Todd E. Cotten,[1] Melanie M. Davis,[2] and Charles D. Shackelford[3]

Effects of Test Duration and Specimen Length on Diffusion Testing of Unconfined Specimens

ABSTRACT: Effective diffusion coefficients, D^*, of chloride and zinc diffusing in saturated, unconfined specimens of a compacted sand-clay mixture are measured for three specimen lengths, L (2.91, 5.83, and 11.60 cm) and three test durations (7, 14, and 21 days). For a specimen length of 2.91 cm, both the chloride and zinc D^* values tend to decrease with increasing test duration, possibly due to the measurement of concentration-dependent D^* values. For a 14-day test duration, no consistent trend in D^* with specimen length is observed, but the overall effect of specimen length on D^* is minor relative to the range of measured D^* values. A 21-day test duration provides the best correlation between the D^* values based on reservoir concentrations, D^*_{Res}, and the D^* values based on soil concentrations, D^*_{Soil}, for chloride for a given test regardless of the specimen length. The effect of test duration on the correlation between D^*_{Res} and D^*_{Soil} for zinc is minor based on the relatively narrow range of measured zinc D^* values. The observed effects of specimen length on the correlation between D^*_{Res} and D^*_{Soil} for a given test are consistent with the more uniform final porosity distributions in the shorter specimens and the contrasting effects of the non-linear distributions in porosity and dry density that become less significant as the specimen length increases.

KEYWORDS: adsorption, attapulgite clay, batch equilibrium, chloride diffusion, contaminant transport, diffusion testing, Freundlich isotherm, sand-clay mixture, swelling, zinc diffusion

Over the past ~30 years, diffusion testing has been performed in several different disciplines (e.g., soil science, geology, oceanography, geotechnical engineering) for several different purposes, including diffusion of nutrients to plant roots (Olsen and Kemper 1968), characterization of pore water in geologic deposits (Manheim 1970; Desaulniers et al. 1982), diffusion of ions in deep-sea sediments (Duursma 1966; Li and Gregory 1974; Lerman 1978, 1979), and, more recently, diffusion of contaminants through waste containment barriers (Gillham et al. 1984; Rowe et al. 1985; Shackelford et al. 1989, 1997a; Shackelford 1991; Shackelford and Daniel 1991b; Airey and Carter 1995). While these studies have advanced our knowledge of the process of diffusive transport in porous materials, considerable confusion regarding testing procedures also has resulted. In particular, there is no consistency with respect to the type of diffusion test, the diffusion test duration, and/or the size of the specimens that have been used for diffusion testing.

Several different types of diffusion testing procedures can be used, test durations have ranged from a few hours to several months, and the specimen volumes have ranged from as small as 10 cm^3 to more than 944 cm^3 (Shackelford 1991). Practical limitations to some, if not all, of the different test methods undoubtedly exist, and variability in test duration and specimen size may have an effect on determination of the measured diffusion coefficients. As a result, an evaluation of the factors potentially affecting the measurement of effective diffusion coefficients is needed. Such an evaluation is particularly of interest to geotechnical engineers associated with the design and evaluation of waste containment barriers because of the increasing importance placed on contaminant transport, in general, and diffusive transport, in particular, in such applications.

The primary objective of this study is to evaluate the potential influence of test duration and specimen length on the diffusion of chloride and zinc in compacted, unconfined specimens of a sand-clay mixture. The evaluation is based on the single reservoir, decreasing source concentration method that has been used extensively in the measurement of effective diffusion coefficients associated with waste disposal applications (Barone et al. 1989; Shackelford et al. 1989; Shackelford 1991; Shackelford and Daniel 1991a,b; Myrand et al. 1992; Verga and Manassero 1994; Airey and Carter 1995; Manassero et al. 1995, 1996, 1997; Shackelford et al. 1997a).

Materials and Methods

Soil

The soil used in this study is a mixture of 75% sand and 25% attapulgite clay (dry weight basis). Physical and chemical properties of the sand and attapulgite clay are provided in Table 1. The chemical properties of the soil constituents were measured using the procedures described by Shackelford and Redmond (1995). Attapulgite clay previously has been evaluated as a potential admixture soil for waste containment applications (Tobin and Wild 1986; Ryan 1987; Broderick and Daniel 1990; Howell and Shackelford 1997; Stern and Shackelford 1998).

[1]Geoenvironmental engineer, CH2M Hill, 825 N. E. Multnomah, Suite 1300, Portland, OR 97232; formerly, graduate research assistant, Geotechnical Engineering Program, Department of Civil Engineering, Colorado State University, Fort Collins, CO 80523.

[2]Geotechnical engineer, Shepherd Miller, Inc., 3801 Automation Way, Suite 100, Fort Collins, CO 80525; formerly graduate research assistant, Geotechnical Engineering Program, Department of Civil Engineering, Colorado State University, Fort Collins, CO 80523.

[3]Associate professor, Geotechnical Engineering Program, Department of Civil Engineering, Colorado State University, Fort Collins, CO 80523.

TABLE 1—*Physical and chemical properties of soil constituents used for sand-clay mixture.*

Property/Characterization	Method	Soil Constituent	
		Attapulgite Clay	Sand
Source	NA	Floridin Co., Quincy, FL	Colorado Lien Co., LaPorte, CO
Trade name	NA	Min-U-Gel FG	40–140 Silica Sand
Liquid limit, LL (%)	ASTM D 4318	338	...
Plastic limit, PL (%)	ASTM D 4318	122	NP
Plasticity index, PI (%)	ASTM D 4318	216	NP
Specific gravity, G_s	ASTM D 854	2.56	2.65
% Sand (0.074–4.75 mm)	ASTM D 421	0	99
% Silt (0.002–0.074 mm)	ASTM D 422	34	1
% Clay (<2 μm)	ASTM D 422	66	0
Classification (USCS)	ASTM D 2487	CH	SP
Cation exchange capacity, CEC (meq/100 g)	...[a]	29.1	0
Exchangeable metals (meq/100 g):	...[a]		NA
Ca		8.0	
Mg		17.8	
Na		<0.1	
K		2.7	
Al		0.3	
Si		<0.1	
Sum		28.8	
Soluble salts (mg/kg)[b]:	...[a]		
Ca		16.5	25.9
Mg		77.0	6.8
Na		8.5	23.3
K	...	<0.5	7.4
Cl^-	...	1.5	0.5
Soil pH (1:1 soil:solution)	...	9.7	8.0

[a] Method described in Shackelford and Redmond (1995).

[b] Based on 1:5 soil:solution ratio.

Liquids

Three liquids were used in this study: deionized distilled water (DDW, pH = 5.8), an acetic acid/sodium acetate (HOAc/NaOAc) buffer solution, and $ZnCl_2$ dissolved in the buffer solution. The DDW was used in compacting specimens of the sand-attapulgite clay mixture. The 1.0 M HOAc/1.4 M NaOAc buffer solution (pH = 4.8) was permeated through the specimens prior to diffusion testing for two reasons (Shackelford et al. 1997a): (1) to saturate the specimens to minimize advective transport due to suction in the compacted specimens, and (2) to buffer the pH of the specimens from pH ~9 to pH ~4.8 to minimize the potential for zinc precipitation during diffusion testing.

Solutions of anhydrous $ZnCl_2$ dissolved in the 1.0 M HOAc/1.4 M NaOAc buffer were used for evaluating chloride and zinc migration in the diffusion tests. Chloride was chosen to represent a non-reactive (i.e., non-adsorbing) solute, whereas zinc was chosen to represent a reactive (adsorbing) toxic metal species. Previous analysis reported by Shackelford et al. (1997a) indicates that complexed species of zinc, such as $Zn(OAc)^+$, also exist in this solution. However, the common practice is to attribute the measured diffusion coefficients to the free ionic form of zinc, Zn^{2+}, even though the diffusion and adsorption of any existing complexed species undoubtedly are different than the diffusion and adsorption of Zn^{2+} (Shackelford and Daniel 1991b; Shackelford et al. 1997a).

Chloride concentrations were measured in the Soil, Water, and Plant Testing Laboratory at Colorado State University using an ion selective electrode (ISE) containing an Orion chloride solid state electrode (Orion model No. 941700). The resulting measured chloride concentrations in the $ZnCl_2$ solutions ranged from 217 to 304 mg/L. Aqueous zinc concentrations were measured in the Department of Chemistry at Colorado State University using a Perkin Elmer P400 ICP atomic emission spectrometer. The result-ing measured zinc concentrations in the $ZnCl_2$ solutions ranged from 445 to 544 mg/L.

The range of measured chloride (Cl^-) concentrations is lower than that expected on the basis of the ratio of atomic weights for Cl and Zn in $ZnCl_2$. However, this lower range of Cl^- concentrations may be attributed, in part, to the measurement of only the free (uncomplexed) Cl^- concentrations using ISE, whereas total zinc concentrations (ionic plus complexed) are measured using ICP. As a result, the measured Cl^- concentrations will not include any chlorine (Cl) that exists in a complexed species (e.g., $ZnCl^+$), whereas the measured zinc concentrations will include zinc that exists in complexed species. Therefore, measured diffusion coefficients for chlorine (Cl) in this study are attributed to diffusion of free chloride (Cl^-), whereas the measured diffusion coefficients for zinc probably represent some average value based on the mobilities of all forms of zinc present in the mixture (Shackelford and Daniel 1991b; Shackelford et al. 1997a).

Batch Equilibrium Adsorption Tests

Batch equilibrium adsorption tests (BEATs) were performed with the sand-attapulgite clay mixture and the $ZnCl_2$ solution to quantify the potential adsorption of zinc and chloride, if any. The procedures used for the BEATs generally followed the guidelines given by Roy et al. (1992). However, a special soil preparation procedure was required because initial BEATs proved unsuccessful, presumably due to precipitation of zinc resulting from the high initial pH of the soil mixture (pH ~9) as described by Shackelford et al. (1997a,b). The soil preparation procedure consisted of mixing ~1000 g of the soil mixture used for each BEAT by hand with the buffer solution in a 2:1 soil:buffer solution ratio (by weight), and placing the entire soil-buffer solution mixture in an oven at a relatively low temperature of 40°C for drying.

Approximately 90 g of the oven-dried and buffered soil mixture were added to 500-mL flasks containing solutions of the $ZnCl_2$ in a 1:4 soil:solution ratio (by weight). The concentrations of chloride and zinc in the flasks were varied by serial dilution. An additional flask containing only the undiluted $ZnCl_2$ solution was tested as a control. All flasks were stoppered, placed in an end-over-end, rotary mixer and mixed for 48 h at ambient laboratory temperatures of 20.5° ± 2.5°C. The 48-h mixing period, twice the mixing period recommended by ASTM ES 10, was used to improve the likelihood of establishing equilibrium conditions. The slurry from each flask then was poured into a centrifuge tube and centrifuged at 2400 g for a minimum of 30 min. After centrifuging, the supernatant from the centrifuge tubes was passed through a 0.45-μm filter and collected in a 20-mL scintillation vial. Aliquots of the supernatant were prepared by diluting in a 1:3 ratio of supernatant to buffer solution to minimize potential changes in pH resulting from dilution with DDW. Separate aliquots were prepared for chemical analysis of chloride by ISE and zinc by ICP.

Diffusion Testing Apparatus

The test apparatus used in this study is the same as described by Shackelford et al. (1997a,b). The test apparatus essentially consists of a permeation/diffusion test cell located between clear acrylic influent and effluent accumulators used to store permeant liquid and to collect effluent, respectively, during the permeation stage of the test prior to diffusion testing.

The diffusion test cell is shown schematically in Fig. 1. The liquid reservoir contains one sampling port and two inflow/outflow ports. Reservoir sampling ports are fitted with Mininert® valves (VICI Precision Sampling Corp., Baton Rouge, LA) containing a septum through which a needle can be inserted for collection of a reservoir sample when the valve is open. The positioning of the inflow/outflow ports permits solution mixing during reservoir filling and draining. One reservoir fill/drain tube (Valve 1) and the effluent collection tube (Valve 2) were open during permeation, but were closed upon commencement of diffusion testing.

The swelling that occurs in unconfined specimens during permeation prior to diffusion testing results in non-uniform porosity and density distributions that may have an effect in the interpretation of the test results (Shackelford and Daniel 1991b; Manassero et al. 1994, 1995, 1996; Shackelford et al. 1997a,b). As a result, the sizes of the stainless-steel compaction molds used in this study were varied to evaluate the potential influence of specimen size

on the measured effective diffusion coefficients. Three different specimen sizes were achieved by using 10.3-cm (4.0-in.)-diameter compaction molds with three different lengths, L: 2.91, 5.83, or 11.60 cm. These three specimen lengths resulted in specimen volumes of 243, 485, and 966 cm^3 that subsequently are referred to as quarter-, half-, and full-size cells, respectively.

Diffusion Specimen Preparation

The sand-clay mixtures were mixed with water (DDW) incrementally, as described by Shackelford et al. (1997a), until the water content was at least six percentage points above the optimum water content of 23.1% based on ASTM Test Method for Laboratory Compaction Characteristics of Soil Using Standard Effect (12 400 ft-lbf (600 kN-m/m³)) (D 698). These relatively high initial water contents were desired to achieve a relatively high initial degree of saturation of the specimens, thereby minimizing the time required for permeation before diffusion testing. The wetted soil mixture was sealed in double Ziplock® freezer bags and allowed to cure for 24 h before compaction.

After the 24-h curing period, the wetted soil mixture was placed and compacted into the quarter-, half-, and full-size cells. Compaction of the full-size specimens generally followed ASTM D 698; however, due to the slight variation in the cell volumes, this procedure resulted in ~98% of standard Proctor compaction energy (ASTM D 698). Compaction of the half-size specimens was achieved by using two lifts of soil and 19 blows per lift, resulting in ~99% of the standard Proctor compaction energy. The quarter-size specimens were compacted using one lift at 19 blows for ~98% of the standard Proctor compaction energy. After compaction, the top and the base of the soil cylinder were trimmed and two samples of the excess soil were collected to determine the as-compacted water content. The compacted specimens then were weighed and covered in Saran® wrap. The covered compacted specimens were sealed in double Ziplock® freezer bags for storage before testing.

Diffusion Testing Procedure

The diffusion tests followed the procedure outlined by Shackelford et al. (1997a). As previously described, all specimens were permeated prior to diffusion testing with the acetic acid/sodium acetate buffer solution until pH ~ 4.8 was achieved. At the end of permeation, excess pore water pressures were allowed to dissipate, Valve 2 (Fig. 1) was closed, and the permeant liquid was drained from the reservoir. Diffusion was initiated by introducing the buffer solution containing zinc chloride into the liquid reservoir. Samples of the reservoir liquid were recovered periodically with the syringes and needles previously described. Reservoir liquid height, H_L (see Fig. 1), also was measured before and after reservoir sampling with a cathetometer, as described in ASTM Test Method for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter (D 5084), to provide an indication of mass flow into the specimen. Measured changes in H_L during diffusion testing were small (<0.1%) in all cases. All diffusion tests were performed at ambient laboratory temperatures of 20.5 ± 2.5°C.

At the completion of the test, the diffusion cell was disassembled and the soil specimen was extruded carefully from the mold using an extrusion device similar to the one described by Shackelford et al. (1989). The soil specimen was sliced at selected intervals during extrusion into ~5-mm-thick slices, and the pore fluid was squeezed from each slice using a large capacity (20-kip) load
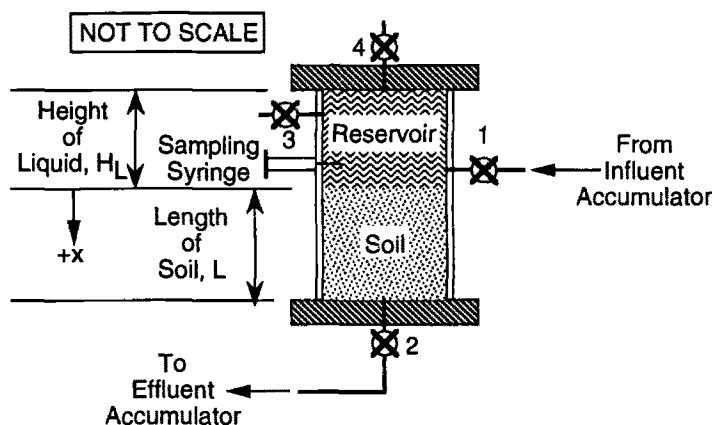

FIG. 1—*Diffusion test cell.*

frame. Chloride and zinc concentrations were measured to provide the final distributions of chloride and zinc in the pore fluid with depth in the specimen.

The diffusion test data were evaluated using the following analytical solution to Fick's second law for one-dimensional diffusion through saturated soil for the case of a decreasing source concentration and finite cell length (Crank 1975; Shackelford 1991; Shackelford et al. 1997a):

$$\frac{c(x \geq 0,t)}{c_0} = \frac{\alpha}{1 + \alpha} + \sum_{m=1}^{\infty} \frac{2\alpha}{1 + \alpha + \alpha^2 q_m^2}$$

$$\exp\left(\frac{-D^* q_m^2 t}{R_d L^2}\right) \frac{\cos\left[q_m\left(1 - \frac{x}{L}\right)\right]}{\cos(q_m)} \quad (1)$$

where c_0 is the initial concentration of the solute in the source reservoir, D^* is the effective diffusion coefficient as defined by Shackelford and Daniel (1991a), R_d is the retardation factor for linear, instantaneous, and reversible sorption, L is the length of the soil specimen, and x is the direction of diffusive transport. The q_ms in Eq 1 are the non-zero positive roots of the following function:

$$\tan(q_m) = -\alpha q_m \quad (2)$$

where α is a constant defined as follows:

$$\alpha = \frac{H_L}{nR_d L} \quad (3)$$

and n is the total porosity of the soil specimen. The measured concentration data were regressed using Eqs 1–3 with the computer software program, Mathcad® (Version 3.1, 1988–1993, MathSoft, Inc., Cambridge, Massachusetts). Regressions were performed on the reservoir concentration data to determine an effective diffusion coefficient, D^*_{Res} ($=D^*$ in Eq 1 for $x = 0$), as well as on the soil concentration data to determine an effective diffusion coefficient, D^*_{Soil} ($=D^*$ in Eq 1 for $x > 0$). The retardation factor, R_d, used in the regression analyses was determined from the results of the BEATs.

The diffusion testing program consisted of a total of the ten diffusion tests summarized in Table 2. The effect of test duration is evaluated by performing three sets of duplicate tests using quarter-size specimens with test durations, $t_f (= t)$, of 7 days (Tests 1a and 1b), 14 days (Tests 2a and 2b), and 21 days (Tests 3a and 3b). The effect of specimen length is evaluated by comparing the results of Tests 2a and 2b for 14-day test durations with two additional sets of duplicate tests with 14-day test durations using half-size specimens (Tests 4a and 4b) and full-size specimens (Tests 5a and 5b).

TABLE 2—*Summary of diffusion testing program.*

Test Series	Test No.	Test Duration, days	Cell Size	Specimen Volume, V (cm³)	Specimen Length, L (cm)
1	1a 1b	7	Quarter	243	2.91
2	2a 2b	14	Quarter	243	2.91
3	3a 3b	21	Quarter	243	2.91
4	4a 4b	14	Half	485	5.83
5	5a 5b	14	Full	966	11.60

Results

Batch Equilibrium Adsorption Tests (BEATs)

As expected, no measurable adsorption of chloride was discerned from the results of the BEATs, and the control test indicated no measurable adsorption of either chloride or zinc to the test apparatus. However, as shown in Fig. 2, adsorption of zinc to the sand-attapulgite clay mixture was observed from the results of the BEATs. Thus, unlike the unsuccessful BEAT results mentioned by Shackelford et al. (1997a), the buffering of the soil mixture prior to batch equilibrium adsorption testing apparently was successful in preventing or minimizing precipitation of zinc.

Both linear and non-linear (Freundlich) adsorption equations were regressed against the measured BEAT data for zinc. The linear adsorption equation is given as follows:

$$c_s = K_d c \quad (4)$$

where c_s is the adsorbed (solid-phase) concentration of zinc (mg of adsorbed zinc/g of dry soil), c is the equilibrium (liquid-phase) concentration (mg/L), and K_d is the distribution coefficient (cm³/g). As indicated in Fig. 2, $K_d = 0.731$ cm³/g, which compares favorably with three of the four K_d values (0.70, 0.43, 0.76, and 0.72 cm³/g) determined from column tests performed with the same soil and solutes as reported by Shackelford et al. (1997a).

The effect of the non-linearity in the measured BEAT data shown in Fig. 2 was quantified by regressing the data with the Freundlich adsorption equation defined as follows:

$$c_s = K_f c^a \quad (5)$$

where K_f and a are Freundlich fitting parameters. Comparison of Eqs 4 and 5 indicates that as $a \rightarrow 1$, $K_f \rightarrow K_d$ and the Freundlich adsorption equation approaches the linear adsorption equation.

As indicated in Fig. 2, the regressed values for K_f and a are 1.11 and 0.940, respectively. Thus, although regressing the measured BEAT data with Eq 5 results in a slight improvement in the coefficient of determination ($r^2 = 0.982$) relative to the linear regression
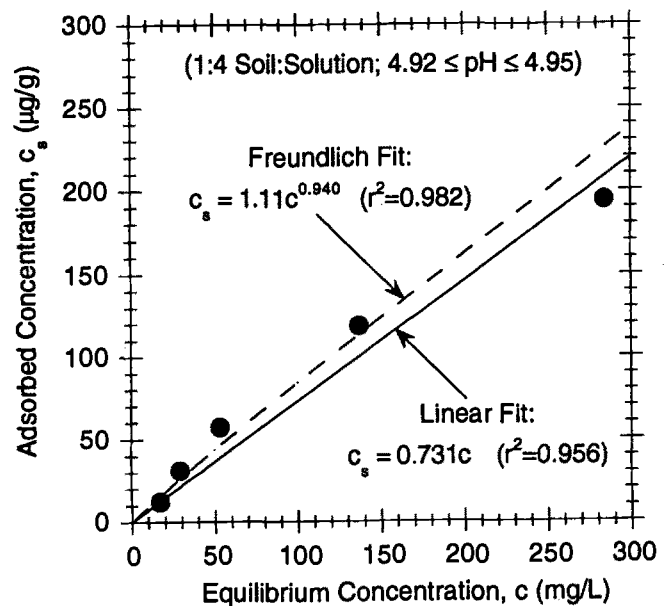

FIG. 2—*Batch equilibrium adsorption test (BEAT) results for zinc adsorption with a 75% sand–25% attapulgite clay (w/w) mixture.*
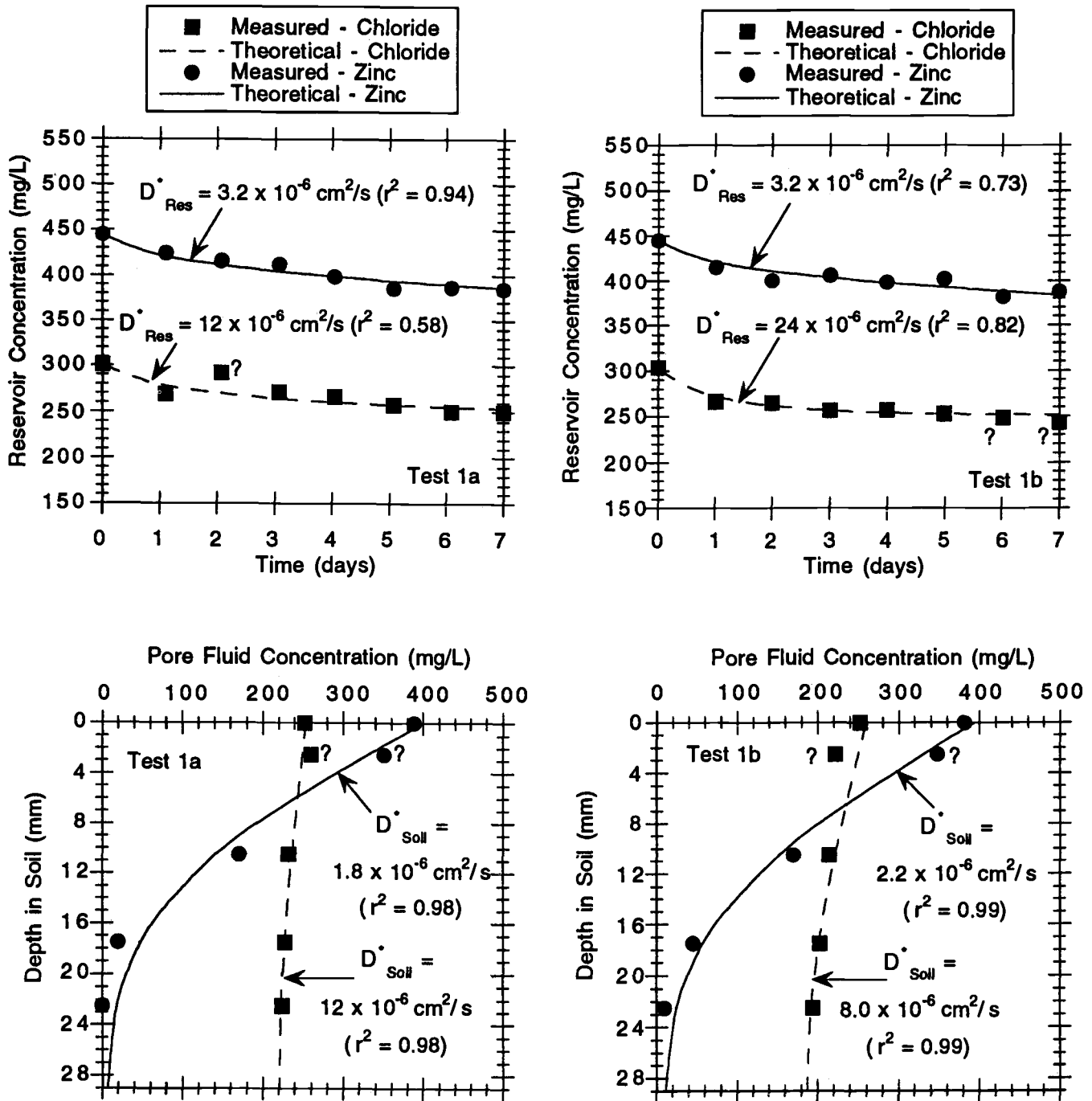
FIG. 3—*Reservoir and soil concentration profiles for diffusion Test Series No. 1.*

($r^2 = 0.956$), the measured BEAT data reflect only a slight non-linearity since $a = 0.940$ is close to unity.

Diffusion Test Results

The measured reservoir and soil concentration profiles for both chloride and zinc for Test Series Nos. 1 to 5 outlined in Table 2 are provided in Figs. 3 through 7, respectively. The expected trends of a decrease in solute concentration with time in the source reservoir during the test and a decrease in solute concentration with depth in the soil specimen at the end of the test are apparent in all figures.

As expected, the extent of diffusive migration of the chloride generally is greater than the extent of zinc migration in all tests due to the apparent adsorption of zinc. Although the extents of migration of both solutes increase with an increase in test duration for the same specimen length (Figs. 3–5), the final chloride concentration profiles for these tests are almost vertical, indicating that the chloride diffusion process is noticeably closer to completion (i.e., equilibrium) than is the zinc diffusion process within the given test duration. Also, for the tests involving a 14-day duration but different specimen lengths (i.e., Figs. 4, 6, and 7), the extents of migration of the chloride and the zinc are such that the chloride reaches the bottom of the specimen regardless of specimen length, L, albeit just barely in the case
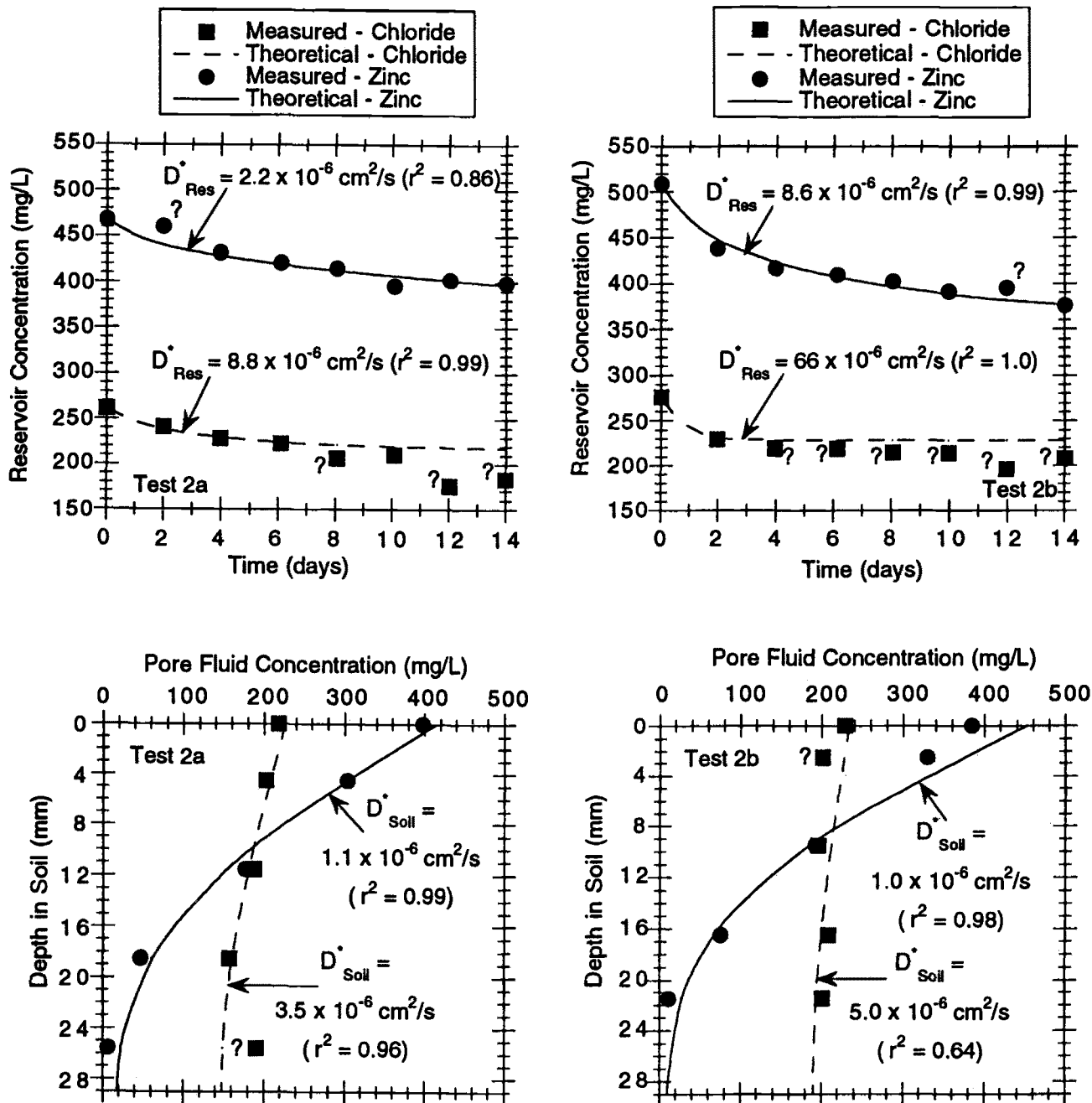
FIG. 4—*Reservoir and soil concentration profiles for diffusion Test Series No. 2.*

of the full cells ($L = 11.60$ cm), whereas the zinc essentially reaches the bottom of the specimen only in the case of the quarter cells ($L = 2.91$ cm). Thus, the differences in the extents of migration between the chloride and the zinc are consistent with the expected differences in the adsorption behavior of the two solutes, the test durations, and the specimen lengths.

The specimen swelling that occurs during permeation prior to diffusion testing results in non-linear distributions in the final soil properties as described by Shackelford et al. (1989, 1997a,b), Shackelford and Daniel (1991b), and Manassero et al. (1995, 1996, 1997). For example, the distributions in the final porosity values

determined from the individual slices of soil ~5 mm thick) recovered at the end of the diffusion tests reported in this study are plotted versus depth in the specimen in Fig. 8. As described by Shackelford et al. (1997a), the degree of specimen swelling typically is significantly greater for the smaller specimens (e.g., quarter cells) relative to the larger specimens (e.g., half or full cells). However, the distribution of the final porosity values typically is more uniform in the smaller specimens (e.g., quarter cells) than the larger specimens (e.g., half or full cells). Both of these effects are apparent from the data shown in Fig. 8.

As a result of the non-linearity in the final properties of the

specimens, the final property values typically are based on values obtained from individual slices recovered at the end of the diffusion test and weighted with respect to the representativeness of the slice as described by Shackelford and Daniel (1991b) and Shackelford et al. (1997a). The resulting final average properties, as well as the corresponding initial properties, of the specimens in this study are summarized in Table 3. Two values for the final n and γ_d of each specimen, one for chloride migration and one for zinc migration, are reported for each specimen in Table 3. The difference between these two values of n or γ_d for a given specimen reported in Table 3 is due to the difference in the extent of migration of

the two solutes upon which the weighted-average values of n and γ_d are based. For example, the weighted-average n and γ_d values based on the extent of zinc migration are higher and lower, respectively, than the corresponding values for the chloride migration since the extent of zinc migration typically is less than the extent of chloride migration. In all cases, the final n and γ_d values reported for the chloride in Table 3 also represent the final values for the entire specimen since the chloride reached the end of the specimen in all tests.

As indicated in Table 3, all specimens had similar initial (compacted) properties, indicating that the specimen preparation proce-
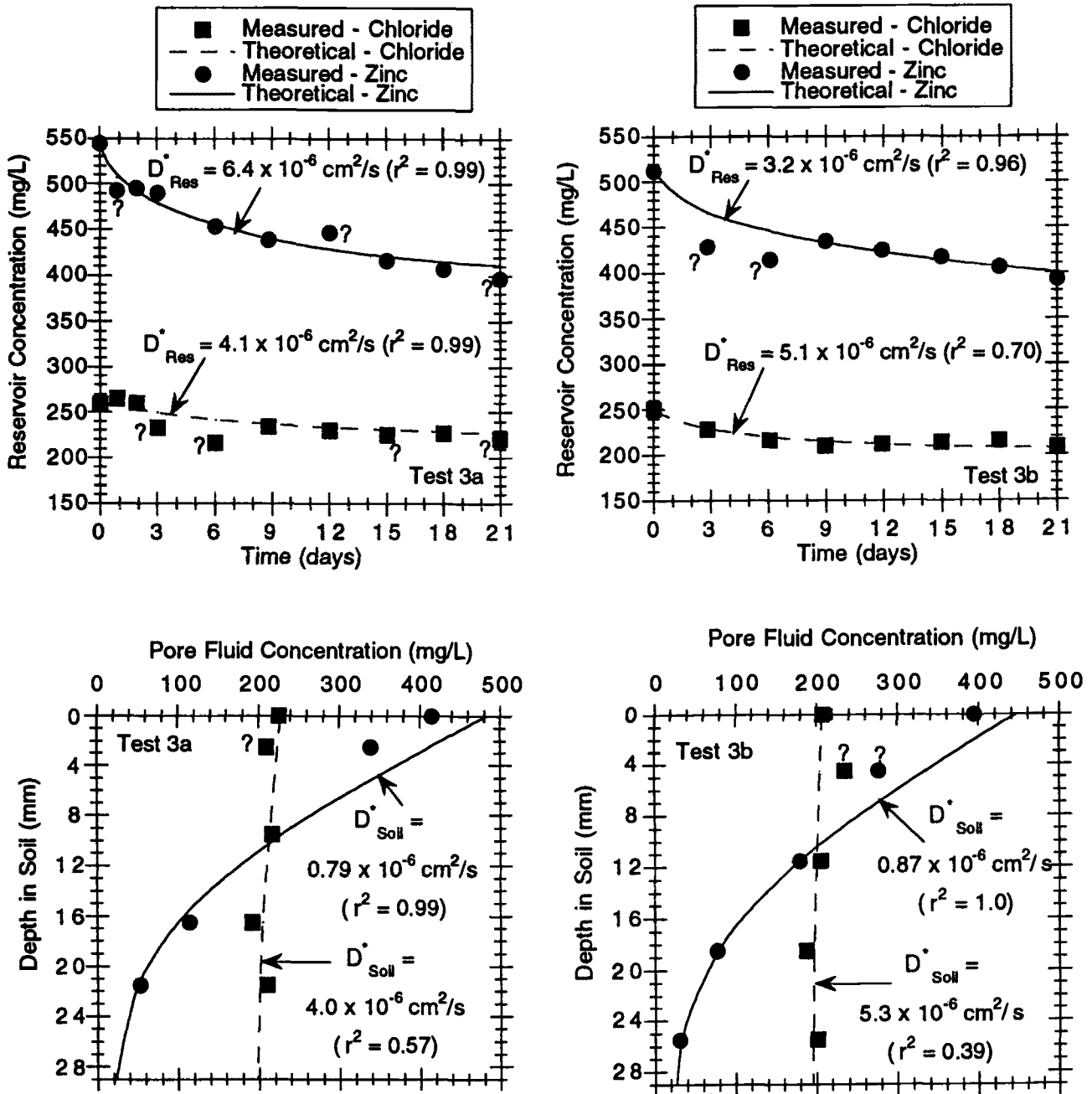

FIG. 5—*Reservoir and soil concentration profiles for diffusion Test Series No. 3.*
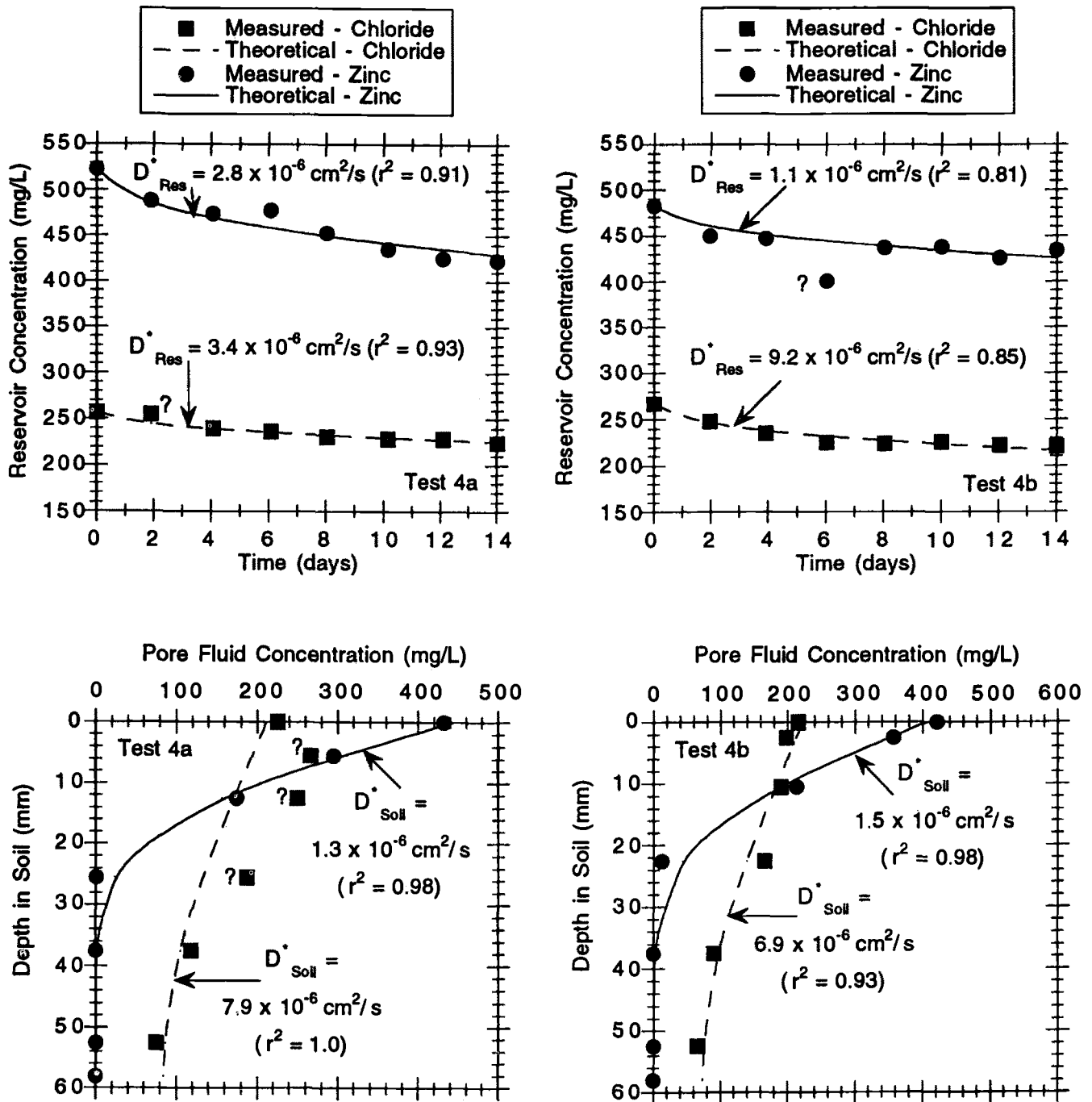
FIG. 6—*Reservoir and soil concentration profiles for diffusion Test Series No. 4.*

dure resulted in reproducible specimens. For example, the average (± 1 standard deviation) of all the initial values for the water content (w), the dry unit weight (γ_d), and the porosity (n) reported in Table 3 are 28.9 (± 0.4) %, 14.3 (± 0.1) kN/m³, and 0.447 (± 0.003), respectively. In contrast, the differences between the final (after testing) property values and the initial property values of the specimens given in Table 3 reflect the effect of swelling previously described. In addition, the degree of swelling relative to the three different cell sizes previously mentioned also is appar-

ent from the data in Table 3. For example, the final, weighted-average n values tend to decrease with an increase in the specimen size, whereas the final, weighted-average γ_d values tend to increase with an increase in specimen size.

Retardation Factors

Based on the data shown in Fig. 2, the differences between the linear and Freundlich (non-linear) regressions of the data are

relatively small, with the Freundlich equation fitting the data better at relatively low equilibrium concentrations (e.g., $c < 150$ mg/L) and the linear adsorption equation fitting the data better at relatively high concentrations. Thus, the differences between the retardation factors based on either the linear or the Freundlich adsorption equations should be small.

Nonetheless, as a result of the slight non-linearity in the observed adsorption behavior of zinc, a secant retardation factor was used in the analysis of the zinc concentration profiles measured in this study in accordance with the procedures described by Davidson et al. (1976), Shackelford et al. (1989), Shackelford and Daniel (1991b), Roy et al. (1992), and Shackelford (1993). The secant retardation factor, R'_d, is defined as follows:

$$R'_d = 1 + \left(\frac{\rho_d}{n}\right) K'_d \qquad (6)$$

where ρ_d and n are the final (average) dry density (g/cm^3) and porosity, respectively, of the specimen in the diffusion test cell,
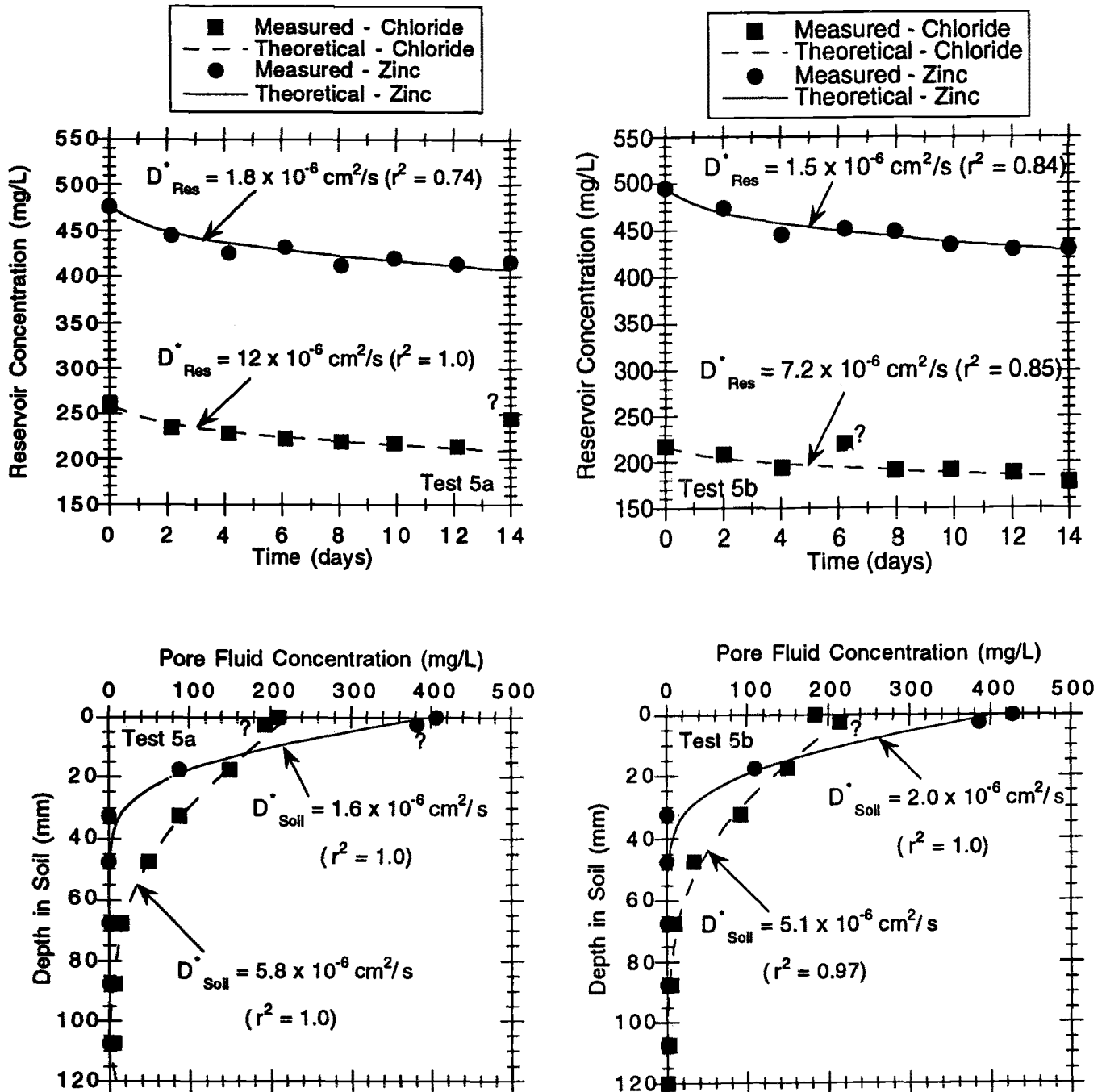

FIG. 7—*Reservoir and soil concentration profiles for diffusion Test Series No. 5.*

and K'_d is a secant distribution coefficient defined as follows (e.g., see Shackelford 1993):

$$K'_d = K_f c^{a-1} \tag{7}$$

where K_f and a are the previously defined Freundlich adsorption equation parameters, and c is the equilibrium concentration upon which the value of K'_d is based. The secant distribution coefficient represents the slope of a straight-line approximation to the non-linear adsorption data that passes through the origin and the point (c, c_s), where c_s is defined by Eq 5.

In all of the cited previous studies, K'_d was evaluated at an equilibrium concentration corresponding to the initial, source concentration, c_0 (i.e., $c = c_0$ in Eq 7). However, defining K'_d with respect to c_0 is strictly valid only for the case where the source concentration is time invariant. Since the source concentration is time variant in decreasing source concentration diffusion testing, K'_d in this study is defined with respect to the final reservoir concentration, c_f, as follows:

$$K'_d = K_f c^{a-1}\big|_{c=c_f} = K_f c_f{}^{a-1} \tag{8}$$
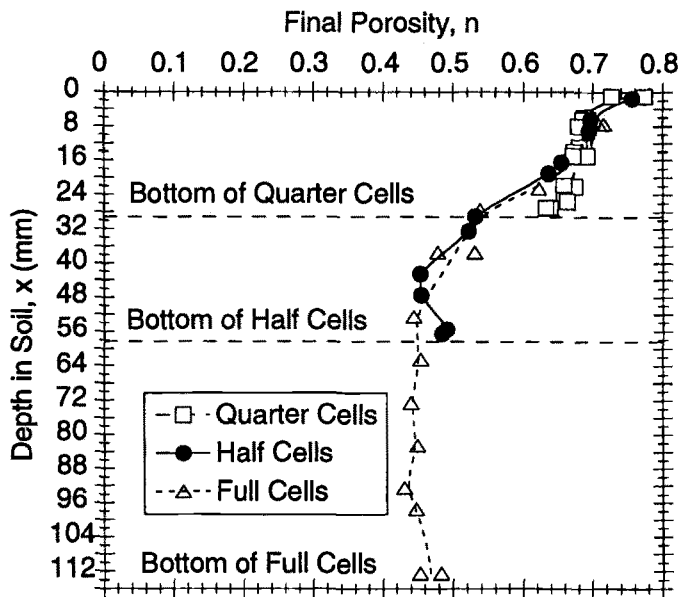
Final Porosity, n

FIG. 8—*Final porosity distributions for all tests.*

Since the final reservoir concentration, c_f, also represents the maximum possible concentration of the solute existing in the soil at the end of the test [i.e., $c(x, t = t_f) \le c_f$], the value of K'_d resulting from use of Eq 8 represents the limiting value of K'_d for the conditions corresponding to the end of the test. Thus, in this case, the secant retardation factor, R'_d, is defined as follows:

$$R'_d = 1 + \left(\frac{\rho_d}{n}\right) K_f c_f{}^{a-1} \tag{9}$$

The resulting values of R'_d used in this study for evaluation of the effective diffusion coefficients, D^*, for zinc are given in Table 4.

The values of linear retardation factor, R_d, also are provided in Table 4, where R_d is defined as follows:

$$R_d = 1 + \left(\frac{\rho_d}{n}\right) K_d \tag{10}$$

where K_d is the distribution coefficient resulting from the linear regression shown in Fig. 2 (i.e., $K_d = 0.731 \text{ cm}^3/\text{g}$). In all cases, R'_d from Eq 9 is only 3% greater than R_d from Eq 10 for all tests (i.e., $R'_d/R_d = 1.03$). Therefore, the differences between the R'_d values used in this study and the corresponding R_d values are relatively minor, as expected (i.e., since the Freundlich parameter, a, is ~1).

Analysis of Diffusion Test Results

The diffusion test data shown in Figs. 3 to 7 were regressed against Eqs 1 to 3 using the appropriate final, weighted average porosity values given in Table 3 and either $R_d = 1$ for the case of chloride diffusion or $R'_d (=R_d$ in Eqs 1 and 3) as given in Table 4 for the case of zinc diffusion. A summary of the effective diffusion coefficients resulting from these regression analyses is provided in Table 5, and the theoretical curves based on the regressed D^* values given in Table 5 are shown in Figs. 3 to 7 for comparison. Some observations regarding these analyses are considered before a general comparison of the test results is discussed.

First, measured concentrations denoted by a question mark (?) in Figs. 3 to 7 were not included in the regression analyses since the regression analyses would not converge when these data were included in the analyses. In most cases, these excluded concentrations clearly do not conform with the general trend of the majority of the data and, therefore, are excluded on the basis of experimental

TABLE 3—*Initial and final physical properties of test specimens.*

Test No.	Initial Properties[a] Water Content, w (%)	Initial Properties[a] Porosity, n	Initial Properties[a] Dry Unit Weight, γ_d (kN/m³)	Final Properties[b] Water Content, w (%)	Final Properties[b] Porosity, n Chloride	Final Properties[b] Porosity, n Zinc	Final Properties[b] Dry Unit Weight, γ_d (kN/m³) Chloride	Final Properties[b] Dry Unit Weight, γ_d (kN/m³) Zinc
1a	29.0	0.441	14.4	76.7	0.668	0.672	6.9	6.8
1b	29.3	0.453	14.1	76.5	0.668	0.671	7.7	7.6
2a	28.3	0.445	14.3	77.3	0.684	0.684	6.6	6.6
2b	28.5	0.445	14.3	80.8	0.679	0.679	7.7	7.7
3a	28.9	0.449	14.2	79.7	0.676	0.676	6.6	6.6
3b	28.5	0.445	14.3	83.6	0.692	0.692	7.2	7.2
4a	29.0	0.445	14.3	67.4	0.569	0.687	11.3	8.2
4b	29.5	0.449	14.2	65.2	0.568	0.662	11.2	8.8
5a	28.7	0.445	14.3	50.7	0.523	0.666	12.6	8.8
5b	29.4	0.449	14.2	48.1	0.498	0.642	12.8	9.1

[a] Values based on as-compacted specimen.
[b] Values based on weighted-averages of incremental slices of specimen after testing.

TABLE 4—*Zinc retardation factors.*

Test No.	Final, Average Dry Density, ρ_d (g/cm³)	Final, Average Porosity, n	Final Reservoir Concentration, c_f (mg/L)	Secant Distribution Coefficient, K'_d (cm³/g)	Secant Retardation Factor, R'^a_d	Linear Retardation Factor, R^b_d
1a	0.694	0.672	385	0.779	1.80	1.75
1b	0.776	0.671	387	0.779	1.90	1.85
2a	0.673	0.684	400	0.778	1.77	1.72
2b	0.786	0.679	376	0.780	1.90	1.85
3a	0.673	0.676	407	0.777	1.78	1.73
3b	0.735	0.692	393	0.778	1.83	1.78
4a	0.837	0.687	423	0.775	1.94	1.89
4b	0.898	0.662	434	0.774	2.05	1.99
5a	0.898	0.666	416	0.776	2.05	1.99
5b	0.929	0.642	430	0.774	2.12	2.06

$^a R'_d = 1 + (\rho_d/n)K'_d$.
$^b R_d = 1 + (\rho_d/n)K_d$ where $K_d = 0.731$ cm³/g (see Fig. 2).

TABLE 5—*Results of regression analyses for determination of effective diffusion coefficients.*

Cell Size	Specimen Volume, cm³	Specimen Length, L (cm)	Test Duration, days	Test No.	Liquid Height, H_L (cm)	Res Chloride D^*_{Res}	r^2	N	Res Zinc D^*_{Res}	r^2	N	Soil Chloride D^*_{Soil}	r^2	N	Soil Zinc D^*_{Soil}	r^2	N
Quarter	243	2.91	7	1a	9.52	12^b	0.58	7	3.2	0.94	8	12	0.98	4	1.8	0.98	4
				1b	9.48	24^b	0.82	6	3.2	0.73	8	8.0	0.99	4	2.2	0.99	4
				Mean	...	12	...	...	3.2	...	...	10	...	...	2.0	...	...
			14	2a	9.77	8.8	0.99	5	2.2	0.86	7	3.5	0.96	4	1.1	0.99	5
				2b	9.40	66^b	1.0	2	8.6^c	0.99	7	5.0	0.64	4	1.0	0.98	5
				Mean	...	8.8	...	...	2.2	...	...	4.25	...	...	1.05	...	...
			21	3a	9.83	4.1	0.99	6	6.4	0.99	7	4.0	0.57	4	0.79	0.99	5
				3b	9.38	5.1	0.70	8	3.2	0.96	6	5.3	0.39	4	0.87	1.0	4
				Mean	...	4.6	...	...	4.8	...	...	4.65	...	...	0.83	...	...
Half	485	5.83	14	4a	9.57	3.4	0.93	7	2.8	0.91	8	7.9	1.0	3	1.3	0.98	7
				4b	9.41	9.2	0.85	8	1.1	0.81	7	6.9	0.93	6	1.5	0.98	7
				Mean	...	6.3	...	...	1.95	...	...	7.4	...	...	1.4	...	...
Full	966	11.60	14	5a	9.60	12	1.0	7	1.8	0.74	8	5.8	1.0	7	1.6	1.0	7
				5b	9.35	7.2	0.85	7	1.5	0.84	8	5.1	0.97	8	2.0	1.0	9
				Mean	...	9.6	...	...	1.65	...	...	5.45	...	...	1.8	...	...

Header spans: Effective Diffusion Coefficients, D^* ($\times 10^{-6}$ cm²/s)^a — Based on Reservoir Concentrations, $D^* = D^*_{Res}$ (Chloride, Zinc); Based on Soil Concentrations, $D^* = D^*_{Soil}$ (Chloride, Zinc).

$^a r^2$ = coefficient of determination from regression analysis, N = number of concentrations upon which r^2 is based.

^{b} This D^* value is not included in the reported mean D^* value since this value is greater than free-solution, D_0, value of 20.3×10^{-6} cm²/s (Shackelford and Daniel 1991a) and, therefore, is not possible physically.

^{c} This D^* value is not included in the reported mean D^* value since this value is greater than free-solution, D_0, value of 7.02×10^{-6} cm²/s (Shackelford and Daniel 1991a) and, therefore, is not possible physically.

error. However, in some cases, the excluded concentrations do not appear to vary substantially from the general trend established by the majority of the data. In these cases, exclusion has been based solely on the ability to perform the regression analyses using Math-Cad®. Second, the r^2 values (i.e., to two significant figures) typically are better for the regressions based on the soil concentrations versus the reservoir concentrations. In the case of the smaller, quarter-size specimens (Test Series 1–3), the typically higher r^2 values for the regressions associated with the measured soil concentrations may be attributed, in part, to the typically lower number of measured concentrations, N, upon which these regressions are based. Third, the number of concentrations upon which the regressed D^*_{Soil} values are based tends to increase with an increase in specimen length due to the greater amount of soil available for recovering soil slices and, therefore, soil concentrations.

Discussion

Effective Diffusion Coefficients

The limiting (maximum) value of D^* for a given chemical species is the diffusion coefficient measured in the absence of soil, commonly referred to as the free-solution or aqueous diffusion coefficient, D_0 (Shackelford and Daniel 1991a). As described by Shackelford (1989) and Shackelford and Daniel (1991a), several different values for D_0 for a given chemical species have been reported depending on the conditions governing the diffusion of the chemical species. However, the conditions upon which these reported D_0 values are based typically are not relevant to the conditions associated with the measurement of the effective diffusion coefficients in soil. Nonetheless, the common practice is to assume

that the appropriate D_0 values correspond to the self-diffusion coefficients of the simplest ionic form at infinite dilution (Shackelford and Daniel 1991b). In this case, the appropriate values of D_0 for chloride and zinc are 20.3×10^{-6} cm²/s and 7.02×10^{-6} cm²/s, respectively (Shackelford and Daniel 1991a).

Based on the D_0 values for chloride and zinc, all of the D^* values reported in Table 5 are physically acceptable (i.e., $D^* < D_0$) except for the D^*_{Res} values for chloride from Test Nos. 1b and 2b and the D^*_{Res} value for zinc from Test No. 2b. Also, 38 of the 40 D^* values reported in Table 5 (i.e., excluding only the chloride D^*_{Res} values for Test Nos. 1b and 2b) are in the relatively narrow range 0.79×10^{-6} cm²/s $\leq D^* \leq 12 \times 10^{-6}$ cm²/s, which is consistent with previously reported test results for diffusion of inorganic chemical species in saturated specimens (e.g., see Shackelford 1991).

The range of chloride D^*_{Res} values excluding the D^*_{Res} values from Test Nos. 1b and 2b (i.e., for 8 out of the 10 tests) is 3.4×10^{-6} cm²/s $\leq D^*_{Res} \leq 12 \times 10^{-6}$ cm²/s. This range of chloride D^*_{Res} values is reduced to 3.4×10^{-6} cm²/s $\leq D^*_{Res} \leq 9.2 \times 10^{-6}$ cm²/s when the results of Test Nos. 1a and 5a are excluded from consideration. The range of chloride D^*_{Soil} values considering all 10 tests is 3.5×10^{-6} cm²/s $\leq D^*_{Soil} \leq 12 \times 10^{-6}$ cm²/s, which is almost same as the range of chloride D^*_{Res} values (i.e., excluding the D^*_{Res} values from Test Nos. 1b and 2b). This range of chloride D^*_{Soil} values improves to 3.5×10^{-6} cm²/s $\leq D^*_{Res} \leq 8.0 \times 10^{-6}$ cm²/s if the chloride D^*_{Soil} value from Test No. 1a is excluded. Thus, the range of physically acceptable D^*_{Res} values for chloride measured in this study compares favorably with the range of D^*_{Soil} values for chloride measured in this study. In addition, the overall range of physically acceptable D^* values (either D^*_{Res} or D^*_{Soil}) for all 10 tests (i.e., excluding the D^*_{Res} values from Test Nos. 1b and 2b) compares favorably to the range of chloride D^* values of 1.5×10^{-6} cm²/s $\leq D^* \leq 10 \times 10^{-6}$ cm²/s reported by Shackelford (1991) for tests previously performed by several different investigators with a variety of soils. Thus, the majority of the chloride D^* values measured in this study are consistent with previously measured chloride D^* values reported in the literature.

In terms of the zinc D^* values reported in Table 5, 9 of the 10 zinc D^*_{Res} values are in the range 1.1×10^{-6} cm²/s $\leq D^*_{Res} \leq 6.4 \times 10^{-6}$ cm²/s, whereas 8 of the 10 zinc D^*_{Res} values are in the narrower range 1.1×10^{-6} cm²/s $\leq D^*_{Res} \leq 3.2 \times 10^{-6}$ cm²/s. In terms of D^*_{Soil} values, all 10 zinc D^*_{Soil} values are in the range 0.79×10^{-6} cm²/s $\leq D^*_{Soil} \leq 2.2 \times 10^{-6}$ cm²/s, and 8 of the 10 zinc D^*_{Soil} values are in the narrower range of 1.0×10^{-6} cm²/s $\leq D^*_{Soil} \leq 2.2 \times 10^{-6}$ cm²/s. Thus, 80% of the D^* values (either D^*_{Res} or D^*_{Soil}) for zinc are in the narrow range 1.0×10^{-6} cm²/s $\leq D^* \leq 3.2 \times 10^{-6}$ cm²/s, indicating relatively consistent test results for zinc. In addition, this range of D^* values for zinc compares favorably with the range of physically acceptable D^* values for zinc of 1.5×10^{-6} cm²/s $\leq D^* \leq 5.1 \times 10^{-6}$ cm²/s reported by Shackelford (1991) for tests previously performed by two different investigators using different soils. Thus, the majority of the zinc D^* values measured in this study are consistent with previously measured zinc D^* values reported in the literature.

Effect of Test Duration

The D^*_{Soil} versus D^*_{Res} values for both chloride and zinc from all tests are plotted as a function of test duration regardless of cell size (specimen length) in Fig. 9. Only D^* values $< D_0$ for chloride are shown in Fig. 9, whereas all D^* values for zinc are shown
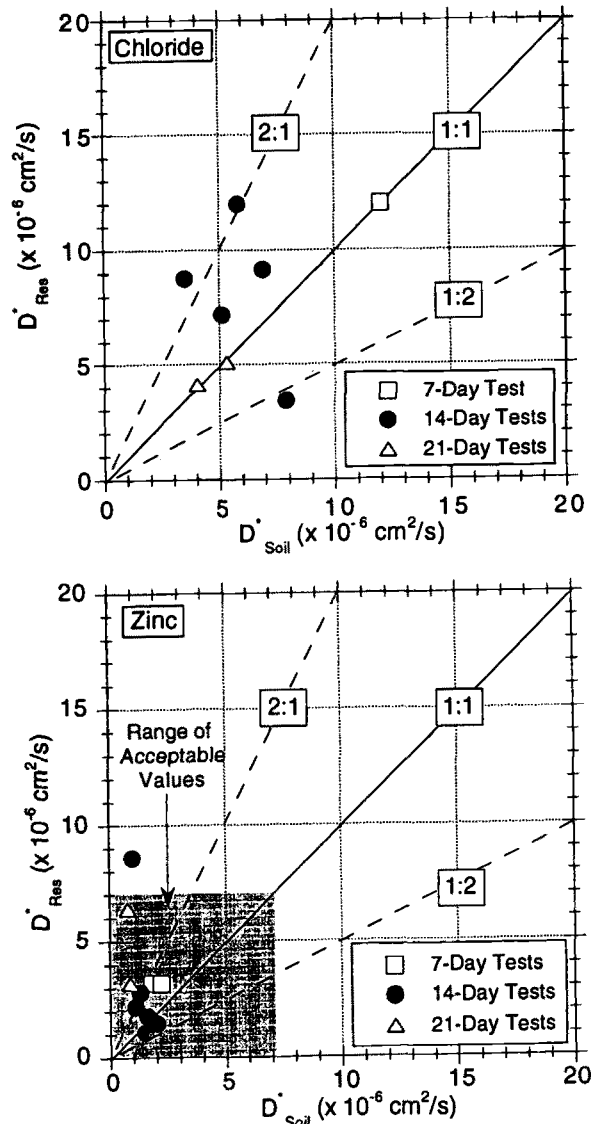

FIG. 9—*Effective diffusion coefficients based on soil concentrations, D^*_{Soil}, versus effective diffusion coefficients based on reservoir concentrations, D^*_{Res}, for all tests as a function of test duration.*

along with the range of physically acceptable D^* values (i.e., $D^* \leq D_0$) for zinc.

In general, test results from single reservoir, decreasing source concentration diffusion tests consistently have indicated $D^*_{Res} > D^*_{Soil}$ for diffusion of non-adsorbing chemical species, typically anions. For example, the relationship between D^*_{Res} and D^*_{Soil} for anion (Br⁻, Cl⁻) diffusion in two unconfined, compacted clay soils was reported by Shackelford and Daniel (1991b) to be in the range $1.18 < D^*_{Res}/D^*_{Soil} < 3.13$ for seven of the eight test results for Cl⁻ and $1.18 < D^*_{Res}/D^*_{Soil} < 1.90$ for three of the five test results for Br⁻. Van Rees et al. (1991) report measured D^*_{Res}/D^*_{Soil} of 1.18 and 1.36 for tests involving tritium diffusion in packed saturated littoral sediments. The improved correlation between D^*_{Res} and D^*_{Soil} for the results of Van Rees et al. (1991) relative to those of Shackelford and Daniel (1991b) may be due, in part, to the inherently improved detection sensitivity associated with measuring the activities of the radioactive tracer, tritium.

In the present study, the correlation between D^*_{Res} and D^*_{Soil} for chloride for the 7- and 21-day tests indicated in Fig. 9 is excellent

$(0.96 \le D_{Res}^*/D_{Soil}^* \le 1.03)$, whereas the same correlation for the 14-day tests is more typical of previously reported results in that four of the five reported test results indicate $D_{Res}^* > D_{Soil}^*$ $(0.43 \le D_{Res}^*/D_{Soil}^* \le 2.67)$. However, the excellent correlation between D_{Res}^* and D_{Soil}^* for chloride for the 7-day test duration is considered inconclusive since this correlation is based on the results of only one test. In addition, the range of D^* values for the duplicate 21-day tests $(4.0 \times 10^{-6} \text{ cm}^2/\text{s} \le D^* \le 5.3 \times 10^{-6} \text{ cm}^2/\text{s})$ is narrower than the range of D^* values for the six 14-day tests $(3.4 \times 10^{-6} \text{ cm}^2/\text{s} \le D^* \le 12 \times 10^{-6} \text{ cm}^2/\text{s})$. Thus, the 21-day test duration tends to provide the best correlation between D_{Res}^* and D_{Soil}^* for the chloride diffusion measured in this study.

The zinc D_{Res}^* values plotted in Fig. 9 tend to be greater than zinc D_{Soil}^* except for the 14-day tests where there is no apparent trend. However, as previously noted, the range of the majority (80%) of all D^* values measured for zinc (either D_{Res}^* or D_{Soil}^*) is relatively narrow $(1.0 \times 10^{-6} \text{ cm}^2/\text{s} \le D^* \le 3.2 \times 10^{-5} \text{ cm}^2/\text{s})$ such that the differences in D_{Res}^* and D_{Soil}^* for zinc indicated in Fig. 9 are considered insignificant.

The data reported in Fig. 9 include D^* values for tests performed using all three specimen sizes. In order to explore the potential effect of test duration on the relationship between D_{Res}^* and D_{Soil}^* for tests performed using the same specimen size, the D_{Res}^* /D_{Soil}^* values based on the mean values for D_{Res}^* and D_{Soil}^* reported in Table 5 for only the quarter cells (Test Series 1–3) with specimen lengths, L, of 2.91 cm are plotted versus test duration in Fig. 10a. The data indicate that the best correlation between D_{Res}^* and D_{Soil}^* for chloride occurs for the longest test duration of 21 days, whereas the best correlation between D_{Res}^* and D_{Soil}^* for zinc occurs for the shortest test duration of 7 days. These observations generally are consistent with those previously made considering all specimen sizes.

All of the mean D^* values for the quarter cells ($L = 2.91$ cm) reported in Table 3 are plotted as a function of test duration in Fig. 10b. In general, D^* for zinc is typically lower than D^* for chloride for a given test duration, and D^* for either chloride or zinc typically decreases with an increase in test duration from 7 days to 21 days. Since the solute concentration gradient between the source reservoir and the soil decreases with increasing test duration, the apparent decrease in D^* with increase in test duration illustrated in Fig. 10b may be an indication that D^* is a function of the solute concentration (e.g., see Achari et al. 1997). However, no assessment of concentration-dependent D^* values is attempted in this study.

Effect of Specimen Length

The D_{Soil}^* versus D_{Res}^* values for both chloride and zinc from all tests are plotted as a function of specimen length regardless of test duration in Fig. 11. Only the physically acceptable D^* values for chloride are shown in Fig. 11, whereas all of the D^* values for zinc are shown along with the range of physically acceptable D^* values for zinc.

The data in Fig. 11 indicate that the best correlation between D_{Res}^* and D_{Soil}^* for chloride occurs for specimen lengths, L, of 2.91 cm (quarter cells) where the D_{Res}^*/D_{Soil}^* values range from 0.96 to 1.03 for three of the four quarter cell tests. This excellent correlation between D_{Res}^* and D_{Soil}^* for chloride may be attributable to a more accurate assessment of the final porosity distribution on the basis of a single, weighted-mean porosity value due to the typically more uniform distributions in final porosity for the quarter cells (see Fig. 8).
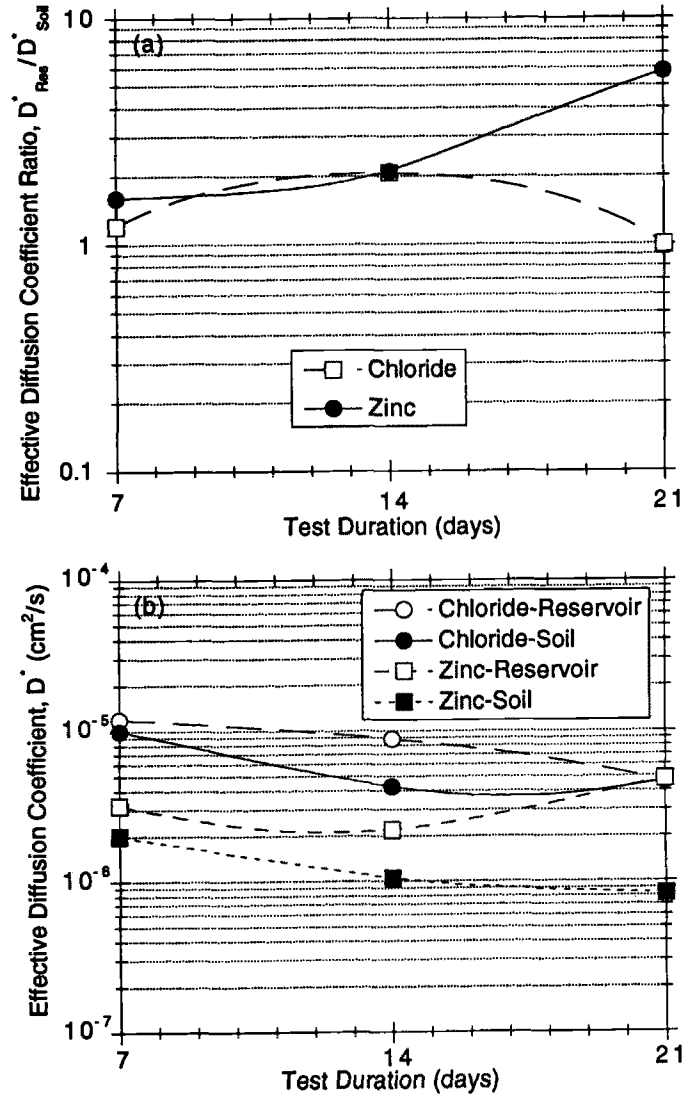

FIG. 10—Effect of test duration for diffusion tests performed with a specimen length of 2.91 cm (quarter cells): (a) ratio of mean D^* based on reservoir concentrations, D_{Res}^*, to mean D^* based on soil concentrations, D_{Soil}^*; (b) all mean D^* values.

As indicated in Fig. 11, the correlation between D_{Res}^* and D_{Soil}^* for zinc improves as the specimen length increases, a trend opposite to that observed for chloride. For example, the D_{Res}^*/D_{Soil}^* values for three of the four tests performed with either half cells ($L = 5.83$ cm) or full cells ($L = 11.90$ cm) ranges from 0.73 to 1.13, whereas the D_{Res}^*/D_{Soil}^* values for the tests performed with the quarter cells ($L = 2.91$ cm) range from 1.45 to 8.10 excluding the two physically unacceptable D_{Res}^* values.

The data reported in Fig. 11 include D^* values for tests performed using all three test durations. As a result, the D_{Res}^*/D_{Soil}^* values based on the mean values for D_{Res}^* and D_{Soil}^* reported in Table 5 for the same test duration of 14 days (i.e., Test Series 2, 4, and 6) are plotted versus specimen length in Fig 12a. The data indicate that the best correlation between the mean D_{Res}^* and D_{Soil}^* values for chloride occurs for the half-size specimens ($L = 5.83$ cm), whereas the best correlation between D_{Res}^* and D_{Soil}^* for zinc occurs for the full-size specimens ($L = 11.60$ cm).

All of the mean D^* values for a 14-day test duration reported in Table 5 are plotted as a function of specimen length in Fig. 12b.

The mean zinc D^* values again are consistently lower than the mean chloride D^* values regardless of specimen length. In addition, the overall ranges in the mean chloride D^* values and the mean zinc D^* values plotted in Fig. 12b considering all specimen lengths are small. For example, the mean chloride D^* values range from 4.25×10^{-6} cm^2/s to 9.6×10^{-6} cm^2/s and the mean zinc D^* values range from 1.05×10^{-6} cm^2/s to 2.2×10^{-6} cm^2/s for all specimen lengths. Thus, the effect of specimen length on the measured D^* values is relatively small for both solutes and is smaller for zinc diffusion relative to chloride diffusion. However, the trends in the D^*_{Res} values with respect to specimen length are noticeably opposite to the trends in D^*_{Soil} with respect to specimen length for a given solute, with the minimum D^*_{Res} and the maximum D^*_{Soil} for chloride occurring at specimen lengths intermediate between 2.91 cm and 11.60 cm, and the minimum D^*_{Res} and the maximum D^*_{Soil} for zinc both occurring at the maximum specimen length of 11.60 cm.

Conclusions

The following conclusions are made for the test procedures and materials used in this study.
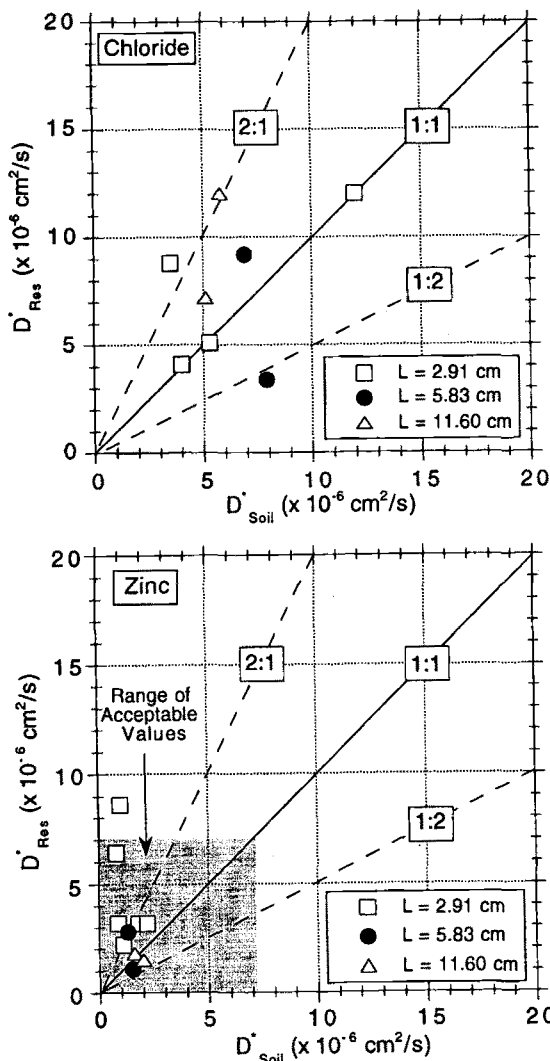
FIG. 11—*Effective diffusion coefficients based on soil concentrations, D$^*_{Soil}$, versus effective diffusion coefficients based on reservoir concentrations, D$^*_{Res}$, for all tests as a function of specimen length (L).*
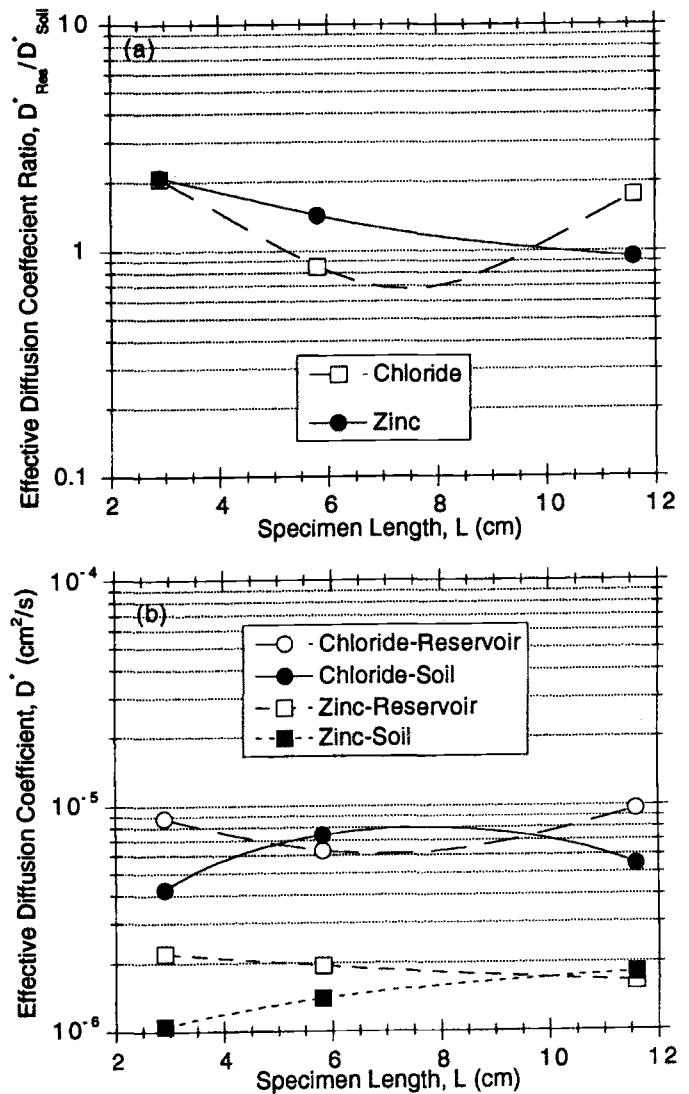
FIG. 12—*Effect of specimen length for diffusion tests performed for a test duration of 14 days:* (a) *ratio of mean* D* *based on reservoir concentrations,* D$^*_{Res}$, *to mean* D* *based on soil concentrations,* D$^*_{Soil}$; (b) *all mean* D* *values.*

1. Consistent results were obtained from the majority of tests performed in this study, with 95% (38/40) of the measured effective diffusion coefficients, D^*, for both chloride and zinc in the relatively narrow range 0.79×10^{-6} cm^2/s $\leq D^* \leq 12 \times 10^{-6}$ cm^2/s, and only 3 of 40 measured D^* values considered as being unacceptably high (greater than the free-solution diffusion coefficient).

2. The chloride D^* values typically are greater than the zinc D^* values, with 75% (15/20) of the measured D^* values for chloride in the range 3.4×10^{-6} cm^2/s $\leq D^* \leq 9.2 \times 10^{-6}$ cm^2/s, and 80% (16/20) of the measured D^* values for zinc in the narrow range 1.0×10^{-6} cm^2/s $\leq D^* \leq 3.2 \times 10^{-6}$ cm^2/s

3. For tests performed with a specimen length, L, of 2.91 cm (quarter-sized cells) and test durations of 7, 14, and 21 days, the mean D^* values from duplicate tests (excluding physically unacceptable D^* values) for both chloride and zinc tended to decrease with increasing test duration, possibly due to the measurement of concentration-dependent D^* values.

4. A 21-day test duration tended to provide the best correlation between the $D*$ values based on reservoir concentrations, D^*_{Res}, for chloride and the $D*$ values based on soil concentrations, D^*_{Soil}, for chloride for a given test regardless of the specimen length.

5. The effect of test duration on the correlation between D^*_{Res} and D^*_{Soil} for zinc tended to be a function of the specimen length, but the relatively narrow range associated with these $D*$ values (i.e., 1.0×10^{-6} cm^2/s $\leq D* \leq 3.2 \times 10^{-6}$ cm^2/s) suggests that differences between the zinc D^*_{Res} and D^*_{Soil} values for a given test were minor.

6. For tests performed with a duration of 14 days and specimen lengths, L, of 2.91, 5.83, and 11.90 cm, the effect of specimen length on the measured $D*$ values was minor as suggested by the narrow ranges of mean $D*$ values for chloride (4.25×10^{-6} cm^2/s $\leq D* \leq 9.6 \times 10^{-6}$ cm^2/s) and zinc (1.05×10^{-6} cm^2/s $\leq D* \leq 2.2 \times 10^{-6}$ cm^2/s).

7. The shorter specimen lengths (2.91 and 5.83 cm) generally provided better correlation between D^*_{Res} and D^*_{Soil} for chloride for a given test regardless of test duration, probably due to the more accurate representation of the non-linear porosity distribution in the specimen by the single, weighted-mean porosity value used in the analysis for $D*$.

8. The longer specimen lengths (5.83 and 11.60 cm) generally provided better correlation between D^*_{Res} and D^*_{Soil} for zinc for a given test regardless of test duration, probably due to the contrasting effects of the non-linear distributions in porosity and dry density that become less significant as the specimen length increases.

Acknowledgments

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