/1/2000 11:45	2.06	59.65	9.04	0.14	6.44	0.068	0.108	94.6	0.1	2.1	0.048	0.035
6/2/2000 20:05	1.35	61.00	9.19	0.15	6.59	0.111	0.108	94.5	0.1	2.2	0.074	0.036
6/3/2000 18:30	0.93	61.93	9.21	0.02	6.61	0.021	0.107	94.5	0.0	2.2	0.000	0.036
6/4/2000 15:35	0.88	62.81	9.32	0.11	6.72	0.125	0.107	94.4	0.1	2.3	0.114	0.037
6/5/2000 21:50	1.26	64.07	9.43	0.11	6.83	0.087	0.107	94.4	0.0	2.3	0.000	0.036
6/7/2000 17:05	1.80	65.88	9.53	0.10	6.93	0.055	0.105	94.3	0.1	2.4	0.055	0.036
6/10/2000 19:53	3.12	68.99	9.83	0.30	7.23	0.096	0.105	94.3	0.0	2.4	0.000	0.035
6/14/2000 0:13	3.18	72.17	10.13	0.30	7.53	0.094	0.104	94.2	0.1	2.5	0.031	0.035
6/15/2000 20:35	1.85	74.02	10.30	0.17	7.70	0.092	0.104	94.1	0.1	2.6	0.054	0.035
6/16/2000 21:50	1.05	75.07	10.40	0.10	7.80	0.095	0.104	94.0	0.1	2.7	0.095	0.036
6/18/2000 10:46	1.54	76.61	10.55	0.15	7.95	0.097	0.104	94.0	0.0	2.7	0.000	0.035
6/19/2000 9:35	0.95	77.56	10.60	0.05	8.00	0.053	0.103	94.0	0.0	2.7	0.000	0.035
6/20/2000 19:35	1.42	78.98	10.72	0.12	8.12	0.085	0.103	93.9	0.1	2.8	0.071	0.035
6/21/2000 22:50	1.14	80.11	10.81	0.09	8.21	0.079	0.102	93.9	0.0	2.8	0.000	0.035
6/22/2000 16:10	0.72	80.84	10.89	0.08	8.29	0.111	0.103	93.9	0.0	2.8	0.000	0.035
6/24/2000 7:15	1.63	82.47	11.02	0.13	8.42	0.080	0.102	93.8	0.1	2.9	0.061	0.035
6/25/2000 20:05	1.53	84.00	11.15	0.13	8.55	0.085	0.102	93.8	0.0	2.9	0.000	0.035
6/26/2000 8:35	0.52	84.52	11.18	0.03	8.58	0.058	0.102	93.8	0.0	2.9	0.000	0.034
6/27/2000 0:25	0.66	85.18	11.22	0.04	8.62	0.061	0.101	93.7	0.1	3.0	0.152	0.035
6/27/2000 20:10	0.82	86.00	11.30	0.08	8.70	0.097	0.101	93.7	0.0	3.0	0.000	0.035
6/28/2000 18:00	0.91	86.91	11.34	0.04	8.74	0.044	0.101	93.7	0.0	3.0	0.000	0.035
6/30/2000 23:55	2.25	89.16	11.50	0.16	8.90	0.071	0.100	93.6	0.1	3.1	0.045	0.035
7/2/2000 20:45	1.87	91.03	11.56	0.06	8.96	0.032	0.098	93.6	0.0	3.1	0.000	0.034
7/3/2000 11:55	0.63	91.66	11.65	0.09	9.05	0.142	0.099	93.6	0.0	3.1	0.000	0.034
7/4/2000 10:35	0.94	92.60	11.70	0.05	9.10	0.053	0.098	93.5	0.1	3.2	0.106	0.035
7/7/2000 18:50	3.34	95.95	11.89	0.19	9.29	0.057	0.097	93.4	0.1	3.3	0.030	0.034
7/8/2000 16:05	0.89	96.83	11.97	0.08	9.37	0.090	0.097	93.4	0.0	3.3	0.000	0.034
7/10/2000 0:30	1.35	98.18	12.09	0.12	9.49	0.089	0.097	93.4	0.0	3.3	0.000	0.034
7/11/2000 9:10	1.36	99.55	12.14	0.05	9.54	0.037	0.096	93.4	0.0	3.3	0.000	0.033
7/12/2000 21:20	1.51	101.05	12.27	0.13	9.67	0.086	0.096	93.3	0.1	3.4	0.066	0.034
7/14/2000 22:08	2.03	103.09	12.37	0.10	9.77	0.049	0.095	93.2	0.1	3.5	0.049	0.034
7/16/2000 1:50	1.15	104.24	12.44	0.07	9.84	0.061	0.094	93.2	0.0	3.5	0.000	0.034
7/18/2000 11:25	2.40	106.64	12.60	0.16	10.00	0.067	0.094	93.1	0.1	3.6	0.042	0.034
7/21/2000 7:25	2.83	109.47	12.75	0.15	10.15	0.053	0.093	93.1	0.0	3.6	0.000	0.033
7/23/2000 5:28	1.92	111.39	12.91	0.16	10.31	0.083	0.093	93.0	0.1	3.7	0.052	0.033
7/24/2000 22:15	1.70	113.09	13.03	0.12	10.43	0.071	0.092	92.9	0.1	3.8	0.059	0.034
7/26/2000 6:50	1.36	114.45	13.10	0.07	10.50	0.052	0.092	92.9	0.0	3.8	0.000	0.033
7/28/2000 7:00	2.01	116.45	13.25	0.15	10.65	0.075	0.091	92.9	0.0	3.8	0.000	0.033
8/1/2000 16:05	4.38	120.83	13.49	0.24	10.89	0.055	0.090	92.8	0.1	3.9	0.023	0.032
8/3/2000 7:00	1.62	122.45	13.67	0.18	11.07	0.111	0.090	92.8	0.0	3.9	0.000	0.032
8/4/2000 0:20	0.72	123.18	13.70	0.03	11.10	0.042	0.090	92.8	0.0	3.9	0.000	0.032
8/6/2000 0:10	1.99	125.17	13.81	0.11	11.21	0.055	0.090	92.8	0.0	3.9	0.000	0.031
8/7/2000 4:20	1.17	126.34	13.90	0.09	11.30	0.077	0.089	92.8	0.0	3.9	0.000	0.031
8/7/2000 17:35	0.55	126.90	13.90	0.00	11.30	0.000	0.089	92.8	0.0	3.9	0.000	0.031
8/9/2000 13:10	1.82	128.71	14.00	0.10	11.40	0.055	0.089	92.7	0.1	4.0	0.055	0.031
8/10/2000 12:10	0.96	129.67	14.22	0.22	11.62	0.230	0.090	92.7	0.0	4.0	0.000	0.031

Laboratory Temperature

Total Meas'mt	Days	Avg T	SD	Freq/d
574	285	22.9	0.24	2.01

Date &Time	Meas'mt Number	Δt (days)	Σ Δt (days)	T (°C)
12/24/2002 9:00	1	0.00	0.00	23.0
12/24/2002 21:17	2	0.51	0.51	22.8
12/25/2002 9:50	3	0.52	1.03	23.0
12/25/2002 21:10	4	0.47	1.51	22.8
12/26/2002 10:05	5	0.54	2.05	23.0
12/26/2002 21:57	6	0.49	2.54	22.8
12/27/2002 10:42	7	0.53	3.07	23.0
12/27/2002 22:40	8	0.50	3.57	22.8
1/3/2003 17:40	9	6.79	10.36	22.5
1/4/2003 7:15	10	0.57	10.93	22.8
1/4/2003 17:45	11	0.44	11.36	22.5
1/5/2003 11:10	12	0.73	12.09	22.8
1/5/2003 21:25	13	0.43	12.52	22.5
1/6/2003 13:45	14	0.68	13.20	23.0
1/7/2003 9:10	15	0.81	14.01	23.0
1/8/2003 14:00	16	1.20	15.21	22.5
1/9/2003 9:45	17	0.82	16.03	23.0
1/10/2003 13:35	18	1.16	17.19	23.0
1/11/2003 19:30	19	1.25	18.44	22.8
1/12/2003 13:07	20	0.73	19.17	23.0
1/13/2003 13:41	21	1.02	20.20	23.0
1/14/2003 4:10	22	0.60	20.80	22.8
1/15/2003 13:13	23	1.38	22.18	22.7
1/16/2003 2:15	24	0.54	22.72	23.0
1/17/2003 15:00	25	1.53	24.25	22.9
1/19/2003 14:24	26	1.97	26.22	22.6
1/23/2003 9:37	27	3.80	30.03	23.1
1/24/2003 16:44	28	1.30	31.32	22.7
1/25/2003 10:30	29	0.74	32.06	22.8
1/26/2003 10:00	30	0.98	33.04	22.8
1/27/2003 8:42	31	0.95	33.99	22.8
1/28/2003 12:32	32	1.16	35.15	22.6
1/29/2003 8:27	33	0.83	35.98	22.8
1/31/2003 10:25	34	2.08	38.06	22.7
2/1/2003 10:05	35	0.99	39.05	22.7
2/3/2003 8:32	36	1.94	40.98	22.8
2/4/2003 9:13	37	1.03	42.01	22.9
2/5/2003 8:37	38	0.97	42.98	22.9
2/6/2003 9:08	39	1.02	44.01	23.0
2/7/2003 22:10	40	1.54	45.55	23.0
2/8/2003 14:14	41	0.67	46.22	24.3
2/9/2003 13:29	42	0.97	47.19	23.7
2/10/2003 13:32	43	1.00	48.19	23.1
2/11/2003 9:33	44	0.83	49.02	23.3
2/12/2003 18:48	45	1.39	50.41	23.0
2/15/2003 17:17	46	2.94	53.35	23.0
2/16/2003 17:19	47	1.00	54.35	23.2
2/17/2003 17:13	48	1.00	55.34	22.8
2/18/2003 16:16	49	0.96	56.30	22.9
2/19/2003 9:37	50	0.72	57.03	22.9
2/20/2003 13:43	51	1.17	58.20	23.0
2/21/2003 12:45	52	0.96	59.16	22.9
2/22/2003 12:54	53	1.01	60.16	22.9
2/23/2003 14:14	54	1.06	61.22	23.0
2/24/2003 8:28	55	0.76	61.98	23.2
2/25/2003 17:01	56	1.36	63.33	23.0
2/27/2003 19:20	57	2.10	65.43	22.8
2/28/2003 17:13	58	0.91	66.34	22.9
3/1/2003 10:03	59	0.70	67.04	22.8
3/3/2003 8:35	60	1.94	68.98	22.8
3/5/2003 14:00	61	2.23	71.21	23.0
3/6/2003 11:01	62	0.88	72.08	22.8
3/7/2003 9:48	63	0.95	73.03	22.7
3/8/2003 17:00	64	1.30	74.33	22.6
3/9/2003 10:25	65	0.73	75.06	22.7
3/10/2003 9:10	66	0.95	76.01	22.7
3/11/2003 10:12	67	1.04	77.05	23.0
3/12/2003 9:43	68	0.98	78.03	22.9
3/13/2003 7:42	69	0.92	78.95	23.0
3/14/2003 7:35	70	1.00	79.94	23.0
3/15/2003 6:40	71	0.96	80.90	22.8

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8/12/2000 23:55	2.49	132.16	14.30	0.08	11.70	0.032	0.089	92.5	0.2	4.2	0.080	0.032
8/14/2000 18:40	1.78	133.94	14.34	0.04	11.74	0.022	0.088	92.2	0.3	4.5	0.168	0.034
8/15/2000 12:30	0.74	134.68	14.42	0.08	11.82	0.108	0.088	92.1	0.1	4.6	0.135	0.034
8/15/2000 22:00	0.40	135.08	14.43	0.01	11.83	0.025	0.088	92.1	0.0	4.6	0.000	0.034
8/19/2000 4:50	3.28	138.36	14.69	0.26	12.09	0.079	0.087	92.1	0.0	4.6	0.000	0.033
8/20/2000 10:30	1.24	139.60	14.79	0.10	12.19	0.081	0.087	92.0	0.1	4.7	0.081	0.034
8/22/2000 7:00	1.85	141.45	14.90	0.11	12.30	0.059	0.087	92.0	0.0	4.7	0.000	0.033
8/23/2000 8:40	1.07	142.52	15.00	0.10	12.40	0.094	0.087	92.0	0.0	4.7	0.000	0.033
8/24/2000 8:25	0.99	143.51	15.05	0.05	12.45	0.051	0.087	92.0	0.0	4.7	0.000	0.033
8/27/2000 18:35	3.42	146.94	15.30	0.25	12.70	0.073	0.086	91.9	0.1	4.8	0.029	0.033
8/30/2000 9:30	2.62	149.56	15.46	0.16	12.86	0.061	0.086	91.9	0.0	4.8	0.000	0.032
8/30/2000 23:15	0.57	150.13	15.50	0.04	12.90	0.070	0.086	91.9	0.0	4.8	0.000	0.032
9/1/2000 7:00	1.32	151.45	15.60	0.10	13.00	0.076	0.086	91.8	0.1	4.9	0.076	0.032
9/2/2000 21:56	1.62	153.08	15.69	0.09	13.09	0.055	0.086	91.7	0.1	5.0	0.062	0.033
9/4/2000 9:00	1.46	154.54	15.80	0.11	13.20	0.075	0.085	91.6	0.1	5.1	0.068	0.033
9/5/2000 21:10	1.51	156.05	15.93	0.13	13.33	0.086	0.085	91.6	0.0	5.1	0.000	0.033
9/8/2000 10:55	2.57	158.62	16.11	0.18	13.51	0.070	0.085	91.5	0.1	5.2	0.039	0.033
9/10/2000 6:20	1.81	160.43	16.27	0.16	13.67	0.088	0.085	91.4	0.1	5.3	0.055	0.033
9/11/2000 2:55	0.86	161.28	16.31	0.04	13.71	0.047	0.085	91.4	0.0	5.3	0.000	0.033
9/13/2000 9:15	2.26	163.55	16.54	0.23	13.94	0.102	0.085	91.3	0.1	5.4	0.044	0.033
9/13/2000 17:03	0.33	163.87	16.57	0.03	13.97	0.092	0.085	91.3	0.0	5.4	0.000	0.033
9/14/2000 7:00	0.58	164.45	16.60	0.03	14.00	0.052	0.085	91.2	0.1	5.5	0.172	0.033
9/16/2000 6:56	2.00	166.45	16.79	0.19	14.19	0.095	0.085	91.2	0.0	5.5	0.000	0.033
9/17/2000 6:58	1.00	167.45	16.88	0.09	14.28	0.090	0.085	91.1	0.1	5.6	0.100	0.033
9/18/2000 17:55	1.46	168.91	17.00	0.12	14.40	0.082	0.085	91.1	0.0	5.6	0.000	0.033
9/19/2000 20:55	1.13	170.03	17.10	0.10	14.50	0.089	0.085	91.0	0.1	5.7	0.089	0.034
9/20/2000 22:45	1.08	171.11	17.20	0.10	14.60	0.093	0.085	91.0	0.0	5.7	0.000	0.033
9/21/2000 5:52	0.30	171.41	17.21	0.01	14.61	0.034	0.085	91.0	0.0	5.7	0.000	0.033
9/22/2000 6:14	1.02	172.42	17.30	0.09	14.70	0.089	0.085	91.0	0.0	5.7	0.000	0.033
9/23/2000 7:10	1.04	173.46	17.39	0.09	14.79	0.087	0.085	90.9	0.1	5.8	0.096	0.033
9/23/2000 19:45	0.52	173.99	17.42	0.03	14.82	0.057	0.085	90.9	0.0	5.8	0.000	0.033
9/24/2000 17:12	0.89	174.88	17.51	0.09	14.91	0.101	0.085	90.9	0.0	5.8	0.000	0.033
9/25/2000 19:35	1.10	175.98	17.64	0.13	15.04	0.118	0.085	90.8	0.1	5.9	0.091	0.034
9/26/2000 7:53	0.51	176.49	17.69	0.05	15.09	0.098	0.085	90.8	0.0	5.9	0.000	0.033
9/28/2000 19:25	2.48	178.97	17.91	0.22	15.31	0.089	0.086	90.7	0.1	6.0	0.040	0.034
9/29/2000 7:48	0.52	179.49	17.99	0.08	15.39	0.155	0.086	90.6	0.1	6.1	0.194	0.034
10/1/2000 6:35	1.95	181.44	18.11	0.12	15.51	0.062	0.085	90.5	0.1	6.2	0.051	0.034
10/1/2000 17:55	0.47	181.91	18.16	0.05	15.56	0.106	0.086	90.5	0.0	6.2	0.000	0.034
10/2/2000 16:30	0.94	182.85	18.24	0.08	15.64	0.085	0.086	90.5	0.0	6.2	0.000	0.034
10/3/2000 20:22	1.16	184.01	18.36	0.12	15.76	0.103	0.086	90.4	0.1	6.3	0.086	0.034
10/5/2000 19:37	1.97	185.98	18.50	0.14	15.90	0.071	0.085	90.3	0.1	6.4	0.051	0.034
10/6/2000 9:42	0.59	186.57	18.55	0.05	15.95	0.085	0.085	90.3	0.0	6.4	0.000	0.034
10/7/2000 6:20	0.86	187.43	18.63	0.08	16.03	0.093	0.086	90.2	0.1	6.5	0.116	0.035
10/8/2000 19:45	1.56	188.99	18.80	0.17	16.20	0.109	0.086	90.2	0.0	6.5	0.000	0.034
10/9/2000 8:47	0.54	189.53	18.85	0.05	16.25	0.092	0.086	90.1	0.1	6.6	0.184	0.035
10/11/2000 2:40	1.75	191.27	19.01	0.16	16.41	0.092	0.086	90.1	0.0	6.6	0.000	0.035
10/11/2000 10:30	0.33	191.60	19.04	0.03	16.44	0.092	0.086	90.0	0.1	6.7	0.306	0.035
10/12/2000 10:10	0.99	192.59	19.12	0.08	16.52	0.081	0.086	90.0	0.0	6.7	0.000	0.035
10/14/2000 1:05	1.62	194.21	19.29	0.17	16.69	0.105	0.086	89.9	0.1	6.8	0.062	0.035
10/16/2000 11:55	2.45	196.66	19.51	0.22	16.91	0.090	0.086	89.9	0.0	6.8	0.000	0.035
10/17/2000 19:55	1.33	197.99	19.63	0.12	17.03	0.090	0.086	89.8	0.1	6.9	0.075	0.035
10/19/2000 2:40	1.28	199.27	19.78	0.15	17.18	0.117	0.086	89.8	0.0	6.9	0.000	0.035
10/19/2000 23:08	0.85	200.13	19.86	0.08	17.26	0.094	0.086	89.7	0.1	7.0	0.117	0.035
10/21/2000 23:43	2.02	202.15	20.00	0.14	17.40	0.069	0.086	89.6	0.1	7.1	0.049	0.035
10/23/2000 8:40	1.37	203.52	20.17	0.17	17.57	0.124	0.086	89.5	0.1	7.2	0.073	0.035
10/24/2000 15:50	1.30	204.82	20.31	0.14	17.71	0.108	0.086	89.5	0.0	7.2	0.000	0.035
10/25/2000 13:25	0.90	205.72	20.37	0.06	17.77	0.067	0.086	89.5	0.0	7.2	0.000	0.035
10/27/2000 9:18	1.83	207.55	20.55	0.18	17.95	0.098	0.086	89.4	0.1	7.3	0.055	0.035
10/28/2000 2:15	0.71	208.26	20.60	0.05	18.00	0.071	0.086	89.4	0.0	7.3	0.000	0.035
10/28/2000 14:42	0.52	208.78	20.66	0.06	18.06	0.116	0.087	89.4	0.0	7.3	0.000	0.035
10/30/2000 5:00	1.64	210.41	20.80	0.14	18.20	0.085	0.086	89.3	0.1	7.4	0.061	0.035
10/30/2000 17:50	0.53	210.95	20.85	0.05	18.25	0.094	0.087	89.3	0.0	7.4	0.000	0.035
11/2/2000 0:05	2.26	213.21	21.02	0.17	18.42	0.075	0.086	89.1	0.2	7.6	0.088	0.036
11/2/2000 22:25	0.93	214.14	21.10	0.08	18.50	0.086	0.086	89.1	0.0	7.6	0.000	0.035
11/4/2000 8:55	1.44	215.58	21.30	0.20	18.70	0.139	0.087	89.0	0.1	7.7	0.070	0.036
11/4/2000 21:28	0.52	216.10	21.33	0.03	18.73	0.057	0.087	89.0	0.0	7.7	0.000	0.036
11/5/2000 11:20	0.58	216.68	21.40	0.07	18.80	0.121	0.087	89.0	0.0	7.7	0.000	0.036
11/5/2000 23:15	0.50	217.17	21.45	0.05	18.85	0.101	0.087	89.0	0.0	7.7	0.000	0.035
11/7/2000 13:35	1.60	218.77	21.66	0.21	19.06	0.131	0.087	88.9	0.1	7.8	0.063	0.036
11/8/2000 9:05	0.81	219.58	21.75	0.09	19.15	0.111	0.087	88.9	0.0	7.8	0.000	0.036
11/9/2000 9:47	1.03	220.61	21.87	0.12	19.27	0.117	0.087	88.8	0.1	7.9	0.097	0.036
11/10/2000 2:18	0.69	221.30	21.94	0.07	19.34	0.102	0.087	88.8	0.0	7.9	0.000	0.036
11/11/2000 9:40	1.31	222.61	22.08	0.14	19.48	0.107	0.088	88.7	0.1	8.0	0.077	0.036
11/12/2000 7:45	0.92	223.53	22.20	0.12	19.60	0.130	0.088	88.7	0.0	8.0	0.000	0.036
11/12/2000 16:25	0.36	223.89	22.22	0.02	19.62	0.055	0.088	88.7	0.0	8.0	0.000	0.036
11/15/2000 10:15	2.74	226.63	22.57	0.35	19.97	0.128	0.088	88.5	0.2	8.2	0.073	0.036
11/16/2000 9:20	0.96	227.59	22.68	0.11	20.08	0.114	0.088	88.4	0.1	8.3	0.104	0.036

3/16/2003 6:50	72	1.01	81.91	22.7
3/16/2003 17:56	73	0.46	82.37	23.0
3/17/2003 8:18	74	0.60	82.97	22.8
3/17/2003 17:35	75	0.39	83.36	22.8
3/18/2003 7:20	76	0.57	83.93	23.0
3/18/2003 14:14	77	0.29	84.22	23.0
3/19/2003 6:50	78	0.69	84.91	23.2
3/19/2003 17:13	79	0.43	85.34	23.0
3/20/2003 4:55	80	0.49	85.83	22.7
3/20/2003 14:20	81	0.39	86.22	23.3
3/21/2003 7:30	82	0.72	86.94	23.2
3/21/2003 21:00	83	0.56	87.50	23.0
3/22/2003 6:00	84	0.38	87.88	23.1
3/22/2003 18:00	85	0.50	88.38	22.8
3/23/2003 5:50	86	0.49	88.87	23.1
3/23/2003 17:50	87	0.50	89.37	22.7
3/24/2003 5:00	88	0.47	89.83	23.0
3/24/2003 17:00	89	0.50	90.33	22.8
3/25/2003 6:00	90	0.54	90.88	23.1
3/25/2003 16:00	91	0.42	91.29	23.0
3/26/2003 7:00	92	0.63	91.92	23.0
3/26/2003 18:43	93	0.49	92.40	22.9
3/27/2003 7:10	94	0.52	92.92	23.0
3/27/2003 20:51	95	0.57	93.49	23.1
3/28/2003 7:50	96	0.46	93.95	23.2
3/28/2003 19:20	97	0.48	94.43	23.3
3/29/2003 9:00	98	0.57	95.00	23.2
3/29/2003 20:10	99	0.47	95.47	23.2
3/30/2003 6:00	100	0.41	95.88	23.2
3/30/2003 18:30	101	0.52	96.40	22.9
3/31/2003 6:30	102	0.50	96.90	23.0
3/31/2003 20:10	103	0.57	97.47	22.8
4/1/2003 8:00	104	0.49	97.96	22.7
4/1/2003 19:00	105	0.46	98.42	22.7
4/2/2003 6:00	106	0.46	98.88	23.0
4/2/2003 21:00	107	0.63	99.50	22.7
4/3/2003 7:00	108	0.42	99.92	22.9
4/3/2003 21:00	109	0.58	100.50	22.7
4/4/2003 8:00	110	0.46	100.96	23.1
4/4/2003 22:00	111	0.58	101.54	23.0
4/5/2003 6:00	112	0.33	101.88	23.0
4/5/2003 18:30	113	0.52	102.40	22.8
4/6/2003 8:00	114	0.52	102.92	23.0
4/6/2003 19:10	115	0.47	103.38	22.8
4/7/2003 7:00	116	0.49	103.87	23.0
4/7/2003 18:40	117	0.49	104.36	23.0
4/8/2003 7:30	118	0.53	104.90	23.1
4/8/2003 20:30	119	0.54	105.44	22.7
4/9/2003 7:00	120	0.44	105.87	23.0
4/9/2003 21:00	121	0.58	106.46	22.7
4/10/2003 7:40	122	0.44	106.90	23.0
4/11/2003 2:30	123	0.78	107.69	22.8
4/11/2003 11:20	124	0.37	108.06	22.8
4/11/2003 23:20	125	0.50	108.56	22.7
4/12/2003 8:00	126	0.36	108.92	22.9
4/12/2003 18:00	127	0.42	109.33	22.6
4/12/2003 23:50	128	0.24	109.58	22.7
4/13/2003 7:00	129	0.30	109.87	22.9
4/13/2003 13:00	130	0.25	110.12	22.8
4/13/2003 21:40	131	0.36	110.49	22.7
4/14/2003 5:30	132	0.33	110.81	22.8
4/14/2003 13:00	133	0.31	111.12	22.7
4/14/2003 20:00	134	0.29	111.42	22.7
4/15/2003 5:00	135	0.38	111.79	22.9
4/15/2003 11:30	136	0.27	112.06	22.7
4/15/2003 18:10	137	0.28	112.34	22.6
4/16/2003 7:30	138	0.56	112.90	23.0
4/16/2003 13:30	139	0.25	113.15	23.0
4/16/2003 21:00	140	0.31	113.46	22.9
4/17/2003 7:00	141	0.42	113.87	22.9
4/17/2003 12:00	142	0.21	114.08	22.9
4/17/2003 21:00	143	0.38	114.46	22.7
4/18/2003 6:00	144	0.38	114.83	22.8
4/18/2003 14:00	145	0.33	115.17	22.7
4/18/2003 22:30	146	0.35	115.52	22.7
4/19/2003 6:00	147	0.31	115.83	22.7
4/19/2003 12:30	148	0.27	116.10	22.9

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11/17/2000 8:57	0.98	228.58	22.80	0.12	20.20	0.122	0.088	88.4	0.0	8.3	0.000	0.036
11/17/2000 16:53	0.33	228.91	22.83	0.03	20.23	0.091	0.088	88.4	0.0	8.3	0.000	0.036
11/18/2000 8:35	0.65	229.56	22.92	0.09	20.32	0.138	0.089	88.3	0.1	8.4	0.153	0.037
11/19/2000 8:05	0.98	230.54	23.00	0.08	20.40	0.082	0.088	88.3	0.0	8.4	0.000	0.036
11/20/2000 21:55	1.58	232.12	23.20	0.20	20.60	0.127	0.089	88.2	0.1	8.5	0.063	0.037
11/21/2000 8:00	0.42	232.54	23.24	0.04	20.64	0.095	0.089	88.2	0.0	8.5	0.000	0.037
11/22/2000 8:00	1.00	233.54	23.35	0.11	20.75	0.110	0.089	88.1	0.1	8.6	0.100	0.037
11/23/2000 9:38	1.07	234.61	23.50	0.15	20.90	0.140	0.089	88.0	0.1	8.7	0.094	0.037
11/25/2000 22:45	2.55	237.15	23.78	0.28	21.18	0.110	0.089	87.9	0.1	8.8	0.039	0.037
11/27/2000 21:10	1.93	239.09	23.99	0.21	21.39	0.109	0.089	87.8	0.1	8.9	0.052	0.037
11/28/2000 12:15	0.63	239.72	24.04	0.05	21.44	0.080	0.089	87.8	0.0	8.9	0.000	0.037
11/28/2000 19:10	0.29	240.00	24.07	0.03	21.47	0.104	0.089	87.8	0.0	8.9	0.000	0.037
11/29/2000 8:15	0.55	240.55	24.12	0.05	21.52	0.092	0.089	87.8	0.0	8.9	0.000	0.037
12/1/2000 4:10	1.83	242.38	24.33	0.21	21.73	0.115	0.090	87.7	0.1	9.0	0.055	0.037
12/2/2000 14:30	1.43	243.81	24.49	0.16	21.89	0.112	0.090	87.6	0.1	9.1	0.070	0.037
12/3/2000 8:35	0.75	244.56	24.60	0.11	22.00	0.146	0.090	87.5	0.1	9.2	0.133	0.038
12/3/2000 16:05	0.31	244.88	24.62	0.02	22.02	0.064	0.090	87.5	0.0	9.2	0.000	0.038
12/4/2000 19:45	1.15	246.03	24.76	0.14	22.16	0.121	0.090	87.4	0.1	9.3	0.087	0.038
12/5/2000 9:15	0.56	246.59	24.81	0.05	22.21	0.089	0.090	87.4	0.0	9.3	0.000	0.038
12/6/2000 1:42	0.69	247.28	24.90	0.09	22.30	0.131	0.090	87.3	0.1	9.4	0.146	0.038
12/7/2000 8:40	1.29	248.57	25.01	0.11	22.41	0.085	0.090	87.2	0.1	9.5	0.078	0.038
12/7/2000 14:05	0.23	248.79	25.03	0.02	22.43	0.089	0.090	87.2	0.0	9.5	0.000	0.038
12/8/2000 10:48	0.86	249.65	25.11	0.08	22.51	0.093	0.090	87.2	0.0	9.5	0.000	0.038
12/9/2000 9:25	0.94	250.60	25.20	0.09	22.60	0.096	0.090	87.1	0.1	9.6	0.106	0.038
12/10/2000 14:38	1.22	251.81	25.34	0.14	22.74	0.115	0.090	87.0	0.1	9.7	0.082	0.039
12/10/2000 21:05	0.27	252.08	25.39	0.05	22.79	0.186	0.090	87.0	0.0	9.7	0.000	0.038
12/11/2000 8:42	0.48	252.57	25.43	0.04	22.83	0.083	0.090	86.9	0.1	9.8	0.207	0.039
12/11/2000 12:28	0.16	252.72	25.45	0.02	22.85	0.127	0.090	86.9	0.0	9.8	0.000	0.039
12/13/2000 11:20	1.95	254.68	25.67	0.22	23.07	0.113	0.091	86.9	0.0	9.8	0.000	0.038
12/14/2000 8:55	0.90	255.58	25.79	0.12	23.19	0.133	0.091	86.8	0.1	9.9	0.111	0.039
12/15/2000 7:50	0.95	256.53	25.90	0.11	23.30	0.115	0.091	86.8	0.0	9.9	0.000	0.039
12/15/2000 22:32	0.61	257.14	25.97	0.07	23.37	0.114	0.091	86.8	0.0	9.9	0.000	0.038
12/16/2000 22:45	1.01	258.15	26.07	0.10	23.47	0.099	0.091	86.7	0.1	10.0	0.099	0.039
12/18/2000 13:10	1.60	259.75	26.23	0.16	23.63	0.100	0.091	86.6	0.1	10.1	0.062	0.039
12/18/2000 21:25	0.34	260.10	26.30	0.07	23.70	0.204	0.091	86.6	0.0	10.1	0.000	0.039
12/20/2000 17:07	1.82	261.92	26.50	0.20	23.90	0.110	0.091	86.5	0.1	10.2	0.055	0.039
12/21/2000 0:20	0.30	262.22	26.52	0.02	23.92	0.067	0.091	86.5	0.0	10.2	0.000	0.039
12/22/2000 9:00	1.36	263.58	26.67	0.15	24.07	0.110	0.091	86.4	0.1	10.3	0.073	0.039
12/22/2000 13:52	0.20	263.78	26.70	0.03	24.10	0.148	0.091	86.4	0.0	10.3	0.000	0.039
12/23/2000 17:15	1.14	264.92	26.82	0.12	24.22	0.105	0.091	86.4	0.0	10.3	0.000	0.039
12/24/2000 14:00	0.86	265.79	26.90	0.08	24.30	0.093	0.091	86.4	0.0	10.3	0.000	0.039
12/25/2000 15:52	1.08	266.87	27.02	0.12	24.42	0.111	0.092	86.3	0.1	10.4	0.093	0.039
12/26/2000 9:31	0.74	267.60	27.10	0.08	24.50	0.109	0.092	86.3	0.0	10.4	0.000	0.039
12/26/2000 13:16	0.16	267.76	27.12	0.02	24.52	0.128	0.092	86.3	0.0	10.4	0.000	0.039
12/28/2000 14:00	2.03	269.79	27.31	0.19	24.71	0.094	0.092	86.2	0.1	10.5	0.049	0.039
12/28/2000 18:20	0.18	269.97	27.34	0.03	24.74	0.166	0.092	86.2	0.0	10.5	0.000	0.039
12/29/2000 9:20	0.63	270.59	27.40	0.06	24.80	0.096	0.092	86.1	0.1	10.6	0.160	0.039
12/30/2000 12:00	1.11	271.70	27.51	0.11	24.91	0.099	0.092	86.0	0.1	10.7	0.090	0.039
12/31/2000 17:25	1.23	272.93	27.68	0.17	25.08	0.139	0.092	86.0	0.0	10.7	0.000	0.039
1/1/2001 10:35	0.72	273.65	27.72	0.04	25.12	0.056	0.092	85.9	0.1	10.8	0.140	0.039
1/2/2001 19:35	1.38	275.02	27.89	0.17	25.29	0.124	0.092	85.9	0.0	10.8	0.000	0.039
1/3/2001 9:25	0.58	275.60	27.95	0.06	25.35	0.104	0.092	85.9	0.0	10.8	0.000	0.039
1/3/2001 18:50	0.39	275.99	28.00	0.05	25.40	0.127	0.092	85.9	0.0	10.8	0.000	0.039
1/5/2001 14:10	1.81	277.80	28.18	0.18	25.58	0.100	0.092	85.9	0.0	10.8	0.000	0.039
1/5/2001 22:25	0.34	278.14	28.20	0.02	25.60	0.058	0.092	85.9	0.0	10.8	0.000	0.039
1/6/2001 19:55	0.90	279.03	28.30	0.10	25.70	0.112	0.092	85.8	0.1	10.9	0.112	0.039
1/7/2001 18:55	0.96	279.99	28.40	0.10	25.80	0.104	0.092	85.8	0.0	10.9	0.000	0.039
1/8/2001 11:06	0.67	280.67	28.49	0.09	25.89	0.133	0.092	85.8	0.0	10.9	0.000	0.039
1/9/2001 19:45	1.36	282.03	28.62	0.13	26.02	0.096	0.092	85.7	0.1	11.0	0.074	0.039
1/10/2001 18:15	0.94	282.97	28.73	0.11	26.13	0.117	0.092	85.7	0.0	11.0	0.000	0.039
1/11/2001 8:15	0.58	283.55	28.80	0.07	26.20	0.120	0.092	85.6	0.1	11.1	0.171	0.039
1/11/2001 21:47	0.56	284.11	28.88	0.08	26.28	0.142	0.092	85.6	0.0	11.1	0.000	0.039
1/12/2001 14:27	0.69	284.81	28.95	0.07	26.35	0.101	0.093	85.6	0.0	11.1	0.000	0.039
1/13/2001 7:35	0.71	285.52	29.02	0.07	26.42	0.098	0.093	85.5	0.1	11.2	0.140	0.039
1/13/2001 21:35	0.58	286.10	29.06	0.04	26.46	0.069	0.092	85.5	0.0	11.2	0.000	0.039
1/14/2001 10:20	0.53	286.64	29.10	0.04	26.50	0.075	0.092	85.4	0.1	11.3	0.188	0.039
1/15/2001 7:57	0.90	287.54	29.22	0.12	26.62	0.133	0.093	85.4	0.0	11.3	0.000	0.039
1/15/2001 21:52	0.58	288.12	29.30	0.08	26.70	0.138	0.093	85.3	0.1	11.4	0.172	0.040
1/17/2001 8:20	1.44	289.55	29.43	0.13	26.83	0.091	0.093	85.3	0.0	11.4	0.000	0.039
1/17/2001 21:59	0.57	290.12	29.50	0.07	26.90	0.123	0.093	85.2	0.1	11.5	0.176	0.040
1/18/2001 8:08	0.42	290.54	29.55	0.05	26.95	0.118	0.093	85.2	0.0	11.5	0.000	0.040
1/19/2001 19:43	1.48	292.03	29.70	0.15	27.10	0.101	0.093	85.1	0.1	11.6	0.067	0.040
1/20/2001 5:10	0.39	292.42	29.77	0.07	27.17	0.178	0.093	85.1	0.0	11.6	0.000	0.040
1/20/2001 19:35	0.60	293.02	29.82	0.05	27.22	0.083	0.093	85.1	0.0	11.6	0.000	0.040
1/21/2001 17:58	0.93	293.95	29.92	0.10	27.32	0.107	0.093	85.0	0.1	11.7	0.107	0.040
1/22/2001 8:38	0.61	294.56	30.00	0.08	27.40	0.131	0.093	85.0	0.0	11.7	0.000	0.040
1/23/2001 17:00	1.35	295.91	30.13	0.13	27.53	0.096	0.093	85.0	0.0	11.7	0.000	0.040

4/19/2003 23:59	149	0.48	116.58	23.0
4/20/2003 7:00	150	0.29	116.87	23.0
4/20/2003 13:00	151	0.25	117.12	22.8
4/20/2003 20:00	152	0.29	117.42	22.8
4/21/2003 7:00	153	0.46	117.87	22.9
4/21/2003 15:50	154	0.37	118.24	22.7
4/21/2003 21:00	155	0.22	118.46	22.6
4/22/2003 6:40	156	0.40	118.86	22.8
4/22/2003 16:00	157	0.39	119.25	22.6
4/22/2003 23:30	158	0.31	119.56	22.7
4/23/2003 5:00	159	0.23	119.79	22.7
4/23/2003 12:00	160	0.29	120.08	22.7
4/23/2003 20:30	161	0.35	120.44	22.9
4/24/2003 6:00	162	0.40	120.83	23.0
4/24/2003 13:30	163	0.31	121.15	22.8
4/24/2003 21:30	164	0.33	121.48	22.7
4/25/2003 5:20	165	0.33	121.81	22.8
4/25/2003 13:30	166	0.34	122.15	22.7
4/25/2003 21:30	167	0.33	122.48	22.6
4/26/2003 3:00	168	0.23	122.71	22.7
4/26/2003 16:00	169	0.54	123.25	22.6
4/26/2003 23:00	170	0.29	123.54	22.8
4/27/2003 5:00	171	0.25	123.79	22.9
4/27/2003 14:00	172	0.38	124.17	22.6
4/27/2003 22:30	173	0.35	124.52	22.7
4/28/2003 6:50	174	0.35	124.87	22.7
4/28/2003 13:00	175	0.26	125.12	22.7
4/28/2003 23:30	176	0.44	125.56	22.5
4/29/2003 6:00	177	0.27	125.83	22.6
4/29/2003 13:00	178	0.29	126.12	22.5
4/29/2003 21:00	179	0.33	126.46	22.6
4/30/2003 6:00	180	0.38	126.83	22.7
4/30/2003 13:00	181	0.29	127.12	22.6
4/30/2003 21:30	182	0.35	127.48	22.7
5/1/2003 6:00	183	0.35	127.83	22.9
5/1/2003 13:00	184	0.29	128.12	22.6
5/1/2003 22:30	185	0.40	128.52	22.8
5/2/2003 7:00	186	0.35	128.87	22.8
5/2/2003 13:00	187	0.25	129.12	22.7
5/2/2003 20:30	188	0.31	129.44	22.6
5/3/2003 6:30	189	0.42	129.85	22.8
5/3/2003 13:30	190	0.29	130.15	22.6
5/3/2003 21:30	191	0.33	130.48	22.7
5/4/2003 5:50	192	0.35	130.83	22.9
5/4/2003 13:30	193	0.32	131.15	22.7
5/4/2003 21:30	194	0.33	131.48	22.7
5/5/2003 7:00	195	0.40	131.87	22.9
5/5/2003 13:00	196	0.25	132.12	22.8
5/5/2003 21:30	197	0.35	132.48	22.9
5/6/2003 6:00	198	0.35	132.83	23.1
5/6/2003 13:00	199	0.29	133.12	22.7
5/6/2003 21:00	200	0.33	133.46	22.7
5/7/2003 7:50	201	0.45	133.91	22.8
5/7/2003 14:30	202	0.28	134.19	22.7
5/7/2003 22:30	203	0.33	134.52	22.7
5/8/2003 6:30	204	0.33	134.85	22.8
5/8/2003 12:30	205	0.25	135.10	22.6
5/8/2003 22:30	206	0.42	135.52	22.7
5/9/2003 7:30	207	0.38	135.90	22.7
5/9/2003 13:00	208	0.23	136.12	22.8
5/9/2003 21:40	209	0.36	136.49	22.7
5/10/2003 8:30	210	0.45	136.94	23.0
5/10/2003 14:00	211	0.23	137.17	23.0
5/10/2003 22:00	212	0.33	137.50	23.0
5/11/2003 7:00	213	0.38	137.87	23.0
5/11/2003 13:30	214	0.27	138.15	22.7
5/11/2003 22:30	215	0.38	138.52	22.7
5/12/2003 6:00	216	0.31	138.83	22.9
5/12/2003 12:30	217	0.27	139.10	22.7
5/12/2003 22:00	218	0.40	139.50	22.8
5/13/2003 2:30	219	0.19	139.69	22.8
5/13/2003 6:30	220	0.17	139.85	22.7
5/13/2003 14:30	221	0.33	140.19	22.6
5/13/2003 22:30	222	0.33	140.52	22.6
5/14/2003 7:00	223	0.35	140.87	22.8
5/14/2003 13:00	224	0.25	141.12	22.7
5/14/2003 22:00	225	0.38	141.50	22.6

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1/24/2001 13:49	0.87	296.78	30.22	0.09	27.62	0.104	0.093	84.9	0.1	11.8	0.115	0.040
1/25/2001 17:25	1.15	297.93	30.34	0.12	27.74	0.104	0.093	84.9	0.0	11.8	0.000	0.040
1/26/2001 8:34	0.63	298.56	30.40	0.06	27.80	0.095	0.093	84.8	0.1	11.9	0.158	0.040
1/26/2001 18:25	0.41	298.97	30.45	0.05	27.85	0.122	0.093	84.8	0.0	11.9	0.000	0.040
1/27/2001 17:40	0.97	299.94	30.57	0.12	27.97	0.124	0.093	84.7	0.1	12.0	0.103	0.040
1/28/2001 18:23	1.03	300.97	30.67	0.10	28.07	0.097	0.093	84.7	0.0	12.0	0.000	0.040
1/29/2001 8:50	0.60	301.57	30.73	0.06	28.13	0.100	0.093	84.6	0.1	12.1	0.166	0.040
1/29/2001 21:40	0.53	302.11	30.79	0.06	28.19	0.112	0.093	84.6	0.0	12.1	0.000	0.040
1/31/2001 21:29	1.99	304.10	31.00	0.21	28.40	0.105	0.093	84.5	0.1	12.2	0.050	0.040
2/2/2001 8:30	1.46	305.56	31.15	0.15	28.55	0.103	0.093	84.4	0.1	12.3	0.069	0.040
2/2/2001 21:10	0.53	306.09	31.20	0.05	28.60	0.095	0.093	84.4	0.0	12.3	0.000	0.040
2/3/2001 9:00	0.49	306.58	31.27	0.07	28.67	0.142	0.094	84.4	0.0	12.3	0.000	0.040
2/4/2001 21:36	1.53	308.10	31.41	0.14	28.81	0.092	0.094	84.3	0.1	12.4	0.066	0.040
2/5/2001 22:15	1.03	309.13	31.52	0.11	28.92	0.107	0.094	84.3	0.0	12.4	0.000	0.040
2/7/2001 5:40	1.31	310.44	31.66	0.14	29.06	0.107	0.094	84.2	0.1	12.5	0.076	0.040
2/7/2001 21:56	0.68	311.12	31.72	0.06	29.12	0.089	0.094	84.1	0.1	12.6	0.148	0.040
2/8/2001 11:25	0.56	311.68	31.79	0.07	29.19	0.125	0.094	84.1	0.0	12.6	0.000	0.040
2/9/2001 20:46	1.39	313.07	31.96	0.17	29.36	0.122	0.094	84.0	0.1	12.7	0.072	0.041
2/11/2001 5:15	1.35	314.42	32.10	0.14	29.50	0.103	0.094	84.0	0.0	12.7	0.000	0.040
2/11/2001 21:03	0.66	315.08	32.15	0.05	29.55	0.076	0.094	83.9	0.1	12.8	0.152	0.041
2/13/2001 19:51	1.95	317.03	32.38	0.23	29.78	0.118	0.094	83.9	0.0	12.8	0.000	0.040
2/15/2001 18:00	1.92	318.95	32.60	0.22	30.00	0.114	0.094	83.8	0.1	12.9	0.052	0.040
2/16/2001 12:03	0.75	319.71	32.66	0.06	30.06	0.080	0.094	83.7	0.1	13.0	0.133	0.041
2/17/2001 20:07	1.34	321.04	32.80	0.14	30.20	0.105	0.094	83.7	0.0	13.0	0.000	0.040
2/18/2001 21:07	1.04	322.08	32.90	0.10	30.30	0.096	0.094	83.6	0.1	13.1	0.096	0.041
2/19/2001 23:20	1.09	323.18	33.00	0.10	30.40	0.092	0.094	83.6	0.0	13.1	0.000	0.041
2/21/2001 8:05	1.36	324.54	33.13	0.13	30.53	0.095	0.094	83.5	0.1	13.2	0.073	0.041
2/21/2001 21:28	0.56	325.10	33.20	0.07	30.60	0.126	0.094	83.5	0.0	13.2	0.000	0.041
2/23/2001 22:00	2.02	327.12	33.39	0.19	30.79	0.094	0.094	83.4	0.1	13.3	0.049	0.041
2/24/2001 17:08	0.80	327.92	33.48	0.09	30.88	0.113	0.094	83.3	0.1	13.4	0.125	0.041
2/25/2001 22:06	1.21	329.13	33.60	0.12	31.00	0.099	0.094	83.2	0.1	13.5	0.083	0.041
2/27/2001 10:10	1.50	330.63	33.77	0.17	31.17	0.113	0.094	83.1	0.1	13.6	0.067	0.041
2/27/2001 23:05	0.54	331.17	33.80	0.03	31.20	0.056	0.094	83.1	0.0	13.6	0.000	0.041
3/1/2001 23:13	2.01	333.17	34.02	0.22	31.42	0.110	0.094	83.0	0.1	13.7	0.050	0.041
3/3/2001 0:27	1.05	334.22	34.12	0.10	31.52	0.095	0.094	82.9	0.1	13.8	0.095	0.041
3/3/2001 9:53	0.39	334.62	34.17	0.05	31.57	0.127	0.094	82.9	0.0	13.8	0.000	0.041
3/3/2001 23:07	0.55	335.17	34.23	0.06	31.63	0.109	0.094	82.8	0.1	13.9	0.181	0.041
3/4/2001 10:50	0.49	335.66	34.30	0.07	31.70	0.143	0.094	82.8	0.0	13.9	0.000	0.041
3/5/2001 22:40	1.49	337.15	34.43	0.13	31.83	0.087	0.094	82.7	0.1	14.0	0.067	0.042
3/6/2001 22:22	0.99	338.14	34.55	0.12	31.95	0.122	0.094	82.7	0.0	14.0	0.000	0.041
3/7/2001 19:50	0.89	339.03	34.62	0.07	32.02	0.078	0.094	82.6	0.1	14.1	0.112	0.042
3/9/2001 9:23	1.56	340.60	34.77	0.15	32.17	0.096	0.094	82.5	0.1	14.2	0.064	0.042
3/9/2001 19:13	0.41	341.01	34.81	0.04	32.21	0.098	0.094	82.5	0.0	14.2	0.000	0.042
3/11/2001 6:45	1.48	342.49	34.96	0.15	32.36	0.101	0.094	82.4	0.1	14.3	0.068	0.042
3/11/2001 19:53	0.55	343.03	35.01	0.05	32.41	0.091	0.094	82.4	0.0	14.3	0.000	0.042
3/12/2001 23:23	1.15	344.18	35.12	0.11	32.52	0.096	0.094	82.3	0.1	14.4	0.087	0.042
3/13/2001 17:24	0.75	344.93	35.20	0.08	32.60	0.107	0.095	82.2	0.1	14.5	0.133	0.042
3/14/2001 9:50	0.68	345.61	35.26	0.06	32.66	0.088	0.094	82.1	0.1	14.6	0.146	0.042
3/14/2001 17:00	0.30	345.91	35.30	0.04	32.70	0.134	0.095	82.1	0.0	14.6	0.000	0.042
3/15/2001 17:35	1.02	346.94	35.40	0.10	32.80	0.098	0.095	82.0	0.1	14.7	0.098	0.042
3/16/2001 8:10	0.61	347.55	35.48	0.08	32.88	0.132	0.095	82.0	0.0	14.7	0.000	0.042
3/17/2001 6:33	0.93	348.48	35.56	0.08	32.96	0.086	0.095	81.9	0.1	14.8	0.107	0.042
3/17/2001 18:48	0.51	348.99	35.60	0.04	33.00	0.078	0.095	81.9	0.0	14.8	0.000	0.042
3/18/2001 7:26	0.53	349.51	35.67	0.07	33.07	0.133	0.095	81.9	0.0	14.8	0.000	0.042
3/18/2001 18:00	0.44	349.95	35.70	0.03	33.10	0.068	0.095	81.8	0.1	14.9	0.227	0.043
3/19/2001 17:45	0.99	350.94	35.80	0.10	33.20	0.101	0.095	81.8	0.0	14.9	0.000	0.042
3/20/2001 8:15	0.60	351.55	35.86	0.06	33.26	0.099	0.095	81.7	0.1	15.0	0.166	0.043
3/21/2001 18:00	1.41	352.95	36.00	0.14	33.40	0.100	0.095	81.6	0.1	15.1	0.071	0.043
3/22/2001 7:22	0.56	353.51	36.05	0.05	33.45	0.090	0.095	81.6	0.0	15.1	0.000	0.043
3/23/2001 8:53	1.06	354.57	36.14	0.09	33.54	0.085	0.095	81.5	0.1	15.2	0.094	0.043
3/23/2001 19:10	0.43	355.00	36.19	0.05	33.59	0.117	0.095	81.5	0.0	15.2	0.000	0.043
3/24/2001 8:31	0.56	355.56	36.23	0.04	33.63	0.072	0.095	81.5	0.0	15.2	0.000	0.043
3/24/2001 18:40	0.42	355.98	36.28	0.05	33.68	0.118	0.095	81.5	0.0	15.2	0.000	0.043
3/25/2001 18:15	0.98	356.97	36.38	0.10	33.78	0.102	0.095	81.4	0.1	15.3	0.102	0.043
3/26/2001 9:25	0.63	357.60	36.43	0.05	33.83	0.079	0.095	81.4	0.0	15.3	0.000	0.043
3/27/2001 10:19	1.04	358.63	36.52	0.09	33.92	0.087	0.095	81.3	0.1	15.4	0.096	0.043
3/27/2001 19:26	0.38	359.01	36.56	0.04	33.96	0.105	0.095	81.3	0.0	15.4	0.000	0.043
3/28/2001 8:35	0.55	359.56	36.61	0.05	34.01	0.091	0.095	81.3	0.0	15.4	0.000	0.043
3/29/2001 18:38	1.42	360.98	36.76	0.15	34.16	0.106	0.095	81.2	0.1	15.5	0.070	0.043
3/30/2001 10:10	0.65	361.63	36.80	0.04	34.20	0.062	0.095	81.2	0.0	15.5	0.000	0.043
3/31/2001 18:51	1.36	362.99	36.94	0.14	34.34	0.103	0.095	81.1	0.1	15.6	0.073	0.043
4/1/2001 10:52	0.63	363.62	37.00	0.06	34.40	0.096	0.095	81.0	0.1	15.7	0.160	0.043
4/2/2001 20:53	1.42	365.03	37.13	0.13	34.53	0.092	0.095	80.9	0.1	15.8	0.071	0.043
4/3/2001 10:59	0.59	365.62	37.19	0.06	34.59	0.102	0.095	80.9	0.0	15.8	0.000	0.043
4/3/2001 22:00	0.46	366.08	37.24	0.05	34.64	0.109	0.095	80.9	0.0	15.8	0.000	0.043
4/4/2001 20:28	0.94	367.02	37.30	0.06	34.70	0.064	0.095	80.8	0.1	15.9	0.107	0.043
4/5/2001 12:23	0.66	367.68	37.37	0.07	34.77	0.106	0.095	80.8	0.0	15.9	0.000	0.043

5/15/2003 7:00	226	0.38	141.87	22.7
5/15/2003 14:30	227	0.31	142.19	22.7
5/15/2003 21:30	228	0.29	142.48	22.5
5/16/2003 6:00	229	0.35	142.83	22.5
5/16/2003 14:20	230	0.35	143.18	22.5
5/16/2003 21:30	231	0.30	143.48	22.5
5/17/2003 5:30	232	0.33	143.81	22.7
5/17/2003 13:00	233	0.31	144.12	22.6
5/17/2003 21:00	234	0.33	144.46	22.6
5/18/2003 6:00	235	0.38	144.83	22.7
5/18/2003 14:00	236	0.33	145.17	22.5
5/18/2003 23:00	237	0.38	145.54	22.6
5/19/2003 6:00	238	0.29	145.83	22.8
5/19/2003 13:30	239	0.31	146.15	22.8
5/19/2003 21:30	240	0.33	146.48	22.8
5/20/2003 6:30	241	0.38	146.85	23.0
5/20/2003 12:30	242	0.25	147.10	23.0
5/20/2003 22:00	243	0.40	147.50	22.8
5/21/2003 5:00	244	0.29	147.79	22.9
5/21/2003 13:00	245	0.33	148.12	22.7
5/21/2003 21:30	246	0.35	148.48	22.7
5/22/2003 5:30	247	0.33	148.81	22.8
5/22/2003 13:00	248	0.31	149.12	22.6
5/22/2003 23:00	249	0.42	149.54	22.7
5/23/2003 7:00	250	0.33	149.87	22.5
5/23/2003 14:30	251	0.31	150.19	22.4
5/23/2003 23:00	252	0.35	150.54	22.5
5/24/2003 5:30	253	0.27	150.81	23.0
5/24/2003 13:00	254	0.31	151.12	23.5
5/24/2003 21:00	255	0.33	151.46	23.4
5/25/2003 6:30	256	0.40	151.85	23.4
5/25/2003 12:00	257	0.23	152.08	23.5
5/25/2003 22:30	258	0.44	152.52	23.4
5/26/2003 8:00	259	0.40	152.92	23.5
5/26/2003 12:00	260	0.17	153.08	23.8
5/26/2003 21:30	261	0.40	153.48	23.4
5/27/2003 7:00	262	0.40	153.87	23.5
5/27/2003 13:30	263	0.27	154.15	23.5
5/27/2003 22:00	264	0.35	154.50	23.3
5/28/2003 4:00	265	0.25	154.75	23.3
5/28/2003 15:00	266	0.46	155.21	23.4
5/28/2003 22:00	267	0.29	155.50	23.3
5/29/2003 9:30	268	0.48	155.98	23.3
5/29/2003 15:00	269	0.23	156.21	23.5
5/29/2003 22:00	270	0.29	156.50	23.4
5/30/2003 6:00	271	0.33	156.83	23.4
5/30/2003 14:00	272	0.33	157.17	23.3
5/30/2003 21:00	273	0.29	157.46	23.3
5/31/2003 3:00	274	0.25	157.71	23.3
5/31/2003 13:00	275	0.42	158.12	23.3
5/31/2003 20:30	276	0.31	158.44	23.3
6/1/2003 6:30	277	0.42	158.85	23.3
6/1/2003 13:00	278	0.27	159.12	23.4
6/1/2003 20:30	279	0.31	159.44	23.3
6/2/2003 2:30	280	0.25	159.69	23.3
6/2/2003 8:00	281	0.23	159.92	23.5
6/2/2003 12:30	282	0.19	160.10	23.4
6/3/2003 0:30	283	0.50	160.60	23.4
6/3/2003 7:00	284	0.27	160.87	23.4
6/3/2003 14:00	285	0.29	161.17	23.2
6/3/2003 21:30	286	0.31	161.48	22.3
6/4/2003 7:00	287	0.40	161.87	23.0
6/4/2003 13:00	288	0.25	162.12	23.0
6/4/2003 20:00	289	0.29	162.42	23.0
6/5/2003 6:30	290	0.44	162.85	23.2
6/5/2003 12:00	291	0.23	163.08	23.0
6/5/2003 22:30	292	0.44	163.52	23.0
6/6/2003 7:00	293	0.35	163.87	23.2
6/6/2003 13:30	294	0.27	164.15	23.0
6/6/2003 23:30	295	0.42	164.56	23.0
6/7/2003 17:00	296	0.73	165.29	23.1
6/7/2003 20:00	297	0.13	165.42	23.2
6/7/2003 22:00	298	0.08	165.50	23.2
6/8/2003 7:00	299	0.38	165.87	23.2
6/8/2003 12:00	300	0.21	166.08	23.1
6/8/2003 22:30	301	0.44	166.52	23.2
6/9/2003 10:00	302	0.48	167.00	23.5

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4/6/2001 9:40	0.89	368.57	37.44	0.07	34.84	0.079	0.095	80.7	0.1	16.0	0.113	0.043
4/6/2001 20:30	0.45	369.02	37.48	0.04	34.88	0.089	0.095	80.7	0.0	16.0	0.000	0.043
4/7/2001 10:40	0.59	369.61	1.15	0.08	34.96	0.136	0.095	80.7	0.0	16.0	0.000	0.043
4/8/2001 20:40	1.42	371.02	1.36	0.21	35.17	0.148	0.095	80.6	0.1	16.1	0.071	0.043
4/9/2001 9:05	0.52	371.54	1.43	0.07	35.24	0.135	0.095	80.6	0.0	16.1	0.000	0.043
4/9/2001 20:16	0.47	372.01	1.50	0.07	35.31	0.150	0.095	80.5	0.1	16.2	0.215	0.044
4/10/2001 20:32	1.01	373.02	1.60	0.10	35.41	0.099	0.095	80.5	0.0	16.2	0.000	0.043
4/11/2001 11:06	0.61	373.63	1.70	0.10	35.51	0.165	0.095	80.4	0.1	16.3	0.165	0.044
4/12/2001 20:30	1.39	375.02	1.86	0.16	35.67	0.115	0.095	80.3	0.1	16.4	0.072	0.044
4/13/2001 20:43	1.01	376.03	1.99	0.13	35.80	0.129	0.095	80.2	0.1	16.5	0.099	0.044
4/14/2001 20:52	1.01	377.03	2.10	0.11	35.91	0.109	0.095	80.1	0.1	16.6	0.099	0.044
4/16/2001 9:05	1.51	378.54	2.30	0.20	36.11	0.133	0.095	80.0	0.1	16.7	0.066	0.044
4/17/2001 6:45	0.90	379.44	2.39	0.09	36.20	0.100	0.095	80.0	0.0	16.7	0.000	0.044
4/18/2001 20:56	1.59	381.04	2.58	0.19	36.39	0.119	0.096	79.9	0.1	16.8	0.063	0.044
4/19/2001 9:15	0.51	381.55	2.63	0.05	36.44	0.097	0.096	79.9	0.0	16.8	0.000	0.044
4/20/2001 13:45	1.19	382.74	2.80	0.17	36.61	0.143	0.096	79.8	0.1	16.9	0.084	0.044
4/20/2001 21:10	0.31	383.05	2.83	0.03	36.64	0.097	0.096	79.8	0.0	16.9	0.000	0.044
4/21/2001 8:55	0.49	383.53	2.89	0.06	36.70	0.123	0.096	79.8	0.0	16.9	0.000	0.044
4/22/2001 9:35	1.03	384.56	3.00	0.11	36.81	0.107	0.096	79.7	0.1	17.0	0.097	0.044
4/23/2001 8:40	0.96	385.52	3.10	0.10	36.91	0.104	0.096	79.7	0.0	17.0	0.000	0.044
4/23/2001 21:56	0.55	386.08	3.19	0.09	37.00	0.163	0.096	79.6	0.1	17.1	0.181	0.044
4/25/2001 10:43	1.53	387.61	3.34	0.15	37.15	0.098	0.096	79.5	0.1	17.2	0.065	0.044
4/26/2001 9:00	0.93	388.54	3.46	0.12	37.27	0.129	0.096	79.5	0.0	17.2	0.000	0.044
4/27/2001 8:53	1.00	389.53	3.57	0.11	37.38	0.111	0.096	79.4	0.1	17.3	0.100	0.044
4/27/2001 21:05	0.51	390.04	3.60	0.03	37.41	0.059	0.096	79.4	0.0	17.3	0.000	0.044
4/28/2001 21:07	1.00	391.04	3.72	0.12	37.53	0.120	0.096	79.3	0.1	17.4	0.100	0.044
4/29/2001 6:53	0.41	391.45	3.77	0.05	37.58	0.123	0.096	79.3	0.0	17.4	0.000	0.044
4/29/2001 21:05	0.59	392.04	3.81	0.04	37.62	0.068	0.096	79.3	0.0	17.4	0.000	0.044
4/30/2001 21:32	1.02	393.06	3.92	0.11	37.73	0.108	0.096	79.2	0.1	17.5	0.098	0.045
5/1/2001 7:32	0.42	393.48	3.99	0.07	37.80	0.168	0.096	79.2	0.0	17.5	0.000	0.044
5/1/2001 19:35	0.50	393.98	4.03	0.04	37.84	0.080	0.096	79.2	0.0	17.5	0.000	0.044
5/3/2001 9:50	1.59	395.57	4.20	0.17	38.01	0.107	0.096	79.1	0.1	17.6	0.063	0.044
5/3/2001 22:26	0.53	396.10	4.27	0.07	38.08	0.133	0.096	79.1	0.0	17.6	0.000	0.044
5/4/2001 11:28	0.54	396.64	4.31	0.04	38.12	0.074	0.096	79.1	0.0	17.6	0.000	0.044
5/5/2001 8:05	0.86	397.50	4.40	0.09	38.21	0.105	0.096	79.0	0.1	17.7	0.116	0.045
5/5/2001 22:27	0.60	398.10	4.49	0.09	38.30	0.150	0.096	79.0	0.0	17.7	0.000	0.044
5/7/2001 9:01	1.44	399.54	4.61	0.12	38.42	0.083	0.096	78.9	0.1	17.8	0.069	0.045
5/7/2001 21:30	0.52	400.06	4.69	0.08	38.50	0.154	0.096	78.9	0.0	17.8	0.000	0.044
5/9/2001 9:45	1.51	401.57	4.83	0.14	38.64	0.093	0.096	78.8	0.1	17.9	0.066	0.045
5/9/2001 23:00	0.55	402.12	4.89	0.06	38.70	0.109	0.096	78.8	0.0	17.9	0.000	0.045
5/11/2001 9:01	1.42	403.54	5.02	0.13	38.83	0.092	0.096	78.7	0.1	18.0	0.071	0.045
5/11/2001 21:43	0.53	404.07	5.09	0.07	38.90	0.132	0.096	78.7	0.0	18.0	0.000	0.045
5/12/2001 8:03	0.43	404.50	5.11	0.02	38.92	0.046	0.096	78.7	0.0	18.0	0.000	0.044
5/12/2001 21:46	0.57	405.07	5.16	0.05	38.97	0.087	0.096	78.6	0.1	18.1	0.175	0.045
5/13/2001 16:35	0.78	405.85	5.21	0.05	39.02	0.064	0.096	78.5	0.1	18.2	0.128	0.045
5/14/2001 12:57	0.85	406.70	5.32	0.11	39.13	0.130	0.096	78.5	0.0	18.2	0.000	0.045
5/15/2001 16:05	1.13	407.83	5.41	0.09	39.22	0.080	0.096	78.5	0.0	18.2	0.000	0.045
5/16/2001 21:28	1.22	409.06	5.52	0.11	39.33	0.090	0.096	78.4	0.1	18.3	0.082	0.045
5/17/2001 21:50	1.02	410.07	5.61	0.09	39.42	0.089	0.096	78.4	0.0	18.3	0.000	0.045
5/18/2001 9:48	0.50	410.57	5.67	0.06	39.48	0.120	0.096	78.3	0.1	18.4	0.201	0.045
5/18/2001 21:51	0.50	411.07	5.70	0.03	39.51	0.060	0.096	78.3	0.0	18.4	0.000	0.045
5/20/2001 7:52	1.42	412.49	5.81	0.11	39.62	0.078	0.096	78.2	0.1	18.5	0.071	0.045
5/21/2001 7:05	0.97	413.46	5.90	0.09	39.71	0.093	0.096	78.2	0.0	18.5	0.000	0.045
5/22/2001 18:20	1.47	414.93	6.10	0.20	39.91	0.136	0.096	78.2	0.0	18.5	0.000	0.045
5/23/2001 7:25	0.55	415.47	6.16	0.06	39.97	0.110	0.096	78.1	0.1	18.6	0.183	0.045
5/24/2001 8:38	1.05	416.52	6.26	0.10	40.07	0.095	0.096	78.1	0.0	18.6	0.000	0.045
5/24/2001 18:20	0.40	416.93	6.30	0.04	40.11	0.099	0.096	78.1	0.0	18.6	0.000	0.045
5/25/2001 8:30	0.59	417.52	6.37	0.07	40.18	0.119	0.096	78.0	0.1	18.7	0.169	0.045
5/27/2001 9:00	2.02	419.54	6.56	0.19	40.37	0.094	0.096	77.9	0.1	18.8	0.049	0.045
5/27/2001 18:39	0.40	419.94	6.59	0.03	40.40	0.075	0.096	77.8	0.1	18.9	0.249	0.045
5/28/2001 8:33	0.58	420.52	6.62	0.03	40.43	0.052	0.096	77.8	0.0	18.9	0.000	0.045
5/28/2001 18:34	0.42	420.94	6.64	0.02	40.45	0.048	0.096	77.8	0.0	18.9	0.000	0.045
5/29/2001 19:30	1.04	421.98	6.70	0.06	40.51	0.058	0.096	77.8	0.0	18.9	0.000	0.045
5/31/2001 18:46	1.97	423.95	6.87	0.17	40.68	0.086	0.096	77.7	0.1	19.0	0.051	0.045
6/1/2001 9:10	0.60	424.55	6.93	0.06	40.74	0.100	0.096	77.7	0.0	19.0	0.000	0.045
6/2/2001 10:15	1.05	425.59	6.99	0.06	40.80	0.057	0.096	77.7	0.0	19.0	0.000	0.045
6/3/2001 9:50	0.98	426.57	7.11	0.12	40.92	0.122	0.096	77.7	0.0	19.0	0.000	0.045
6/3/2001 19:05	0.39	426.96	7.13	0.02	40.94	0.052	0.096	77.7	0.0	19.0	0.000	0.045
6/4/2001 8:05	0.54	427.50	7.19	0.06	41.00	0.111	0.096	77.6	0.1	19.1	0.185	0.045
6/4/2001 19:02	0.46	427.96	7.20	0.01	41.01	0.022	0.096	77.6	0.0	19.1	0.000	0.045
6/5/2001 19:05	1.00	428.96	7.29	0.09	41.10	0.090	0.096	77.5	0.1	19.2	0.100	0.045
6/6/2001 7:10	0.50	429.46	7.30	0.01	41.11	0.020	0.096	77.5	0.0	19.2	0.000	0.045
6/6/2001 19:15	0.50	429.97	7.37	0.07	41.18	0.139	0.096	77.5	0.0	19.2	0.000	0.045
6/7/2001 5:40	0.43	430.40	7.40	0.03	41.21	0.069	0.096	77.5	0.0	19.2	0.000	0.045
6/7/2001 19:05	0.56	430.96	7.42	0.02	41.23	0.036	0.096	77.5	0.0	19.2	0.000	0.045
6/8/2001 7:45	0.53	431.49	7.45	0.03	41.26	0.057	0.096	77.5	0.0	19.2	0.000	0.044
6/8/2001 19:25	0.49	431.97	7.49	0.04	41.30	0.082	0.096	77.4	0.1	19.3	0.206	0.045

6/9/2003 15:30	303	0.23	167.23	23.1
6/9/2003 20:30	304	0.21	167.44	23.2
6/10/2003 9:00	305	0.52	167.96	23.1
6/10/2003 13:00	306	0.17	168.12	23.2
6/10/2003 22:00	307	0.38	168.50	23.2
6/11/2003 9:30	308	0.48	168.98	23.0
6/11/2003 13:00	309	0.15	169.12	23.2
6/11/2003 23:30	310	0.44	169.56	23.2
6/12/2003 9:00	311	0.40	169.96	23.0
6/12/2003 13:00	312	0.17	170.12	23.1
6/12/2003 22:00	313	0.38	170.50	23.2
6/13/2003 9:00	314	0.46	170.96	23.0
6/13/2003 14:00	315	0.21	171.17	23.0
6/13/2003 20:30	316	0.27	171.44	23.0
6/14/2003 7:00	317	0.44	171.87	23.0
6/14/2003 19:00	318	0.50	172.37	23.0
6/14/2003 23:00	319	0.17	172.54	23.0
6/15/2003 8:00	320	0.38	172.92	22.9
6/15/2003 12:00	321	0.17	173.08	23.0
6/15/2003 23:00	322	0.46	173.54	23.0
6/16/2003 13:00	323	0.58	174.12	23.0
6/16/2003 17:30	324	0.19	174.31	23.0
6/16/2003 21:00	325	0.15	174.46	23.0
6/17/2003 9:00	326	0.50	174.96	23.0
6/17/2003 17:00	327	0.33	175.29	23.0
6/17/2003 23:00	328	0.25	175.54	23.0
6/18/2003 9:00	329	0.42	175.96	23.0
6/18/2003 14:00	330	0.21	176.17	22.9
6/18/2003 23:00	331	0.38	176.54	22.9
6/19/2003 6:30	332	0.31	176.85	22.8
6/19/2003 16:30	333	0.42	177.27	22.8
6/19/2003 23:00	334	0.27	177.54	22.9
6/20/2003 10:00	335	0.46	178.00	22.8
6/20/2003 15:00	336	0.21	178.21	22.9
6/21/2003 0:00	337	0.38	178.58	22.9
6/21/2003 7:00	338	0.29	178.87	22.8
6/21/2003 14:00	339	0.29	179.17	23.0
6/21/2003 22:00	340	0.33	179.50	22.9
6/22/2003 6:00	341	0.33	179.83	22.9
6/22/2003 15:00	342	0.38	180.21	23.0
6/22/2003 23:00	343	0.33	180.54	23.0
6/23/2003 6:00	344	0.29	180.83	23.0
6/23/2003 14:00	345	0.33	181.17	23.0
6/23/2003 22:00	346	0.33	181.50	22.8
6/24/2003 7:50	347	0.41	181.91	23.0
6/24/2003 13:30	348	0.24	182.15	23.0
6/24/2003 22:00	349	0.35	182.50	23.2
6/25/2003 7:00	350	0.38	182.87	23.1
6/25/2003 14:00	351	0.29	183.17	23.0
6/25/2003 22:00	352	0.33	183.50	23.0
6/26/2003 5:30	353	0.31	183.81	23.2
6/26/2003 17:00	354	0.48	184.29	23.0
6/27/2003 10:00	355	0.71	185.00	23.1
6/27/2003 22:00	356	0.50	185.50	23.1
6/28/2003 9:00	357	0.46	185.96	23.1
6/28/2003 23:00	358	0.58	186.54	22.8
6/29/2003 12:00	359	0.54	187.08	23.0
6/29/2003 22:00	360	0.42	187.50	22.8
6/30/2003 11:00	361	0.54	188.04	22.8
6/30/2003 16:00	362	0.21	188.25	22.7
6/30/2003 23:00	363	0.29	188.54	22.8
7/1/2003 10:00	364	0.46	189.00	22.9
7/1/2003 20:00	365	0.42	189.42	22.9
7/2/2003 5:30	366	0.40	189.81	23.0
7/2/2003 14:00	367	0.35	190.17	23.0
7/2/2003 22:00	368	0.33	190.50	23.0
7/3/2003 10:00	369	0.50	191.00	23.0
7/3/2003 20:00	370	0.42	191.42	23.0
7/4/2003 8:30	371	0.52	191.94	23.0
7/4/2003 21:00	372	0.52	192.46	23.0
7/5/2003 5:30	373	0.35	192.81	23.0
7/5/2003 18:00	374	0.52	193.33	22.9
7/5/2003 23:00	375	0.21	193.54	23.0
7/6/2003 7:00	376	0.33	193.87	23.0
7/6/2003 12:00	377	0.21	194.08	23.0
7/6/2003 18:00	378	0.25	194.33	23.1
7/7/2003 8:40	379	0.61	194.94	23.0

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6/10/2001 9:50	1.60	433.57	7.62	0.13	41.43	0.081	0.096	77.2	0.2	19.5	0.125	0.045
6/10/2001 19:15	0.39	433.97	7.64	0.02	41.45	0.051	0.096	77.2	0.0	19.5	0.000	0.045
6/11/2001 9:05	0.58	434.54	7.70	0.06	41.51	0.104	0.096	77.2	0.0	19.5	0.000	0.045
6/12/2001 9:50	1.03	435.57	7.80	0.10	41.61	0.097	0.096	77.2	0.0	19.5	0.000	0.045
6/12/2001 17:30	0.32	435.89	7.82	0.02	41.63	0.063	0.096	77.1	0.1	19.6	0.313	0.045
6/13/2001 9:40	0.67	436.57	7.89	0.07	41.70	0.104	0.096	77.1	0.0	19.6	0.000	0.045
6/13/2001 20:30	0.45	437.02	7.90	0.01	41.71	0.022	0.095	77.1	0.0	19.6	0.000	0.045
6/14/2001 19:37	0.96	437.98	8.00	0.10	41.81	0.104	0.095	77.1	0.0	19.6	0.000	0.045
6/15/2001 19:40	1.00	438.98	8.10	0.10	41.91	0.100	0.095	77.0	0.1	19.7	0.100	0.045
6/16/2001 12:45	0.71	439.69	8.18	0.08	41.99	0.112	0.095	77.0	0.0	19.7	0.000	0.045
6/16/2001 20:00	0.30	440.00	8.20	0.02	42.01	0.066	0.095	77.0	0.0	19.7	0.000	0.045
6/17/2001 11:50	0.66	440.66	8.24	0.04	42.05	0.061	0.095	77.0	0.0	19.7	0.000	0.045
6/18/2001 9:25	0.90	441.56	8.35	0.11	42.16	0.122	0.095	76.9	0.1	19.8	0.111	0.045
6/19/2001 9:40	1.01	442.57	8.43	0.08	42.24	0.079	0.095	76.9	0.0	19.8	0.000	0.045
6/20/2001 7:30	0.91	443.48	8.51	0.08	42.32	0.088	0.095	76.9	0.0	19.8	0.000	0.045
6/20/2001 20:00	0.52	444.00	8.57	0.06	42.38	0.115	0.095	76.8	0.1	19.9	0.192	0.045
6/22/2001 8:25	1.52	445.51	8.67	0.10	42.48	0.066	0.095	76.7	0.1	20.0	0.066	0.045
6/23/2001 8:10	0.99	446.50	8.73	0.06	42.54	0.061	0.095	76.7	0.0	20.0	0.000	0.045
6/23/2001 20:35	0.52	447.02	8.75	0.02	42.56	0.039	0.095	76.7	0.0	20.0	0.000	0.045
6/24/2001 10:00	0.56	447.58	8.82	0.07	42.63	0.125	0.095	76.6	0.1	20.1	0.179	0.045
6/25/2001 13:45	1.16	448.74	8.89	0.07	42.70	0.061	0.095	76.5	0.1	20.2	0.086	0.045
6/25/2001 21:45	0.33	449.07	8.93	0.04	42.74	0.120	0.095	76.5	0.0	20.2	0.000	0.045
6/27/2001 9:45	1.50	450.57	9.02	0.09	42.83	0.060	0.095	76.5	0.0	20.2	0.000	0.045
6/28/2001 9:20	0.98	451.55	9.10	0.08	42.91	0.081	0.095	76.4	0.1	20.3	0.102	0.045
6/30/2001 20:38	2.47	454.02	9.20	0.10	43.01	0.040	0.095	76.4	0.0	20.3	0.000	0.045
7/1/2001 9:17	0.53	454.55	9.29	0.09	43.10	0.171	0.095	76.4	0.0	20.3	0.000	0.045
7/2/2001 10:07	1.03	455.58	9.35	0.06	43.16	0.058	0.095	76.3	0.1	20.4	0.097	0.045
7/3/2001 9:33	0.98	456.56	9.40	0.05	43.21	0.051	0.095	76.3	0.0	20.4	0.000	0.045
7/4/2001 9:25	0.99	457.56	9.49	0.09	43.30	0.091	0.095	76.2	0.1	20.5	0.101	0.045
7/5/2001 21:42	1.51	459.07	9.53	0.04	43.34	0.026	0.094	76.2	0.0	20.5	0.000	0.045
7/7/2001 9:33	1.49	460.56	9.63	0.10	43.44	0.067	0.094	76.2	0.0	20.5	0.000	0.045
7/7/2001 21:00	0.48	461.04	9.68	0.05	43.49	0.105	0.094	76.1	0.1	20.6	0.210	0.045
7/8/2001 9:59	0.54	461.58	9.70	0.02	43.51	0.037	0.094	76.1	0.0	20.6	0.000	0.045
7/9/2001 9:31	0.98	462.56	9.78	0.08	43.59	0.082	0.094	76.1	0.0	20.6	0.000	0.045
7/10/2001 10:15	1.03	463.59	9.83	0.05	43.64	0.049	0.094	76.1	0.0	20.6	0.000	0.044
7/10/2001 21:27	0.47	464.06	9.87	0.04	43.68	0.086	0.094	76.1	0.0	20.6	0.000	0.044
7/12/2001 16:15	1.78	465.84	9.99	0.12	43.80	0.067	0.094	76.0	0.1	20.7	0.056	0.044
7/13/2001 10:25	0.76	466.60	10.02	0.03	43.83	0.040	0.094	76.0	0.0	20.7	0.000	0.044
7/14/2001 7:52	0.89	467.49	10.09	0.07	43.90	0.078	0.094	76.0	0.0	20.7	0.000	0.044
7/15/2001 7:38	0.99	468.48	10.16	0.07	43.97	0.071	0.094	76.0	0.0	20.7	0.000	0.044
7/15/2001 20:22	0.53	469.01	10.19	0.03	44.00	0.057	0.094	76.0	0.0	20.7	0.000	0.044
7/16/2001 8:52	0.52	469.53	10.23	0.04	44.04	0.077	0.094	75.9	0.1	20.8	0.192	0.044
7/17/2001 8:40	0.99	470.52	10.30	0.07	44.11	0.071	0.094	75.9	0.0	20.8	0.000	0.044
7/18/2001 9:30	1.03	471.56	10.39	0.09	44.20	0.087	0.094	75.9	0.0	20.8	0.000	0.044
7/18/2001 18:26	0.37	471.93	10.40	0.01	44.21	0.027	0.094	75.9	0.0	20.8	0.000	0.044
7/19/2001 9:50	0.64	472.57	10.46	0.06	44.27	0.094	0.094	75.8	0.1	20.9	0.156	0.044
7/20/2001 8:55	0.96	473.53	10.51	0.05	44.32	0.052	0.094	75.8	0.0	20.9	0.000	0.044
7/20/2001 18:15	0.39	473.92	10.53	0.02	44.34	0.051	0.094	75.8	0.0	20.9	0.000	0.044
7/21/2001 8:40	0.60	474.52	10.58	0.05	44.39	0.083	0.094	75.8	0.0	20.9	0.000	0.044
7/21/2001 22:23	0.57	475.10	10.61	0.03	44.42	0.052	0.093	75.7	0.1	21.0	0.175	0.044
7/22/2001 9:03	0.44	475.54	10.66	0.05	44.47	0.112	0.094	75.7	0.0	21.0	0.000	0.044
7/23/2001 8:00	0.96	476.50	10.71	0.05	44.52	0.052	0.093	75.7	0.0	21.0	0.000	0.044
7/24/2001 9:17	1.05	477.55	10.80	0.09	44.61	0.085	0.093	75.7	0.0	21.0	0.000	0.044
7/24/2001 16:40	0.31	477.86	10.81	0.01	44.62	0.033	0.093	75.7	0.0	21.0	0.000	0.044
7/25/2001 8:42	0.67	478.53	10.86	0.05	44.67	0.075	0.093	75.6	0.1	21.1	0.150	0.044
7/26/2001 8:25	0.99	479.51	10.92	0.06	44.73	0.061	0.093	75.6	0.0	21.1	0.000	0.044
7/27/2001 8:53	1.02	480.53	10.97	0.05	44.78	0.049	0.093	75.6	0.0	21.1	0.000	0.044
7/27/2001 15:17	0.27	480.80	11.00	0.03	44.81	0.112	0.093	75.6	0.0	21.1	0.000	0.044
7/28/2001 8:50	0.73	481.53	11.03	0.03	44.84	0.041	0.093	75.6	0.0	21.1	0.000	0.044
7/28/2001 22:15	0.56	482.09	11.06	0.03	44.87	0.054	0.093	75.5	0.1	21.2	0.179	0.044
7/30/2001 8:22	1.42	483.51	11.18	0.12	44.99	0.084	0.093	75.5	0.0	21.2	0.000	0.044
7/30/2001 17:03	0.36	483.87	11.20	0.02	45.01	0.055	0.093	75.5	0.0	21.2	0.000	0.044
7/31/2001 10:38	0.73	484.61	11.26	0.06	45.07	0.082	0.093	75.4	0.1	21.3	0.136	0.044
7/31/2001 17:32	0.29	484.89	11.27	0.01	45.08	0.035	0.093	75.4	0.0	21.3	0.000	0.044
8/2/2001 8:17	1.61	486.51	11.38	0.11	45.19	0.068	0.093	75.3	0.1	21.4	0.062	0.044
8/2/2001 17:05	0.37	486.88	11.40	0.02	45.21	0.055	0.093	75.3	0.0	21.4	0.000	0.044
8/3/2001 7:52	0.62	487.49	11.44	0.04	45.25	0.065	0.093	75.3	0.0	21.4	0.000	0.044
8/3/2001 15:18	0.31	487.80	11.46	0.02	45.27	0.065	0.093	75.3	0.0	21.4	0.000	0.044
8/5/2001 17:50	2.11	489.91	11.53	0.07	45.34	0.033	0.093	75.2	0.1	21.5	0.047	0.044
8/6/2001 15:50	0.92	490.82	11.60	0.07	45.41	0.076	0.093	75.2	0.0	21.5	0.000	0.044
8/7/2001 9:42	0.74	491.57	11.66	0.06	45.47	0.081	0.093	75.2	0.0	21.5	0.000	0.044
8/8/2001 9:07	0.98	492.54	11.70	0.04	45.51	0.041	0.092	75.1	0.1	21.6	0.102	0.044
8/8/2001 17:44	0.36	492.90	11.73	0.03	45.54	0.084	0.092	75.1	0.0	21.6	0.000	0.044
8/9/2001 18:17	1.02	493.93	11.80	0.07	45.61	0.068	0.092	75.1	0.0	21.6	0.000	0.044
8/10/2001 21:30	1.13	495.06	11.88	0.08	45.69	0.071	0.092	75.0	0.1	21.7	0.088	0.044
8/11/2001 10:02	0.52	495.58	11.90	0.02	45.71	0.038	0.092	75.0	0.0	21.7	0.000	0.044
8/11/2001 22:40	0.53	496.11	11.93	0.03	45.74	0.057	0.092	75.0	0.0	21.7	0.000	0.044

7/7/2003 15:00	380	0.26	195.21	22.8
7/7/2003 22:00	381	0.29	195.50	22.8
7/8/2003 9:00	382	0.46	195.96	22.9
7/8/2003 15:00	383	0.25	196.21	22.8
7/8/2003 22:00	384	0.29	196.50	22.8
7/9/2003 2:30	385	0.19	196.69	23.0
7/9/2003 10:00	386	0.31	197.00	23.0
7/9/2003 16:00	387	0.25	197.25	22.8
7/9/2003 23:00	388	0.29	197.54	22.9
7/10/2003 8:00	389	0.38	197.92	23.0
7/10/2003 16:00	390	0.33	198.25	23.0
7/10/2003 22:00	391	0.25	198.50	22.9
7/11/2003 8:30	392	0.44	198.94	23.0
7/11/2003 17:00	393	0.35	199.29	22.7
7/11/2003 23:00	394	0.25	199.54	22.7
7/12/2003 5:30	395	0.27	199.81	22.7
7/12/2003 11:00	396	0.23	200.04	22.7
7/12/2003 17:00	397	0.25	200.29	22.6
7/13/2003 8:00	398	0.63	200.92	22.8
7/13/2003 17:00	399	0.38	201.29	22.8
7/13/2003 23:00	400	0.25	201.54	22.9
7/14/2003 7:00	401	0.33	201.87	23.0
7/14/2003 13:00	402	0.25	202.12	23.0
7/14/2003 22:00	403	0.38	202.50	22.9
7/15/2003 8:00	404	0.42	202.92	22.8
7/15/2003 12:00	405	0.17	203.08	22.8
7/15/2003 22:00	406	0.42	203.50	22.6
7/16/2003 7:00	407	0.38	203.87	22.8
7/16/2003 14:00	408	0.29	204.17	22.8
7/16/2003 22:00	409	0.33	204.50	22.8
7/17/2003 7:00	410	0.38	204.87	22.8
7/17/2003 15:00	411	0.33	205.21	22.7
7/17/2003 22:00	412	0.29	205.50	22.9
7/18/2003 7:00	413	0.38	205.87	23.0
7/18/2003 21:00	414	0.58	206.46	23.4
7/19/2003 6:30	415	0.40	206.85	22.4
7/19/2003 12:30	416	0.25	207.10	22.4
7/19/2003 22:00	417	0.40	207.50	22.4
7/20/2003 4:30	418	0.27	207.77	22.4
7/20/2003 13:00	419	0.35	208.12	22.4
7/20/2003 21:00	420	0.33	208.46	22.5
7/21/2003 8:30	421	0.48	208.94	22.6
7/21/2003 23:30	422	0.63	209.56	22.5
7/22/2003 10:00	423	0.44	210.00	22.6
7/22/2003 23:00	424	0.54	210.54	22.5
7/23/2003 9:00	425	0.42	210.96	22.7
7/23/2003 21:30	426	0.52	211.48	22.6
7/24/2003 9:00	427	0.48	211.96	22.7
7/24/2003 23:00	428	0.58	212.54	22.6
7/25/2003 7:30	429	0.35	212.90	22.7
7/25/2003 16:40	430	0.38	213.28	22.7
7/26/2003 1:00	431	0.35	213.62	22.6
7/26/2003 9:00	432	0.33	213.96	22.7
7/26/2003 23:00	433	0.58	214.54	22.7
7/27/2003 7:00	434	0.33	214.87	22.7
7/27/2003 23:00	435	0.67	215.54	22.7
7/28/2003 8:00	436	0.38	215.92	22.7
7/28/2003 23:30	437	0.65	216.56	22.5
7/29/2003 9:30	438	0.42	216.98	22.7
7/29/2003 20:00	439	0.44	217.42	22.6
7/30/2003 9:00	440	0.54	217.96	22.7
7/30/2003 20:00	441	0.46	218.42	22.6
7/31/2003 9:00	442	0.54	218.96	22.9
7/31/2003 22:00	443	0.54	219.50	22.8
8/1/2003 8:30	444	0.44	219.94	22.9
8/1/2003 22:30	445	0.58	220.52	22.6
8/2/2003 8:30	446	0.42	220.94	22.8
8/2/2003 22:00	447	0.56	221.50	22.7
8/3/2003 10:00	448	0.50	222.00	22.7
8/3/2003 22:00	449	0.50	222.50	22.7
8/4/2003 9:00	450	0.46	222.96	22.7
8/4/2003 23:00	451	0.58	223.54	22.7
8/5/2003 6:00	452	0.29	223.83	23.0
8/5/2003 23:30	453	0.73	224.56	22.8
8/6/2003 9:00	454	0.40	224.96	22.9
8/6/2003 23:00	455	0.58	225.54	22.8
8/7/2003 7:00	456	0.33	225.87	22.8

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8/12/2001 22:33	1.00	497.10	12.00	0.07	45.81	0.070	0.092	75.0	0.0	21.7	0.000	0.044
8/13/2001 8:10	0.40	497.50	12.02	0.02	45.83	0.050	0.092	75.0	0.0	21.7	0.000	0.044
8/13/2001 21:25	0.55	498.06	12.06	0.04	45.87	0.072	0.092	74.9	0.1	21.8	0.181	0.044
8/14/2001 11:25	0.58	498.64	12.10	0.04	45.91	0.069	0.092	74.9	0.0	21.8	0.000	0.044
8/15/2001 8:55	0.90	499.53	12.16	0.06	45.97	0.067	0.092	74.9	0.0	21.8	0.000	0.044
8/15/2001 22:25	0.56	500.10	12.20	0.04	46.01	0.071	0.092	74.9	0.0	21.8	0.000	0.044
8/16/2001 8:05	0.40	500.50	12.24	0.04	46.05	0.099	0.092	74.8	0.1	21.9	0.248	0.044
8/16/2001 21:45	0.57	501.07	12.27	0.03	46.08	0.053	0.092	74.8	0.0	21.9	0.000	0.044
8/17/2001 8:09	0.43	501.50	12.30	0.03	46.11	0.069	0.092	74.8	0.0	21.9	0.000	0.044
8/18/2001 8:33	1.02	502.52	12.38	0.08	46.19	0.079	0.092	74.7	0.1	22.0	0.098	0.044
8/18/2001 16:34	0.33	502.85	12.39	0.01	46.20	0.030	0.092	74.7	0.0	22.0	0.000	0.044
8/19/2001 6:30	0.58	503.43	12.46	0.07	46.27	0.121	0.092	74.7	0.0	22.0	0.000	0.044
8/20/2001 7:38	1.05	504.48	12.53	0.07	46.34	0.067	0.092	74.7	0.0	22.0	0.000	0.044
8/20/2001 16:10	0.36	504.84	12.55	0.02	46.36	0.056	0.092	74.7	0.0	22.0	0.000	0.044
8/21/2001 9:35	0.73	505.56	12.61	0.06	46.42	0.083	0.092	74.6	0.1	22.1	0.138	0.044
8/22/2001 9:17	0.99	506.55	12.69	0.08	46.50	0.081	0.092	74.6	0.0	22.1	0.000	0.044
8/23/2001 9:30	1.01	507.56	12.76	0.07	46.57	0.069	0.092	74.6	0.0	22.1	0.000	0.044
8/24/2001 17:07	1.32	508.88	12.81	0.05	46.62	0.038	0.092	74.5	0.1	22.2	0.076	0.044
8/25/2001 21:19	1.18	510.05	12.93	0.12	46.74	0.102	0.092	74.5	0.0	22.2	0.000	0.044
8/26/2001 9:50	0.52	510.57	12.99	0.06	46.80	0.115	0.092	74.4	0.1	22.3	0.192	0.044
8/27/2001 21:58	1.51	512.08	13.07	0.08	46.88	0.053	0.092	74.4	0.0	22.3	0.000	0.044
8/28/2001 8:39	0.45	512.52	13.11	0.04	46.92	0.090	0.092	74.4	0.0	22.3	0.000	0.044
8/29/2001 7:40	0.96	513.48	13.19	0.08	47.00	0.083	0.092	74.3	0.1	22.4	0.104	0.044
8/29/2001 17:38	0.42	513.90	13.20	0.01	47.01	0.024	0.091	74.3	0.0	22.4	0.000	0.044
8/30/2001 17:00	0.97	514.87	13.29	0.09	47.10	0.092	0.091	74.2	0.1	22.5	0.103	0.044
8/31/2001 7:39	0.61	515.48	13.33	0.04	47.14	0.066	0.091	74.2	0.0	22.5	0.000	0.044
9/1/2001 11:00	1.14	516.62	13.39	0.06	47.20	0.053	0.091	74.1	0.1	22.6	0.088	0.044
9/1/2001 21:56	0.46	517.08	13.41	0.02	47.22	0.044	0.091	74.1	0.0	22.6	0.000	0.044
9/2/2001 10:10	0.51	517.59	13.46	0.05	47.27	0.098	0.091	74.1	0.0	22.6	0.000	0.044
9/3/2001 18:40	1.35	518.94	13.53	0.07	47.34	0.052	0.091	74.0	0.1	22.7	0.074	0.044
9/4/2001 18:57	1.01	519.95	13.60	0.07	47.41	0.069	0.091	74.0	0.0	22.7	0.000	0.044
9/5/2001 7:38	0.53	520.48	13.65	0.05	47.46	0.095	0.091	74.0	0.0	22.7	0.000	0.044
9/5/2001 22:20	0.61	521.09	13.69	0.04	47.50	0.065	0.091	73.9	0.1	22.8	0.163	0.044
9/6/2001 8:59	0.44	521.54	13.73	0.04	47.54	0.090	0.091	73.9	0.0	22.8	0.000	0.044
9/7/2001 7:50	0.95	522.49	13.78	0.05	47.59	0.053	0.091	73.9	0.0	22.8	0.000	0.044
9/7/2001 20:40	0.53	523.02	13.82	0.04	47.63	0.075	0.091	73.9	0.0	22.8	0.000	0.044
9/8/2001 20:04	0.97	524.00	13.90	0.08	47.71	0.082	0.091	73.8	0.1	22.9	0.103	0.044
9/9/2001 20:36	1.02	525.02	13.99	0.09	47.80	0.088	0.091	73.8	0.0	22.9	0.000	0.044
9/10/2001 15:00	0.77	525.79	14.05	0.06	47.86	0.078	0.091	73.8	0.0	22.9	0.000	0.044
9/10/2001 22:19	0.30	526.09	14.08	0.03	47.89	0.098	0.091	73.8	0.0	22.9	0.000	0.044
9/12/2001 11:32	1.55	527.64	14.20	0.12	48.01	0.077	0.091	73.7	0.1	23.0	0.064	0.044
9/14/2001 7:37	1.84	529.48	14.34	0.14	48.15	0.076	0.091	73.6	0.1	23.1	0.054	0.044
9/15/2001 8:50	1.05	530.53	14.39	0.05	48.20	0.048	0.091	73.6	0.0	23.1	0.000	0.044
9/16/2001 8:34	0.99	531.52	14.46	0.07	48.27	0.071	0.091	73.5	0.1	23.2	0.101	0.044
9/17/2001 11:33	1.12	532.64	14.53	0.07	48.34	0.062	0.091	73.5	0.0	23.2	0.000	0.044
9/17/2001 20:55	0.39	533.03	14.56	0.03	48.37	0.077	0.091	73.5	0.0	23.2	0.000	0.044
9/18/2001 19:25	0.94	533.97	14.60	0.04	48.41	0.043	0.091	73.4	0.1	23.3	0.107	0.044
9/19/2001 21:50	1.10	535.07	14.66	0.06	48.47	0.055	0.091	73.4	0.0	23.3	0.000	0.044
9/20/2001 9:26	0.48	535.56	14.70	0.04	48.51	0.083	0.091	73.4	0.0	23.3	0.000	0.044
9/20/2001 22:32	0.55	536.10	14.73	0.03	48.54	0.055	0.091	73.4	0.0	23.3	0.000	0.043
9/22/2001 21:20	1.95	538.05	14.89	0.16	48.70	0.082	0.091	73.3	0.1	23.4	0.051	0.043
9/23/2001 8:35	0.47	538.52	14.92	0.03	48.73	0.064	0.090	73.3	0.0	23.4	0.000	0.043
9/23/2001 19:00	0.43	538.95	14.96	0.04	48.77	0.092	0.090	73.3	0.0	23.4	0.000	0.043
9/24/2001 7:42	0.53	539.48	15.00	0.04	48.81	0.076	0.090	73.3	0.0	23.4	0.000	0.043
9/25/2001 9:36	1.08	540.56	15.08	0.08	48.89	0.074	0.090	73.2	0.1	23.5	0.093	0.043
9/26/2001 15:40	1.25	541.82	15.16	0.08	48.97	0.064	0.090	73.2	0.0	23.5	0.000	0.043
9/27/2001 13:30	0.91	542.73	15.24	0.08	49.05	0.088	0.090	73.1	0.1	23.6	0.110	0.043
9/27/2001 22:52	0.39	543.12	15.27	0.03	49.08	0.077	0.090	73.1	0.0	23.6	0.000	0.043
9/29/2001 14:20	1.64	544.76	15.38	0.11	49.19	0.067	0.090	73.1	0.0	23.6	0.000	0.043
9/30/2001 7:50	0.73	545.49	15.41	0.03	49.22	0.041	0.090	73.0	0.1	23.7	0.137	0.043
9/30/2001 21:50	0.58	546.07	15.46	0.05	49.27	0.086	0.090	73.0	0.0	23.7	0.000	0.043
10/1/2001 11:16	0.56	546.63	15.50	0.04	49.31	0.071	0.090	73.0	0.0	23.7	0.000	0.043
10/2/2001 21:47	1.44	548.07	15.60	0.10	49.41	0.070	0.090	73.0	0.0	23.7	0.000	0.043
10/3/2001 22:00	1.01	549.08	15.68	0.08	49.49	0.079	0.090	72.9	0.1	23.8	0.099	0.043
10/4/2001 9:26	0.48	549.56	15.72	0.04	49.53	0.084	0.090	72.9	0.0	23.8	0.000	0.043
10/5/2001 9:25	1.00	550.56	15.80	0.08	49.61	0.080	0.090	72.9	0.0	23.8	0.000	0.043
10/5/2001 22:59	0.57	551.12	15.85	0.05	49.66	0.088	0.090	72.9	0.0	23.8	0.000	0.043
10/7/2001 11:30	1.52	552.64	16.00	0.15	49.81	0.099	0.090	72.8	0.1	23.9	0.066	0.043
10/7/2001 22:00	0.44	553.08	16.03	0.03	49.84	0.069	0.090	72.8	0.0	23.9	0.000	0.043
10/9/2001 9:13	1.47	554.55	16.14	0.11	49.95	0.075	0.090	72.7	0.1	24.0	0.068	0.043
10/10/2001 9:25	1.01	555.56	16.22	0.08	50.03	0.079	0.090	72.7	0.0	24.0	0.000	0.043
10/10/2001 20:29	0.46	556.02	16.27	0.05	50.08	0.108	0.090	72.7	0.0	24.0	0.000	0.043
10/11/2001 9:33	0.54	556.56	16.32	0.05	50.13	0.092	0.090	72.6	0.1	24.1	0.184	0.043
10/12/2001 11:13	1.07	557.63	16.41	0.09	50.22	0.084	0.090	72.6	0.0	24.1	0.000	0.043
10/12/2001 22:03	0.45	558.08	16.46	0.05	50.27	0.111	0.090	72.6	0.0	24.1	0.000	0.043
10/13/2001 9:20	0.47	558.55	16.50	0.04	50.31	0.085	0.090	72.6	0.0	24.1	0.000	0.043
10/14/2001 6:12	0.87	559.42	16.58	0.08	50.39	0.092	0.090	72.5	0.1	24.2	0.115	0.043

8/7/2003 23:30	457	0.69	226.56	22.7
8/8/2003 3:00	458	0.15	226.71	22.7
8/8/2003 18:00	459	0.63	227.33	22.7
8/9/2003 7:00	460	0.54	227.87	22.7
8/9/2003 23:00	461	0.67	228.54	22.7
8/10/2003 9:00	462	0.42	228.96	22.7
8/10/2003 23:30	463	0.60	229.56	22.7
8/11/2003 7:30	464	0.33	229.90	22.7
8/11/2003 21:30	465	0.58	230.48	22.6
8/12/2003 9:00	466	0.48	230.96	22.7
8/12/2003 23:30	467	0.60	231.56	22.7
8/13/2003 8:30	468	0.38	231.94	22.6
8/13/2003 22:00	469	0.56	232.50	22.7
8/14/2003 9:30	470	0.48	232.98	22.8
8/14/2003 23:30	471	0.58	233.56	22.8
8/15/2003 9:00	472	0.40	233.96	23.0
8/15/2003 23:00	473	0.58	234.54	22.9
8/16/2003 9:00	474	0.42	234.96	22.8
8/16/2003 23:30	475	0.60	235.56	22.8
8/17/2003 9:00	476	0.40	235.96	22.7
8/17/2003 23:00	477	0.58	236.54	22.7
8/18/2003 9:00	478	0.42	236.96	22.8
8/18/2003 22:00	479	0.54	237.50	22.8
8/19/2003 9:00	480	0.46	237.96	22.8
8/19/2003 22:00	481	0.54	238.50	22.8
8/20/2003 9:00	482	0.46	238.96	22.8
8/20/2003 23:00	483	0.58	239.54	22.9
8/21/2003 9:00	484	0.42	239.96	23.0
8/21/2003 23:30	485	0.60	240.56	22.8
8/22/2003 9:00	486	0.40	240.96	22.9
8/22/2003 23:30	487	0.60	241.56	22.9
8/23/2003 9:00	488	0.40	241.96	22.8
8/23/2003 23:30	489	0.60	242.56	22.8
8/24/2003 8:00	490	0.35	242.92	22.9
8/24/2003 23:30	491	0.65	243.56	22.7
8/25/2003 9:00	492	0.40	243.96	22.8
8/25/2003 22:00	493	0.54	244.50	22.8
8/26/2003 9:00	494	0.46	244.96	22.8
8/26/2003 22:30	495	0.56	245.52	22.9
8/27/2003 9:00	496	0.44	245.96	23.0
8/27/2003 22:00	497	0.54	246.50	22.9
8/28/2003 9:00	498	0.46	246.96	22.9
8/28/2003 22:00	499	0.54	247.50	23.0
8/29/2003 9:00	500	0.46	247.96	23.0
8/29/2003 22:30	501	0.56	248.52	22.8
8/30/2003 9:00	502	0.44	248.96	23.0
8/30/2003 21:00	503	0.50	249.46	22.9
8/31/2003 9:00	504	0.50	249.96	22.9
8/31/2003 22:00	505	0.54	250.50	23.0
9/1/2003 9:00	506	0.46	250.96	23.0
9/1/2003 22:00	507	0.54	251.50	23.0
9/2/2003 9:00	508	0.46	251.96	23.0
9/2/2003 23:00	509	0.58	252.54	23.0
9/3/2003 9:00	510	0.42	252.96	23.0
9/3/2003 22:30	511	0.56	253.52	22.9
9/4/2003 9:00	512	0.44	253.96	23.0
9/4/2003 23:00	513	0.58	254.54	22.9
9/5/2003 9:00	514	0.42	254.96	23.0
9/5/2003 22:00	515	0.54	255.50	22.9
9/6/2003 9:30	516	0.48	255.98	23.0
9/6/2003 22:00	517	0.52	256.50	22.9
9/7/2003 9:00	518	0.46	256.96	23.0
9/7/2003 23:00	519	0.58	257.54	23.0
9/8/2003 9:00	520	0.42	257.96	23.0
9/8/2003 22:00	521	0.54	258.50	22.9
9/9/2003 9:00	522	0.46	258.96	23.0
9/9/2003 23:00	523	0.58	259.54	22.8
9/10/2003 9:00	524	0.42	259.96	23.0
9/10/2003 23:30	525	0.60	260.56	23.2
9/11/2003 9:00	526	0.40	260.96	23.2
9/11/2003 23:30	527	0.60	261.56	23.0
9/12/2003 9:00	528	0.40	261.96	23.2
9/12/2003 22:00	529	0.54	262.50	23.0
9/13/2003 9:00	530	0.46	262.96	23.2
9/13/2003 22:30	531	0.56	263.52	23.3
9/14/2003 9:00	532	0.44	263.96	23.3
9/14/2003 23:30	533	0.60	264.56	23.2

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10/14/2001 20:16	0.59	560.01	16.63	0.05	50.44	0.085	0.090	72.5	0.0	24.2	0.000	0.043
10/15/2001 12:15	0.67	560.67	16.69	0.06	50.50	0.090	0.090	72.5	0.0	24.2	0.000	0.043
10/16/2001 8:35	0.85	561.52	16.76	0.07	50.57	0.083	0.090	72.4	0.1	24.3	0.118	0.043
10/17/2001 17:35	1.38	562.90	16.89	0.13	50.70	0.095	0.090	72.4	0.0	24.3	0.000	0.043
10/17/2001 22:17	0.20	563.09	16.90	0.01	50.71	0.051	0.090	72.4	0.0	24.3	0.000	0.043
10/18/2001 13:05	0.62	563.71	16.97	0.07	50.78	0.114	0.090	72.3	0.1	24.4	0.162	0.043
10/20/2001 9:10	1.84	565.55	17.11	0.14	50.92	0.076	0.090	72.2	0.1	24.5	0.054	0.043
10/21/2001 9:46	1.03	566.57	17.20	0.09	51.01	0.088	0.090	72.2	0.0	24.5	0.000	0.043
10/21/2001 21:37	0.49	567.06	17.26	0.06	51.07	0.122	0.090	72.2	0.0	24.5	0.000	0.043
10/22/2001 21:48	1.01	568.07	17.33	0.07	51.14	0.069	0.090	72.2	0.0	24.5	0.000	0.043
10/23/2001 8:25	0.44	568.51	17.39	0.06	51.20	0.136	0.090	72.1	0.1	24.6	0.226	0.043
10/24/2001 11:21	1.12	569.64	17.48	0.09	51.29	0.080	0.090	72.1	0.0	24.6	0.000	0.043
10/25/2001 9:28	0.92	570.56	17.58	0.10	51.39	0.109	0.090	72.0	0.1	24.7	0.109	0.043
10/26/2001 7:41	0.93	571.48	17.67	0.09	51.48	0.097	0.090	72.0	0.0	24.7	0.000	0.043
10/27/2001 21:25	1.57	573.06	17.81	0.14	51.62	0.089	0.090	71.9	0.1	24.8	0.064	0.043
10/28/2001 8:25	0.50	573.56	17.87	0.06	51.68	0.120	0.090	71.9	0.0	24.8	0.000	0.043
10/28/2001 21:01	0.53	574.08	17.91	0.04	51.72	0.076	0.090	71.8	0.1	24.9	0.190	0.043
10/29/2001 13:15	0.68	574.76	17.97	0.06	51.78	0.089	0.090	71.8	0.0	24.9	0.000	0.043
10/30/2001 13:20	1.00	575.76	18.06	0.09	51.87	0.090	0.090	71.8	0.0	24.9	0.000	0.043
10/30/2001 22:05	0.36	576.13	18.10	0.04	51.91	0.110	0.090	71.7	0.1	25.0	0.274	0.043
10/31/2001 11:33	0.56	576.69	18.12	0.02	51.93	0.036	0.090	71.7	0.0	25.0	0.000	0.043
11/1/2001 7:43	0.84	577.53	18.20	0.08	52.01	0.095	0.090	71.6	0.1	25.1	0.119	0.043
11/1/2001 22:31	0.62	578.14	18.26	0.06	52.07	0.097	0.090	71.6	0.0	25.1	0.000	0.043
11/2/2001 20:58	0.94	579.08	18.34	0.08	52.15	0.086	0.090	71.5	0.1	25.2	0.107	0.044
11/3/2001 8:55	0.50	579.58	18.40	0.06	52.21	0.121	0.090	71.5	0.0	25.2	0.000	0.043
11/3/2001 20:10	0.47	580.05	18.43	0.03	52.24	0.064	0.090	71.5	0.0	25.2	0.000	0.043
11/4/2001 9:34	0.56	580.60	18.48	0.05	52.29	0.090	0.090	71.4	0.1	25.3	0.179	0.044
11/4/2001 20:25	0.45	581.06	18.53	0.05	52.34	0.111	0.090	71.4	0.0	25.3	0.000	0.044
11/6/2001 8:45	1.51	582.57	18.66	0.13	52.47	0.086	0.090	71.3	0.1	25.4	0.066	0.044
11/6/2001 22:50	0.59	583.16	18.70	0.04	52.51	0.068	0.090	71.3	0.0	25.4	0.000	0.044
11/7/2001 12:23	0.56	583.72	18.75	0.05	52.56	0.089	0.090	71.3	0.0	25.4	0.000	0.044
11/7/2001 22:47	0.43	584.15	18.79	0.04	52.60	0.092	0.090	71.3	0.0	25.4	0.000	0.043
11/8/2001 9:17	0.44	584.59	18.83	0.04	52.64	0.091	0.090	71.2	0.1	25.5	0.229	0.044
11/9/2001 15:40	1.27	585.86	18.94	0.11	52.75	0.087	0.090	71.2	0.0	25.5	0.000	0.044
11/10/2001 20:22	1.20	587.05	19.06	0.12	52.87	0.100	0.090	71.1	0.1	25.6	0.084	0.044
11/11/2001 23:30	1.13	588.18	19.16	0.10	52.97	0.088	0.090	71.1	0.0	25.6	0.000	0.044
11/12/2001 7:40	0.34	588.52	19.19	0.03	53.00	0.088	0.090	71.1	0.0	25.6	0.000	0.043
11/12/2001 21:59	0.60	589.12	19.23	0.04	53.04	0.067	0.090	71.0	0.1	25.7	0.168	0.044
11/14/2001 11:49	1.58	590.70	19.40	0.17	53.21	0.108	0.090	70.9	0.1	25.8	0.063	0.044
11/14/2001 22:48	0.46	591.15	19.42	0.02	53.23	0.044	0.090	70.9	0.0	25.8	0.000	0.044
11/15/2001 9:47	0.46	591.61	19.47	0.05	53.28	0.109	0.090	70.9	0.0	25.8	0.000	0.044
11/15/2001 21:58	0.51	592.12	19.51	0.04	53.32	0.079	0.090	70.9	0.0	25.8	0.000	0.044
11/16/2001 7:38	0.40	592.52	19.55	0.04	53.36	0.099	0.090	70.8	0.1	25.9	0.248	0.044
11/16/2001 17:30	0.41	592.93	19.58	0.03	53.39	0.073	0.090	70.8	0.0	25.9	0.000	0.044
11/17/2001 10:55	0.73	593.66	19.65	0.07	53.46	0.096	0.090	70.8	0.0	25.9	0.000	0.044
11/17/2001 20:38	0.40	594.06	19.68	0.03	53.49	0.074	0.090	70.7	0.1	26.0	0.247	0.044
11/18/2001 22:35	1.08	595.15	19.77	0.09	53.58	0.083	0.090	70.7	0.0	26.0	0.000	0.044
11/19/2001 20:43	0.92	596.07	19.86	0.09	53.67	0.098	0.090	70.6	0.1	26.1	0.108	0.044
11/20/2001 13:05	0.68	596.75	19.92	0.06	53.73	0.088	0.090	70.6	0.0	26.1	0.000	0.044
11/21/2001 10:40	0.90	597.65	20.00	0.08	53.81	0.089	0.090	70.5	0.1	26.2	0.111	0.044
11/22/2001 10:15	0.98	598.63	20.10	0.10	53.91	0.102	0.090	70.5	0.0	26.2	0.000	0.044
11/23/2001 10:45	1.02	599.65	20.19	0.09	54.00	0.088	0.090	70.4	0.1	26.3	0.098	0.044
11/24/2001 11:10	1.02	600.67	20.30	0.11	54.11	0.108	0.090	70.3	0.1	26.4	0.098	0.044
11/25/2001 10:10	0.96	601.63	20.40	0.10	54.21	0.104	0.090	70.3	0.0	26.4	0.000	0.044
11/27/2001 13:10	2.13	603.75	20.67	0.27	54.48	0.127	0.090	70.2	0.1	26.5	0.047	0.044
11/28/2001 7:28	0.76	604.52	20.76	0.09	54.57	0.118	0.090	70.1	0.1	26.6	0.131	0.044
11/29/2001 13:30	1.25	605.77	20.90	0.14	54.71	0.112	0.090	70.1	0.0	26.6	0.000	0.044
11/30/2001 7:30	0.75	606.52	20.98	0.08	54.79	0.107	0.090	70.0	0.1	26.7	0.133	0.044
12/2/2001 12:55	2.23	608.74	21.20	0.22	55.01	0.099	0.090	69.9	0.1	26.8	0.045	0.044
12/3/2001 7:47	0.79	609.53	21.29	0.09	55.10	0.114	0.090	69.9	0.0	26.8	0.000	0.044
12/4/2001 20:41	1.54	611.07	21.40	0.11	55.21	0.072	0.090	69.8	0.1	26.9	0.065	0.044
12/5/2001 7:35	0.45	611.52	21.50	0.10	55.31	0.220	0.090	69.8	0.0	26.9	0.000	0.044
12/6/2001 11:48	1.18	612.70	21.60	0.10	55.41	0.085	0.090	69.7	0.1	27.0	0.085	0.044
12/7/2001 7:30	0.82	613.52	21.71	0.11	55.52	0.134	0.090	69.7	0.0	27.0	0.000	0.044
12/8/2001 10:02	1.11	614.62	21.80	0.09	55.61	0.081	0.090	69.6	0.1	27.1	0.090	0.044
12/9/2001 11:40	1.07	615.69	21.91	0.11	55.72	0.103	0.090	69.6	0.0	27.1	0.000	0.044
12/10/2001 7:30	0.83	616.52	22.00	0.09	55.81	0.109	0.091	69.6	0.0	27.1	0.000	0.044
12/10/2001 20:45	0.55	617.07	22.09	0.09	55.90	0.163	0.091	69.5	0.1	27.2	0.181	0.044
12/11/2001 9:50	0.55	617.61	22.15	0.06	55.96	0.110	0.091	69.4	0.1	27.3	0.183	0.044
12/13/2001 9:50	2.00	619.61	22.35	0.20	56.16	0.100	0.091	69.3	0.1	27.4	0.050	0.044
12/14/2001 12:22	1.11	620.72	22.52	0.17	56.33	0.154	0.091	69.1	0.2	27.6	0.181	0.044
12/15/2001 9:40	0.89	621.61	22.62	0.10	56.43	0.113	0.091	69.0	0.1	27.7	0.113	0.045
12/16/2001 9:13	0.98	622.59	22.72	0.10	56.53	0.102	0.091	69.0	0.0	27.7	0.000	0.044
12/17/2001 7:00	0.91	623.50	22.80	0.08	56.61	0.088	0.091	68.9	0.1	27.8	0.110	0.045
12/18/2001 6:45	0.99	624.49	22.90	0.10	56.71	0.101	0.091	68.9	0.0	27.8	0.000	0.045
12/18/2001 22:35	0.66	625.15	23.02	0.12	56.83	0.182	0.091	68.8	0.1	27.9	0.152	0.045
12/19/2001 9:00	0.43	625.58	23.07	0.05	56.88	0.115	0.091	68.8	0.0	27.9	0.000	0.045

9/15/2003 9:00	534	0.40	264.96	23.3
9/15/2003 22:00	535	0.54	265.50	23.1
9/16/2003 9:00	536	0.46	265.96	23.2
9/16/2003 23:30	537	0.60	266.56	23.0
9/17/2003 9:00	538	0.40	266.96	23.2
9/17/2003 22:00	539	0.54	267.50	23.2
9/18/2003 9:00	540	0.46	267.96	23.3
9/18/2003 22:00	541	0.54	268.50	23.2
9/19/2003 9:00	542	0.46	268.96	23.3
9/19/2003 22:00	543	0.54	269.50	23.1
9/20/2003 9:00	544	0.46	269.96	23.3
9/20/2003 22:00	545	0.54	270.50	23.1
9/21/2003 9:00	546	0.46	270.96	23.3
9/21/2003 22:00	547	0.54	271.50	23.1
9/22/2003 9:00	548	0.46	271.96	23.3
9/22/2003 22:00	549	0.54	272.50	23.1
9/23/2003 9:00	550	0.46	272.96	23.3
9/23/2003 22:00	551	0.54	273.50	23.1
9/24/2003 9:00	552	0.46	273.96	23.2
9/24/2003 22:00	553	0.54	274.50	23.1
9/25/2003 9:00	554	0.46	274.96	23.3
9/25/2003 22:00	555	0.54	275.50	23.1
9/26/2003 9:00	556	0.46	275.96	23.3
9/26/2003 22:00	557	0.54	276.50	23.1
9/27/2003 9:00	558	0.46	276.96	23.2
9/27/2003 22:00	559	0.54	277.50	23.0
9/28/2003 9:00	560	0.46	277.96	23.3
9/28/2003 22:00	561	0.54	278.50	23.0
9/29/2003 9:00	562	0.46	278.96	23.3
9/29/2003 22:00	563	0.54	279.50	23.1
9/30/2003 9:00	564	0.46	279.96	23.3
9/30/2003 22:00	565	0.54	280.50	23.1
10/1/2003 9:00	566	0.46	280.96	23.3
10/1/2003 22:00	567	0.54	281.50	23.2
10/2/2003 9:00	568	0.46	281.96	23.3
10/2/2003 22:00	569	0.54	282.50	23.1
10/3/2003 9:00	570	0.46	282.96	23.3
10/3/2003 22:00	571	0.54	283.50	23.2
10/4/2003 9:00	572	0.46	283.96	23.3
10/4/2003 22:00	573	0.54	284.50	23.1
10/5/2003 9:00	574	0.46	284.96	23.2

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12/20/2001 9:00	1.00	626.58	23.16	0.09	56.97	0.090	0.091	68.8	0.0	27.9	0.000	0.045
12/20/2001 19:12	0.43	627.00	23.21	0.05	57.02	0.118	0.091	68.7	0.1	28.0	0.235	0.045
12/21/2001 9:27	0.59	627.60	23.28	0.07	57.09	0.118	0.091	68.7	0.0	28.0	0.000	0.045
12/21/2001 20:20	0.45	628.05	23.31	0.03	57.12	0.066	0.091	68.6	0.1	28.1	0.221	0.045
12/22/2001 18:12	0.91	628.96	23.42	0.11	57.23	0.121	0.091	68.6	0.0	28.1	0.000	0.045
12/23/2001 9:28	0.64	629.60	23.50	0.08	57.31	0.126	0.091	68.5	0.1	28.2	0.157	0.045
12/23/2001 20:23	0.45	630.05	23.54	0.04	57.35	0.088	0.091	68.5	0.0	28.2	0.000	0.045
12/24/2001 6:50	0.44	630.49	23.60	0.06	57.41	0.138	0.091	68.4	0.1	28.3	0.230	0.045
12/24/2001 19:50	0.54	631.03	23.65	0.05	57.46	0.092	0.091	68.4	0.0	28.3	0.000	0.045
12/25/2001 20:27	1.03	632.06	23.77	0.12	57.58	0.117	0.091	68.3	0.1	28.4	0.097	0.045
12/26/2001 8:00	0.48	632.54	23.82	0.05	57.63	0.104	0.091	68.3	0.0	28.4	0.000	0.045
12/26/2001 20:02	0.50	633.04	23.88	0.06	57.69	0.120	0.091	68.3	0.0	28.4	0.000	0.045
12/27/2001 7:55	0.50	633.53	23.93	0.05	57.74	0.101	0.091	68.2	0.1	28.5	0.202	0.045
12/27/2001 21:12	0.55	634.09	24.00	0.07	57.81	0.126	0.091	68.2	0.0	28.5	0.000	0.045
12/28/2001 7:50	0.44	634.53	24.05	0.05	57.86	0.113	0.091	68.2	0.0	28.5	0.000	0.045
12/28/2001 20:30	0.53	635.06	24.10	0.05	57.91	0.095	0.091	68.2	0.0	28.5	0.000	0.045
12/29/2001 8:50	0.51	635.57	24.16	0.06	57.97	0.117	0.091	68.1	0.1	28.6	0.195	0.045
12/29/2001 20:11	0.47	636.05	24.20	0.04	58.01	0.085	0.091	68.1	0.0	28.6	0.000	0.045
12/30/2001 7:52	0.49	636.53	24.27	0.07	58.08	0.144	0.091	68.1	0.0	28.6	0.000	0.045
12/30/2001 21:02	0.55	637.08	24.32	0.05	58.13	0.091	0.091	68.1	0.0	28.6	0.000	0.045
12/31/2001 8:50	0.49	637.57	24.38	0.06	58.19	0.122	0.091	68.0	0.1	28.7	0.203	0.045
1/1/2002 8:14	0.97	638.55	24.50	0.12	58.31	0.123	0.091	68.0	0.0	28.7	0.000	0.045
1/1/2002 21:58	0.57	639.12	24.57	0.07	58.38	0.122	0.091	68.0	0.0	28.7	0.000	0.045
1/2/2002 9:25	0.48	639.60	24.61	0.04	58.42	0.084	0.091	67.9	0.1	28.8	0.210	0.045
1/2/2002 21:27	0.50	640.10	24.65	0.04	58.46	0.080	0.091	67.9	0.0	28.8	0.000	0.045
1/3/2002 9:25	0.50	640.60	24.71	0.06	58.52	0.120	0.091	67.9	0.0	28.8	0.000	0.045
1/3/2002 22:08	0.53	641.13	24.78	0.07	58.59	0.132	0.091	67.8	0.1	28.9	0.189	0.045
1/4/2002 9:26	0.47	641.60	24.82	0.04	58.63	0.085	0.091	67.8	0.0	28.9	0.000	0.045
1/4/2002 22:02	0.53	642.12	24.89	0.07	58.70	0.133	0.091	67.8	0.0	28.9	0.000	0.045
1/5/2002 9:03	0.46	642.58	24.93	0.04	58.74	0.087	0.091	67.7	0.1	29.0	0.218	0.045
1/5/2002 20:47	0.49	643.07	24.99	0.06	58.80	0.123	0.091	67.7	0.0	29.0	0.000	0.045
1/6/2002 8:58	0.51	643.58	25.05	0.06	58.86	0.118	0.091	67.7	0.0	29.0	0.000	0.045
1/6/2002 21:18	0.51	644.09	25.10	0.05	58.91	0.097	0.091	67.6	0.1	29.1	0.195	0.045
1/7/2002 8:35	0.47	644.56	25.15	0.05	58.96	0.106	0.091	67.6	0.0	29.1	0.000	0.045
1/7/2002 20:56	0.51	645.08	25.20	0.05	59.01	0.097	0.091	67.5	0.1	29.2	0.194	0.045
1/8/2002 9:18	0.52	645.59	25.25	0.05	59.06	0.097	0.091	67.5	0.0	29.2	0.000	0.045
1/9/2002 9:30	1.01	646.60	25.36	0.11	59.17	0.109	0.092	67.4	0.1	29.3	0.099	0.045
1/9/2002 21:55	0.52	647.12	25.41	0.05	59.22	0.097	0.092	67.4	0.0	29.3	0.000	0.045
1/10/2002 9:40	0.49	647.61	25.47	0.06	59.28	0.123	0.092	67.4	0.0	29.3	0.000	0.045
1/10/2002 21:52	0.51	648.12	25.51	0.04	59.32	0.079	0.092	67.3	0.1	29.4	0.197	0.045
1/11/2002 9:16	0.47	648.59	25.56	0.05	59.37	0.105	0.092	67.3	0.0	29.4	0.000	0.045
1/11/2002 21:43	0.52	649.11	25.61	0.05	59.42	0.096	0.092	67.3	0.0	29.4	0.000	0.045
1/12/2002 9:40	0.50	649.61	25.67	0.06	59.48	0.121	0.092	67.2	0.1	29.5	0.201	0.045
1/13/2002 9:35	1.00	650.60	25.77	0.10	59.58	0.100	0.092	67.2	0.0	29.5	0.000	0.045
1/13/2002 21:12	0.48	651.09	25.81	0.04	59.62	0.083	0.092	67.2	0.0	29.5	0.000	0.045
1/14/2002 20:15	0.96	652.05	25.92	0.11	59.73	0.115	0.092	67.1	0.1	29.6	0.104	0.045
1/15/2002 8:35	0.51	652.56	26.00	0.08	59.81	0.156	0.092	67.1	0.0	29.6	0.000	0.045
1/15/2002 20:25	0.49	653.06	26.05	0.05	59.86	0.101	0.092	67.1	0.0	29.6	0.000	0.045
1/16/2002 9:25	0.54	653.60	26.10	0.05	59.91	0.092	0.092	67.0	0.1	29.7	0.185	0.045
1/16/2002 23:15	0.58	654.17	26.17	0.07	59.98	0.121	0.092	67.0	0.0	29.7	0.000	0.045
1/17/2002 19:50	0.86	655.03	26.27	0.10	60.08	0.117	0.092	67.0	0.0	29.7	0.000	0.045
1/18/2002 9:19	0.56	655.59	26.34	0.07	60.15	0.125	0.092	66.9	0.1	29.8	0.178	0.045
1/18/2002 19:35	0.43	656.02	26.39	0.05	60.20	0.117	0.092	66.9	0.0	29.8	0.000	0.045
1/19/2002 9:50	0.59	656.61	26.46	0.07	60.27	0.118	0.092	66.9	0.0	29.8	0.000	0.045
1/19/2002 22:27	0.53	657.14	26.51	0.05	60.32	0.095	0.092	66.8	0.1	29.9	0.190	0.046
1/20/2002 21:05	0.94	658.08	26.62	0.11	60.43	0.117	0.092	66.8	0.0	29.9	0.000	0.045
1/21/2002 10:01	0.54	658.62	26.69	0.07	60.50	0.130	0.092	66.7	0.1	30.0	0.186	0.046
1/21/2002 21:45	0.49	659.11	26.74	0.05	60.55	0.102	0.092	66.7	0.0	30.0	0.000	0.046
1/22/2002 23:07	1.06	660.17	26.86	0.12	60.67	0.114	0.092	66.7	0.0	30.0	0.000	0.045
1/23/2002 22:15	0.96	661.13	26.97	0.11	60.78	0.114	0.092	66.6	0.1	30.1	0.104	0.046
1/24/2002 18:53	0.86	661.99	27.07	0.10	60.88	0.116	0.092	66.5	0.1	30.2	0.116	0.046
1/25/2002 9:10	0.60	662.59	27.13	0.06	60.94	0.101	0.092	66.5	0.0	30.2	0.000	0.046
1/25/2002 23:35	0.60	663.19	27.19	0.06	61.00	0.100	0.092	66.4	0.1	30.3	0.166	0.046
1/26/2002 10:08	0.44	663.63	27.27	0.08	61.08	0.182	0.092	66.4	0.0	30.3	0.000	0.046
1/26/2002 21:08	0.46	664.09	27.30	0.03	61.11	0.065	0.092	66.4	0.0	30.3	0.000	0.046
1/27/2002 8:50	0.49	664.57	27.36	0.06	61.17	0.123	0.092	66.3	0.1	30.4	0.205	0.046
1/27/2002 22:23	0.56	665.14	27.41	0.05	61.22	0.089	0.092	66.3	0.0	30.4	0.000	0.046
1/28/2002 23:45	1.06	666.19	27.53	0.12	61.34	0.114	0.092	66.2	0.1	30.5	0.095	0.046
1/29/2002 11:57	0.51	666.70	27.60	0.07	61.41	0.138	0.092	66.2	0.0	30.5	0.000	0.046
1/29/2002 23:15	0.47	667.17	27.65	0.05	61.46	0.106	0.092	66.1	0.1	30.6	0.212	0.046
1/30/2002 19:53	0.86	668.03	27.74	0.09	61.55	0.105	0.092	66.1	0.0	30.6	0.000	0.046
1/31/2002 8:36	0.53	668.56	27.81	0.07	61.62	0.132	0.092	66.0	0.1	30.7	0.189	0.046
1/31/2002 22:35	0.58	669.15	27.88	0.07	61.69	0.120	0.092	66.0	0.0	30.7	0.000	0.046
2/1/2002 17:27	0.79	669.93	27.97	0.09	61.78	0.114	0.092	66.0	0.0	30.7	0.000	0.046
2/1/2002 23:35	0.26	670.19	28.00	0.03	61.81	0.117	0.092	66.0	0.0	30.7	0.000	0.046
2/2/2002 22:19	0.95	671.13	28.10	0.10	61.91	0.106	0.092	65.9	0.1	30.8	0.106	0.046
2/3/2002 9:25	0.46	671.60	28.16	0.06	61.97	0.130	0.092	65.9	0.0	30.8	0.000	0.046

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2/3/2002 19:20	0.41	672.01	28.20	0.04	62.01	0.097	0.092	65.9	0.0	30.8	0.000	0.046					
2/4/2002 9:15	0.58	672.59	28.28	0.08	62.09	0.138	0.092	65.8	0.1	30.9	0.172	0.046					
2/4/2002 22:26	0.55	673.14	28.32	0.04	62.13	0.073	0.092	65.8	0.0	30.9	0.000	0.046					
2/5/2002 23:10	1.03	674.17	28.45	0.13	62.26	0.126	0.092	65.7	0.1	31.0	0.097	0.046					
2/6/2002 23:28	1.01	675.18	28.57	0.12	62.38	0.119	0.092	65.7	0.0	31.0	0.000	0.046					
2/7/2002 23:50	1.02	676.20	28.67	0.10	62.48	0.098	0.092	65.6	0.1	31.1	0.098	0.046					
2/8/2002 8:55	0.38	676.58	28.71	0.04	62.52	0.106	0.092	65.6	0.0	31.1	0.000	0.046					
2/9/2002 0:33	0.65	677.23	28.80	0.09	62.61	0.138	0.092	65.5	0.1	31.2	0.154	0.046					
2/9/2002 17:15	0.70	677.92	28.88	0.08	62.69	0.115	0.092	65.5	0.0	31.2	0.000	0.046					
2/10/2002 22:12	1.21	679.13	29.01	0.13	62.82	0.108	0.093	65.4	0.1	31.3	0.083	0.046					
2/11/2002 8:59	0.45	679.58	29.08	0.07	62.89	0.156	0.093	65.4	0.0	31.3	0.000	0.046					
2/11/2002 20:32	0.48	680.06	29.12	0.04	62.93	0.083	0.093	65.3	0.1	31.4	0.208	0.046					
2/12/2002 8:24	0.49	680.55	29.19	0.07	63.00	0.142	0.093	65.3	0.0	31.4	0.000	0.046					
2/12/2002 22:10	0.57	681.13	29.24	0.05	63.05	0.087	0.093	65.2	0.1	31.5	0.174	0.046					
2/13/2002 9:10	0.46	681.59	29.30	0.06	63.11	0.131	0.093	65.2	0.0	31.5	0.000	0.046					
2/13/2002 22:32	0.56	682.14	29.36	0.06	63.17	0.108	0.093	65.1	0.1	31.6	0.180	0.046					
2/14/2002 16:39	0.75	682.90	29.45	0.09	63.26	0.119	0.093	65.1	0.0	31.6	0.000	0.046					
2/15/2002 8:52	0.68	683.57	29.52	0.07	63.33	0.104	0.093	65.1	0.0	31.6	0.000	0.046					
2/17/2002 1:40	1.70	685.27	29.70	0.18	63.51	0.106	0.093	65.0	0.1	31.7	0.059	0.046					
2/17/2002 12:05	0.43	685.71	29.75	0.05	63.56	0.115	0.093	65.0	0.0	31.7	0.000	0.046					
2/18/2002 9:14	0.88	686.59	29.84	0.09	63.65	0.102	0.093	64.9	0.1	31.8	0.113	0.046					
2/18/2002 22:45	0.56	687.15	29.90	0.06	63.71	0.107	0.093	64.9	0.0	31.8	0.000	0.046					
2/19/2002 8:42	0.41	687.57	29.95	0.05	63.76	0.121	0.093	64.9	0.0	31.8	0.000	0.046					
2/20/2002 9:05	1.02	688.58	30.06	0.11	63.87	0.108	0.093	64.8	0.1	31.9	0.098	0.046					
2/21/2002 0:22	0.64	689.22	30.12	0.06	63.93	0.094	0.093	64.8	0.0	31.9	0.000	0.046					
2/21/2002 12:40	0.51	689.73	30.17	0.05	63.98	0.098	0.093	64.7	0.1	32.0	0.195	0.046					
2/21/2002 22:10	0.40	690.13	30.21	0.04	64.02	0.101	0.093	64.7	0.0	32.0	0.000	0.046					
2/22/2002 12:13	0.59	690.71	30.29	0.08	64.10	0.137	0.093	64.7	0.0	32.0	0.000	0.046					
2/22/2002 22:33	0.43	691.14	30.32	0.03	64.13	0.070	0.093	64.6	0.1	32.1	0.232	0.046					
2/23/2002 8:50	0.43	691.57	30.38	0.06	64.19	0.140	0.093	64.6	0.0	32.1	0.000	0.046					
2/23/2002 18:30	0.40	691.98	30.41	0.03	64.22	0.074	0.093	64.6	0.0	32.1	0.000	0.046					
2/24/2002 20:03	1.06	693.04	30.54	0.13	64.35	0.122	0.093	64.5	0.1	32.2	0.094	0.046					
2/25/2002 6:54	0.45	693.49	30.60	0.06	64.41	0.133	0.093	64.5	0.0	32.2	0.000	0.046					
2/25/2002 14:37	0.32	693.81	30.63	0.03	64.44	0.093	0.093	64.5	0.0	32.2	0.000	0.046					
2/25/2002 23:52	0.39	694.20	30.69	0.06	64.50	0.156	0.093	64.5	0.0	32.2	0.000	0.046					
2/26/2002 9:01	0.38	694.58	30.73	0.04	64.54	0.105	0.093	64.4	0.1	32.3	0.262	0.047					
2/26/2002 15:30	0.27	694.85	30.75	0.02	64.56	0.074	0.093	64.4	0.0	32.3	0.000	0.046					
2/27/2002 0:50	0.39	695.24	30.79	0.04	64.60	0.103	0.093	64.4	0.0	32.3	0.000	0.046					
2/28/2002 2:45	1.08	696.32	30.92	0.13	64.73	0.120	0.093	64.3	0.1	32.4	0.093	0.047					
2/28/2002 11:05	0.35	696.67	30.96	0.04	64.77	0.115	0.093	64.3	0.0	32.4	0.000	0.047					
3/1/2002 5:03	0.75	697.42	31.05	0.09	64.86	0.120	0.093	64.2	0.1	32.5	0.134	0.047					
3/2/2002 2:48	0.91	698.32	31.15	0.10	64.96	0.110	0.093	64.2	0.0	32.5	0.000	0.047					
3/2/2002 7:08	0.18	698.50	31.17	0.02	64.98	0.111	0.093	64.2	0.0	32.5	0.000	0.047					
3/2/2002 14:05	0.29	698.79	31.20	0.03	65.01	0.104	0.093	64.1	0.1	32.6	0.345	0.047					
3/3/2002 13:42	0.98	699.78	31.39	0.19	65.20	0.193	0.093	64.1	0.0	32.6	0.000	0.047					
3/4/2002 6:40	0.71	700.48	31.44	0.05	65.25	0.071	0.093	64.1	0.0	32.6	0.000	0.047					
3/4/2002 22:55	0.68	701.16	31.50	0.06	65.31	0.089	0.093	64.0	0.1	32.7	0.148	0.047					
3/5/2002 17:50	0.79	701.95	31.58	0.08	65.39	0.101	0.093	64.0	0.0	32.7	0.000	0.047					
3/6/2002 8:55	0.63	702.58	31.66	0.08	65.47	0.127	0.093	63.9	0.1	32.8	0.159	0.047					
3/6/2002 23:00	0.59	703.16	31.71	0.05	65.52	0.085	0.093	63.9	0.0	32.8	0.000	0.047					
3/7/2002 8:40	0.40	703.57	31.76	0.05	65.57	0.124	0.093	63.9	0.0	32.8	0.000	0.047					
3/7/2002 22:10	0.56	704.13	31.80	0.04	65.61	0.071	0.093	63.8	0.1	32.9	0.178	0.047					
3/8/2002 8:55	0.45	704.58	31.86	0.06	65.67	0.134	0.093	63.8	0.0	32.9	0.000	0.047					
3/8/2002 19:33	0.44	705.02	31.90	0.04	65.71	0.090	0.093	63.7	0.1	33.0	0.226	0.047					
3/9/2002 9:45	0.59	705.61	31.96	0.06	65.77	0.101	0.093	63.7	0.0	33.0	0.000	0.047					
3/9/2002 22:47	0.54	706.15	31.99	0.03	65.80	0.055	0.093	63.6	0.1	33.1	0.184	0.047					
3/10/2002 12:10	0.56	706.71	32.10	0.11	65.91	0.197	0.093	63.6	0.0	33.1	0.000	0.047					
3/11/2002 10:15	0.92	707.63	32.13	0.03	65.94	0.033	0.093	63.5	0.1	33.2	0.109	0.047					
3/11/2002 23:20	0.55	708.18	32.22	0.09	66.03	0.165	0.093	63.5	0.0	33.2	0.000	0.047					
3/12/2002 10:23	0.46	708.64	32.30	0.08	66.11	0.174	0.093	63.4	0.1	33.3	0.217	0.047					
3/12/2002 23:55	0.56	709.20	32.35	0.05	66.16	0.089	0.093	63.4	0.0	33.3	0.000	0.047					
3/13/2002 11:57	0.50	709.70	32.39	0.04	66.20	0.080	0.093	63.3	0.1	33.4	0.199	0.047					
3/14/2002 0:05	0.51	710.21	32.44	0.05	66.25	0.099	0.093	63.2	0.1	33.5	0.198	0.047					
3/14/2002 9:35	0.40	710.60	32.48	0.04	66.29	0.101	0.093	63.2	0.0	33.5	0.000	0.047					
3/14/2002 23:15	0.57	711.17	32.55	0.07	66.36	0.123	0.093	63.1	0.1	33.6	0.176	0.047					
3/15/2002 9:16	0.42	711.59	32.59	0.04	66.40	0.096	0.093	63.1	0.0	33.6	0.000	0.047					
3/15/2002 20:33	0.47	712.06	32.65	0.06	66.46	0.128	0.093	63.1	0.0	33.6	0.000	0.047					
3/16/2002 13:20	0.70	712.76	32.76	0.11	66.57	0.157	0.093	63.1	0.0	33.6	0.000	0.047					
3/16/2002 21:25	0.34	713.10	32.83	0.07	66.64	0.208	0.093	63.1	0.0	33.6	0.000	0.047					
3/17/2002 9:06	0.49	713.58	32.90	0.07	66.71	0.144	0.093	63.1	0.0	33.6	0.000	0.047					
3/17/2002 21:10	0.50	714.09	32.96	0.06	66.77	0.119	0.094	63.1	0.0	33.6	0.000	0.047					
3/18/2002 9:00	0.49	714.58	33.00	0.04	66.81	0.081	0.093	63.0	0.1	33.7	0.203	0.047					
3/18/2002 19:42	0.45	715.03	33.03	0.03	66.84	0.067	0.093	63.0	0.0	33.7	0.000	0.047					
3/19/2002 8:22	0.53	715.55	33.08	0.05	66.89	0.095	0.093	63.0	0.0	33.7	0.000	0.047					
3/19/2002 21:03	0.53	716.08	33.12	0.04	66.93	0.076	0.093	63.0	0.0	33.7	0.000	0.047					
3/20/2002 9:12	0.51	716.59	33.18	0.06	66.99	0.119	0.093	63.0	0.0	33.7	0.000	0.047					
3/20/2002 23:52	0.61	717.20	33.24	0.06	67.05	0.098	0.093	62.9	0.1	33.8	0.164	0.047					

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3/21/2002 8:18	0.35	717.55	33.29	0.05	67.10	0.142	0.094	62.9	0.0	33.8	0.000	0.047					
3/21/2002 22:52	0.61	718.16	33.36	0.07	67.17	0.115	0.094	62.9	0.0	33.8	0.000	0.047					
3/22/2002 8:30	0.40	718.56	33.41	0.05	67.22	0.125	0.094	62.9	0.0	33.8	0.000	0.047					
3/22/2002 21:32	0.54	719.10	33.46	0.05	67.27	0.092	0.094	62.8	0.1	33.9	0.184	0.047					
3/23/2002 10:01	0.52	719.62	33.51	0.05	67.32	0.096	0.094	62.8	0.0	33.9	0.000	0.047					
3/24/2002 12:05	1.09	720.71	33.63	0.12	67.44	0.110	0.094	62.8	0.0	33.9	0.000	0.047					
3/25/2002 0:03	0.50	721.21	33.68	0.05	67.49	0.100	0.094	62.8	0.0	33.9	0.000	0.047					
3/25/2002 12:06	0.50	721.71	33.72	0.04	67.53	0.080	0.094	62.7	0.1	34.0	0.199	0.047					
3/26/2002 8:41	0.86	722.57	33.82	0.10	67.63	0.117	0.094	62.7	0.0	34.0	0.000	0.047					
3/26/2002 22:30	0.58	723.14	33.88	0.06	67.69	0.104	0.094	62.7	0.0	34.0	0.000	0.047					
3/27/2002 8:43	0.43	723.57	33.92	0.04	67.73	0.094	0.094	62.6	0.1	34.1	0.235	0.047					
3/28/2002 8:55	1.01	724.58	34.03	0.11	67.84	0.109	0.094	62.6	0.0	34.1	0.000	0.047					
3/29/2002 11:15	1.10	725.67	34.12	0.09	67.93	0.082	0.094	62.5	0.1	34.2	0.091	0.047					
3/29/2002 23:50	0.52	726.20	34.16	0.04	67.97	0.076	0.094	62.4	0.1	34.3	0.191	0.047					
3/30/2002 11:28	0.48	726.68	34.22	0.06	68.03	0.124	0.094	62.4	0.0	34.3	0.000	0.047					
3/31/2002 11:35	1.00	727.69	34.33	0.11	68.14	0.109	0.094	62.3	0.1	34.4	0.100	0.047					
3/31/2002 21:35	0.42	728.10	34.37	0.04	68.18	0.096	0.094	62.3	0.0	34.4	0.000	0.047					
4/1/2002 9:02	0.48	728.58	34.42	0.05	68.23	0.105	0.094	62.3	0.0	34.4	0.000	0.047					
4/2/2002 12:55	1.16	729.74	34.55	0.13	68.36	0.112	0.094	62.2	0.1	34.5	0.086	0.047					
4/2/2002 19:30	0.27	730.02	34.59	0.04	68.40	0.146	0.094	62.1	0.1	34.6	0.365	0.047					
4/3/2002 8:55	0.56	730.58	34.64	0.05	68.45	0.089	0.094	62.1	0.0	34.6	0.000	0.047					
4/4/2002 8:45	0.99	731.57	34.75	0.11	68.56	0.111	0.094	62.0	0.1	34.7	0.101	0.047					
4/4/2002 22:50	0.59	732.16	34.80	0.05	68.61	0.085	0.094	62.0	0.0	34.7	0.000	0.047					
4/5/2002 20:00	0.88	733.04	34.90	0.10	68.71	0.113	0.094	62.0	0.0	34.7	0.000	0.047					
4/7/2002 6:33	1.40	734.44	35.01	0.11	68.82	0.079	0.094	61.9	0.1	34.8	0.072	0.047					
4/8/2002 9:00	1.10	735.54	35.12	0.11	68.93	0.100	0.094	61.8	0.1	34.9	0.091	0.047					
4/8/2002 21:43	0.53	736.07	35.17	0.05	68.98	0.094	0.094	61.8	0.0	34.9	0.000	0.047					
4/9/2002 8:16	0.44	736.51	35.20	0.03	69.01	0.068	0.094	61.7	0.1	35.0	0.227	0.048					
4/9/2002 15:35	0.30	736.81	35.22	0.02	69.03	0.066	0.094	61.7	0.0	35.0	0.000	0.048					
4/10/2002 9:10	0.73	737.55	35.30	0.08	69.11	0.109	0.094	61.7	0.0	35.0	0.000	0.047					
4/10/2002 23:05	0.58	738.13	35.34	0.04	69.15	0.069	0.094	61.7	0.0	35.0	0.000	0.047					
4/11/2002 23:45	1.03	739.15	35.45	0.11	69.26	0.107	0.094	61.6	0.1	35.1	0.097	0.047					
4/12/2002 20:28	0.86	740.02	35.53	0.08	69.34	0.093	0.094	61.6	0.0	35.1	0.000	0.047					
4/13/2002 8:45	0.51	740.53	35.58	0.05	69.39	0.098	0.094	61.5	0.1	35.2	0.195	0.048					
4/14/2002 9:30	1.03	741.56	35.68	0.10	69.49	0.097	0.094	61.5	0.0	35.2	0.000	0.047					
4/14/2002 22:30	0.54	742.10	35.72	0.04	69.53	0.074	0.094	61.4	0.1	35.3	0.185	0.048					
4/15/2002 22:50	1.01	743.11	35.80	0.08	69.61	0.079	0.094	61.4	0.0	35.3	0.000	0.048					
4/16/2002 8:30	0.40	743.52	35.86	0.06	69.67	0.149	0.094	61.3	0.1	35.4	0.248	0.048					
4/17/2002 23:45	1.64	745.15	36.02	0.16	69.83	0.098	0.094	61.3	0.0	35.4	0.000	0.048					
4/18/2002 8:20	0.36	745.51	36.06	0.04	69.87	0.112	0.094	61.2	0.1	35.5	0.280	0.048					
4/19/2002 8:46	1.02	746.53	36.17	0.11	69.98	0.108	0.094	61.2	0.0	35.5	0.000	0.048					
4/19/2002 19:30	0.45	746.98	36.20	0.03	70.01	0.067	0.094	61.2	0.0	35.5	0.000	0.048					
4/20/2002 12:08	0.69	747.67	36.28	0.08	70.09	0.115	0.094	61.1	0.1	35.6	0.144	0.048					
4/20/2002 18:51	0.28	747.95	36.30	0.02	70.11	0.071	0.094	61.0	0.1	35.7	0.357	0.048					
4/22/2002 8:52	1.58	749.53	0.80	0.26	70.37	0.164	0.094	61.0	0.0	35.7	0.000	0.048					
4/22/2002 20:40	0.49	750.02	0.89	0.09	70.46	0.183	0.094	61.0	0.0	35.7	0.000	0.048					
4/23/2002 21:00	1.01	751.04	1.03	0.14	70.60	0.138	0.094	61.0	0.0	35.7	0.000	0.048					
4/24/2002 19:00	0.92	751.95	1.13	0.10	70.70	0.109	0.094	60.9	0.1	35.8	0.109	0.048					
4/25/2002 8:20	0.56	752.51	1.20	0.07	70.77	0.126	0.094	60.9	0.0	35.8	0.000	0.048					
4/26/2002 16:06	1.32	753.83	1.40	0.20	70.97	0.151	0.094	60.8	0.1	35.9	0.076	0.048					
4/27/2002 1:13	0.38	754.21	1.43	0.03	71.00	0.079	0.094	60.8	0.0	35.9	0.000	0.048					
4/28/2002 11:00	1.41	755.62	1.58	0.15	71.15	0.107	0.094	60.7	0.1	36.0	0.071	0.048					
4/29/2002 8:50	0.91	756.53	1.68	0.10	71.25	0.110	0.094	60.7	0.0	36.0	0.000	0.048					
4/30/2002 0:10	0.64	757.17	1.75	0.07	71.32	0.110	0.094	60.6	0.1	36.1	0.157	0.048					
4/30/2002 8:52	0.36	757.53	1.80	0.05	71.37	0.138	0.094	60.6	0.0	36.1	0.000	0.048					
4/30/2002 20:25	0.48	758.01	1.85	0.05	71.42	0.104	0.094	60.5	0.1	36.2	0.208	0.048					
5/1/2002 11:13	0.62	758.63	1.90	0.05	71.47	0.081	0.094	60.5	0.0	36.2	0.000	0.048					
5/1/2002 15:20	0.17	758.80	1.92	0.02	71.49	0.117	0.094	60.5	0.0	36.2	0.000	0.048					

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APPENDIX C

PROPERTIES OF BENTONITES

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Table C.1 – Specific Gravity of Bentonites Taken from Two GCLs.

Specific Gravity Measurements (ASTM D 854)							
Lower Quality Bentonite (LQB)							
Test Number	$V_{pycnometer}$ (mL)	$M_{pycnometer}$ (g)	$M_{pycnometer+water}$ (g)	M_{soil} (g)	$M_{pycnometer+water+soil}$ (g)	Temperature (°C)	Specific Gravity G_s
1	1000	258.72	1255.15	30.52	1274.53	22.7	2.740
2	1000	252.32	1249.02	29.45	1267.72	22.7	2.740
3	1000	258.72	1255.15	24.15	1270.48	22.7	2.738
						Avg:	**2.74**
Higher Quality Bentonite (HQB)							
Test Number	$V_{pycnometer}$ (mL)	$M_{pycnometer}$ (g)	$M_{pycnometer+water}$ (g)	M_{soil} (g)	$M_{pycnometer+water+soil}$ (g)	Temperature (°C)	Specific Gravity G_s
1	1000	252.32	1254.22	32.79	1275.20	22.7	2.776
2	1000	258.72	1255.15	31.99	1275.65	22.7	2.784
						Avg:	**2.78**

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Table C.2 – Sieve Analysis of Air-Dried Bentonites Taken from Two GCLs.

Sieve Analysis for Air-Dried Bentonite (ASTM D 422)
Lower Quality Bentonite (LQB)
Test No. 1

Sample Mass:	315	g		Dry Mass:	305.6	g
Sieve	Size of Opening (mm)	Mass of Sieve (g)	Mass of Soil and Sieve (g)	Mass of Soil (g)	% retained	% passing
#10	2.00	386.50	386.50	0.00	0.0	100.0
#20	0.85	388.80	391.80	3.00	1.0	99.0
#40	0.425	346.30	397.40	51.10	17.7	82.3
#60	0.25	375.40	471.70	96.30	49.2	50.8
#100	0.15	351.60	424.80	73.20	73.2	26.8
#200	0.075	345.25	402.28	57.03	91.8	8.2
Pan		288.56	312.30	23.74	100.0	
Sum		2482.41	2786.78	304.37		

Test No. 2

Sample Mass:	300	g		Dry Mass:	292.7	g
Sieve	Size of Opening (mm)	Mass of Sieve (g)	Mass of Soil and Sieve (g)	Mass of Soil (g)	% retained	% passing
#10	2.00	436.3	436.3	0.00	0.0	100.0
#20	0.85	388.80	392.35	3.55	1.2	98.8
#40	0.425	346.30	400.70	54.40	19.8	80.2
#60	0.25	375.40	465.20	89.80	50.5	49.5
#100	0.15	351.60	423.90	72.30	75.2	24.8
#200	0.075	345.25	395.28	50.03	92.3	7.7
Pan		301.56	324.10	22.54	100.0	
Sum		2545.21	2837.83	292.62		

Test No. 3

Sample Mass:	372.6	g		Dry Mass:	363.6	g
Sieve	Size of Opening (mm)	Mass of Sieve (g)	Mass of Soil and Sieve (g)	Mass of Soil (g)	% retained	% passing
#10	2.00	466.20	466.20	0.00	0.0	100.0
#20	0.85	372.70	375.50	2.80	0.8	99.2
#40	0.425	399.20	452.40	53.20	15.4	84.6
#60	0.25	320.60	433.60	113.00	46.5	53.5
#100	0.15	353.30	443.70	90.40	71.4	28.6
#200	0.075	344.50	416.90	72.40	91.3	8.7
Pan		283.70	315.40	31.70	100.0	
Sum		2540.20	2903.70	363.50		

Higher Quality Bentonite (HQB)
Test No. 1

Sample Mass:	346.75	g		Dry Mass:	335.4	g
Sieve	Size of Opening (mm)	Mass of Sieve (g)	Mass of Soil and Sieve (g)	Mass of Soil (g)	% retained	% passing
#10	2.00	466.2	468.3	2.10	0.6	99.4
#20	0.85	372.70	530.50	157.80	47.7	52.3
#40	0.425	399.10	518.60	119.50	83.3	16.7
#60	0.25	320.60	346.90	26.30	91.1	8.9
#100	0.15	353.30	364.20	10.90	94.4	5.6
#200	0.075	344.50	356.00	11.50	97.8	2.2
Pan		283.76	290.88	7.12	100.0	
Sum		2540.16	2875.38	335.22		

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Table C.3 – Hydrometer Analysis of Bentonites Taken from Two GCLs.

Hydrometer Test (ASTM D 422)

Hydrometer: 152H, ID #: 887246

Dispersing Agent: 5 g of Sodium Hexametaphosphate $(NaPO3)_6$

Hydrometer Calibration: Reading for Deionized Water = 0.0 and 50 g/L of KCl = 50.0

Lower Quality Bentonite (LQB)

Test No. 1

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	22.5	5.5	33.20	27.70	11.76	5.88	0.01265	0.03066	91.48
5	22.5	5.5	32.60	27.10	11.86	2.37	0.01265	0.01947	89.49
15	22.5	5.5	32.10	26.60	11.94	0.80	0.01265	0.01128	87.84
30	22.5	5.5	31.80	26.30	11.99	0.40	0.01265	0.00799	86.85
60	22.5	5.5	31.40	25.90	12.05	0.20	0.01265	0.00567	85.53
250	22.5	5.5	30.50	25.00	12.20	0.05	0.01265	0.00279	82.56
1440	22.5	5.5	28.00	22.50	12.61	0.01	0.01265	0.00118	74.30
2870	22.5	5.5	27.00	21.50	12.77	0.00	0.01265	0.00084	71.00
4293	22.5	5.5	26.10	20.60	12.92	0.00	0.01265	0.00069	68.03

Test No. 2

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	22.5	5.1	33.00	27.90	11.72	5.86	0.01265	0.03062	92.14
5	22.5	5.1	32.20	27.10	11.86	2.37	0.01265	0.01947	89.49
15	22.5	5.1	32.00	26.90	11.89	0.79	0.01265	0.01126	88.83
30	22.5	5.1	31.20	26.10	12.02	0.40	0.01265	0.00800	86.19
60	22.5	5.1	30.80	25.70	12.09	0.20	0.01265	0.00568	84.87
250	22.5	5.1	29.70	24.60	12.27	0.05	0.01265	0.00280	81.24
1440	22.5	5.1	27.00	21.90	12.71	0.01	0.01265	0.00119	72.32
2932	22.5	5.1	25.80	20.70	12.91	0.00	0.01265	0.00084	68.36
4280	22.5	5.1	24.80	19.70	13.07	0.00	0.01265	0.00070	65.06

Test No. 3

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	22.5	5.5	33.20	27.70	11.76	5.88	0.01265	0.03066	93.95
5	22.5	5.5	32.60	27.10	11.86	2.37	0.01265	0.01947	91.92
15	22.5	5.5	32.10	26.60	11.94	0.80	0.01265	0.01128	90.22
30	22.5	5.5	31.80	26.30	11.99	0.40	0.01265	0.00799	89.20
60	22.5	5.5	31.40	25.90	12.05	0.20	0.01265	0.00567	87.85
250	22.5	5.5	30.50	25.00	12.20	0.05	0.01265	0.00279	84.79
1440	22.5	5.5	28.00	22.50	12.61	0.01	0.01265	0.00118	76.31
2870	22.5	5.5	27.00	21.50	12.77	0.00	0.01265	0.00084	72.92
4293	22.5	5.5	26.10	20.60	12.92	0.00	0.01265	0.00069	69.87

Test No. 4

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	22.0	6.1	29.80	23.70	12.41	6.21	0.01272	0.03169	80.38
5	22.0	6.1	29.00	22.90	12.54	2.51	0.01272	0.02015	77.67
15	22.0	6.1	28.70	22.60	12.59	0.84	0.01272	0.01166	76.65
30	22.0	6.1	28.20	22.10	12.68	0.42	0.01272	0.00827	74.96
60	22.0	6.1	27.90	21.80	12.72	0.21	0.01272	0.00586	73.94
250	22.0	6.1	27.10	21.00	12.86	0.05	0.01272	0.00288	71.23
1440	21.0	6.1	25.70	19.60	13.09	0.01	0.01287	0.00123	66.48
2880	21.0	6.1	24.90	18.80	13.22	0.00	0.01287	0.00087	63.76
4320	22.0	6.1	23.20	17.10	13.50	0.00	0.01272	0.00071	58.00

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Test No. 5

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	22.7	5	33.30	28.30	11.66	5.83	0.01262	0.03046	93.43
5	22.7	5	33.10	28.10	11.69	2.34	0.01262	0.01929	92.77
15	22.7	5	33.00	28.00	11.71	0.78	0.01262	0.01115	92.44
30	22.7	5	32.80	27.80	11.74	0.39	0.01262	0.00789	91.78
60	22.7	5	32.00	27.00	11.87	0.20	0.01262	0.00561	89.14
250	22.7	5	31.00	26.00	12.04	0.05	0.01262	0.00277	85.84
1440	22.7	5	30.10	25.10	12.18	0.01	0.01262	0.00116	82.86
2880	22.7	5	29.70	24.70	12.25	0.00	0.01262	0.00082	81.54
4320	22.7	5	29.40	24.40	12.30	0.00	0.01262	0.00067	80.55

Test No. 6

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	22.7	5	32.60	27.60	11.77	5.89	0.01262	0.03061	91.12
5	22.7	5	32.10	27.10	11.86	2.37	0.01262	0.01943	89.47
15	22.7	5	32.00	27.00	11.87	0.79	0.01262	0.01122	89.14
30	22.7	5	31.70	26.70	11.92	0.40	0.01262	0.00795	88.15
60	22.7	5	31.10	26.10	12.02	0.20	0.01262	0.00565	86.17
250	22.7	5	30.90	25.90	12.05	0.05	0.01262	0.00277	85.51
1440	22.7	5	29.70	24.70	12.25	0.01	0.01262	0.00116	81.54
2880	22.7	5	29.10	24.10	12.35	0.00	0.01262	0.00083	79.56
4320	22.7	5	28.40	23.40	12.46	0.00	0.01262	0.00068	77.25

Test No. 7

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	22.7	5	32.60	27.60	11.77	5.89	0.01262	0.03061	91.12
5	22.7	5	32.00	27.00	11.87	2.37	0.01262	0.01944	89.14
15	22.7	5	31.90	26.90	11.89	0.79	0.01262	0.01123	88.81
30	22.7	5	31.10	26.10	12.02	0.40	0.01262	0.00799	86.17
60	22.7	5	30.80	25.80	12.07	0.20	0.01262	0.00566	85.18
250	22.7	5	30.50	25.50	12.12	0.05	0.01262	0.00278	84.19
1440	22.7	5	29.10	24.10	12.35	0.01	0.01262	0.00117	79.56
2880	22.7	5	28.30	23.30	12.48	0.00	0.01262	0.00083	76.92
4320	22.7	5	27.60	22.60	12.59	0.00	0.01262	0.00068	74.61

Higher Quality Bentonite (HQB)

Test No. 1

Elapsed Time, t (min.)	Temperature (°C)	Composite Correction C_c	Hydrometer Pre-Reading	Actual Hydrometer Reading	L (cm)	L/T (cm/min)	K [mm(min/cm)$^{0.5}$]	D (mm)	% Finer in Dispersed
2	23.0	5	33.80	28.80	11.58	5.79	0.01254	0.03016	94.92
5	23.0	5	33.30	28.30	11.66	2.33	0.01254	0.01914	93.27
15	23.0	5	32.70	27.70	11.76	0.78	0.01254	0.01110	91.30
30	23.0	5	32.10	27.10	11.86	0.40	0.01254	0.00788	89.32
60	23.0	5	31.90	26.90	11.89	0.20	0.01254	0.00558	88.66
250	23.0	5	31.50	26.50	11.95	0.05	0.01254	0.00274	87.34
1440	23.0	5	31.20	26.20	12.00	0.01	0.01254	0.00114	86.35
2880	23.0	5	30.40	25.40	12.13	0.00	0.01254	0.00081	83.72
4320	23.0	5	30.20	25.20	12.17	0.00	0.01254	0.00067	83.06

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Table C.4 – Atterberg limits of Bentonites Taken from Two GCLs.

Atterberg Limit Test (ASTM D 4318)

1) Liquid Limit (LL)

Deionized Water

GCL Type	No of blows	Mdish	Mdish+soln+soil	Mdish+soil	w	w corrected
	(N)	(g)			(%)	
LQB	36	1.575	20.514	5.22	419.6	419.6
	27	1.567	21.921	5.46	422.8	422.8
	31	1.556	21.205	5.308	423.7	423.7
	20	1.562	21.182	5.215	437.1	437.1
	20	1.56	24.204	5.785	436.0	436.0
	22	1.558	21.695	5.327	434.3	434.3
	16	1.558	22.963	5.497	443.4	443.4
	17	1.55	17.574	4.499	443.4	443.4
HQB	16	1.547	21.421	4.351	608.8	608.8
	14	1.542	21.454	4.381	601.4	601.4
	17	1.553	21.372	4.36	606.1	606.1
	31	1.568	21.967	4.575	578.4	578.4
	36	1.542	22.309	4.618	575.1	575.1
	31	1.545	20.006	4.261	579.7	579.7
	28	1.543	22.652	4.609	588.5	588.5
	24	1.548	21.551	4.431	593.8	593.8
	23	1.55	21.592	4.443	592.8	592.8
	18	1.556	22.672	4.571	600.4	600.4

2) Plastic Limit (PL) & Plasticity Index (PI)

GCL Type	Mdish	Mdish+soln+soil	Mdish+soil	w	PL	PI
	(g)			(%)		
LQB	1.575	12.771	9.831	35.6	36.3	393
	1.564	14.542	11.037	37.0		
HQB	1.534	9.812	7.368	41.9	41.4	548
	1.551	13.613	10.112	40.9		

LQB = GCL with Lower Quality Bentonite
HQB = GCL with Higher Quality Bentonite

5 mM $CaCl_2$

GCL Type	No of blows	Mdish	Mdish+soln+soil	Mdish+soil	w	w corrected
	(N)	(g)			(%)	
LQB	30	0.946	20.439	5.136	365.2	366.0
	33	0.954	20.873	5.249	363.8	364.5
	29	0.947	20.51	5.093	371.9	372.6
	24	0.947	18.986	4.694	381.4	382.2
	19	0.947	21.619	5.21	384.9	385.7
	17	0.945	20.526	4.959	387.8	388.7
HQB	32	0.946	21.454	4.104	549.4	551.1
	28	0.942	22.411	4.206	557.8	559.5
	19	0.935	19.443	3.735	561.0	562.8
	22	0.941	22.725	4.24	560.3	562.1
	22	0.946	22.22	4.169	560.1	561.8
	18	0.946	22.651	4.18	571.2	573.0

10 mM $CaCl_2$

GCL Type	No of blows	Mdish	Mdish+soln+soil	Mdish+soil	w	w corrected
	(N)	(g)			(%)	
LQB	36	0.949	19.599	5.183	340.5	341.8
	31	0.953	19.05	5.024	344.5	345.9
	26	0.948	19.219	5.02	348.7	350.1
	23	0.948	19.106	4.991	349.1	350.5
	17	0.947	21.391	5.423	356.7	358.2
	17	0.947	19.259	4.95	357.5	358.9
HQB	40	0.957	22.442	4.496	507.1	510.0
	27	0.951	23.231	4.551	518.9	521.9
	25	0.953	21.625	4.304	516.9	519.9
	23	0.95	22.048	4.351	520.3	523.4
	21	0.943	20.467	4.077	523.0	526.0
	16	0.94	22.309	4.323	531.7	534.8

20 mM $CaCl_2$

GCL Type	No of blows	Mdish	Mdish+soln+soil	Mdish+soil	w	w corrected
	(N)	(g)			(%)	
LQB	34	0.946	21.611	6.258	289.0	290.9
	33	0.944	20.662	6.023	288.2	290.1
	28	0.945	20.879	6.016	293.1	295.0
	27	0.948	19.137	5.591	291.8	293.7
	20	0.953	21.614	6.128	299.2	301.2
	22	0.955	20.4	5.842	297.9	299.9
HQB	46	0.947	22.38	5.006	428.0	432.1
	37	0.945	19.738	4.457	435.1	439.4
	27	0.941	21.86	4.786	444.1	448.5
	26	0.942	22.009	4.809	444.8	449.2
	22	0.946	21.484	4.659	453.1	457.7
	14	0.949	22.03	4.674	465.9	470.8

50 mM $CaCl_2$

GCL Type	No of blows	Mdish	Mdish+soln+soil	Mdish+soil	w	w corrected
	(N)	(g)			(%)	
LQB	39	0.946	25.101	9.239	191.3	193.3
	33	0.941	23.872	8.774	192.7	194.8
	24	0.94	22.342	8.172	195.9	198.1
	23	0.941	23.422	8.521	196.6	198.8
	15	0.945	23.605	8.475	200.9	203.2
	17	0.947	19.936	7.291	199.3	201.6
HQB	43	0.942	21.68	6.753	256.9	260.6
	36	0.946	19.414	6.081	259.6	263.4
	29	0.947	20.291	6.282	262.6	266.5
	32	0.945	18.633	5.832	261.9	265.8
	26	0.947	19.684	6.082	264.9	268.8
	21	0.947	20.103	6.105	271.4	275.5

100 mM $CaCl_2$

GCL Type	No of blows	Mdish	Mdish+soln+soil	Mdish+soil	w	w corrected
	(N)	(g)			(%)	
LQB	32	0.956	15.356	6.959	139.9	142.1
	30	0.957	13.32	6.103	140.2	142.5
	29	0.959	12.693	5.815	141.6	143.9
	25	0.959	13.076	5.954	142.6	144.9
	24	0.955	13.768	6.227	143.0	145.3
	22	0.96	13.399	6.075	143.2	145.5
	18	0.961	14.046	6.291	145.5	148.0
HQB	33	0.955	21.191	8.967	152.6	155.2
	30	0.96	20.272	8.567	153.9	156.5
	27	0.956	20.102	8.432	156.1	158.9
	23	0.957	19.596	8.123	160.1	163.0
	20	0.959	21.122	8.628	162.9	165.9
	17	0.955	20.538	8.36	164.5	167.5

500 mM $CaCl_2$

GCL Type	No of blows	Mdish	Mdish+soln+soil	Mdish+soil	w	w corrected
	(N)	(g)			(%)	
LQB	34	0.943	26.87	14.06	97.7	103.3
	35	0.951	28.239	14.773	97.4	103.0
	29	0.951	26.048	13.462	100.6	106.5
	21	0.946	23.785	12.257	101.9	108.0
	20	0.942	26.091	13.413	101.7	107.7
	15	0.942	23.534	11.958	105.1	111.6
	17	0.942	26.911	13.738	102.9	109.2
HQB	41	0.95	26.572	14.258	92.5	97.5
	30	0.945	25.258	13.406	95.1	100.4
	22	0.944	23.444	12.365	97.0	102.5
	22	0.946	26.112	13.72	97.0	102.5
	21	0.943	23.272	12.204	98.3	104.0
	15	0.952	26.858	13.853	100.8	106.8

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Table C.5 – Swell Index of Bentonites Taken from Two GCLs.

Swell Index Test (ASTM D 5890)
Testing Liquid: Deionized Water
Lower Quality Bentonite (LQB)

Test No.	1	2	3	4	5	6	7	8	9
Swell Index (mL/2 g)	29.5	26.0	27.8	28.0	25.5	27.6	27.0	27.3	27.0
Test No.	10	11	12	13	14	15	16	17	
Swell Index (mL/2 g)	26.7	29.5	28.6	27.0	27.1	26.9	26.5	27.1	

Higher Quality Bentonite (HQB)

Test No.	1	2
Swell Index (mL/2 g)	30.0	30.5

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Table C.6 – Bentonite Mass per Unit Area for Two GCLs.

Mass Per Unit Area of GCL (ASTM D 5993)

GCL with Lower Quality Bentonite (GCL-LQB)
Specimen Size: 5" x 5" (12.7 cm x 12.7 cm)
Specimen Area: 161.29 cm^2
No. of Specimens: 5
Nominal Mass Per Unit Area of GCL Synthetic Components:
1) Cap Nonwoven: 200 g/m^2
2) Woven Scrim: 105 g/m^2
3) Total: 305 g/m^2

Test No.	M_{dish} (g)	$M_{dish+sample}$ (g)	$M_{dish+dry\ sample}$ (g)	$M_{dry\ sample}$ (g)	m_{GCL} (g/m^2)	m_{clay} (g/m^2)	w_{clay} (%)
1	28.37	119.03	116.28	87.91	5450.43	5145.43	3.31
2	28.31	111.1	108.67	80.36	4982.33	4677.33	3.22
3	29.07	119.07	116.37	87.3	5412.61	5107.61	3.28
4	29.04	122.49	119.68	90.64	5619.69	5314.69	3.28
5	29.01	122.8	119.92	90.91	5636.43	5331.43	3.35
				Avg:	5420.30	5115.30	3.29

GCL with Higher Quality Bentonite (GCL-HQB)
Specimen Size: 5" x 5" (12.7 cm x 12.7 cm)
Specimen Area: 161.29 cm^2
No. of Specimens: 5
Nominal Mass Per Unit Area of GCL Synthetic Components:
1) Cap Nonwoven: 200 g/m^2
2) Woven Scrim: 200 g/m^2
3) Total: 400 g/m^2

Test No.	M_{dish} (g)	$M_{dish+sample}$ (g)	$M_{dish+dry\ sample}$ (g)	$M_{dry\ sample}$ (g)	m_{GCL} (g/m^2)	m_{clay} (g/m^2)	w_{clay} (%)
1	215.66	297.97	294.94	79.28	4915.37	4515.37	4.16
2	205.34	289.09	285.82	80.48	4989.77	4589.77	4.42
3	216.4	301.91	298.47	82.07	5088.35	4688.35	4.55
4	204.86	291.07	287.77	82.91	5140.43	4740.43	4.32
5	331.61	413.6	410.7	79.09	4903.59	4503.59	3.99
				Avg:	5007.50	4607.50	4.29

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Table C.7 – Chemical Properties of Bentonites Taken from Two GCLs.

Soil Chemical Analysis

Lower Quality Bentonite (LQB)

Sample #	Soil Paste		CEC	Cl	Exchangeable Bases				
	pH	EC			Ca	Mg	Na	K	Sum
		(mS/cm)	(meq/100g)	(mg/kg)	(meq/100g)				
1	8.90	3.10	73.5	116	12.0	4.0	56.1	0.58	72.7
2	8.90	2.90	65.2	162	15.7	4.8	40.0	0.78	61.3
3	8.82	3.15	53.1	2.7	6.9	2.2	41.3	0.80	51.2
Average	8.87	3.05	63.9	93.6	11.5	3.7	45.8	0.7	61.7

Sample #	1N NH_4OAc Extractables				Water Extract				
	Ca	Mg	Na	K	Ca	Mg	Na	K	Sum
	(meq/100g)				(meq/100g)				
1	14	4.5	62	0.84	2.0	0.48	5.9	0.26	8.6
2	16	4.8	64	0.90	0.4	0	24.0	0	24.4
3	7.8	2.3	55.3	0.90	0.9	0.1	14.0	0.11	15.1
Average	12.6	3.9	60.4	0.9	1.1	0.2	14.6	0.1	16.1

Sample #	Soluble Salts				
	Ca	Mg	Na	K	Sum
	(mg/kg)				
1	240.0	29.0	3430.0	50.0	3749.0
2	241.0	29.4	3444.0	51.6	3766.0
3	174.4	14.1	3220.0	42.5	3451.0
Average	218.5	24.2	3364.7	48.0	3655.3

Higher Quality Bentonite (HQB)

Sample #	Soil Paste		CEC	Exchangeable Bases				
	pH	EC		Ca	Mg	Na	K	Sum
		(mS/cm)	(meq/100g)	(meq/100g)				
1	8.8	2.10	90.6	15.9	7.0	64.8	0.70	88.4
2	8.8	2.20	96.1	14.7	7.0	73.2	0.80	95.7
3	8.9	2.70						
Average	8.8	2.33	93.4	15.3	7.0	69.0	0.75	92.1

Sample #	1N NH_4OAc Extractables				Water Extract				
	Ca	Mg	Na	K	Ca	Mg	Na	K	Sum
	(meq/100g)				(meq/100g)				
1	19.5	8.3	97.2	1.2	3.6	1.3	32.4	0.5	37.8
2	18.5	7.6	102.6	1.40	3.8	1.3	29.4	0.6	35.1
Average	19	8.0	100	1.30	3.7	1.3	30.9	0.6	36.5

Sample #	Soluble Salts			
	Ca	Mg	Na	K
	(mg/kg)			
1	720.0	160	7452	200
2	754.0	160	6762	231
Average	737.0	160.0	7107.0	215.5

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Table C.8 – Mineralogical Compositions of Bentonites Taken from Two GCLs.

Results of X-Ray Diffraction (XRD) Analyses

Mineral Constituent	Lower Quality Bentonite (LQB)				Higher Quality Bentonite (HQB)		
	1	2	3	Avg	1	2	Avg
Quartz	4	3	3.3	3.4	4	3	3.5
Cristobalite	15	9	6.8	10.3	5	4	4.5
Tridymite	0	2	0	0.67	0	1	0.50
Plagioclase Feldspar	4	4	7.4	5.1	3	2	2.5
K-Feldspar	1	trace	0	0.33	trace	trace	0.00
Calcite	1	1	0	0.67	1	1	1.0
Gypsum	0	1	0.7	0.57	0	trace	0.00
Heulandite	0	0	0.4	0.13	0	0	0.00
Pyrite	0	0	0	0.00	trace	0	0.00
Clinoptilolite	1	1	0	0.67	trace	1	0.50
Kaolinite	trace	trace	0	0.00	0	trace	0.00
Chlorite	0	trace	0	0.00	0	1	0.50
Illite/Mica	0	1	1.7	0.90	0	2	1.0
Montmorillonite	74	78	79.6	77.2	87	85	86.0
Total	100	100	100	100.0	100	100	100.0

1, 2: Based on X-ray diffraction analysis performed by Mineralogy Inc., Tulsa, OK.
3: Based on X-ray diffraction analysis performed by K/T GeoServices Inc., Argyle, TX.

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APPENDIX D

STATISTICAL ANALYSES ON HYDRAULIC CONDUCTIVITY TEST DATA

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Table D.1 – Statistical analyses on hydraulic conductivity versus pore volumes of flow.

Permeant Liquid	Test No.	Prehydration	GCL Type	Pore Volumes of Flow @ Slope of k ~ 0
5 mM $CaCl_2$	5 mM-1	No	LQB	54.1
	5 mM-2	No	LQB	77.7
	5 mM-P	Yes	LQB	42.2
	5 mM-HQB	No	HQB	68.0
10 mM $CaCl_2$	10 mM-1	No	LQB	26.1
	10 mM-2	No	LQB	38.1
	10 mM-P	Yes	LQB	20.1
	10 mM-HQB	No	HQB	51.1
20 mM $CaCl_2$	20 mM-1	No	LQB	13.3
	20 mM-2	No	LQB	18.1
	20 mM-P	Yes	LQB	10.4
	20 mM-HQB	No	HQB	19.2
50 mM $CaCl_2$	50 mM-1	No	LQB	6.97
	50 mM-2	No	LQB	4.76
	50 mM-P	Yes	LQB	11.4
	50 mM-HQB-1	No	HQB	23.5
	50 mM-HQB-2	No	HQB	18.1
100 mM $CaCl_2$	100 mM-1	No	LQB	9.08
	100 mM-2	No	LQB	5.25
	100 mM-P	Yes	LQB	13.5
	100 mM-HQB-1	No	HQB	19.0
	100 mM-HQB-2	No	HQB	21.7
500 mM $CaCl_2$	500 mM-1	No	LQB	7.47
	500 mM-2	No	LQB	6.34
	500 mM-HQB-1	No	HQB	17.7
	500 mM-HQB-2	No	HQB	4.92

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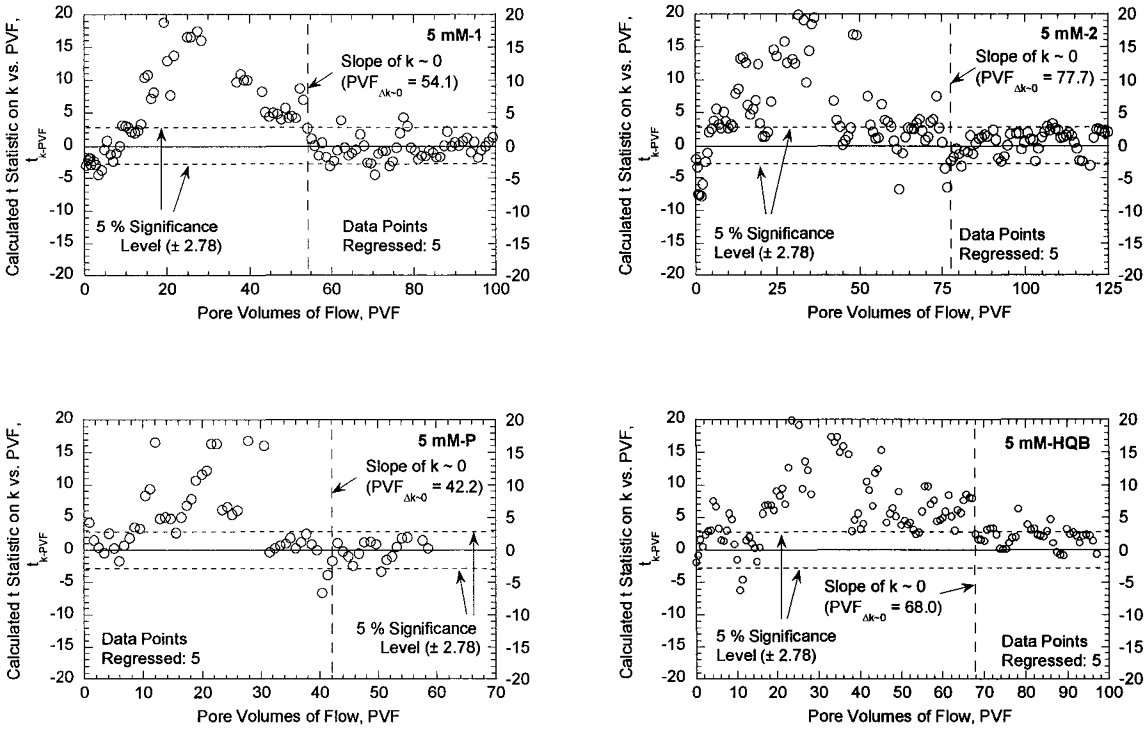

Fig. D.1 - Statistical analyses on the tests performed with 5 mM $CaCl_2$ solution.

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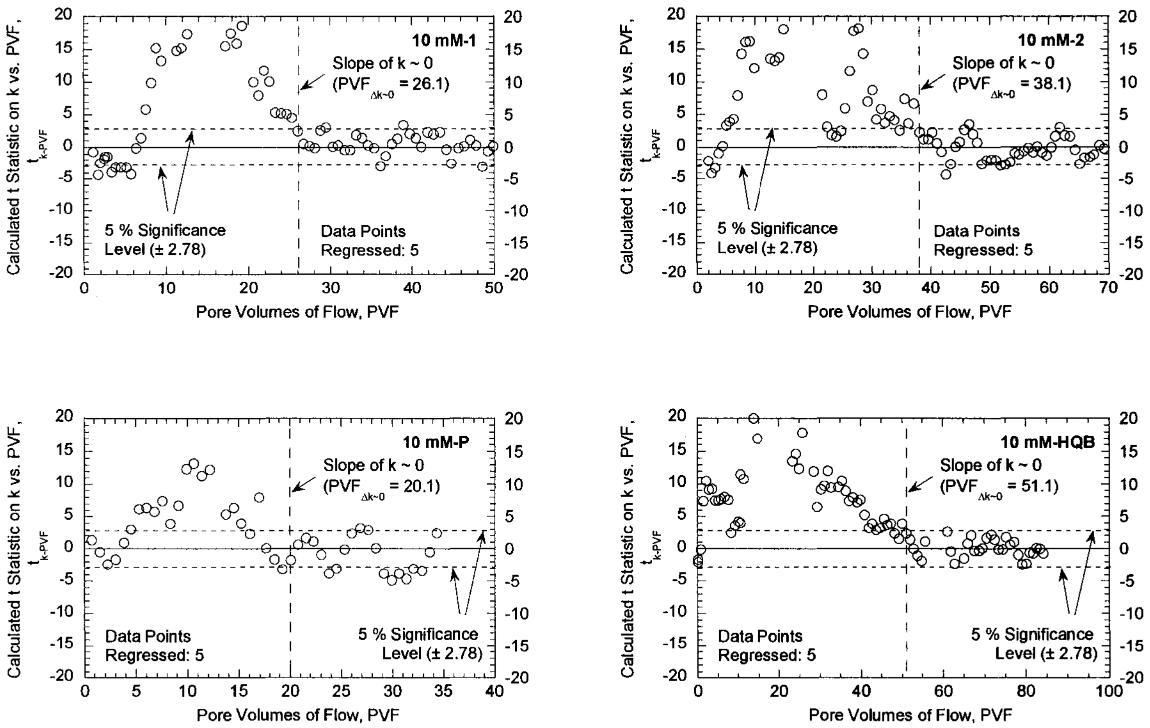

Fig. D.2 - Statistical analyses on the tests performed with 10 mM $CaCl_2$ solution.

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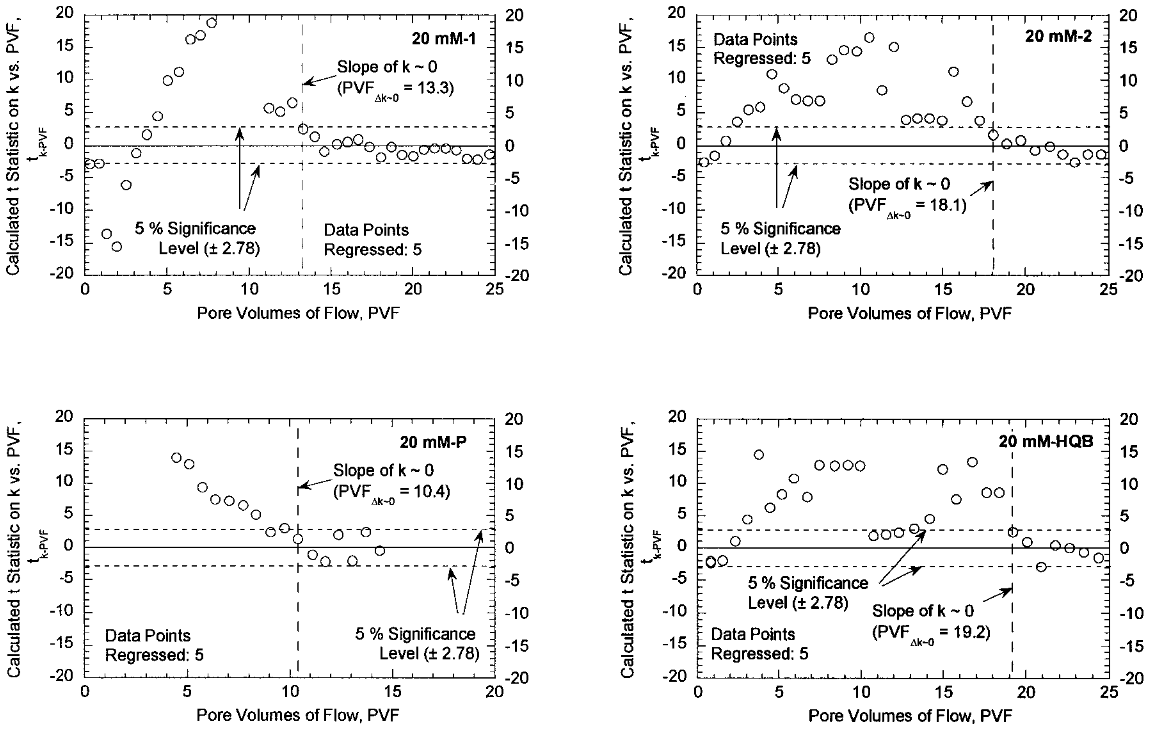

Fig. D.3 - Statistical analyses on the tests performed with 20 mM $CaCl_2$ solution.

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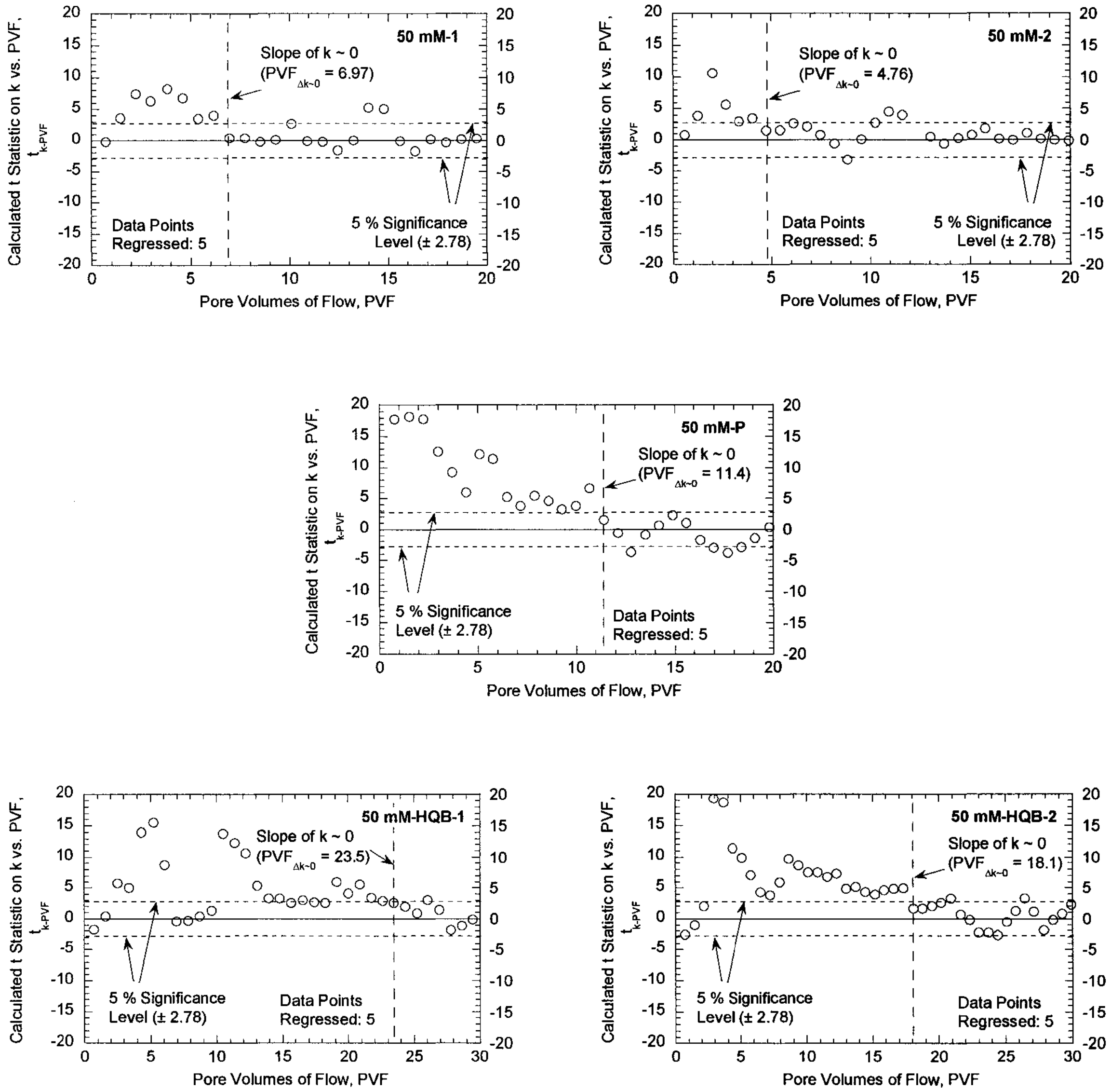

Fig. D.4 - Statistical analyses on the tests performed with 50 mM $CaCl_2$ solution.

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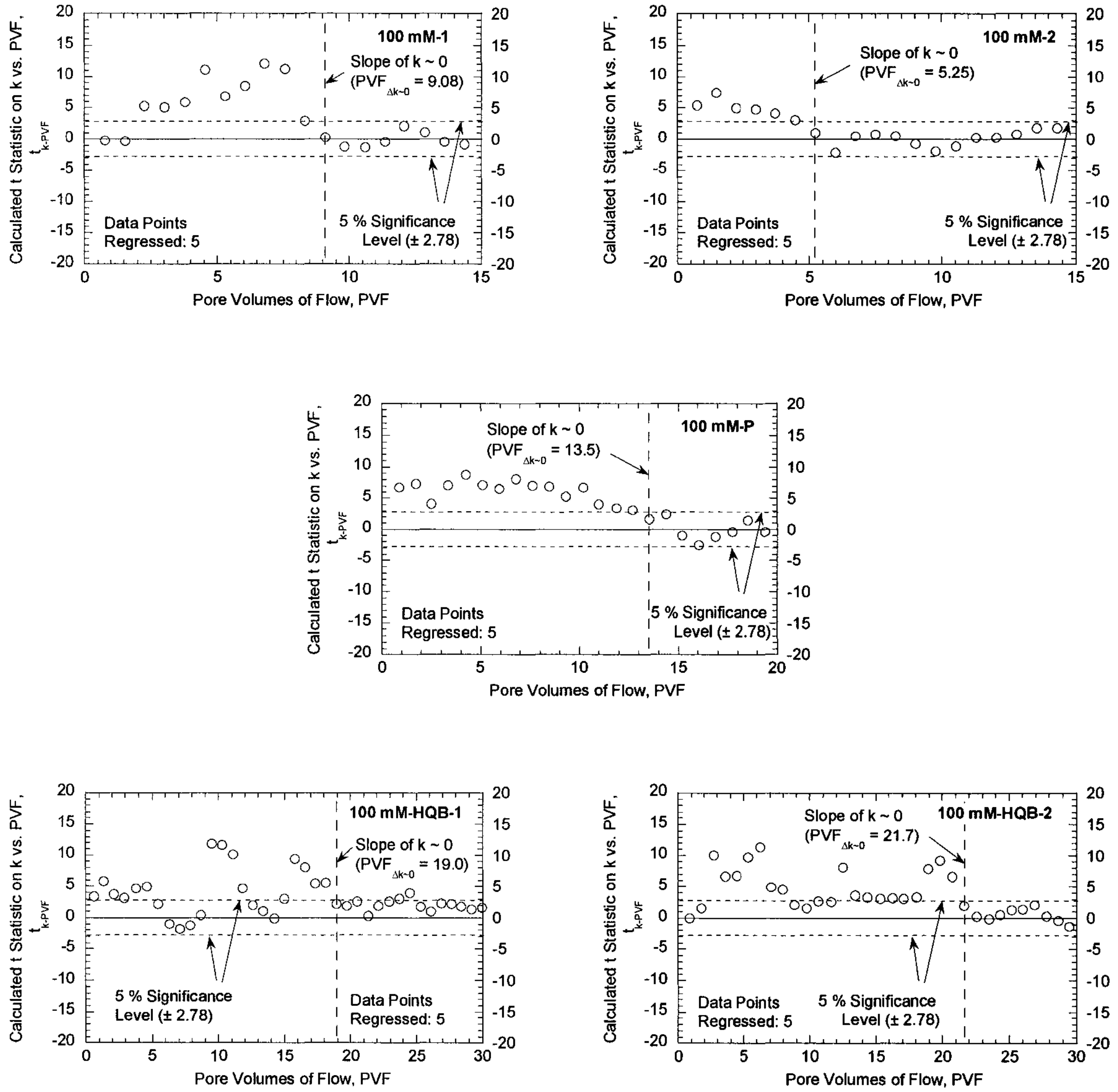

Fig. D.5 - Statistical analyses on the tests performed with 100 mM $CaCl_2$ solution.

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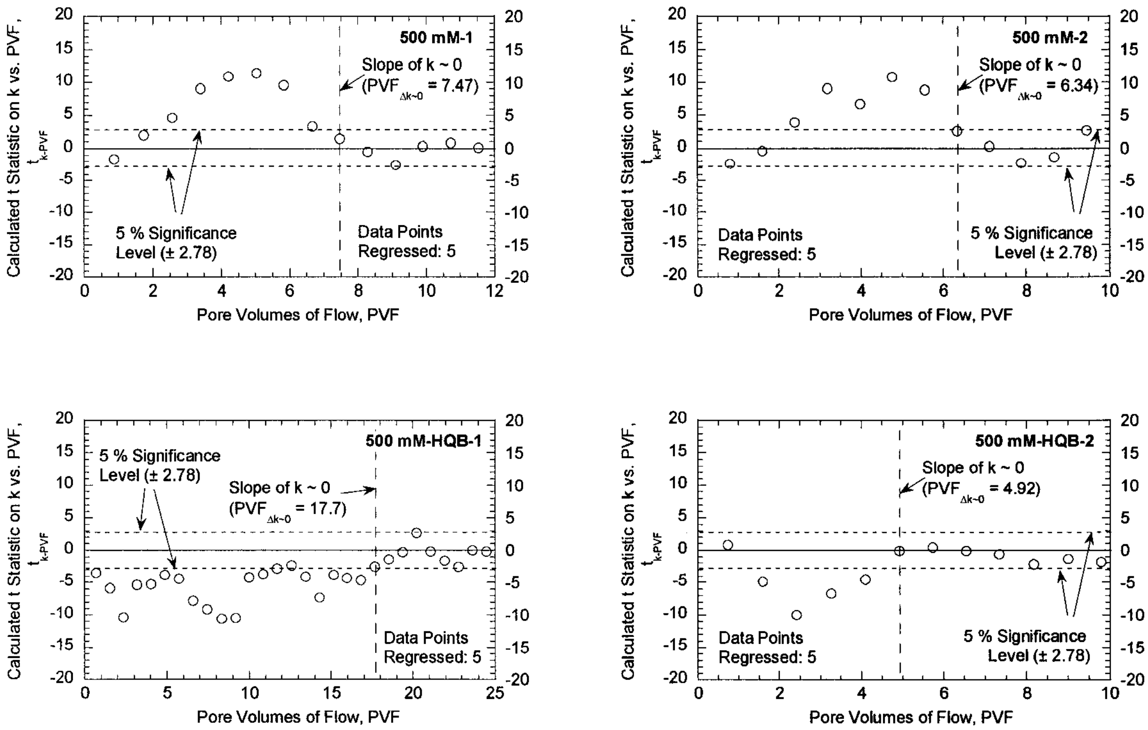

Fig. D.6 - Statistical analyses on the tests performed with 500 mM $CaCl_2$ solution.

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APPENDIX E

COMBINED CHEMICO-OSMOTIC/DIFFUSION TEST DATA

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Table E.1 - Combined Chemico-Osmotic/Diffusion Test Data.

Flushing Stage												
Δt	Σt	Qout	Σ Qout	PVF	pH	EC	pH	EC	k			
(days)	(days)	(cm3)	(cm3)			(mS/m)	Ratio		(cm/s)			
0.0	0.0	0.0	0.0	0.0								
8.8	8.8	22.7	22.7	1.5	8.2	594.0	1.4	2970.0	5.3E-10			
13.7	22.5	24.6	47.3	3.2	8.5	234.0	1.4	1170.0	3.7E-10			
14.4	36.9	21.8	69.1	4.6	8.6	127.4	1.4	637.0	3.1E-10			
15.1	52.0	22.4	91.5	6.1	8.8	89.0	1.5	445.0	3.1E-10			
16.4	68.5	23.5	115.0	7.7	8.7	73.7	1.4	368.5	3.0E-10			
11.1	79.6	16.0	131.0	8.7	9.0	65.7	1.5	328.5	3.0E-10			
Chemico-Osmotic Test												
t			Cot	ΔP		EC		Measured			ΔPavg	w
						(mS/m)		Ca2+ (N)	Cl- (N)	Ca2+ (ppm)		
(min)	(hr)	(days)	(M CaCl2)	(psi)	(kPa)	Top	Bottom	Bottom	Bottom	Bottom	(psi)	
-7200	-120	-5.0	0	0.05	0.32						0.00	0.0000
-6960	-116	-4.8	0	0.05	0.32						0.00	0.0000
-6720	-112	-4.7	0	0.03	0.22						0.00	0.0000
-6480	-108	-4.5	0	0.02	0.14						0.00	0.0000
-6240	-104	-4.3	0	0.02	0.17						0.00	0.0000
-6000	-100	-4.2	0	0.02	0.14						0.00	0.0000
-5760	-96	-4.0	0	0.02	0.13	12.40	17.20				0.00	0.0000
-5520	-92	-3.8	0	0.06	0.41						0.00	0.0000
-5280	-88	-3.7	0	0.08	0.53						0.00	0.0000
-5040	-84	-3.5	0	0.12	0.85						0.00	0.0000
-4800	-80	-3.3	0	0.12	0.83						0.00	0.0000
-4560	-76	-3.2	0	0.13	0.91						0.00	0.0000
-4320	-72	-3.0	0	0.15	1.01	8.50	8.80				0.00	0.0000
-4080	-68	-2.8	0	0.13	0.87						0.00	0.0000
-3840	-64	-2.7	0	0.12	0.83						0.00	0.0000
-3600	-60	-2.5	0	0.13	0.86						0.00	0.0000
-3360	-56	-2.3	0	0.14	0.97						0.00	0.0000
-3120	-52	-2.2	0	0.14	0.97						0.00	0.0000
-2880	-48	-2.0	0	0.15	1.01	8.30	7.00				0.00	0.0000
-2640	-44	-1.8	0	0.12	0.83						0.00	0.0000
-2400	-40	-1.7	0	0.10	0.68						0.00	0.0000
-2160	-36	-1.5	0	0.08	0.58						0.00	0.0000
-1920	-32	-1.3	0	0.07	0.50						0.00	0.0000
-1680	-28	-1.2	0	0.06	0.41						0.00	0.0000
-1440	-24	-1.0	0	0.05	0.32	7.90	6.00				0.00	0.0000
-1200	-20	-0.8	0	0.04	0.28						0.00	0.0000
-960	-16	-0.7	0	0.04	0.26						0.00	0.0000
-720	-12	-0.5	0	0.04	0.26						0.00	0.0000
-480	-8	-0.3	0	0.01	0.06						0.00	0.0000
-240	-4	-0.2	0	0.01	0.06						0.00	0.0000
0	0	0.0	0	0.00	0.02	7.00	5.40				0.00	0.0000
240	4	0.2	0.005	0.30	2.10						5.36	0.0568
480	8	0.3	0.005								5.36	
720	12	0.5	0.005								5.36	
960	16	0.7	0.005								5.36	
1200	20	0.8	0.005	1.01	6.97						5.36	0.1887
1440	24	1.0	0.005	1.18	8.11	106.00	6.40	0.0000	0.0002	0.08	5.36	0.2195
1680	28	1.2	0.005	1.32	9.11						5.36	0.2466
1920	32	1.3	0.005	1.46	10.04						5.36	0.2718
2160	36	1.5	0.005	1.57	10.85						5.36	0.2938
2400	40	1.7	0.005	1.68	11.60						5.36	0.3142
2640	44	1.8	0.005	1.80	12.41						5.36	0.3360
2880	48	2.0	0.005	1.89	13.06	115.20	9.10	0.0000	0.0004	0.04	5.36	0.3536
3120	52	2.2	0.005	1.96	13.48						5.36	0.3650
3360	56	2.3	0.005								5.36	

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3600	60	2.5	0.005								5.36	
3840	64	2.7	0.005								5.36	
4080	68	2.8	0.005	2.21	15.25						5.36	0.4129
4320	72	3.0	0.005	2.27	15.62	116.10	9.50	0.0000	0.0004	0.05	5.36	0.4230
4560	76	3.2	0.005	2.30	15.86						5.36	0.4296
4800	80	3.3	0.005	2.33	16.09						5.36	0.4355
5040	84	3.5	0.005	2.36	16.29						5.36	0.4411
5280	88	3.7	0.005	2.40	16.52						5.36	0.4473
5520	92	3.8	0.005	2.43	16.74						5.36	0.4533
5760	96	4.0	0.005	2.46	16.94	116.50	9.40	0.0000	0.0003	0.03	5.36	0.4587
6000	100	4.2	0.005	2.48	17.09						5.36	0.4628
6240	104	4.3	0.005								5.36	
6480	108	4.5	0.005								5.36	
6720	112	4.7	0.005	2.53	17.42						5.36	0.4716
6960	116	4.8	0.005	2.55	17.57						5.36	0.4759
7200	120	5.0	0.005	2.58	17.81	116.20	9.30	0.0000	0.0005	0.00	5.36	0.4822
7440	124	5.2	0.005	2.60	17.92						5.36	0.4852
7680	128	5.3	0.005	2.61	18.01						5.36	0.4876
7920	132	5.5	0.005	2.63	18.10						5.36	0.4900
8160	136	5.7	0.005	2.64	18.22						5.36	0.4934
8400	140	5.8	0.005	2.66	18.37						5.36	0.4973
8640	144	6.0	0.005	2.68	18.48	116.40	9.00	0.0000	0.0005	0.08	5.36	0.5005
8880	148	6.2	0.005	2.68	18.46						5.36	0.4998
9120	152	6.3	0.005	2.68	18.49						5.36	0.5007
9360	156	6.5	0.005	2.69	18.52						5.36	0.5014
9600	160	6.7	0.005	2.70	18.61						5.36	0.5039
9840	164	6.8	0.005	2.72	18.73						5.36	0.5072
10080	168	7.0	0.005	2.74	18.90	115.70	8.90	0.0000	0.0005	0.01	5.36	0.5117
10320	172	7.2	0.005	2.73	18.82						5.36	0.5096
10560	176	7.3	0.005								5.36	
10800	180	7.5	0.005								5.36	
11040	184	7.7	0.005	2.75	18.95						5.36	0.5130
11280	188	7.8	0.005	2.76	19.06						5.36	0.5160
11520	192	8.0	0.005	2.78	19.15	115.90	9.30	0.0000	0.0006	0.03	5.36	0.5186
11760	196	8.2	0.005	2.75	18.93						5.36	0.5126
12000	200	8.3	0.005	2.74	18.90						5.36	0.5117
12240	204	8.5	0.005	2.74	18.91						5.36	0.5121
12480	208	8.7	0.005	2.75	18.98						5.36	0.5139
12720	212	8.8	0.005	2.78	19.16						5.36	0.5188
12960	216	9.0	0.005	2.80	19.28	115.20	9.40	0.0000	0.0006	0.04	5.36	0.5220
13200	220	9.2	0.005								5.36	
13440	224	9.3	0.005								5.36	
13680	228	9.5	0.005								5.36	
13920	232	9.7	0.005	2.73	18.84						5.36	0.5102
14160	236	9.8	0.005	2.73	18.84						5.36	0.5102
14400	240	10.0	0.005	2.74	18.92	114.30	9.70	0.0000	0.0007	0.04	5.36	0.5123
14640	244	10.2	0.005	2.72	18.75						5.36	0.5076
14880	248	10.3	0.005	2.70	18.64						5.36	0.5048
15120	252	10.5	0.005	2.69	18.55						5.36	0.5022
15360	256	10.7	0.005	2.70	18.58						5.36	0.5031
15600	260	10.8	0.005	2.70	18.59						5.36	0.5033
15840	264	11.0	0.005	2.70	18.58	114.60	10.00	0.0000	0.0007	0.00	5.36	0.5031
16080	268	11.2	0.005	2.67	18.37						5.36	0.4975
16320	272	11.3	0.005	2.65	18.27						5.36	0.4947
16560	276	11.5	0.005	2.64	18.19						5.36	0.4925
16800	280	11.7	0.005	2.62	18.09						5.36	0.4899
17040	284	11.8	0.005	2.62	18.04						5.36	0.4886
17280	288	12.0	0.005	2.60	17.95	113.70	10.00	0.0000	0.0007	0.08	5.36	0.4861
17520	292	12.2	0.005	2.57	17.71						5.36	0.4794

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17760	296	12.3	0.005	2.56	17.68						5.36	0.4787
18000	300	12.5	0.005	2.56	17.62						5.36	0.4770
18240	304	12.7	0.005	2.54	17.50						5.36	0.4738
18480	308	12.8	0.005	2.53	17.41						5.36	0.4714
18720	312	13.0	0.005	2.50	17.26	113.70	10.80	0.0000	0.0008	0.04	5.36	0.4675
18960	316	13.2	0.005	2.47	17.02						5.36	0.4607
19200	320	13.3	0.005	2.46	16.93						5.36	0.4585
19440	324	13.5	0.005	2.43	16.78						5.36	0.4544
19680	328	13.7	0.005	2.41	16.64						5.36	0.4505
19920	332	13.8	0.005	2.40	16.51						5.36	0.4471
20160	336	14.0	0.005	2.40	16.52	113.40	11.20	0.0000	0.0008	0.01	5.36	0.4473
20400	340	14.2	0.005	2.33	16.09						5.36	0.4357
20640	344	14.3	0.005	2.32	15.98						5.36	0.4325
20880	348	14.5	0.005	2.30	15.83						5.36	0.4286
21120	352	14.7	0.005	2.28	15.69						5.36	0.4247
21360	356	14.8	0.005	2.26	15.60						5.36	0.4225
21600	360	15.0	0.005	2.23	15.39	113.10	11.50	0.0000	0.0007	0.23	5.36	0.4167
21840	364	15.2	0.005	2.18	15.05						5.36	0.4075
22080	368	15.3	0.005	2.16	14.89						5.36	0.4032
22320	372	15.5	0.005	2.13	14.69						5.36	0.3978
22560	376	15.7	0.005	2.13	14.66						5.36	0.3969
22800	380	15.8	0.005	2.12	14.62						5.36	0.3958
23040	384	16.0	0.005	2.07	14.29	112.20	12.00	0.0000	0.0008	0.13	5.36	0.3868
23280	388	16.2	0.005	1.99	13.74						5.36	0.3721
23520	392	16.3	0.005	1.98	13.63						5.36	0.3691
23760	396	16.5	0.005	1.97	13.55						5.36	0.3668
24000	400	16.7	0.005	1.96	13.49						5.36	0.3653
24240	404	16.8	0.005	1.96	13.48						5.36	0.3650
24480	408	17.0	0.005	1.93	13.27	111.50	12.50	0.0000	0.0007	0.07	5.36	0.3594
24720	412	17.2	0.005	1.84	12.69						5.36	0.3435
24960	416	17.3	0.005	1.82	12.52						5.36	0.3390
25200	420	17.5	0.005	1.80	12.40						5.36	0.3357
25440	424	17.7	0.005	1.79	12.33						5.36	0.3340
25680	428	17.8	0.005	1.77	12.17						5.36	0.3295
25920	432	18.0	0.005	1.74	12.01	111.60	13.00	0.0000	0.0007	0.17	5.36	0.3252
26160	436	18.2	0.005	1.68	11.60						5.36	0.3140
26400	440	18.3	0.005	1.66	11.47						5.36	0.3106
26640	444	18.5	0.005	1.65	11.34						5.36	0.3071
26880	448	18.7	0.005	1.63	11.24						5.36	0.3043
27120	452	18.8	0.005	1.61	11.10						5.36	0.3006
27360	456	19.0	0.005	1.60	11.04	110.90	13.20	0.0000	0.0010	0.20	5.36	0.2989
27600	460	19.2	0.005	1.54	10.60						5.36	0.2869
27840	464	19.3	0.005	1.52	10.45						5.36	0.2828
28080	468	19.5	0.005	1.49	10.27						5.36	0.2782
28320	472	19.7	0.005	1.47	10.10						5.36	0.2735
28560	476	19.8	0.005	1.44	9.96						5.36	0.2696
28800	480	20.0	0.005	1.42	9.81	110.60	13.90	0.0000	0.0010	0.44	5.36	0.2657
29040	484	20.2	0.005	1.35	9.31						5.36	0.2522
29280	488	20.3	0.005	1.33	9.18						5.36	0.2487
29520	492	20.5	0.005	1.31	9.05						5.36	0.2451
29760	496	20.7	0.005	1.31	9.00						5.36	0.2438
30000	500	20.8	0.005	1.28	8.85						5.36	0.2397
30240	504	21.0	0.005	1.26	8.68	110.00	14.60	0.0000	0.0013	0.74	5.36	0.2350
30480	508	21.2	0.005	1.16	8.00						5.36	0.2167
30720	512	21.3	0.005	1.13	7.80						5.36	0.2113
30960	516	21.5	0.005	1.11	7.64						5.36	0.2068
31200	520	21.7	0.005	1.11	7.62						5.36	0.2063
31440	524	21.8	0.005	1.08	7.43						5.36	0.2011
31680	528	22.0	0.005	1.06	7.29	109.10	15.50	0.0001	0.0013	1.04	5.36	0.1973

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31920	532	22.2	0.005	1.00	6.87						5.36	0.1859
32160	536	22.3	0.005	0.97	6.69						5.36	0.1813
32400	540	22.5	0.005	0.95	6.54						5.36	0.1772
32640	544	22.7	0.005	0.93	6.38						5.36	0.1729
32880	548	22.8	0.005	0.91	6.24						5.36	0.1689
33120	552	23.0	0.005	0.87	6.02	108.80	15.80	0.0001	0.0014	1.76	5.36	0.1630
33360	556	23.2	0.005	0.82	5.63						5.36	0.1525
33600	560	23.3	0.005	0.80	5.51						5.36	0.1492
33840	564	23.5	0.005	0.78	5.38						5.36	0.1458
34080	568	23.7	0.005	0.76	5.27						5.36	0.1426
34320	572	23.8	0.005	0.75	5.14						5.36	0.1393
34560	576	24.0	0.005	0.73	5.04	107.70	16.10	0.0001	0.0015	2.71	5.36	0.1365
34800	580	24.2	0.005	0.68	4.69						5.36	0.1269
35040	584	24.3	0.005	0.66	4.56						5.36	0.1236
35280	588	24.5	0.005	0.64	4.39						5.36	0.1187
35520	592	24.7	0.005	0.62	4.30						5.36	0.1165
35760	596	24.8	0.005	0.60	4.14						5.36	0.1122
36000	600	25.0	0.005	0.58	3.99	108.30	16.60	0.0002	0.0014	3.90	5.36	0.1081
36240	604	25.2	0.005	0.53	3.67						5.36	0.0993
36480	608	25.3	0.005	0.53	3.65						5.36	0.0988
36720	612	25.5	0.005	0.52	3.55						5.36	0.0961
36960	616	25.7	0.005	0.50	3.43						5.36	0.0928
37200	620	25.8	0.005	0.48	3.28						5.36	0.0887
37440	624	26.0	0.005	0.46	3.16	107.80	17.10	0.0003	0.0016	6.28	5.36	0.0857
37680	628	26.2	0.005	0.41	2.84						5.36	0.0769
37920	632	26.3	0.005	0.40	2.74						5.36	0.0743
38160	636	26.5	0.005	0.39	2.70						5.36	0.0732
38400	640	26.7	0.005	0.39	2.67						5.36	0.0722
38640	644	26.8	0.005	0.37	2.56						5.36	0.0694
38880	648	27.0	0.005	0.36	2.45	107.60	17.70	0.0004	0.0014	7.36	5.36	0.0663
39120	652	27.2	0.005	0.32	2.23						5.36	0.0605
39360	656	27.3	0.005	0.32	2.22						5.36	0.0601
39600	660	27.5	0.005	0.31	2.16						5.36	0.0586
39840	664	27.7	0.005	0.30	2.03						5.36	0.0551
40080	668	27.8	0.005	0.29	1.99						5.36	0.0540
40320	672	28.0	0.005	0.29	1.97	107.20	17.90	0.0006	0.0017	11.39	5.36	0.0532
40560	676	28.2	0.005	0.23	1.59						5.36	0.0429
40800	680	28.3	0.005	0.24	1.65						5.36	0.0448
41040	684	28.5	0.005	0.23	1.61						5.36	0.0437
41280	688	28.7	0.005	0.23	1.59						5.36	0.0431
41520	692	28.8	0.005	0.21	1.45						5.36	0.0394
41760	696	29.0	0.005	0.21	1.42	107.40	18.00	0.0007	0.0017	13.89	5.36	0.0385
42000	700	29.2	0.005	0.17	1.19						5.36	0.0323
42240	704	29.3	0.005								5.36	
42480	708	29.5	0.005	0.16	1.08						5.36	0.0293
42720	712	29.7	0.005	0.16	1.12						5.36	0.0304
42960	716	29.8	0.005	0.16	1.12						5.36	0.0304
43200	720	30.0	0.005	0.15	1.05	107.60	18.80	0.0007	0.0017	14.14	5.36	0.0286
43440	724	30.2	0.005	0.13	0.90						5.36	0.0243
43680	728	30.3	0.005	0.14	0.96						5.36	0.0259
43920	732	30.5	0.005	0.15	1.02						5.36	0.0276
44160	736	30.7	0.005	0.15	1.03						5.36	0.0278
44400	740	30.8	0.005	0.14	0.94						5.36	0.0256
44640	744	31.0	0.005	0.15	1.00	107.00	18.60	0.0009	0.0016	18.04	5.36	0.0271
44880	748	31.2	0.005	0.10	0.67						5.36	0.0181
45120	752	31.3	0.005	0.10	0.66						5.36	0.0179
45360	756	31.5	0.005	0.09	0.64						5.36	0.0174
45600	760	31.7	0.005	0.10	0.66						5.36	0.0177
45840	764	31.8	0.005	0.12	0.79						5.36	0.0215

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46080	768	32.0	0.005	0.12	0.80	107.30	19.60	0.0010	0.0014	19.62	5.36	0.0217
46320	772	32.2	0.005	0.09	0.61						5.36	0.0166
46560	776	32.3	0.005	0.10	0.68						5.36	0.0183
46800	780	32.5	0.005	0.10	0.67						5.36	0.0181
47040	784	32.7	0.005	0.09	0.63						5.36	0.0170
47280	788	32.8	0.005	0.10	0.66						5.36	0.0179
47520	792	33.0	0.005	0.09	0.65	106.90	18.70	0.0008	0.0014	16.09	5.36	0.0175
47760	796	33.2	0.005	0.09	0.59						5.36	0.0159
48000	800	33.3	0.005	0.09	0.65						5.36	0.0175
48240	804	33.5	0.005	0.09	0.65						5.36	0.0175
48480	808	33.7	0.005	0.10	0.66						5.36	0.0177
48720	812	33.8	0.005	0.10	0.67						5.36	0.0181
48960	816	34.0	0.005	0.10	0.68	107.10	19.60	0.0011	0.0015	21.52	5.36	0.0185
49200	820	34.2	0.005	0.07	0.50						5.36	0.0134
49440	824	34.3	0.005	0.08	0.54						5.36	0.0146
49680	828	34.5	0.005	0.08	0.57						5.36	0.0155
49920	832	34.7	0.005	0.10	0.66						5.36	0.0179
50160	836	34.8	0.005	0.09	0.63						5.36	0.0170
50400	840	35.0	0.005	0.09	0.61	107.20	18.80	0.0011	0.0014	22.28	5.36	0.0166
50640	844	35.2	0.005	0.16	1.10						5.36	0.0297
50880	848	35.3	0.005	0.18	1.24						5.36	0.0336
51120	852	35.5	0.005	0.19	1.28						5.36	0.0347
51360	856	35.7	0.005	0.18	1.25						5.36	0.0340
51600	860	35.8	0.005	0.20	1.34						5.36	0.0364
51840	864	36.0	0.005	0.18	1.25	107.20	18.20	0.0011	0.0014	21.61	5.36	0.0340
52080	868	36.2	0.005	0.16	1.12						5.36	0.0302
52320	872	36.3	0.005	0.17	1.14						5.36	0.0310
52560	876	36.5	0.005	0.16	1.12						5.36	0.0302
52800	880	36.7	0.005	0.17	1.19						5.36	0.0323
53040	884	36.8	0.005	0.17	1.15						5.36	0.0312
53280	888	37.0	0.005	0.17	1.14	107.20	18.70	0.0011	0.0014	22.30	5.36	0.0308
53520	892	37.2	0.005	0.15	1.04						5.36	0.0282
53760	896	37.3	0.005	0.15	1.04						5.36	0.0282
54000	900	37.5	0.005	0.15	1.05						5.36	0.0284
54240	904	37.7	0.005	0.15	1.06						5.36	0.0287
54480	908	37.8	0.005	0.15	1.03						5.36	0.0280
54720	912	38.0	0.005	0.15	1.01	107.40	19.60	0.0012	0.0015	24.11	5.36	0.0273
54960	916	38.2	0.005	0.17	1.20						5.36	0.0325
55200	920	38.3	0.005	0.18	1.22						5.36	0.0330
55440	924	38.5	0.005	0.17	1.17						5.36	0.0317
55680	928	38.7	0.005	0.16	1.12						5.36	0.0304
55920	932	38.8	0.005	0.17	1.16						5.36	0.0314
56160	936	39.0	0.005	0.16	1.10	107.10	19.00	0.0012	0.0015	23.65	5.36	0.0297
56400	940	39.2	0.005	0.16	1.08						5.36	0.0293
56640	944	39.3	0.005	0.17	1.14						5.36	0.0308
56880	948	39.5	0.005	0.16	1.08						5.36	0.0291
57120	952	39.7	0.005	0.15	1.04						5.36	0.0282
57360	956	39.8	0.005	0.14	0.98						5.36	0.0265
57600	960	40.0	0.005	0.14	0.97	107.10	18.80	0.0012	0.0015	23.91	5.36	0.0263
57840	964	40.2	0.005	0.13	0.92						5.36	0.0248
58080	968	40.3	0.005	0.13	0.90						5.36	0.0243
58320	972	40.5	0.005	0.13	0.92						5.36	0.0250
58560	976	40.7	0.005	0.12	0.85						5.36	0.0231
58800	980	40.8	0.005	0.12	0.79						5.36	0.0215
59040	984	41.0	0.005	0.11	0.77	107.20	18.70	0.0012	0.0016	23.75	5.36	0.0207
59280	988	41.2	0.005	0.10	0.72						5.36	0.0194
59520	992	41.3	0.005	0.11	0.74						5.36	0.0202
59760	996	41.5	0.005	0.10	0.69						5.36	0.0187
60000	1000	41.7	0.005	0.11	0.77						5.36	0.0207

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60240	1004	41.8	0.005	0.11	0.74						5.36	0.0200
60480	1008	42.0	0.005	0.10	0.67	107.30	18.70	0.0012	0.0015	24.27	5.36	0.0181
60720	1012	42.2	0.005	0.07	0.48						5.36	0.0131
60960	1016	42.3	0.005	0.08	0.57						5.36	0.0153
61200	1020	42.5	0.005	0.09	0.59						5.36	0.0161
61440	1024	42.7	0.005	0.09	0.61						5.36	0.0166
61680	1028	42.8	0.005	0.08	0.56						5.36	0.0151
61920	1032	43.0	0.005	0.08	0.55	107.50	19.20	0.0012	0.0016	24.26	5.36	0.0149
62160	1036	43.2	0.005	0.08	0.52						5.36	0.0140
62400	1040	43.3	0.005	0.08	0.52						5.36	0.0142
62640	1044	43.5	0.005	0.08	0.52						5.36	0.0142
62880	1048	43.7	0.005	0.08	0.53						5.36	0.0144
63120	1052	43.8	0.005	0.08	0.52						5.36	0.0142
63360	1056	44.0	0.005	0.08	0.52	107.40	19.00	0.0012	0.0015	24.04	5.36	0.0142
63600	1060	44.2	0.005	0.05	0.37						5.36	0.0099
63840	1064	44.3	0.005	0.06	0.38						5.36	0.0103
64080	1068	44.5	0.005	0.06	0.38						5.36	0.0103
64320	1072	44.7	0.005	0.06	0.43						5.36	0.0116
64560	1076	44.8	0.005	0.06	0.44						5.36	0.0119
64800	1080	45.0	0.005	0.06	0.41	107.30	18.90	0.0012	0.0015	24.22	5.36	0.0112
65040	1084	45.2	0.005	0.05	0.35						5.36	0.0095
65280	1088	45.3	0.005	0.05	0.35						5.36	0.0095
65520	1092	45.5	0.005	0.05	0.35						5.36	0.0095
65760	1096	45.7	0.005	0.06	0.39						5.36	0.0105
66000	1100	45.8	0.005	0.05	0.37						5.36	0.0101
66240	1104	46.0	0.005	0.05	0.32	107.00	19.00	0.0012	0.0015	24.40	5.36	0.0086
66480	1108	46.2	0.005	0.04	0.28						5.36	0.0077
66720	1112	46.3	0.005	0.05	0.31						5.36	0.0084
66960	1116	46.5	0.005	0.05	0.31						5.36	0.0084
67200	1120	46.7	0.005	0.04	0.29						5.36	0.0078
67440	1124	46.8	0.005	0.04	0.29						5.36	0.0078
67680	1128	47.0	0.005	0.05	0.37	107.50	19.10	0.0012	0.0015	24.63	5.36	0.0101
67920	1132	47.2	0.005	0.02	0.12						5.36	0.0034
68160	1136	47.3	0.005	0.02	0.15						5.36	0.0041
68400	1140	47.5	0.005	0.02	0.16						5.36	0.0043
68640	1144	47.7	0.005	0.03	0.21						5.36	0.0058
68880	1148	47.8	0.005	0.03	0.17						5.36	0.0047
69120	1152	48.0	0.005	0.03	0.23	107.20	19.20	0.0012	0.0015	24.73	5.36	0.0062
69360	1156	48.2	0.005	0.01	0.03						5.36	0.0009
69600	1160	48.3	0.005	0.02	0.13						5.36	0.0035
69840	1164	48.5	0.005	0.03	0.20						5.36	0.0054
70080	1168	48.7	0.005	0.04	0.26						5.36	0.0069
70320	1172	48.8	0.005	0.04	0.24						5.36	0.0065
70560	1176	49.0	0.005	0.04	0.24	107.10	19.00	0.0012	0.0015	24.88	5.36	0.0065
70800	1180	49.2	0.005	0.01	0.10						5.36	0.0026
71040	1184	49.3	0.005	0.02	0.14						5.36	0.0039
71280	1188	49.5	0.005	0.04	0.24						5.36	0.0065
71520	1192	49.7	0.005	0.03	0.23						5.36	0.0062
71760	1196	49.8	0.005	0.04	0.29						5.36	0.0078
72000	1200	50.0	0.005	0.04	0.30	107.50	18.90	0.0012	0.0015	25.04	5.36	0.0080
72240	1204	50.2	0.005	0.02	0.10						5.36	0.0028
72480	1208	50.3	0.005	0.02	0.11						5.36	0.0030
72720	1212	50.5	0.005	0.02	0.11						5.36	0.0030
72960	1216	50.7	0.005	0.02	0.11						5.36	0.0030
73200	1220	50.8	0.005	0.01	0.08						5.36	0.0021
73440	1224	51.0	0.005	0.01	0.06	107.60	19.20	0.0012	0.0015	24.99	5.36	0.0015
73680	1228	51.2	0.005	0.01	0.06						5.36	0.0015
73920	1232	51.3	0.005	0.00	0.03						5.36	0.0007
74160	1236	51.5	0.005	0.01	0.08						5.36	0.0021

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74400	1240	51.7	0.005	0.02	0.10						5.36	0.0028
74640	1244	51.8	0.005	0.02	0.14						5.36	0.0037
74880	1248	52.0	0.005	0.01	0.08	107.80	19.10	0.0013	0.0015	25.06	5.36	0.0022
75120	1252	52.2	0.005	0.01	0.05						5.36	0.0013
75360	1256	52.3	0.005	0.01	0.06						5.36	0.0015
75600	1260	52.5	0.005	0.01	0.08						5.36	0.0022
75840	1264	52.7	0.005	0.01	0.08						5.36	0.0022
76080	1268	52.8	0.005	0.01	0.05						5.36	0.0013
76320	1272	53.0	0.005	0.01	0.10	107.00	18.90	0.0013	0.0015	25.19	5.36	0.0026
76560	1276	53.2	0.005	0.00	0.01						5.36	0.0004
76800	1280	53.3	0.005	0.01	0.06						5.36	0.0015
77040	1284	53.5	0.005	0.02	0.12						5.36	0.0034
77280	1288	53.7	0.005	0.02	0.10						5.36	0.0028
77520	1292	53.8	0.005	0.01	0.08						5.36	0.0021
77760	1296	54.0	0.005	0.01	0.06	107.50	19.00	0.0013	0.0015	25.23	5.36	0.0015
78000	1300	54.2	0.005								5.36	
78240	1304	54.3	0.005	0.01	0.06						5.36	0.0017
78480	1308	54.5	0.005	0.01	0.09						5.36	0.0024
78720	1312	54.7	0.005	0.02	0.14						5.36	0.0039
78960	1316	54.8	0.005	0.02	0.14						5.36	0.0039
79200	1320	55.0	0.005	0.02	0.11	107.40	19.00	0.0013	0.0015	25.13	5.36	0.0030
79440	1324	55.2	0.005	0.01	0.03						5.36	0.0009
79680	1328	55.3	0.005	0.01	0.03						5.36	0.0009
79920	1332	55.5	0.005	0.01	0.06						5.36	0.0015
80160	1336	55.7	0.005	0.02	0.15						5.36	0.0041
80400	1340	55.8	0.005	0.02	0.14						5.36	0.0039
80640	1344	56.0	0.005	0.02	0.12	107.60	19.20	0.0013	0.0015	25.20	5.36	0.0034
80880	1348	56.2	0.005	0.01	0.05						5.36	0.0013
81120	1352	56.3	0.005	0.01	0.06						5.36	0.0017
81360	1356	56.5	0.005	0.02	0.13						5.36	0.0035
81600	1360	56.7	0.005	0.02	0.13						5.36	0.0035
81840	1364	56.8	0.005	0.02	0.17						5.36	0.0045
82080	1368	57.0	0.005	0.03	0.17	107.70	19.30	0.0013	0.0015	25.94	5.36	0.0047
82320	1372	57.2	0.005	0.01	0.05						5.36	0.0013
82560	1376	57.3	0.005	0.01	0.03						5.36	0.0009
82800	1380	57.5	0.005	0.02	0.12						5.36	0.0032
83040	1384	57.7	0.005	0.03	0.19						5.36	0.0052
83280	1388	57.8	0.005	0.02	0.15						5.36	0.0041
83520	1392	58.0	0.005	0.02	0.17	107.90	19.10	0.0012	0.0016	25.04	5.36	0.0045
83760	1396	58.2	0.005	0.01	0.04						5.36	0.0011
84000	1400	58.3	0.005	0.01	0.04						5.36	0.0011
84240	1404	58.5	0.005	0.01	0.08						5.36	0.0021
84480	1408	58.7	0.005	0.02	0.14						5.36	0.0037
84720	1412	58.8	0.005	0.03	0.21						5.36	0.0056
84960	1416	59.0	0.005	0.01	0.10	107.50	19.20	0.0013	0.0015	25.47	5.36	0.0026
85200	1420	59.2	0.005	0.01	0.06						5.36	0.0017
85440	1424	59.3	0.005	0.00	0.03						5.36	0.0007
85680	1428	59.5	0.005	0.01	0.06						5.36	0.0015
85920	1432	59.7	0.005	0.02	0.14						5.36	0.0037
86160	1436	59.8	0.005	0.01	0.08						5.36	0.0022
86400	1440	60.0	0.005	0.01	0.10	107.80	19.40	0.0013	0.0015	26.05	5.36	0.0026
86640	1444	60.2	0.005	0.01	0.06						5.36	0.0017
86880	1448	60.3	0.005	0.00	0.01						5.36	0.0004
87120	1452	60.5	0.005	0.01	0.06						5.36	0.0017
87360	1456	60.7	0.005	0.00	0.02						5.36	0.0006
87600	1460	60.8	0.005	0.00	0.01						5.36	0.0002
87840	1464	61.0	0.005	0.01	0.03	107.90	19.30	0.0013	0.0016	26.03	5.36	0.0009
88080	1468	61.2	0.005	0.01	0.09						5.36	0.0024
88320	1472	61.3	0.005	0.01	0.03						5.36	0.0009

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88560	1476	61.5	0.005	0.01	0.07						5.36	0.0019
88800	1480	61.7	0.005	0.03	0.19						5.36	0.0050
89040	1484	61.8	0.005	0.03	0.22						5.36	0.0060
89280	1488	62.0	0.005	0.04	0.28	108.00	19.20	0.0013	0.0016	26.06	5.36	0.0077
89520	1492	62.2	0.005	0.02	0.14						5.36	0.0039
89760	1496	62.3	0.005	0.02	0.11						5.36	0.0030
90000	1500	62.5	0.005	0.00	0.02						5.36	0.0006
90240	1504	62.7	0.005	0.01	0.10						5.36	0.0026
90480	1508	62.8	0.005	0.02	0.12						5.36	0.0034
90720	1512	63.0	0.005	0.01	0.04	107.60	19.40	0.0013	0.0016	26.31	5.36	0.0011
90960	1516	63.2	0.005	0.03	0.20						5.36	0.0054
91200	1520	63.3	0.005	0.03	0.18						5.36	0.0049
91440	1524	63.5	0.005	0.03	0.18						5.36	0.0049
91680	1528	63.7	0.005	0.01	0.05						5.36	0.0013
91920	1532	63.8	0.005	0.02	0.11						5.36	0.0030
92160	1536	64.0	0.005	0.01	0.10	107.80	19.90	0.0013	0.0016	26.95	5.36	0.0026
92400	1540	64.2	0.005	0.00	0.01						5.36	0.0004
92640	1544	64.3	0.005	0.00	0.02						5.36	0.0006
92880	1548	64.5	0.005	0.00	0.01						5.36	0.0002
93120	1552	64.7	0.005	0.01	0.04						5.36	0.0011
93360	1556	64.8	0.005	0.02	0.10						5.36	0.0028
93600	1560	65.0	0.005	0.00	0.02	107.90	19.70	0.0013	0.0015	26.45	5.36	0.0006
93840	1564	65.2	0.005	0.02	0.11						5.36	0.0030
94080	1568	65.3	0.005	0.01	0.05						5.36	0.0013
94320	1572	65.5	0.005	0.01	0.07						5.36	0.0019
94560	1576	65.7	0.005	0.03	0.18						5.36	0.0049
94800	1580	65.8	0.005	0.03	0.21						5.36	0.0056
95040	1584	66.0	0.005	0.03	0.20	108.10	19.60	0.0013	0.0015	26.70	5.36	0.0054
95280	1588	66.2	0.005	0.01	0.06						5.36	0.0015
95520	1592	66.3	0.005	0.01	0.10						5.36	0.0026
95760	1596	66.5	0.005	0.03	0.19						5.36	0.0050
96000	1600	66.7	0.005	0.04	0.25						5.36	0.0067
96240	1604	66.8	0.005	0.02	0.12						5.36	0.0032
96480	1608	67.0	0.005	0.01	0.06	108.00	19.40	0.0013	0.0014	26.75	5.36	0.0015
96720	1612	67.2	0.005	0.00	0.03						5.36	0.0007
96960	1616	67.3	0.005	0.01	0.08						5.36	0.0022
97200	1620	67.5	0.005	0.01	0.06						5.36	0.0015
97440	1624	67.7	0.005	0.02	0.10						5.36	0.0028
97680	1628	67.8	0.005	0.02	0.11						5.36	0.0030
97920	1632	68.0	0.005	0.01	0.09	107.90	19.60				5.36	0.0024
98160	1636	68.2	0.005	-0.01	-0.03						5.36	-0.0009
98400	1640	68.3	0.005	-0.02	-0.12						5.36	-0.0032
98640	1644	68.5	0.005	-0.01	-0.08						5.36	-0.0022
98880	1648	68.7	0.005	-0.03	-0.18						5.36	-0.0049
99120	1652	68.8	0.005	-0.04	-0.26	107.60	19.70				5.36	-0.0069
99360	1656	69.0	0.005	-0.06	-0.39						5.36	-0.0105
99600	1660	69.2	0.005	-0.06	-0.40						5.36	-0.0108
99840	1664	69.3	0.005	-0.05	-0.35						5.36	-0.0095
100080	1668	69.5	0.005	-0.05	-0.32						5.36	-0.0088
100320	1672	69.7	0.005	-0.05	-0.34						5.36	-0.0093
100560	1676	69.8	0.005	-0.05	-0.32	107.10	19.60				5.36	-0.0086
100800	1680	70.0	0.005	-0.06	-0.44						5.36	-0.0119
101040	1684	70.2	0.005	-0.04	-0.25						5.36	-0.0067
101280	1688	70.3	0.005	-0.04	-0.28						5.36	-0.0077
101520	1692	70.5	0.005	-0.04	-0.25						5.36	-0.0067
101760	1696	70.7	0.005	-0.01	-0.08						5.36	-0.0021
102000	1700	70.8	0.005	0.00	-0.03	107.20	19.40				5.36	-0.0007
102240	1704	71.0	0.005	-0.05	-0.32						5.36	-0.0086
102480	1708	71.2	0.005	-0.04	-0.26						5.36	-0.0071

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102720	1712	71.3	0.005	-0.04	-0.28						5.36	-0.0077
102960	1716	71.5	0.005	-0.05	-0.34						5.36	-0.0091
103200	1720	71.7	0.005	-0.04	-0.30						5.36	-0.0080
103440	1724	71.8	0.005	-0.04	-0.28	107.00	19.60				5.36	-0.0077
103680	1728	72.0	0.005	-0.07	-0.49						5.36	-0.0133
103920	1732	72.2	0.005	-0.06	-0.41						5.36	-0.0110
104160	1736	72.3	0.005	-0.06	-0.39						5.36	-0.0105
104400	1740	72.5	0.005	-0.06	-0.39						5.36	-0.0106
104640	1744	72.7	0.005	-0.05	-0.37						5.36	-0.0099
104880	1748	72.8	0.005	-0.05	-0.37	107.00	19.60				5.36	-0.0101
105120	1752	73.0	0.005	-0.05	-0.37						5.36	-0.0099
105360	1756	73.2	0.005	-0.04	-0.26						5.36	-0.0069
105600	1760	73.3	0.005	-0.03	-0.23						5.36	-0.0062
105840	1764	73.5	0.005	-0.03	-0.20						5.36	-0.0054
106080	1768	73.7	0.005	-0.03	-0.18						5.36	-0.0049
106320	1772	73.8	0.005	-0.03	-0.21	107.20	19.40				5.36	-0.0056
106560	1776	74.0	0.005	-0.06	-0.42						5.36	-0.0114
106800	1780	74.2	0.005	-0.05	-0.31						5.36	-0.0084
107040	1784	74.3	0.005	-0.04	-0.28						5.36	-0.0077
107280	1788	74.5	0.005	-0.06	-0.38						5.36	-0.0103
107520	1792	74.7	0.005	-0.04	-0.26						5.36	-0.0071
107760	1796	74.8	0.005	-0.03	-0.23	107.00	20.10				5.36	-0.0063

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