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EFFECTIVE POROSITY OF GEOLOGIC MATERIALS

FIRST ANNUAL REPORT

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Effective Porosity of Geologic Materials

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First Annual Report

by

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I. INTRODUCTION

Effective porosity is that portion of the total void space of a porous material that is capable of transmitting a fluid. Total porosity is the ratio of the total void volume to the total bulk volume. Porosity ratios traditionally are multiplied by 100 and expressed as a percent.

Effective porosity occurs because a fluid in a saturated porous media will not flow through all voids, but only through the voids which are interconnected. Unconnected pores are often called dead-end pores. Particle size, shape, and packing arrangement are among the factors that determine the occurance of dead-end pores. In addition, some fluid contained in interconnected pores is held in place by molecular and surface-tension forces. This "immobile" fluid volume also does not participate in fluid flow.

Increased attention is being given to the effectiveness of fine grain materials as a retardant to flow. The calculation of travel time (t) of contaminants through fine grain materials, considering advection only, requires knowledge of effective porosity (n_e):

$$t = \frac{n_e x}{KI} \tag{1}$$

where x is the distance travelled, K is the hydraulic conductivity, and I is the hydraulic gradient. The lack of a reliable method for determining effective porosity has necessitated the estimation of this parameter. Currently, this is an undesirable but unavoidable practice.

Effective porosity is an important parameter in calculation of contaminant transport. This study documents laboratory technique for measuring effective porosity of fine-grained soils. Confusion about the meaning of effective porosity and its relation to total porosity also is explained.

This project is of benefit to ground-water professionals who are involved in prevention and mitigation of contamination. Planners and regulators involved in ground water pollution prevention strategies and regulation also will have more definitive data on which appropriate decisions can be made.

Relationships identified between effective porosity and physical characteristics may permit estimation of the importance and magnitude of effective porosity from the total porosity and physical characteristics without its direct measurement. The review of work in associated sciences is an important starting point for research in fine-grain saturated soils.

II. OBJECTIVES AND SCOPE

The objective of this project is to document the value of an effective porosity measurement technique of fine-grain soils and to relate effective porosity to total porosity and other physical characteristics. The documentation of undisturbed soil sample collection techniques, a comparison of field measured and laboratory measured hydraulic conductivities, and documentation of static and dynamic porosity measurements are to be accomplished in this project. An extensive literature search of associated sciences also has been conducted.

To simplfy the task of studying effective porosity in geologic materials, non-lithified sedimentary rocks with no secondary porosity are considered. Samples to be studied will be glacial till deposits with 10^{-4} to 10^{-7} cm/sec hydraulic conductivity.

Total porosity can be classified as primary or secondary. Primary porosity is the porosity that forms when the sediment is deposited, whereas secondary porosity is formed after the sediment was deposited. Secondary porosity includes cavities produced by the solutioning of carbonates and by fractures. Secondary porosity is avoided here because analysis methods used would be substantially complicated by small scale heterogeneities that are typical of the voids caused by solution cavities and fractures.

Indurated rocks which have been lithified by cement are of interest because cementation increases the number of dead-end pores; therefore, a significant amount of previous work applies to these materials. Lithified rocks are not considered for use as liner materials and are not considered here.

III. PAST ACTIVITIES (LITERATURE REVIEW)

A literature search of associated sciences was conducted to perform a comprehensive examination of pertinent work on the subject. Past activities have been divided into five categories to separate work from different disciplines. Selected categories are:

Hydrodynamic and physical properties of soil;
Flow in saturated porous media;
Tracer movement in saturated porous media;
Measurement of effective porosity of saturated porous media; and
Chemical reactions in porous media.

One can easily become confused when surveying the use of the term "porosity" in the literature. Few authors state whether they are referring to the total or effective porosity. More important than this is that many authors refer to total porosity in contexts where effective porosity should be used, even if they are approximately the same. When volumetric considerations are required, such as aquifer compressibility, total porosity is appropriate. However, when flow is considered, such as tracer migration, effective porosity is appropriate.

There was considerable interest in effective porosity before it became of importance to ground-water professionals. Interest in the past has been by soil scientists, petroleum engineers and physical chemists. Study in these disciplines are pertinent; however, caution is required in a review of multi-disciplinary literature in translating the varieties of terminology used by authors in various fields.

As previously indicated, in this study, flow is considered under saturated conditions. This is referred to as single-phase flow, i.e. the flow of one fluid, in this case, water. Soil scientists often also considered unsaturated conditions. Unsaturated flow is two-phase, air and water. Three-phase flow, oil, natural gas, and water, is of interest to petroleum engineers and is also important. Persistence of multiphase flow is because immiscible fluids create dead-end pores. This is because one fluid may prevent flow of another fluid through narrow pathways.

A. Hydrodynamic and physical properties of soil.

Introductory texts in sedimentology, petrology and soil science provide key information to the physical characteristics of soils. Selley (1976) summarized other authors work on the relationships between physical properties and total porosity. The grain size, sorting, grain shape (sphericity), grain roundness (angularity) and packing are the factors that determine total porosity when sedimentation occurs. This is primary porosity. Table 1 shows the relationship of total porosity to physical characteristics. Total porosity generally increases with decreasing grain size, however, this is caused by other properties. Theoretically, for spherical grains of uniform size the grain diameter will not effect porosity. Total porosity increases with increasing sorting. Total porosity decreases with increasing sphericity and roundness. Total porosity decreases with closer packing. Graton and Fraser (1935) determined the total porosity of spherical particles of uniform size with different packing arrangements (figure 1). Biella et al. (1983) studied percentage of small grain size to total porosity and found that as the percentage of small grain size particles decreased, the total porosity also decreased to a minimum and then increased. The above studies were conducted using silica sand as the material of interest.

Table 1. The Relationships between Total Porosity and Physical Characteristics

Property	Primary total porosity low	Primary total porosity high	Reason
Grain size	NA	NA	grain size has no influence on porosity
Sorting	poor	good	small grains fill in voids between large grains
Packing	close	loose	close packing has less voids between grains
Shape	spherical	oblong	spherical grains tend to pack more closely
Roundness	rounded	angular	rounded grains tend to pack more closely

Because the scope of this project is directed toward fine grain materials, clay minerals are also of interest. Williams et al. (1954) described the layer, or sheet, structure which are characteristic of clays. Illite and montmorillonite have a very similar structure to mica which have a platy habit. Kaolinite does not exhibit this type of structure. Clay minerals when settled out of water tend to assume a parallel orientation. This leads to a tighter packing and a resulting lower total porosity.

Techniques used to characterize soils are summarized by Das (1979). Optimum moisture content, the moisture content at which the maximum dry unit weight is obtained, is determined by the standard Proctor test. The liquid

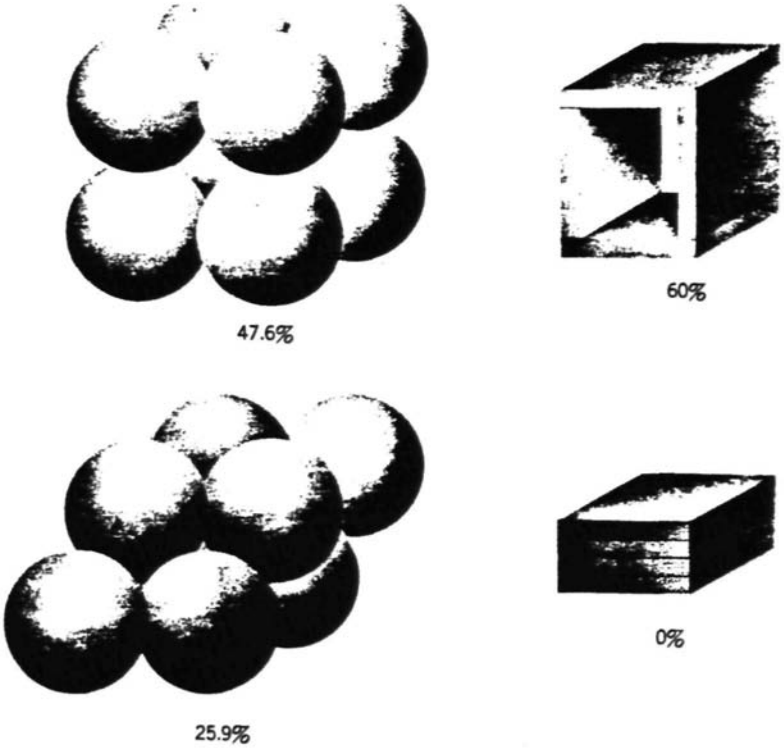


Figure 1. Packing arrangements available for spherical particles of uniform size.

limit and plastic limit define the moisture contents where the transition from semi-solid to plastic and plastic to liquid occur.

Bear (1979) defined the "interconnected pore space" as the effective pore space with respect to the total pore space. He stated, "This happens when the porous medium contains dead-end pores, i.e. pores or channels with only a narrow single connection to the interconnected pore space, so that almost no flow occurs through them." Hantush (1964) included water held in place by molecular and surface tension forces in this category. Davis and DeWiest (1966) illustrated the relationship of total porosity n, to specific yield S_y, and specific retention S_r (figure 2). Bear (1979) stated:

$$n = S_y + S_r \tag{2}$$

and that S_y ($<n$) is sometimes called effective porosity. This is the case in Rawls et al. (1983) where the effective porosity was considered as the difference of the total porosity and the residual soil-water content. The residual soil-water content being the specific retention.

B. Flow in saturated porous media.

Flow of ground water in saturated porous media has been described by Bear (1979). Hydraulic conductivity is the coefficient which relates discharge to head loss. The coefficient was first presented by Darcy in 1856. The relationship has been termed Darcy's Law and can be expressed as:

$$Q = K\ I\ A \tag{3}$$

where Q is the discharge (L^3/L), K is the hydraulic conductivity (L/T), I is the hydraulic gradient (L/L), and A is the cross-sectional area (L^2). Darcy's law was developed while examining coarse-grain sands. Many studies have questioned the validity of Darcy's law for soils containing clays.

Swartzendruber (1962) gave a conscientious review of work by Darcy and others considering the applicability of Darcy's law. In reviewing the work

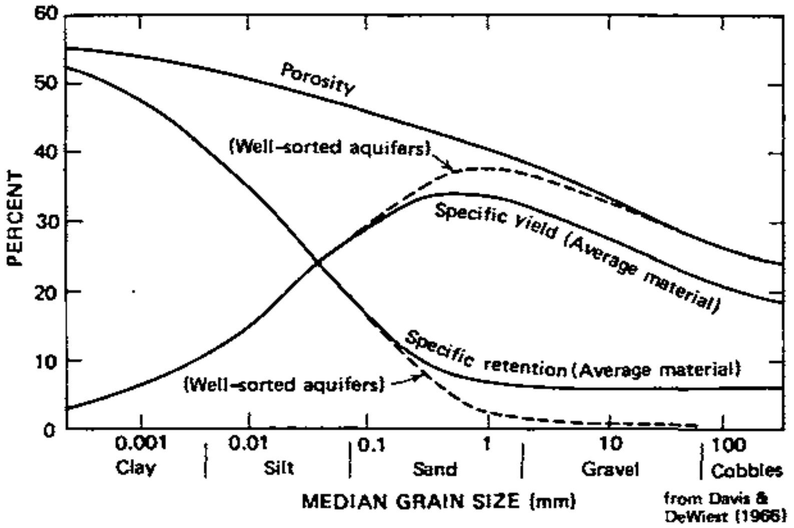


Figure 2. Illustration of the interrelationship between median grain size and total porosity, specific yield and specific retention.

of Stearns (1927), who addressed grain-size distribution and used some samples with clay size particles, he concluded that Darcy's law is not applicalbe when clay was present above 5 percent. In a study of saturated kaolinite Olsen (1966) stated "... the evidence as a whole suggests that Darcy's law is obeyed in many natural sediments, but that exceptions may occur in very fine-grained clays, specifically montmorillonite, and also in shallow, unconfined clays or in granular soils containing small amounts of clay." Von Engelhardt and Tunn (1955) found that there was no linear relationship between pressure drop and fluid velocity in sandstones with clay contents of 1 to 5 percent.

Hydraulic conductivity of saturated porous media may be determined by field methods or by laboratory methods, see Olson and Daniel (1979). Several field and laboratory methods are described by Freeze and Cherry (1979). Many tests are not viable in the field depending on the soil types and information desired. Because of the special requirements of this project a different procedure than described will be used.

Before laboratory methods for determining hydraulic conductivity can be summarized, consideration of collection of a representative sample must first be addressed.

The collection of truly undisturbed samples for tests in the laboratory is difficult. Elzeftawy and Cartwright (1983), Daniel (1983), and Smetten (1984) used "undisturbed cores" in their studies. Problems identified include: small sample size, storage, and development of acceptable sample interface to a porous plate. In addition to these and other problems, comparisons of undisturbed and disturbed (recompacted) samples rarely agree.

Laboratory methods include the constant-head and falling-head permeameter tests. Daniel et al. (1984) describe two types of permeameters, flexible-wall and fixed-wall, and presents their advantages and disadvantages.

C. Tracer movement in porous media.

Migration or flow through a porous media can be evaluated by means of tracers. For a tracer to be effective it should react similarly to the eluant both physically and chemically. Ideally, it should be totally unreactive toward the substance forming the bed of the column. No exchange or adsorption reactions should occur and concentrations of a magnitude that cause precipitation must be avoided.

Various tracers have been used in laboratory core column studies. Because of interest in the mobility of radionuclides in ground-water flow systems, Champ et al. (1982) used a mixture of plutonium isotopes, predominantly 239Pu (77%), as the tracer. "Undisturbed horizontal cores" were used not only to determine the transport of 239Pu but also to identify the chemical speciation of 239Pu in the effluent.

An agronomic approach was used by Elrick, Erh, and Krupp (1966) because of an interest in pesticide movement in soils. The herbicide, atrazine, as a 14C-ring labeled isotope, was used as the tracer. This enabled the use of a tracer which was a natural chemical compond used in agriculture and which would be affected by a variety of chemical and physical proccesses (i.e. adsorption, fixation, precipitation, degradation or decay). Glass beads and packed soils, Honeywood silt loam and Guelph loam, were used as the media in these miscible displacement studies.

Nielsen and Biggar (1961, 1963) and Biggar and Nielsen (1962) in a series of articles observed miscible displacement of soils under both saturated and unsaturated conditions. Chloride ion and tritium were used as the observed tracers with various soils (Oakley sand, Yolo loam, Columbia silt loam, and/or Niken clay loam) and two sizes of glass beads (200 and 390μ) serving as the porous media. By using tracers of different diffusion coefficients, the authors hoped to define the contribution of diffusion to the spreading of the breakthrough curves. No separation of tracers could be measured at 2.11 cm per hour. However, at low average flow velocity, v = 0.20 cm/hr, translation of chloride curve to the left did occur yielding separate breakthrough curves both in unsaturated conditions, with Columbia silt loam, and in saturated conditions, with Niken clay loam. The authors concluded from the data that diffusion had indeed manifested itself.

Corey and Horton (1968) employed a triply tagged solution of 3H, 2H, and

and with miscible displacement techniques observed no differences in the relative rates of tracer movement in a water-saturated acidic kaolinite soil. This finding is not similar to the results of Nielsen and Biggar because the flow velocity, 1.22 cm/hr, was still too high to allow observance of the molecular diffusion contribution to dispersion. Also the diffusion coefficients of the water tracer did not vary to the degree seen between chloride and tritium. Diffusion coefficients in water for $^{1}H^{2}H^{16}0$, $^{1}H3H^{I6}0$, and $^{1}H_{2}^{18}0$ at 25°C are 2.34 x 10"5, 2.44 x 10"5, and 2.66 x 10^{-5}, respectively. Whereas, chloride and tritium have diffusion coefficients of 6.21 x 10^{-5} cm^{2}/sec and 5.22 x 10^{-5} cm^{2}/sec, respectively.

The exchange of tritiated water, HTO, between the atmosphere and soil and crops was investigated by G. A. Garland (1980). These experiments were carried out in the field and in a wind tunnel along with other laboratory studies. In short exposures it was found that uptake by moist soil was controlled by atmospheric mixing with most vapor interaction occurring within two to three days. The tritiated water absorbed during exposure evaporated over a period of several weeks. Rain washed activity into the soil and impeded evaporation.

Miscible displacement principles were utilized by Sadler, Taylor, Williardson, and Keller in 1965. They flushed salts, Cl^-,Na^+ and $Ca^{++}Mg^{++}$, from a humic gley, silt loam soil in a soil reclamation project. Experimental field plots were selected with each adjacent to an open drain. Results indicated that both hydrodynamic dispersion and ionic diffusion actively contribute salt to the effluent. The salt in the soil directly over the line of the drain is removed primarily by velocity flow and dispersion. The importance of diffusion as a removal process seems to increase with increasing distance from the drain.

D. Measurement of effective porosity.

Field Techniques

Field techniques to calculate effective porosity have been presented; however, their application to this study is limited. Rawls et al. (1983) determined the effective porosity of soils using information available in soils surveys. As indicated earlier, they consider effective porosity of shallow soils (less than five feet deep) as specific yield, S_y, by

$$n_e = n - \theta_r \qquad (4)$$

where n is the total porosity calculated as the bulk density divided by the particle density and θ_r is the residual soil water content which is equivalent to the specific retention (S_r). Rawls et al. do not identify the effective porosity they calculate to be a measure of dead-end pore volumes. Therefore, its application here is merely informative.

Loo (1984) identified three methods for determining effective porosity from field tests: a tracer method, Jacob's method, and seismic tomography.

A tracer method was presented by Halevy et al. (1962) where tracer was injected at a well 250 meters from a pumped well. They assumed a homogeneous medium with a negligible natural gradient. Effective porosity was stated as:

$$n_e = \frac{v}{\pi r^2 b} \tag{5}$$

where v is the volume pumped, b is the thickness of the aquifer, and r is the distance between wells. Determination of the volume of the tracer pumped was most difficult to obtain. They used a functional relationship with breakthrough curves. Application of this method to fine grain soils (the field test was performed on dolomite) would be nearly impossible because of the travel times involved.

Review of Loo's reference to Jacob's work, Jacob (1940), shows no specific reference to effective porosity. Mention of porosity was made in the context of determining the total water volume rather than the effective water volume.

Methods used to determine effective porosity by seismology require extensive geophysical work in the field as well as core analysis in the laboratory. This effort was so substantial and was not within the scope of this work so that it was not critically reviewed.

Measurement of effective porosity has been a laboratory pursuit since the early 1950's. A concerted effort to compare methods was made by Dotson et al. (1951) using ten selected natural and synthetic samples. All samples were indurated. Comparative measurements were made at five different laboratories. Methods used were Boyle's Law, water-saturation and organic liquid-saturation. The average deviation of porosity values (%) from the group mean was ±0.5 porosity percent. The authors did not consider reproducibility of porosity measurements a problem; however, samples with a high clay content gave highly variable results with the water saturation techniques and this is exactly the type of soil under investigation in landfill liners because of its low hydraulic conductivity, i.e., less than 1 x 10^{-7} cm/sec.

Porosity, by definition, involves the volume of voids present within a porous solid matrix. Effective porosity, however, pertains exclusively to that portion of the total void volume available for flow. Various nomenclature can be found in the literature which defines that space which is not contributing to flow and papers which address this topic are approaching effective porosity although from a different viewpoint.

Nielsen and Biggar (1961) discussed "'holdback' as a relative measure of the volume of water not displaced but remaining within the sample." Jackson and Klute (1967) employed the term "dead-end pore volume" and used both transient- and steady-state diffusion coefficients as a method of achieving estimation.

Relyea (1982) uses a porosity term, e, in the transport equation for a one-dimensional porous medium:

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{dx^2} - V_w\,\frac{\partial C}{dx} - \frac{\rho b}{\varepsilon}\,\frac{\partial S}{\partial t} \qquad (6)$$

where S = radionuclide concentration adsorbed on the solid (µg/g)
C = radionuclide concentration in solution (µg/cm3)
D = the dispersion coefficient (cm^2/sec)
x = distance along the flow path (cm)
V_w = ground water velocity (cm/sec)
pb = bulk density of the porous medium (g/cm3)
e = porosity of the medium (cm3/cm3)
t = time (sec)

The same term was used in defining the retardation factor, Rf, and the mass transport units, n, in a column. Following the author's definition of porosity,

$$\varepsilon = \frac{\text{pore or void volume}}{\text{total volume of column}} \tag{7}$$

it is clear that e is equivalent to total porosity and not effective porosity.

In migration studies of radioactive wastes Carlsen and Batsberg (1982) employ column techniques and use a "volume porosity" defined as

$$\varepsilon = V_o/AL = \frac{V_o}{AL} \tag{8}$$

where V_o = dead-volume of an unretarded solute (L^3)

A = cross-sectional area of the column (L^2)

L = length of column (L)

By definition this volume porosity is equivalent to Relyea's porosity; however, Carlsen and Batsberg do caution that V_o should be corrected for the system's dead volume.

By 1984 several new methods appeared further defining void volumes of columns. Street used fluorescence detectors in determining V_m, the void volume of a column experienced by a solute of a given molecular volume. A static exclusion method was developed by Wei Cheng to determine specific pore volume of porous materials, on the basis of size exclusion of some polymer from pore volume in an appropriate solvent.

Obviously, a variety of terminology abounds in the present literature which addresses the topic of "volume available for flow" as related to effective porosity. Despite the "definition" be it chromatographic, agronomic (travel time of nutrients through soil), or environmental (migration of a leachate through an "impervious" soil boundary), the basic question is identical: What is the transport time for a solute to move through a porous media from point A to point B? The thrust of this current study is to better understand effective porosity and develop a technique for measuring it. All relevant information on "effective porosity" has been incorporatedinto a cohesive bibliography.

E. Chemical reactions in porous media.

McAuliffe et al. (1947) studied the direct exchange of deuterium oxide with the hydroxyl groups of two clay minerals, kaolinite and halloysite. They found a rapid H-D exchange with surface OH groups but a slow diffusion into the lattice at elevated temperatures (27°C-170°C).

Five different soil types were chosen by Fancher and Thomas (1954) to study exchange between heavy water and clay mineral samples. Kaolinite samples had no exchange with D_2O within the limits of error of the determination. The halloysite, attapulgite, chabazite, and montmorillonite samples showed large exchanges with D_2O indicating the participation of not only surface hydroxyls but also intralattice hydroxyls. Determinations were done at 200°C for a twenty-four hour period in a Parr bomb.

By using infrared spectroscopy, Romo (1956) observed the exchange of hydroxyl hydrogens with deuterium, D_2O. Samples were of kaolinite (<2μ) and were treated hydrothermically at 300°C and 10,000 psi. The rate of exchange appeared to be a stepwise process in which initially surface hydroxyls participated and finally (post 28 hours) intralattice hydroxyls exchanged by means of diffusion.

A. Klinkenberg (1961) employed a mathematical approach to demonstrate band broadening tendencies as the roles of chemical exchange between species altered. An application of this theory was postulated to be in the area of chromatography of hydrogen and could possibly be used as the technique to monitor for hydrogen when included as a tracer.

Halevy (1964) also investigated the exchangeability of hydroxyl groups in kaolinite and, in contradiction to McAuliffe et al (1947), reported that exchange never exceeded 1 percent. Halevy also determined the exchanging species to be the hydroxyl group as opposed to the hydrogen ion.

Hashimoto et al. (1964) used a mathematical formulation to interpret empirical descriptions of column behavior, a representation of column performance in terms of equivalent column volume and an additional parameter, a Peclet number. By use of sand and soil columns and evaluation of the hydraulic characteristics of each, the empirical formulation gave excellent agreement for the case of a slow isotopic exchange.

Over the period of a decade Stewart (1967, 1972) studied the relationship of tritium and deuterium with soils. In 1967 he investigated the fractionation of both isotopes in the soil water of four clay samples. In Davidson clay samples the isotope effect, E_T for tritium and E_D for deuterium, ratio was initially one and built to a 3-to-1 ratio for E_T/E_D after 17 months of equilibration. A Georgia kaolinite sample did not exhibit the large isotope exchange characteristic of the Davidson clay; this fact is believed attributable to a smaller number of exposed surface hydroxyls. Data covering a montmorillonite exhibited an initial, rapid isotope exchange and that this exchange was equal for tritium and deuterium. Illite results suggested an exchange occurred but with no additional exchange between the 1 1/2 month and 8 month equilibration periods. The illite data seemed to support, to some extent, the belief that more net isotope exchange occurred with deuterium than with tritium.

In 1972 Stewart followed with another study concerning the fractionation in which he stated that "the difference in physical state between tenaciously adsorbed water and bulk pore water does not appear to be sufficient to result in appreciable isotopic fractionation." As such, this factor would not contribute appreciably to retardation of tracer flow velocity. These data support the feasibility of using isotopes of both hydrogen and oxygen and of using isotope effect phenomenon to monitor soil/water interactions.

IV. CURRENT WORK

A. Approach to the problem.

The current study is being approached in two phases, phase one includes work conducted at each field site and phase two includes all work conducted in the laboratory. The field work consists of collecting undisturbed soil samples of sufficient quantity to perform all laboratory tests including replicates. In addition, hydraulic conductivity tests are performed in the field to determine the in-situ vertical hydraulic conductivity of the zone where soil wa3 collected. Laboratory tasks include the determination of standard engineering and agricultural soil and soil/solution characteristics, hydraulic conductivity, dynamic porosity, and static porosity.

Collection of the soil sample.

Illinois State Geological Survey records were examined to select three potential sites for sample collection. Site selection criteria included: sites where samples could be obtained with less than 50 feet of overlying materials to reduce drilling costs, and the soil to be sampled contained no weathered or oxidized zones to maximize the stability of chemical species. The soil to be sampled should further: contain no gravel-sized grains, a small percentage of sand-sized grains (less than 30%), clay minerals limited to primarily illite, and minimal organic carbon. The soils would be collected from below the zone of saturation, and be of sufficient thickness to obtain an adequate amount of sample from one borehole.

Sample collection was accomplished utilizing a specially constructed split-spoon sampler. The sampler contains a 24-inch length of polycarbonate plastic tubing sized to minimize disturbance to the sample and to be used for the column in subsequent laboratory studies. The borehole was drilled with 3 3/4 inch inside diameter hollow stem auger(s). Samples were collected with a standard split spoon sampler until the desired interval was reached. A series of samples were then collected in the specially constructed sampler fitted with polycarbonate tubing.

Conducting the field injection test.

To conduct the field vertical hydraulic conductivity testing, a second borehole was constructed to the same level from which soil samples were collected. A standard split spoon sample was taken and the sampler was pushed back into the same hole to a depth about 6 inches deeper than that penetrated during sample collection. A slug test was then conducted by filling the center of the A rods and sampler with water to a measured level. The water level was then monitored as it declined over time. The vertical hydraulic conductivity was calculated using the analysis method for falling-head permeameter tests (Todd, 1959).

Determining the soil and soil/solution properties.

To determine the various soil and soil/solution properties, samples were preserved in the polycarbonate tubing and transported to the laboratory. The ends of the polycarbonate tubing were sealed to prevent the samples from drying out. After reaching the laboratory, one length of tubing was used to determine liquid limit, plastic limit, optimum moisture content, grain size distribution, clay mineralogy and wilting point. All tests were done following ASTM methods.

Conducting column studies to determine hydraulic conductivities and dynamic porosities.

To determine hydraulic conductivities and dynamic porosities, the polycarbonate tubing was cut such that four 7-inch lengths of soil could be prepared for the column studies. Soil from the end of each tube was removed to a depth of approximately 1 inch, the porous frits and end caps were inserted. Each tube was then ready to be attached to the laboratory apparatus. Hydraulic conductivity determinations of fine-grained soils using constant head permeameter methods is a time consuming test. Therefore, the apparatus allows continual measurement and determination of the hydraulic conductivity while additional tracer tests are performed. The dynamic porosity measurements are determined by injecting triated water, a conservative tracer, into the soil and then eluting the tracer from the soil. Samples of the.outflow from the soil are retreived and breakthrough curves are drawn based on the concentration of tritium measured with a scintillation counter. The dynamic porosity is calculated as the arrival in the outflow of a specified percentage of the conservative tracer.

Determination of static (total) porosity.

After the dynamic porosity tests are completed the sample is removed from the polycarbonate tube, the soil is dried and weighed to calculate the total porosity.

The above tests and procedures will be repeated for soil samples from all three sites.

As column tests are completed, attempts will be made to determine if any statistically significant relationship between effective porosity and other soil characteristics can be identified. Any significant relationship encountered could' be used for estimating effective porosity from other characteristics. If no significant relationship is found, modification of experimental procedures will be investigated to recommend standard testing methods for effective porosity measurements.

B. Equipment design.

The laboratory tests required specially designed equipment to accomodate the demands of successful tracer studies (figure 3). Extremely low flow rates and the resulting great length of time required to conduct tests under normal hydraulic gradients required the use of special apparatus. A computerized flow control and sample collection system was designed and constructed. Integral parts of the system include: the fixed head source, the flow measurement accumulator, the inlet pressure sensor, the tracer injection port, the soil column, the outlet pressure sensor, and the sample collection device.

The fixed pressure source is maintained by a regulated supply of a mixture of nitrogen and carbon dioxide. The pressurized gas contacts the water in the supply reservoir and in each accumulator. The supply reservoir is capable of supplying water to the four accumulators simultaneously.

The flow measurement accumulator is a device used when very low flow rates are encountered (Daniel et al., 1984). The accumulators in this system are constructed of 2 ml glass pipets enclosed in a plexiglass cylinder. Flow is determined by measuring the time it takes the water/gas interface in the accumulator to move from an upper to a lower level sensing device. This is accomplished by the triggering of two electric eyes and recording the time

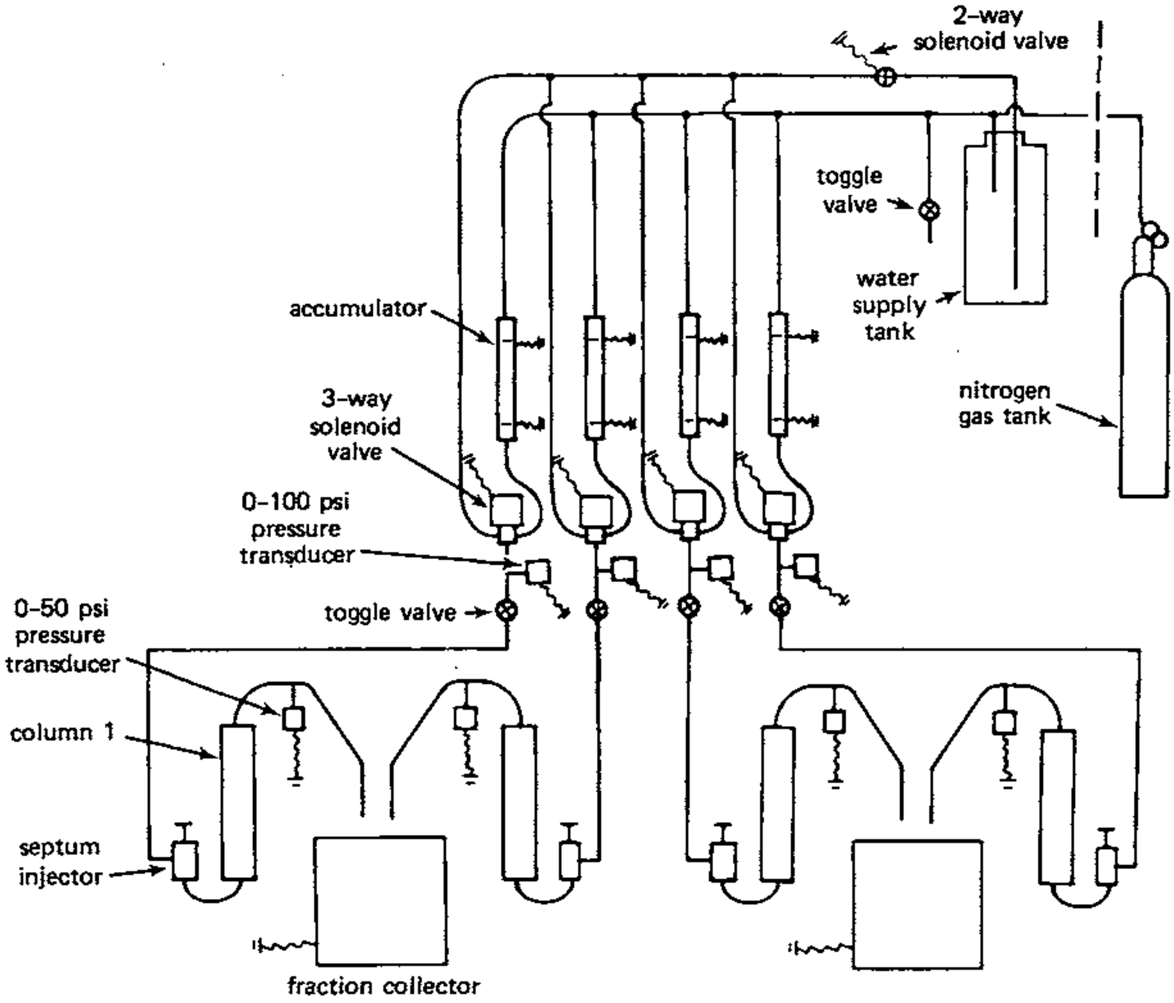


Figure 3. Diagram of the automated four-column system

when the level reaches the upper and lower sensors. Also, the electric eye sensors control the actuation of a three-way valve to refill the accumulator.

The inlet pressure sensor is a strain-gage transducer. The transducer is connected to the flow system with appropriate stainless steel fittings designed to minimize dead space.

The tracer injection port allows insertion of small quantities of solute into the flow system with minimal disturbance of the system.

The soil column is constructed of polycarbonate plastic which has an inside diameter of 1.25 inches and an outside diameter of 1.50 inches. The outside diameter of the tubing is accommodated by the split-spoon sampling device which was adapted for the soil sample collection.' The top and bottom of each column (end caps) is constructed of Delrin plastic. The end caps are milled to accept a stainless steel frit of 5 micrometers pore size and a stainless steel fitting to connect to the inflow and outflow tubing.

The outlet pressure sensor is a strain-gage type transducer similar to the inflow sensor, however, it is rated for a lower pressure. The transducer is connected to the flow system with a specially constructed stainless steel fitting to minimize the internal volume.

The sample collection device is an ISCO Retriever II fraction collector. This device controls the separation of column outflow for analysis. It also provides a measure of the column outflow rate. The fraction collector signals the computer when sample changes are made.

V. RESULTS TO DATE

A. Accuracy and precision of all measurements.

The accuracy, the closeness to the correct number, and the precision, repeatability of successive measurements of that number, are dependent on the experimental procedures and quality assurance of the test. All of the experimental procedures follow standard chemical and engineering methods, and a quality assurance report was prepared for the project manager; however, these are merely prerequisites to explanation of actual performance of equipment and procedures. The accuracy and precision of hydraulic conductivity, effective porosity and other soil/solution properties are presented below.

Hydraulic conductivity.

Hydraulic conductivity will be determined in the field by a variation of the slug test and analyzed by the falling-head permeameter method (Freeze and Cherry, 1979). The hydraulic conductivity (K) is calculated as

$$K = \frac{aL}{At} \ln \left(\frac{H_o}{H_1}\right) \qquad (9)$$

where a is the cross-sectional area of the drop pipe, L is the length of the soil, A is the cross-sectional area of the soil column, t is the time of the test, H_0 is the head at the beginning of the test, and H_1 is the head at time, t, of the test.

The accuracy of the test is dependent on: the effectiveness of the seal between the split-spoon sampler used as the test orifice and the borehole; the measurement of the length of soil in the sampler; and the measurement of the reference head at the bottom of the split-spoon sampler from which H_0 and H_1 are measured.

A poor seal cannot be monitored unless it appears that results are unrealistic. Error in measurement of the volume of water injected (the slug) and of water levels are known.

In the laboratory, hydraulic conductivity (K) will be measured by the constant-head permeameter method (Freeze and Cherry, 1979) by

$$K = \frac{QL}{AH} \qquad (10)$$

where Q is the flow rate into the column (assuming steady-state flow), L is the length of the soil, A is the cross-sectional area of the soil, and H is head differential across the column (the difference measured from the transducers minus a premeasured friction loss due to fittings).

The hydraulic conductivity is determined every five seconds so the size of the data set will be large, such that statistically significant information of the precision will be obtained. Changes in conductivity over time will also be observed.

To date, measurements of hydraulic conductivity are determined neglecting head loss in the column end fittings. Though this loss should be equivalent throughout all tests, it has not been evaluated. Therefore, the calculated hydraulic conductivity is not the actual conductivity of the medium itself.

B. Experimental results.

Initial experiments were conducted on a temporary apparatus in order to study the behavior of various sized particles in a chromatographic situation. The apparatus consisted of an Altex pump, Model 110 A, in series with a Data Instruments pressure transducer (100 psi), SSI septum injector, column, a second pressure transducer (50 psi), and a Gilson Filter Fluorometer, Model 121. Both inlet and outlet pressure transducers were monitored on a Cole Parmer dual-pen strip chart recorder. Fluorometric data was interpreted on a Hewlett-Packard 3390 A Integrator.

Four ranges of particle sizes were utilized as the column packing in these experiments:

Table 2. Description of Column Packing Particles

Column Parameters #	Particle Size µm	Particle Composition	U.S.G.S. Size Classification
1	250-500	Ottawa Sand	Medium Sand
2	106-250	Ottawa Sand	Fine Sand
3	10- 75	Glass Beads	Silt
4	5- 20.	Glass Beads	Silt/Clay

Particles of this size fall within the constraints, as mentioned by Gray, (1968) regarding column diameter versus particle diameter. By maintaining a 30 or 40 to 1 ratio between the column and particle diameters, local velocity effects, such as channeling or radial velocity gradient, can be effectively minimized. This system was used as a column for the separation of an organic tracer, Rhodamine WT, from the $1X10^{-3}M$ $NaHC0_3$ buffered water. All columns were run at a minimum of seven different flow rates in the range of 5 ml/min to 0.1 ml/min and all runs were done in duplicate.

Results to date indicated that columns of this nature can and do perform as an effective chromatographic tool. Separation of the Rhodamine WT spike was attained with the expected Gaussian curve observed at greater pore water velocities. Recovery of the tracer was greater than 85% in all cases. However, effluent concentration curves broadened more at lower pore water velocities, i.e. 10^{-3} cm/sec. This phenomenon was to be expected since diffusive transport became more significant at these velocities. Band broadening is a real-time measure of diffusion processes under controlled flow conditions.

Batch sorption tests were conducted on the four column packing materials. Concentrations tested ranged from 0.119 ppm to 119 ppm. The tests were conducted for a period of eight days. The only material which showed a statistically significant decrease in fluorescence was the glass beads, 10-75 µm diameter, and this trend was noted only at the end of the eight day test.

The decrease in fluorescence was observed at three tracer concentrations, 119 ppm, 11.9 ppm and 0.119 ppm. The largest sand size particles, 250-500 µm, exhibited a 4.73% variance from standards but only at the maximum time exposure.

Hydraulic conductivities, K, were calculated at every flow for each column. With increasing flow (or pressure) K increased linearly to a maximum after which it tailed off (see figure 4). This trend would be supportive of Relyea's statement that at high velocities effective pore volume of a sample can decrease. With the diminished pore volume a rise in pressure is necessitated if velocity is to remain constant. This trend for a non-linear increase in pressure gradient at higher flow velocities can be seen in figure (5). This trend also served to support the theory of diminished pore volumes at higher velocities.

The total porosity of all columns has been determined statically (refer to Table 3) according to the following formulation:

$$V_v = V_{column} - V_{solid} \qquad (11)$$

where:

V_v = volume of voids

V_{column} = total volume of column

V_{solid} = total volume of solids
[(wt. of solid in column)/(bulk density of solid)]

and $$E_{TOT} = (V_v/V_{column}) \times 100 \qquad (12)$$

where:

E_{TOT} = total porosity (%)

By this definition total porosity includes all void space whether interconnected or isolated. This concurs with the use of the term as given by Dotson et al. (1951), Coats and Smith (1964), and Corey and Horton (1968).

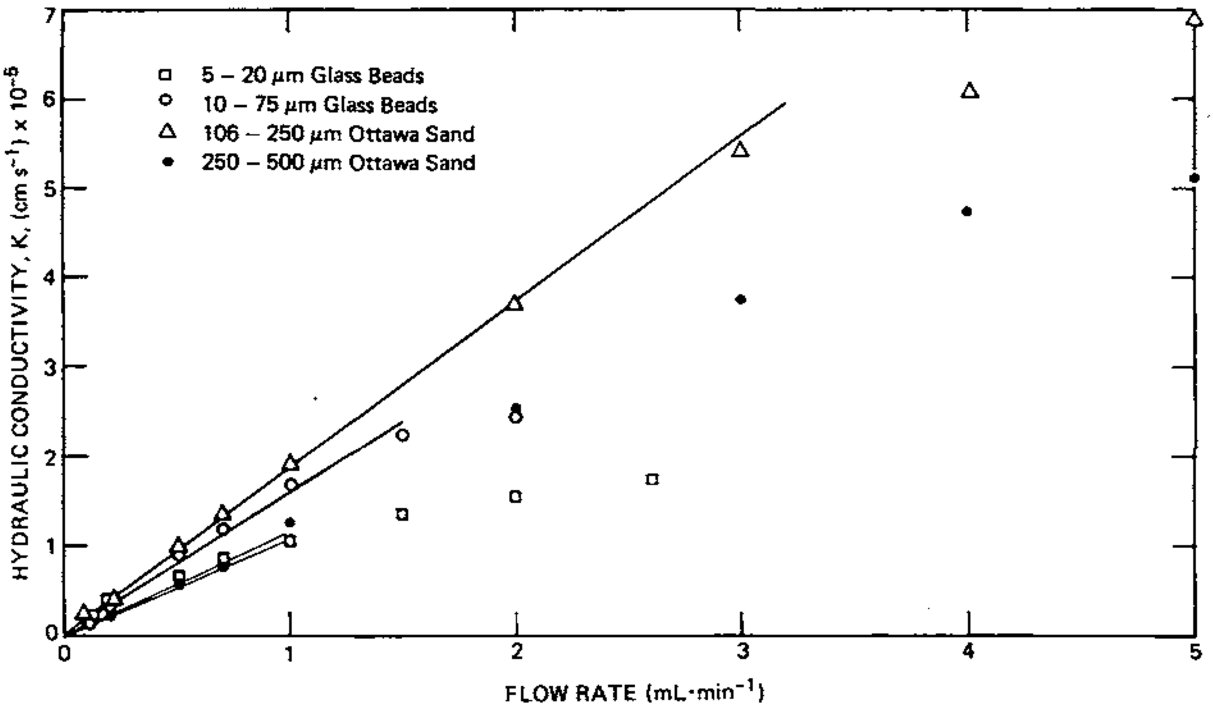


Figure 4. Comparisons of flow rate and hydraulic conductivity.

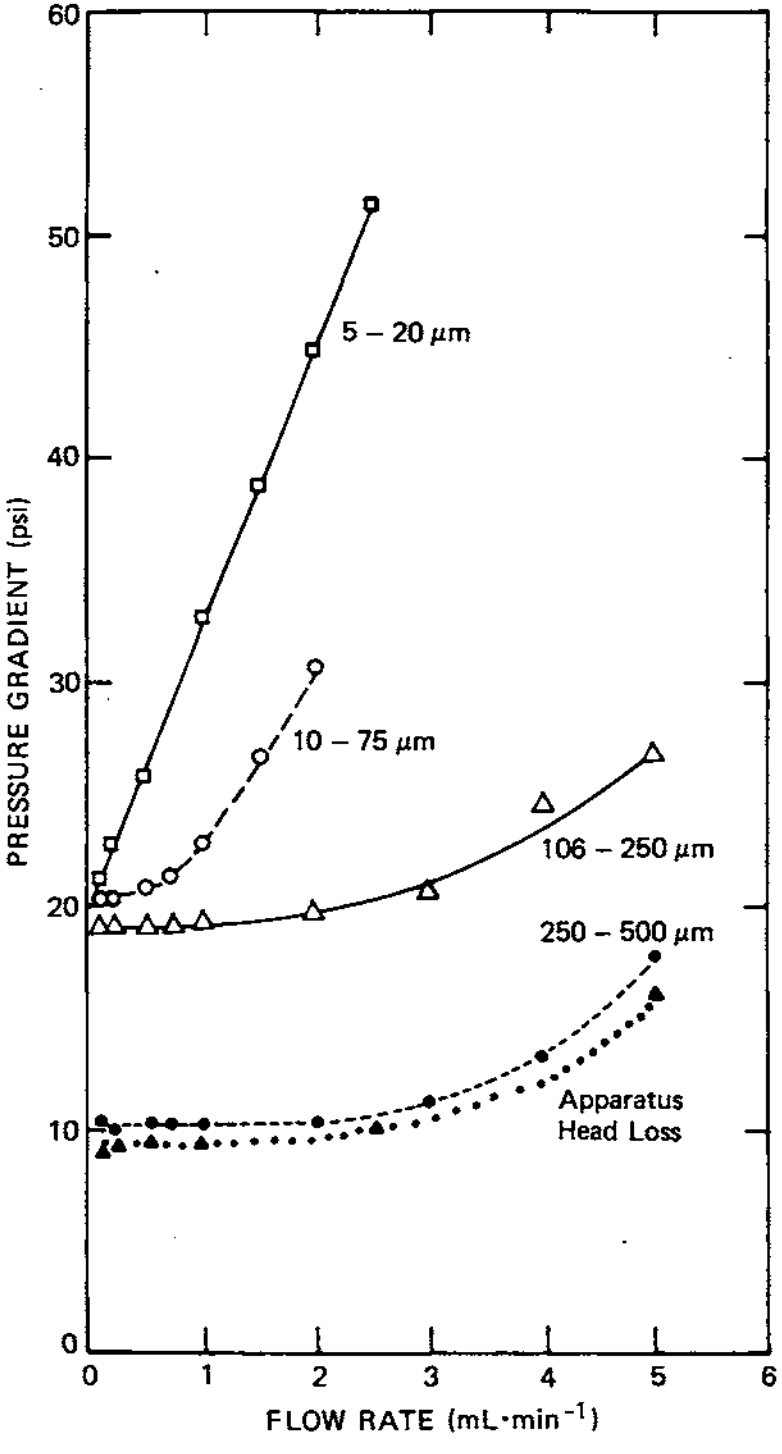


Figure 5. Comparisons of flow rate and resultant pressure gradient.

Table 3. Static and Dynamic Porosity Measurements

	V_v	E_{TOT}	V_{DYN}*	n_d
Column	Void Volume (Static)	Total Porosity	Pore Volume (Dynamic)	Dynamic Porosity
#	ml	%	ml	%
1	35.6	36.5	38.64±.33⊙	40.0H.3⊙
2	43.1	45.3	37.68±.28⊙	39.5±0.4⊙
3	37.1	38.4	37.64±.30•	39.2±0.7•
4	29.1	29.1	30.49±.34⊙	34.0±0.3⊙

⊙ Average of 16 Runs
• Average of 10 Runs
* V_{DYN} is equivalent to V_0 (as defined by Horvath and Lin)

A porosity based upon elution data may be defined as a dynamic porosity. This definition is also employed by Carlsen and Batsberg (1982), Dotson et al. (1951), Horvath and Lin (1976), Relyea (1982), and Schweich and Sardin (1981). The method of calculation is:

$$n_d = (V_{DYN}/V_{column}) \times 100 \qquad (13)$$

where n_d = dynamic porosity

V_{DYN} = volume determined by fluid flow of a tracer

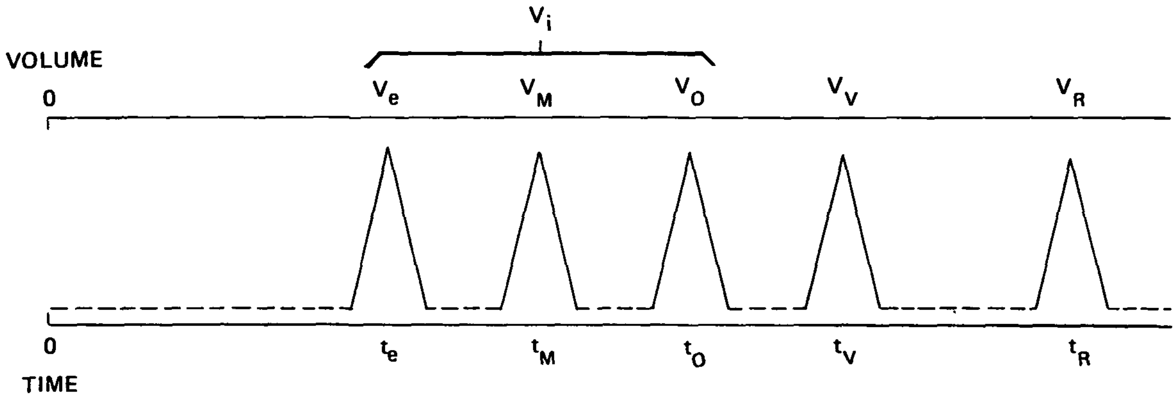
The values of dynamic porosity are equal to or greater than those calculated for total porosity in these four cases. This can not be attributed to retention due to the results of the adsorption studies. A combination of experimental error, packing, and size distribution are more likely causes. This was expected since the materials used for columns 3 and 4 were uniform glass spheres and exhibited little variability of size distribution. Consequently, these types of packing yield little, if any, detectible dead-end pore space (Graton and Fraser, 1935). Columns 1 and 2 were composed of Ottawa sand two to five hundred times greater in particle diameter than the glass beads composing columns 3 and 4. This large grain size and the decrease in both sphericity and roundness contributed to a porosity which is equal to the total porosity within experimental error.

Horvath and Lin (1976) defined three different hold-up times, t_e, t_m, and t_o, and corresponding hold-up volumes, V_e, V_m, and V_o for a variety of solutes in the mobile phase. These factors will be evaluated by varying the size of the tracer in a series of experiments and are graphically illustrated in figure 7.

With respect to the preliminary experiments for columns 1 and 2, the chromatographic volume equals the volume of voids, $V_o = V_v$. (Horvath and Lin's V_o is equivalent, by definition, to the previous V_{DYN}, a volume determined by fluid flow of a tracer.) Therefore, all voids within the column participate in fluid flow. The large grain size, the narrow grain size distribution, and the lack of both sphericity and roundness of particles are all factors contributing to the equivalency of dynamic and static void volumes. Thus, the unsorbed solute, Rhodamine WT, explored mainly the interstitial volume, V_e. The intrastitial volume, V_i, was very small.

Columns 3 and 4 are composed of non-porous glass beads, a column material impervious to solute and allowing no intrastitial fluid volume, i.e. $V_i = 0$. The use of Rhodamine WT therefore provides an exact indication of interstitial volume, V_e. Again, in these two columns V_O is coincidental with V_e (i.e. $V_0 = V_e = V_v$) the narrow grain size distribution is probably the overriding factor for these close porosity measurements.

The soils chosen for this project are to be of fine-grained materials with a clay component. Expected hydraulic conductivities (1×10^{-7} cm/sec) are a hundred-fold lower than those observed with the four columns. Resulting porosities, therefore are expected to have considerable intrastitial



where V_e – interstitial fluid volume
V_i – intrastitial fluid volume
$V_i = V_O - V_e$
V_M – unabsorbed solute volume
$V_M = V_e + \psi V_i$
V_O – chromatographic hold-up volume
V_V – void volume (statically determined)
V_R – volume of a retarded solute
ψ – fraction of intraparticulate fluid space accessible to solute

Figure 6. Schematic representation of different mobile phase hold-up volumes (and hold-up times) measured with tracers in chromatography experiments.

volumes. Dead-end pore volume will become a recognizable factor with these pore and particle size distributions over a range of flow rates. The chromatographic hold-up volume, V_o, can be measured by use of the conservative tracer, HTO. A second tracer of larger molecular dimension, i.e. Rhodamine WT or poly (ethylene oxide), can be used to determine the minimum interstitial volume available for flow. This information should lead to a bank of porosity values as defined by the molecular dimensions of the two tracer molecules.

VI. FIRST YEAR PROGRESS

Progress during the first year has been as planned. • The review of pertinent literature has been completed and is briefly summarized in this report. The agronomic and hydrogeologic literature confirmed the lack of a straight-forwarded method for measuring effective porosity. Chemical or chromotographic literature supports the application of chromographic tracer studies as a means for measuring effective porosity.

Preliminary development and testing of the soil sampling and laboratory testing apparatus has been completed. Soil samples were collected from a site where drilling was being conducted for another project. Tracer studies and hydraulic conductivity measurements have been completed on glass spheres and Ottawa sand. Hydraulic conductivity tests have been conducted on the collected soil sample.

Progress during the first year has been rewarding. The research team has confidence in its research plan and is in a position to complete the project on time. The results of the completed project should fulfill the goals of this project and provide the scientific community with a significant step toward understanding the movement of solutes through fine grained geologic materials.

VII. SECOND YEAR SCHEDULE

Samples from one of the three selected sites will be collected within the first two months of year two. Simultaneous hydraulic conductivity and tracer tests will be conducted on these samples during the winter months. Samples from the second site will be collected in February and those from the third site will be collected in June 1985. Approximately three months are allocated for samples from each site.

Traditional engineering and agricultural tests will be performed on all samples as soon as collected. Regression of test results will be performed to search for predictive or suitable estimation procedures.

In addition to the final project report, papers documenting the effective porosity measurement technique are planned for two scientific journals. A third paper addressing the importance of effective porosity measurements in predicting rates of solute migration through geologic materials also is planned.

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