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Characterizing zinc migration through a high pH sand-clay mixture

Caractérisation de la migration du zinc à travers un mélange d'argile et de sable à pH élevé

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ABSTRACT: The results of laboratory column tests performed to characterize the migration of zinc, a toxic chemical, in a $ZnCl_2$ solution through a compacted sand-clay soil mixture are presented. The results of the column tests were potentially affected by the existence of a high initial pH (~ 8.6) in the pore water of the test specimens, an apparent effective porosity effect, and a non-uniform porosity distribution resulting from swelling of unconfined test specimens.

RESUME: Les résultats de tests de colonne en laboratoire faits pour caractériser la migration du zinc, un produit chimique toxique, dans une solution de $ZnCl_2$ à travers un mélange de sable et d'argile tassé sont présentés ici. Les résultats du tests de colonne ont été potentiellement affectés par l'existence d'un taux initial élevé de pH (~ 8,6) dans l'eau des pores de l'échantillon, un effet effectif apparent de la porosité, et une distribution non-uniforme de porosité résultant d'un gonflement d'échantillons non enclos.

1 INTRODUCTION

The importance of contaminant migration through waste containment barriers, such as compacted soil liners and slurry walls, has been established (e.g., Crooks and Quigley 1984, Shackelford 1990). As a result, characterization of the miscible transport parameters for specific pollutants migrating through specific barrier materials is an important consideration in the design of waste containment barriers.

The results of laboratory column tests performed to characterize the migration of zinc, a toxic chemical, contained in a $ZnCl_2$ solution through a compacted sand-clay soil mixture are presented. Two factors potentially affected the characterization of zinc migration: (1) existence of a high initial pH in the pore water of the test specimens, and (2) swelling of the unconfined test specimens prior to column testing resulting in measurement of an apparent effective porosity effect and inconsistent zinc retardation factors.

2 MATERIALS AND METHODS

2.1 Soil

A mixture of 75 percent (dry weight) quartz sand and 25 percent attapulgite clay (Min-U-Gel FG, Floridin Company, Quincy, Florida) was used in this study. Attapulgite is a clay mineral with a chain-like crystal structure that is less susceptible to chemical attack than bentonite (Shackelford 1994). Some physical and chemical properties of the two soil constituents are given in Table 1.

The soil constituents were mixed with deionized distilled water (DDW) at a water content ~ 3 percentage points wet of the optimum water content ($w_{opt} = 26\%$) based on ASTM D 698. Test specimens were prepared by compacting the wetted soil mixture into stainless-steel molds with lengths, L , of either 2.91, 5.83, or 11.60 cm corresponding to mold volumes of 243, 485, or 966 cm^3 , respectively. Compaction of the test specimens followed ASTM D 698 except the compaction energies were ~ 98 percent of the standard energy due to differences in the mold volumes.

2.2 Permeant liquids

The permeant liquids used in this study include DDW (pH = 5.8), an acetic acid/sodium acetate (HOAc/NaOAc) buffer solution, and $ZnCl_2$ dissolved in the buffer solution. The buffer solution consisted of 1.0 M HOAc and 1.4 M NaOAc with a measured pH

Table 1. Properties of soil mixture constituents.

Property	ASTM Standard	Constituent	
		Sand	Attapulgite Clay
Liquid Limit, LL (%)	D 4318	-----	338
Plasticity Index, PI (%)	D 4318	-----	216
Sand (0.075-4.75 mm)	D 422	99%	0
Sil/Clay (<0.075 mm)	D 422	1%	100%
Classification (USCS)	D 2487	SP	CH
Soil pH (1:1 paste)	-----	8.0	9.7
CEC ¹ (meq/100g)	-----	0	29.1

¹CEC = Cation Exchange Capacity

of 4.8. Solutions of anhydrous $ZnCl_2$ dissolved in the buffer solution were used in the column tests. Measured zinc concentrations in these solutions ranged from 445 mg/L to 525 mg/L.

2.3 Test apparatus and procedure

Constant-head column tests were performed using the apparatus shown schematically in Fig. 1. The influent accumulator is a Mariotte device that provides a constant head at the bottom of the small diameter inflow tube as described by Daniel (1994). A constant head also exists at the top of the elevated exit tube in the effluent accumulator. A constant, applied pressure through the inlet tube of the influent accumulator drives the flow.

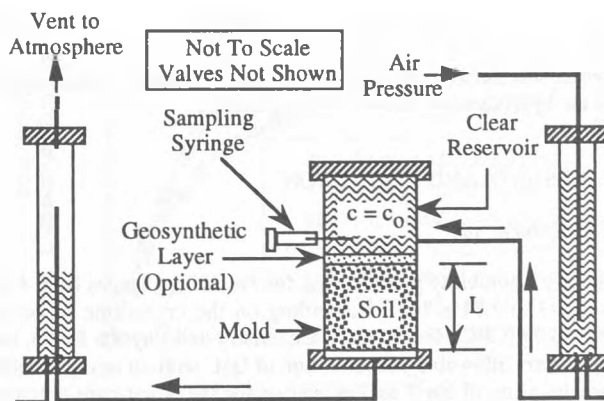


Figure 1. Constant-head column testing apparatus.

The compacted specimens generally were unconfined at the interface between the mold and the reservoir and, therefore, were allowed to swell into the reservoir during permeation. In such cases, the swollen soil was trimmed flush with the top of the mold before performing the column stage of the test. Some compacted test specimens also were confined from swelling with a geosynthetic layer consisting of a Synthetics Industries non-woven needle-punched geotextile with a layer of Tensar NS1305 geonet. Influent liquid samples were collected with a sampling syringe through a reservoir sampling port fitted with a Mininert® (VICI Precision Sampling Corp., Baton Rouge, Louisiana) valve containing a septum. Effluent samples were collected periodically by draining the effluent accumulator.

The column tests were performed using the cumulative mass procedure described by Shackelford (1995a,b). The steps in this procedure are as follows: (1) allow the effluent to collect in the effluent reservoir over a pore volume increment, ΔT ; (2) determine the increment of effluent volume, $\Delta V_e (= \Delta T \cdot V_p$, where V_p is the pore volume of the soil), that has entered the reservoir during this pore volume increment; (3) shake the collected volume of effluent before removing an aliquot of effluent for measurement of the average effluent concentration, \bar{c}_e ; and (4) determine the increment of solute mass in the collected volume of effluent, $\Delta m (= \bar{c}_e \cdot \Delta V_e)$. This procedure is repeated for each subsequent pore volume increment, and the cumulative mass values $\Sigma(\Delta m) (= \Sigma \bar{c}_e \cdot \Delta V_e)$ are normalized with respect to the solute mass in the pore fluid of the soil at steady-state transport, $m_0 (= V_p c_0$, where c_0 is the initial, constant solute concentration in the influent reservoir), to provide the dimensionless cumulative mass ratio, $CMR (= \Sigma(\Delta m)/m_0)$. Thus, the analysis of the effluent data in the cumulative mass approach is based on the total or cumulative solute mass that has collected in the effluent reservoir.

Column testing was initiated with the buffer solution containing $ZnCl_2$ following initial permeation only with the buffer solution. Chloride concentrations were measured using an ion selective electrode (ISE) and zinc concentrations were measured using an inductively coupled plasmatometer (ICP).

The measured chloride and zinc concentrations in the effluent from the column tests were regressed against the following analytical solution for the cumulative mass ratio, CMR , based on the one-dimensional advection-dispersion equation with linear adsorption to determine the retardation factor, R_d , and the column Peclet number, P_L (Shackelford 1995a,b):

$$CMR = \frac{\sum_{i=1}^j \Delta m_i}{m_0} = \left(\frac{T - R_d}{2} \right) \operatorname{erfc} \left(\frac{R_d - T}{2\sqrt{TR_d/P_L}} \right) + \left(\frac{T + R_d}{2} \right) \exp(P_L) \operatorname{erfc} \left(\frac{R_d + T}{2\sqrt{TR_d/P_L}} \right) \quad (1)$$

where j is the number of effluent samples, and T and P_L are defined as follows:

$$T = \frac{vt}{L} \quad ; \quad P_L = \frac{vL}{D} \quad (2)$$

where v is the average linear or seepage velocity, t is time, and D is the hydrodynamic dispersion coefficient.

3 RESULTS AND DISCUSSION

3.1 Effluent pH

Since the solubility product, K_{sp} , for $Zn(OH)_2(s)$ ranges from 4.12×10^{-17} to 7.71×10^{-17} depending on the crystalline phase of $Zn(OH)_2$ (CRC Handbook of Chemistry and Physics 1991), the maximum allowable concentration of OH^- without any allowable precipitation of Zn^{2+} as $Zn(OH)_2(s)$ for the worst-case scenario and the zinc concentration used in this study ($\sim 0.007 \text{ M Zn}^{2+}$) is

7.67×10^{-8} ($pH = 6.9$). Consequently, if the soil pH is greater than 6.9, some aqueous Zn^{2+} will precipitate as $Zn(OH)_2(s)$.

Initial permeation of compacted soil specimens with DDW revealed effluent pH values of ~ 8.6 which are consistent with the relatively high pH values for the soil constituents (see Table 1). Thus, there was a concern that zinc precipitation during migration through the soil would result in inaccurate R_d values due to precipitation. As a result, all test specimens were pre-saturated by permeation with the HOAc/NaOAc buffer solution designed to reduce and maintain the pH of the soil pore water to a value of ~ 4.8 .

An example of the results of this pre-saturated permeation procedure is shown in Fig. 2. Initial permeation with ~ 4 pore volumes of DDW indicates an effluent pH of ~ 8.6 . Subsequent permeation with the buffer solution results in a rapid decrease in pH to a value of 4.8 which is the same as the influent pH for the buffer solution. A pH of 4.8 is sufficiently below the desired maximum pH of 6.9, but not too low to cause concern regarding clay particle dissolution which typically occurs only for $pH \leq 2$ (e.g., Shackelford 1994). The effluent pH for the test results shown in Fig. 2 remained stable at ~ 4.8 for ~ 16 pore volumes before the column testing stage of the test commenced using the $ZnCl_2$ solution.

Weak acids have an inherent advantage over strong acids in terms of pH-lowering capacity in that, for a given original solution pH, weak acids provide more equivalents of hydrogen ions (H_3O^+) than strong acids. More concentrated solutions of a strong acid (e.g., HNO_3) also could be used, but the extremely low original pH values of strong acid solutions are undesirable due to the potential for clay particle attack. Thus, in this case, the HOAc/NaOAc solution proved to be effective in buffering the effluent pH of the high pH soil to a value of ~ 4.8 . More detail regarding the effective acid buffering of this high pH soil is provided in Shackelford et al. (1997).

3.2 Specimen swelling and effective porosity

One unconfined column test was performed for each of the three column lengths, L (i.e., 2.91, 5.83, and 11.60 cm). Typical cumulative mass breakthrough curves for chloride (Cl^-) in the form of $T - CMR$ versus T , where T is the cumulative pore volumes of flow, $T (= \Sigma(\Delta T))$, are shown in Fig. 3. The retardation factor, R_d , defined with respect to mass balance for a finite column approaches asymptotically the value of $T - CMR$ on a plot of T versus $T - CMR$. Values of $R_d < 1$ for non-reactive tracers, typically anions, are indicative of an effective porosity (n_e) effect in which not all of the pore space is available for contaminant migration. In this case, the value for R_d equals the effective porosity ratio, n_e/n , where n is the total porosity (Shackelford 1995a).

For example, Wierenga and van Genuchten (1989) attributed R_d values for Cl^- of 0.78 to an effective porosity effect due to anion

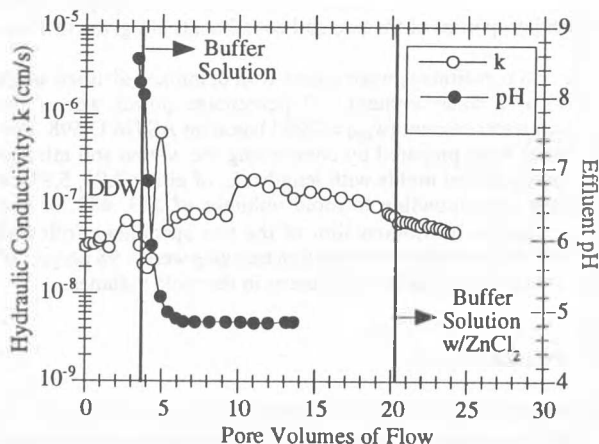


Figure 2. Typical effluent pH and hydraulic conductivity trends for buffered column test specimens.

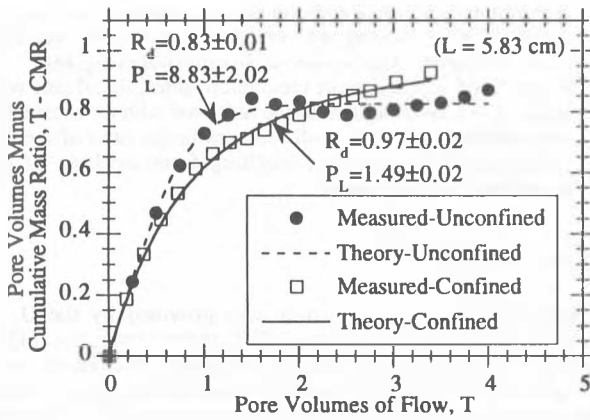


Figure 3. Chloride (Cl⁻) column test results.

exclusion. Anion exclusion or negative adsorption results in some clay soils from the repulsion of anions from the negatively charged surfaces of clay particles (e.g., Bohn et al. 1985). The exclusion of anions from the pores of clay soils during transport contributes to an effective porosity effect in terms of anion migration. However, an effective porosity effect due to anion exclusion would not pertain necessarily to the migration of zinc when zinc is in a cationic form (e.g., Zn²⁺, ZnCl⁺). Thus, an accurate assessment of the cause as well as the existence of an effective porosity effect is important in terms of characterizing the migration of zinc.

The values of n_e/n ($=R_d$) based on the Cl⁻ breakthrough curves for all three unconfined column tests are plotted versus the column length in Fig. 4. Although the n_e/n values < 1 may indicate a possibility of anion exclusion, these values also may simply reflect an inaccurate estimate of the total porosity used in the analysis. For example, the final porosity distributions for the unconfined specimens, shown in Fig. 5, were significantly non-uniform and generally higher than the initial values, which ranged from 0.43 to 0.46, due to the effect of swelling near the soil-reservoir interface. As a result of the non-uniform porosity distributions, a weighted-average porosity value was used to estimate V_p for analysis of the column data. Thus, an inaccurate estimate of the final porosity may have contributed to the observed effective porosity effect.

In an attempt to evaluate further the effect of a non-uniform porosity distribution on the column test results for Cl⁻, three additional column tests on confined specimens were performed. A typical Cl⁻ breakthrough curve for these confined column tests also is shown in Fig. 3, and the regressed n_e/n values for all three confined tests are plotted versus the column length in Fig. 4. Based on the results shown in Fig. 4, an effective porosity effect is more prevalent for the smallest specimens ($L = 2.91$ cm) and less prevalent for largest specimens ($L = 11.60$ cm). In addition, the effect of confinement tends to decrease the tendency for an effective porosity effect for the intermediate size specimens ($L = 5.83$ cm). These results are consistent with the different final porosity distributions in the confined versus unconfined specimens.

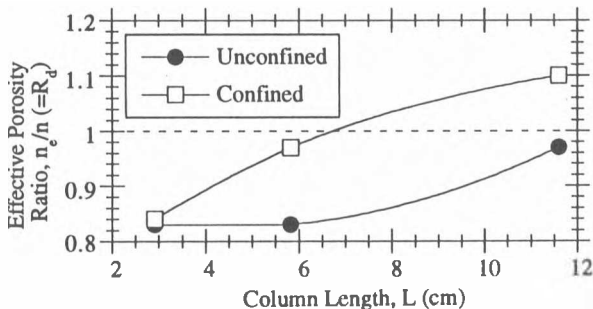


Figure 4. Effective porosity ratio versus column length for unconfined and confined column test specimens.

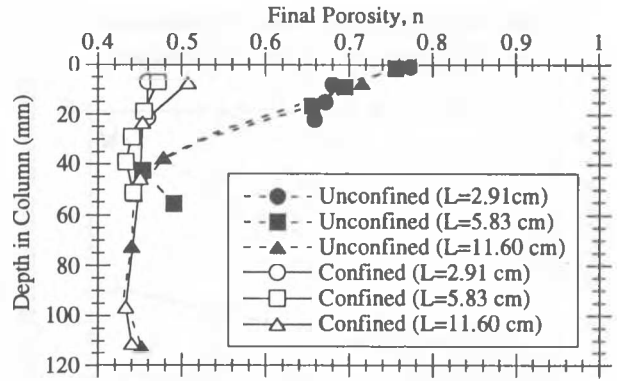


Figure 5. Final porosity distributions in unconfined and confined test specimens.

As shown in Fig. 5, the final porosity values for the confined specimens are very close to the initial range of porosity values (i.e., 0.43 to 0.46) indicating that the geosynthetic layer was relatively effective in minimizing swelling of the specimens. Also, the resulting final porosity distributions for the confined specimens are more uniform than those of the unconfined specimens. Thus, the weighted-average final porosity value for the confined specimens was more representative of the actual porosity distribution which is reflected in no observed effective porosity effect for the two largest ($L = 5.83$ cm and $L = 11.60$ cm) confined specimens. However, the geosynthetic layer apparently was not sufficiently rigid to preclude a significant porosity variation relative to the analysis for the smallest ($L = 2.91$ cm) confined specimen since a n_e/n value of ~ 0.84 was measured. In any case, this analysis indicates that failure to account for the possibility of non-uniform porosity distribution, particularly in the case of unconfined specimens, may lead to an incorrect conclusion regarding both the existence and cause (e.g., anion exclusion) of an effective porosity effect.

3.3 Specimen swelling and retardation of zinc

The CMR breakthrough curves based on the zinc analysis of the effluent from the unconfined specimens are shown in Fig. 6 along with the regressed retardation factors. The test results shown in Fig. 6 have been corrected for the apparent effective porosity effect using the procedure described by Shackelford (1995b).

As shown in Fig. 7, the R_d values corrected for the apparent effective porosity effect are higher than the uncorrected R_d values for all column lengths. Thus, neglecting the apparent porosity

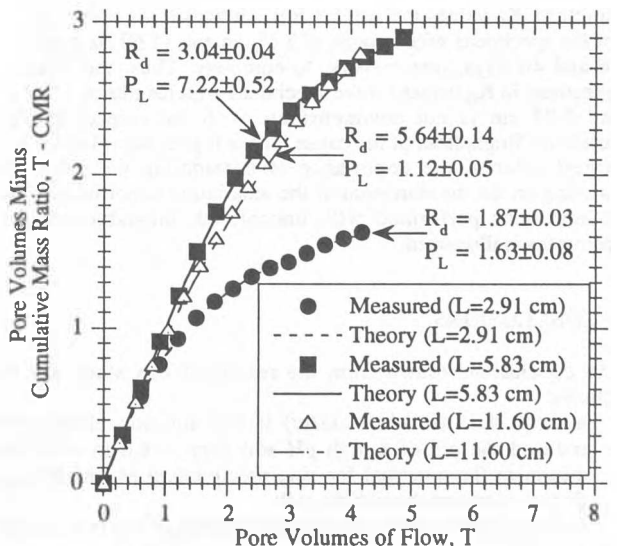


Figure 6. Unconfined column test results for zinc.

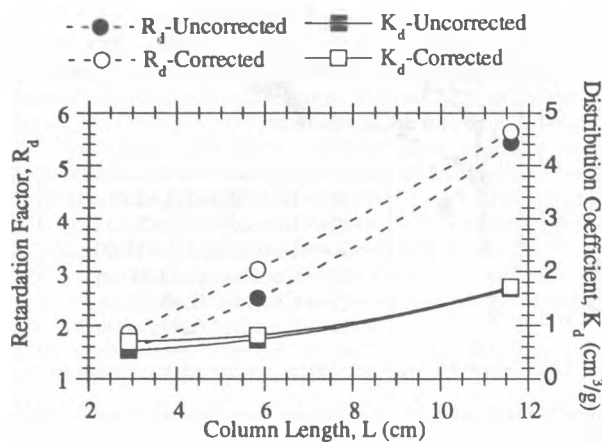


Figure 7. Retardation factor, R_d , and distribution coefficient, K_d , for zinc as a function of column length.

effect in terms of the retardation factor for zinc results in lower, more conservative estimates of R_d .

Also, as indicated in Fig. 7, the R_d values tend to increase with an increase in cell length. Since the same soil with the same CEC was used in each column, this trend is unexpected (i.e., R_d should be the same in all columns). However, part of this discrepancy between measured and expected results for R_d can be attributed to a decrease in dry density (ρ_d) and an increase in the porosity (n) near the inflow boundary due to swelling of the unconfined test specimens. This effect is evaluated by calculating distribution coefficients, K_d , representing linear, reversible sorption from the measured R_d values in accordance with the following equation:

$$K_d = \frac{n}{\rho_d} (R_d - 1) \quad (3)$$

The calculated distribution coefficients, plotted in Fig. 7, are nearly independent of the column length (i.e., constant) for $L = 2.91$ cm and $L = 5.83$ cm, which is consistent with linear, reversible sorption and a constant CEC. At least two possible explanations can be offered for the higher K_d value associated with the largest ($L = 11.60$ cm) column.

First, non linear adsorption may have been prevalent. However, independently performed batch equilibrium tests indicated that the adsorption of zinc to the sand-attapulgite clay mixture was linear over the concentration range used in this study. Second, non-equilibrium or rate-dependent (kinetic), rather than equilibrium, conditions may have dominated the adsorption of zinc, particularly for the small column test ($L = 2.91$ cm) that was completed in only 6.5 hours. Kinetic conditions would result in measured R_d and, therefore, K_d values that are too low. However, the column tests for the specimens with lengths of 5.83 cm and 11.60 cm required 36 and 40 days, respectively, to complete. Thus, the relative agreement in K_d values for the specimens with lengths of 2.91 cm and 5.83 cm is not commensurate with the respective test durations. Regardless of the cause for the higher K_d value for the largest column, the importance of considering the effect of swelling on the measurement of the retardation factor of zinc for column tests performed with unconfined, pre-saturated test specimens is illustrated.

4 CONCLUSIONS

The conclusions drawn from the results of this study are as follows:

- a weak acid (HOAc/NaOAc) buffer solution effectively reduced the pH of a high pH soil from ~ 8.6 to ~ 4.8 to minimize the potential for zinc precipitation as $Zn(OH)_2(s)$ during migration through the soil;
- a non-uniform porosity distribution resulting from swelling of unconfined column test specimens may result in an apparent effective porosity effect when, in reality, none exists;

- neglecting the apparent effective porosity effect due to swelling in terms of evaluating the retardation factor, R_d , for zinc resulted in lower, more conservative estimates of R_d ; and
- an observed increase in the retardation factor, R_d , of zinc with increase in column length for the same soil with the same CEC was attributed, in part, to differences in the ratio of the dry density to porosity, ρ_d/n , resulting from swelling of the unconfined test specimens.

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REFERENCES

- Bohn, H., McNeal, B., and O'Connor, G. 1985. *Soil chemistry*, 2nd Ed. John Wiley and Sons, Inc., New York, 341 pp.
- Crooks, V. E. and Quigley, R. M. 1984. Saline leachate migration through clay: A comparative laboratory and field investigation. *Canadian Geotechnical Journal*, 21(2):349-362.
- Daniel, D. E. 1994. State-of-the-art: Laboratory hydraulic conductivity tests for saturated soils. *Hydraulic Conductivity and Waste Contaminant Transport in Soil*, ASTM STP 1142, D. E. Daniel and S. J. Trautwein, Eds., ASTM, Philadelphia, 30-78.
- Shackelford, C. D. 1990. Transit-time design of earthen barriers. *Engineering Geology*, Elsevier Publ., Amsterdam, 29:79-94.
- Shackelford, C. D. 1994. Waste-soil interactions that alter hydraulic conductivity. *Hydraulic Conductivity and Waste Contaminant Transport in Soil*, ASTM STP 1142, D. E. Daniel and S. J. Trautwein, Eds., ASTM, Philadelphia, 111-168.
- Shackelford, C. D. 1995a. Analytical models for cumulative mass column testing. *Geoenvironment 2000*, ASCE Geotech. Spec. Publ. No. 46, Y. B. Acar and D. E. Daniel, Eds., ASCE, New York, 355-372.
- Shackelford, C. D. 1995b. Cumulative mass approach for column testing. *Journal of Geotechnical Engineering*, ASCE, New York, 121(10):696-703.
- Shackelford, C. D., Cotten, T. E., Rohal, K. M., and Strauss, S. H. 1997. Acid buffering a high pH soil for zinc diffusion. *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE, New York, 123(3).
- Wierenga, P. J. and van Genuchten, M. Th. 1989. Solute transport through small and large unsaturated soil columns. *Ground Water*, 27(1):35-42.