

**LABORATORY DETERMINATION OF DIFFUSION AND DISTRIBUTION  
COEFFICIENTS OF INORGANIC CHEMICALS FOR UNSATURATED SOIL.**

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**Abstract** A technique is proposed in this paper for determining the diffusion and distribution coefficients for inorganic chemicals in unsaturated soils. The technique integrates the concept of single reservoir diffusion testing with the axis-translation principle for the control of soil suction. The approach adopted provides a fundamental basis for understanding how decreasing water content alters the pathway, and the open area available for the diffusion of solutes under unsaturated conditions. The main objectives are to demonstrate the feasibility of using this technique to determine both the diffusion and distribution coefficients from a single test, and to establish the functional relationships for the diffusion and distribution coefficients for an unsaturated soil. The test results showed that the diffusion coefficient decreases non-linearly with decreasing water content. Results from mass balance calculations indicate that the mass adsorbed per mass of dry soil drops below the equilibrium isotherm as the water content decreases. This seems to suggest that either the distribution coefficient varies with water content or that a fraction of the soil solids may be inactive as the water content decreases.

**Introduction**

The processes that govern the transport of inorganic chemicals through saturated soils are equally valid for unsaturated soils; however, the key difference hinges on the nature of the transport parameters. Transport parameters such as hydraulic conductivity for advection, diffusion coefficient for molecular diffusion and distribution coefficient for adsorption-exchange phenomenon are constants for saturated soil. However, in unsaturated soils, there may need to be functional relationships between these parameters and the water content of the soil. Characterization of these parameters for unsaturated soil is of fundamental importance to the prediction of contaminant migration.

In this paper, a technique for determining the diffusion coefficient and the distribution coefficient for inorganic chemicals in an unsaturated soil is described. This approach allows the stress state of the soil and pore water to be controlled throughout the test. The main objectives

of this paper are to demonstrate the feasibility of using this new technique to determine both the diffusion and distribution coefficients of an unsaturated soil in a single test, and to establish the functional relationships for the diffusion coefficient and the distribution coefficient as the soil desaturates.

Functional relationships for the diffusion coefficient of an unsaturated soil have emerged primarily through the soil science literature. It is known that the diffusion coefficient varies with the water content, but the form of the functionals as reported by different researchers seems to differ. Results showing the relationship between the diffusion coefficient, normalised with respect to the diffusion coefficient in a free solution, and the volumetric water content of various geologic materials are as shown in Fig. 1.

Data on the distribution coefficient for unsaturated soils are scarce, and a fundamental understanding of whether the adsorption characteristics change with water content is lacking. The paper by Brown (1953) is the only reference in the literature known

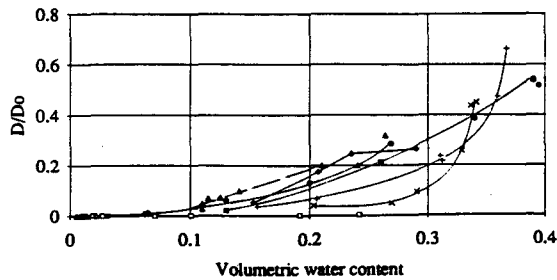
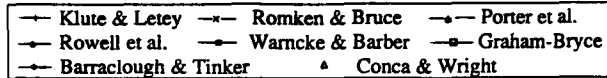


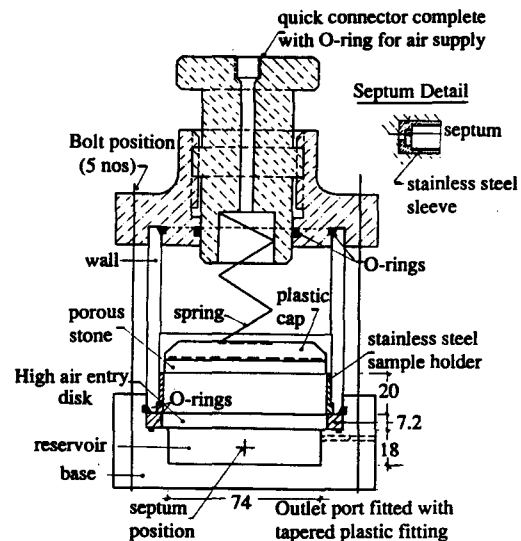
Fig. 1 Functional Relationship between  $D/D_0$  and volumetric water content where  $D$  is the diffusion coefficient of the soil and  $D_0$  is the diffusion coefficient in a free solution.

to the authors. His results showed that the amount of cation exchange in soil decreases with decreasing water content. The test durations however, were only 4 days and it may be questionable as to whether chemical equilibrium had been attained. The computation of the distribution coefficient from the apparent diffusion coefficient deduced from transient diffusion tests is also complicated by its dependency on the solution concentration. The effect of desaturation on the adsorption phenomenon is still unknown at present although, it appears that most researchers have been using the distribution coefficient obtained by batch-type test, regardless of the degree of saturation of the soil.

Many researchers attribute the decrease in the rate of diffusion as the water content decreases, to the increased tortuosity of the pathway for diffusion. Mobility of ions through water absorbed on soil surfaces has been reported to be very small (Kemper, 1960 and Porter et al., 1960). The presence of discontinuous water filled pores or water films, and the small mobility of ionic species in the thin water films could have serious implications on the adsorption characteristics of an unsaturated soil. The role of water content on the pathway for diffusion and on the adsorption characteristics are essential information that needs to be verified.

## TEST EQUIPMENT

A new diffusion testing technique for unsaturated soil has been developed at the University of Saskatchewan. A cross-section of the apparatus is shown in Fig. 2. This equipment integrates the concept of single reservoir diffusion testing with the axis-translation principle for the control of soil suction. The single reservoir method is similar to the modified column test with a decreasing source concentration as used by Rowe et al. (1988). The diffusion cell was made of plastic. The main features of this equipment are (i) zero advection, (ii) diffusion and distribution coefficients can be determined independently and, (iii) control of the stress states of the soil and pore water throughout the test.



All dimensions are in millimeters.

Fig. 2 A Cross-Section of the Diffusion Cell for Unsaturated Soil Testing.

## Material

A natural aeolian sand, called Beaver Creek sand was used for this study. It is an olive brown, oxidized, calcareous, fine to medium sand which is poorly sorted. Sand was selected for this study because of the low silt and clay content, and the low water retention characteristics would provide some insights as to the role of thin water films and discontinuous water-filled pores. The fines content

(i.e., % passing No. 200 U.S. standard sieve) of this clean sand was only 1%. The dominant mineralogy of this sand was quartz mineral and 38% of the fines were of smectite mineral. The cation exchange capacity of the sand was relatively small at 1.45 meq/100g of soil. The major exchangeable cations were calcium and magnesium at 0.86 meq/100g and 0.5 meq/100g, respectively.

## Procedure

Laboratory tests simulating one-dimensional diffusion were conducted on the sand at various suctions. The suctions corresponded to a range of water contents where the degree of saturation varied from 100% to residual saturation. Deaired, deionised, distilled water was used throughout the test from preparation stages to sampling.

Prior to specimen preparation, the high-flow air entry disk was first saturated, soaked and flushed at least 3 times with water until the level of electrical conductivity was undetectable. The soil was then placed in a slurry form and preloaded under a constant spring load to ensure relatively consistent void ratios for all specimens. The soil was allowed to consolidate under the preload for at least 24 hours before application of a matric suction. At the end of consolidation under the total stress, the air pressure was applied in order to drain the pore water to the desired matric suction. The specimen was left to equilibrate for at least 48 hours under the applied suction.

After moisture equilibrium was attained, the reservoir was spiked with a potassium chloride solution by injecting a stock solution into the reservoir below the specimen. The reservoir was stirred continuously during the injection with a magnetic stir bar at slow motion for 2 minutes. A sample was taken immediately to measure the initial reservoir concentration. Decreases in the reservoir concentration with time were monitored by sampling a volume of 0.6 to 0.7 ml of the reservoir solution at various time intervals. The tests were curtailed when chemical equilibrium was attained as indicated by zero or very small

changes in the reservoir concentration. Stirring of the solution in the reservoir was only carried out for about 2 minutes before and during sampling. A slow motion was used to ensure uniform concentration. Sampling was made with a 1 ml gas-tight syringe and at each sampling, the sampled volume was replaced with deaired, deionised and distilled water.

Upon completion of the test, the final weight of the cell was determined. The solution was then drained from the reservoir before dismantling the diffusion cell to prevent rewetting of the soil specimen. The soil specimens were extruded and sectioned into slices for moisture content and mass balance determination. Barium chloride at 0.1N was used for extracting potassium ions by soaking the air-dried soil in solution for at least 24 hours. This procedure was repeated three times. An Atomic Adsorption Spectrometer in the emission mode was used for the analysis of  $K^+$  extracted by the barium chloride solution. Flame photometry was used for the analysis of the change in  $K^+$  in the reservoir.

Three series of diffusion tests were performed with the sand subjected to different levels of suction in order to determine the effect of water content on the diffusion and distribution coefficients. The suction values were 2.7 kPa, 3.1 kPa and 3.8 kPa.

## Presentation of Test Results

The physical properties of the soil specimens tested were obtained at the end of the diffusion test. The volumetric water content profile was fairly uniform across the soil specimen for cases at 2.7 kPa and 3.1 kPa. The volumetric water content and the degree of saturation at 2.7 kPa and 3.1 kPa were 0.308 and 0.205, and 81% and 52%, respectively. For the case at 3.8 kPa, the volumetric water content was found to vary with depth. The values of the volumetric water content and the degree of saturation ranged from 0.081 to 0.034 and 21% to 9%, respectively. The void ratio and the dry density of the soil are fairly uniform across the soil profile with an average value of 0.63 and 1650 kg/m<sup>3</sup>, respectively. The amount of

moisture loss over the test duration varied from 0.2g to 0.36g of water. The initial concentration of  $K^+$  and  $Cl^-$  in the pore water at the start of the test was only 1.5 mg/l. This amount was assumed to be negligible.

The adsorption equilibrium isotherm for  $K^+$  is presented in Fig. 3. The adsorption isotherm is nonlinear. There are two aspects of the batch test that are different from a conventional batch test. First, these data were obtained using a diffusion-type batch test where the soil was first saturated in a reservoir of deionised distilled water which was then spiked with  $K^+$  at various concentrations. The soil sample was left to equilibrate by diffusion over a 5 day period. Second, the presentation of the partitioning relationship differs from conventional form. The mass adsorbed by the soil solids is being normalised with respect to the surface area of the soil solids rather than with the dry mass of the soil.

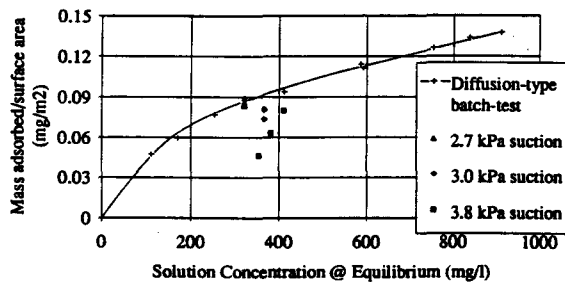


Fig. 3 Partitioning Relationship of  $K^+$  between the solids and the solution phases.

Computation of the surface area for the coarse fraction and the quartz fraction of the fines was based on distribution of particle sizes as described by Bear (1960). For the smectite and illite minerals, the surface area was obtained by assuming a specific surface of 500 m<sup>2</sup>/g and 2.8 m<sup>2</sup>/g, respectively. This approach gives a better representation of the interfacial phenomenon and in normalising the distribution coefficient with respect to the surface area, the isotherm is made independent of the soil type.

Results of the mass of  $K^+$  that was adsorbed by the soil at various suctions are also plotted on the

same figure. The mass adsorbed was deduced from the total mass released by Barium Chloride after deducting the mass of  $K^+$  in solution and the background  $K^+$  present in the soil. This mass of  $K^+$  was checked against that obtained by simple mass accounting of the initial mass, the mass removed during sampling, and the mass in solution assuming chemical equilibrium at end of test. The difference in computed mass was between 1 to 2%.

Variations in the concentration of  $K^+$  in the reservoir versus time for the soil samples at three different suctions are plotted in Figure 4. In addition, to the experimental data points, a theoretical curve determined using the analytical solution "POLLUTE" (Rowe et al. 1983) was also shown in the same figure. The distribution coefficient was based on Freundlich equation for saturated soil. The constant terms  $K_f$  and  $N$  in the Freundlich equation adopted in the simulation were 1.95 and 0.76, respectively. For cases which fall below the equilibrium isotherm, the dry density,  $\rho_d$ , associated with the mass adsorption term,  $\rho_d K_d$ , in the continuity equation was modified to account for the reduction in the mass adsorbed by the soil. It was assumed that the reduction in the adsorption characteristics is due to physical inaccessibility to the adsorption sites. Modification was made by reducing the actual dry density by the ratio of  $S_e$  to  $S_s$ , where  $S_e$  is the actual mass absorbed by the soil per unit surface area, and  $S_s$  is the potential mass absorbed by the soil per unit surface area under fully saturated conditions, at the same equilibrium solution concentration. The diffusion coefficient was backcalculated by fitting various values to match the experimental data. The goodness of the fit was measured by the residual sum of squares.

All simulations were based on a diffusion and distribution coefficient for the high air entry disk of  $0.75 \times 10^{-5}$  cm<sup>2</sup>/s and 0.08 ml/g, respectively, for the high air entry disk. These coefficients were determined from a separate diffusion test on the high air entry disk. The tests on the high air entry disk were carried out in duplicates. No diffusion tests were performed on the porous stone over the specimen but simulations showed that the concentration versus time profile were not sensitive to the parameters of the stone.

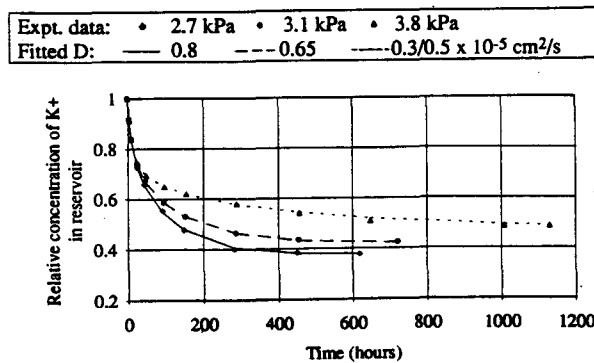


Fig. 4 Concentration-time profile of  $K^+$  in the reservoir for various stages of suctions ( $D_0 = 1.8 \times 10^{-5} \text{ cm}^2/\text{s}$  at  $19.6^\circ\text{C}$ ).

The concentration versus depth profile of  $K^+$  in the soil as obtained from the simulation was found to be uniform at the end of the test except for the case at 3.8 kPa. Numerical simulation results showed that the solution concentration at the top of the specimen for this case was only 80% of that in the reservoir at the end of test. Back-analysis of the  $Cl^-$  ions in the soil at the end of test showed that the  $Cl^-$  profile was uniform across the soil profile for all cases except for the case at 3.8 kPa. This further validates the attainment of chemical equilibrium in the soil. Results of  $Cl^-$  was however, not presented because of additional mass loss caused by the reactions between  $Cl^-$  and aluminium foil.

### Interpretation of Test Results

The results of the concentration versus time profiles for all the three series were reasonably good and consistent. The data showed that the reservoir concentration tends toward equilibrium at large times. The maximum moisture loss encountered throughout the test duration was only 0.36g. Steps have been taken to eliminate moisture losses by minimizing fluctuations in temperature and relative humidity as the plastic diffusion cell responds quite significantly to changes of these factors.

The results on the mass absorbed by the soil were normalised with respect to the total surface area of all the soil solids. For the case at a matric suction of 2.7 kPa as shown in Fig. 3, the test data fall along the equilibrium isotherm line. This shows that all the soil solids are actively participating in the adsorption phenomenon even at a degree of saturation of 80%. As matric suction increases, or as the degree of saturation decreases, the amount of mass adsorbed by the soil drops below the equilibrium isotherm. This seems to suggest either that the distribution coefficient is dependent on water content or that a fraction of the soil solids is inactive.

The fraction of the active mass of soil solids participating in the adsorption phenomenon is estimated by expressing the actual mass absorbed per total surface area as a ratio to that given by the equilibrium isotherm at the same concentration. The functional relationship for the adsorption phenomenon given by the ratio of active mass of soil participating in the adsorption phenomenon to the total mass of soil is plotted in Fig. 5, as a function of the degree of saturation. The results indicate that there is a gradual but small decrease in the mass of soil participating in adsorption as the degree of saturation decreases from 80% to 20%. At near residual saturation ( $S < 20\%$ ), it decrease rapidly.

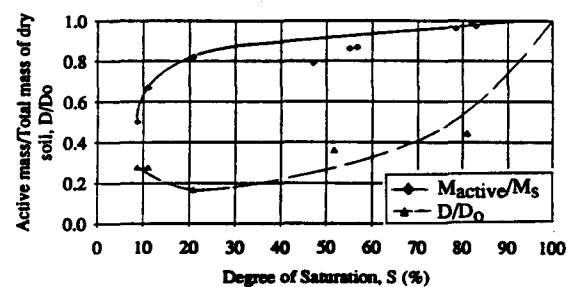


Fig. 5 Effect of water content on the magnitude of active mass of soil solids participating in the adsorption phenomenon, and the normalised diffusion coefficient.

Results of the normalised diffusion coefficient,  $D/D_0$ , are plotted as functions of the degree of saturation in Fig. 5. The functional relationship for the diffusion coefficient is slightly nonlinear. The form of the functional relationship is quite

similar to that given by Rowell et al. (1967), and Warncke and Barber (1972). One anomaly in the data is the increase in the diffusion coefficient at low water contents. The explanation for this may be attributed to the fact that at higher matric suctions the water is confined to small pores congregated at isolated spots where the pathways are less tortuous.

## CONCLUDING REMARKS

The results obtained using this new technique for diffusion testing of unsaturated soil provide a reasonable basis for the interpretation of the adsorption phenomenon and the diffusion mechanism. The functional relationships for adsorption as reflected by the ratio of active mass to the total dry mass of soil is relatively linear between 80% saturation to near residual saturation. The functional relationships for the normalized diffusion coefficient on the other hand is slightly nonlinear. Beyond a 20% degree of saturation, the fraction of soil mass participating in adsorption decreases rapidly but the normalized diffusion coefficient increases. Further studies will have to be carried to verify these results and the anomaly in the diffusion coefficient at low water content.

The key factor affecting adsorption and diffusion phenomena in unsaturated soil is the distribution of water in the soil at various suctions. The importance of the presence of water is seen in its role in providing physical access to ionic species along continuous water filled pores or water films to the vicinity of the solid surfaces where adsorption occurs.

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