SOLUTE BREAKTHROUGH CURVES FOR PROCESSED KAOLIN AT LOW FLOW RATES

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ABSTRACT: Solute breakthrough curves for a 0.01-M NaCl solution permeated through two compacted test specimens of processed kaolin soil are measured at two volumetric flow rates (2.65×10^{-4} cm^3/s and 2.65×10^{-5} cm^3/s) using a flow pump system. Regression analyses of the effluent solute concentrations with two analytical models resulted in hydrodynamic dispersion coefficients D ranging from 1.49×10^{-6} cm^2/s to 3.95×10^{-6} cm^2/s for chloride and from 2.11×10^{-6} cm^2/s to 8.74×10^{-6} cm^2/s for sodium indicating that diffusion dominated the transport process in the two column tests. The effluent electrical conductance values measured immediately after sampling also tend to reflect the dominance of diffusion on the solute migration process. An observed decrease in effluent pH from between 4.8 and 5.5 during permeation with distilled water to about 4.5 during subsequent permeation with the NaCl solution is consistent with Na^+ for H^+ exchange at relatively low pH previously reported for studies involving kaolinite soils. The results of this laboratory study tend to confirm previous field studies that indicate diffusion-dominated transport at the low flow rates common in fine-grained barrier materials.

INTRODUCTION

Column testing traditionally has been performed in the fields of soil science, ground-water hydrology, and process (chemical and environmental) engineering. In most of the studies in soil science and ground-water hydrology, either coarse-grained soils have been used to simulate transport through aquifer materials and/or artificially high flow rates have been imposed to shorten the test duration. In the process engineering fields, the porous medium typically is a synthetically produced material (e.g., resin) with highly controlled material properties.

Column tests have been performed only in a few instances for purposes related to the design and evaluation of soil barriers for waste containment [e.g., Crooks and Quigley (1984); Acar and Haider (1990); van Ree et al. (1992)]. However, some simulation and field studies have indicated that diffusion is the dominant contaminant transport process through fine-grained barrier materials [e.g., see Goodall and Quigley (1977); Crooks and Quigley (1984); Shackelford (1988); Johnson et al. (1989)]. As a result, there is a need for additional study of transport processes related to waste containment (e.g., soil liners) and remediation (e.g., slurry walls) at flow rates more representative of field conditions. The primary objective of the present study is to evaluate the significance of diffusive migration on the transport of a simple NaCl salt solution through a homogeneous compacted clay soil at relatively low flow rates.

THEORY

The advection-dispersion equation describing one-dimensional transient solute transport through a homogeneous soil column can be written as follows [e.g. Freeze and Cherry (1979)]:

$$\frac{\partial c_r}{\partial t} = \frac{D}{R_d}\left(\frac{\partial^2 c_r}{\partial x^2}\right) - \frac{v}{R_d}\left(\frac{\partial c_r}{\partial x}\right) \tag{1}$$

where D = hydrodynamic dispersion coefficient; c_r = solute (resident) concentration in the pore water of the soil; R_d = retardation factor; t = time; x = macroscopic distance in the direction of transport; and v = average pore water (seepage) velocity given by Darcy's law.

The retardation factor R_d accounts for linear, reversible, and instantaneous equilibrium adsorption of reactive solutes. For reactive (adsorbing) solutes, $R_d > 1$, whereas for nonreactive (nonadsorbing) solutes, $R_d = 1$ on the basis that all of the pore space conducts flow.

The hydrodynamic dispersion coefficient is the sum of the effective diffusion coefficient D^* and the mechanical dispersion coefficient D_m as follows (Freeze and Cherry 1979):

$$D = D^* + D_m \tag{2}$$

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where D_m = a function of the seepage velocity; that is, as $v \rightarrow 0$, $D_m \rightarrow 0$ and (1) reduces to Fick's second law describing transient diffusive transport through porous media. Therefore, as $v \rightarrow 0$, miscible transport approaches the pure diffusion case.

Analytical Model

Analytical solutions to (1) in the form $c_r = c_r(x, t)$ have been derived for several different initial and boundary conditions [e.g., see van Genuchten and Alves (1982)]. Based on the work of van Genuchten and Parker (1984), the following initial and boundary conditions are considered appropriate:

$$c_r(x, 0) = c_i; \quad vc_r(0^+, t) - D\frac{\partial c_r(0^+, t)}{\partial x} = vc_o; \quad \frac{\partial c_r(\infty, t)}{\partial x} = 0 \tag{3}$$

where 0^+ indicates evaluation at the influent boundary just inside the soil column. The solution to (1) and (3) is (Lindstrom et al. 1967; Gershon and Nir 1969; van Genuchten and Alves 1982)

$$\frac{c_r(x, t) - c_i}{c_o - c_i} = \frac{1}{2}\left[\operatorname{erfc}(\xi_1) + 2\sqrt{\frac{\xi_4}{\pi}}\exp(-\xi_1^2) - (1 + \xi_2 + \xi_4)\exp(\xi_2)\operatorname{erfc}(\xi_3)\right] \tag{4}$$

where erfc is the complementary error function, and the dimensionless arguments are given by

$$\xi_1 = \frac{1 - T_R}{2\sqrt{\dfrac{T_R}{P_L}}}; \quad \xi_2 = P_L; \quad \xi_3 = \frac{1 + T_R}{2\sqrt{\dfrac{T_R}{P_L}}}; \quad \xi_4 = T_R P_L \tag{5}$$

and

$$T_R = \frac{vt}{R_d L} = \frac{T}{R_d}; \quad P_L = \frac{vL}{D} \tag{6}$$

where T = a dimensionless time factor representing the number of pore volumes of flow; and P_L = the column Péclet number [see Shackelford (1994b)].

Although (4) is strictly applicable only to a semiinfinite porous medium, effluent concentrations c_e for finite soil columns can be evaluated by considering the requirement for continuity of solute mass flux across the lower or exit boundary of a finite column [e.g., see Gershon and Nir (1969); Kreft and Zuber (1978); Parker and van Genuchten (1984); van Genuchten and Parker (1984)] or

$$c_e = \frac{J(L^-, t)}{q} \tag{7}$$

where L^- indicates evaluation just inside the exit end of the column and $c_e = c_e(L, t)$. In terms of (4), the solute flux J is given by (Shackelford 1994b)

$$J(x, t) = qc_i + \frac{1}{2}q(c_o - c_i)[\operatorname{erfc}(\xi_1) + \exp(\xi_2)\operatorname{erfc}(\xi_3)] \tag{8}$$

and substitution of (8) into (7) results in the following model for describing effluent solute breakthrough curves from finite laboratory columns:

$$\frac{c_e(L, t) - c_i}{c_o - c_i} = \frac{1}{2}[\operatorname{erfc}(\xi_1) + \exp(\xi_2)\operatorname{erfc}(\xi_3)] \tag{9}$$

which has the same form, but not the same meaning, as the well-known Ogata and Banks (1961) solution [e.g., see Kreft and Zuber 1978; Parker and van Genuchten (1984); van Genuchten and Parker 1984)]. On the basis of mass balance constraints, ease of use, and physical relevance to actual flow systems at low flow rates, van Genuchten and Parker (1984) and Shackelford (1994b) recommend the use of (9) [i.e., relative to several other analytical solutions to (1)] for evaluation of effluent concentrations from finite soil columns.

MATERIALS AND METHODS

Soil

The soil used in the present study is Standard Air Float (SAF) kaolin, produced by the Georgia Kaolin Company of Union, New Jersey. The Georgia Kaolin Company reports that SAF kaolin soil consists, on average, of 96% (dry weight) kaolinite mineral. The physical and chemical properties of the processed kaolin soil are shown in Tables 1 and 2, respectively.

The soluble salt concentrations were determined by washing specimens of the kaolin with deionized water. The exchangeable cation concentrations were determined by subtracting the soluble salt concentrations from the extractable cation concentrations for the same ions based on the procedure by Thomas (1982) in which separate specimens of kaolin are washed with

TABLE 1. Physical Properties of Processed Kaolin Soil Used in Study

Property (1)	Reference (2)	Value (3)
Source	Product information[a]	—
Trade name	Product information	"Standard air float"
Principal mineral	Product information	Kaolinite
Color	—	White
Water content (*w*)	ASTM D 4959	0.4%
Specific gravity (G_s)	ASTM D 854	2.65
Liquid limit (*LL*)	ASTM D 4318	41.0%
Plasticity index (*PI*)	ASTM D 4318	17.0%
Particle sizes:		
silt (0.002–0.074 mm)	ASTM D 422	39%
clay (<0.002 mm)	ASTM D 422	61%
Activity, A[b]	—	0.28
USCS classification	ASTM D 2487	CL
Maximum dry unit weight ($\gamma_{d\max}$)	ASTM D 698(A)	15.9 kN/m^3 (101.0 pcf)
Optimum water content (w_{opt})	ASTM D 698(A)	22.0%

[a] Georgia Kaolin Co., Union, N.J.

[b] A = $PI(\%)/\% < 2\ \mu$m.

TABLE 2. Chemical Properties of Processed Kaolin Soil Used in Study

Property (1)	Value(s) (2)
(*a*) Saturated paste	
Percent saturation, g/g	91.2
pH at 25°C	4.8
Electrical (specific) conductance, *EC* at 25°C, μS/cm	100
(*b*) Soluble salts, mg/L (meq/L)[a]	
Ca^{2+}	1.53 (0.08)
Mg^{2+}	0.092 (0.01)
Na^{+}	0.01 (<0.01)
K^{+}	<0.01 (<0.01)
Br^{-}	<0.1 (<0.01)
Cl^{-}	17.2 (0.49)
(*c*) Exchangeable cations (meq/100 g)[a]	
Ca^{2+}	1.94
Mg^{2+}	0.10
Na^{+}	<0.01
K^{+}	0.02
Li^{+}	<0.01
Al^{3+}	0.77
Fe^{2+}, Fe^{3+}	0.12
[sum]	<2.97
(*d*) Exchange capacities at pH = 6.6[a]	
Anion exchange capacity, AEC (meq/100 g)	<1
Cation exchange capacity, CEC (meq/100 g)	12.7

[a] Values reported are averages of three measurements.

ammonium acetate (NH_4OAc). The cation exchange capacity (CEC) was determined by a method modified after Rhoades (1982) in which the soil is washed repeatedly with a saturating solution of NaOAc plus $NaNO_3$, rinsed with pure ethanol, and exposed to a 0.5N $Mg(NO_3)_2$ solution to determine the release of Na^+ and, therefore, the CEC of the soil. Differences between the sum of the exchangeable cations and the CEC can result from failure to account for all exchangeable cations and/or differences in the test procedures, as described by Rhoades (1982).

Several attempts also were made to determine an anion exchange capacity (AEC) using both chloride and phosphorous solutions. However, only a slight AEC (<1 meq/100g) was measured for the kaolin at the equilibrium pH of 6.6.

Soil Preparation

The bulk kaolin soil was prepared for compaction by mixing the air-dried soil with distilled water (DW) with an electrical (specific) conductance *EC* < 1 μS/cm (1 μS/cm = 1 μmho/cm). Distilled water was used in soil preparation to minimize the introduction of additional ions into the soil pore water. Based on the optimum water content of 22% (see Table 1), a target water content of 24% was chosen for soil preparation to minimize the hydraulic conductivity of the compacted test specimens in accordance with standard procedures for the construction of compacted clay barriers for waste containment. After wetting and mixing the soil to the desired water content, the wetted soil was passed through a No. 4 sieve to remove wetted clods with average diameters greater than 4.75 mm. The wetted soil passing the No. 4 sieve was placed and sealed in double-sealed plastic bags. The bags subsequently were placed and sealed in a large polyethylene container with a saturated sponge to maintain a relatively humid environment and minimize evaporation. The soil was allowed to hydrate for at least 7 days prior to compaction to promote a uniform water content.

Test Specimen Properties

Compaction

After hydration, the soil was removed from the polyethylene container and passed again through a No. 4 sieve to minimize the effect of clod size on the compacted material. Clods retained on the No. 4 sieve were broken up with a spatula and added to the soil that had passed the No. 4 sieve. The exact amount of the resulting soil mixture required to achieve a dry unit weight of 15.1 kN/m^3 (96.0 pcf) was placed into a mold with an inner diameter of 10.12 cm (3.985 in.) for compaction.

Two compacted soil specimens were tested in the present study. A static compaction procedure was used to minimize differences between the compacted test specimens. The static compaction was achieved by placing an acrylic disc on top of the wetted soil in the mold and compressing the soil with a hydraulic jack for a period of 30 min to minimize specimen rebound upon release of the confining stress. The compacted specimens were extruded from the mold in the same direction as compaction to minimize specimen disturbance. Each extruded specimen was measured and weighed before placement into a flexible-wall permeameter for consolidation and back-pressure saturation prior to permeation. The lengths L of the soil specimens after extrusion from the mold were 3.05 cm (1.20 in.). A short specimen length was desired to minimize both testing time and volume changes in the test specimens during permeation. The properties of the compacted test specimens are summarized in Table 3. As shown in this table, the compacted dry unit weights of both test specimens were reduced to values somewhat less than the desired value of 15.1 kN/m^3 (96.0 pcf) presumably due to a small amount of rebound after compaction.

Back Pressure

The compacted specimens for the column tests were submitted to back pressure before permeation to achieve essentially full saturation. Back-pressure saturation was achieved by first consolidating the test specimen under no back pressure to an effective stress of 34.5 kPa (5 psi), and then increasing the confining pressure and the back pressure in increments of 69 kPa (10 psi) to maintain the difference between confining pressure and back pressure of 34.5 kPa (5 psi). The back-pressure increment was applied within 60 s after application of the confining pressure increment to reestablish the 34.5 kPa (5 psi) difference and minimize additional consolidation of the test specimen. Pressure increases were limited to one per day to allow equilibration of pore pressures within the test specimen that should have occurred relatively rapidly due to the short specimens. The final confining and cell pressures as well as the final B-values for each test specimen are summarized in Table 3.

TABLE 3. Test Specimen Properties

Stage of test (1)	Parameter (2)	Test 1 (3)	Test 2 (4)
Compaction	Dry unit weight (γ_d), kN/m^3 (pcf)	14.8 (94.1)	14.7 (93.7)
Compaction	Water content (w), percent	23.5	23.9
Compaction	Degree of saturation (S_r), percent	81.5	82.2
Compaction	Porosity (n)	0.433	0.435
Compaction	Volume, cm^3	245.4	245.2
Compaction	Void volume, cm^3	106.3	106.8
Back pressure	Final cell pressure, kPa (psi)	552 (80)	552 (80)
Back pressure	Final back pressure, kPa (psi)	517 (75)	517 (75)
Back pressure	Final Skempton's B parameter	0.993	0.974
Permeation	Induced flow rate with DW, cm^3/s	2.65×10^{-4}	2.65×10^{-4}
Permeation	Induced flow rate with NaCl solution, cm^3/s	2.65×10^{-4}	2.65×10^{-5}
End	Dry unit weight (γ_d), kN/m^3 (pcf)	14.4 (91.6)	14.2 (90.6)
End	Water content (w), percent	30.4	31.1
End	Degree of saturation (S_r), percent	100.0	100.0
End	Porosity (n)	0.446	0.452
End	Volume, cm^3	253.7	255.5
End	Void volume, cm^3	113.1	115.5

TABLE 4. Measured Chemical Properties of NaCl Solutions

Parameter (1)	Test 1 (2)	Test 2 (3)
Electrical (specific) conductance (EC_o) at 25°C, μS/cm	1,208	1,187
pH at 25°C	6.2	6.5
Sodium (Na^+) concentration (c_o), mg/L	228	234
Chloride (Cl^-) concentration (c_o), mg/L	347	356

Permeation

After back-pressure saturation, each test specimen was permeated with deaired DW prior to permeation with a 0.01-M NaCl solution. Permeation with DW was performed to flush excess soluble salts from the test specimens and minimize the influence of background solute concentrations c_i on the test results. The test specimens were flushed with DW under identical volumetric flow rates (2.65×10^{-4} cm³/s) to minimize differences between specimen properties before introduction of the NaCl solution.

A deaired 0.01-M NaCl solution was introduced into the influent of each test specimen immediately after flushing with DW to evaluate the migration of solutes, Na^+ and Cl^-, through the process kaolin. The measured chemical properties of the NaCl solutions for each test are shown in Table 4. Introduction of the NaCl solution represents commencement of the column test from the standpoint of evaluation of the transport parameters (D and R_d). The volumetric flow rate was maintained at 2.65×10^{-4} cm³/s for test 1, whereas volumetric flow rate for test 2 was reduced to 2.65×10^{-5} cm³/s to evaluate the effect of a lower flow rate on the migration of the solutes.

Effluent samples from the soil columns were recovered periodically throughout permeation for chemical analysis. The pH and EC of the effluent samples were measured and recorded in the laboratory immediately after sampling. In addition, separate effluent samples were recovered for chemical analysis of solute concentrations. Chloride (Cl^-) and sodium (Na^+) concentrations were measured by ion chromatography (IC) and inductively coupled plasma-optical emissions spectroscopy (ICP-OES), respectively.

The effluent from the soil columns was allowed to accumulate in a collection reservoir between sampling intervals. As a result, the measured values of pH, EC, and solute concentrations represent average values over the increment of time between sampling. Schnabel and Ritchie (1989) and Shackelford (1994b) indicate that plotting the average effluent concentrations at the midpoint of the interval between sampling generally results in $\leq 10\%$ error in P_L and R_d for $P_L \leq 50$ when the data are regressed against (9) with the errors decreasing to zero for $P_L = 1.00$. As a result, the effluent concentrations, pH, and EC values in the present study are plotted at the midpoints of the intervals between sampling.

Breakdown

After completion of a test, the test specimen was removed carefully from the flexible-wall permeameter. The specimen was reweighed and remeasured, and the entire specimen was placed in an oven at 105°C to determine the final water content. Based on the total weight, the measured volume, and the final water content of each specimen, the total porosity n and void volumes shown in Table 3 were calculated. The volume of voids at the end of the test were used in calculating the pore volumes of flow assuming that all voids conducted fluid flow.

Flow Pump System

A flow pump system was used to permeate the test specimens. Flow pump systems differ from more traditional hydraulic systems (e.g., constant-head or falling-head systems) in that the flow pump maintains a constant volumetric flow rate Q through the test specimen. The hydraulic conductivity k is calculated from pressure drop (head loss) Δu across the specimen measured with a differential pressure transducer in accordance with the following form of Darcy's law:

$$k = \frac{Q\gamma_f L}{A\Delta u} \qquad (10)$$

where γ_f = unit weight of the permeant fluid (usually water); and A = total cross-sectional area of the test specimen. A flow pump system is attractive for column testing since (1) the induced constant volumetric flow rate under steady-state conditions (no volume change) results in a constant seepage velocity that is assumed in the derivation of the advection-dispersion equation [(1)]; and (2) waste-soil interactions that may alter soil hydraulic conductivity do not alter the volumetric flow rate (Redmond and Shackelford 1994).

With respect to the current study, a flow pump with two reciprocating syringes is used to allow refilling of one syringe with fresh permeant solution while the second syringe is infusing permeant solution through the test specimen. In this manner, the flow pump can provide continuous flow of permeant solution to the specimen that is essential to produce the several pore volumes of flow required for measurement of solute (effluent) breakthrough curves for laboratory column testing. A detailed description of the design and evaluation process of the flow pump system used in the present study is provided by Redmond and Shackelford (1994).

RESULTS AND DISCUSSION

Hydraulic Parameters

The hydraulic conductivity k, the pressure loss Δu, and the temperature as a function of the net pore volumes of flow T for permeation with both DW and the NaCl solution for both tests are shown in Fig. 1. Net pore volumes of flow are calculated as follows:

$$T = T_{\Sigma} - T_{\mathrm{DW}} \qquad (11)$$

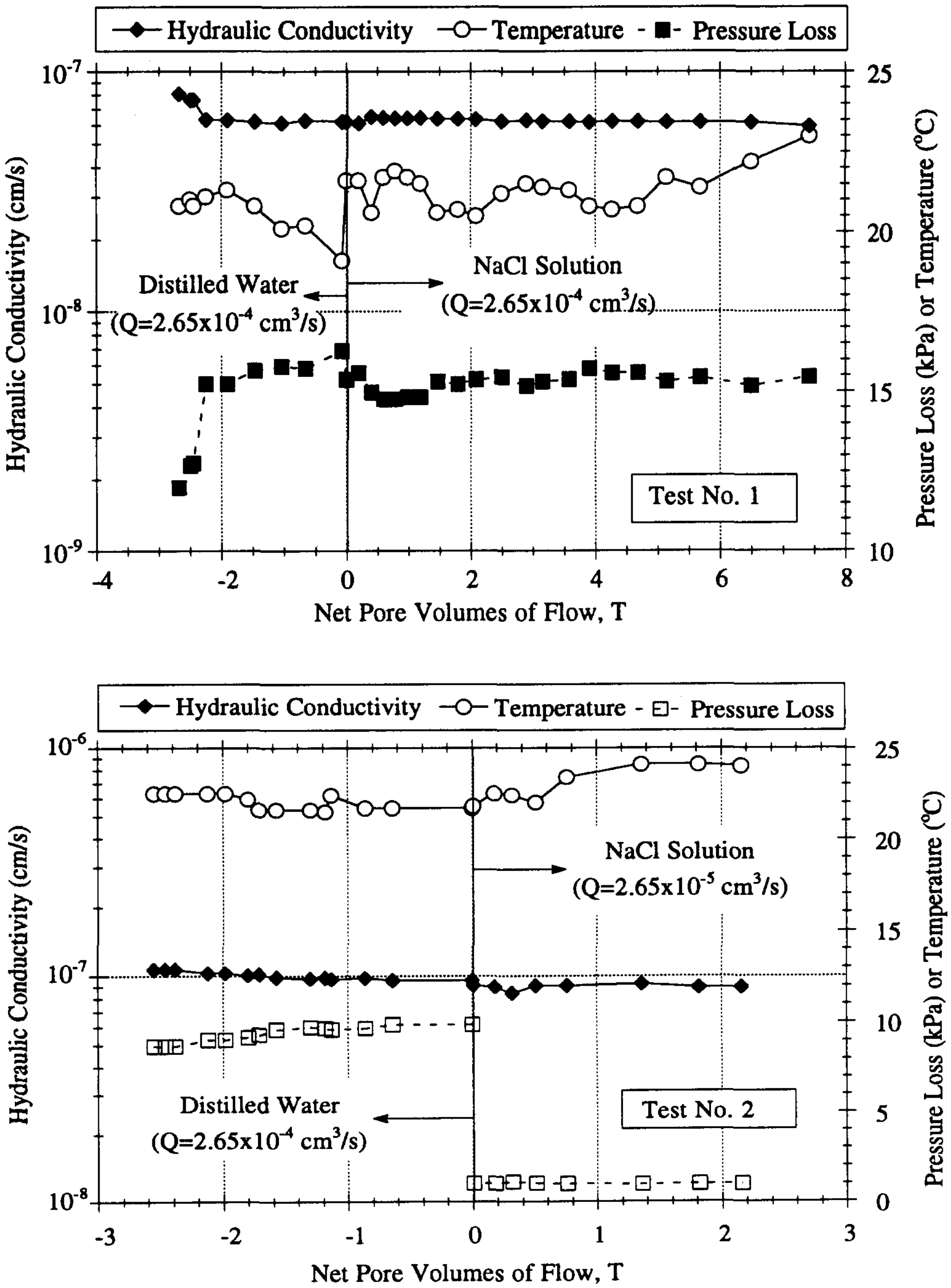

FIG. 1. Hydraulic Conductivity, Pressure Loss, and Temperature versus Net Pore Volumes of Flow for Tests 1 and 2

TABLE 5. Summary of Hydraulic Parameter Results

Permeant Liquid (1)	Parameter (2)	Test 1 (3)	Test 2 (4)
Distilled water	Induced flow rate (Q), cm^3/s	2.65×10^{-4}	2.65×10^{-4}
Distilled water	Test duration, days	13.7	14.1
Distilled water	Pore volumes of flow	2.75	2.68
Distilled water	Averaged induced hydraulic gradient	49.1 ± 5.2	31.2 ± 1.5
Distilled water	Average hydraulic conductivity (k_1), cm/s	$6.7(\pm 0.8) \times 10^{-8}$	$10.1(\pm 0.4) \times 10^{-8}$
NaCl solution	Induced flow rate, cm^3/s	2.65×10^{-4}	2.65×10^{-5}
NaCl solution	Test duration, days	37.1	108.9
NaCl solution	Pore volumes of flow	7.42	2.16
NaCl solution	Averaged induced hydraulic gradient	51.0 ± 1.0	3.41 ± 0.14
NaCl solution	Average hydraulic conductivity (k_2), cm/s	$6.3(\pm 0.1) \times 10^{-8}$	$9.0(\pm 0.3) \times 10^{-8}$
NaCl solution	k_2/k_1	0.94	0.89
NaCl solution	Seepage velocity (v), cm/s	7.1×10^{-6}	7.0×10^{-7}

where T_Σ = pore volumes of flow since the start of permeation with the DW; and T_{DW} = total number of pore volumes of flow for permeation only with DW given in Table 5. Therefore, $T < 0$ corresponds to the flushing stage of the test, and $T = 0$ corresponds to the beginning of the column stage of the test where $T \geq 0$ is the same as the dimensionless time factor given in (6).

Based on the plots in Fig. 1, the effect of temperature on the measured hydraulic conductivity is small. Also, introduction of the NaCl solution resulted in very little change in the hydraulic conductivity of both test specimens. Finally, the decrease in volumetric flow rate Q on introduction of the NaCl solution in the low flow rate test (test 2) is compensated by an equal decrease in pressure loss across the test specimen.

The hydraulic parameters for both tests are summarized in Table 5. The test durations for the flushing stages of the tests (13.7 days and 14.1 days) are similar and relatively short in both tests due to permeation at the same volumetric flow rate (2.65×10^{-4} cm^3/s). However, the durations of the column stages of the tests are considerably greater and relatively long at 37.1 days for the high flow rate test (test 1) and 108.9 days for the low flow rate test (test 2). The greater test durations associated with the column stages of the tests result from the requirements (1) to provide as complete a description as possible of the solute breakthrough curves in the effluent; and (2) to achieve a relative effluent concentration, $(c_e - c_i)/(c_o - c_i)$, of at least 0.5 for both Cl^- and Na^+. Also, the column stage of test 2 is 2.94 times greater than that of the test 1 due to the 10-fold decrease in volumetric flow rate for test 2 relative to test 1. Therefore, even though the attempt was made to decrease test times by using relatively short (3.05 cm) test specimens, test 1 required 50.8 days of permeation, whereas test 2 required 123.0 days of permeation.

The average induced hydraulic gradient of 51.0 for the column stage of the high flow rate test (test 1) is more typical of laboratory hydraulic conductivity testing on saturated fine-grained soils. However, the average induced hydraulic gradient of 3.41 for the column stage of the low flow rate test (test 2) probably is closer to field conditions.

The slightly lower average hydraulic conductivity values for test 1 relative to test 2 may be due, in part, to relatively greater dry unit weights of test 1 both after compaction and at the end of the test (see Table 3). In each test, the hydraulic conductivity based on permeation with the NaCl solution is slightly lower than the initial hydraulic conductivity based on permeation with DW. The increase in ionic strength of the 0.01-M NaCl solution relative to the DW apparently is not sufficiently large to cause particle rearrangement, flocculation, and an increase in hydraulic conductivity in the presence of the induced effective stresses in the test specimens (Mitchell 1993; Shackelford 1994a). In addition, the lower value of k_2/k_1 reported in Table 5 for test 2 relative to test 1 probably is due, in part, to an overall increase in effective stress within the soil specimen in test 2 resulting from the decrease in induced flow rate under constant confining stress. In either case, the effect of the NaCl solution on the hydraulic conductivity values of both specimens is small.

The seepage velocities reported in Table 5 were calculated using the final values for the total porosity and total volume of the test specimens shown in Table 3 assuming all of the voids conducted fluid flow and a specimen length of 3.05 cm (1.20 in.). These assumptions are believed to be reasonable given the short lengths and corresponding small volumes of the test specimens. Based on these assumptions, the calculated seepage velocity for the low flow rate test is about 10 times less than that of the high flow rate test corresponding to the same relative difference between induced volumetric flow rates.

pH

The measured pH values in the effluent for both tests 1 and 2 are shown in Fig. 2(a). Although some differences exist, the trend in pH is the same; that is, a relatively high pH during the

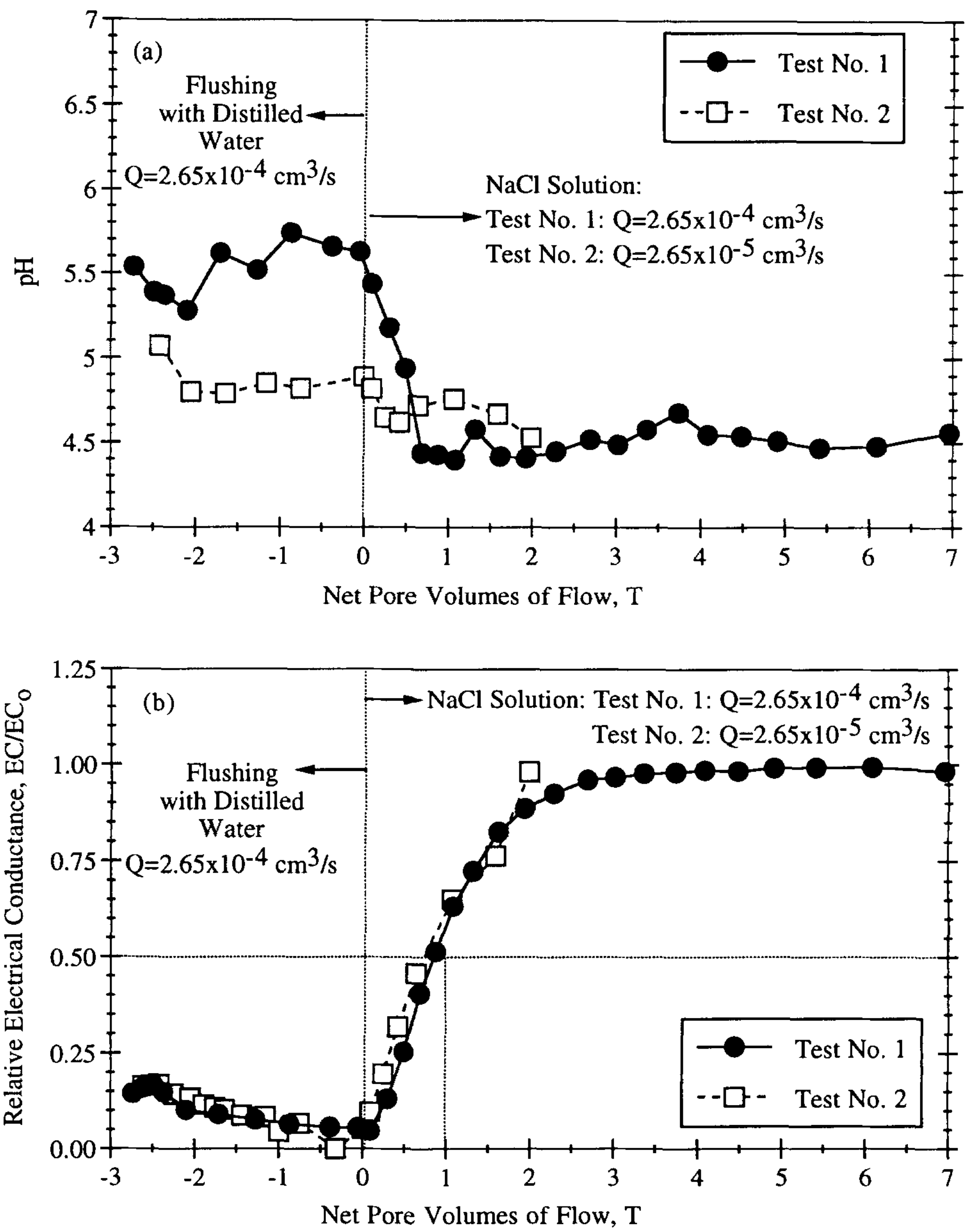

FIG. 2. Effluent: (a) pH; and (b) Relative Electrical Conductance versus Net Pore Volumes of Flow for Tests 1 and 2

flushing stage of the test in which DW (pH ≈ 5.8) is the permeant fluid followed by a decrease in pH upon permeation with the NaCl solution. This trend is consistent with replacement of the protons (H^+) attached to exposed hydroxyls on the surfaces of kaolinite clay particles due to exchange of Na^+ for H^+ at relatively low pH conditions [e.g., see Grim (1968); Ferris and Jepson (1975); Bolland et al. (1976); McBride (1978); Bohn et al. (1985)]. The relatively low pH of 4.8 measured on a saturated paste tends to substantiate the observed decrease in effluent pH (see Table 2). Since the DW contains only trace amounts of cations (low electrical conductance), significant release of protons from the soil due to exchange reactions during the flushing stage is not expected.

The final pH values for both tests are approximately 4.5 indicating relatively acidic conditions existing in the test specimens. In addition, the capacity for release of protons from the test specimens apparently was not exhausted during the tests since there is no indication of a subsequent increase in pH.

Electrical Conductance

The measured EC values normalized with respect to the initial electrical conductance EC_o for the NaCl solution (see Table 4) for both tests 1 and 2 are shown as a function of the net pore volumes of flow in Fig. 2(b). In general, the trends in EC/EC_o data for both tests are the same. The decrease in *EC*/*EC*$_o$ values during the flushing stage of the test reflects a decrease in soluble salt (ion) concentrations within the pore water of the test specimens due to permeation with DW. After permeation with DW, the *EC*/*EC*$_o$-values increase as increasing concentrations of ions, particularly Na^+ and Cl^-, appear in the effluent.

Due to a requirement for electrical neutrality in solution, there is no distinction between the contributions of nonreactive and reactive solutes (ions) to the overall *EC* of the effluent. Therefore, no information regarding the migration of individual solute species can be ascertained from *EC* measurements. Nonetheless, the trends in relative *EC*-values shown in Fig. 2(b) are indicative more or less of the expected behavior of solute breakthrough curves; that is, an *EC*/*EC*$_o$-value of 0.5 is reached close to $T = 1$ and the *EC*/*EC*$_o$ values subsequently approach a value of unity upon further permeation with the NaCl solution. The fact that *EC*/*EC*$_o$ = 0.5 at *T*-values slightly less than unity for both tests probably reflects the expected dominance of molecular diffusion at the low flow rates imposed in this study (Shackelford 1988).

Solute Breakthrough Curves

The measured solute concentrations for Cl^- and Na^+ in the effluent of tests 1 and 2 are shown in Fig. 3. The data indicate that there is a slight but noticeable decrease in both Cl^- and

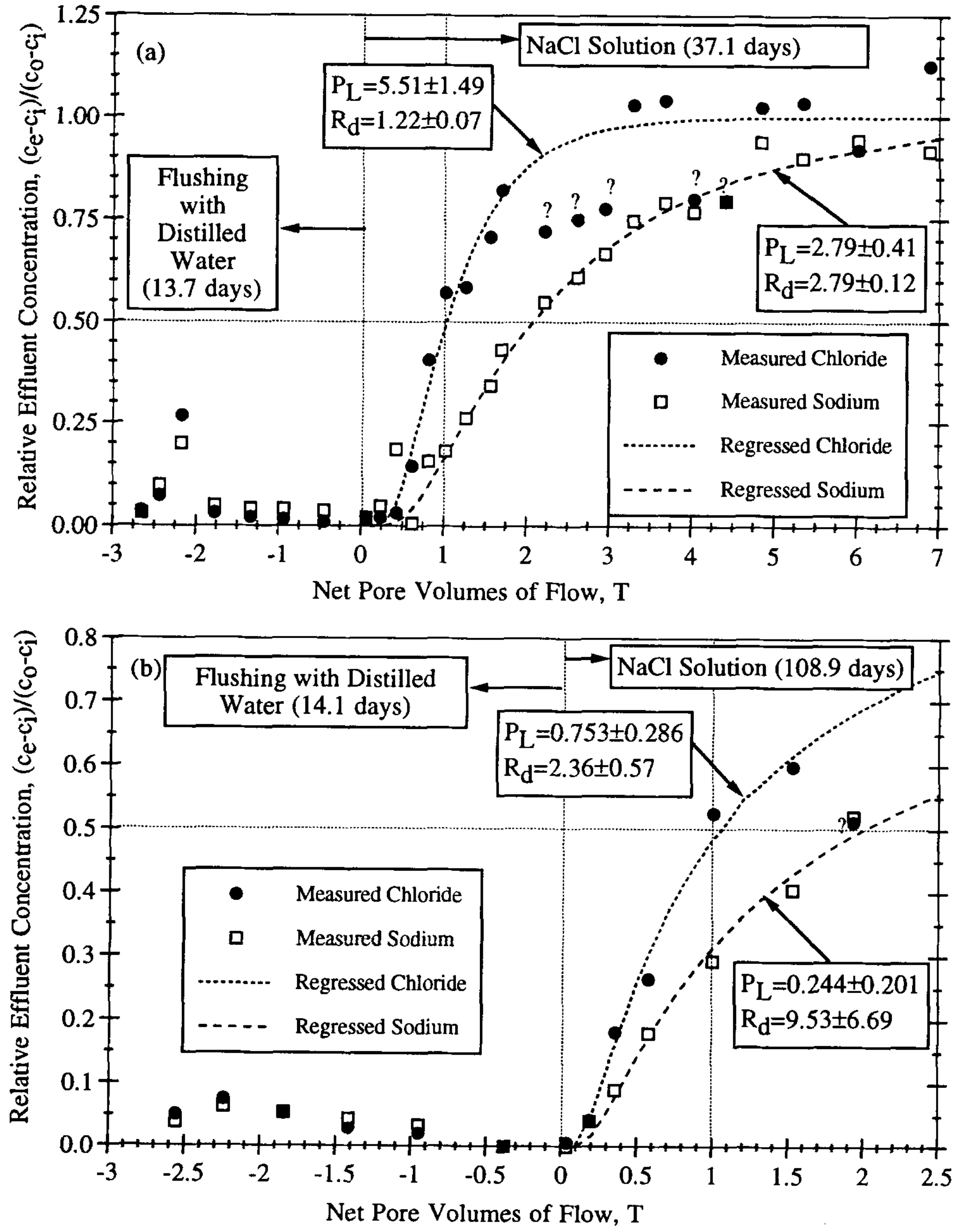

FIG. 3. Measured and Regressed Solute Breakthrough Curves Based on Full Analytical Model (Eq. 9): (a) Test 1; and (b) Test 2

TABLE 6. Summary of Transport Parameter Results Based on Regression Analyses

Analytical model (1)	Test (2)	Flow rate (Q)[a] (cm³/s) (3)	Chemical species (4)	Fitted Parameters (value ± std. dev.): Péclet number (P_L) (5)	Fitted Parameters (value ± std. dev.): Retardation factor (R_d) (6)	Dispersion coefficient (D) (cm²/s) (7)	D/R_d (8)
Full (Eq. 9)	1	2.65×10^{-4}	Cl^-	5.51 ± 1.49	1.22 ± 0.07	3.95×10^{-6}	3.24×10^{-6}
Full (Eq. 9)	1	2.65×10^{-4}	Na^+	2.79 ± 0.41	2.79 ± 0.12	7.81×10^{-6}	2.80×10^{-6}
Full (Eq. 9)	2	2.65×10^{-5}	Cl^-	0.753 ± 0.286	2.36 ± 0.57	2.84×10^{-6}	1.20×10^{-6}
Full (Eq. 9)	2	2.65×10^{-5}	Na^+	0.244 ± 0.201	9.53 ± 6.69	8.75×10^{-6}	0.918×10^{-6}
Truncated (Eq. 13)	1	2.65×10^{-4}	Cl^-	5.96 ± 1.53	1.04 ± 0.05	3.66×10^{-6}	3.51×10^{-6}
Truncated (Eq. 13)	1	2.65×10^{-4}	Na^+	3.33 ± 0.28	2.09 ± 0.04	6.54×10^{-6}	3.13×10^{-6}
Truncated (Eq. 13)	2	2.65×10^{-5}	Cl^-	1.43 ± 0.28	1.06 ± 0.06	1.49×10^{-6}	1.41×10^{-6}
Truncated (Eq. 13)	2	2.65×10^{-5}	Na^+	1.01 ± 0.16	1.98 ± 0.11	2.11×10^{-6}	1.07×10^{-6}

[a] Flow rate during column testing stage of test.

Na^+ concentrations during the flushing stage of the test, which reflects the decrease in electrical conductance previously noted. Overall, the Cl^- and Na^+ concentrations were reduced before permeation with the NaCl solution to 3.3 mg/L and 4.5 mg/L, respectively, for test 1 and to 3.4 mg/L and 2.6 mg/L, respectively, for test 2. In terms of the column stages of the tests, scatter in the measured Cl^- concentrations is noticeable, particularly for the $2.2 \leq T \leq 3$ and $4.0 \leq T \leq 4.4$ in test 1. However, there are sufficient data previous to this scatter to establish a trend in the measured concentrations.

The theoretical solute breakthrough curves as well as the best-fit values for the column Peclet number P_L and retardation factor R_d for each solute based on (9) also are shown in Fig. 3. The best-fit values for P_L and R_d were determined using a nonlinear least squares regression analysis in the IGOR software program distributed by WaveMetrics, Inc. (Lake Oswego, Ore). The best-fit values of P_L and R_d as well as the resulting dispersion coefficients D are summarized in Table 6. The D-values were calculated in accordance with (6) using the seepage velocity values shown in Table 5.

Three aspects of the data in Table 6 and plots in Fig. 3 warrant discussion: (1) the effect of low flow rates on the measured dispersion coefficients; (2) the apparent retardation of chloride; and (3) the effect of low flow rates on measured retardation factors. Each of these three aspects is discussed in the following subsections.

Effect of Low Flow Rates on Dispersion

The calculated hydrodynamic dispersion coefficients D for both Cl^- and Na^+ based on (9) fall within a narrow range from 2.84×10^{-6} cm²/s to 8.75×10^{-6} cm²/s, although there is significant uncertainty (large standard deviation) associated with the determination of D for Na^+ in test 2. This range of dispersion coefficients is within the range of effective diffusion coefficients D^* measured under no-flow conditions (i.e., $v = 0$) for both Cl^- and Na^+ with similar soils (Shackelford 1991). Therefore, for the assumptions inherent in the advection-dispersion theory and (9), the transport of the Cl^- and Na^+ under the relatively low flow rates imposed in the present study is dominated by diffusion; that is, mechanical dispersion is negligible (i.e., $D_m \approx 0$ and $D \approx D^*$).

The dispersion coefficient D of Cl^- at the relatively high flow rate (test 1) is approximately 1.3 times greater than dispersion coefficient for Cl^- at the relatively low flow rate (test 2). This difference in D-values is consistent with classical advection-dispersion transport theory indicating that D increases as the seepage velocity increases (Freeze and Cherry 1979). However, the Na^+ dispersion coefficient at the relatively high flow rate is 0.89 times the Na^+ dispersion coefficient at the relatively low flow rate. Therefore, differences in D-values for a given solute at the different flow rates probably reflect scatter in the measured concentration data more than compliance to the advection-dispersion theory. In any case, the differences between D-values for a given solute for the low flow rates in the present study are small.

In each test, the Cl^- dispersion coefficient is less than the Na^+ dispersion coefficient. The Na^+ dispersion coefficient is about two times greater than the Cl^- dispersion coefficient for test 1, and about three times greater than the Cl^- dispersion coefficient for test 2. This trend is visually apparent from the shape of the solute breakthrough curves in Fig. 3, where the spreading of Na^+ is noticeably greater than the spreading of the Cl^-. Cherry et al. (1984) have noted that the dispersion of reactive solutes ($R_d > 1$) generally is greater than the dispersion of nonreactive ($R_d = 1$) solutes. However, in the present study, both solutes are reactive based on the analyses with (9).

In general, the larger the value of R_d, the greater the magnitude of D required to maintain a constant value of the ratio D/R_d appearing in the advection-dispersion equation [(1)]. Therefore, for a given effluent concentration distribution and flow rate, a greater dispersion might be expected for a solute that exhibits greater retardation, such as Na^+ in this case. This comparison presumes that the values of D/R_d for both Cl^- and Na^+ are identical for the same flow rate. Based on the data in Table 6, the ratio of D/R_d for Cl^- to D/R_d for Na^+ is 1.16 for test 1 and 1.31 for test 2. As a result, the values of D/R_d for both Cl^- and Na^+ are not identical for the same flow rate. However, the difference between D/R_d values for both Cl^- and Na^+ is not large and cannot totally compensate for the difference between Na^+ and Cl^- dispersion coefficients previously noted. Therefore, the fact that the D-values for Cl^- are less than the D-values for Na^+ in the present study is not necessarily surprising.

Apparent Retardation of Chloride

As indicated in Table 6 and Fig. 3, both chloride (Cl^-) and sodium (Na^+) exhibit a retardation effect (i.e., $R_d > 1$). While a retardation factor for Na^+ is expected due to the CEC associated with kaolinite, Cl^- generally is assumed to be a nonreactive (nonadsorbing) solute (i.e., $R_d = 1$). As a result, some discussion of the apparent retardation effect of chloride is warranted.

The scatter in the concentration data may account for a portion of the measured retardation effect for chloride. However, based on the standard deviations reported in Table 6 for the retardation factor of Cl^-, the scatter in the measured concentration data cannot totally account for the measured retardation effect.

As previously mentioned, the effluent concentrations are plotted at the middle of the effluent sampling interval to account for the average nature of the measured effluent concentrations that are allowed to collect over an increment in time. However, the studies by Schnabel and Ritchie (1987) and Shackelford (1994b) indicate that the errors in regressed values of P_L and R_d are generally $\leq 10\%$. Therefore, the measured retardation effect for Cl^- also cannot be attributed totally to the measurement of incremental, average effluent concentrations.

The existence of dead-end or unconnected pore space and/or viscous (adsorbed) pore water may lead to an effective porosity in which all of the pore space does not contribute to fluid flow [e.g., Bear (1972)]. One method commonly used to determine this effect is to measure the number of pore volumes of flow required for advective breakthrough [i.e., T at $(c_e - c_i)/(c_o - c_i) = 0.5$] of a nonreactive tracer. However, the measured retardation effect for the Cl^- and the low induced flow rates (diffusion-dominated transport) preclude the using of the chloride breakthrough curve for determining an effective porosity effect in the present study [e.g., see Shackelford (1993)]. Nevertheless, the existence of an effective porosity effect for the kaolin test specimens would result in a larger, not smaller, measured retardation effect, since the pore volumes of flow associated with any given effluent concentration would be larger than assumed in the present analyses.

The total ion exchange capacity of kaolinite generally is attributed to a combination of broken bonds on particle edges, isomorphic substitution, and replacement of the protons (H^+) from exposed hydroxyls (OH^-) on the surfaces of kaolinite clay particles [e.g., see Grim (1968); Bohn et al. (1985); and Mitchell (1993)]. In addition, the exchange capacity of kaolinite traditionally has been considered to be pH dependent. A pH-dependent adsorption behavior of kaolinite is consistent with the metal oxide (e.g., Fe_2O_3) model in which an abundance of protons (H^+) in the pore water at relatively low pH results in adsorption of protons to exposed hydroxyls at the solid-liquid interface resulting in a net positive charge (solid-$OH_2^{+1/2}$) which, in turn, represents positive exchange sites for the adsorption of Cl^- from solution [e.g., see Bohn et al. (1985)]. The opposite situation occurs at high pH (low H^+ concentration) resulting in negative exchange sites and adsorption of Na^+. The pH at which there is zero net charge on the particle surface is referred to as the zero point of charge (ZPC). A ZPC of 3.5 for kaolinite has been reported by Grim (1968), whereas a ZPC of 6.5 for kaolinite has been reported by Bohn et al. (1985). Differences in ZPC may result, in part, from differences in the type and purity of the kaolinite as well as differences in the test procedure. As a result, anion exchange capacities (AEC) at low pH which, in some cases, may be greater than the CEC at high pH have been reported for some kaolinites [e.g., Grim (1968)].

The existence of a net positive charge at relatively low pH does not mean necessarily that only anion adsorption is possible; that is, negative exchange sites may exist even though the overall net charge on the surface of the clay particle is positive. For example, the exchange of Na^+ for H^+ on the surfaces of kaolinite clay particles at relatively low pH values (pH < 7) is well recognized [e.g., Ferris and Jepson (1975); Bolland et al. (1976); McBride (1978)]. In transient systems such as the column tests performed in the present study, exchange of Na^+ for H^+ would be expected to result in release of protons (H^+) to the effluent and a decrease in effluent pH.

The pH of 4.8 measured for a saturated paste of the kaolin soil (Table 2) is within the reported range of ZPC values for kaolinite soils and indicates that the process kaolin in the present study is relatively acidic. In addition, the effluent pH in both column tests decreased to a value of approximately 4.5 upon permeation with the NaCl solution and remained at this value throughout the duration of the test. This trend is consistent with the prior description for Na^+ adsorption at low pH. Therefore, the observed retardation factors for both Cl and Na$^+$ are consistent with adsorption of anions as well as cations at low pH in soils with pH-dependent surface charges, for example, soils with appreciable kaolinite.

Batch equilibrium tests were performed by mixing 50 g of kaolin (dry weight) with 200 mL of NaCl solution at different initial concentrations to further evaluate a potential for anion adsorption. The 1:4 soil:solution ratio (by weight) is the largest recommended soil:solution ratio for batch equilibrium testing [see Roy et al. (1991)]. The soil was prewashed three times with DW before mixing with the NaCl solution. The soil:solution slurries were mixed for 48 h, a portion of the slurry was removed after mixing and centrifuging, and the supernatant was analyzed for chloride (Cl$^-$) and sodium (Na$^+$) concentrations. The results of the tests are plotted in Fig. 4. Each data point in Fig. 4 represents the average of three separate tests performed at the same initial concentration of NaCl solution.

The data in Fig. 4 indicate that (1) adsorption of Na$^+$ and Cl$^-$ are possible at pH values as high as 5.9; and (2) the adsorption behaviors are linear over the range of concentrations considered in the present study. The relatively high equilibrium pH values ranging from 5.4 to 5.9 probably represent the greater dilution of H$^+$ associated with the lower soil:solution ratios used in the batch tests relative to either the saturated paste extract (Table 2) or the soil columns.

The retardation factor also can be estimated from the results of batch equilibrium tests using the following equation (Freeze and Cherry 1979):

$$R_d = 1 + \frac{\rho_d}{n} K_d \qquad (12)$$

where n and ρ_d = porosity and dry density of the soil in the soil column, respectively; and K_d = slope of the adsorption curve known as the "distribution coefficient." The retardation factors based on (12), the slopes of the adsorption relationships shown in Fig. 4, and the soil properties at the end of the tests presented in Table 3, are 1.9 for Cl$^-$ and 2.4 for Na$^+$ in tests 1 and 2, respectively. These R_d-values are between the respective solute R_d-values reported in Table 6 from the column test results analyzed on the basis of (9). Besides the differences in pH previously noted, differences between R_d-values determined from batch equilibrium versus column tests can arise due to the lower soil:solution ratios used in batch tests and the difference between static (no flow) conditions in the batch tests relative to transient conditions in the column tests (Cherry et al. 1984).

The existence of anion adsorption in the batch equilibrium tests is not supported by the negligible AEC reported in Table 2. However, the pH of the AEC measurements was larger than the pH of the batch equilibrium tests and, therefore, may be beyond the ZPC of this particular kaolin. Nonetheless, no conclusion in this regard is made since an evaluation of the ZPC, AEC, and anion adsorption of the kaolin is beyond the objective of the present study. Indeed, there is some controversy regarding the nature of the permanent and pH-dependent charge of kaolinite soils that cannot be resolved by the tests performed in the present study [e.g., see Bolland et al. (1980)].

Finally, the retardation factors for both Cl$^-$ and Na$^+$ based on the column test results (Table 6) for the low flow rate test are significantly greater than the corresponding values for the relatively high flow rate test. The larger standard deviations associated with the retardation

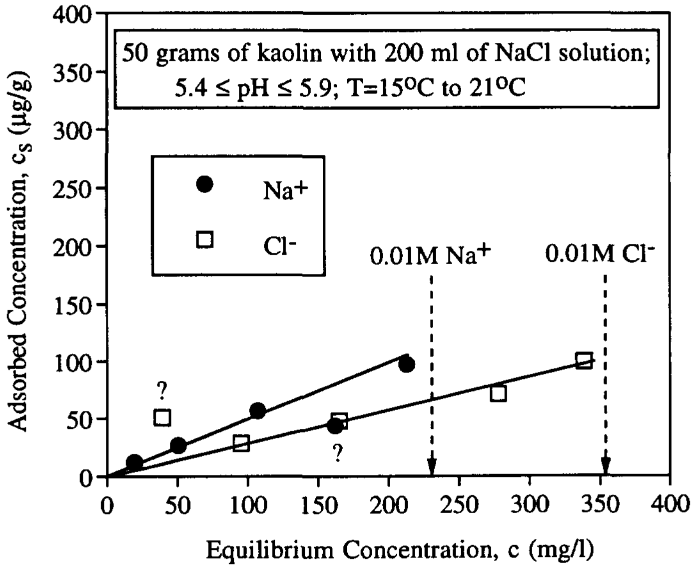

FIG. 4. Batch Equilibrium Test Results for Sodium (Na$^+$) and Chloride (Cl$^-$)

factors for the low flow rate test suggest that test duration may be a significant factor. As a result of the relatively long duration of the low flow rate test (~109 days), chemical reactions (e.g., precipitation) and/or biochemical degradation of solute concentrations may have existed, resulting in lower effluent concentrations than otherwise would be measured for a given time and, therefore, the measurement of larger retardation effect. The significance of such reactions in the high flow rate test is less likely due to the shorter test duration (~37 days) and the fact that the relative effluent chloride concentrations reached unity for the high flow rate test [see Fig. 3(a)]. As a result, the retardation factors measured in the low flow rate tests may encompass sinks other than the linear, reversible, and instantaneous equilibrium adsorption of reactive solutes assumed by the advection-dispersion equation [(1)].

Effect of Low Flow Rates on Retardation

To illustrate the effect of flow rate on the determination of R_d, a "truncated" form of (9) or

$$\frac{c_e(L, t) - c_i}{c_o - c_i} = \frac{1}{2}\,\mathrm{erfc}(\xi_1) \qquad (13)$$

also is used to model the measured effluent concentrations in the present study. Eq. 13 commonly

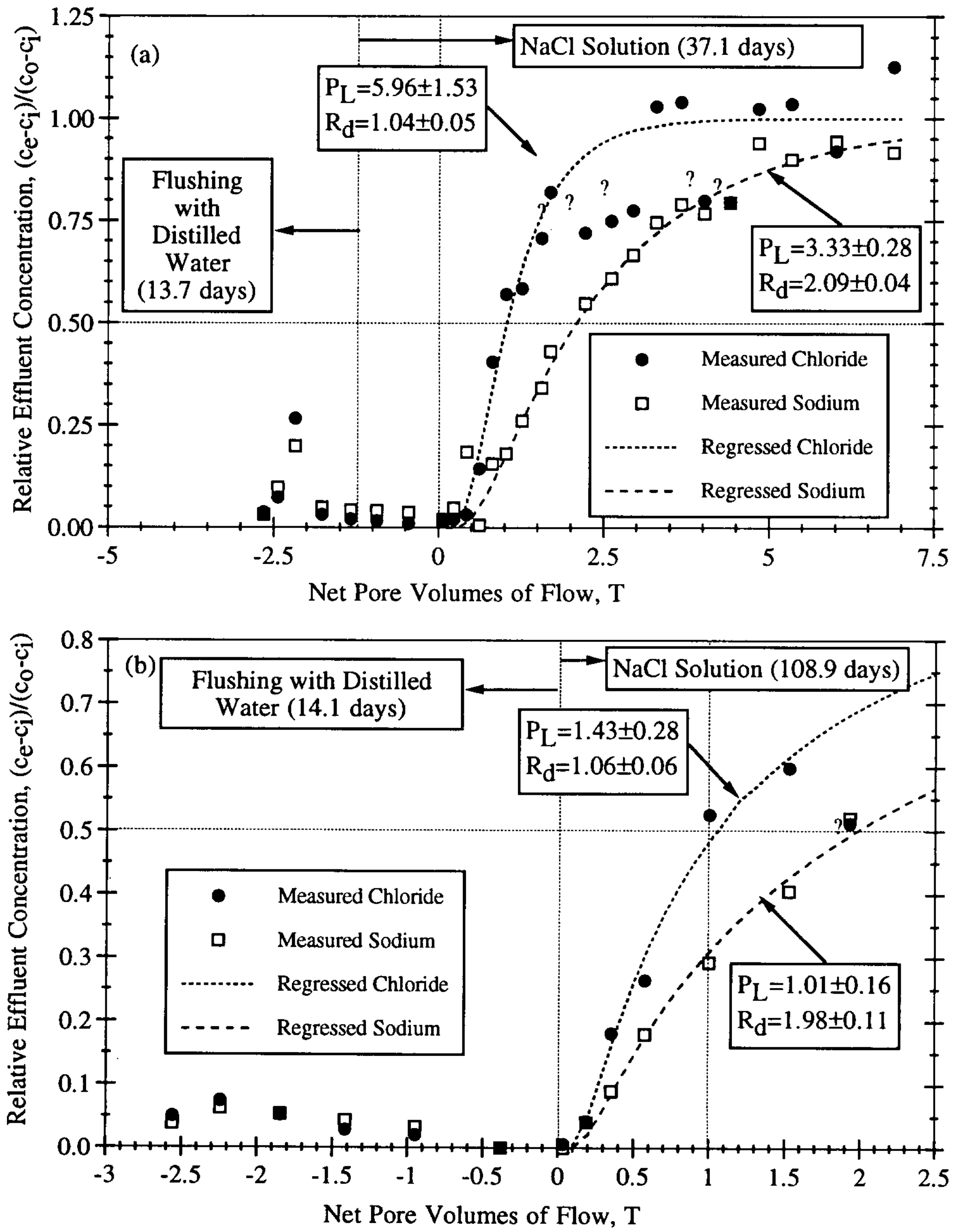

FIG. 5. Measured and Regressed Solute Breakthrough Curves Based on Truncated Analytical Model (Eq. 13): (a) Test 1; and (b) Test 2

is used to describe solute migration for advective-dominated transport, since the second term in (9) becomes negligible at relatively high flow rates [e.g., see Ogata and Banks (1961); De Weist (1965); Domenico and Schwartz (1990); and Fetter (1993)]. Although (13) is applicable strictly at only relatively high flow rates, it does predict that $R_d = T$ at a relative concentration of 0.5 for all values of P_L (Shackelford 1994b).

The best-fit values of P_L and R_d based on regression of the measured solute breakthrough curves in terms of the "truncated" solution, (13), also are summarized in Table 6. The theoretical curves based on the values of P_L and R_d in Table 6 for tests 1 and 2 are shown in Fig. 5.

A comparison of the R_d-values in Table 6 with the theoretical curves shown in Fig. 5 shows, in all cases, that $R_d = T$ at a relative concentration of 0.5. The values of R_d based on (9) are larger than the values of R_d based on (13), although the dispersion coefficients are relatively close. In addition, the values of R_d for Cl^- based on (13) are very close to unity with the slight deviation most likely being attributable to scatter in the measured effluent concentrations. Therefore, the common assumption that Cl^- is a nonreactive solute (i.e., $R_d = 1$) is approximated very closely by the analyses with the "truncated" analytical model [(13)].

However, (9) satisfies the mass balance constraint for finite columns and provides a correct measure of the retardation factor at all flow rates, whereas (13) does not (Shackelford 1994b). Also, (9) reduces to an appropriate solution for Fick's second law of diffusion when $v = 0$, whereas (13) does not (Shackelford 1994b). Therefore, the R_d-values for both Cl^- and Na^+ based on (9) should be more representative in terms of the mass balance constraint for finite columns and physical relevance to diffusion dominated transport systems at low flow rates.

For a given flow rate, the retardation factors for Cl^- are smaller than the retardation factors for Na^+ regardless of whether the values are determined using (9) or (13). This trend is consistent with preferential adsorption of Na^+ relative to Cl^-. For a given solute, the retardation factors at the lower flow rate are larger than the retardation factors at the higher flow rate when the data are analyzed in terms of (9), whereas the retardation factors determined with (13) are essentially independent of flow rate. A larger retardation factor for a given solute at a lower flow rate is consistent with conditions that are more favorable for equilibrium adsorption due to a greater retention time for the solute within the soil.

PRACTICAL SIGNIFICANCE

The results of the present study support the results of previous field studies and model simulations suggesting that diffusion is the dominant transport process at the low flow rates expected in the field for transport through clayey soils. Thus, realistic estimates of transport parameters for clayey soils in laboratory column tests are likely only when relatively low flow rates are imposed in the test. The application of relatively low flow rates typically requires relatively long test durations to provide sufficient data for analysis. However, longer test durations generally subject the solutes to greater exposure to chemical and/or biochemical degradation processes that can affect the accuracy of the measured transport parameters. For example, a large standard deviation is associated with the regressed retardation factor for Na^+ ($R_d = 9.53 \pm 6.69$) in the lower flow rate test (test 2) even though the observed scatter in the effluent concentrations does not appear to be significant [see Fig. 3(b)]. This uncertainty in the measured R_d-value suggests that chemical and/or biochemical processes were operative in the test, which required ~109 days to complete. Also, analytical solutions to the one-dimensional advection-dispersion equation that account only for linear, reversible, and instantaneous retardation may not be appropriate for evaluation of transport parameters in such long-term tests.

SUMMARY AND CONCLUSIONS

Solute breakthrough curves for a 0.01-M NaCl solution permeated through two compacted test specimens of processed kaolin soil are measured at two flow rates (2.65×10^{-4} cm^3/s and 2.65×10^{-5} cm^3/s) using a flow pump system. Regression analyses of the effluent solute concentrations resulted in hydrodynamic dispersion coefficients D ranging from 1.49×10^{-6} cm^2/s to 3.95×10^{-6} cm^2/s for chloride and from 2.11×10^{-6} cm^2/s to 8.74×10^{-6} cm^2/s for sodium. Since these D-values are within the range of effective diffusion coefficients (D^*) reported for the same solutes in similar soils, diffusion apparently dominated the transport processes in both column tests. Therefore, the results of this laboratory study tend to confirm previous field studies indicating that diffusion dominates miscible transport at the low flow rates common in fine-grained barrier materials.

Effluent pH decreases from between 4.8 and 5.5 during permeation with distilled water to about 4.5 during subsequent permeation with the NaCl solution. The decrease in effluent pH is consistent with Na^+ for H^+ exchange at low pH previously reported for studies involving kaolinite soils.

The relative electrical conductance EC/EC_o-values in the effluent of both tests reached a magnitude of 0.5 before one net pore volume of flow and, therefore, tend to substantiate the solute breakthrough curve analyses indicating diffusion-dominated transport.

Analysis of the effluent concentrations for the column tests displays a retardation effect ($R_d > 1$) for Cl^- as well as Na^+. Several factors, including anion adsorption at low pH, are suggested as possible reasons for the observed retardation effect for Cl^-. The relatively acidic effluent (pH $\approx$ 4.5) tends to substantiate the analyses indicating the potential for anion adsorption of Cl^- at pH < 7. The possibility for anion adsorption also is supported by the results of batch equilibrium tests. However, other factors, such as scatter in measured concentration data, use of incremental, average effluent concentrations, and chemical and/or biochemical reactions, also may have contributed to the measurement of a retardation effect for Cl^-.

Two analytical models are considered in the analyses of the effluent concentration data. One commonly assumed analytical model based on advective-dominated transport conditions [i.e., (13)] indicates that the measured retardation factors are approximately equal to the value for the pore volumes of flow at a relative effluent concentration of 0.5. However, another analytical model [(9)] indicates that the retardation factors are not equal to the value for the pore volumes of flow at a relative effluent concentration of 0.5. The apparent discrepancy is explained as a result of the failure of the second analytical model [(13)] to account for the diffusion dominated transport at the low flow rates imposed in the study.

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