

## A New Technique for Diffusion Testing of Unsaturated Soil

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**ABSTRACT:** A technique is proposed for determining the coefficients of diffusion and adsorption for ions in unsaturated soils. The method integrates the single reservoir diffusion testing of saturated soil with the axis-translation technique for the control of matric suction. The procedure allows for the application of a net total stress and matric suction to the soil during the diffusion test. The use of this new technique to determine the coefficients of diffusion and adsorption of ions from a single test is demonstrated. The effects of the degree of saturation on the coefficients of diffusion and adsorption were evaluated on a sandy soil with water contents ranging from saturation to near the residual degree of saturation. Potassium and chloride ions were used as the primary tracers.

The test results showed that both the coefficients of diffusion and adsorption can be determined from a single test. The results illustrate a decrease in both the effective diffusion and adsorption coefficients with a decrease in the degree of saturation. The extent of the decrease in the effective diffusion coefficient from saturation to near the residual degree of saturation was approximately 80%. The decrease in the adsorption coefficient was gradual and small from saturation to a degree of saturation of approximately 10%; however, it then decreased rapidly as the water content approached the residual degree of saturation.

**KEYWORDS:** unsaturated soil, diffusion test, inorganic chemicals, effective diffusion coefficient, adsorption coefficient

### Nomenclature

- $J_d$  = Diffusive mass flux
- $\Theta_w$  = Volumetric water content
- $D_i^*$  = Effective diffusion coefficient of ion  $i$  in soil
- $dC_i/dz$  = Concentration gradient
- $Q_i$  = Mass of ion  $i$  adsorbed by the solids per unit mass of dry soil
- $C_{ei}$  = Concentration of ion  $i$  at equilibrium
- $K_f$  = Freundlich adsorption coefficient
- $m$  = Freundlich constant
- $\sigma$  = Total stress
- $u_a$  = Pore-air pressure
- $u_w$  = Pore-water pressure

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### Introduction

Compacted, unsaturated soils are often present as one of the components in the design of barriers for the containment of waste. Zones of unsaturated soil can be found in covers or in the granular drainage layers in the leachate collection system in landfills. Unsaturated layers of gravel are also being proposed as a backfill around subsurface nuclear and hazardous waste repositories (Conca and Wright 1990). Other geoenvironmental problems such as remediation of hydrocarbon or chemical spills and prediction of the fate of agricultural-related contaminants in surficial soils and soil salinity also require an understanding of chemical transport in unsaturated soils.

The processes governing contaminant transport in saturated soils are also valid for unsaturated soils; however, the transport parameters may be quite different. Transport parameters such as hydraulic conductivity and the coefficients of diffusion and adsorption are generally assumed to be constant for saturated soils. In unsaturated soils, however, there needs to be functional relationships between these parameters and the water content.

This study focuses primarily on diffusion and adsorption as the dominant transport and attenuation processes governing the movement of contaminants in an unsaturated soil. A number of studies have emerged in the soil science literature which show that the effective diffusion coefficient varies with the water content of the soil. The shape of the functional relationships reported by different researchers vary for different textured soils; however, limitations in the test procedures used may have an effect on the measured diffusion coefficients. Existing data pertaining to the dependency of the adsorption coefficient on the degree of saturation are limited. Various hypotheses have been suggested by Bear and Verruijt (1987), but there has been no experimental verification to date.

The objective of this paper is to describe the principle and test procedure for a new technique for determining the coefficients of diffusion and adsorption of ions for an unsaturated soil. The principle of the new test method is based on the integration of the single reservoir method for diffusion testing of saturated soil with the axis-translation technique (Hilf 1956) for the control of the matric suction. With the axis-translation technique, the soil specimen can be brought to a specified degree of saturation by drainage of the soil-water. The new test method allows both the matric suction and the net total stress to be controlled independently before and during the diffusion test. For the purpose of evaluating the proposed test method, simple ions such as potassium and chloride were selected as the primary reactive and non-reactive tracers.

## Background

The migration of contaminants in soil is governed by two key processes: transport and attenuation. In the absence of advection, movement by diffusion becomes the dominant transport process. Changes in concentration can also occur as a result of chemical or biological reactions within the liquid phase or by transfer of the contaminants to the solid phase of the soil matrix.

### Diffusion in Soils

Diffusion is a process whereby dissolved mass is transported from higher chemical potential toward lower by random molecular motion (Robinson and Stokes 1959). The equation describing a one-dimensional diffusive flux in soil given by Porter et al. (1960) is based on Fick's first law and is written as follows:

$$J_d = -\theta_w D_i^* \frac{dC_i}{dz} \quad (1)$$

where

$$\begin{aligned} J_d &= \text{diffusive mass flux, } ML^{-2} T^{-1}, \\ \theta_w &= \text{volumetric water content, } L^3 L^{-3}, \\ D_i^* &= \text{effective diffusion coefficient of ion } i \text{ in soil, } \\ &L^2 T^{-1}, \text{ and} \\ \frac{dC_i}{dz} &= \text{concentration gradient, } ML^{-3} L^{-1}. \end{aligned}$$

The volumetric water content in Eq 1 represents the fraction of the total cross section of the soil that is occupied by water and through which diffusion takes place. The effective diffusion coefficient is a constant for a saturated soil. As the soil desaturates, numerous experimental data have shown that the effective diffusion coefficient decreases either linearly or non-linearly with a decrease in the water content (Klute and Letey 1958; Porter et al. 1960; Graham-Bryce 1963; Romkens and Bruce 1964; Rowell et al. 1967; Warncke and Barber 1972; Barraclough and Tinker 1981).

The two methods used most widely by the soil scientists in determining the effect of water content on the effective diffusion coefficient are the two half cell method (Klute and Letey 1958; Porter et al. 1960; Graham-Bryce 1963; Romkens and Bruce 1964; Rowell et al. 1967) and the one half cell method with ion-exchange resin paper (Warncke and Barber 1972) or ion-exchange membrane (Barraclough and Tinker 1981).

The two half cell method consists of two cells of soil. Soil specimens are either equilibrated with different salt solutions of the same molarity or the same salt solution, one of which is spiked with an isotope tracer. One face of each soil specimen is then exposed, and the two half cells are joined together to allow diffusion to proceed. At the end of the test, the water content and the quantity of the labeled ions in each half cell are measured. The effective diffusion coefficient is back-calculated based on the quantity of the labeled ions that had diffused into the other half cell (Barrer 1951; Carslaw and Jaeger 1959).

The one half cell method, which uses ion-exchange resin paper or membrane, is essentially the same as the two half cell method, the difference being that one of the cells is replaced by an ion-exchange membrane or resin paper that acts as an ion sink. At the end of the test, the quantity of the cations or anions that has diffused into the resin paper or membrane is measured. The method for calculating the effective diffusion coefficient is described by Vaidyanathan and Nye (1966).

Various methods of soil specimen preparation have been used. In most procedures, the soil is first wetted to a predetermined water content (Porter et al. 1960; Rowell et al. 1967; Warncke and Barber 1972; Barraclough and Tinker 1981). The soil is then packed into the half cell, and, if necessary, additional water is added to the soil specimen. Although the soil specimen is compacted to a consistent dry density, soils with differing water contents have different soil structures and are therefore "different" soils (Fredlund 1989; Lambe 1958). Another approach that provides better control of the stress state of the soil is to drain the soil-water to the desired water content using a pressure plate apparatus (Klute and Letey 1958; Romkens and Bruce 1964).

The coefficient of diffusion for unsaturated gravel has also been determined using electrical conductivity measurements (Conca and Wright 1990). The electrical conductance of the pore-water was measured under a steady-state flow condition using a two-electrode method. The water content in the gravel was brought to the required degree of saturation by varying the speed of the centrifuge and the flow rate of a pump that feeds a 0.01 M potassium chloride solution continuously into the soil specimen. The diffusion coefficient is calculated based on the assumption that the electrical conductance is analogous to the diffusion coefficient using the Nernst-Einstein equation.

### Adsorption

Adsorption is the phenomenon by which a portion of the mass of a dissolved substance (e.g., contaminant) is held to the solid at a liquid-solid interface (Bear and Verruijt 1987). The partitioning characteristics of an ion between the liquid and the solid phases at constant temperature and pressure is described quantitatively by an adsorption function. The form of the adsorption function could be linear or non-linear depending upon the affinity of the solids for the adsorbate. Among the numerous empirical models for describing the adsorption characteristics of soil (Helferich 1962), the Freundlich equation is quite widely used.

$$Q_i = K_f (C_{e_i})^m \quad (2)$$

where

$$\begin{aligned} Q_i &= \text{mass of ion } i \text{ adsorbed by the solids per unit mass of} \\ &\text{dry soil, } MM^{-1}, \\ C_{e_i} &= \text{concentration of ion } i \text{ at equilibrium, } ML^{-3}, \\ K_f &= \text{Freundlich adsorption coefficient } (L^3 M^{-1})^m, \text{ and} \\ m &= \text{Freundlich constant.} \end{aligned}$$

The coefficients  $K_f$  and  $m$  can be determined using a 24-h batch-type measurement or a short-term batch method in accordance with ASTM Test Method for 24-Hour Batch-Type Measurement of Contaminant Sorption by Soils and Sediments (D 4646-87) or ASTM Test Method for Distribution Ratios by the Short-Term Batch Method (D 4319-83), respectively. In both methods, a high solution to solid ratio was specified. The affinity of the soil for the ion defined on the basis of D 4646-87 or D 4319-83, therefore, corresponds to the adsorption characteristics for a saturated soil.

Rowe et al. (1988) have also demonstrated that it is possible to back-calculate both the coefficients of diffusion and adsorption for a saturated soil using a single reservoir method. The test setup consists of a soil column with a source reservoir at the top and a zero flux boundary at the base. The reservoir contains a mass source with some concentration,  $C_0$ , at time equal to zero, and the decrease in concentration with time is monitored. The coefficients

of diffusion and adsorption are determined by fitting a theoretical solution using "POLLUTE/3.0" (Rowe and Booker 1983) to both the concentration versus time profile and the concentration versus depth profile in the soil specimen measured at the end of the test.

The effect of water content on the adsorption coefficient is not well defined for unsaturated soils. Brown (1953) tested the influence of water content on the adsorption characteristics of various geologic materials using a test setup similar to the one half cell method with ion-exchange membrane. Synthetic Ca-exchange membranes are first washed with 4N hydrochloric acid to displace  $\text{Ca}^{2+}$  with  $\text{H}^+$ . Excess chlorides are removed by rinsing the membranes with distilled water. The membranes are then placed into the bottom of a container, followed by 100 g of the moistened soil. The soil samples are pre-wetted to various water contents extending from saturation to the wilting point. At the end of the test, the various major cations exchanged with  $\text{H}^+$  were extracted from the membranes. An exchange period of 96 h was established for each treatment. The results showed that the mass exchanged per unit mass of soil decreases with a decrease in the water content; however, the decrease in adsorption could also be related to a decrease in diffusive flux associated with a decrease in the effective diffusion coefficient.

#### Shortcomings of Existing Test Methods

One of the key shortcomings of the two half cell method or the one half cell method with ion-exchange membrane is the lack of control of the stress state within the soil specimen. Soils with differing water contents and densities should be considered as "different" soils (Fredlund 1989) because of differences in the soil structures (Lambe 1958). Therefore, any measured changes in the effective diffusion coefficient could encompass both the effects of changing water content and soil structure. In addition, the soil suction was either not controlled during the test or there was no proper control of the water content of the resin paper or membrane. Consequently, mass flow of the contaminants due to a suction gradient could occur (Shackelford 1991; Barraclough and Tinker 1981). Hence, the movement of the contaminants is no longer driven by diffusion alone but rather by both advection and diffusion. Another limitation is related to the interconnectivity of the liquid phase along the soil-soil interface or the soil-membrane interface, particularly at low water contents.

In the case of reactive ions, the coefficient of diffusion determined from the two half cell method or the one half cell method with the ion-exchange paper method is not a fundamental parameter but is comprised of the effective diffusion and distribution coefficients. The need for an independent determination of the transport parameters was illustrated by Rowe et al. (1985). However, independent determination of the coefficients of diffusion and adsorption from a single test is not feasible because the effects of water content on these coefficients are both unknown.

#### A New Method for Diffusion Testing of Unsaturated Soil

The design concept of the new test method evolves out of the need for a control of the stress state of the soil [i.e., net normal stress ( $\sigma - u_a$ ) and matric suction ( $u_a - u_w$ )] and an independent measurement of the coefficients of diffusion and adsorption. One other problem encountered in the diffusion testing of unsaturated soil is related to the difficulty in determining the pore-water concentrations. Disturbances to the soil specimen in the course of extracting the pore-water will expose additional potential adsorp-

tion sites (i.e., sites associated with the soil particles that are isolated from the liquid phase under unsaturated conditions). Consequently, the amount of adsorption would be overestimated.

Difficulties associated with the determination of the concentrations of the ions in the soil-water can be overcome by allowing the system to reach chemical equilibrium (i.e., when the rate of change in concentration,  $dC/dt$ , approached zero at large times). At equilibrium, the concentration of the ions would be uniform throughout the system. The amount of adsorption can then be computed using the principle of mass conservation if the equilibrium concentration is known. A procedure that allows the matric suction to be controlled throughout the test and the monitoring of the attainment of chemical equilibrium is therefore required for the diffusion testing of unsaturated soils. These requirements can be satisfied by integrating the principles of the single reservoir method with a flux-controlled boundary (Rowe et al. 1988) and the pressure plate apparatus [ASTM Test Method for Capillary-Moisture Relationships for Coarse- and Medium-Textured Soil by Porous Plate Apparatus (D 2325-68)].

#### The Apparatus for Diffusion Testing of Unsaturated Soil

The apparatus for diffusion testing of unsaturated soils is shown in Fig. 1 (Lim 1995). The advantages of the apparatus include: (1) independent control of the stress state of the soil throughout the test duration; (2) no advection; and (3) independent determination of the coefficients of diffusion and adsorption from a single test.

The various components that make up the diffusion cell are a base, a high air-entry disk, a soil specimen holder, a bronze porous stone, a loading cap, a spring, an external ring, and a top with a loading platen and a quick connection to an air supply. The base houses a source reservoir of known volume, a septum for sampling

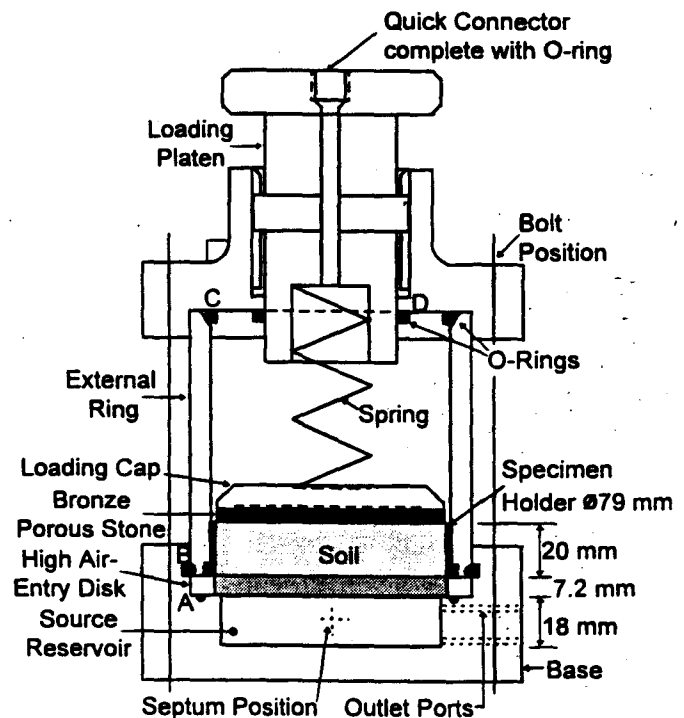


FIG. 1—A cross section of the apparatus for diffusion testing of unsaturated soil.

purposes, two tapered plastic outlets, and O-rings at locations "A" and "B". The ends of each of the outlets are connected to another short piece of plastic tubing that can be opened or closed via a clamp. The outlet located just beneath the high air-entry disk functions both as a drainage outlet and an inlet during sampling. The lower outlet near the base of the reservoir is used for draining the source reservoir at the end of the test.

The external ring with an outside diameter of 9.525 cm and a wall thickness of 0.635 cm was made of acrylic. The external ring is pressure-sealed against the base and the top via the O-rings at locations "B" and "C". The top cover and the loading platen were fabricated from acetyl plastic. Potential air and moisture leakage between the top cover and the loading platen and at the quick connection were sealed with O-rings. The loading accessories, which include a porous stone, a plastic cap, and a spring, are placed over the soil specimen in the order shown in Fig. 1. Application of the preload is achieved by lowering the loading platen through a screw mechanism.

The high air-entry disks manufactured by Soilmoisture Equipment Corporation, Santa Barbara, CA 93105 were made from ceramic, which is formed from sintered kaolin. The high air-entry disk is placed between the source reservoir and the soil specimen to facilitate the control of the matric suction through the use of the axis-translation technique. The high air-entry disk is encased in a stainless steel ring to provide a better sealing of the source reservoir. The soil specimen holder with an internal diameter of 7.9 cm and 2.0 cm high was made of stainless steel.

### Test Setup

A schematic diagram of a typical setup for diffusion testing of unsaturated soil is shown in Fig. 2. The incoming air was first regulated to a pressure of 80 kPa by Regulator  $R_1$ . The air was then passed through an air filter that removes condensed water and dirt in the air pressure line. The air pressure was further

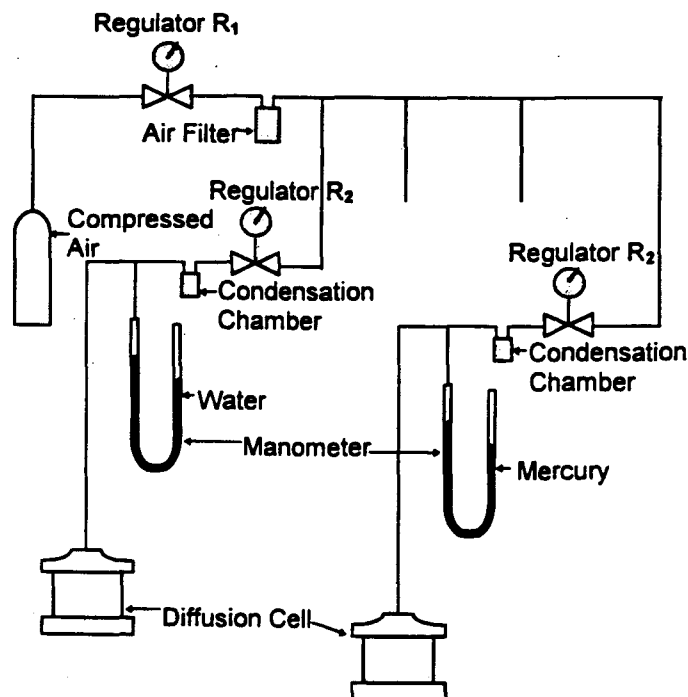


FIG. 2—A schematic diagram of a typical setup for diffusion testing of unsaturated soil.

regulated to the desired matric suction using Regulator  $R_2$ . A condensation chamber was placed after Regulator  $R_2$  for collecting the condensing water vapor. The magnitude of the air pressure was registered by either a water- or mercury-filled manometer for the low-pressure range or a pressure gage for the high-pressure range.

Prior to the commencement of the test program, checks were undertaken to eliminate any leakage along the air pressure line and to ensure that the regulators and the pressure gages were in good working condition. All the regulators and the gages were calibrated against a standardized gage and a manometer. The stability of the regulated air pressure was also checked prior to the diffusion tests by monitoring the fluctuation of the fluid levels in the manometer or the needle position in the case of the pressure gage. A small volume of distilled water was also placed in the condensation chamber to ensure that the air pressure line was saturated with water vapor.

### Soil

The selection of the soil type for this study was based on two considerations. The two considerations are: first, to evaluate the feasibility of the proposed apparatus in determining the coefficients of diffusion and adsorption; second, to provide an understanding of the fundamental role of the liquid phase on the coefficients of diffusion and adsorption. A sand with low silt and clay content and with low water retention characteristics was therefore selected. The soil, called Beaver Creek Sand, is an olive brown, oxidized, uniform, fine-to-medium aeolian sand. The physical index characteristics, mineralogical composition, cation exchange capacity, and chemistry of this soil are summarized in Table 1.

The grain-size distribution of the soil was measured by mechanical sieving in accordance with ASTM Test Method for Particle-Analysis of Soils (D 422-63). The fines content of the soil was determined by saturating the soil in a sodium hexametaphosphate solution in accordance to ASTM Test Method for Amount of Material in Soils Finer than the No. 200 (75- $\mu\text{m}$ ) Sieve (D 1140-92). The fines in the soil were dispersed by shaking the soil-solution mixture and then washing the mixture with distilled water through a U.S. No. 200 sieve. Tests for the mineralogy of the soil were performed by Saskatchewan Research Council, Saskatoon, Saskatchewan, Canada, using an X-ray diffraction method. The cation exchange capacity and the exchangeable cations provided by PLAINS—Innovative Laboratory Services, Saskatoon, Saskatchewan, Canada, were determined based on the methods described by Page et al. (1982).

### Chemical Tracers

In order to illustrate the application of the diffusion cell in determining the coefficients of diffusion and adsorption, potassium and chloride ions prepared from potassium chloride salt were selected as the reactive and non-reactive tracers, respectively. Potassium is considered to be a relatively stable ion in that it does not complex with anions such as sulphates or carbonates. The diffusion coefficient of potassium and chloride in free water are also similar (Cussler 1984).

### Test Program and Test Procedure

Diffusion tests were conducted on the sand at six different values of suction (0, 2.75, 3.1, 3.6, 3.9, and 6.0 kPa). The procedure for

TABLE 1—A summary of the physical index, mineralogical composition, cation exchange capacity, and chemistry of the soil.

| Grain-size distribution   |       |
|---|-------|
| Percentage of sand  | 98.9  |
| % retained on 0.417-mm sieve  | 3.5   |
| % retained on 0.297-mm sieve  | 30.0  |
| % retained on 0.246-mm sieve  | 26.8  |
| % retained on 0.149-mm sieve  | 37.3  |
| % retained on 0.075-mm sieve  | 1.3   |
| Percentage of silt and clay   | 1.1   |
| Coefficient of uniformity   | 1.8   |
| Specific gravity  | 2.67  |
| Mineralogy, %   |       |
| Quartz  | 89.6  |
| Plagioclase   | 8.71  |
| Illite  | 1.24  |
| Smectite  | 0.42  |
| Fe-Mg chlorite  | 0.03  |
| Cation exchange capacity, meq/100 g of dry soil                         | 1.30  |
| Exchangeable cations, meq/100 g of dry soil                             |       |
| Ca <sup>2+</sup>  | 0.86  |
| Mg <sup>2+</sup>  | 0.50  |
| K <sup>+</sup>  | 0.04  |
| Na <sup>+</sup>   | 0.06  |
| Dissolved ionic species in the 5:1 solution to solid extract, meq/100 g |       |
| Ca <sup>2+</sup>  | 0.45  |
| Mg <sup>2+</sup>  | 0.20  |
| K <sup>+</sup>  | 0.016 |
| Na <sup>+</sup>   | 0.014 |
| Cl <sup>-</sup>   | 0.003 |
| SO <sub>4</sub> <sup>2-</sup>   | 0.009 |
| HCO <sub>3</sub> <sup>-</sup>   | 0.19  |

soil specimen preparation, diffusion testing of the soil, and the high air-entry disk are described in the following sections. De-aired, distilled, and de-ionized water was used throughout the test from preparation to sampling.

#### Soil Specimen Preparation

The soil specimen for the diffusion test was prepared from a slurry. This method of specimen preparation was adopted because it minimizes entrapped air bubbles and therefore ensures complete saturation of the soil specimen. After placing the saturated high air-entry disk into the base, the specimen holder was centered over the disk. A known weight of air-dried soil was then placed into the specimen holder in small increments, and water was added as the specimen height increased. The slurry was stirred intermittently to remove any entrapped air bubbles. To ensure consistency in the porosity and dry density, the mass of air-dried soil and the applied preload were approximately the same for each soil specimen.

Once the soil was in place, the bronze porous stone, loading cap, and spring were placed over the soil and the cell was assembled. A small preload was applied onto the soil specimen by lowering the loading platen, which in turn compressed the spring to give a required pressure of 10 kPa. Application of the preload was to ensure continuity between the liquid phase of the soil and the high air-entry disk. The soil specimen was left to equilibrate in a controlled environmental chamber for at least 24 h. The relative humidity and temperature in the environmental chamber were

maintained constant at  $84 \pm 2\%$  and  $19.6 \pm 0.2^\circ\text{C}$ , respectively. Following the initial moisture equilibration, the upper outlet was opened to allow the soil to consolidate under the applied preload.

#### Procedure for the Diffusion Testing of Soil

The preliminary preparation work involved the cleaning of the base, external ring, high air-entry disk, bronze porous stone, and loading cap to ensure chemical cleanliness. The base and external ring were washed with running water and then rinsed thoroughly with distilled deionized water. The high air-entry disk and the bronze porous stone were soaked in numerous pore volumes of distilled and de-ionized water. Chemical cleanliness of the high air-entry disk and the bronze porous stone was monitored by measuring the electrical conductance of the supernatant. Additional pore volumes of water were flushed through the high air-entry disk to ensure complete saturation and chemical cleanliness of the disk. Flushing was discontinued when the electrical conductance of the flushed-out water was less than  $0.1 \mu\text{S}$ .

After cleaning, the weight of the various components of the cell was measured and the source reservoir was filled with water. Upon filling the reservoir, a magnetic stir bar was placed into the reservoir, followed by the high air-entry disk and placement of the soil specimen. The cell was assembled, and, after consolidation, the upper outlet was left open and the cell was connected to a regulated air-pressure line via the quick connection to drain the soil-water to the required matric suction. At the end of drainage, the hydraulic head is a constant (i.e., zero hydraulic gradient), and since the pore-water pressure,  $u_w$ , is zero (i.e., the upper outlet is opened to atmosphere during drainage), the matric suction of the soil is therefore equal to the applied air pressure.

Once drainage was complete, the diffusion test was initiated by spiking the source reservoir with a stock solution containing potassium and chloride. The water in the source reservoir was spiked by injecting a known volume of the stock solution through the septum using a syringe. To accommodate the stock solution and without causing backflow of water from the source reservoir into the high air-entry disk and the soil specimen, the upper outlet was opened to allow drainage of the displaced water. In this manner, the volume of water in the source reservoir remained constant. To further ensure a uniform concentration at the start of the test, the solution was stirred gently for approximately 2 min. A 1-mL sample was then taken from the source reservoir to establish the initial concentrations of the various ions.

Changes in the concentrations of the various ions in the source reservoir were monitored continuously by sampling at various time intervals. The sample size was generally less than 1 mL. Prior to any sampling, a glass tube filled with de-aired, distilled, and de-ionized water was first connected to the upper outlet port. Care was also taken to remove any air bubbles trapped between the outlet and the glass tube. During sampling, the upper outlet was opened and water in the source reservoir was withdrawn using a 1-mL gas-tight syringe. The sampled volume was replaced simultaneously with de-aired, distilled, and de-ionized water. After each sampling, the upper outlet was closed immediately.

Various precautionary measures were undertaken to minimize moisture loss from the diffusion cell during the test: first, stirring of the water in the source reservoir was carried out only during sampling; second, the diffusion cell was housed in an insulated box to protect the cell from draught; and third, the complete test setup was located in a controlled environmental chamber where

it was maintained at a constant relative humidity of  $84 \pm 2\%$  and room temperature of  $19.6 \pm 0.2^\circ\text{C}$ .

The test was terminated when the changes in the concentration of potassium in the source reservoir with time were insignificant. Upon completion of the test, the final weight of the diffusion cell was determined. To prevent possible flow of water from the source reservoir into the high air-entry disk and the soil specimen, the water in the source reservoir was first drained before dismantling the cell. After drainage, the cell was weighed again, and, as the cell was being dismantled, the weight of the various components was measured.

The soil specimen was extruded from the specimen holder with a specially designed extruder. The soil specimen was sectioned into three smaller slices approximately 4 to 5 mm thick for water content and chemical mass balance determinations. The rationale in sectioning the soil specimen was to check for possible variations of the water content and to verify the attainment of chemical equilibrium. For the case with a matric suction of 0 kPa, the soil specimen was left whole since it was saturated and not stable during slicing.

Water contents of the sliced specimens were measured by air-drying the soil at a room temperature of  $21 \pm 2^\circ\text{C}$ . After drying, the total mass of chloride and also potassium in each sliced specimen were determined by saturating the soil in distilled de-ionized water. The supernatant was decanted after 48 h. The remaining mass of potassium in each sliced specimen was extracted by saturating the soil in a barium chloride solution. The mixture was left to equilibrate for at least three days. At the end of each equilibration, the supernatant was decanted. The extraction process was repeated at least three times to ensure complete removal of the adsorbed potassium from the soil. During each saturation, the soil specimen was shaken periodically.

#### *Procedure for the Diffusion Testing of the High Air-Entry Disk*

The high air-entry disk that was used for controlling the matric suction of the soil formed an integral part of the setup for the diffusion testing of unsaturated soil. The effective diffusion and adsorption coefficients of the high air-entry disk are, therefore, pertinent to the determination of the coefficients of diffusion and adsorption for the soil. The general procedure for the diffusion testing of the high air-entry disk alone was done in a similar manner as the diffusion testing of the soil. In order to minimize the test duration, the water level over the high air-entry disk was kept to a minimum. The excess water above the high air-entry disk was flushed by applying a small air pressure to the cell. When the water level was drained to just above the high air-entry disk, the air-pressure line was disconnected, but the quick connector was left open to the atmosphere to allow continued drainage of the remaining water. Once drainage was complete, the quick connector was closed and the test was initiated by spiking the source reservoir.

#### *Analytical Methods*

The concentrations of the various tracers in the source reservoir were measured using various analytical methods. Concentrations of chloride and potassium in the samples and the distilled water extract were measured using ion chromatography and flame photometry, respectively. In the case of the barium chloride extract, the concentrations of potassium in the supernatant were measured using atomic adsorption spectrometry. Dilution of the samples was required to bring the concentration to within the measuring range

of the equipment, and all samples were filtered through a 0.45- $\mu\text{m}$  filter paper.

#### **Test Results**

The test results for the high air-entry disk and the sand at different matric suctions, defined on the basis of a single reservoir diffusion test (Lim 1995), are presented in the following sections.

#### *High Air-Entry Disk*

Diffusion tests were conducted on two 0.5-bar high air-entry disks designated as D1.05 and D2.05. The porosity and dry density of the high air-entry disks are 51.0% and  $1550 \text{ kg/m}^3$ , respectively. The concentration versus time profiles for potassium and chloride in the source reservoir for D1.05 and D2.05 are given in Fig. 3. The concentrations were normalized with respect to the initial concentration at time equal to zero. The results showed that the variations in the concentrations of potassium and chloride in the source reservoir with time were characterized by a smooth decreasing trend, and the concentration profiles for potassium and chloride were almost identical.

A simple mass balance calculation at the end of the test showed that the final mass in the system was generally smaller than the initial mass after discounting the mass removed during sampling. The difference in mass, which ranged from 3.4 to 5.0% of the total mass, was relatively small and could be related to adsorption or small analytical errors. Regardless of the various possible causes, the difference in mass was represented mathematically as an adsorption reaction. The adsorption coefficient was calculated assuming a linear adsorption function, and chemical equilibrium was attained at the end of the test. The back-calculated distribution coefficients of potassium and chloride for the 0.5-bar high air-entry disk were 0.1 and 0.07 mL/g, respectively.

The effective diffusion coefficients of potassium and chloride for the 0.5-bar high air-entry disk were determined by fitting a theoretical solution to the measured concentration versus time profile in the source reservoir. The diffusion coefficient corresponding to a profile that matched the measured concentration versus time profile would be the effective diffusion coefficient. The theoretical solution was obtained using "CTRAN/W": a numerical solution based on a finite element formulation (CTRAN/W 1991). "CTRAN/W" is a proprietary computer software developed and distributed by Geo-Slope International Ltd., Calgary, Alberta, Canada. The simulated concentration versus time profiles for potassium and chloride corresponding to an effective diffusion coefficient of  $0.75 \times 10^{-5} \text{ cm}^2/\text{s}$ , for both D1.05 and D2.05, are plotted on Fig. 3. The results showed that the match between the measured and the simulated profiles for the two disks were satisfactory.

#### *Beaver Creek Sand at Various Matric Suctions*

The soil-water retention characteristics and the variations of the degree of saturation across the soil specimen for cases at different matric suctions are shown in Figs. 4 and 5, respectively. The results showed that the variations in the degree of saturation, in general, were uniform except for the case with a matric suction of 3.9 kPa. The variations of the porosity and dry density among the various soil specimens and across the soil profile were also small. The average porosity and dry density of the soil specimen were 38.2% and  $1650 \text{ kg/m}^3$ , respectively. The differences between the initial and final mass of water in the cell in general were less than 0.4

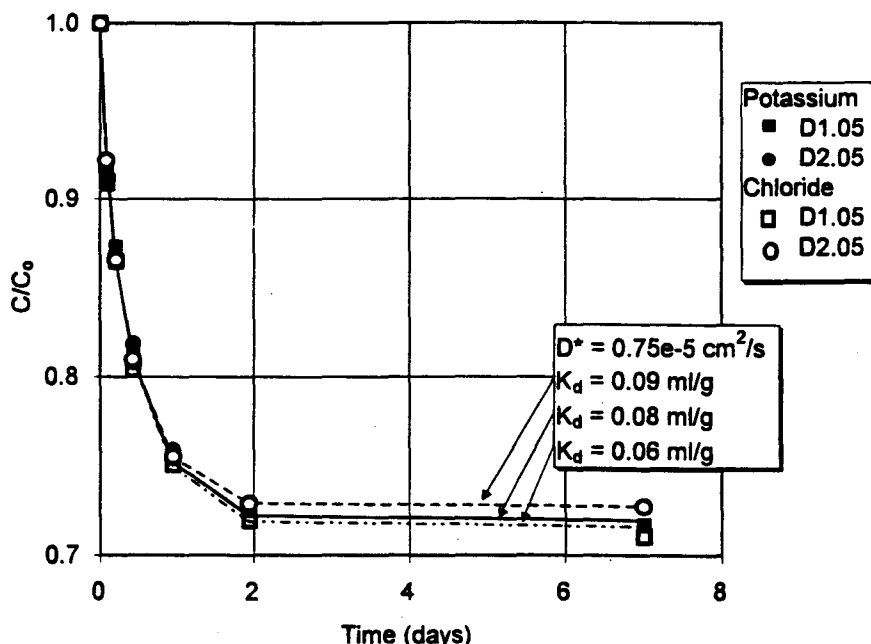


FIG. 3—Variations of the concentrations of potassium and chloride in the source reservoir normalized with respect to the initial concentration at time zero versus time for 0.5-bar high air-entry disks.

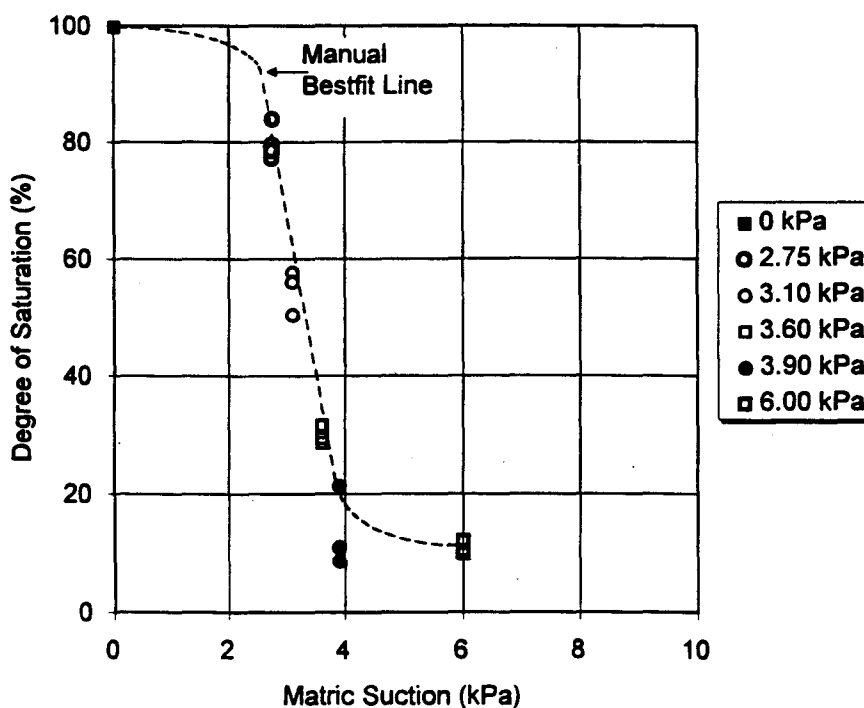


FIG. 4—The soil-water retention characteristics of the soil specimen at different matric suctions.

g (i.e., the moisture loss over the test duration was less than 0.4% of the total volume of water).

Plots of the concentration versus time profile for potassium and chloride in the source reservoir for the different cases are given in Figs. 6 and 7, respectively. The results showed that the concentration versus time profiles for potassium were characterized by a smooth decreasing trend. For chloride, the results also showed a smooth decreasing trend, but the concentration continued to

decrease at a constant rate at larger times. In general, the results showed that the rate of change of the concentration in the source reservoir decreased with an increase in matric suction. For a non-reactive ion, the decreasing rate of change in concentration with increases in matric suction could be associated with a decrease in the effective diffusion coefficient. In the case of a reactive ion, the decreasing rate of change in concentration could also be related to a decrease in the adsorption coefficient.

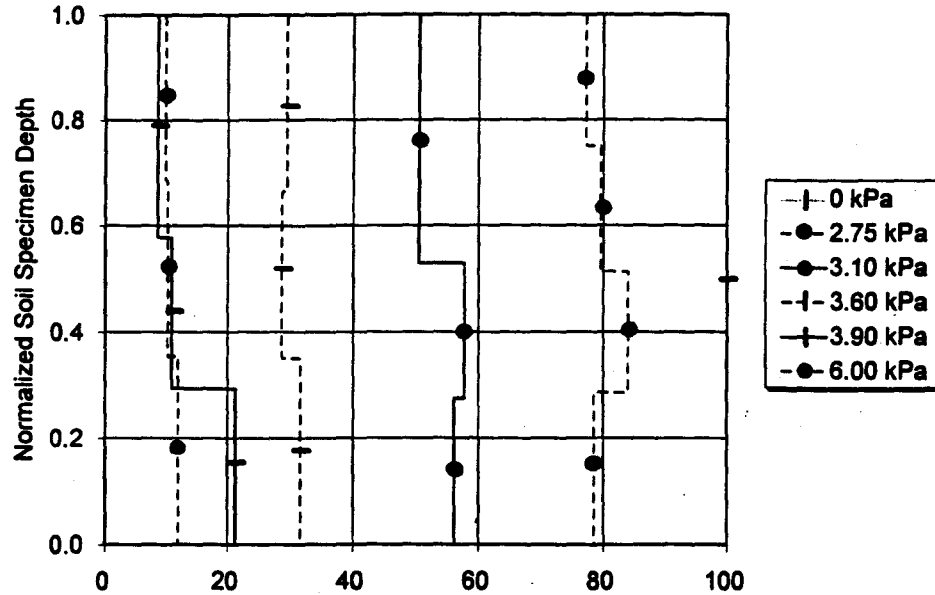


FIG. 5—Variations of the degree of saturation across the soil profile for cases at different matric suctions.

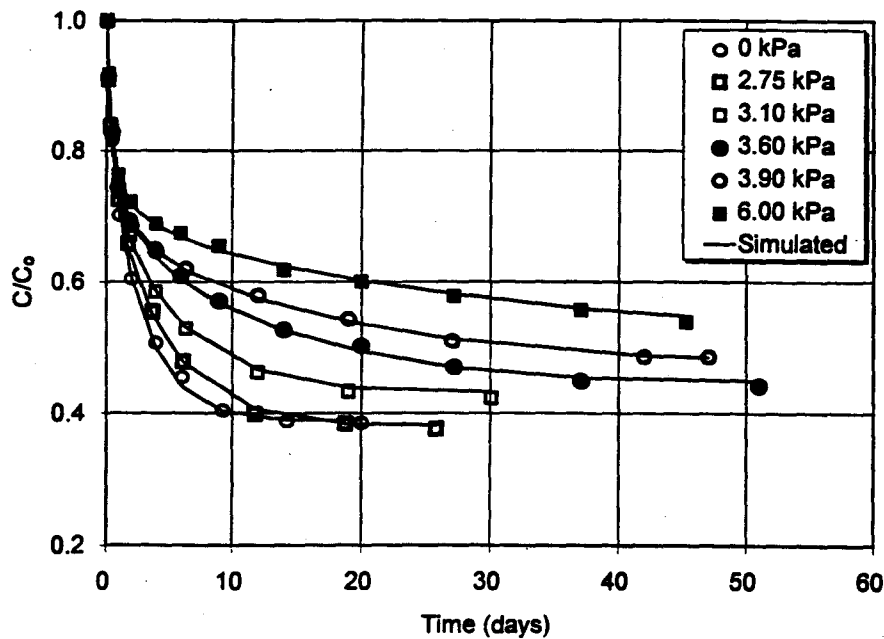


FIG. 6—Variations of the concentration of potassium in the source reservoir normalized with respect to the initial concentration at time zero versus time for cases at different matric suctions.

Results of the total mass of potassium extracted from the soil specimen at the end of the test and the theoretical mass obtained from a simple mass calculation are provided in Table 2. The theoretical total mass of potassium in the soil specimen was calculated based on the principle of mass conservation, assuming that chemical equilibrium was attained at the end of the test and assuming zero adsorption in the bronze porous stone. The mass removed during sampling was accounted for in the mass balance calculations. The results showed that except for the case with a matric suction of 0 kPa, the difference between the theoretical and the measured total mass ranged from 1 to 5%. The difference could be related to possible errors in the analytical method or the possible

fixation of potassium by the smectite minerals. For the case with a matric suction of 0 kPa, the significant difference could be due to possible retention of a fraction of the soluble potassium on the tare during drying.

In the case of chloride, the final concentration in the source reservoir was also verified against a theoretical concentration calculated on the basis of mass balance at the end of the test. The results of the final and the theoretical concentrations for the different cases are given in Table 2. The results showed that the final concentrations were generally smaller than the theoretical concentrations except for cases with matric suctions of 0 and 6 kPa. The smaller measured concentrations would represent a loss of chloride.



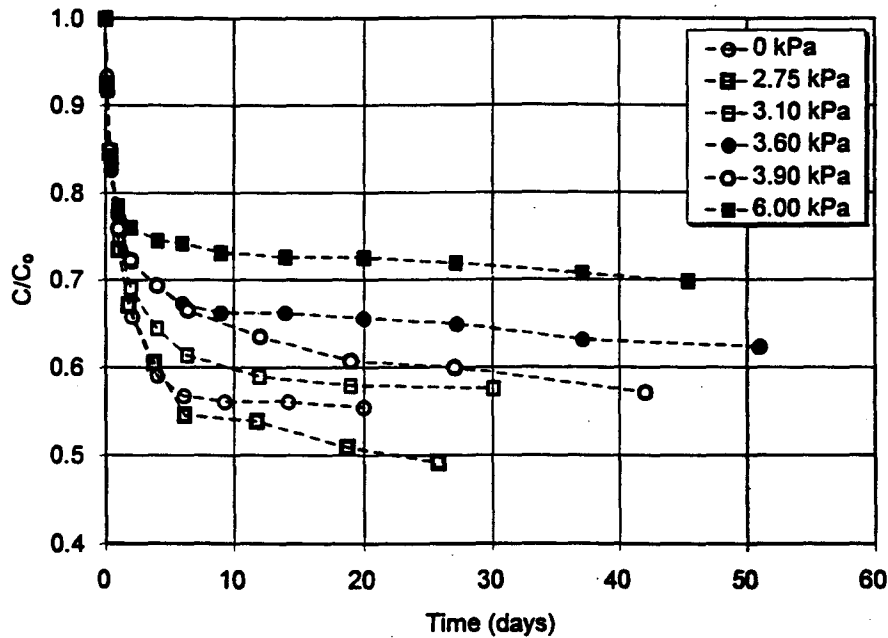


FIG. 7—Variations of the concentration of chloride in the source reservoir normalized with respect to the initial concentration at time zero versus time for cases at different matric suctions.

TABLE 2—A comparison of the measured and theoretical mass for potassium and the final and theoretical concentration for chloride for cases at different matric suctions.

| Case, kPa | Total Mass of K <sup>+</sup> in Soil |                 | Percent Difference | Chloride Concentration |                   | Differences in Mass, mg |
|-----------|--------------------------------------|-----------------|--------------------|------------------------|-------------------|-------------------------|
|           | Extracted, mg                        | Theoretical, mg |                    | Final, mg/L            | Theoretical, mg/L |                         |
| 0.00      | 29.3 ± 0.3                           | 33.1            | 12 ± 1.0           | 426                    | 448               | -3 (-5%)                |
| 2.75      | 28.6 ± 0.1                           | 29.8            | 4 ± 0.4            | 401                    | 491               | -11 (-18%)              |
| 3.10      | 25.0 ± 0.2                           | 26.3            | 5 ± 0.7            | 476                    | 533               | -7 (-11%)               |
| 3.60      | 22.7 ± 0.1                           | 24.0            | 5 ± 0.5            | 525                    | 570               | -5 (-8%)                |
| 3.90      | 19.1 ± 0.2                           | 19.7            | 3 ± 0.8            | 480                    | 584               | -11 (19%)               |
| 6.00      | 14.9 ± 0.1                           | 15.1            | 1 ± 0.7            | 573                    | 585               | -1 (-2%)                |

The losses were quite significant and may be related to possible complexation-precipitation reactions between chloride and the upper bronze porous stone or the tin foils. For cases with matric suctions of 2.75, 3.1, and 3.9 kPa, additional tin foils were placed over the bronze porous stone to minimize the moisture loss from the soil specimen.

The effective diffusion coefficient was evaluated only for potassium. The method of the back-analysis for the coefficients of diffusion and adsorption differed somewhat depending on whether chemical equilibrium was reached at the end of the test. For cases in which chemical equilibrium was attained, the adsorption coefficient was calculated based on the principle of mass conservation. Once the adsorption coefficient was defined, the effective diffusion coefficient was obtained by fitting a theoretical solution to the measured concentration versus time profile using "CTRAN/W". For cases in which chemical equilibrium was not attained, both the coefficients of diffusion and adsorption were unknown. The unknown coefficients were determined by fitting a theoretical solution to both the concentration versus time profile in the source reservoir and the concentration versus depth profile in the soil specimen simultaneously.

Plots of the simulated concentration versus time profiles for potassium for the various cases are given in Fig. 6. Plots of the

simulated concentration versus depth profile and the average theoretical concentrations of potassium in the soil-water for the different cases are also shown in Fig. 8. The average theoretical concentration of potassium in the soil-water was calculated based on the total mass of potassium in each sliced specimen and the adsorption coefficient assumed in the numerical simulation. The results showed that the match between the measured and the simulated profiles for the various cases was satisfactory.

The effects of matric suction on the coefficients of diffusion and adsorption plotted against the degree of saturation are given in Figs. 9 and 10, respectively. The effective diffusion coefficients were normalized with respect to the effective diffusion coefficient at saturation. The results in Fig. 9 showed that the normalized effective diffusion coefficient decreased with decreases in the degree of saturation. The decrease was quite rapid initially; however, beyond a degree of saturation of 60%, the normalized effective diffusion coefficient decreased almost linearly with a decrease in the degree of saturation. The extent of the decrease from saturation to near the residual degree of saturation was approximately 80%, less than one order of magnitude. The results showed an apparent anomaly in which the normalized effective diffusion coefficient increased as the water content approached the residual degree of saturation. A similar anomaly at low water contents was also

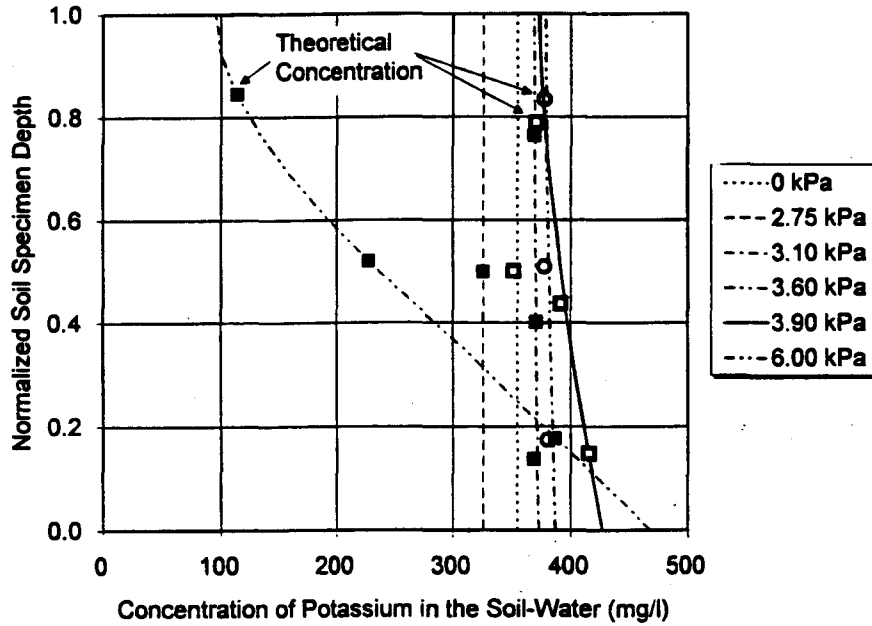


FIG. 8—Results of the simulated concentration versus depth profile and the theoretical concentration of potassium in the soil-water for cases at different matric suctions.

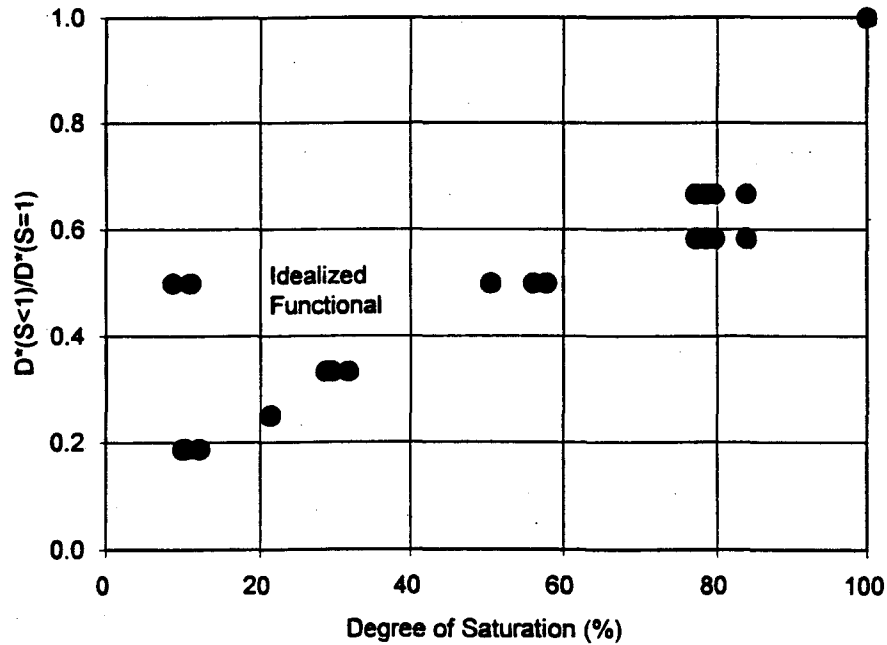


FIG. 9—Relationship between the effective diffusion coefficient normalized with respect to the effective diffusion coefficient at saturation and the degree of saturation.

reported by Graham-Bryce (1963) and Gillham et al. (1984). In general, the form of the functional relationship between the normalized effective diffusion coefficient and the degree of saturation was slightly non-linear.

The relationship between the adsorption coefficient and the degree of saturation given in Fig. 10 showed that the initial decrease was small as the soil desaturated from a degree of saturation of 100 to 60%. The adsorption coefficients, however, remained relatively constant from a degree of saturation of 60 to 20%. As the water content approached the residual degree of saturation, the adsorption coefficient decreased quite abruptly from  $8 \times 10^{-7}$  to

$5.6 \times 10^{-7}$  (L/mg)<sup>m</sup> (i.e., a decrease of approximately 44%). In general, the form of the functional relationship between the adsorption coefficient and the degree of saturation was bi-linear.

**Conclusions**

A new technique for diffusion testing of unsaturated soil in which the stress state of the soil (i.e., the net total stress and the matric suction) can be controlled throughout the test duration is illustrated. The test results showed that a direct determination of

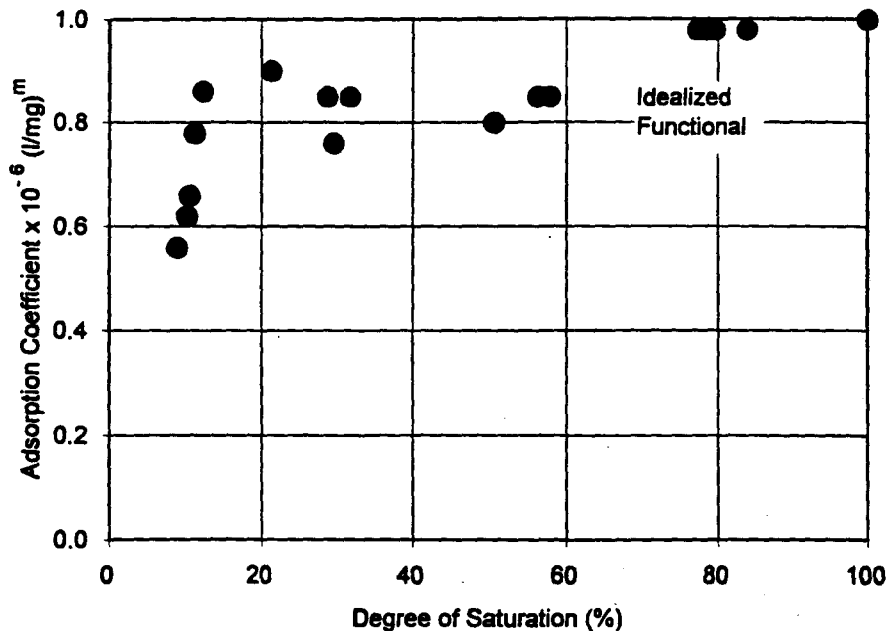


FIG. 10—Relationship between the adsorption coefficient and the degree of saturation.

the coefficients of diffusion and adsorption from a single test is feasible with the new technique.

The results determined from the single reservoir diffusion test for the sand showed that the concentration versus time profiles for potassium in the source reservoir were characterized by a well-defined decreasing trend. At large times, the concentration versus time profiles began to level off, providing a clear indication of the attainment of chemical equilibrium. However, for cases with high matric suctions, a long test duration would be required for complete attainment of chemical equilibrium.

In the case of chloride, the variations of the concentration in the source reservoir with time also showed a well-defined decreasing trend. However, for most cases, the attainment of chemical equilibrium could not be established.

For cases with chemical equilibrium, the required adsorption coefficient could be calculated on the basis of mass balance at the end of the test, and the effective diffusion coefficient could be obtained by fitting a theoretical solution to the measured concentration versus time profile. For cases with incomplete chemical equilibrium, both the concentration versus time profile and the concentration versus depth profile in the soil specimen would be required to determine the unknown coefficients.

The results of this study showed that both the coefficients of diffusion and adsorption for potassium decreased with a decrease in the degree of saturation. For diffusion, the functional relationship between the normalized effective diffusion coefficient and the degree of saturation was slightly non-linear. In the case of adsorption, the effect of the degree of saturation on the adsorption coefficient was quite insignificant from saturation to a degree of saturation of 10%. A significant decrease in the adsorption coefficient was evident only near the residual degree of saturation. The functional relationship between the adsorption coefficient and the degree of saturation was bi-linear.

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