START

0008125

DIFFUSION COEFFICIENTS AND HYDRAULIC CONDUCTIVITY IN UNSATURATED HANFORD SOILS AND SEDIMENTS

J. V. Wright

January 1990

MAR 1990
RECEIVED
EDMC

Presented at the
First Annual International
High-Level Radioactive Waste
Management Conference
April 8-12, 1990
Las Vegas, Nevada

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

92124951878

DIFFUSION COEFFICIENTS AND HYDRAULIC CONDUCTIVITY IN UNSATURATED HANFORD SOILS AND SEDIMENTS

JUDITH WRIGHT
Pacific Northwest Laboratory
Box 999, Mail Stop K6-84
Richland, Washington 99352
(509) 376-7915

ABSTRACT

Two groundwater transport parameters of some Hanford formation materials, the hydraulic conductivity and the diffusion coefficient, were measured to aid in predicting contaminant migration. The hydraulic conductivities and diffusion coefficients for five soil types were determined as functions of the water content for the aqueous phase. The degree of saturation (or the volumetric water content) in the soil was fixed at desired levels by use of a high-speed core ultracentrifuge with an ultralow constant-rate flow pump feeding water into the sample through a rotating seal. After the water content was fixed and the soil was at hydraulic steady-state (within two to four hours), the electrical conductivity was measured using a 1 kHz conductivity bridge. Diffusion coefficient values were calculated from the measured electrical conductivity values using the Nernst-Einstein equation. Hanford formation soils exhibit great heterogeneity regarding hydraulic conductivity in subunit soils. Hydraulic conductivity ranged from 10^{-7} cm/sec to 10^{-4} cm/sec depending on soil type and water content. However, diffusion coefficients depended only on water content, although water content is controlled by the hydraulic properties of each soil under similar hydrologic conditions. Diffusion coefficients ranged from 10^{-8} cm^2/sec at volumetric water contents between about 3% and 5% to 10^{-6} cm^2/sec at volumetric water contents between 15% and 25%.

INTRODUCTION

Modelling the transport of contaminants in vadose zones surrounding nuclear and hazardous waste repositories requires knowledge of the material characteristics under unsaturated conditions. The diffusion coefficient, D, and hydraulic conductivity, K, are two of several unsaturated transport parameters that are poorly known but that are key input parameters to existing and developing models of contaminant release from repository systems.[1,2] Knowledge of D and K as functions of the volumetric water content, θ, is particularly important in the near-field transition zone around waste packages where changes in temperature, water content, compaction of backfill, infiltration of fines, and secondary mineralization will alter the transport character of near-field environments. This study experimentally determined the diffusion coefficient and hydraulic conductivity of five subunits of the Hanford formation at various degrees of saturation for use in modelling of subsurface flow and transport at the site. In addition, preliminary results are reported for unsaturated retardation factors for potassium ion in three different Hanford soils.

Traditional methods of investigating unsaturated systems require very long times to attain homogeneous distributions of water because normal gravity does not provide a large enough driving force relative to the low hydraulic conductivities that characterize highly unsaturated conditions. An unsaturated flow apparatus (UFA™) has been developed in which hydraulic steady-state can be achieved rapidly in most geologic materials at volumetric water contents as low as 0.5%. Soil samples were placed in the UFA™ to achieve hydraulic steady-state with 0.1 *M* KCl as an electrolyte solution. The diffusion coefficient corrected to infinite dilution was determined from the measured electrical conductivity (EC) of the sample using the Nernst-Einstein equation. This method is subsequently referred to as the UFA-EC method and is also described elsewhere in this volume (Conca, "Diffusion Barrier Transport Properties of Unsaturated Paintbrush Tuff Rubble Backfill").

EXPERIMENTAL METHODS

The UFA™ developed for this study consists of a rock core ultracentrifuge with an ultralow constant-rate flow pump which provides fluid to the sample surface through a rotating seal assembly and microdispersal system. A centripetal acceleration (or its inertial effect, the centrifugal field) is a body force like gravity, and so acts simultaneously over the entire system and independently of other driving forces, e.g., gravity or matric suction, and does not induce significant changes in the sample packing, density or other physical properties.[3] Accelerations up to 20,000 g are attainable at temperatures up to 150°C and flow rates as low as 0.1 ml/hr. Effluent is collected in a transparent, volumetrically-calibrated container at the bottom of the sample assembly. Effluent collection can be observed and recorded during centrifugation through a window in the sample assembly using a strobe light.

Under a centripetal acceleration in which the water is driven by both the matric potential and the centrifugal force per unit volume, $\rho\omega^2 r$, Darcy's Law is given by

$$q = -K(\psi)\,[d\psi/dr - \rho\omega^2 r] \qquad (1)$$

where q is the flux density into the sample; K is the hydraulic conductivity, which is a function of the matric suction (ψ) and therefore of water content (θ); r is the radius from the axis of rotation; ρ is the fluid density; and ω is the rotation speed (rad/s). The system reaches steady-state in soils in two to four hours. Moisture distributions in soil samples prepared in the UFA™ are uniform to within at least 3%. Appropriate values of rotation speed and flow rate into the sample are chosen to obtain desired values of flux density, water content, and hydraulic conductivity within the sample. At speeds above about 400 rpm, provided that a sufficient flux density exists, $d\psi/dr \propto \rho\omega^2 r$ and, therefore, equation (1) is reduced to $q = K(\psi)\,[\rho\omega^2 r]$ or $K(\psi) = q/\rho\omega^2 r$. As an example, a 45-gram sample of a silt accelerated to 2000 rpm with a flow rate into the silt of 3 ml/hr achieved hydraulic steady-state in two hours at a volumetric water content of 22.4% and an unsaturated hydraulic conductivity of 2.5×10^{-7} cm/sec.

Electrical conductivity in a potentiostatic or galvanostatic mode provides reliable estimates of diffusion coefficients in dilute electrolyte solutions[4,5] and was developed for this study using a variation of the two-electrode method.[6]

The electrical conductivity cell designed for use in the UFA™ fits inside the centrifuge sample chamber. Two stainless steel ring electrodes 2.5 cm apart maximize contact area with the soil. Stainless steel electrodes are ideal for the water contents and the current densities used in these experiments ($\leq$1 mA/cm^2).[7]

After electrical conductivity measurements are made, they can be related to the diffusion coefficient through the Nernst-Einstein equation.[8] For the experimental design of this study, the Nernst-Einstein equation is

$$D_i = \frac{RT}{F^2} \times \frac{\Theta G t_i}{Z_i C_i} \qquad (2)$$

where D_i is the diffusion coefficient of the *ith* ion (cm^2/sec), R is the gas constant (J/deg mol), T is absolute temperature (Kelvin), F is Faraday's constant (coul/mol), Θ is the cell constant for the UFA™ conductivity cell sample holder (cm^{-1}), G is the measured conductance on the conductivity bridge (mhos), t_i is the transport or transference number of the *ith* ion (t_{K^+} = 0.4898; 0.1*M*), Z_i is the charge number on the *ith* ion (dimensionless) and C_i is the molar concentration of the *ith* ion. The diffusion coefficients determined in this study have been corrected for solution non-ideality using the extended Debye-Hückel approximation.[9]

VERIFICATION OF THE UFA-EC TECHNIQUE

Diffusion coefficient values for Hanford soils were determined using the UFA-EC technique. These values were compared to results from previous studies on similar soils verifying that the UFA-EC technique is valid and compares favorably with traditional techniques for determining diffusion coefficients.

An empirical relationship was developed by Kemper and others to describe diffusion coefficients as a function of water content and soil type.[10,11] This relationship illustrated that the solute diffusion coefficient, D, is a positive exponential function of water content, θ, and is independent of solution ionic strength below about 1 *M*. The relationship is:

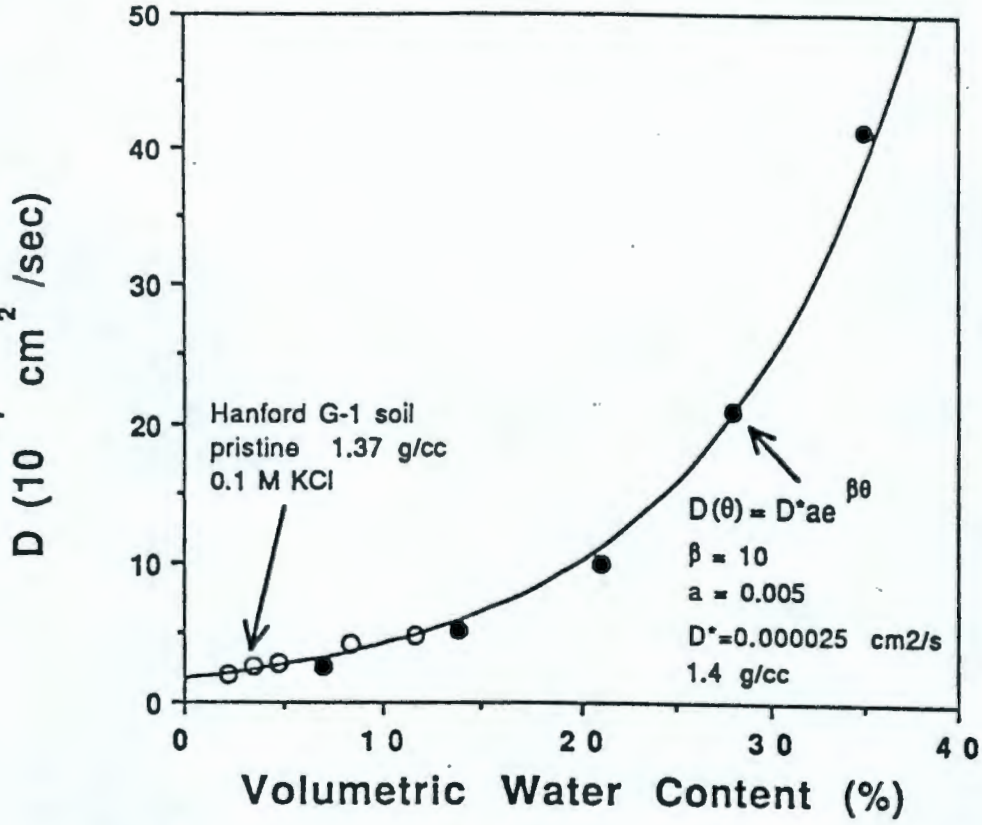

Figure 1. Comparison of diffusion coefficients for the Hanford G-1 soil determined by the UFA-EC method (open circles) and from the literature empirical relationship (closed circles). The regression curve has an R = 0.99.

$$D(\theta) = D^* a e^{b\theta} \qquad (3)$$

where D* is the free diffusion coefficient in a pure-water system, and *a* and *b* are empirical constants determined from experimental results by traditional techniques[12]. Olsen and Kemper[11] reported that data for soils fit this relationship if $b = 10$ and *a* varies from 0.005 to 0.001 depending on soil type and texture (sand to clay, respectively).

Diffusion coefficients for potassium ion in the Hanford G-1 soil obtained using the UFA-EC technique were compared to the relationship in Equation (3). The Hanford G-1 soil is characterized by $a = 0.005$, and $D^* = 2.5 \times 10^{-5}$ cm^2/sec for K^+. Figure 1 shows the results. The exponential regression curve fits both sets of data with an R = 0.99, illustrating that results from the UFA-EC technique are consistent with results for soils reported in the literature, and indicating that diffusion coefficients in the soils determined by the UFA-EC technique are valid.

In the absence of physicochemical processes, simple diffusion coefficients are similar for all ionic aqueous species, differing by, at most, a factor of four. This simple diffusion coefficient is what the electrical conductivity method measures. Numerical models using *D(θ)* as an input parameter require the simple diffusion coefficient, as measured by the UFA-EC method, which can differ from *D(θ)* measured from traditional half-cell methods. Half-cell methods cannot completely eliminate advection, retardation, reaction and osmotic effects over the long experimental durations needed to obtain sufficient data at low water contents. Also, it is extremely difficult to control boundary conditions, or to collect samples, at low water contents using traditional half-cell methods.

SAMPLE AND SOLUTION DESCRIPTION

The Hanford site is underlain by a variety of heterogeneous interbedded river sands and gravels, with numerous loess, volcanic, flood and lacustrine deposits. Sediments comprising the vadose zone are generally Holocene in age The materials selected for this study are subunits of the Hanford G-1 soil collected from an excavation pit at the Central Landfill site in the 200 West area, and composite samples of Hanford G-3 and G-4 soils.[13] There were five different types of sediments observed at the Landfill site; two loesses, a fine gravel, and two coarse sands. Dispersed throughout the sediments were silt lenses and dikes. Each type of sediment was sampled in an air-tight glass-jar for return to the laboratory. A rough breakdown of grain size is as follows: *loess 1* - 4% clay, 15% silt, 81% sand; *loess 2* - 3% clay, 18% silt, 79% sand; *gravel* - 1% clay, 2% silt, 85% sand {very coarse}, 12% gravel; *upper coarse sand* - 3% clay, 3% silt, 94% sand, and *lower coarse sand* - 2% clay, 2% silt, 96% sand.

The coarse sands and the gravel, which occur over much of the site, are different subunits of the highly heterogeneous Hanford G-1 soil, which has an average composition that varies around 91% sand, 3% silt and 6% clay. The fines of each subunit were investigated using X-ray diffraction to determine the presence or absence of expandable clays which are very important with respect to controlling water content and retardation of liquid wastes. Samples were investigated using a Phillips 3600 X-ray diffraction unit operated at 40 KV and 25 Ma using CuK_{α} radiation. Data were collected in a step scanning mode using 0.02 degree steps and a count time of 1 or 2 seconds per step, through a range of 3.0 to 80.0 degrees 2θ. Samples were analyzed as random powder mounts, oriented mounts, and ethylene glycolated oriented mounts. The minimum detection limit for phase identification is typically between 1% and 2%. Table 1 shows some of the results. Also included are results for the Hanford G-3 and G-4 soils. Organic material was negligible for all samples. However, all soil samples contained a significant amount of X-ray amorphous phases.

TABLE 1. X-RAY DIFFRACTION RESULTS FOR THE HANFORD SOILS

Sample	Major Phases	Minor Phases (<5%)
Silt lense in Hanford G-1 soil	quartz muscovite calcite	montmorillonite kaolinite
Silt dike in Hanford G-1 soil	albite quartz diopside/augite	phlogopite chlorite smectite
Hanford G-1 soil composite	quartz albite diopside/augite	phlogopite kaolinite
Hanford G-3 soil composite	quartz albite	muscovite
Hanford G-4 soil composite	quartz albite	smectite muscovite

The conductivity solutions used in these experiments were 0.1*M* KCl. The electrical conductivity of the effluent solutions was monitored during the experiments to observe any changes in conductivity resulting from cation exchange, water/rock interactions, etc., that could affect the determination of the diffusion coefficient. Cation exchange was observed to variable degrees for each soil and sufficient flux was allowed until cation exchange ceased to affect solution chemistry. During measurements used for determination of diffusion coefficients the electrical conductivity of the effluent solutions never varied by more than 0.0005 mhos or 2% of the conductivity of the infiltrating 0.1*M* KCl solution.

RESULTS

The following diffusion coefficients and hydraulic conductivities were obtained in the conductivity cell sample holder immediately after removal from the UFA™ using a conductivity bridge at 1 kHz. Water contents were determined by the difference in sample weights after each run, wet and oven dried at 50°C. Equations (1) and (2) were used to determine the hydraulic conductivities and diffusion coefficients, respectively.

Diffusion Coefficients

Figure 2a shows the diffusion coefficient as a function of water content for all the soil samples in this study. The data for all soil sample groups cluster along a curvilinear trend demonstrating that the diffusion coefficient in these samples is dependent primarily on water content, and only secondarily on soil type. Figure 2a illustrates that at the volumetric water content expected under the Landfill site in the field (i.e., 3-8% for coarse sands and gravels, 8-15% for finer sands and 15-25% for the silt lenses and dikes), the diffusion coefficients should be between 2 and 10×10^{-8} cm^2/sec, 1 and 4×10^{-7} cm^2/sec, and 4 and 11×10^{-7} cm^2/sec, respectively.

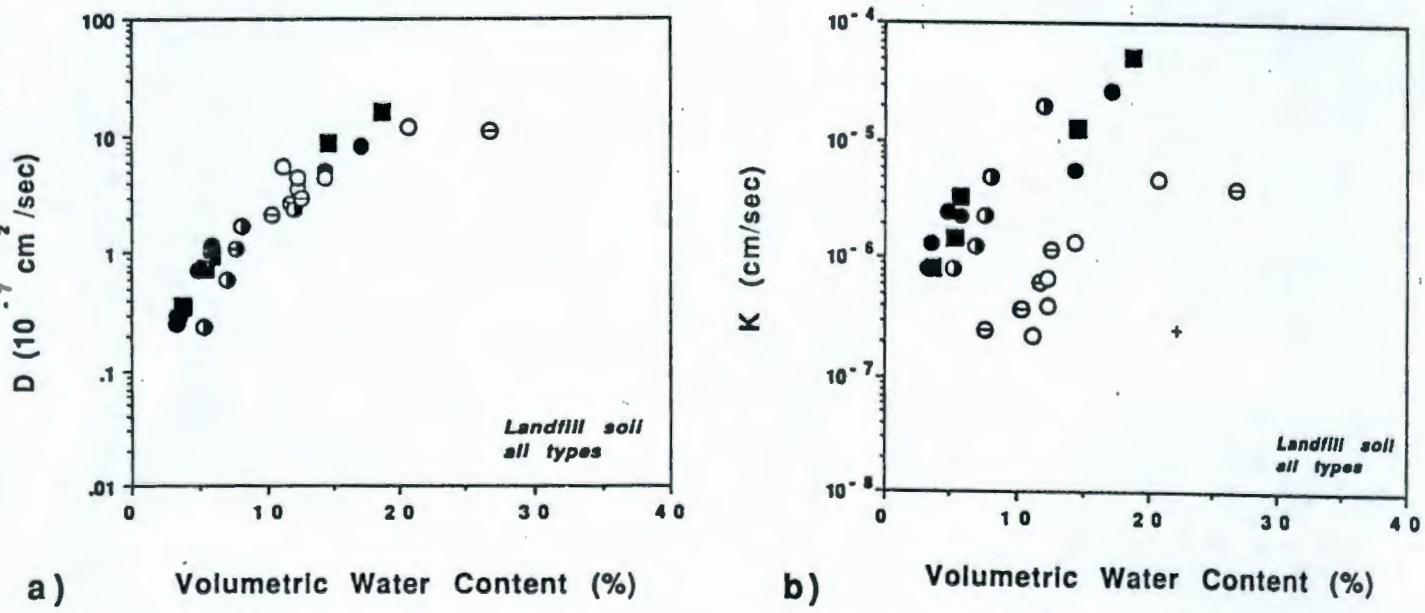

Figure 2. a) Diffusion coefficients for Hanford soils under the Landfill site showing strong dependence on water content and weak dependence on soil type. Open circles are loess 2, slashed-circles are loess 1, closed circles are lower coarse sand, half-closed circles are upper coarse sand, closed squares are gravel. b) Hydraulic conductivity results for the same soils showing dependence on both soil type and water content.

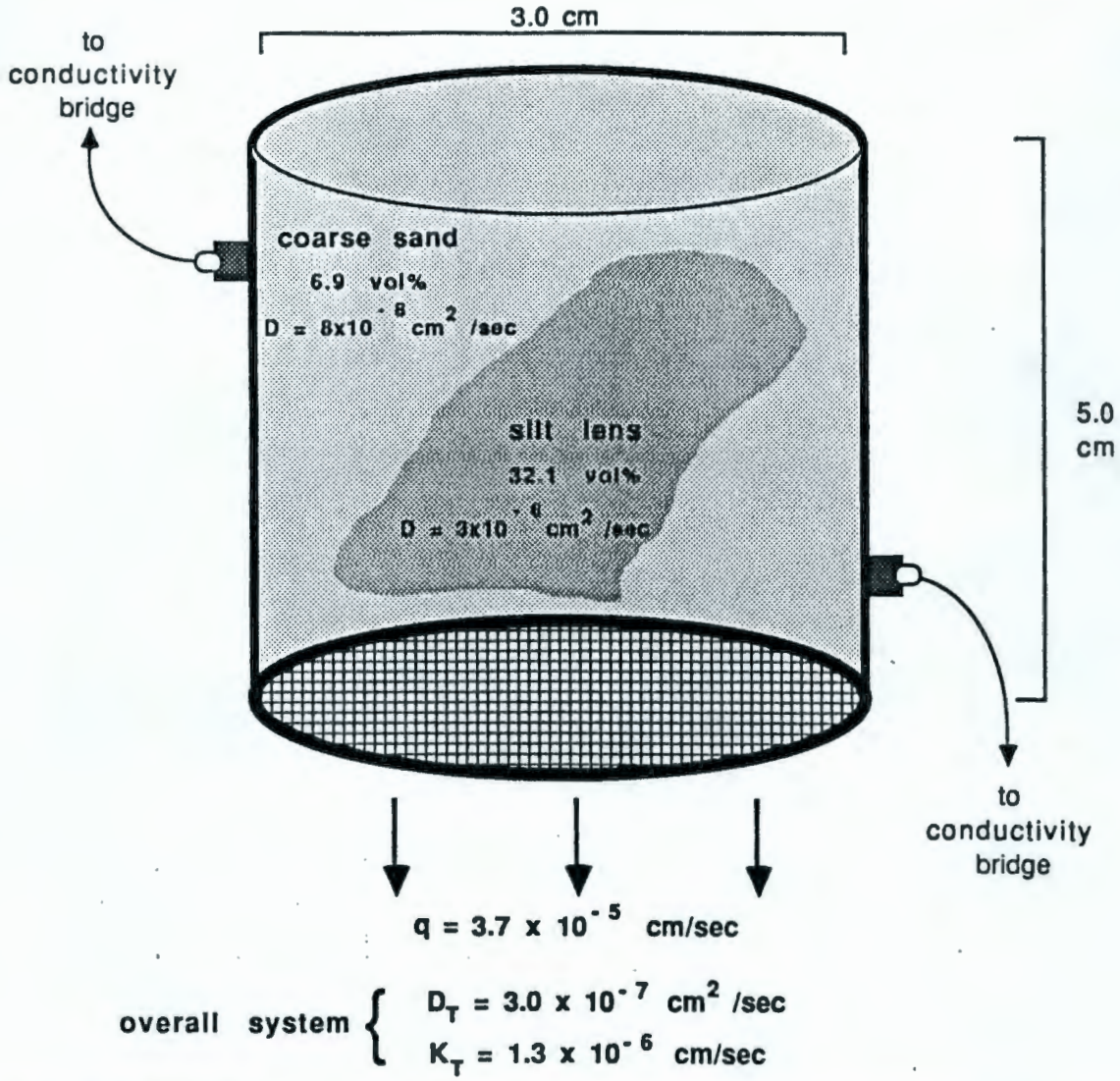

FIGURE 3. Transport through coarse sand containing a silt lens.

2 1 2 4 9 5 1 8 3 4

Unsaturated Hydraulic Conductivity

Figure 2b shows the hydraulic conductivities, $K(\theta)$, as a function of water content for the Hanford G-1 soil samples used in this study. As expected, the hydraulic conductivities differ markedly for the different soils. The coarser- and finer-grained soils define two distinct fields. The coarser-grained soils have hydraulic conductivities approximately an order of magnitude higher than the finer soils. The only data for a pure silt lens suggests that the hydraulic conductivities of the silt lenses and dikes are another order of magnitude less than the fine sands or the loesses.

Flow through a Two-Media System

In the very heterogeneous Hanford G-1 soil, silt lenses and cross-cutting dikes occur throughout the sediments and definitely affect flow through the unit. The silts have lower conductivities, higher water contents and a greater abundance of fines that can influence retardation of contaminants. To investigate the effect of a silt lens on the overall unsaturated hydraulic conductivity and diffusion coefficient of a coarse sand containing silt lenses, a sample of lower coarse sand containing an intact silt lens was placed into the UFA™ (Figure 3). This two-media system was run for four hours at 500 rpm with a flow rate of 1 ml/hr, giving an overall hydraulic conductivity of 1.3×10^{-6} cm/sec. The diffusion coefficient measured was 3.0×10^{-7} cm^2/sec. The total volumetric water content of the system was 13.9%, but seperately the coarse sand had a volumetric water content of 6.9% and the silt lens had a volumetric water content of 32.1%.

The question is: how much does the silt lens affect the conductivity of the overall system? If the silt lens is assumed to have negligible hydraulic conductivity, $K(\theta)$, then the $K(\theta)$ of the overall system would simply be the $K(\theta)$ of the coarse sand, i.e., 2.6 x 10^{-6} cm/sec (the presence of an impermeable barrier the size and shape of the lens decreases the cross-sectional area of flow around the sand, increasing the average flux density through the sand by a factor of 2.) Figure 2 indicates that $K(\theta)$ and $D(\theta)$ range from 2.0 to 4.0 x 10^{-6} cm/sec and 1.0 to 2.0 x 10^{-7} cm^2/sec, respectively, in the lower coarse sand at a volumetric water content of 6.9%. Comparison of these ranges to the total $K(\theta)$ and $D(\theta)$ in the two-media system indicates that the silt lens has no discernible effect on the hydraulic conductivity, except to increase the tortuosity slightly, and only a small effect on the diffusion coefficient.

RETARDATION COEFFICIENTS

Unsaturated retardation factors are presently being studied for Hanford soils and sediments. In these flow experiments, K_d for a particular species is defined as the concentration of that species lost from solution to the solid phases divided by the concentration remaining in solution. The retardation factor for that species is given by:

$$R_f = 1 + \rho K_d/\theta$$

where ρ is the dry bulk density and θ is the volumetric water content. If none of a particular species is lost to the solid phase, then $K_d = 0$ and $R_f = 1$ for that species. Figure 4 shows preliminary results for the Hanford G-1, G-3 and G-4 soils run under the same hydrologic conditions. The Hanford G-1 and G-3 soils are identical in

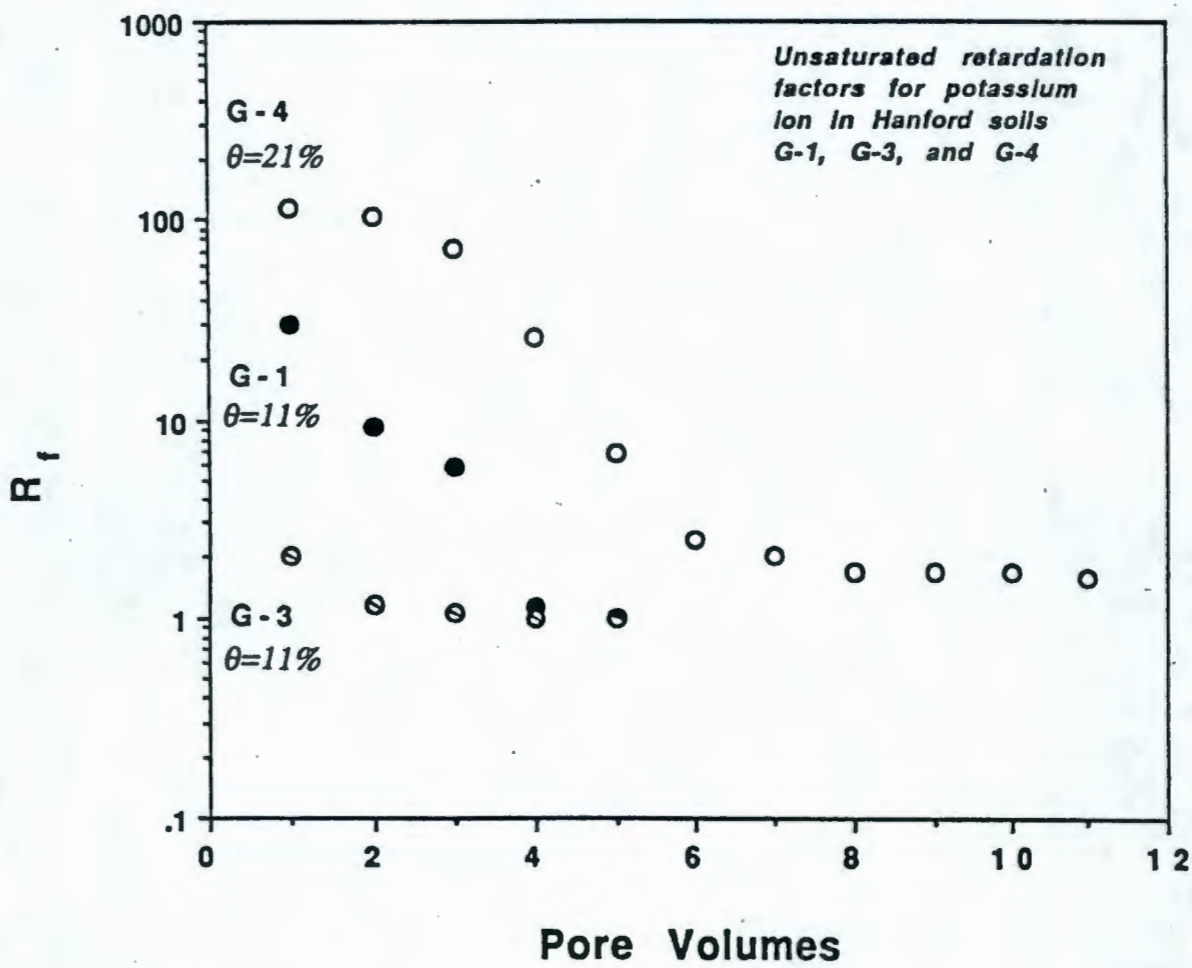

Figure 4. Retardation factors for potassium ion in three Hanford soils under unsaturated conditions.

hand specimen, have the same amount of fines, and have similar water retention properties. The Hanford G-4 soil is similar to G-1 and G-3 but has slightly more fines, a more brownish color and greater water retention properties. Retardation of potassium in these soils was dominated by cation exchange with calcium in clay minerals, but absorption by amorphous phases could also be significant.

As expected, Figure 4 indicates that the Hanford G-4 soil has the highest water content and greatest retardation effects of the three soils under the same hydrologic conditions. However, even though the water contents of the Hanford G-1 and G-3 soils are identical the retardation behavior is very different, and the G-1 soil exhibits greater retardation.

CONCLUSIONS

Although the Hanford formation soils are often grouped as a single unit of coarse or gravelly sand, the data in Figure 2 suggest that there is great heterogeneity regarding hydraulic conductivity in the subunit soils. The transport of water and contaminants will depend significantly on the path taken through these subunits. Hydraulic conductivity ranged from 10^{-7} cm/sec to 10^{-4} cm/sec depending on both soil type and water content. The diffusion coefficients did not depend on soil type but only on water content, although water content is controlled by the hydraulic properties of each soil under similar hydrologic conditions. Diffusion coefficients ranged from 10^{-8} cm^2/sec at volumetric water contents between about 3% and 5% to 10^{-6} cm^2/sec at volumetric water contents between 15% and 25%.

ACKNOWLEDGEMENTS

Stimulating discussions with Glendon Gee, Karl Pool, and Jim Conca provided insight into the physics and chemistry of soils and groundwater. Nancy Uziemblo determined soil mineralogy using XRD. Mozart and Sting provided musical inspiration. The Department of Energy provided support through Pacific Northwest Laboratory under Contract DE-AC06-76RLO 1830.

REFERENCES

1. T. H. Pigford and P. L. Chambré, "Near-field mass transfer in Geologic Disposal Systems: a review," *Mat. Res. Soc. Symp. Proc., 112,* 125-141 (1988).

2. K. Pruess and J. S. Y. Wang, "Numerical Modeling of Isothermal and Nonisothermal Flow in Unsaturated Fractured Rock - A Review," in *Flow and Transport Through Unsaturated Fractured Rock*, D. D. Evans and T. J. Nicholson, Geophysical Monograph 42, American Geophysical Union, Washington, D.C. (1987).

3. J. R. Nimmo and K.C. Akstin, "Hydraulic conductivity of a Sandy Soil at Low Water Content after Compaction by Various Methods," *Soil Sci. Soc. Amer. J., 52,* 303-310 (1988).

4. D. G. Miller, *Estimation of tracer diffusion coefficients of ions in aqueous solution, UCRL-53319,* Lawrence Livermore National Laboratory, Livermore, C. A. (1972).

5. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London (1959).

6. J. D. Rhoades and J. D. Oster, "Solute content," in *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods*, A. Klute, 2nd ed., Amer. Soc. Agronomy and Soil Sci. Soc. Amer., Madison, Wisconsin, 985-1006 (1986).

7. L. A. Geddes, C. P. DaCosta, and G. Wise, "The impedance of stainless-steel electrodes," *Med. & Biol. Eng., 9,* 511-521 (1971).

8. J. J. Jurinak, S. S. Sandhu, and L. M. Dudley, "Ionic diffusion coefficients as predicted by conductometric techniques," *Soil Sci. Soc. Amer. J., 51,* 625-630 (1987).

9. W. Stumm and J. J. Morgan, *Aquatic Chemistry,* John Wiley & Sons, New York (1981).

10. W. D. Kemper and J. C. Van Schaik, "Diffusion of salts in clay water systems," *Soil Sci. Soc. Amer. Proc., 30,* 534 -540 (1966).

11. S. R. Olsen and W. D. Kemper, "Movement of nutrients to plant roots," *Adv. Agron., 30,* 91-151 (1968).

12. E. Bresler, B. McNeal, and D. L. Carter, *Saline and Sodic Soils*, Springer-Verlag, N.Y. (1982).

13. M. J. Fayer, W. Conbere, P. R. Heller and G. W. Gee, *Model Assessment of Protective Barrier Designs*, Battelle Pacific Northwest Laboratories Topical Report, PNL-5604 (1985).