PNNL-11389
UC-900

Final Project Report

CRADA with Beckman Instruments and Pacific Northwest National Laboratory (PNL-013): Development and Commercialization of the Unsaturated Flow Apparatus (UFA) Using Characterization of Aridisols

Judith Wright
James Conca

October 1996

Prepared for U.S. Department of Energy
under Contract DE-AC06-76RLO

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
by Battelle

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Development and Commercialization of the Unsaturated Flow Apparatus (UFA) Using Characterization of Aridisols

PURPOSE

The objective of this Cooperative Research and Development Agreement (CRADA) was to develop and commercialize a technology conceived by scientists at Pacific Northwest National Laboratory (PNNL) and manufactured by Beckman Instruments , Inc. (Beckman), and to apply this technology to the characterization of arid soils. The technology is the Unsaturated Flow Apparatus (UFA). The UFA provides a highly efficient method of direct, rapid measurement of hydraulic conductivity and other flow properties according to Darcy-Buckingham principles because the operator controls both the fluid driving force, using an ultracentrifuge, and the flow into the sample while it is spinning, with a rotating seal assembly. The concept of using centrifugation to significantly decrease the time needed, from years or months to days, for study of subsurface transport, particularly under unsaturated conditions, was conceived by James Conca, Ph.D., and Judith Wright, Ph.D., in 1986. The prototype UFA was developed in 1988 because there was a need to rapidly and accurately determine transport parameters in soils, sediments, and rocks for the Grout Waste Disposal Program. Transport parameters are critical to modeling outcomes for site-specific solutions to environmental remediation and waste disposal problems.

The objective of the CRADA was to design and develop a commercially viable UFA instrument using arid western soils from DOE sites as test materials. Under the original plan, this would expand Beckman's product market from largely biomedical instruments to include an instrument with applications to the environmental, waste disposal, soils, hydrological and agricultural fields. However, during the implementation of the CRADA, Beckman's application research scientists decided that they could not provide appropriate technical application support for these new fields that are outside of their expertise. Therefore, the UFA technology and its commercial development and application became the centerpiece for a DOE spinoff business as the final objective of the CRADA. This business, Northwest Environmental Services, Testing and Training (NESTT): 1) is an innovative soil testing laboratory providing analytical service work to DOE DoD, and private industry, using the UFA Method and other techniques; 2) continues to develop and test new generations of the UFA instrument; and 3) markets and sells the instrument. All of these objectives have been fulfilled.

Established Need For New Technology

Both commercial and government facilities have generated significant amounts of wastes, categorized as hazardous, radioactive, or mixed (both hazardous and radioactive). Much liquid and solid hazardous waste has been directly discharged to shallow land sites above the water table. We have gradually realized that these wastes, and the leached solutions from them, threaten our environment and groundwater resources. Consequently, contaminated sites at DOE and other federal and commercial facilities have been targeted for remediation and restoration under EPA (CERCLA and RCRA) and state regulations. More importantly for the 21st century, and as a result of dwindling global water supplies, municipal, industrial and agricultural water needs require accurate evaluation and determination of water movement and distribution.

The prediction of water migration and contaminant behavior requires input values of transport parameters for the range of soils, sediments, and rocks at each location. These parameters include hydraulic conductivity, diffusion coefficient, vapor diffusivity, and retardation factor. Performance assessment and other predictive models have unanimously identified these parameters, and variations associated with their vertical and lateral distribution, as the key parameters needed to successfully model aqueous systems and determine appropriate remediation and water development strategies. Long experimental times and extreme difficulties in obtaining data by traditional methods have resulted in the use of estimates and extrapolations of these parameters, both of which are non-defensible. The UFA Method directly measures these parameters in hours to days in soils, sediments, or rocks, thus, filling the void in information and data of this type. Appendix A provides a recent article showing the types of problems addressed and solved by the UFA. This article was also written as a marketing publication and appeared in the December 1995 issue of the trade journal *Soil and Groundwater Cleanup*.

SUMMARY OF ACTIVITIES

Figure 1 shows a time line summarizing activities and events significant to this CRADA Project (see also Table 1).

Establishment of CRADA between DOE/PNNL and Beckman

In February 1992, PNNL and Beckman Instrument, Inc. formally entered into this CRADA. Beckman is a wholly U.S.-owned international corporation specializing in the development, marketing, sales and applications support of biomedical and analytical instrumentation. Beckman's headquarters are located in Fullerton, California, and its special products manufacturing facility is located in Palo Alto, California. Beckman has regional sales offices and service support specialists in every region of the United States and key industrial nations.

DOE through the Offices of Energy Research and Environmental Management supported this CRADA between PNNL and Beckman Instruments, Inc. to continue development of the UFA technology and to introduce the UFA Method to other areas of research and application that would benefit from it. This CRADA opened new possibilities for Beckman in environmental fields, such as remediation and restoration, soil science, hydrology, agriculture, and engineering. The CRADA project consisted of two interactive components: the main portion from Energy Research (ER) included research and development at PNNL with observations and feedback from the experimental work on instrument performance to Beckman engineers, and the Environmental Management (EM) portion included joint demonstration, testing and evaluation by PNNL in collaboration with Beckman Instruments. Work activities concentrated on soils, sediments, groundwater chemistries, contaminant/solute/solvent mixtures, and conditions of immediate need at DOE sites. A CRADA Document, a CRADA Joint Work Statement and a CRADA Commercialization Plan were developed (see PNNL Technical Report PNL-9424).

1986	Development of concept
1987	Funding of Prototype development
1988	Manufacture of Prototype
1988-91	Proof of Principle and initial marketing of idea for widespread application
1991	Submittal to ER and EM-50 (RDDT&E)
1991-95	Participation in VOC Arid Integrated Demonstration in support of field demos
1992	Establishment of joint ER/EM CRADA with Beckman Instruments, Inc.
1992	Development of second generation UFA under the CRADA
1990-92	UFA used in Japanese high-level nuclear waste program
1992-94	CRADA Collaborations with INEL, LLNL, PNL, LANL, USGS, Japan and EPRI
1994	CRADA hosted the first International Soil Physics Workshop on Unsaturated Flow
1994	Establishment of UFA spinoff business, NESTT
1994	First commercial UFA sold to Washington State University
1994	Second generation UFA sold to Pacific Northwest Laboratory
1995	Second generation UFA sold to United States Geological Survey
1995	Second generation UFA sold to Los Alamos National Laboratory
1995	Third generation UFA developed under the CRADA
1995	Third generation UFA sold to the Japanese Geological Survey
1996	January - Completion of CRADA NESTT now has six employees and $301K in DOE contracts ASTM Procedure for the UFA accepted by Subcommittee D18.21

Figure 1. Timeline for Major Events In the UFA CRADA

Project Team

The alliance between PNNL and Beckman consisted of a diverse project team. The team had been established to accomplish the commercialization of the UFA (Figure 2). PNNL members possessed expertise in many areas which include geology, geochemistry soil science, hydrology, environmental sciences, and engineering. Beckman brought product development, applications, marketing, engineering, and management expertise. Beckman team members included Philip Hutcherson (product planning program management), Dr. Allen Furst (research and applications management), Dr. Stephen Little (research and applications), David Schiessler (marketing), Curt Talbott (custom products management), Dennis Tragarz (mechanical engineering), and Howard Weir (finance). PNNL team members included Dr. Judith Wright (CRADA program management, geology, soil science, and geochemistry), Dr. James Conca (geology, soil science, and hydrology), Michaela Mann (technical communications), Karen Rose (program administration), and Duane Deonigi (administrative review).

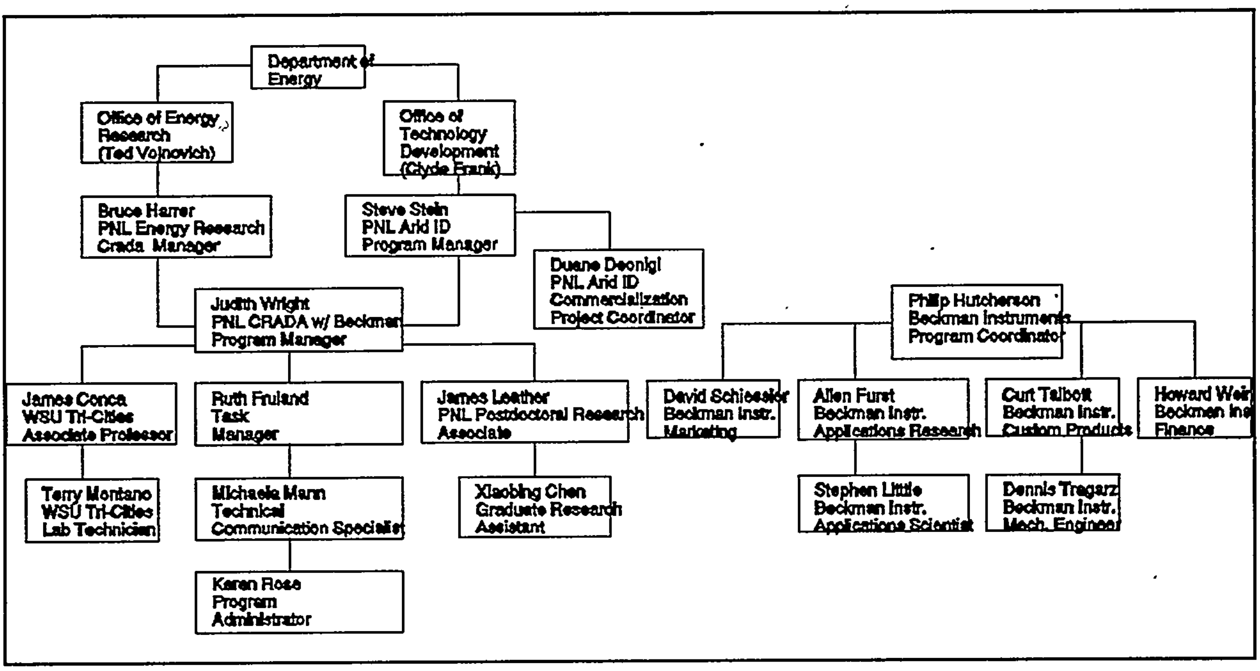

FIGURE 2. Project Organization Structure

Table 1. CRADA Publications (by date from most recent)

ASTM Standard Test Procedure (J. L. Conca, 1996, in press) "The UFA Method for Determining Hydraulic Conductivity and Relative Permeability as a Function of Water Content or other Liquid Content," Submitted to ASTM D18.21 Subcommittee on Ground Water.

Nelson, P. and J. L. Conca, (1996) *Present-Day Porosity and Permeability in Lacustrine Strata and Fallout Tuffs*, U. S. Geol. Survey Open File Report, USGS, Reston, Virginia (in press).

Wright, J. V., L. M. Peurrung, T. E. Moody, J. L. Conca, X. Chen, P. P. Didzerekis and E. Wyse (1995) *In Situ Immobilization of Heavy metals in Apatite Mineral Formulations*, Technical Report to the Strategic Environmental Research and Development Program, Department of Defense, Pacific Northwest Laboratory, Richland, WA, 81 p.

Khaleel, R., J. F. Relyea, and J. L. Conca (1995) "Estimation of van Genuchten-Mualem Relationships to Estimate Unsaturated Hydraulic Conductivity at Low Water Contents", *Water Resources Research*, vol. 31, p. 2659-2668.

Conca, J. L. and J. V. Wright (1995) "Find Transport Data Faster: A New Technology for Determining Transport Properties in Soil and Other Porous Media", *Soil and Groundwater Cleanup*, December, p. 14-26.

Conca, J. L. and J. V. Wright (1995) "A New Technology for Determining Transport Parameters in All Porous Media", in *Proceedings of the American Nuclear Society Topical Meeting on Mathematics and Computations, Reactor Physics, and Environmental Analyses*, American Nuclear Society, La Grange Park, Illinois, vol. 1, p. 165-180.

Moody, Timothy E. and Judith Wright. 1995. *Adsorption Isotherms: North Carolina Apatite Induced Precipitation of Lead, Zinc, Manganese and Cadmium from the Bunker Hill 4000 Soil*, Technical Report BHI 00197, Bechtel Hanford, Inc., Richland, WA, 21 p.

Lindenmeier, C. W., R. J. Serne, J. L. Conca, A. T. Owen, and M. I. Wood (1995) *Solid Waste Leach Characteristic and Contaminant-Sediment Interactions, Volume 2: Contaminant Transport Under Unsaturated Conditions*, Technical Report PNL-10722, Pacific Northwest Laboratory, Richland, WA.

Zhou, W., J. Conca, R. Arthur and M. J. Apted (1995) *Analysis and Confirmation of Robust Performance for the Flow-Diversion Barrier System within the Yucca Mountain Site*, Technical Report IED-9408, INTERA Sciences Inc., Environmental Division, Denver, Colorado.

Conca, J. L. and J. V. Wright (1994) "The UFA Technology for Characterization of In Situ Barrier Materials", in *Proceedings of the 33rd Hanford Symposium on Health and the Environment*, Department of Energy, Pasco, Washington, vol.2, p. 1179-1193.

Wright, J. V. and J. L. Conca (1994) "Direct Measurements of Transport Properties are Essential for Site Characterization", in *Proceedings of the Spectrum '94 International Topical Meeting on Nuclear and Waste Management*, Amer. Nuc. Soc., La Grange Park, Il, vol. 1, 438-446.

Conca, J. L. and I. R. Triay (1994) "Selenite Transport in Unsaturated Tuff from Yucca Mountain," *Proceedings of the Fifth International High-Level Radioactive Waste Management Conference*, American Nuclear Society, La Grange Park, Illinois, vol. 4, p. 2175-2182.

Wright, J. V., J. L. Conca, and X. Chen (1994) *Hydrostratigraphy and Recharge Distributions from Direct Measurements of Hydraulic Conductivity Using the UFA™ Method*, PNL Technical Report PNL-9424, Pacific Northwest Laboratory, Richland, WA, 150 p.

Fredrickson, J. K., F. J. Brockman, B. N. Bjornstad, P. E. Long, S. W. Li, J. P. McKinley, J. L.

Conca, T. L. Kieft, and D. L. Balkwill (1994) "Microbiological Characteristics of Pristine and Contaminated Deep Vadose Sediments", *Geomicrobio. Journal*, vol. 11, p. 95-107.

Conca, J. L. (1993) *Measurement of Unsaturated Hydraulic Conductivity and Chemical Transport in Yucca Mountain Tuff*, Technical Report LA-12596-MS, Los Alamos National Laboratory, Los Alamos, NM, 28 p.

Serne, R. J., J. L. Conca, V. L. LeGore, K. J. Cantrell, C. W. Lindenmeier, J. A. Campbell, J. E. Amonette, and M. I. Wood (1993) *Solid Waste Leach Characteristic and Contaminant-Sediment Interactions, Volume 1: Batch Leach and Adsorption, and Sediment Characterization,* Technical Report PNL-8889, Pacific Northwest Laboratory, Richland, Washington.

Wright, J. V., J. M. Leather, and J. L. Conca (1993) "The UFA™ Method for Site Characterization and Remediation", in *Proceedings of the Environmental Remediation '93 Conference*, Augusta, GA, vol. 2, p. 819-826.

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Conca, J. L., M. J. Apted and R. C. Arthur (1993) "Aqueous Diffusion in Repository and Backfill Environments", *Scientific Basis for Nuclear Waste Management XVI*, Materials Research Society Symposium Proceedings, vol. 294, p. 395-402.

Conca, J. L., M. J. Apted and R. C. Arthur (1993) "Direct Determination of Transport Properties in Repository Materials", *Scientific Basis for Nuclear Waste Management XVI*, Materials Research Society Symposium Proceedings, vol. 294, p. 839-844.

Arthur, R. C., M. J. Apted and J. L. Conca (1993) "Dealing with Uncertainty in the Chemical Environment in Bentonite Backfill", *Scientific Basis for Nuclear Waste Management XVI*, Materials Research Society Symposium Proceedings, vol. 294, p. 389-394.

Conca, J. L. and J. V. Wright (1992) "Flow and Diffusion in Unsaturated Gravel, Soil and Whole Rock", *Applied Hydrogeology*, vol. 1, p. 5-24.

Conca, J. L. and J. V. Wright (1992) "Direct Determinations of Unsaturated Flow and Transport", *Proceedings of the 12th Annual Hydrology Days Conference*, Fort Collins, CO, p. 103-116.

Conca, J. L. and J. V. Wright (1992) "A New Technology for Direct Measurements of Unsaturated Transport", *Proceedings of the Nuclear and Hazardous Waste Management Spectrum '92 Meeting*, American Nuclear Society, vol. 2, p. 1546-1555.

Commercial Instrument Development (Office of Energy Research)

During the course of this CRADA, scientists at PNNL and WSU worked with Beckman engineers to develop several configurations for the UFA. There are two types of ultracentrifuges. The L8-UFA can attain speeds up to 10,000 rpm, temperatures from 0°C to 150°C, and uses all three rotor sizes, and costs approximately $105k. The J6-UFA can attain speeds up to 6,000 rpm, temperatures from -20°C to 40°C, and uses one rotor size (at present), and costs approximately $55k. There are two types of rotors. The Hy-sed 40 rotor accommodates samples sizes up to 50 cm^3, and costs approximately $29k The Hy-sed 90 rotor accommodates two samples sizes; a sample chamber up to 100 cm^3, or a sample chamber that accepts a 2.5-inch diameter by 2-inch long Shelby Tube (280 cm^3). The Hy-sed 90 costs approximately $60k. There are three rotating seal assemblies. The face seal is used with water and for measuring physical transport properties. The mechanical seal is used for chemical studies. The ferrofluidic seal is used for non-aqueous phase liquids. Various small accessories were developed for different sample types and applications. Each client can obtain a particular configuration of the UFA components depending upon application and budgetary constraints.

The VOC-Arid Integrated Demonstration Program (VOC-Arid ID)

The EM-50 VOC-Arid ID Program (1991-95) allowed the UFA instrument to be tested and demonstrated in a large field operation in which the UFA method supported other technologies and programs, e.g., the Expedited Response Action, In Situ Bioremediation, Subsurface Science Program, and Vapor Extraction Projects. During this time, the next generation UFA instruments were designed and built under the CRADA. Presentations of scientific results at numerous professional meetings, invited academic seminars and technical conferences produced increased interest in the technology, both to purchase new UFA instruments and for providing service work using existing UFA instruments.

Establishment of the Spinoff Business

As part of the CRADA, Alan Furst and Stephen Little from Beckman were trained in the UFA Lab and attended meetings and conferences with Judith Wright and James Conca. However, after almost two years, Furst and Little decided that Beckman, whose core market is biomedical, could not effectively market and technically support the UFA with existing personnel. Therefore, Beckman asked Wright and Conca to support and market the UFA. It was decided by the project team that the best option for accomplishing this, as well as meeting the objectives of the CRADA, was to establish a spinoff business, centered around the UFA. This business provides service work and continues to develop, market, and sell the UFA. Staff members from this business provide technical applications support for the UFA technology. This business was established in September, 1994 in Richland, WA, and is called Northwest Environmental Services, Testing and Training (NESTT). At the time of this writing, NESTT has six employees, and contracts with DOE and subcontractors totalling over $300k.

SIGNIFICANT ACCOMPLISHMENTS

There have been several significant accomplishments: 1) a new generation UFA technology was developed and commercialized; 2) five commercial units were sold in the United States and Japan, 3) the DOE spinoff business, NESTT, was established and is performing work for DOE national laboratories and subcontractors that could not be obtained elsewhere, and employs six staff (Appendix B); 4) an ASTM Test Procedure was written and approved for the UFA Method (Appendix C); 5) increased fundamental scientific understanding about unsaturated systems resulted from this CRADA, especially in subsurface hydrostratigraphic and recharge mapping (Table 1 shows the publications generated by this CRADA project), and 6) two masters and one doctoral theses were generated from this CRADA. Several collaborations with national laboratories resulted from the CRADA, including collaborations with INEL, LANL, LLNL, and SNL. Appendix D is a Los Alamos Technical Report that resulted from this CRADA.

SIGNIFICANT PROBLEMS

Several technical problems were overcome during the course of this CRADA. The major scientific problem was the resistance of the scientific community to a new method, but three years of seminars, publications and meetings have resulted in acceptance by the overall community and the approval of an ASTM Test Procedure for the UFA. Another problem was the failure of the DOE Environmental Management program (EM-50) to provide all of the funding it committed to in the original CRADA.

DOE/LABORATORY BENEFITS REALIZED

The two major benefits of this CRADA to the core missions of DOE are the development of a new technology and scientific method that directly measures transport properties in soils, sediments, and rocks, and the establishment of a spinoff business, NESTT, that can provide this testing service to DOE national laboratories and private industry. As a result of the Beckman-DOE collaboration under this CRADA, the UFA is a commercial product. There are six UFAs in operation at NESTT, two at PNNL, one at LANL, one at the U. S. Geological Survey at the Nevada Test Site, and one in Japan. Appendix E contains the UFA Tech Briefs used to market the applications of the UFA, with case histories of DOE projects.

INDUSTRY BENEFITS REALIZED

As a result of this CRADA, Beckman Instruments, whose core market is biomedical, now has a new market in environmental science and has added the UFA product line to its manufacturing. Other testing laboratories in the environmental and petroleum industries have expressed an interest in purchasing a UFA for their laboratories and are using the spinoff business, NESTT, to provide these services for the present.

SCIENTIFIC AND ENGINEERING BENEFITS REALIZED

A new method of measuring transport properties, the UFA Method was developed and has gained acceptance in the scientific and engineering communities. Evidence of the acceptance of the technique came with approval of the ASTM Test Procedure for the UFA Method.

RECOMMENDED FOLLOW-ON WORK

Further development of the UFA technology is possible and is continuing to increase UFA capabilities for future DOE and industrial applications. These developments include larger sample sizes, radioactive waste and sludge adaptations and applications, exotic materials development, further waste management applications, and agronomy applications. Much of the work involves scientific marketing to specific fields and laboratories, nationally and internationally.

APPENDIX A

Background Publication on the UFA Technology in *Soils and Groundwater Cleanup*

Reprint "Fluid Transport Data Faster" removed for
separate cycling.

APPENDIX B

Products and Services List and Published Price List for the UFA Spinoff Business, *NESTT*

NORTHWEST ENVIRONMENTAL SERVICES, TESTING AND TRAINING (NESTT)

2000 Logston Blvd., Richland, WA 99352 (509) 375-3268/FAX 375-4838

PRODUCTS AND SERVICES

Transport Properties of Porous Media - Unsaturated and Saturated

Hydraulic Conductivity
Electrical Conductivity
Thermal Conductivity
Distribution Coefficient
Retardation Factor
Recharge Rate
Moisture Retention
Moisture Potential
Osmotic Potential
Leaching/Desorption
Relative Permeabilities of NAPLs
Vapor Diffusivity/Gas Permeability
Pore Water Extraction and Analysis
Aqueous Diffusion Coefficient
Field Capacity

Physical/Chemical Properties of Porous Media

Grain Size Distribution
Soil Classification
Carbon Content/K_{oc}
Mineralogy
Water Content
Soil pH, Alkalinity, O_2
Density, Specific Gravity, Porosity
Cation Exchange Capacity
Waste:Soil Redox Couple Ratios

Feasibility and Pilot-Scale Studies

Feasibility Studies of all types
Percolation Boxes
Very Large Columns
Lysimeters

Specialty Experimental Equipment

Sample Holders
Dispersion Caps
Conductivity Cells
Sample Packers
Effluent Collection Cups
Sample Corers

Educational Services

Manuals and Training Modules
Earth and Environmental Science Curricula at All Levels
Technical Training
Short Courses/Workshops

Technical Assistance

Site Characterization and Restoration Support
Problematic Samples/Non-Standard Conditions
Program/Project Management at All Levels including RCRA/CRCLA Guidance
Sampling Protocols
Barrier Testing

NORTHWEST ENVIRONMENTAL SERVICES, TESTING AND TRAINING 3/1/96
2000 LOGSTON BLVD, RICHLAND, WASHINGTON 99352 Phone: (509) 375-3268 FAX: (509) 375-4838

PUBLISHED PRICE LIST* - *Transport Properties of Porous Media* (Temperatures from -20° to 150°C)

Hydraulic Conductivity, $K(\theta)$ - from saturated down to 10^{-11} cm/s using the UFA and Falling/Constant Head Methods. Up to eleven points per curve depending upon conductivity.	$2000 per soil sample $4000 per rock sample
$K(\theta)$ measured by column methods	$1400 per soil sample
Electrical Conductivity at any specified water content	$ 200 per soil sample $ 400 per rock sample
Retardation Factor, $R_f(\theta)$ (run time dependant upon flow rates, substrate and water chemistry) - does not include chemical analyses	$2500 per sample per week of run time
Moisture Potential and Retention, $\psi(\theta)$	$1000 per sample
Distribution Coefficient (run time dependant upon substrate and water chemistry) - does not include chemical analyses	$ 300 per batch test
Gas Permeability at any specified water content	$ 300 per soil sample
Total gas permeability from saturated to air dry, $k_a(\theta)$	$ 800 per soil sample
note: total $k_a(\theta)$ must be run with $K(\theta)$	
Pore Water Extraction	$ 500 per soil sample
Aqueous Diffusion Coefficient at any specified water content	$ 200 per soil sample
Relative Permeabilities of NAPLs - from saturated down to 10^{-10} cm/s using the UFA Method	$4000 per soil sample $6000 per rock sample

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*Price discounts - 20% discount for 10 or more samples; 30% discount for 50 or more samples; 40% discount for 100 or more samples. Prices quoted and charged are the same as those quoted our most favored customer for like services and in like quantities. Costs are based upon run times derived from previous work in these systems for the USDOE. No other methods or vendors can provide these measurements over these ranges in conductivities and temperatures. Special materials, fluids, conditions or problems may require additional handling and costs which will be reflected in any price quotes.

APPENDIX C

ASTM Test Procedure developed for the UFA Method

Approved by Subcommittee D18.21

Submitted to ASTM D18.21 Subcommittee on Ground Water

THE UFA METHOD FOR DETERMINING HYDRAULIC CONDUCTIVITY AND RELATIVE PERMEABILITY AS A FUNCTION OF WATER CONTENT OR OTHER LIQUID CONTENT.

1. Scope

1.1 This test method covers the determination of the relative permeability of liquids in any porous media, in particular, the hydraulic conductivity for water in subsurface materials, especially in relatively impermeable materials or materials under unsaturated conditions, e.g. soil, sediment, rock, concrete and ceramic, either natural or artificial.

1.1.1 A procedure for preparing test specimens is provided in section 8 and a procedure for carrying out the hydraulic conductivity measurement is provided in section 10. Calculations are given in Section 11. Specific instructions for operation of the specific ultracentrifuge and micro-infusion pump used should be obtained from the manufacturer of the equipment. The specific equipment discussed in this test method is described in Section 6 and is called the UFA™. Although originally UFA was an acronym for Unsaturated Flow Apparatus, the method is equally applicable to saturated systems and the term UFA is now stand-alone. Also, there is a commercially available UFA unit whose name is simply UFA.

1.2 *This standard may involve hazardous materials operations and equipment. This standard does not purport to address all of the safety issues associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicable regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards*

C 702 Methods for Reducing Field Samples of Aggregate to Testing Size, *Annual Book of ASTM Standards, Vol. 04.02.*

D 420 Practice for Investigating and Sampling Soil and Rock for Engineering Purposes, *Annual Book of ASTM Standards, Vol. 04.08.*

D 653 Terminology Relating to Soil, Rock and Contained Fluids, *Annual Book of ASTM Standards, Vol. 04.08.*

D 2216 Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures, *Annual Book of ASTM Standards, Vol. 04.08.*

2.2 Other References

Conca, James L. 1993 *Measurement of Unsaturated Hydraulic Conductivity and Chemical Transport in Yucca Mountain Tuff*, Technical Report LA-12596-MS, Los Alamos National Laboratory, Los Alamos, NM, 28 p.

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Conca, James L., and Judith Wright. 1990. "Diffusion Coefficients in Gravel Under Unsaturated Conditions." *Water Resources Research*, Vol. 26, p. 1055-1066.

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Nimmo, John R., and Karen A. Mello. 1991. "Centrifugal Techniques for Measuring Saturated Hydraulic Conductivity." *Water Resources Research*, Vol. 27, p.1263-1269.

Nimmo, John R., Jacob Rubin, and D. P. Hammermeister. 1987. "Unsaturated Flow in a Centrifugal Field: Measurement of Hydraulic Conductivity and Testing of Darcy's Law." *Water Resources Research*, Vol. 23, p. 124-134.

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Wright, Judith, James L. Conca, and Xiaobing Chen. 1994. *Hydrostratigraphy and Recharge Distributions from Direct Measurements of Hydraulic Conductivity Using the UFA™ Method*, PNL Technical Report PNL-9424, Pacific Northwest Laboratory, Richland, WA, 150 p.

3. Definitions

3.1 See ASTM D653 for specific terms relating to soil, rock and contained fluids.

3.2 *Porosity* -- the percentage of the bulk volume of a rock, soil or porous material that is occupied by air, vacuum or fluid; the non-solid portion of the total volume.

3.3 *Permeability* (also referred to as *Flow Porosity*) -- the portion or fraction of the total porosity that is interconnected and contributing to the overall flow of fluid through the sample.

3.4 *Water Content* -- the amount of water contained in a porous solid or aggregate; generally expressed either as the weight percent, which is the ratio of the weight of water in the sample determined by weight loss upon heating to the total sample weight, or as the volume percent (θ), which is the volume of water in the sample divided by the total sample volume. The volumetric water content is the weight percent water multiplied by the dry bulk density (ρ) of the sample. When the sample is saturated, the water content expressed as the volume percent equals the porosity.

3.5 *Matric potential (matric suction; water suction, water potential, etc.)* -- The negative pressure potential generated in the pore spaces of the sample resulting from the surface tension of the water and includes all capillary, electric double layer and other water film effects. Matric potential is the negative gauge pressure, relative to the external gas pressure on the soil water, to which a solution identical in composition to the soil water must be subjected in order to be in equilibrium through a porous membrane wall with the water in the soil (Hillel, 1980)

3.6 *Hydraulic steady-state* -- The point at which the flux out of a porous media equals the flux into the porous media; alternatively the point at which the water content of the material is no longer changing.

3.7 *Unsaturated Flow Apparatus* -- the combination of an ultracentrifuge with a constant-flow microinfusion pump and rotating seal assembly. Specific parts are defined as follows:

3.7.1 *Sample Holder* -- the metal, polysulfone, fiberglass or epoxy shell that contains the soil, rock, cement or aggregate to be tested.

3.7.2 *Sample Cup* -- the metal canister that contains the sample holder. It has a cap with o-rings to prevent fluid flow around the sides of the sample holder.

3.7.3 *Bucket* -- the metal shell that holds the sample cup and screws into the rotor.

3.7.4 *Effluent Collection Chamber* -- the plastic graduated vessel at the end of the sample cup that collects the effluent as it exits the sample cup.

3.7.5 *Rotor* -- the central aluminum fixture that holds the sample and bucket and spins on the rotating shaft. The Hy-sed 40.0 rotor holds the 3.33 cm diameter samples and the Hy-sed 90.0 rotor holds the 4.44 cm diameter samples.

3.7.6 *Rotating Seal* -- the mechanism which connects the stationary exterior of the system to the rotating interior; the boundary through which the two fluids must pass from the external pumps to the rotating samples. The components are composed of teflon/graphite polymers and sintered graphite seals, traditional bearing assemblies and heat sinks.

3.8 *Variables used in equations and units*

K = hydraulic conductivity (cm/sec)

r = distance from axis of rotation

ρ = density (gm/cm^3)

ω = rotation speed (radians/sec)

4. Summary of Method

4.1 The UFA Method is effective because it allows the operator to set the variables in Darcy's Law. Darcy's Law states that the fluid flux equals the hydraulic conductivity times the fluid driving force (See section 11). The driving force is fixed by imposing an acceleration on the sample through an adjustable rotation speed. The flux is fixed by setting the flow rate into the sample with an appropriate constant-flow pump and dispersing the flow front evenly over the sample. Thus, the sample reaches the steady-state hydraulic conductivity, or relative permeability if the liquid is non-aqueous, which is dictated by that combined flux and driving force. The operator can impose whatever hydraulic conductivity is desired within the operational range of rotation speeds and flow rates, usually between 10^{-2} cm/s (10 darcy; 10^{-7} cm^2) and 10^{-11} cm/s (10^{-8} darcy; 10^{-16} cm^2). It is most convenient to saturate the sample using a traditional falling head or constant head method (Klute, 1986) followed by step-wise desaturation in the UFA by increasing the speed and decreasing the flow rate, allowing steady-state to be reached at each step. Because a relatively large driving force is used, the UFA achieves hydraulic steady state in a few hours for most geologic materials, even at very low water contents.

4.2 There are specific advantages to using a centripetal acceleration as a fluid driving force. It is a whole-body force similar to gravity and, therefore, acts simultaneously over the entire system and independently of other driving forces, e.g., gravity or matric potential. Additionally, in the UFA the acceleration dominates any matric potential gradients as the Darcy driving force. The use of steady-state centrifugation to measure steady-state hydraulic conductivities has recently been demonstrated on various porous media (Wright et al., 1994; Conca and Wright, 1992; Nimmo et al., 1987).

4.3 Several issues involving flow in an acceleration field have been raised and addressed by previous and current research (Wright et al., 1994; Nimmo et al., 1987; Nimmo and Akstin, 1988; Nimmo and Mello, 1991; Nimmo et al., 1994). These studies have shown that compaction from acceleration is negligible for subsurface soils at or near their field densities. Bulk densities in these samples have remained constant because a whole-body acceleration does not produce high point pressures. The notable exception is surface soils and recently tilled soils, which can have unusually low bulk densities. Special arrangements must be made to preserve their densities. Whole rock, grout, ceramics or other solids are completely unaffected by these accelerations.

4.4 Three-dimensional deviations of the driving force as a function of position in the sample are less than a factor of two. Theoretically, the situation under which unit gradient conditions are achieved in the UFA, in which the change in the matric potential with radial distance equals zero ($d\psi/dr = 0$), is best at higher fluxes, higher speeds, and/or coarser grain-size (Nimmo et al., 1994). This is observed in potential gradient measurements in the normal operational range where $d\psi/dr = 0$. The worst case occurs at the lowest fluxes in the finest-grained materials, but even in the worst case, the hydraulic conductivity appears insensitive to small variations in water content or matric potential (Conca and Wright, 1994).

5. Significance and Use

5.1 Recent results have demonstrated that direct measurements of unsaturated transport parameters, e.g., hydraulic conductivity, vapor diffusivity, retardation factors, thermal and electrical conductivities, and fluid potential, on subsurface materials and engineered systems are essential for defensible site characterization needs of performance assessment as well as restoration or disposal strategies. Predictive models require the transport properties of real systems that can be difficult to obtain over reasonable time periods using traditional methods. The UFA Method greatly decreases the time required to obtain direct measurements of hydraulic conductivity on unsaturated systems and relatively impermeable materials. Traditionally, long times are required to attain steady-state conditions and distributions of water because normal gravity does not provide a large enough driving force relative to the low conductivities that characterize highly unsaturated conditions or highly impermeable saturated systems. Pressure techniques are not effective for measuring unsaturated transport properties because they do not provide a whole-body force and cannot act on the entire sample simultaneously unless the sample is saturated or near-saturated. High pressures used on saturated systems often induce fracturing or grain rearrangements and cause compaction as a result of high point pressures that are generated within the sample. The UFA does not produce high point pressures.

5.2 In the UFA, the measurements of ten evenly-spaced hydraulic conductivities of a typical soil from the saturated hydraulic conductivity down to an unsaturated hydraulic conductivity of 10^{-11} cm/s (10^{-8} darcy; 10^{-16} cm^2) takes only four days. Traditional techniques take many years to measure the same range of hydraulic conductivities. Even numerical estimation techniques take several weeks, require specific knowledge of pore geometry and connectivity, and cannot be used to perform actual experiments under the desired conditions. Where it has been possible to compare UFA results with traditional techniques and with numerical estimation techniques, the agreement has been excellent (Wright et al., 1994; Nimmo et al., 1987).

5.3 The UFA can be used in conjunction with other methods that require precise fixing of the water content of a porous material. The UFA is used to achieve the steady-state water content in the sample and other methods are applied to investigate particular problems as a function of water content. This has been successful in determining diffusion coefficients, vapor diffusivity, electrical conductivity, monitoring the breakthrough of chemical species (retardation factor), pore water extraction, solids characterization and other physical or chemical properties as functions of the water content (Conca and Wright, 1990; Conca and Wright, 1992; Conca 1993; Conca and Triay, 1994; Conca and Wright, 1994; Wright et al., 1994).

6. Apparatus

6.1 The UFA instrument consists of an ultracentrifuge with a constant, ultralow flow pump that provides fluid to the sample surface through a rotating seal assembly and microdispersal system (Figure 1). The only commercial UFA is available from UFA Ventures, 2000 Logston Blvd., Richland, WA 99352, and is manufactured for UFA Ventures by Beckman Instruments, Inc. Figure 2 shows the UFA with two AVI® infusion pumps. This UFA can reach accelerations of up to 20,000 g (soils are generally run only up to 1,000 g), temperatures can be adjusted from -20° to 150°C, and constant flow rates can be set as low as 0.001 ml/h. Effluent from the sample is collected in a transparent, volumetrically-calibrated chamber at the bottom of the sample assembly. Using a strobe light, an observer can check the chamber while the sample is being centrifuged. Two samples are run at the same time in the UFA with fluids flowing into each via the two feeds, the central feed or inlet path, and the annular feed.

6.2 Several variations of the UFA have been developed under the Department of Energy's (DOE) Volatile Organic Compound (VOC) - Arid Site Integrated Demonstration (ID) Program to accommodate the various aspects of multiphase/multicomponent systems encountered in mixed waste environments. Two rotor sizes and three rotating seal designs, e.g., face, mechanical and ferrofluidic, accommodate various applications such as non-aqueous phase liquids, tank waste sludge, and multiphase fluid flow. The prototype face seal is ideal for routine aqueous systems, while the ferrofluidic liquid-metal rotating seal allows temperature-abating sealing against vapor loss during operation with VOCs. The mechanical and ferrofluidic seals allow minimal internal contamination during adsorption/retardation flow experiments using heavy metals, lanthanides and actinides. Excellent agreement among the different designs of the UFA has been demonstrated for splits of the same samples. Various sample holders of different materials, e.g., teflon, titanium, stainless steel, copolymers, and nylon, address the many chemical compatibility requirements and accommodate sample sizes between 20 and 100

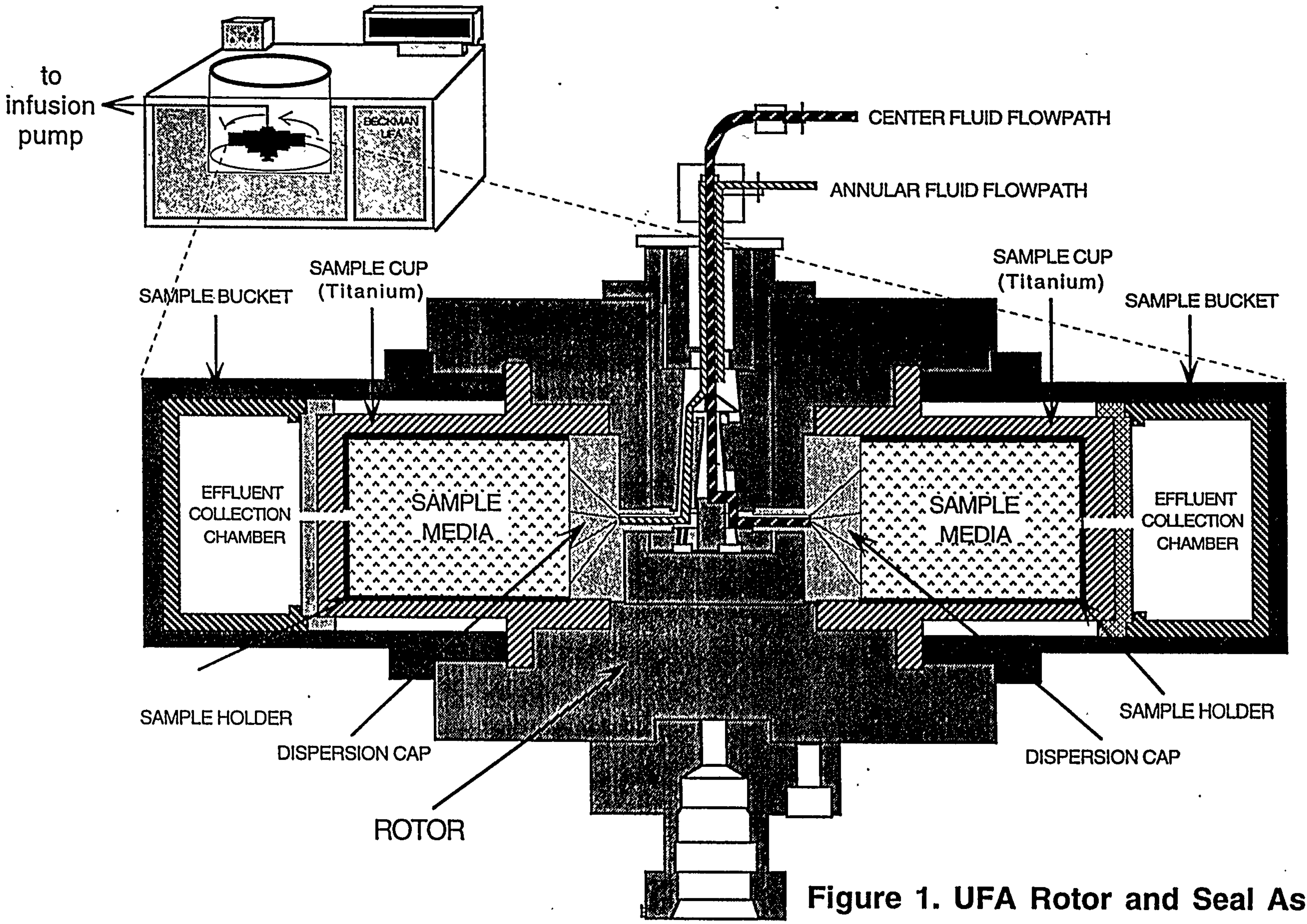


Figure 1. UFA Rotor and Seal Assembly

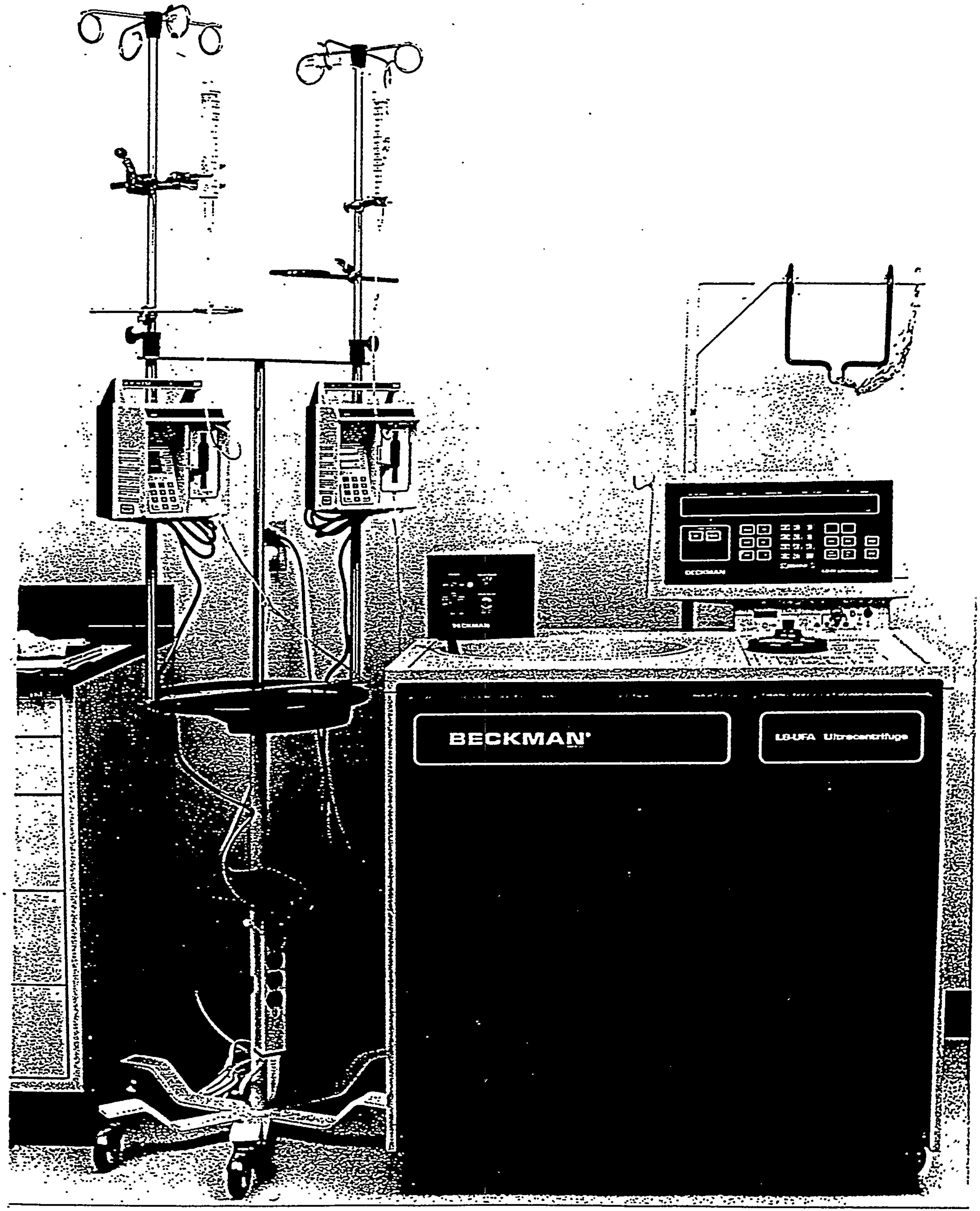


Figure 2. The UFA with AVI Infusion Pumps.

cm^3. Each rotor and seal assembly comes preconfigured and the operator does not need to configure any part of the UFA as part of this procedure.

6.3 Materials can be run in the UFA as recomposited samples or as in situ samples subcored directly into the sample UFA chamber from trench, outcrops or drill cores. Whole rock cores and cores of ceramics, grouts, and other solids are cast in an appropriate epoxy sleeve for use in the UFA (see section 8).

7. Materials

7.1 In addition to the UFA instrument, various materials are necessary for sample preparation and handling of soils, rock, aggregate, concrete and other porous media (see ASTM D 420 and Section 8). However, once the sample is prepared, all that is needed is a balance accurate to ±0.01 g for weighing the sample at each steady-state point for water content determination (see ASTM D 2216) and an oven for drying the sample after the final point to obtain the dry weight. Kim-wipes or other dust-free wipes, clean brushes for cleaning threads, various spoons and spatulas, squeeze bottles, distilled water for cleaning, and other basic laboratory implements are essential for smooth operation. As with any precision instrument, it is important to keep the area clean and dirt free because grit can wear or destroy certain moving parts in the UFA. The UFA comes with specific tools necessary for operation, e.g., spanner wrenches.

7.2 Hydraulic conductivity can be very sensitive to the solution chemistry, especially when samples contain expandable, or swelling, clay minerals. Water should be used that is appropriate to the situation, e.g., ground water from the site from which the sample was obtained, or rainwater if an experiment is being performed to investigate infiltration of precipitation into a disposal site. A standard synthetic pore water solution, similar to the solution expected in the field is also useful. Distilled or deionized water is generally not useful unless it is to be compared to other tests using this water or is specified in pertinent test plans, other ASTM methods, or EPA procedures.

8. Sampling

8.1 *Soil and disaggregated materials*- Depending upon the specific investigation, samples are obtained in many ways. The best possible sampling is to subcore the outcrop, trench, or undisturbed sample directly into the UFA sample holder using a subcoring device that holds a UFA sample holder. Often, however, undisturbed samples are not available and the sample must be recomposited or reassembled into a form that is representative of the field conditions.

Soil scientists have developed numerous methods for preparing disaggregated soils for flow tests (Klute, 1986). Two useful ways for the UFA are fill and tamp (damp; best with fine to medium soils, and with expandable clays) and slurry (wet; best with silts and non-expandable clays). These methods usually result in dry bulk densities of between 1.4 and 1.6 g/cm^3 for most soils and sediments, and between 1.0 and 1.4 g/cm^3 for clay-rich soils. For higher densities, an hydraulic press can be used with an appropriately-sized piston and confining cylinder for the sample holder. Centrifugation in the UFA will generally not affect the density for samples within 0.1 g/cm^3 of their field density, or about 1.4 g/cm^3 and above for most soils. If compaction is a problem, lower rotation speeds must be used. Other established soil sampling and filling methods can also be used.

8.1.1 Fill and Tamp - Rinse sample holder with distilled water and dry. Place filter paper in bottom of sample holder. Weigh sample holder and filter paper and record on data sheet. Check soil sample number against data sheet. Place a folded Kim-Wipe under the sample holder to absorb excess water. Carefully spoon small amounts of the dry sample into the sample holder, tamp down the soil firmly, by hand with a one-kilogram piston, and add enough fluid to dampen but not saturate. Continue this process until the sample holder is full with damp, well compacted soil. Wipe off the top and sides carefully to clear away any grit that might damage the holder O-ring or cap threads.

8.1.2 Slurry - Rinse sample holder with distilled water and dry. Place filter paper in bottom of sample holder. Weigh sample holder and filter paper and record on data sheet.

Sample Volume (cm^3): ____________ Dry Sample Weight: ____________

Orig Wt % Water Content: Volumetric Water Content: ____________

Check soil sample number against data sheet. Spoon an appropriate volume of dry sample into a jar. Add enough water to just saturate the sample and stir thoroughly. Allow mixture to settle. Prepare sample cup and centrifuge in the meantime. Once soil/water mixture has settled, carefully decant or siphon excess water. Place a folded Kim-Wipe under sample holder to absorb excess water and carefully mix and spoon soil mixture into sample holder, constantly mixing to insure homogeneity and reduce layering, and periodically tamping mixture down firmly. When sample holder is full, let sample settle as it loses water slowly to the Kim-Wipe over several hours. Add additional wet soil to sample holder as necessary to top it off. Carefully wipe the top and sides of the sample holder to clean off any grit that might damage the holder O-ring or cap threads.

8.2 *Whole rock cores, concrete or ceramics-* Solid coherent materials can be cored using a coring bit (see ASTM C 702), usually diamond, that produces cylinders that can be potted in a mold with the correct interior diameter (3.97 cm for the Hy-sed 40.0 rotor, 5.08 cm for the Hy-sed 90.0 rotor) using an appropriate epoxy for the intended test. The

material, fill fractures or pores and change its conductivity.

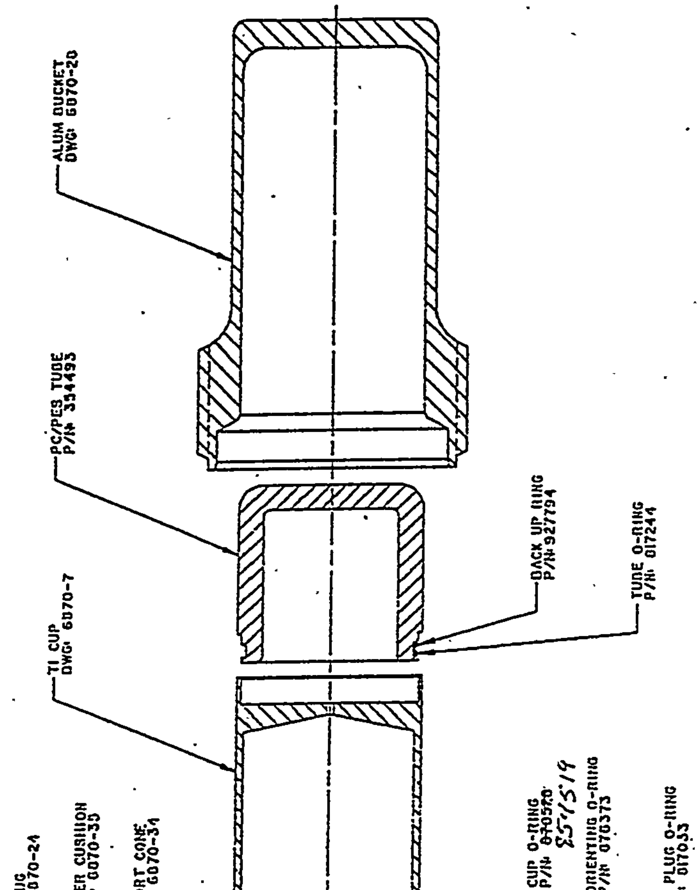
9. Calibration

The UFA should have a manufacturers service contract to maintain calibrations, smooth functioning and long life. Do not attempt to calibrate the UFA manually. The balances used to weigh samples and the oven used for drying samples should be calibrated periodically according to the relevant quality assurance or impact levels for the application.

10. Procedure

10.1 The following procedure refers to the commercially available UFA. However, it is applicable to any centrifuge/infusion pump set-up that allows open flow into the sample during centrifugation. Specific dimensions would have to be adjusted accordingly.

10.2 Before beginning each sequence of unsaturated flow measurements or water content settings the operator will record the setup information for the UFA on a data sheet. A sample of a data sheet is given in Table 1, and was developed for the common type of soil



er and Bucket Assemblies.

taking care that the threads are seated properly, and firmly tighten caps with the spanner wrench until they will not move further. *Do Not Overtighten!* Attach effluent collection chambers to bottom of sample cups. Weigh both sample assemblies and equalize their weights to ±1 gram to maintain balance. Equalization of weights can be obtained by adding teflon, stainless steel beads or water to the effluent collection chamber of the lighter assembly. Figure 3 shows the components and orientation of a Hy-sed 40.0 sample assembly.

10.5.2 If using the Hy-sed 90.0 rotor, clean all 0-rings and lubricate with silicon vacuum grease. Push metal threaded cap (with inserted perforated disc if the sample is a soil or aggregate) onto the top of the sample holder. Carefully clean threads of the metal sample cups and caps with a toothbrush and a Kim-Wipe. Make sure metal cone is in place in the bottom of the cup with the flat, grooved side oriented toward the top of the sample cup. Lubricate cap threads. Place sample holders inside cups and carefully screw down the caps by hand, taking care that the threads are seated properly. *Do Not Overtighten!* Push the fluid dispersal cap (with oriented marking A or C correctly aligned) into the O-ring seal in the metal threaded cap. Attach effluent collection chambers to bottom of sample cups. Weigh both sample assemblies and equalize their weights to ±5 grams to maintain balance. Equalization of weights can be obtained by adding teflon, stainless steel beads or water to the effluent collection chamber of the lighter assembly.

10.5.3 Push the sample assembly with the letter A marked on the cap into position A in the centrifuge rotor with the letter A facing up (this positions the fluid dispersal pattern in the cap in the correct orientation over the top of the sample). Gently screw the metal bucket into the rotor over the sample assembly. Place the second sample assembly (marked C) into position C of the centrifuge rotor with the letter C on the cap of the sample cup assembly facing up. Turn the effluent collection chamber so that the set of calibration markings are facing up. Gently screw the metal bucket into the rotor over the sample assembly. After each bucket is tightened, make sure the calibration lines on the effluent collection chamber are visible through the windows in the top of the buckets.

10.6 The centrifuge should be prepared for a sample run by lowering the rotor assembly into the centrifuge chamber. For low speed operation, turn the key located near the "Start" switch to the low speed setting (zonal). This setting allows the centrifuge to operate with the door open. Set the temperature by pressing the "Temp" button, entering the selected temperature, and pressing the "Enter" button. Set the rotor speed by pressing the "Speed" button, entering the selected speed and pressing the "Enter" button. Put the plexiglass shield or metal plate in place, anchor it with the cable and thread the pump feeder line along the indicated path. The centrifuge settings must be displayed in order to start the machine, so press "Enter" to display settings, and press the "Start" button to start centrifuging. The maximum allowable speed for the Hy-sed 40.0 rotor is 3000 rpm. At the time of publication, the maximum allowable speed for the Hy-sed 90.0 rotor is 6000 rpm. Carefully follow the operating instructions that will be included with the UFA.

10.7 *Some points to remember are*:

10.7.1 Do not set the volume limit on the pumps to more than the available volume in effluent collection chambers, and always empty the effluent collection chambers after each run, or before the chambers are full.

10.7.2 *Never have the microinfusion pumps running unless the centrifuge is rotating. Failure to do so will prevent steady-state from being achieved within the sample.* Always turn the pump off when decelerating the sample to zero rpm. It is best to turn the pump on and off at the same centrifuge speed, preferably three quarters of the final centrifuge speed (e.g., for 1000 rpm, turn the pump on and off when rpm's have reached 750). This eliminates any small error introduced during the ramp up or down periods. Ramp times are usually less than 60 seconds.

10.7.3 Always be aware of the sample chamber, dispersion cap and effluent collection chamber orientation and the fluid level in the effluent collection chamber. Overfilling can cause fluid to run back into the sample or out of the chamber. For example, empty the effluent collection cup of the sample first before opening up the sample cup to reduce the possibility of effluent backflow.

10.7.4 Hydraulic steady-state is achieved when the fluid flux out equals the flux in as set by the microinfusion pump. This is determined

TABLE 2 Typical UFA Parameter Settings For Measuring Hydraulic Conductivity In Porous Media as a Function of Moisture Content

pump rate (ml/hr)	rotation speed (rpm)	time duration (hrs)	
50*	300	2**	
50	600	2**	Day 1
50	1000	2**	
50	1500	2**	
40	2000	2**	
15	2000	3**	Day 2
5	2000	4**	
1	2000	8**	overnight
0.5	2000	10**	Day 3
0.2	2300	10**	overnight
0.1	2500	10**	Day 4
0.01	2500	10***	

---

* The highest flow rates will depend upon the saturated hydraulic conductivity and will be determined for each sample. The first setting of the pump flow rate will be equal to the highest flow rate achievable, and subsequent flow rates will decrease from that value.

** Weigh sample and sample holder after run and enter weight on data sheet.

*** Weigh sample and record on data sheet. Dry sample in oven @ 100°C and weigh to get dry sample weight. Record weight on data sheet. Clean assemblies and prepare next sample.

by using the strobe light to illuminate the effluent collection chamber for reading the volume of water that has exited the sample. At least two observations of the volume must be made at adequately separate times, recorded using a stop-watch. An even more precise method for assuring that hydraulic steady-state has been reached is to determine that the sample is no longer changing its weight by periodically weighing the sample every half hour or so.

10.7.5 Check O-rings frequently to determine if they are damaged. Change O-rings if they show even small nicks or cuts. Remember to grease O-rings to assure proper sealing of sample and fluid delivery, and lubricate all threads to prevent galling and to reduce wear of threaded parts.

10.7.6 Remember to keep the flow rates into each sample approximately the same to maintain balance and reduce wear on the rotating seal during operation.

10.7.7 It is better to begin the run with a saturated sample and use step-wise desaturation of the sample, rather than to begin with a dry sample and use step-wise saturation. This is because steady-state is achieved faster with desaturation and transient flow effects, such as fingering of the flow front, are minimized.

10.8. The choice of run parameters, i.e., rotation speed and flow rate settings, depend upon the intrinsic permeability of the sample and the target water content desired. However, for most soils and sediments Table 2 gives a well-characterized set of run parameters that will provide a hydraulic conductivity curve over a wide range of water contents relevant to vadose zone conditions. After an entire run represented by Table 2, the sample should be dried, and both the weight and volume of the dry sample should be measured.

11. Calculations

11.1 Calculation of Relative Permeability (Hydraulic Conductivity for Water) -
Fluid flux, q, is given by Darcy's Law as the product of the hydraulic conductivity, K, and the fluid driving force. Under a centripetal acceleration, the driving force is a function of rotation speed, distance from the axis of rotation and fluid density (Nimmo et al., 1987; Wright et al., 1994). Therefore, Darcy's Law becomes:

$$q = K(\rho\omega^2 r)$$

where K = hydraulic conductivity (cm/sec), r = distance from axis of rotation, ρ = fluid density (gm/cm^3), ω = rotation speed (radians/sec). The dimensional analysis is:

$$(cm\ s^{-1}) = (cm\ s^{-1})(gm\ \ cm^{-3}\ s^{-2}\ cm) \div 980.67\ (dynes\ cm^{-2}cm^{-1}{}_{H2O})$$

where a dyne = gm cm s^{-2}. The last term converts the units from an acceleration (g-force units) to a force per unit volume relative to water. The flow rate chosen for the pump plus the cross-sectional area of the sample determines flux. Re-arrangement gives:

$$K = q/(\rho\omega^2 r)$$

11.2 For convenience of calculation using run parameters from the instruments and the geometry of the UFA rotor and sample assembly, the working relationship is:

$$K = (2.88)(\text{flow rate in ml/hr}) \div (\text{rotation speed in rpm})^2(\text{X-sectional area in cm}^2)$$

11.3 As an example, a sample of soil packed into a sample holder for the Hy-sed 40.0 rotor with an interior diameter of 3.33 cm has a cross-sectional area of 8.55 cm^2. The sample is run in the UFA at 2000 rpm with a pump flow rate of 5 ml/hr; giving an hydraulic conductivity of 4.2 x 10^{-7} cm/s. Steady-state is achieved after 4 hours. The water content is then measured and the volumetric water content determined from the final dry weight and dry bulk density. The volumetric water content can be plotted against hydraulic conductivity for each point in the step-wise desaturation to give an hydraulic conductivity curve. Such a curve is shown in Figure 4 for borehole sediment core samples from the Hanford Site in Washington State. This data set of 59 directly-measured hydraulic conductivities took only three weeks to obtain with a single UFA. Each point is a direct measurement and independent of all other points. The shape of the curve is dependent upon the pore-size distribution and is unique to each sample.

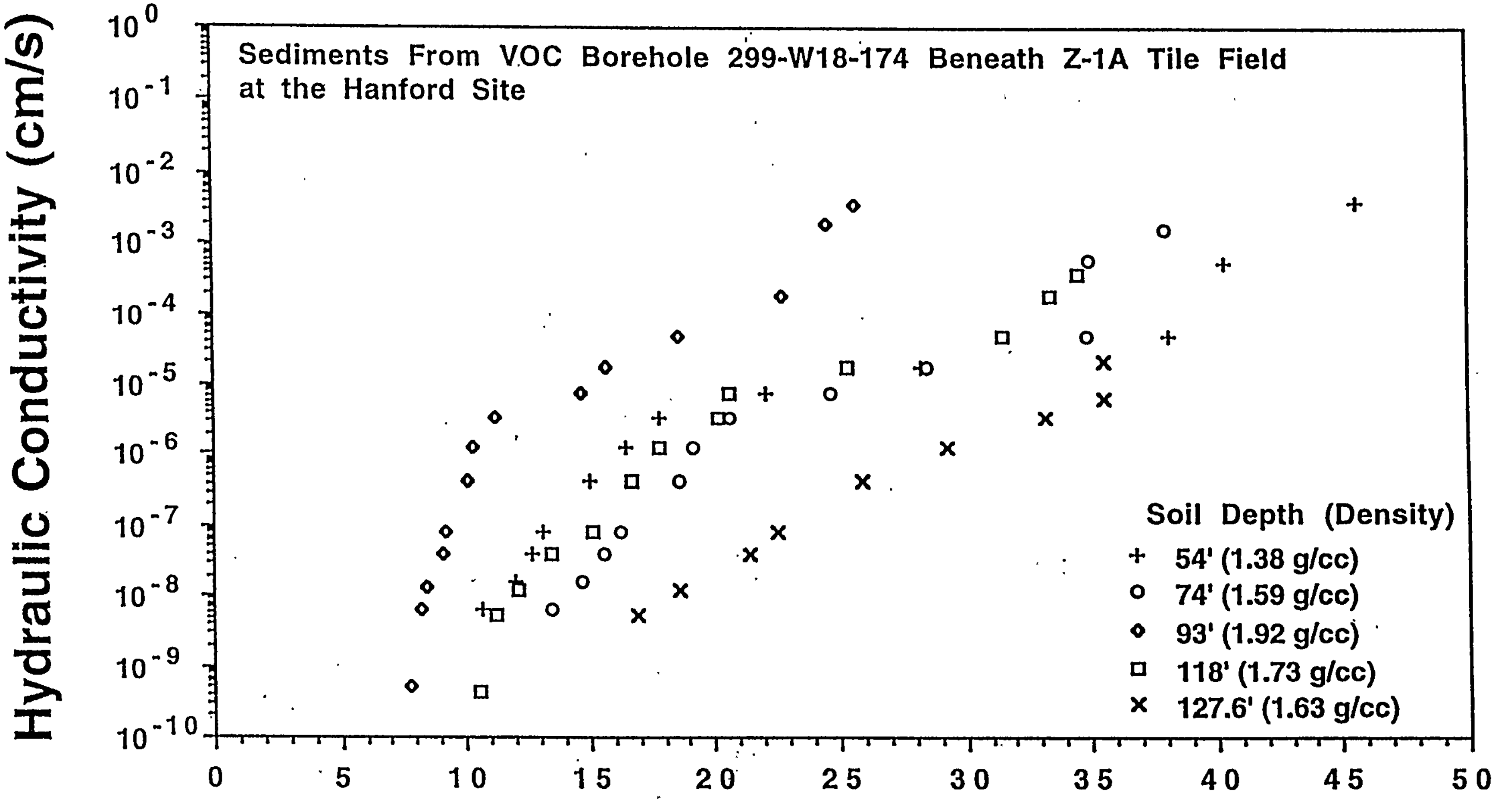


Figure 4. Unsaturated Hydraulic Conductivity Curves Measured by the UFA Method

APPENDIX D

Los Alamos National Laboratory
Technical Report LA-12596-MS

Measurement of Unsaturated Hydraulic Conductivity and Chemical Transport in Yucca Mountain Tuff

LA-12596-MS

UC-814
Issued: December 1993

Measurement of Unsaturated Hydraulic Conductivity and Chemical Transport in Yucca Mountain Tuff

Milestone Report 3044-WBS1.2.3.4.1.4.1

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MEASUREMENT OF UNSATURATED HYDRAULIC CONDUCTIVITY AND CHEMICAL TRANSPORT IN YUCCA MOUNTAIN TUFF

MILESTONE REPORT 3044-WBS1.2.3.4.1.4.1

by

James L. Conca

ABSTRACT

Hydraulic conductivities, K, were experimentally determined as a function of volumetric water content, θ, in tuff from the Yucca Mountain site. In addition, the retardation factor, R_f, in Yucca Mountain tuff with respect to selenium, as the selenite species, was measured under unsaturated conditions. These data were used to determine the feasibility of applying a new unsaturated flow technology (UFA™) to further hydrologic studies at Yucca Mountain. The UFA™ directly measures $K(\theta)$ rapidly in Yucca Mountain tuff and is shown to agree well with traditional methods. Hysteresis does not appear important during this testing. Hydraulic steady-state is achieved fastest during desaturation from a saturated state. Imbibition into dry tuff requires a long time for steady-state to occur because of slow filling of the diffusion porosity which can take a few weeks. The existing UFA™ is a prototype, and a new design of the next generation UFA™ is completed that eliminates some of the earlier problems. These preliminary investigations demonstrate that the UFA™ is a useful investigative technique that should be used to compliment existing techniques for hydrogeochemical characterization at Yucca Mountain.

INTRODUCTION

The scope of this report is four-fold: 1) to determine the feasibility of a new unsaturated flow technology in measuring unsaturated hydraulic conductivity in Yucca Mountain tuff as an additional tool for characterizing hydrologic properties, 2) to compare this method to existing methods for estimating hydraulic conductivity in the unsaturated zone, 3) to review hydraulic conductivities determined for tuff from Yucca Mountain using this method, and 4) to determine the feasibility of using the UFA™ for hydrogeochemical characterization as in the measurement of R_f.

Modeling the transport of contaminants in vadose zones surrounding nuclear and hazardous waste repositories requires knowledge of the material characteristics under unsaturated conditions. The hydraulic conductivity, K, retardation factor, R_f, and diffusion coefficient, D, are the primary transport parameters that are key input parameters to existing and developing models of contaminant release from repository systems and waste sites (*Pigford and Chambré,* 1988). Knowledge of K, R_f, and D, as a function of the volumetric water content, referred to as the characteristic behaviors of a porous medium, is particularly important in the near-field transition zone around high-level waste packages where changes in temperature, water content, compaction of backfill, infiltration of fines, and secondary mineralization will alter transport characteristics. An excellent discussion of transport parameters, processes, and mechanisms in partially saturated media can be found in Wang and Narasimhan, 1993.

However, transport parameters have generally been difficult to obtain as a function of the volumetric water content. 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 unsaturated conditions. The low conductivities of fractured whole rock under normal potential gradients have hampered experimental studies because of the long time scales required for the experiments. Most of the existing transport data on fractured rock comes from saturated flow studies using high pressures that reduce experimental times but lose the natural conditions by inducing new fractures, enlarging existing fractures, and affecting pressure-dependent reactions and phase stabilities. *In situ* measurements of unsaturated flow in whole rock in boreholes or at the surface using surface infiltrometers have provided some excellent results (*Kilbury, et al.* 1986), but are restricted to a narrow range of water contents, and the boreholes themselves can severely disturb the system (*Montazer,* 1987). Lin and co-workers at Lawrence Livermore National Laboratory (*Lin and Daily,* 1984) have shown that computed impedance tomography (CIT) has great promise in the study of unsaturated flow, but CIT still has only coarse resolution and is not developed for aqueous chemical studies. Yang and co-workers at the United States Geological Survey Denver have extracted pore water from unsaturated tuff using triaxial compression (*Yang, et al.* 1988) but this method is not designed to investigate unsaturated flow. To address these problems, an unsaturated flow apparatus (UFA™) based on open centrifugation was developed in which hydraulic steady-state is achieved rapidly in most geologic media at low water contents (*Conca and Wright,* 1992; *Conca and Wright,* 1990).

WATER CONTENT AND CENTRIFUGATION

The application of a centripetal acceleration (or its inertial effect, the centrifugal force) to geologic problems is as old as centrifugation itself (*Russell and Richards,* 1938). However, the use of steady-state centrifugation to fix the water content and to measure unsaturated hydraulic conductivities has only recently been demonstrated by Nimmo and co-workers (*Nimmo et al.,*1987; *Nimmo and Mello,* 1991). There are specific advantages to using a centripetal acceleration as a fluid driving force. It is a body force similar to gravity, and so acts simultaneously over the entire system and independently of other driving forces, e.g., gravity or matric suction. The UFA™ developed for this study consists of a rock core ultracentrifuge with an ultralow constant-rate flow pump which provides any fluid to the sample surface through a rotating seal assembly and microdispersal system (Figure 1). Accelerations up to 20,000 g are attainable at temperatures from 0° to 150°C and flow rates as low as 0.001 ml/hr. The effluent is collected in a transparent, volumetrically calibrated container at the bottom of the sample assembly which can be observed during centrifugation using a strobe light. The maximum sample volume is 40 cm^3 for aggregate materials (soils, gravels, etc. in a polyethersulfone or fiberglass sample holder) and up to 45 cm^3 for solid cores (whole rock, grout, ceramic, etc., potted in casting resin and machined to the correct dimensions). The next generation UFA™ has, among other modifications, a maximum sample volume of 125 cm^3.

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

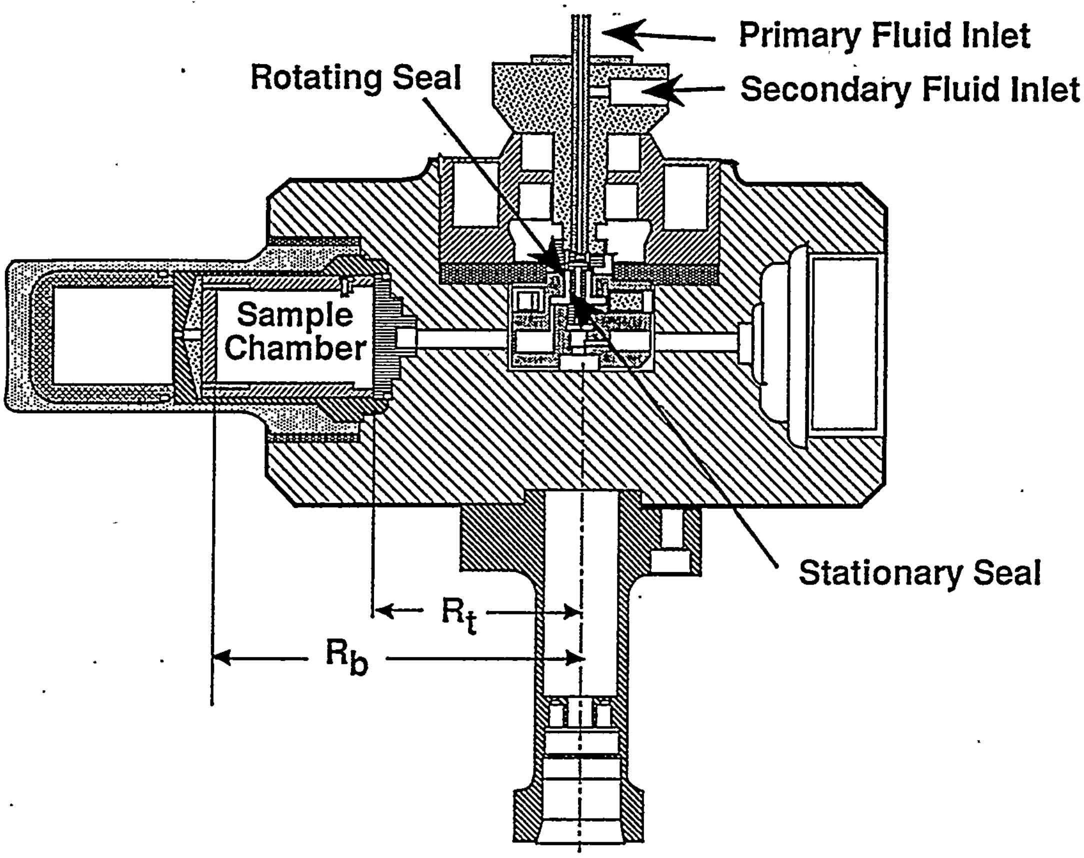


Figure 1. The UFA™ Rotor and Seal Assembly

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

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. Moisture distributions in homogeneous samples run in the UFA™ are uniform to within 3% (*Conca and Wright,* 1990; *Nimmo et al.* 1987). 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 in the sample. At speeds above 300 rpm, provided that sufficient flux density exists, $d\psi/dr \ll \rho\omega^2 r$ and equation 1a reduces to $q = K(\psi)\ [\rho\omega^2 r]$ or

$$K(\psi) = q/\rho\omega^2 r \qquad (1b)$$

As an example, a whole rock core of Topopah Spring Member tuff accelerated to 7500 rpm with a flow rate into the core of 2 ml/hr achieved hydraulic steady-state in 30 hours with a hydraulic conductivity of 8.28×10^{-9} cm/sec at a volumetric water content of 7.0%. Previous studies have verified equation 1b regarding the linear dependence of K on flux and the second order dependence on rotation speed (*Nimmo and Akstin,* 1988; *Conca and Wright,* 1990).

There are several issues surrounding flow in an acceleration field that are frequently raised and that have been successfully addressed by previous and on-going research. These include uniformity of moisture distribution, deviation of the driving force with position in the sample due to deviations in the curvatures of air-water interfaces, and compaction due to acceleration (*Nimmo and Mello,* 1991; *Nimmo and Akstin,* 1988; *Nimmo et al.* 1987; *Conca and Wright,* 1990). These studies have shown that: 1) compaction due to acceleration is negligible in samples over 1.0 g/cm^3 (bulk densities in all samples have remained constant because a whole-body acceleration does not produce high point pressures); 2) three dimensional deviations of the driving force with position in the sample is less than 1%, and 3) moisture distribution is uniform to within 3% in homogeneous systems. In heterogeneous samples or multicomponent systems, each component reaches its own hydraulic conductivity and water content at steady-state, as occurs in the field. This last effect cannot be reproduced with pressure-driven techniques, but only under a whole-body acceleration field such as gravity or centrifugal methods.

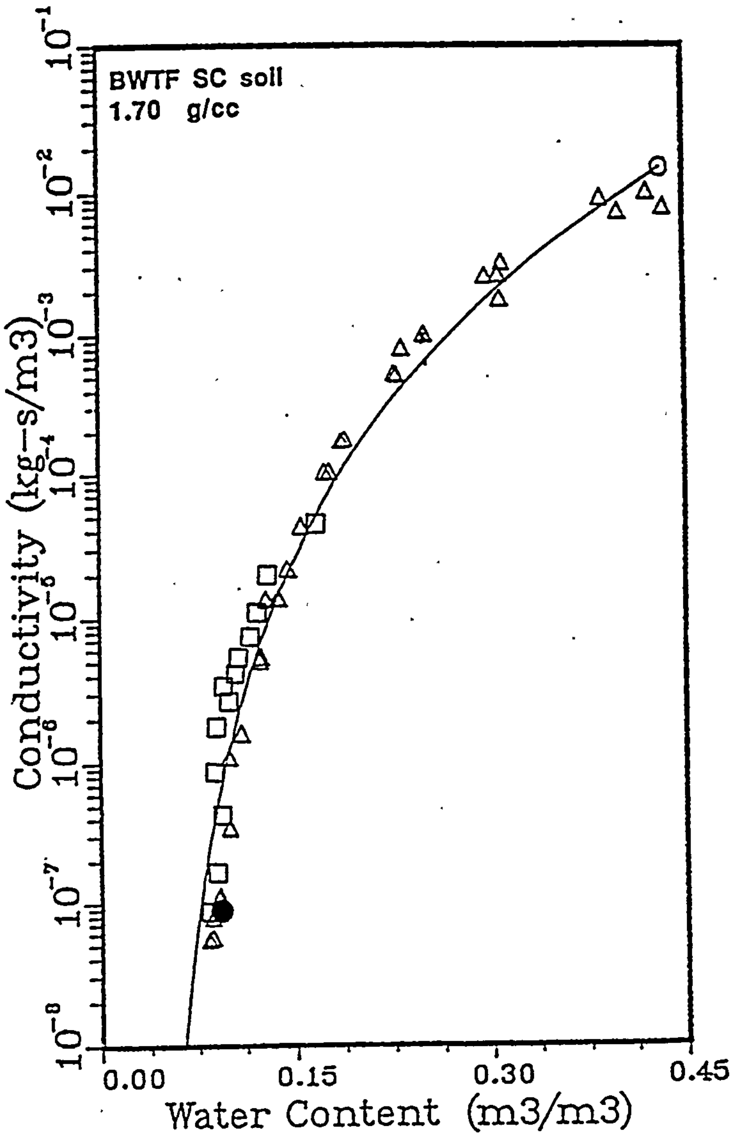
Also, the lower boundary condition of the sample and the relationship of $d\psi/dr$ to $\rho\omega^2 r$ needs to be mentioned. The condition $d\psi/dr = 0$ in the UFA™ only occurs ***after*** the sample has reached hydraulic steady-state. But even before steady-state occurs, as during initial infiltration into a dry sample, $d\psi/dr \ll \rho\omega^2 r$ for all speeds above about 300 rpm, and this includes the lower boundary. Unlike the gravity drain situation, there is no moisture buildup at the air-water interface under a centripetal acceleration because $d\psi/dr \ll \rho\omega^2 r$ at all points within the system. The lower boundary of aggregate samples, such as soil, is a filter paper between the sample bottom and a perforated plastic plate. Additionally, the boundary condition issue of flow down the sample container interior sides, circumventing the sample and affecting $K(\theta)$, has not been observed to occur in the UFA™. Flow down the sample container exterior sides is prevented by O-ring seals.

QUALITY ASSURANCE

The results of this project were carried out in accordance with PNL-MA-70 Impact Level III, Good Practice Standards procedures, with the proper equipment calibrations by Westinghouse Standards Laboratory, and approved technical procedures in place prior to initiating work. All laboratory tests are described in a Laboratory Record Book (LRB EES2) or cited references to standard tests. However, Impact Level I Technical Procedures are in place for this method for use in the Yucca Mountain Project. All measurement and test equipment are identified on an M&TE list. All calculations are performed using protocols described in Hand Calculation Procedures or authorized computer-generated algorithms and macros.

COMPARISONS TO TRADITIONAL TECHNIQUES

Hydraulic conductivities of unsaturated sediments from the Buried Waste Test Facility (BWTF) at the Hanford Site were determined over the water content range from 5% to 40% using the UFA™ method and three traditional techniques (Figure 2). These sediments are coarse to medium grained fluvio-glacial soils of a dominantly volcanic source lithology, having approximately 85-90% sand,5-10% silt and 3-6% clay by weight for the < 2 mm size fraction. Open squares are direct measurements of $K(\theta)$ obtained in a three-day period using the UFA™. Open triangles are direct measurements of $K(\theta)$ using traditional column flow experiments under unit-gradient conditions, requiring about a year of experimental time to achieve the hydraulic steady-states over this water content range (Mike Fayer, personal communication). A Campbell relationship was fit to water retention data for the BWTF soil and used to generate a Mualem relationship (the solid curve). Also shown in Figure 2 is 13-year field lysimeter data obtained under unit-gradient conditions at water contents in the field (Glendon Gee, personal communication), a point which ties the laboratory data to the field conditions. The agreement of the UFA™ data with all three methods is excellent and demonstrates the feasibility and rapidity of the UFA™ method.



- □ UFA™ measurements made over 3-days
- △ Traditional column experiments made over 1-year
- ● Average of field lysimeter measurements made over 13-years
- — Mualem estimation derived from curve-fitted water-retention data made over 6-weeks

Figure 2. Characteristic Curves for the BWTF Soil Obtained Using Four Different Methods.

It was anticipated that different techniques would compare well for the BWTF soils because the traditional techniques were originally developed for sands and sandy loams. However, these techniques have never been validated for silts, clays, rocks or other less permeable media. Therefore, a comparison was run among the UFA™ method and two traditional methods on a fine silt from the Field Lysimeter Test Facility (FLTF) at the Hanford Site that achieves hydraulic conductivities in the low water content range similar to some of the Yucca Mountain tuffs. The results are shown in Figure 3. Circles are data from falling head permeameter studies, and triangles and squares are laboratory data from steady-state soil column studies (Glendon Gee, personal communication). The solid line is the Mualem relationship generated from a van Genuchten relationship fit to water retention data for the FLTF soil (fitting parameters are listed on the figure). The agreement among these methods is still very good. At low water contents, the estimate overpredicts the hydraulic conductivity relative to the UFA™, or conversely, the estimate underpredicts the residual saturation. Considering that these tests for the BWTF and the FLTF soils were performed blind, the agreement is better than expected.

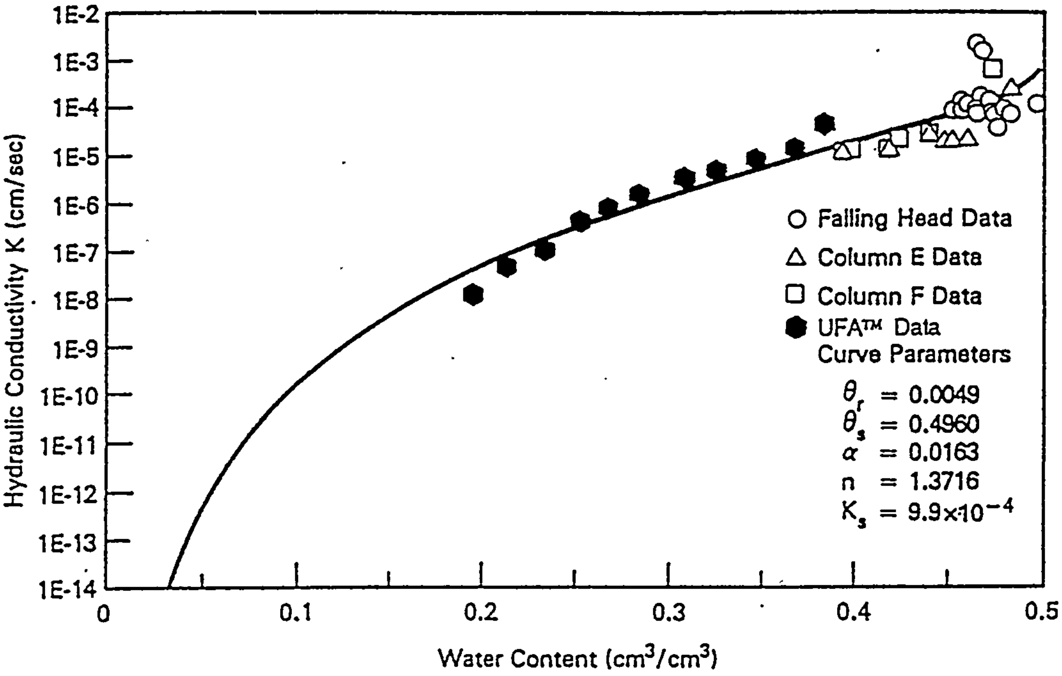
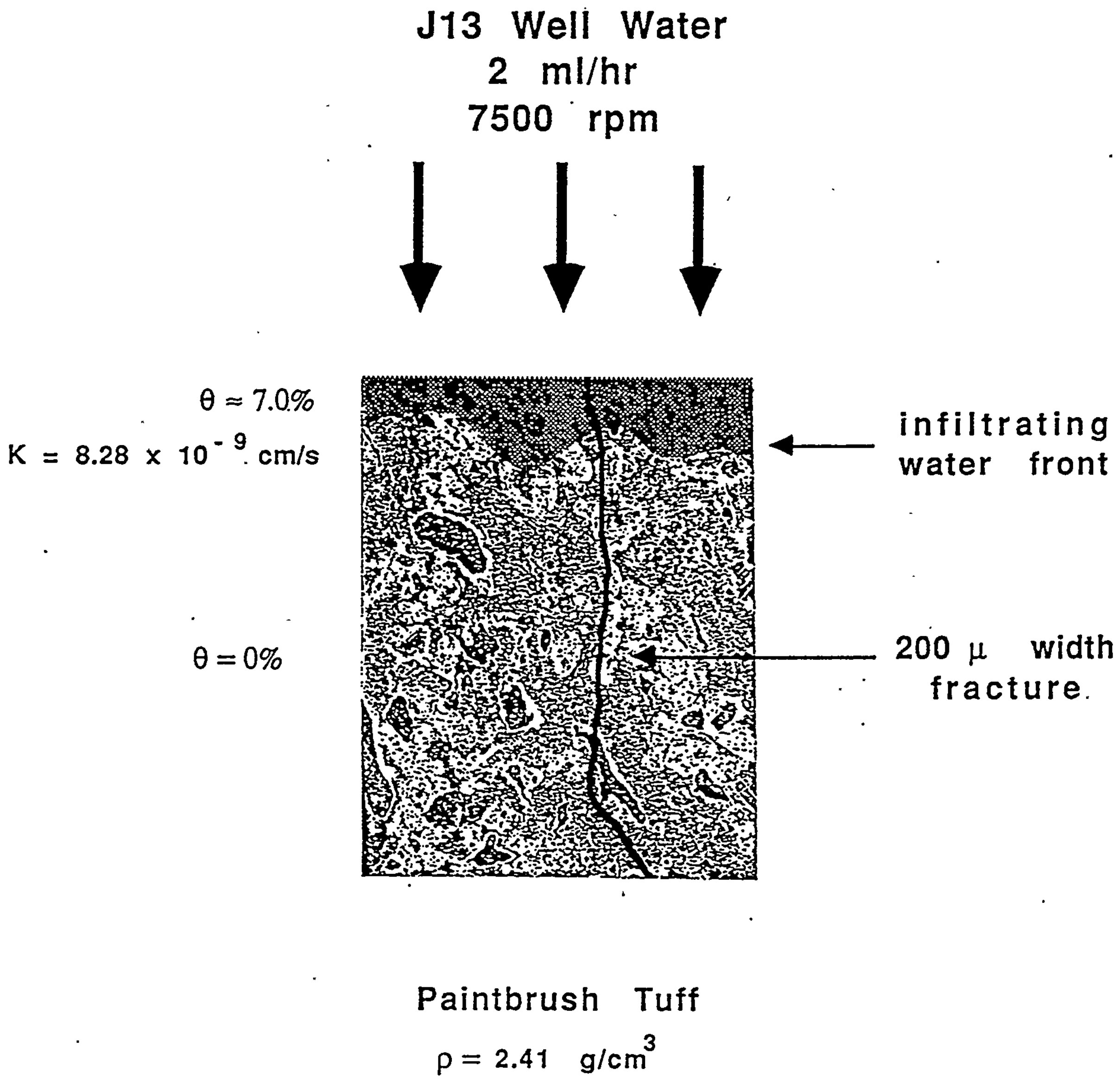


Figure 3. Measured Hydraulic Conductivity Data and van Genuchten Function Fit for FLTF Soil using Three Different Methods.

Whole rock cores of Topopah Spring Member and Calico Hills tuff were run in the UFA™ to generate characteristic hydraulic conductivity relationships for each rock and to investigate the tuff whole rock systems in light of current capillary bundle theory which predicts the desaturation of progressively smaller aperture fractures with decreasing water content. The water distribution in a whole rock core of tuff with a natural single large 200 µm fracture that almost, but not completely, spans the core is shown in Figure 4. The approximate volumetric water content is $\theta \sim 7.0\%$ (88% of saturation) in the wetted rock after two hours at 7500 rpm with a flow rate into the core of 2 ml/hr. Water has infiltrated the matrix but the fracture has not begun conducting any water. K is the unsaturated hydraulic conductivity at the approximate volumetric water content of 7%.

Figure 5 shows the water distribution in the same whole rock core as Figure 4 after the flow rate was increased to 5 ml/hr. The fracture catastrophically drained 6 ml over a ten minute period after one hour under these conditions. K is the hydraulic conductivity of the saturated system, matrix plus fracture, at a volumetric water content of approximately 7.9%. The top portion of the wetted matrix and the fracture walls to a depth of less than 1 mm were saturated. This indicates that while the matric potential at high accelerations does not significantly contribute to the driving force in the Darcy relationship, the matric potential does influence the moisture distribution and flow paths analogously to the 1 g situation as predicted by capillary bundle theory. The matrix immediately adjacent to the fracture must be saturated before the fracture will conduct water.

Characterization of the flow paths within the tuff can also be accomplished using a dyed groundwater (India ink in water has been successful for these thin section analyses) as the infusing liquid. An example is illustrated in Figure 6 which shows a photomicrograph of a thin section through a core perpendicular to the flow direction illustrating fluid flow through the fractured matrix and along cleavage fractures in a large feldspar grain (*Conca and Wright, 1990*). Areas of blue indicate the flow paths. Notice the dendritic pattern of a lateral flow path in the feldspar. These "dead end" flow paths do not contribute significantly to the hydraulic conductivity but greatly influence the aqueous chemistry because of



<u>Figure 4</u>. Water Distribution in a Whole Rock Core of Tuff with a Single Natural Large Fracture that Almost but not Completely Spans the Core. After Two Hours at 7500 rpm Rotation Speed and 2 ml/hr Flow Rate, Water has Infiltrated the Matrix but not the Fracture.

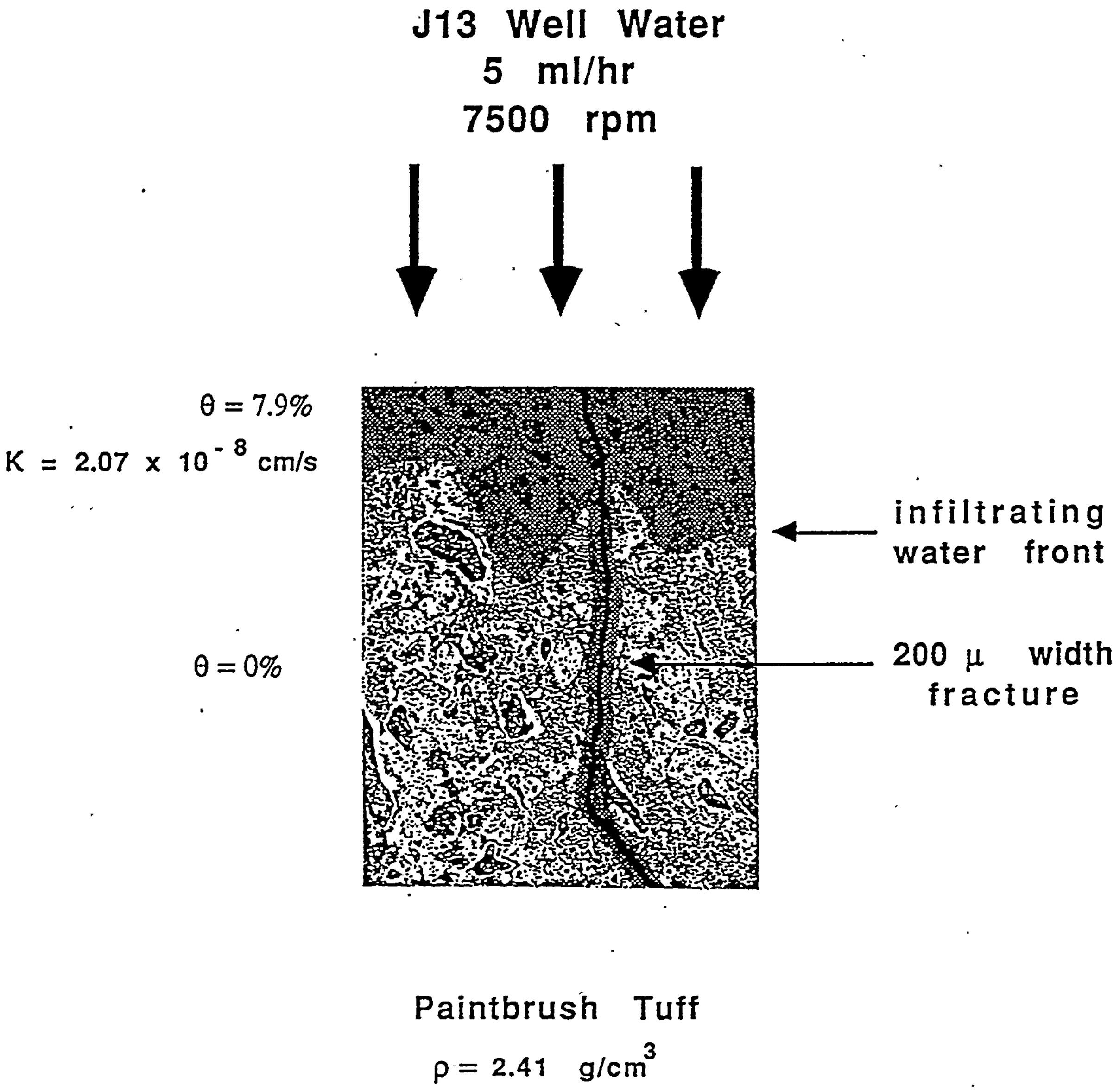


Figure 5. Water Distribution in the Same Core as in Figure 4 One Hour After Flow Rate Increased to 5 ml/hr. The Fracture Drained 6 ml over a Ten Minute Period After the Matrix Began Saturating.

(see color plate)

Figure 6. Photomicrograph of a Thin Section Through a Core of Tiva Canyon Member Tuff Perpendicular to Flow Illustrating Fluid Flow along Cleavage Fractures in a Large Feldspar Grain. Areas of Blue Indicate the Flow Paths, which were Sparse and Unevenly Distributed in Both the Tuff Matrix and in the Phenocrysts. Field of View is 2 mm. Large Fractures have Apertures between 50 and 100 µm, While Smaller Fractures have Apertures less than 10 µm.

long fluid residence times. Once the core sample is infused with dye, thin sections can be mapped using image analysis to produce a 3-dimensional image of the flow porosity. When the resolution of other imaging techniques, such as CT and CIT, reaches the micron level, then the UFA™ will be used in conjunction with them to non-destructively map water distribution as a function of water content within the same core.

Figure 7 and Table 1 show some results of UFA™ studies with the Power Reactor and Nuclear Fuel Development Corporation (PNC) for Japan's high-level nuclear waste geologic repository program. The thrust of this study was to completely characterize the near-field transport characteristics using the UFA™ in conjunction with other techniques. Figure 7 includes the four candidate host rock types investigated and the compacted bentonite barrier material.

Table 1. Transport Parameters in PNC Japan's Repository Host Rocks Using the UFA™

Rock Type		K (cm/s)	D (cm²/s)
basalt	1 *(fractured)*	2.98×10^{-9}	2.52×10^{-8}
basalt	2	2.13×10^{-10}	4.56×10^{-9}
basalt	3 *(fractured)*	4.03×10^{-9}	1.46×10^{-8}
basalt	4	$< 7.1 \times 10^{-12}$	1.90×10^{-8}
granite	1	1.90×10^{-9}	7.73×10^{-9}
granite	2	2.95×10^{-9}	1.13×10^{-8}
granite	3	1.34×10^{-9}	8.30×10^{-9}
granite	4	2.49×10^{-9}	1.77×10^{-8}
mudstone	1	1.45×10^{-10}	4.31×10^{-9}
mudstone	2	1.34×10^{-10}	4.23×10^{-9}
mudstone	3	1.84×10^{-10}	5.54×10^{-9}
mudstone	4	1.40×10^{-10}	- -
tuff	1	- -	7.48×10^{-6}
tuff	2	2.21×10^{-7}	6.17×10^{-6}
tuff	3	8.82×10^{-8}	5.77×10^{-6}

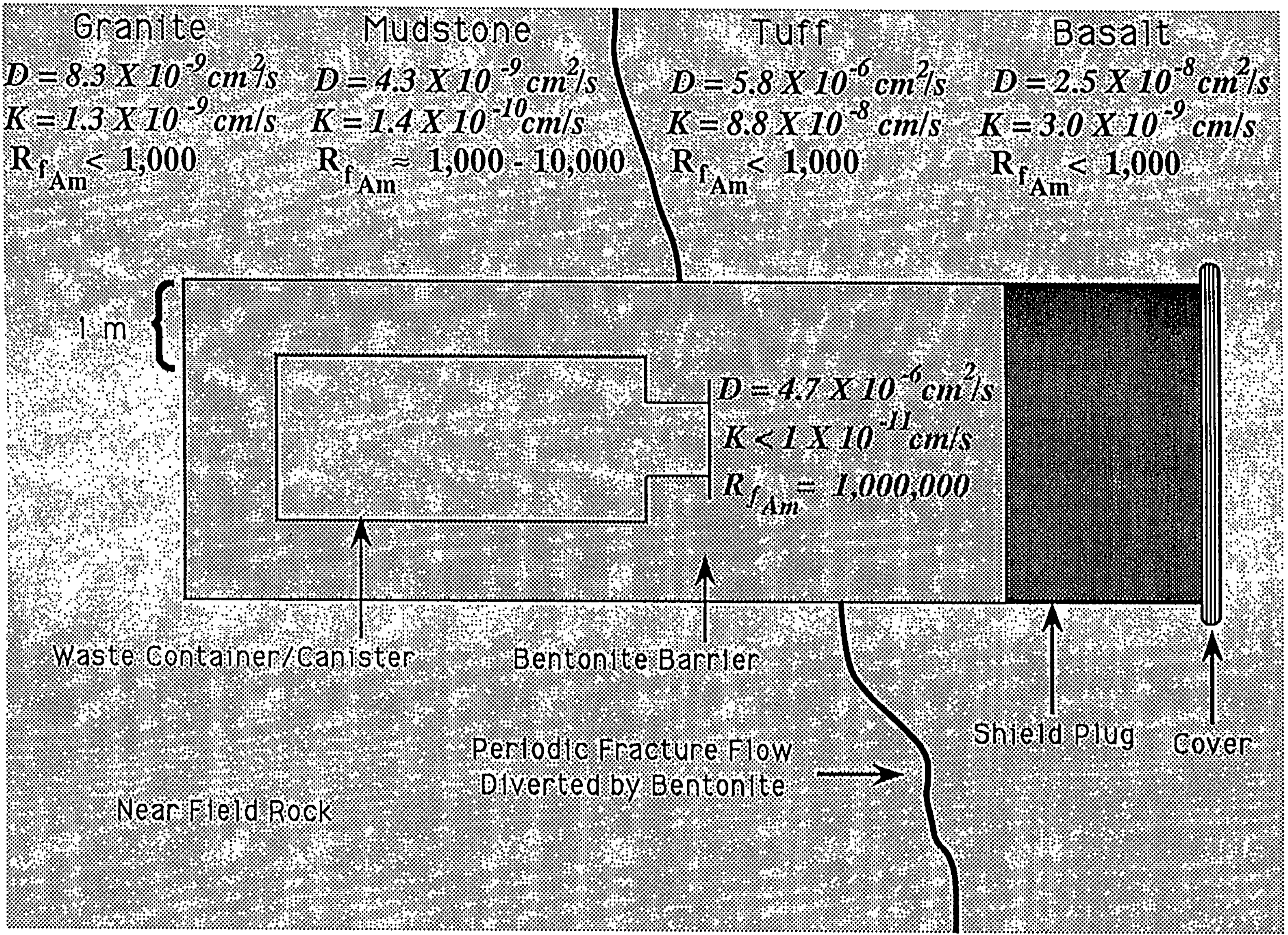


Figure 7. Transport Parameters Measured in the Bentonite and Each Candidate Host Rock. Rf Values in the Host Rocks are Estimated from the Literature and/or Extrapolated from Cs Behavior.

The proposed repository occurs below the water table, so it is assumed that the materials will be saturated after the initial desiccation phase has passed. Italicized values are those that were measured in the UFA™ except for R_{fAm} in the bentonite which was measured by Ashida and co-workers at PNC using half-cell diffusion methods (Ashida et al., 1993). The PNC tuff is a very porous, homogeneous, but relatively impermeable, rock that has less lithic fragments and glass shards than the Yucca Mountain tuffs and is less fractured. Table 1 lists the hydraulic conductivity and diffusion coefficients determined for the PNC candidate host rocks using the UFA™ over a three-week period. Flow effects from fractures or bedding structures can be investigated by running different samples of the same rock type exhibiting different features. As expected, fractures in the basalt strongly effected advection but not diffusion whereas bedding structures in the mudstone had no effect on either advection or diffusion.

RESULTS

The unsaturated hydraulic conductivities for several tuff units from Yucca Mountain investigated using the prototype UFA™ are shown in Figure 8. There are few data because the new generation UFA™, which can achieve lower K and θ, has not been completed. The $K(\theta)$ relationship appears to be steep for each sample when plotted as a function of volumetric water content because the pore size distribution affected over this water content range is very narrow. However, $K(\theta)$ falls in distinct fields for the welded, vitric and zeolitized tuffs indicating that each rock type is controlled by a distinctly different pore size distribution. Figure 9 plots a hysteretic curve for the vitric member that ran for 191.6 hours. Hydraulic steady-state was achieved at each point, and the run began from the saturated state. Because hysteresis is important in relation to the water potential but negligible with respect to hydraulic conductivity, hysteresis is not noticeable when the UFA™ is used to determine the characteristic behavior because the UFA™ directly measures $K(\theta)$ and not $\psi(\theta)$.

Hydraulic steady-state really applies only to the flow porosity, and not to the diffusion porosity which is unconnected to the overall flow porosity (*Norton and Knapp, 1977*). Therefore, one can achieve hydraulic steady-state with respect to the flow porosity and not have reached the steady-state water content with respect to the diffusion porosity. Under normal unit-gradient subsurface conditions, this will not be important, as the diffusion porosity will always be

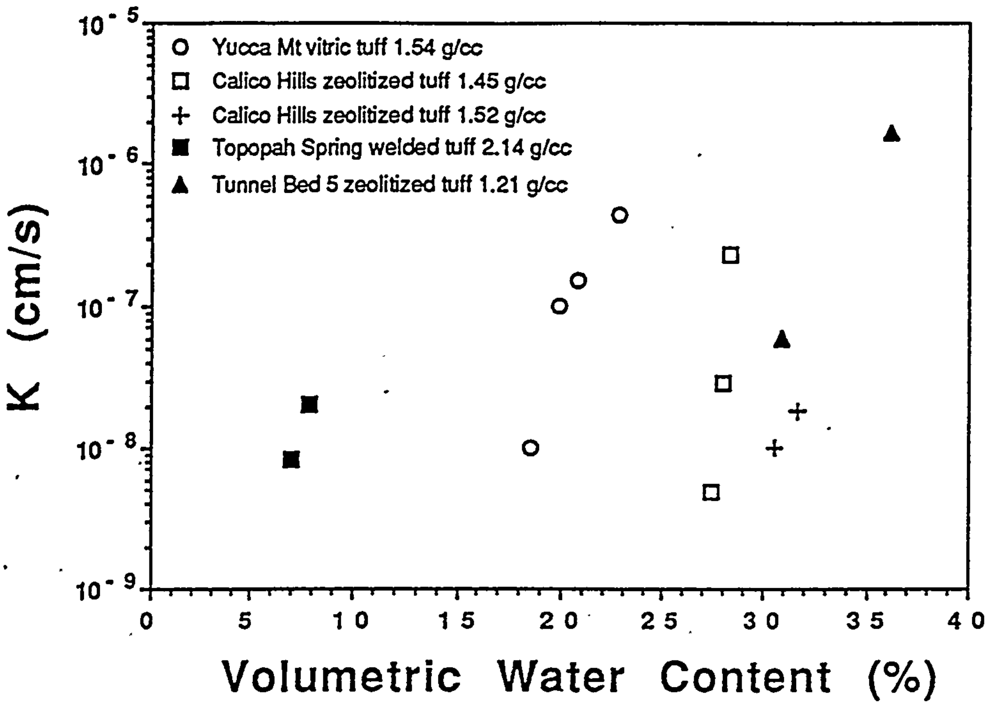


Figure 8. Unsaturated Hydraulic Conductivities for Various Yucca Mountain Tuffs.

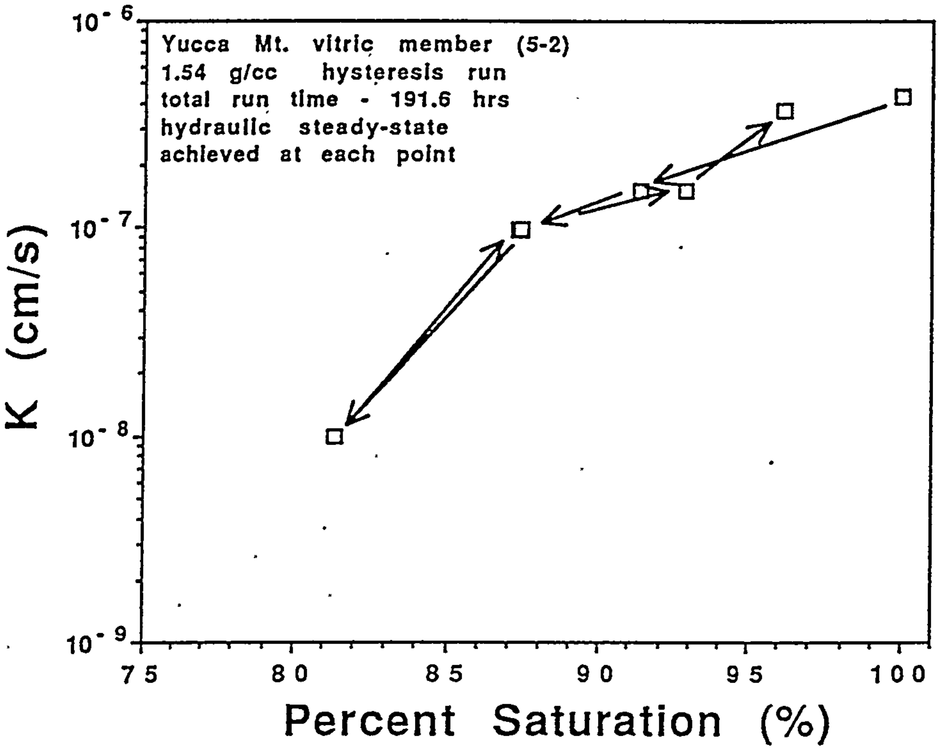


Figure 9. Hysteresis in the Yucca Mt. Vitric Member.

saturated, and changes in water content occur primarily in the flow porosity as expected by capillary bundle theory. However, in the near-field of the repository during re-invasion by the ground water or in the event of a leak, the diffusion porosity will experience changes in saturation from fully dry to fully saturated. Figure 10 shows two curves for the vitric member. The crosses indicate the situation in which hydraulic steady-state was achieved with respect to the flow porosity and with the diffusion porosity saturated, i.e., the tuff was begun saturated. The closed circles indicate the situation in which hydraulic steady-state was achieved with respect to the flow porosity but the diffusion porosity was not saturated, i.e., the tuff was begun dry and the experiment was fast enough that the diffusion porosity did not appreciably saturate, although the diffusion of water into the diffusion pores was constantly taking place. The difference between the two curves indicates a diffusion porosity of about 3% by volume out of a total pore volume of 22.8%, a small but significant volume that is not hydraulically connected to migrating waters but is chemically connected through diffusion.

Figure 11 illustrates this difference for a sample of the zeolitized Calico Hills tuff with a total porosity of 31.7%. The run was started with the core oven-dried at 60°C. This drying was necessary to ensure proper adhesion of the epoxy sample jacket and the effect of drying on the sample properties is considered minimal as repeated cycles did not cause noticeable changes in physical properties or hydraulic conductivity. The initial gravity-fed flow rate was 0.6 ml/hr, a rate which saturated the top of the sample. This rate was the result of the hydraulic conductivity of the sample and the large matric potential occurring during imbibition into dry tuff. This flow rate declined over the next 20 hours as the connected fractures and matrix became saturated to level off at 0.16 ml/hr. At just under 40 hours, breakthrough occurred from the end of the sample. Because the flow rate did not change appreciably over the remaining duration of the run, the flow porosity was evidently saturated prior to or just after breakthrough, and the water content at that point is indicative of the volume of the flow porosity minus whatever diffusion porosity had become saturated. However, the water content continued to slowly increase over the next 380 hours as the diffusion porosity saturated. This data provides some relative rates of migration within this material during advective flow and during diffusion, of both water and dissolved species.

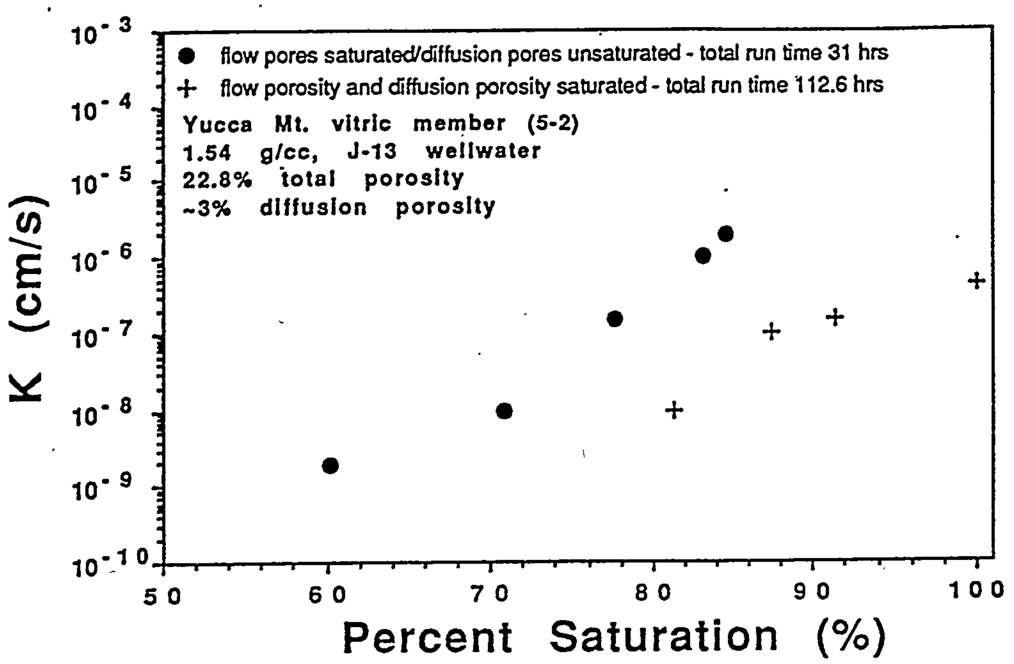


Figure 10. Hydraulic Steady-State Achieved with Respect to the Flow Porosity with and without Saturating the Diffusion Pores

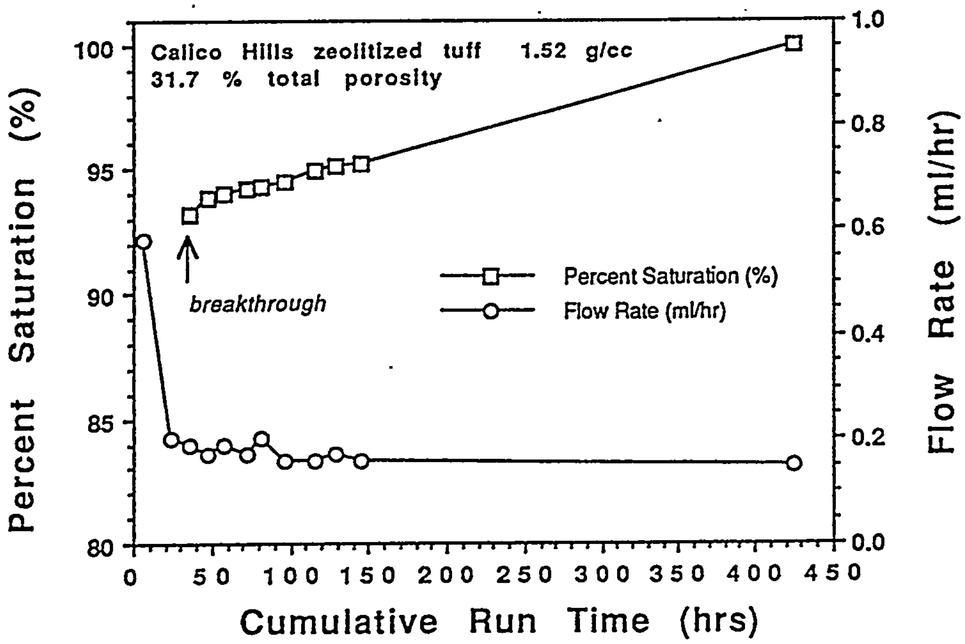
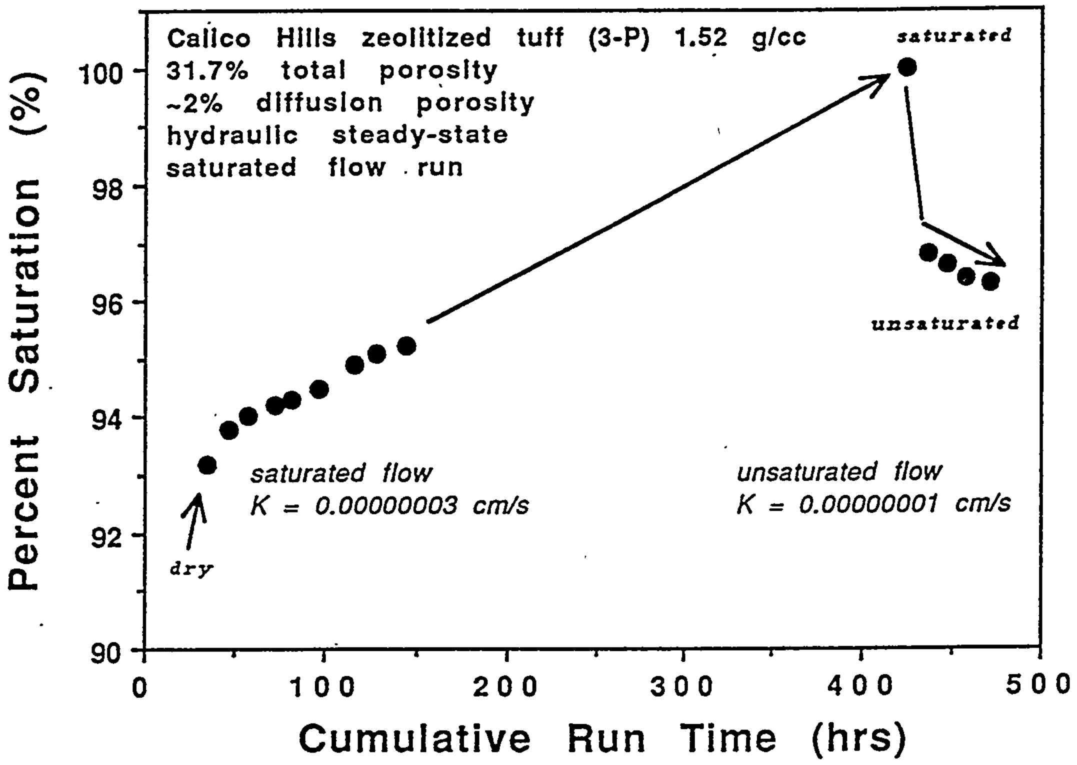


Figure 11. Time Required to Saturate the Diffusion Porosity in the Calico Hills Zeoloitized Tuff After the Flow Porosity has Achieved Hydraulic Steady-State.



<u>Figure 12.</u> Time Required to Achieve Hydraulic Steady-State from the Dry State Compared to the Saturated State.

From the dry state, this sample of the zeolitized Calico Hills tuff took about 425 hours to reach its saturated steady-state water content. After that occurred, the sample was then forced to reach a slightly unsaturated hydraulic steady-state at 96% of saturation (Figure 12). This required significantly less time, only about 50 hours. It is, therefore, more time-efficient to run these samples from the saturated state, and more relevant to the field conditions.

Figure 13 shows the hydraulic conductivity of the Yucca Mountain vitric member and the Topopah Spring welded tuff along with several different geologic materials, putting the tuff *K(θ)* into perspective with other porous media. The two soils bracket most soil behavior, especially arid soils at the Yucca Mountain Site. The gravel made of crushed Topopah Spring welded tuff exhibits the extreme drainage behavior of gravels. The open circles are measured saturated

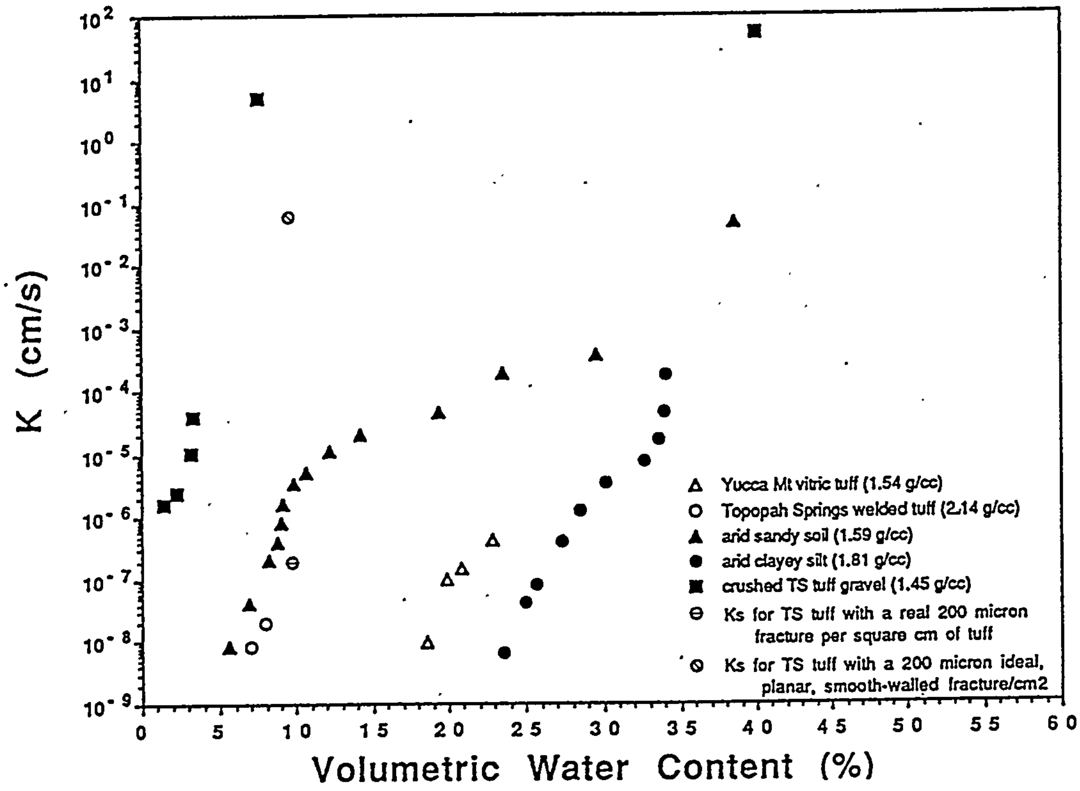


Figure 13. Hydraulic Conductivity as a Function of Volumetric Water Content for Two Yucca Mountain Tuffs Compared to Other Geologic Materials and a Theoretical Calculation.

and near-saturated hydraulic conductivities for the whole rock Topopah Spring welded tuff with a single 200 µm aperture fracture previously mentioned. The circle with the horizontal slash is the measured hydraulic conductivity of that fracture normalized to a fracture abundance of one fracture per square centimeter of tuff (2×10^{-7} cm s^{-1}). The circle with the diagonal slash is the calculated saturated hydraulic conductivity of an impermeable-matrix fractured rock with 200 µm aperture fractures and a fracture abundance of one fracture per centimeter of rock using the idealized fracture flow relationship from Norton and Knapp (1977):

$$k = nd^3/12 \tag{2}$$

where k is the intrinsic permeability (cm^2), n is fracture abundance (cm^{-1}) and d is the fracture aperture (cm). The hydraulic conductivity, K, is related to the intrinsic permeability through the fluidity relationship:

$$K = k\,\rho g/\eta \tag{3}$$

where ρ is the fluid density, g is the gravitational acceleration, and η is the fluid viscosity. For water flowing through a rock with 200 µm aperture fractures with one fracture per centimeter, $n = 1$ cm^{-1}, $d = 0.02$ cm, $\rho = 1$ g cm^{-3}, $\eta = 0.01$ poise (combined units of g s^{-1}), and $g = 980$ cm s^{-2}, giving $K = 0.059$ cm s^{-1}. This calculated value is much higher than the measured value of 2×10^{-7} cm s^{-1} for the 200 µm aperture fracture normalized to a fracture abundance of one fracture per centimeter because the actual fracture is not planar, smooth-walled or of constant aperture size throughout the rock. The 200 µm aperture was measured where the fracture intersected the sample surface, and may not represent the aperture size in the sample interior. This difference of a factor of 2.95×10^5 for the hydraulic conductivity illustrates the difficulty of idealizing fracture characteristics from sparse measurements. Also, the above fluidity relationship was developed for saturated conditions only, and is not applicable to unsaturated conditions where matric potential is as important as the fluid viscosity and density, and is also a strong function of fracture and matrix aperture sizes.

Diffusion coefficients have been determined in a variety of materials using various methods. However, unsaturated conditions present unique experimental problems. Diffusive fluxes through unsaturated materials require longer time periods to collect sufficient data from transient-state experiments. Maintaining proper boundary conditions for direct steady-state techniques under unsaturated conditions is extremely difficult and has yet to be satisfactorily demonstrated. Recently, an indirect method was developed that measures electrical conductivity in a potentiostatic or galvanostatic mode coupled with the Nernst-Einstein relationship, which provides reliable estimates of diffusion coefficients (Miller, 1972). A variation of the two-electrode method was found to be ideal for studies of geologic media. Electrical conductivity is related to the migration of ions in an aqueous solution because the ease with which ions can migrate through an aqueous solution is exactly analogous to the ease with which the aqueous species can align their dipoles along the electric field vector, as long as the frequency is appropriate. Conductivity measurements of aqueous solutions actually measure the impedance (the AC analog of DC resistance) at the impressed frequency which is a complex variable vector sum of the real in-phase (resistive) and the imaginary out-of-phase (reactive) components of the system response. For conductivity measurements (conductivity is the reciprocal of resistivity) using AC excitation, it is the in-phase component of impedance that is a measure of the true solution resistivity (or conductivity) and that can be used to represent the migration of ions in solution in geologic materials. Therefore, the impedance must be totally resistive, i.e., no capacitive elements, for the Nernst-Einstein relationship to be applicable. This was verified for saturated and unsaturated geologic systems with a 1 kHz bridge using electrochemical impedance spectroscopy which gives direct information about the real and imaginary components of impedance as a function of excitation frequency (Conca and Wright, 1990). The impedance in these systems is a constant, frequency-independent quantity in the 600 to 7,000 Hz region, and is totally resistive in the 400 to 10,000 Hz region. Thus, the measured impedance at 1 kHz on unsaturated geologic systems is a good measure of the true system resistance and its reciprocal, conductivity, and will give reliable values for diffusion coefficients calculated from the Nernst-Einstein equation. In addition, we have determined $D(\theta)$ on the same soils using the UFA™-electrical conductivity method and using

Kemper's empirically-derived relationship (Bresler et al., 1982) and the agreement is excellent ($R^2 = 0.99$; Wright, 1990). Once electrical conductivity measurements are made, they can be related to the diffusion coefficient through the Nernst-Einstein equation (Conca and Wright, 1990)

$$D_i = \frac{RT}{\mathcal{F}^2} \times \frac{\Theta G t_i}{Z_i C_i} \qquad (4)$$

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), $\mathcal{F}$ 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 ($t_{K^+} = 0.4898$ at $0.1M$; $t_{Na^+} = 0.3854$ at $0.1M$), 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 (Stumm and Morgan, 1981). Effluent is monitored to correct for possible water/substrate interactions which can change the solution electrolyte concentrations.

Simple diffusion coefficients in aqueous solution at 25°C for almost all chemical species, including organics, are between 0.5×10^{-5} cm^2/sec and 2.1×10^{-5} cm^2/sec (Conca and Wright, 1992; Oelkers, 1991; Robinson and Stokes, 1959). Therefore, simple diffusion coefficients in porous media that are less than 10^{-6} cm^2/sec at 25°C result from mechanisms or conditions other than the inherent mobility differences between the ions themselves. D represents a generic simple diffusion coefficient at infinite dilution that is a bulk property of the system and refers to the various combined physical effects of the porous media. This differs from the apparent diffusion coefficient, D_a, which includes retardation and other transient chemical effects and is specific for each species, medium, and fluid composition. Numerical models using $D(\theta)$ as an input parameter require the simple diffusion coefficient. Once breakthrough has occurred for a particular species, retardation ceases and the diffusion coefficient attains the simple value which can be orders of magnitude higher than the apparent diffusion coefficients for many species in materials such as zeolitized tuff or bentonite. The point at which breakthrough occurs is determined by the capacity of the flow paths in the media for that species under appropriate conditions.

Figure 14 shows over 300 diffusion coefficients in a variety of geologic and engineered barrier materials. The *D(θ)* relationship is characterized at higher water contents by a gradual decline in *D(θ)* as water content decreases, followed by a steep drop-off at low water contents because of the loss of continuous water pathways as the surface films become thin and discontinuous and the pendular water elements become very small, or the saturated apertures become very small. The diffusion coefficients for all materials fall into a narrow range of distribution and demonstrate that the diffusion coefficient is dependent primarily on *volumetric* water content, and only secondarily on material type at any given

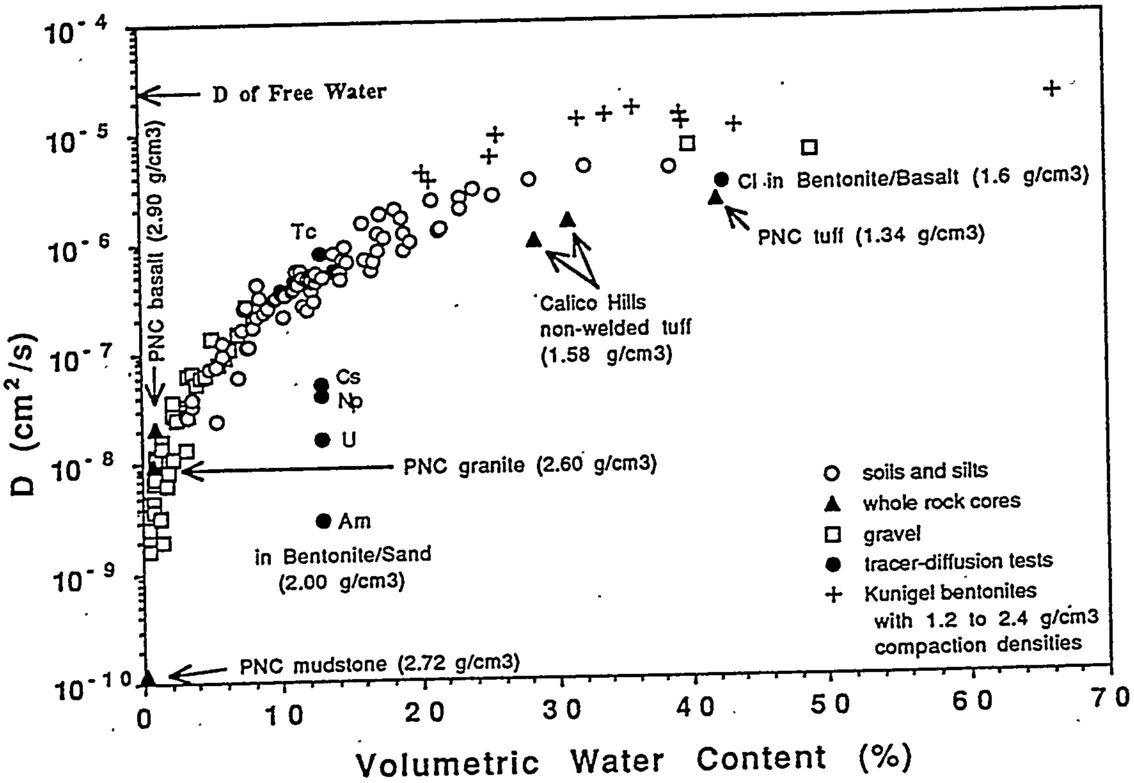


Figure 14. Diffusion Coefficients in Various Geologic Media as a Function of the Free Volumetric Water Content.

water content. No such relationship occurs for wt% water content or degree of saturation. Of course, the material properties determine the unsaturated volumetric water content, especially in aggregate materials such as gravels and soils which can have similar porosities (and, therefore, similar saturated diffusion coefficients) but very different water retention properties under the same hydrologic regime. Whole rock appears to behave similarly to aggregate materials, although not many data have been collected. Therefore, if different materials have the same volumetric water content, then their diffusion coefficients will be the same, within a factor of about two. As an example, a saturated fractured whole rock, with a total porosity of 10%, and an unsaturated gravel, with a total porosity of 40% that is only 25% saturated, both have $\theta =$ 10% with a corresponding D of 3×10^{-7} cm^2/sec. Fractured media can be synthesized with ideal, smooth-walled, planar fractures, or with excessive amounts of water-filled unconnected porosity, that do not follow this relationship, but natural materials have highly tortuous diffusion paths, and log-normal distributions of fracture/fracture apertures or pore volume/throat distributions that are similarly affected by surface and bulk water. Increasing the water content decreases the diffusion path lengths.

Also shown in Figure 14 as closed circles are apparent diffusion coefficients measured on compacted bentonite by half-cell methods (Albinsson and Engkvist, 1989; Relyea et al., 1986). Cl^- and TcO_4^- are considered to be not retarded by bentonite and compare well with the data from the electrical conductivity method. However, once chemical equilibrium is reached in the bentonite, the apparent diffusion coefficients for Cs, Np, U and Am will increase to that of Tc and Cl. The time required to reach equilibrium depends upon the situation and may or may not be important over regulatory time frames.

RETARDATION

Retardation factors can be determined in flow experiments where R_f for a particular species is the ratio of the solution velocity to the species velocity. The retardation factor for that species is given by (Bouwer, 1991):

$$R_f = V_{gw}/V_{sp} = 1 + \rho K_d/n \qquad (5)$$

where V_{gw} is the velocity of groundwater, V_{sp} is the velocity of the species, ρ is the dry bulk density and n is the porosity. If none of a particular species is lost to the solid phase, then $K_d = 0$ and $R_f = 1$ for that species. In column experiments, a breakthrough curve is obtained for the particular species and R_f is determined as the pore volume at which $C/C_o \doteq 0.5$. It is now generally assumed that for unsaturated systems $n = \theta$ (Bouwer, 1991; Conca and Wright, 1992).

The UFA was used to determine the unsaturated retardation behavior of two Yucca Mountain tuffs with respect to J-13 well water spiked with selenite to 1.31 ppm Se. Se concentrations were determined using a Jarrell-Ash Model 976 Plasma Atomcomp inductively coupled argon plasma atomic emission spectrometer. A Dionex Series 4000i Ion Chromatograph was used to speciate the selenium. All selenium in the starting solutions and in all effluent solutions was found as SeO_4^{-2} ion. For these experiments, the UFA rotation speed was set at 2000 rpm with a flow rate of 0.2 ml/hr into each sample. The experiment was run for only 9 days. Figure 15 shows the breakthrough curves for selenite in the Yucca Mountain vitric member at 62.6% saturation, and in the zeolitized non-welded tuff at 52.8% saturation. The unsaturated hydraulic conductivity during these retardation experiments was 2.49×10^{-8} cm/s for the Yucca Mountain vitric member and 1.16×10^{-8} cm/s for the zeolitized non-welded tuff. The experiment was stopped before full breakthrough in the zeolitized non-welded tuff, but the $C/C_o = 0.5$ point was reached. The retardation factor for each tuff sample is only 2.5, giving a K_d of 0.94 for the Yucca Mountain vitric member and 0.79 for the zeolitized non-welded tuff. These K_ds are lower than expected from batch studies on similar materials (Thomas, 1987), but within an order of magnitude. Recent studies by J. Zachara and D. Rai of selenite sorption on various soils gave K_ds between 0.02 and 4.63 (Zachara, personal communication; manuscript in press) which are also fairly low, although consistently higher than selenate and sulfate K_ds in the same materials. A possible explanation for the low K_ds in the tuffs is that the adsorption isotherm for selenite is not linear in this high of a concentration range. Further retardation studies will be performed at 50 ppb Se to examine this possibility.

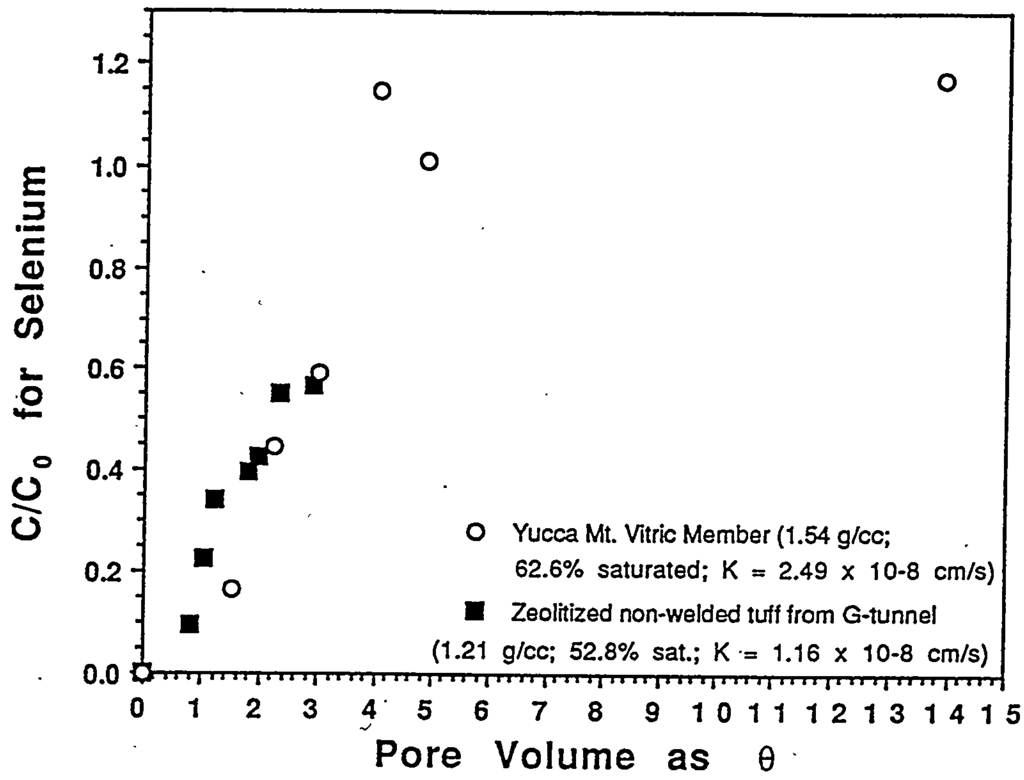


Figure 15. Yucca Mountain Tuff Retardation Experiment for 1.31 ppm Selenium in J-13 Well Water as the Selenite species

THE NEXT GENERATION UFA™

The existing UFA™ is the prototype instrument that has demonstrated that open-flow centrifugation is a useful investigative technique that should be used to compliment existing techniques for hydrologic characterization of any porous media, including rock. However, the prototype as easy and routine to operation as would be desirable. Therefore, the next-generation UFA was designed, and has been built, to have a larger sample size capability (over twice times the present volume, or about 100 cm^3); an improved fluid-dispersion system that is built into the rotor for complete and homogeneous dispersion of fluids across the sample surface, including non-aqueous phase liquids; a new rotating seal that works more efficiently at high speeds; and easy quick-release mechanisms for sample removal and effluent collection. Different sample holders will accommodate different sample sizes. As of this publication data, the new rotor has been built and is being tested. Thus far, it has performed well and results are identical between the prototype and the next-generation instrument.

CONCLUSIONS

Hydraulic conductivities, *K*, that were experimentally determined as a function of volumetric water content, θ, in tuff from the Yucca Mountain site were used to determine the feasibility of applying a new unsaturated flow technique (UFA™) to further hydrologic studies at Yucca Mountain. The UFA™ directly measures *K*(θ) rapidly in Yucca Mountain tuff and is shown to agree well with traditional methods. Hysteresis does not appear important during this testing. Capillary bundle theory holds in the UFA™. Hydraulic steady-state is achieved fastest during desaturation from a saturated state. Imbibition into dry tuff requires a long time for steady-state to occur because of slow filling of the diffusion porosity which can take a few weeks. The retardation factor for the selenite species was only 2.5 in Yucca Mountain vitric member at 62.6% saturation and zeolitized non-welded tuff from G-tunnel at 52.8% saturation with respect to J-13 well water contaminated with selenium at 1.31 mg/l (ppm). The unsaturated hydraulic conductivity during these experiments for each sample was 2.49×10^{-8} cm/s for the Yucca Mountain vitric member and 1.16×10^{-8} cm/s for the zeolitized non-welded tuff. These preliminary investigations demonstrate that the UFA™ is a useful investigative technique that should be used to compliment existing techniques for hydrologic characterization at Yucca Mountain.

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APPENDIX E

Ufa Tech Briefs Developed to Describe Technology Applications and Case Histories

UFA VENTURES TECH BRIEF

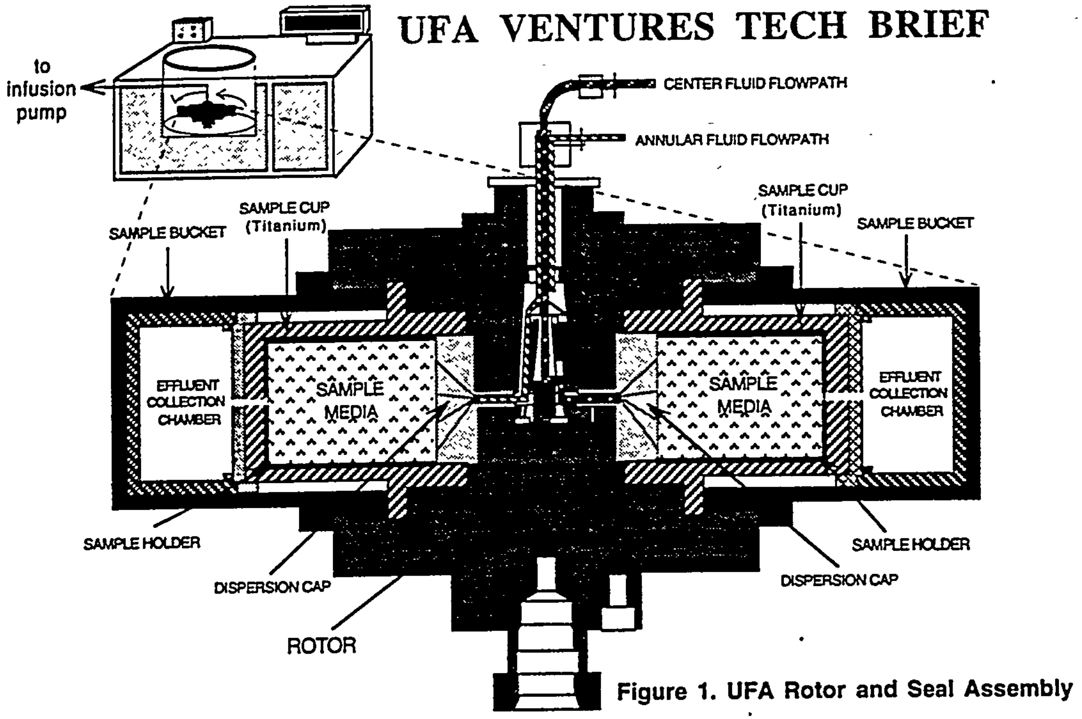

Figure 1. UFA Rotor and Seal Assembly

HYDRAULIC CONDUCTIVITY

Water and contaminant migration in the vadose, or unsaturated, zone have become critical to water resource development, agriculture, site restoration and waste disposal strategies. Because liquid transport is much slower in an unsaturated zone, transport through the vadose zone is usually the limiting factor for contaminant release, nutrient loss and groundwater recharge. Proposed regulations from the United States Environmental Protection Agency will soon require measurement of the unsaturated transport parameters for each geologic unit, soil horizon and engineered component for modelling and performance assessment needs.

The single most important transport property is hydraulic conductivity, K, which is a strong, non-linear function of the volumetric water content, θ. Traditional methods of investigating unsaturated systems require very long times because normal gravity does not provide a large enough driving force relative to the low hydraulic conductivities that characterize unsaturated conditions. Pressure techniques often bypass portions of the sample because pressure is not a whole body force like gravity and will seek the path of least resistance, e.g., fractures, sandy areas and macropores, and can affect the stabilities of common minerals like calcite, clays and gypsum. To solve these problems, an unsaturated flow apparatus (UFA^{TM}) was developed based on open-flow centrifugation. Hydraulic steady-state is achieved in hours in any porous media, even at very low water contents, by using an adjustable, whole-body driving force in combination with precision fluid flow.[1] The UFA is actually a Darcy's Law machine in that the operator adjusts both the flux and the driving force, and attains any desired hydraulic steady-state. The normal operating range is from saturated down to 10^{-11} cm/s (10^{-8} darcy; 10^{-16} cm^2), or 10^{-14} cm/s for only saturated conditions. Temperature can be controlled from -20°C to 150°C. Sample sizes can range from less than 40 cm^3 cores to Shelby-tube sized samples (280 cm^3). Samples can be directly subcored in the field from trenches, outcrops and split-spoon drill cores, or recomposited back to field densities if obtained disaggregated. Whole rock cores and other solids are potted in a resin sleeve. The UFA can isolate and separate advection from other processes, e.g., diffusion or vapor flow, allowing precise measurement of the residual water content. The UFA instrument consists of an open-flow ultracentrifuge with constant, ultralow flow pumps that provide fluid to the sample surface through a rotating seal assembly and microdispersal system (Figure 1). The UFA can control accelerations up to 20,000 g, temperatures from -20° to 150°C, and flow rates down to 0.001 ml/h. Effluent is collected in a transparent, volumetrically-calibrated chamber, which is observed during operation using a strobe light. The UFA Method is effective because it allows the operator to set the variables in Darcy's Law under which the fluid flux equals the hydraulic conductivity times the fluid driving force. Under a centripetal acceleration in which water is driven by both the matric potential gradient, and the centrifugal force per unit volume, Darcy's Law is[2]

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

where q is the flux density into the sample, K is the hydraulic conductivity, ψ is the matric potential, $d\psi/dr$ is the matric gradient, $\rho\omega^2 r$ is the centrifugal force per unit volume, r is the radius from the axis of rotation, ρ is the fluid density, and ω is the rotation speed in radians per second. Above speeds of about 300 rpm, provided that sufficient flux density exists, $d\psi/dr << \rho\omega^2 r$. Rearranging the equation and expressing hydraulic conductivity as a function of volumetric water content, θ, Darcy's Law becomes

$$K(\theta) = q/\rho\omega^2 r \qquad (2)$$

As an example, a silt from the Hanford formation accelerated to 2500 rpm with a flow rate of 0.01 ml/h reached hydraulic steady state in 10 hours at a target volumetric water content of 16.4% and an unsaturated hydraulic conductivity of 4 x 10^{-10} cm/s. Because of the ability to control the flow rate (±1% non-pulsating), rotation speed (±5 rpm) and weight measurement (±0.001 g), hydraulic conductivity is known to within ±8% at a volumetric water content known to within ±2%.[2] Figure 2 shows hydraulic conductivity vs. moisture content data obtained in three weeks for six borehole samples using a single UFA.

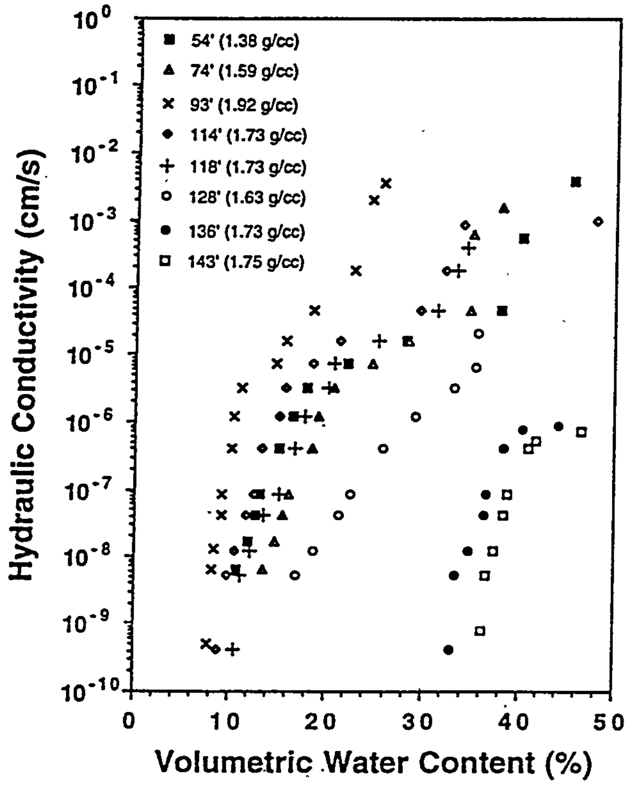

FIGURE 2. UFA-Measured Hydraulic Conductivities for Sediment Cores From Hanford Site Borehole

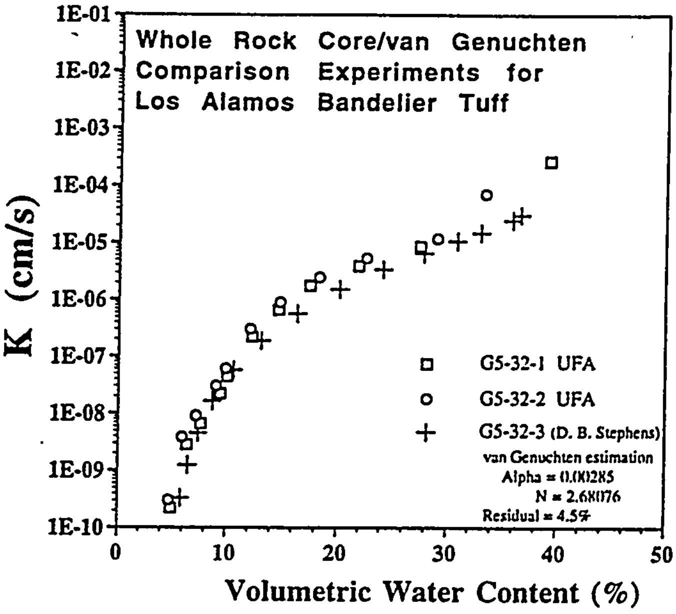

FIGURE 3. Hydraulic Conductivity Results Using a UFA and van Genuchten/Mualem Method on the same rock core.

Comparisons between the UFA Method, soil columns, van Genuchten/Mualem estimations and lysimeter measurements on the same materials show excellent agreement.[1, 2] Figure 3 shows results from a rock core of volcanic tuff using the UFA Method and a van Genuchten/Mualem estimation. Compaction from acceleration is negligible for subsurface soils at or near their field densities. Three dimensional deviations of the driving force with position in the sample are less than a factor of two, and water distribution is uniform in homogeneous samples. In heterogeneous samples each component reaches its own steady-state condition as occurs in the field, conditions which cannot be reproduced with alternative methods, only with a UFA.[1, 2]

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UFA VENTURES TECH BRIEF

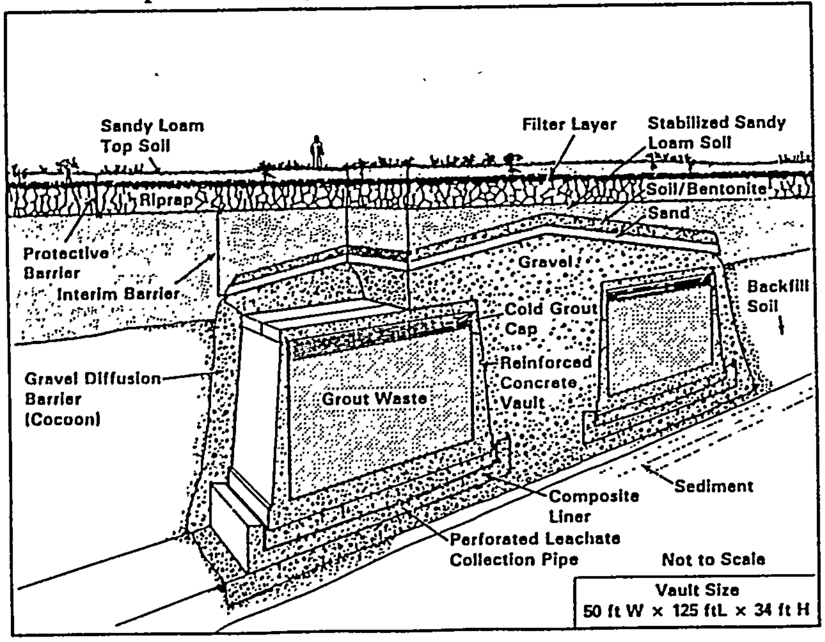
GEOTECHNICAL BARRIER TESTING

The UFA can be used to test materials for various flow and transport properties before final decisions or costly field testing. The UFA can determine optimal operating parameters of other technologies, e.g., testing nutrient formulas for *in situ* bioremediation; determining thermal, vapor and hydraulic conductivities versus moisture content for *in situ* heating and vapor extraction; measuring tank sludge waste behavior for mitigating waste tank safety issues; determining saturated and unsaturated retardation factors and leach rates of heavy metals, uranium and other actinides for emplacing permeable reactive barriers; and measuring fluid conductivity for carbon tetrachloride, ethylene glycol and other organic fluids. These direct measurements can provide remediation strategies and defensible performance assessments on schedule and at lower cost.

Case Study: *Testing A Richards Barrier*

Under unsaturated conditions, gravel acts as an effective hydraulic barrier to inflow of water from the surrounding environment and can be used to isolate subsurface disposal facilities or other structures (Figure 1). This use is referred to as a diversion barrier, capillary barrier or Richards Barrier.[1] A Richards Barrier consists of a slightly sloped layer of gravel below a layer of finer--grained material such as sand or silt. In Figure 2, K_r, K_s, and K_g refer to the hydraulic conductivities of the rock matrix, the sand, and a tuff gravel, respectively, at their respective steady-state unsaturated water contents, θ. Similarly, D refers to their respective diffusion coefficients. At hydraulic steady-state, the matric potential, or capillary pressure, is equal across the boundary, $\psi_g = \psi_s$. A positive pressure in the direction of flow is necessary for flow across the boundary from the sand into the gravel, a condition requiring the bottom of the sand layer to become completely saturated. If the hydraulic conductivity of the sand is sufficiently high, even a slight slope prevents the boundary from ever saturating. The flow rates required to saturate an ordinary sand or coarse silt are greater than occurs in any unsaturated zone saturated, i.e., recharges over 3×10^5 cm^3/cm^2/yr or over 10,000 inches of rain per year. Thus, the sand will never become saturated and no advective flow will occur into the gravel or onto the waste packages it is protecting. The size and nature of the gravel and sand must be chosen to optimize the relative conductivities and potential characteristics of each layer. The UFA was used to test various sands and gravels prior to pilot scale tests of a Richards Barrier for the high-level nuclear waste repository at Yucca Mountain. Different designs of a Richards Barrier made from candidate gravels and soils were run in large Percolation Boxes. Various water fluxes could be put into the top of the system to replicate desired recharge conditions, either as dominant matrix flow, periodic or continuous discreet fracture flow, or both. Table 1 shows results for some candidate soils and gravels. The clayey loam is a poor candidate soil because it has a relatively low saturated hydraulic conductivity and the barrier failed at relatively low recharge ates. On the other hand, the sandy loam was ideal. The size

Figure 1. A Richards Barrier, or gravel cocoon, and other geotechnical layers used to isolate an underground low-level nuclear waste disposal facility.



of the gravel had only secondary effect.

Structural offsets from seismic events were investigated using the Percolation Box by incorporating 10 cm vertical offsets along the sand/gravel boundary oriented to pool the flow and cause failure. Since this is a dynamic flow system, the flux or flow rate that can be handled by any particular height of offset should be predictable using the unsaturated hydraulic conductivity curve, K(θ), together with the water content/height distribution, h(θ) or ψ(θ), for the soil adjacent and upgradient to the offset. To test the predictive capability of the UFA, the hydraulic conductivity and matric potential of each soil was obtained using the UFA. Figure 3 shows the results for the sandy loam. The K(θ) curve gives the steady-state flux or recharge for this soil at any water content. Choosing a particular offset, e.g., 10 cm, the respective volumetric water content will be 44% and the maximum flux that this soil can handle is about 10^{-3} cm/s. Normalizing to the flow area across the top of the offset in the Percolation Box, that translates to a predicted fracture flow rate of 500 ml/hr at which the 10 cm offset should fail. The 10 cm offset actually failed at 800 ml/hr. This is eqivalent to a recharge of 3.6×10^3 cm/yr, a truly robust performance.

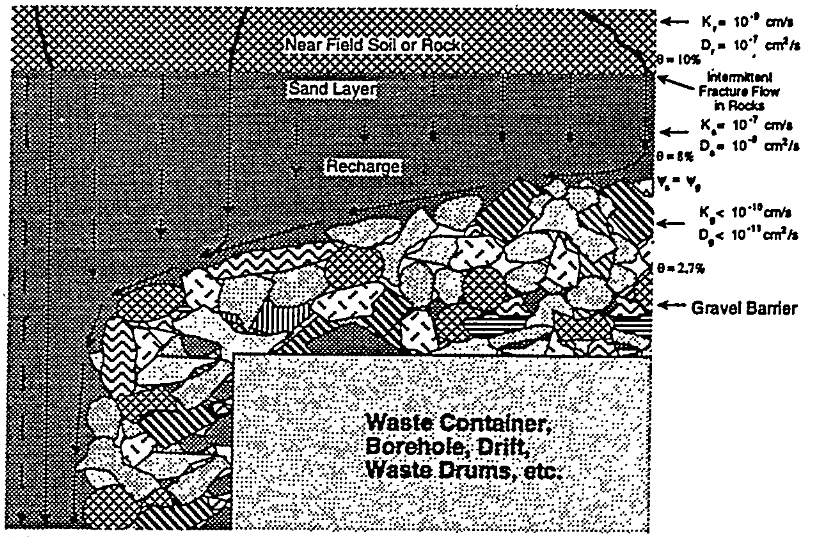


FIGURE 2. Features of a Richards Barrier (Gravel Barrier)

The UFA can be used in similar ways to predict or test the performance of various materials and remediation strategies for any situation involving flow and transport.

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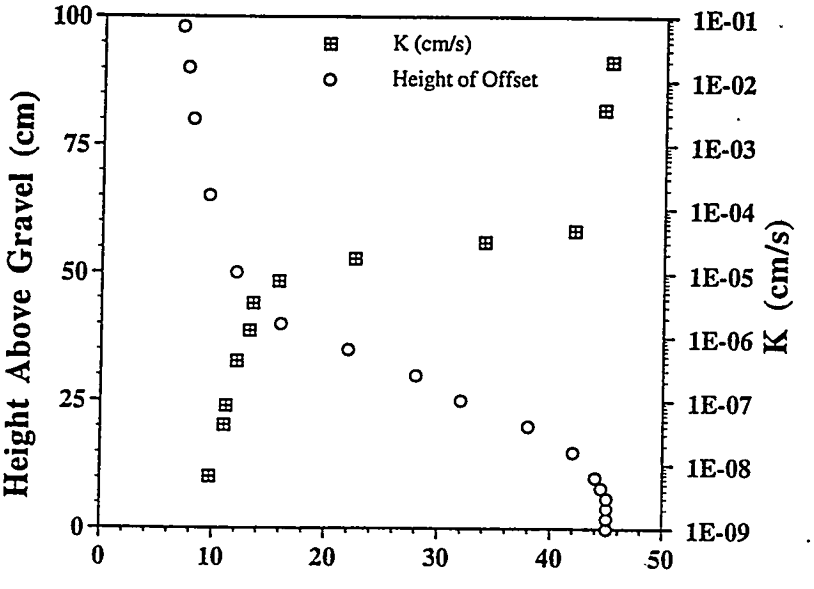


FIGURE 3. Properties Measured by the UFA to Determine the Performance of Geotechnical Layers.

TABLE 1. Maximum Recharge Rates Diverted Around Waste Package by Soil and Gravel Geotechnical Layers.

Soil Type	Gravel Type	Maximum Recharge
sandy loam	3/4" tuff	6.8×10^4 cm/yr
sandy loam	3/8" tuff	1.4×10^5 cm/yr
clayey loam	3/8" tuff	<0.5 cm/yr
sand	1/2" basalt	1.0×10^5 cm/yr
sand	1/8" quartz	2.5×10^5 cm/yr
sandy loam with 10 cm faulted offset at sand/gravel interface	3/8" tuff	3.6×10^3 cm/yr

UFA VENTURES TECH BRIEF

CHEMICAL RETARDATION

The migration of contaminants and water in the subsurface environment is controlled by several transport properties of the soil or rock. The hydraulic conductivity describes the physical movement of the water through the material, while the movement of chemicals dissolved in the water is described by the retardation factor. The retardation factor for any particular chemical includes all of the interactions between the many chemical species and the solid surfaces of the porous media. These interactions tend to retard the migration of the chemical relative to the water and delay its arrival downstream or downgradient. To model or predict contaminant transport and plan remediation activities at a site, both hydrologic and chemical behaviors need to be known.

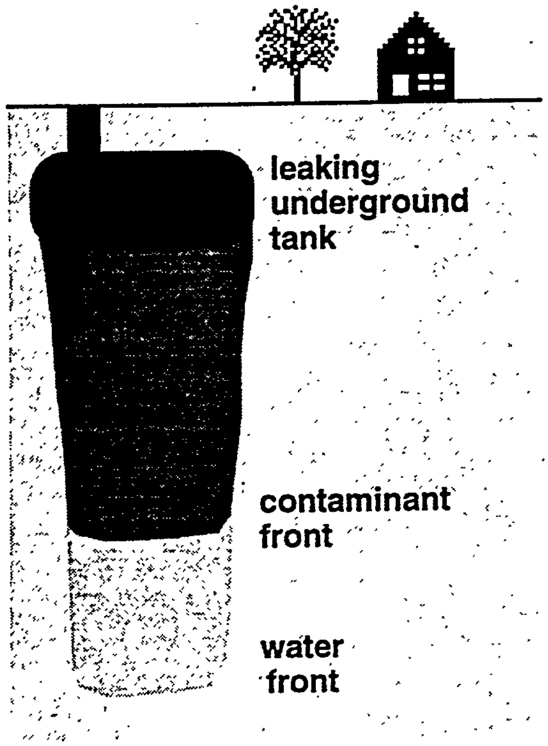
Retardation factors, R_f, can be determined in flow experiments where R_f for a particular species is the ratio of the solution velocity to the contaminant velocity. The retardation factor for that species is given by[1]

$$R_f = V_{gw}/V_{sp} \qquad (1)$$

where V_{gw} is the velocity of the water and V_{sp} is the velocity of the contaminant species. This is a bulk property that describes the overall migration of the chemical species with respect to the water and can be thought of as a chemical front moving somewhere behind the water front, but retarded by the various chemical interactions (Figure 1). If none of a particular species is retarded then $R_f = 1$ and the contaminant travels along with the water at the groundwater flow rate. When R_f are large, as for plutonium ($R_f > 10^4$ in most soils) the contaminant can take many years to migrate offsite. Because R_f describes the chemical behavior, it depends upon any factor strongly affecting chemistry, e.g., temperature, pH, redox potential, salinity, organic content, and concentrations of other chemical species. Each chemical species has its own R_f which changes as the chemistry changes. This complexity has resulted in unsuccessful predictions of retardation factors from general principles. R_f must be measured experimentally for each species under each condition for each system. Because this can be time consuming, batch tests have traditionally been performed to measure the distribution coefficient, K_d, where one part solid is placed into ten parts solution and shaken for 24 or 48 hours to observe the amount that is sorbed onto the solid. K_d can be used to estimate R_f by[1]

$$R_f = 1 + \rho K_d/n \qquad (2)$$

where ρ is the dry bulk density and n is the porosity. But for most subsurface conditions, batch experiments do not reproduce behavior in the field and can overestimate the retardation of soils and rocks. It is better to perform column experiments using the actual soil or rock, groundwater and contaminants under field conditions. In column experiments, contaminated groundwater is pumped into a column of soil packed to field density. The effluent from the column is monitored for the contaminant of interest. A breakthrough curve is obtained for the particular contaminant and R_f is determined as the



$$R_f = \frac{\text{velocity of water}}{\text{velocity of contaminant}}$$

pore volume at which the concentration of the chemical species exiting the sample is 50% of the entering solution, or $C/C_o = 0.5$. However, under unsaturated conditions or in very low permeability materials these experiments can take years because of low flow rates. Pressure systems cannot be used for unsaturated conditions and can cause significant chemistry changes in pressure-sensitive phases such as calcite, clay minerals, or gypsum.

The UFA method can be used to reduce these times dramatically by allowing flow rates to increase and by being able to target the desired water content or permeability of the system and reach hydraulic steady-state in hours.[2] The UFA achieves steady-state in any porous media by using an adjustable, whole-body driving force together with precision flow. The UFA instrument consists of an ultracentrifuge with a constant, ultralow flow pump that provides fluid to the sample surface through a rotating seal assembly and microdispersal system. The ultracentrifuge can reach accelerations of up to 20,000 g (soils are generally run only up to 1,000 g), temperatures can be adjusted from -20° to 150°C, and constant flow rates can be reduced to 0.001 ml/h. Effluent from the sample is collected in a transparent, volumetrically-calibrated chamber at the bottom of the sample assembly.

Case Study: *Uranium Transport in Hanford Soils*

Figure 2 shows some transport results for uranium in a fine-grained Hanford soil under the unsaturated conditions existing in the field. The UFA was used to achieve field water content and conditions, i.e., 20°C, a volumetric water content of 29%, and a hydraulic conductivity of 6.6×10^{-8} cm/s using Hanford vadose zone water contaminated with uranium to 50 ppb. These steady-state conditions were achieved in 3 hours using the UFA. Similar experiments on the same soil using both traditional soil columns and negative-suction, or vacuum, columns took several months, and in one case over a year, to achieve steady-state under these conditions. However, results were consistent among all methods. Tritium experiments performed in the UFA gave $R_f = 1$ demonstrating that no preferential flow paths were being produced in the UFA and that all assumptions were correct. The breakthrough experiment for uranium itself took one month, e.g., the soil required almost 15 pore volumes of water pumping at 0.2 ml/hr to saturate the uranium sorption sites in the soil such that the contaminant could migrate unimpeded. The retardation factor was 7.6, a reasonably high value for soils of the Hanford Formation, especially under unsaturated conditions where there is a tendency to lower the effective retardation factor.[2] Chemical retardation can also be affected by the gas phase under unsaturated conditions, especially in this case, because the partial pressure of CO_2 adversely affects the solubility of uranium by forming relatively mobile carbonate complexes. This is why it is necessary to carry out column experiments under field conditions.

1. Bouwer, H. 1991.*Ground Water, 29*:41-46.
2. Lindenmeier, C. W., R. J. Serne, J. L. Conca, A. T. Owen, and M. I. Wood 1995. Technical Report PNL-10722, Pacific Northwest Labs, Richland, WA.

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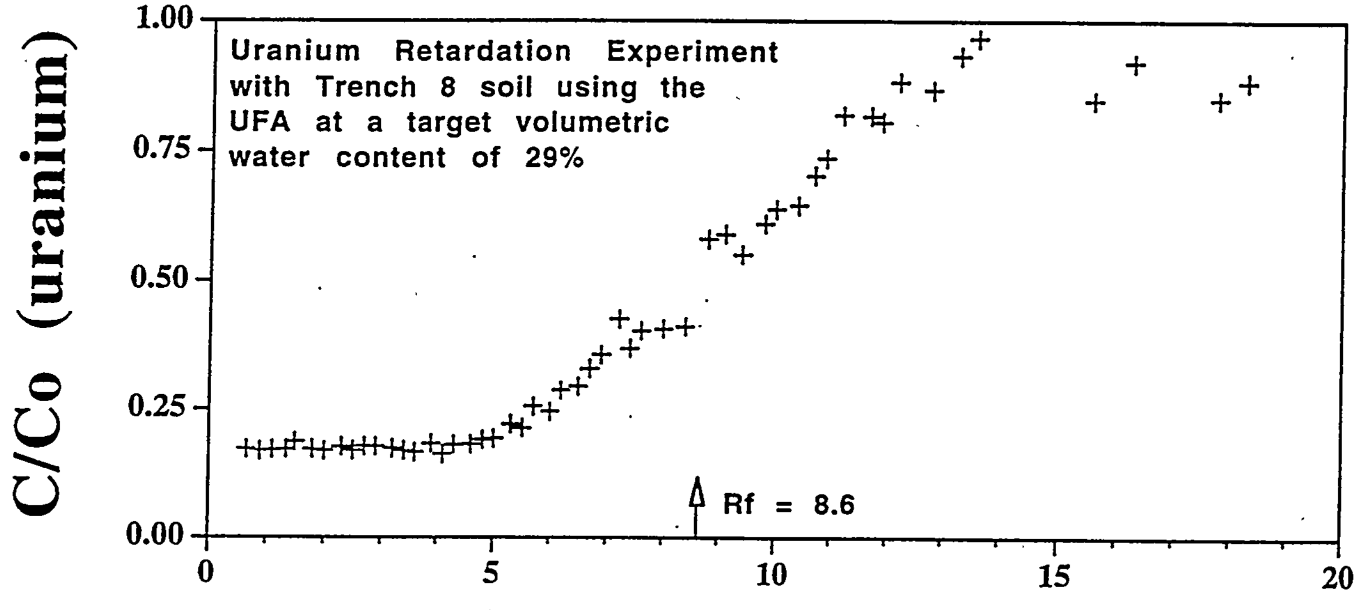

Figure 2

UFA VENTURES TECH BRIEF

HYDROSTRATIGRAPHIC MAPPING

To predict contaminant migration, implement remediation strategies or design a disposal facility, the transport properties must be known for the units beneath the site. The single most important transport property is the hydraulic conductivity which is a non-linear function of the water content. Traditionally, long times are required to attain hydraulic steady-state, but the UFA achieves steady-state in hours using an adjustable, whole-body driving force together with precision flow.[1]

Case Study: *Hydrostratigraphic Mapping*

Subsurface mapping involves knowing the spatial distribution of particular physical or chemical properties. In the study area, measurements of hydraulic conductivity using the UFA Method allowed detailed spatial mapping of the permeability, a hydrostratigraphic map, beneath the site which replaced a traditional layer-cake geology that did not provide enough detailed permeability information for targeting clean-up activities. The Plutonium Finishing Plant in the 200-West Area at the Hanford Site is the site of a mixed-waste contaminant plume containing carbon tetrachloride (CCl_4) with plutonium (Pu) and americium (Am).[2] The water table at this site is approximately 73 m (240 ft) below the surface. The overlying vadose zone consists of unconsolidated clastic sediments of poorly sorted glacio-fluvial gravel, sand, and silt (designated as the Hanford formation). Beneath it lie semi-continuous layers of loess, paleosols, and low-permeability paleoplaya lake deposits that have developed extensive caliche (grouped as Early Palouse and Plio-Pleistocene units). These sediments have a variety of water contents and a wide range of field hydrologic properties with respect to water and organic liquids. Previously, traditional layer-cake geology was used to define the hydrostratigraphy (Figure 1), with a single hydraulic behavior for each unit inferred from sediment type and a few saturated hydraulic conductivity measurements. Figure 1 is a projection onto a NE-SW trending vertical plane. Perspective is given by the apparent width of each borehole. Shown are the borehole sample positions and boundaries between different sediment units and subunits. The inset shows

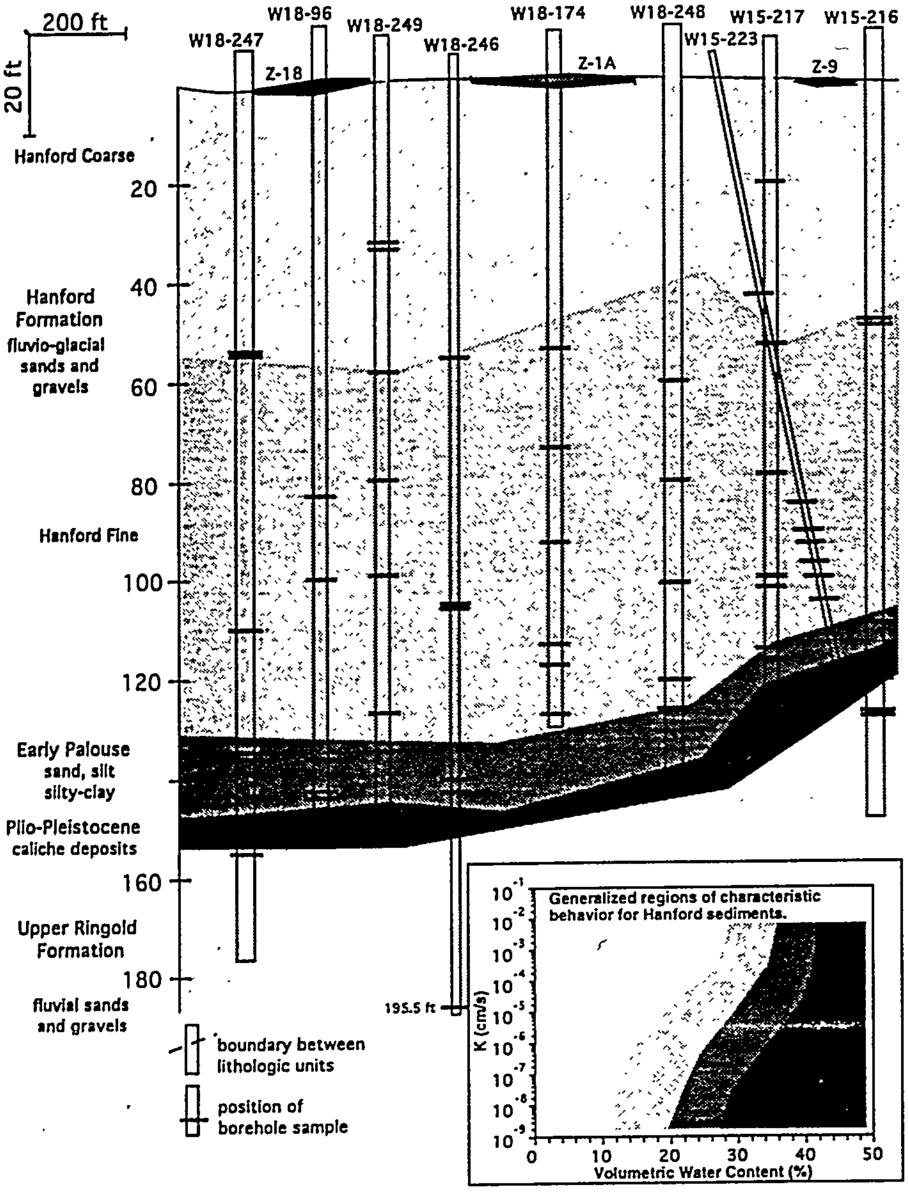

Figure 1. Hydrostratigraphic Map Inferred from Lithology and Sediment Type.

generalized regions of hydraulic behavior *roughly* correlated with gravel and sands, silty-sand, sandy-silt, and fine silts and clays moving from left to right in the inset and describes the hydraulic behavior of the units of the same shading shown in the cross-section. However, different samples which appear to be similar in appearance, grain-size distribution and other characteristics can have very different transport behaviors. The hydraulic conductivity data provided by the UFA Method allow the subsurface to be mapped with respect to the hydrologic properties of the sediments which is more relevant to predictive modelling, conceptual test plans and actual behavior than sediment type. Figure 2 gives results from one of the boreholes directly beneath Z-18 Crib. Each curve has from eight to twelve independent, unsaturated hydraulic conductivity measurements obtained in three days using the UFA Method. These hydraulic conductivities can now be assigned the shading of the region from the inset in Figure 1 in which they fall, generating a true hydrostratigraphic map (Figure 3). This map provides direct information of subsurface transport behavior and shows sufficient detail for developing a defensible restoration strategy and predicting contaminant transport. Compared to Figure 1, Figure 3 illustrates that the Early Palouse unit is not homogeneous as is indicated in hand specimen and by grain-size distribution, but has two completely different behaviors. Perched water was found on top of the right-most subunit which would not have been possible using the inferred hydrostratigraphy from Figure 1. The Hanford Fine subunit is also seen to be similar to the Hanford Coarse subunit only with local areas of different behavior. Hydrostratigraphy with the detail obtainable with the UFA provides answers to many more questions about the subsurface than can be answered traditionally.

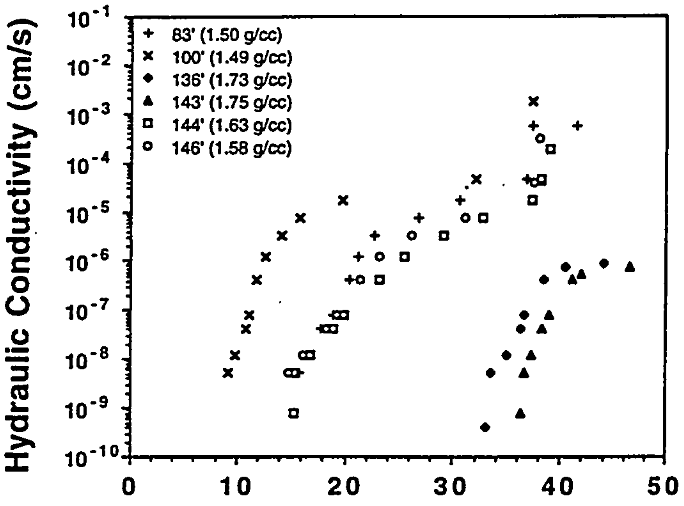

Figure 2. **Unsaturated Hydraulic Conductivities for Borehole Samples from Beneath Z-18 Disposal Crib.**

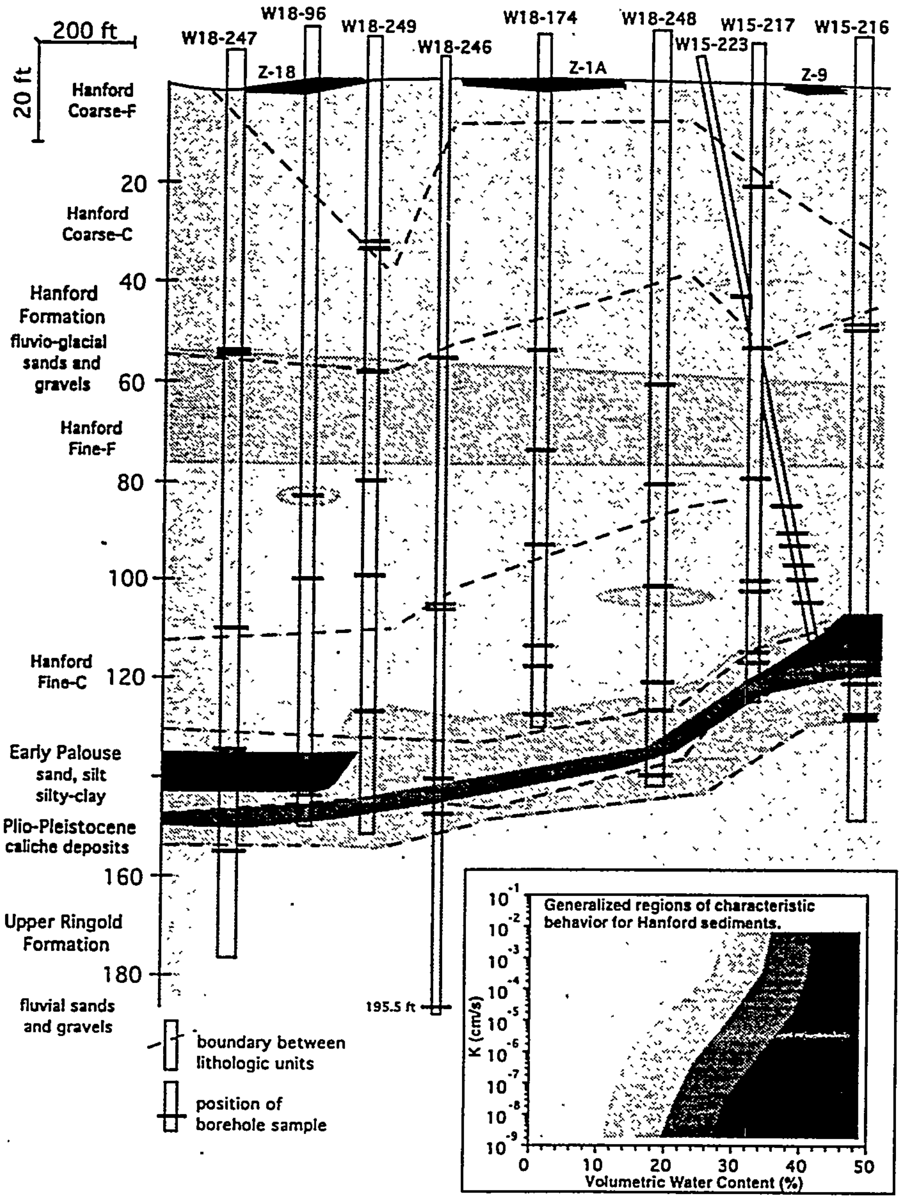

Figure 3. Hydrostratigraphic Map of Subsurface Below Z-Plant Determined from Actual Hydraulic Behavior Measured in the UFA.

1. Conca, J. L. and J. V. Wright. 1992. *Applied Hydrogeology* 1:5-24.

2. Last, G., and V. Rohay. 1993. Technical Report PNL-8597, Pacific Northwest Laboratory, Richland, WA

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UFA VENTURES TECH BRIEF

RECHARGE MAPPING

To predict contaminant migration, implement remediation strategies or design a disposal facility, one must know the transport properties of the units beneath the site as well as any engineered parts of the system, e.g., grout, gravel, or geotechnical barriers. The single most important transport property is the hydraulic conductivity (K) which is a strong, non-linear function of the volumetric water content (θ). For many performance assessments and licensing requirements by the EPA and NRC, contaminant release rates and groundwater travel times must be determined. For the vadose zone, the most important factor for travel time is the recharge, defined as the amount of precipitation that passes the upper few meters of soil to enter the vadose zone.

Case Study: *Recharge Mapping at a VOC Site*

Measurements of hydraulic conductivity using the UFA Method allow detailed mapping of the subsurface flux or recharge. The UFA achieves hydraulic steady-state in any porous media in hours by using an adjustable, whole-body driving force together with precision fluid flow.[1] The Plutonium Finishing Plant in the 200-West Area at Hanford in Washington State is the site of a mixed-waste contaminant plume containing carbon tetrachloride (CCl_4) with plutonium (Pu) and americium (Am).[2] The water table at this site is the top of an unconfined aquifer approximately 73 m (240 ft) below the surface. The overlying vadose zone consists of clastic sediments of poorly sorted glacio-fluvial gravel, sand, and silt, and semi-continuous layers of loess, paleosols, and low-permeability paleoplaya lake deposits that have developed extensive caliche. These sediments have a variety of water contents and a wide range of hydrologic properties.

The recharge at any point in the subsurface depends upon precipitation rate, type of surface cover, and any lateral recharge that may occur from perched saturated zones or artificial recharge within the vadose zone. For a normally vegetated fine-grained cover soil at this site, the recharge is less than 10^{-10} cm/s. However, this has been locally increased by human influence. Under normal conditions, hydraulic steady state is usually achieved within a few meters of the surface, i.e., the recharge is everywhere the same, each material has reached its steady-state volumetric water content for that water flux, and the recharge is equal to the hydraulic conductivity of the materials at that water content. Because borehole samples were collected as undisturbed as possible, the in situ volumetric water content and the actual hydraulic conductivity behavior can be measured and used together to determine the recharge into each sample just prior to sampling. The UFA Method was used to measure the hydraulic conductivity of over sixty samples from boreholes drilled in an around these disposal facilities. Figure 1 is a plot of hydraulic conductivity curves for two samples from the same borehole. A line is drawn from the sample's field moisture content on the horizontal axis to the hydraulic conductivity curve. A second line is drawn from the point intersected on the curve to the vertical axis. This point on the vertical axis indicates the subsurface flux in the sample at the time of sampling. The sample at 55.3 ft has a flux that is less than 10^{-9} cm/s. Arid soils in the vadose zone in this region require tens to hundreds of years to achieve hydraulic steady state when fluxes are 10^{-9} cm/s or less; therefore, it can be assumed that this sample has not undergone artificially high flux from recent

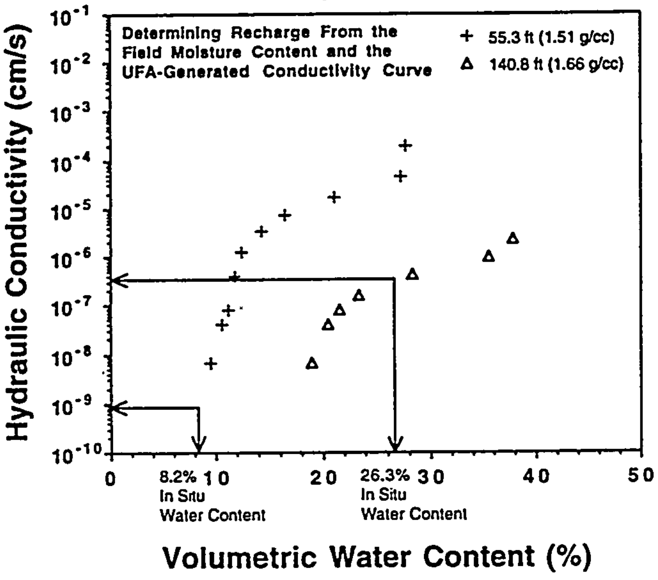

Figure 1. Determination of Recharge.

disposal of wastewater to the ground, and this flux is probably close to the actual recharge rate. For the sample at 140.8 ft below the surface, the flux is much higher, 3×10^{-7} cm/s. This result indicates that the sample has recently been subjected to increased flux, but does not provide any specific information about the timing and/or magnitude of the subsurface flux. The sample could have experienced a flux of 3×10^{-7} cm/s the day before sampling and never been subjected to any greater flux, or the sample could have experienced a flux of 3×10^{-5} cm/s 10 years ago and still be draining.

This type of determination was made on each sample and then used to assemble a subsurface flux or recharge distribution map for the subsurface beneath the site showing which samples have had artificially high recharges, presumably from the disposal facilities. Figure 2 is the resultant recharge or subsurface flux distribution map projected onto a NE-SW trending vertical plane showing the disposal facilities at the surface, the eight boreholes and samples at various depths, and a possible plume geometry that is consistent with these observations and with the hydrostratigraphy of the site. It can be seen that most borehole samples investigated have natural recharges expected at the Hanford Site. Recharge through the Hanford formation is essentially vertical and channelized as evidenced by the lack of increased recharge into borehole samples from the Hanford formation adjacent to the cribs. The only Hanford samples showing increased recharge are those directly below the cribs. No extensive lateral sheet flow is occurring in this area.

On the other hand, lateral dispersion of the plume and increased recharge is definitely occurring within the Palouse/Plio-Pleistocene units and along or near their boundaries. These results show that the plume is heterogeneously distributed and which specific areas should be targeted for remediation. This method of subsurface flux or recharge mapping works in any arid to semi-arid region.

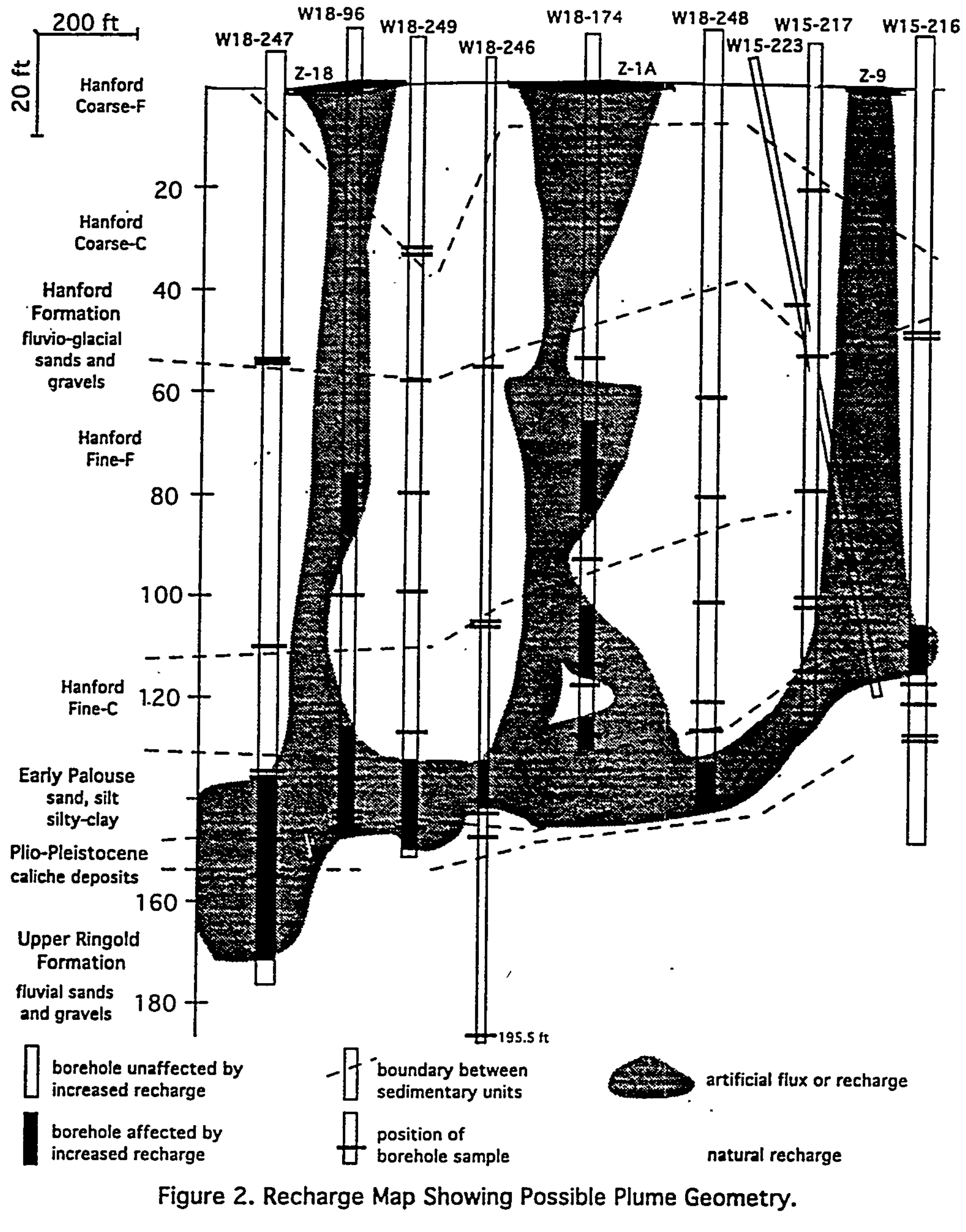

Figure 2. Recharge Map Showing Possible Plume Geometry.

1. Conca, J. L. and J. V. Wright. 1992. *Applied Hydrogeology* 1:5-24.

2. Last, G., and V. Rohay. 1993. Technical Report PNL-8597, Pacific Northwest Laboratory, Richland, WA.

3. Gee, G. W., M. J. Fayer, M. L. Rockhold, and M. D. Campbell. 1992. "Variations in Recharge at the Hanford Site," *Northwest Science*, 66:237-250.

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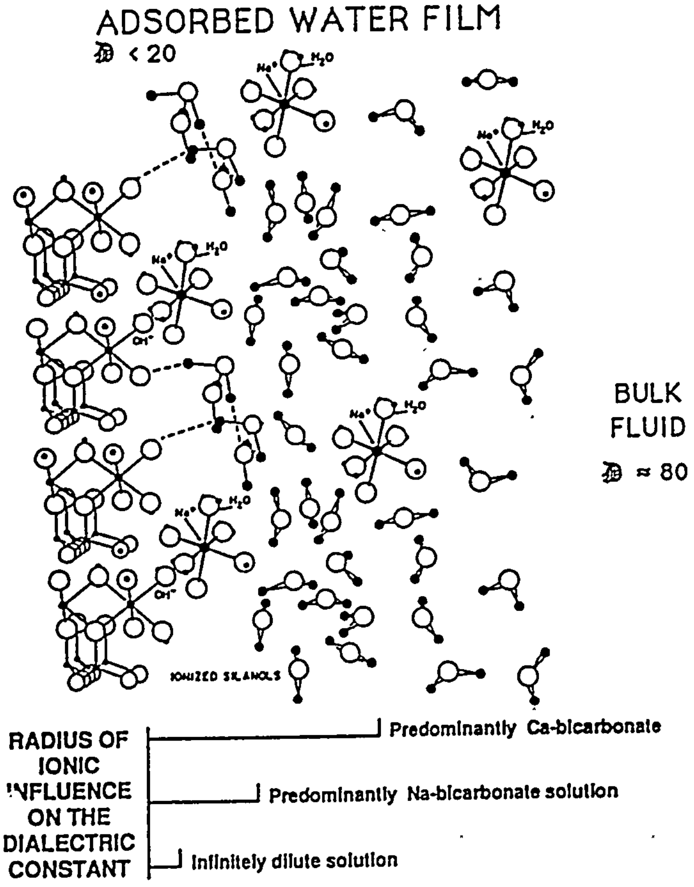
MEASURING DIFFUSION COEFFICIENTS

The aqueous diffusion coefficient describes how individual molecules and ions migrate, or randomly walk, through subsurface soils and rocks, independent of the water or carrier fluid (Figure 1). Diffusion coefficients often control the ultimate source of a contaminant, i.e., how it comes out of the waste form or how it gets through some containment barrier or liner. Once a contaminant gets out into the environment, advection or flow usually becomes the dominant transport process. Diffusion coefficients control many remediation processes, such as adsorption or chemical filtering, Diffusion becomes important in unsaturated environments where the flow of water is very slow.

Direct and indirect techniques have been used to determine diffusion coefficients in porous media. Both techniques employ steady-state and transient-state techniques. Fick's first law forms the basis of steady-state experiments, while Fick's second law describes the transient-state. Unfortunately, it has been extremely difficult to measure diffusion coefficients below 10^{-8} cm²/s, using direct steady-state techniques (tracer diffusion tests) because it is difficult to maintain proper boundary conditions. This necessitates an indirect method to measure diffusion coefficients in unsaturated or relatively impermeable soils and rocks. The most widely used indirect method is to measure electrical conductivity in a potentiostatic mode. During the run, the degree of saturation and other physical conditions can be fixed in the sample using the Unsaturated Flow Apparatus (UFA).[1] Electrical conductivity cells designed for use in the UFA have two stainless steel electrodes in contact with the sample. Once electrical conductivity is measured, it is related to the diffusion coefficient through the Nernst-Einstein equation[2] which is given by:

$$D_i = \frac{RT}{F^2} \times \frac{\Lambda_i}{Z_i} = 8.92 \times 10^{-7} \times \frac{\Theta Gt_i}{ZC_i}$$

where D_i is the diffusion coefficient of the ith ion (cm^2/s), R is the gas constant (J/deg mol), T is absolute temperature (Kelvin), F is Faraday's constant (coul/mol), Λ is equivalent conductance of



DIELECTRIC CONSTANT, 𝕯

Vacuum	1.0000
Air	1.0005
Teflon	2.1
Pyrex	4.5
Distilled Water	78.0

Figure 1. The nature of ionic diffusion and electrical conductivity for water films in subsurface materials. In this example, the complexation of hydrated sodium ions on the exposed edge oxygens of a mineral surface alters the dielectric constant of the water, lowering the electrical conductivity. In an analogous way, weak bonds between the hydrated ions, edge oxygens and water molecules inhibit ionic diffusion and lowers the overall diffusion coefficient of the water film. Higher valent ions have a greater effect on the system. If the water film is more than about 20 Å thick then the diffusion coefficient will be unaffected by complexation and will be determined only by the volumetric water content and ionic strength of the solution. In natural systems, aqueous diffusion is always through bulk water.

the ith ion (cm^2 S/mol), Z_i is the charge number on the ith ion (dimensionless), t_i is the transference number of the ith ion, C_i is the molar concentration of the ith ion, Θ is the cell constant for the conductivity cell sample holder (cm^{-1}), and G is the measured conductance on a conductivity bridge (S). All of these parameters are known or easily measured. This method is the foundation of diffusion and upon which all subsequent methods are based. The ease with which molecules diffuse through the water is exactly related to the ease with which the water molecules can align their dipoles along the electric field vector (Figure 1). There are different representations of diffusion, describing various physicochemical properties of the media:

$$D_a(\varepsilon + \rho K_d) = D_e = D_s = \varepsilon D_v \phi = \varepsilon D_v \delta_D/\tau^2$$

where D_a is the apparent diffusion coefficient, D_e is the effective diffusion coefficient which is usually equal to the simple diffusion coefficient, D_s measured by electrical conductivity methods, D_p is the diffusion coefficient in the pore water, D_v is the diffusion coefficient in free water, ε is the porosity, ρ is the density, K_d is the distribution coefficient, ϕ is a geometric factor, δ_D is the constrictivity, and τ is the tortuosity. The distribution coefficient and the extent of retardation used in transport models need to be determined separately for each specific ionic species, media, and fluid composition. Retardation can significantly affect the migration of species in porous media, resulting in an apparent diffusion coefficient that can be markedly different from the simple diffusion coefficient. However, this apparent diffusion coefficient is transient and will approach the simple diffusion coefficient as the sorption sites are filled or as the system otherwise tends toward chemical equilibrium. The diffusion coefficient for most aqueous species, including organics, are similar, differing by, at most, a factor of two from the self-diffusion coefficient of water which is 2.4 x 10^{-5} cm^2/s at 25°C. Diffusion coefficients in porous media that are less than 10^{-5} cm^2/s result from mechanisms or conditions other than the inherent mobility differences between the species themselves. These mechanisms include path length differences due to water content differences and retardation due to sorption and transient chemical effects. Figure 2 shows over 300 diffusion coefficients for various geologic media as a function of volumetric water content determined using the Nersnt-Einstein method. The UFA was used to fix the target water content with 0.01 *M* KCl or NaCl solutions. It can be seen that the simple, or effective, diffusion coefficient is primarily a function of the water content and not of the material type.

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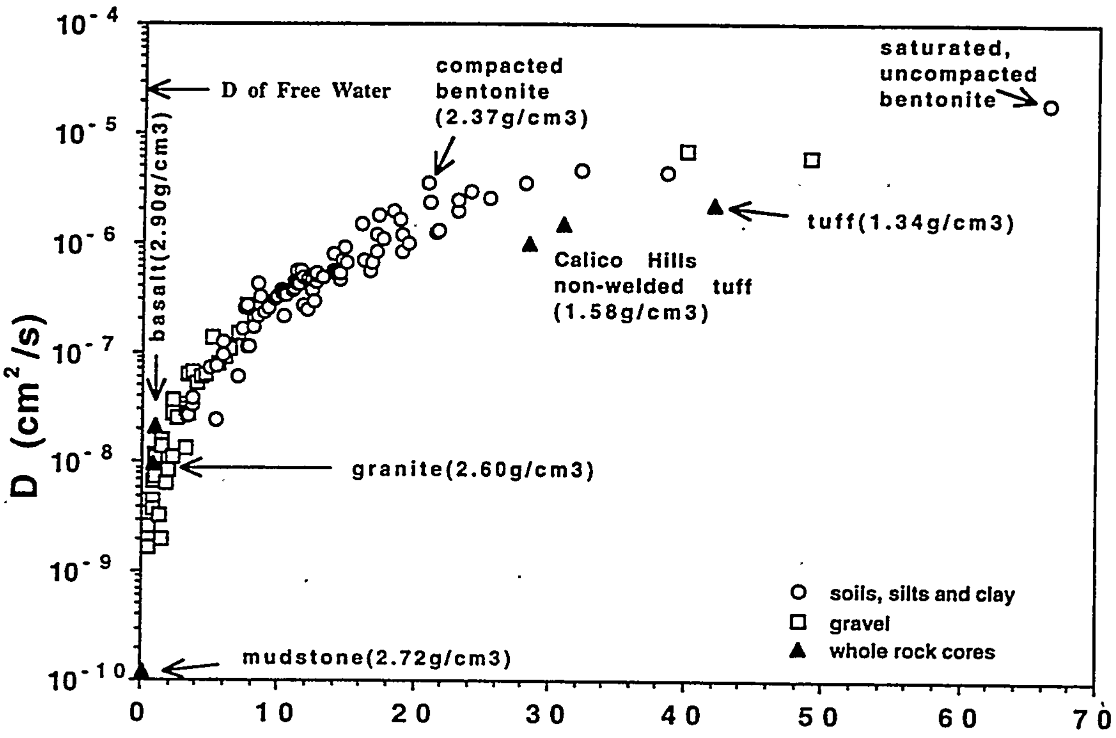

Figure 2.

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