Field Studies at the Apache Leap Research Site in Support of Alternative Conceptual Models

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ABSTRACT

This is a final technical report for a project of the U.S. Nuclear Regulatory Commission (sponsored contract NRC-04-090-051) with the University of Arizona. The contract was an optional extension that was initiated on July 21, 1994 and that expired on May 31, 1995. The project manager was Thomas J. Nicholson, Office of Nuclear Regulatory Research. The objectives of this contract were to examine hypotheses and conceptual models concerning unsaturated flow and transport through fractured rock, and to design and execute confirmatory field and laboratory experiments to test these hypotheses and conceptual models at the Apache Leap Research Site near Superior, Arizona.

The results discussed here are products of specific tasks that address a broad spectrum of issues related to flow and transport through fractures. Each chapter in this final report summarizes research related to a specific set of objectives and can be read and interpreted as a separate entity. The tasks include detection and characterization of historical rapid fluid flow through fractured rock and the relationship to perched water systems using environmental isotopic tracers of ^3H and ^{14}C , fluid- and rock-derived $^{2343}\text{U}/^{238}\text{U}$ measurements, and geophysical data. The water balance in a small watershed at the ALRS demonstrates the methods of accounting for ET, and estimating the quantity of water available for infiltration through fracture networks. Grain density measurements were made for core-sized samples using a newly designed gas pycnometer. The distribution and magnitude of air permeability measurements have been measured in a three-dimensional setting; the subsequent geostatistical analysis is presented. Electronic versions of the data presented here are available from authors; more detailed discussions and analyses are available in technical publications referenced herein, or soon to appear in the professional literature.

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This report has been prepared to document work performed to date by researchers in the Department of Hydrology and Water Resources at the University of Arizona, under contract NRC-04-90-51, FIN L1282, entitled "Validation Studies for Assessing Unsaturated Flow and Transport Through Fractured Rock." The project manager is Thomas J. Nicholson who provided substantial input to the preparation of this report. The report is an independent product and does not necessarily reflect the views or regulatory position of the NRC.

FOREWORD

This final technical report, NUREG/CR-6459, was prepared by the University of Arizona as a research project for the Waste Management Branch, Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission (FIN L1282). It is the final report documenting completed research to evaluate various conceptual models involving two-phase flow (gas and liquid) and transport through heterogeneous, fractured rock. Detailed information is provided on: the occurrence and significance of fluid flow through fractures in unsaturated tuffs; use of isotope geochemistry to interpret unsaturated zone conditions and processes; geophysical studies used to characterize moisture content, movement, and redistribution; water-balance methods for estimating infiltration; gas and water sampling methods; and air-injection experiments. Data summaries are provided in companion reports (NUREG/CR-5457 and -6458). The research results are relevant to site characterization and data analysis issues encountered in review and confirmation of high-level radioactive waste disposal licensing information.

NUREG/CR-6459 is not a substitute for NRC regulations, and compliance is not required. The approaches and/or methods described in this NUREG/CR are provided for information only. Publication of this report does not necessarily constitute NRC approval or agreement with the information contained herein. Use of product or trade names is for identification purposes only and does not constitute endorsement by the NRC or the University of Arizona.

1. INTRODUCTION

This document provides a final technical report for U.S. Nuclear Regulatory Commission sponsored contract, NRC-04090-51 (FIN L1282) with the University of Arizona. The contract was an optional extension initiated on July 12, 1994 and expired on May 31, 1995. The project manager is Thomas J. Nicholson, Office of Nuclear Regulatory Research. The Principal Investigator is R.L. Bassett, and S. P. Neuman and P. J. Wierenga are Co-Principal Investigators.

This contract arises from a statement of work based upon NRC regulatory needs that originated in the technical review of DOE's Site Characterization Plan and research needs identified in two symposium peer reviews of the earlier research programs conducted at the University of Arizona (Evans and Nicholson, 1987). The broad objectives of this contract are to examine various hypotheses and conceptual models concerning unsaturated flow and transport through heterogeneous fractured rock and to design and execute confirmatory field and laboratory experiments to test these hypotheses and conceptual models. Conceptual models and hypotheses relevant to flow and transport processes in unsaturated fractured rock have been recently identified and prioritized through the Peer Review of the Yucca Mountain Site Characterization Project (Freeze et. al., 1991). The specific objectives under this contract are (1) to investigate continuum scales for predicting gas and liquid flow in matrix-fracture systems, (2) to determine the relationships between relative permeability of air and water in unsaturated fractured tuff, (3) to investigate the use of effective hydraulic, pneumatic and transport properties to predict transport, (4) to investigate the use of isotope and reaction path studies to determine the rate and pathway of solute flux in and unsaturated fractured tuff, (5) to investigate the role of fracture zones in unsaturated flow and transport in a region above the water table and (6) to determine the relationships between measurements performed at different scales. Objectives (1), (3), and (6) are to be addressed in cooperation with another project also at the University of Arizona lead by Shlomo P. Neuman (FIN L1283).

The research approach to the above objectives was divided into five related tasks:

- Task 1 Hydraulic/Pneumatic/ and Tracer Field Tests
- Task 2 Geochemical Studies
- Task 3 Infiltration, Deep Percolation and Recharge Studies
- Task 4 Workshop on Fracture Flow and Transport Studies

Progress reports for the above tasks are provided in this document.

2. OCCURRENCE AND SIGNIFICANCE OF FLUID FLOW THROUGH FRACTURES IN UNSATURATED TUFF AT THE ALRS

by G.R. Davidson, R.L. Bassett, E.L. Hardin, and D.L. Thompson

2.1 INTRODUCTION

If aqueous fracture flow is significant at the Apache Leap, it is most likely to be found beneath the ephemeral streams where fractures are periodically exposed to water under positive head. For this reason, the Deep Slant Borehole (DSB-1) was placed in the bed of an ephemeral stream (Fig. 2.1) and drilled at an angle to intersect a series of nearly vertical fractures. The surface trace of DSB-1 roughly follows the wash down-stream. The bottom of the borehole penetrates a perched aquifer believed to be part of a regional perched system shown in Fig. 2.2. A diagram of DSB-1 is provided in Fig. 2.3.

Contamination of pore fluids was minimized by using atmospheric air to cool the bit and remove cuttings. Continuous core was retrieved from DSB-1 and immediately preserved in Protec Core® to isolate pore fluids from atmospheric contaminants and to prevent evaporation (Davidson, 1995). A log of core recovery is given in Appendix A.

The occurrence and significance of water and gas flow through fractures is investigated here using geochemical and isotopic measurements from surface water, soil gas, formation gas, pore water, and perched aquifer water. Carbon-14 and tritium measurements, obtained primarily by distillation of pore water from preserved core (Davidson, 1995), provide evidence that close to half the water in the aquifer in a mixing zone beneath DSB-1 may be derived from nearby fractures. Geochemical models further suggest that older aquifer water moving into the local mixing zone is also derived largely from fracture recharge. Gaseous diffusion of $^{14}\text{CO}_2$ has been offered as a possible mechanism by which the ^{14}C distribution is established in the unsaturated zone, but the DSB-1 system is thought to be controlled by flow of water through fractures with partial imbibition into the surrounding matrix.

2.2 SAMPLING SCHEDULE

Flow through specific fractures in unsaturated fractured rock is difficult to document for several reasons. In the absence of a tunnel network beneath the surface, relatively small diameter boreholes provide the only access to water flowing through a fracture. Flows are often episodic with preferential pathways within each fracture plane or set, and water may bypass an intersecting borehole without entering it. Flows that do enter a borehole may be of short duration, making them difficult to locate and sample. Collection of water, when it is found, poses its own set of problems. Simply collecting a sample can be a major undertaking. For radioisotope work, additional difficulties are added by requiring isolation from the atmosphere and larger sample volumes relative to geochemical measurements.

Figure 2.1 Location maps for the ALRS. The drainage basin containing DSB-1 is outlined in the lower map. "AQ-" and "SG-" refer to runoff water sampling sites and soil gas sampling sites, respectively.

Figure 2.2 Approximate perched water table elevations (in meters above sea level) around the ALRS based on well data collected by Bassett et al. (1994). Surface elevations are in feet.

Figure 2.3 Cross-section of DSB-1 with changes in pitch and diameter identified. Pitch is given in degrees from vertical. Casing start and end identifies the location where casing became lodged in the borehole and could not be removed.

An attempt was made to circumvent these difficulties by extracting water for radioisotope analyses from core samples located adjacent to suspected ephemerally water-bearing fractures. If water flows rapidly through a fracture with some loss into the adjacent matrix, pore waters from these core should appear younger than core from unfractured zones.

Sampling sites were identified using video and geophysical logs of the DSB-1 borehole. The highlighted bands in Fig. 2.4 identify three intervals where fracture flow was suspected. Other intervals could also have been selected, but time and monetary constraints limited the investigation to the most promising intervals. All figures and discussion refer to vertical depths rather than linear distance along the borehole unless otherwise noted.

At 72 m, the video log recorded water seeping into the borehole. The geophysical logs at this depth show an increase in neutron capture, coupled with sharp drops in resistivity and density readings. Increasing neutron capture and decreasing resistivity readings can be caused by increased saturation in the formation. Sharp, short-duration drops in density are typical of isolated fracture sets. When occurring together, these records may indicate that water flowing through fractures has partially imbibed into the local matrix resulting in increased saturation.

At 47 m, no resistivity data are available because the casing remains in the borehole at that depth, but the neutron and density logs are consistent with the readings at 72 m. Gravimetric and vacuum-distillation results also demonstrate anomalously high water content at this depth (Fig. 2.5).

Below 120 m, the formation becomes much more fractured. Although matrix porosity is considerably lower in the gray unit relative to the white unit (Table 2.1), air permeability below 120 m is much higher due to the high frequency of open fractures (Fig. 2.6). Maximum neutron capture, and minimum resistivity and density readings occur at 134 m. Core records also indicate particularly high fracture density here. Only 0.3 meter of core was retrieved from a 3 meter interval at this depth due to the highly fractured condition of the rock (Appendix A).

Sampling points from unfractured intervals were selected by locating areas on the geophysical logs with lower neutron capture, higher density and higher resistivity responses.

2.3 RADIOISOTOPE MEASUREMENTS FROM DSB-1

2.3.1 Aqueous ^{14}C and ^3H Distribution

Uncorrected ^{14}C activity and tritium results are plotted in Figs. 2.7 and 2.8 with the same fracture zones from Fig. 2.4 identified. Tables of all isotopic data are provided in Appendix B. The distilled samples provide the most complete record of the borehole. Carbon-14 trends reverse direction toward increasing activity five times in these data. Three of the reversals occur at or near the highlighted zones. The other two reversals occur in the upper 30 m and just above the water table. At 20.5 m, the reversal is probably caused by flow through an unidentified

Figure 2.4 Neutron, density, and resistivity logs of DSB-1. Highlighted bands are shown at depths where ephemeral water-bearing fracture zones were suspected based on video and geophysical logs. Additional zones bound by the two dashed lines were not specifically targeted, but their influence is also observed in the isotope data. The two locations where the borehole narrows are marked as "bn". (Geophysical data from E. Hardin, 1993, written communication.)

Figure 2.5 Water content of DSB-1 core measured by gravimetric analysis (open circles) and by vacuum distillation (filled circles). (Data from Geddis, 1994, and Davidson, 1995, respectively) Highlighted and dashed bands identify the suspected water-bearing fractures from Fig. 2.4.

Figure 2.6 Cumulative air purged (STP). Each interval is labeled with the depth. Intervals where flow rate data are of uncertain quality are shown as dashed lines. Note the different scales on the two graphs.

Figure 2.7 Carbon-14 activity of all samples measured from DSB-1. Highlighted and dashed bands identify the suspected water-bearing fractures from Fig. 2.4. The broken line connecting the lowest formation air intervals signifies possible contamination at these depths. Analytical precision (1σ) is roughly the size of the data points. DOC and DIC refer to dissolved organic carbon and dissolved inorganic carbon, respectively.

Figure 2.8 Tritium concentration of all samples measured from DSB-1. Highlighted and dashed bands identify the suspected water-bearing fractures from Fig. 2.4. Error bars reflect the analytical precision (1σ).

Table 2.1 Porosity measurements on Apache Leap Tuff. Only the white and gray units are penetrated by DSB-1. The upper-most unit (white) is estimated to be about 30 m thick.

Unit	Porosity (%)	Method	Source
All	0.4 - 16 n = 12	powder density and bulk specific gravity data	Peterson (1961)
White	9.2 - 47.6* 14.6 mean n = 105	mercury intrusion	Vogt (1988)
Gray	5.9 mean* n = 4	mercury intrusion	Vogt (1988)
Brown	7.2 mean* n = 4	mercury intrusion	Vogt (1988)
White	12 - 21** 16.4 mean n = 15	air pycnometer	Geddis (1994)
Gray	2 - 11** 5.3 mean n = 94	air pycnometer	Geddis (1994)

* Vogt (1988) used pressures which he felt slightly underestimated actual porosity.

** Recent measurements using water intrusion on the same core have given higher porosities (E. Hardin, 1995, personal communication).

fracture zone. This could not be confirmed because the interval in the borehole is hidden by the casing, and the core sample was crushed after distillation.

Increased ^{14}C activity in pore water from the perched aquifer may result from additions of recent water to the aquifer through fractures. Similarity between the two points below the water table and the nearest point above suggests that the elevation of the water table may have been higher in the past.

Several possible water-bearing fractures are identified between the dashed lines at 89 and 98 m in Figs. 2.4 - 2.8. These fractures were not specifically targeted for sampling, but the influence of flow through at least the lowest feature can be seen in the peak activity at 101.8 m.

Several other observations are of interest: (1) the smallest increase in activity is near the only zone flowing into the borehole at the time core was collected, (2) the fracture zones are not anomalous points along an otherwise monotonically decreasing activity plot, (3) though the increase in activity is always near the predicted zones, the increase does not always fall within the

zone, and (4) the pore waters extracted from core within the saturated zone have much higher activities than perched water samples drawn from the open borehole. These observations are discussed in the following sections.

2.3.1.1 Limitations on Imbibition of Fracture Flow into the Matrix

Pores in the matrix surrounding an ephemeral water-bearing fracture will contain water from many discrete flow events. The ^{14}C activity of this water is an integrated value representing the proportional contribution from each event. If the pores adjacent to the fracture are already near saturation when flow begins, imbibition will be low. Most of the flow will continue down the fracture. These pores will contain a smaller portion of the most recent flows relative to less saturated pores surrounding other fractures.

At 129-133 m, the formation is highly fractured. Successive flows may take variable routes allowing adjacent matrix pores more time to drain between flows. At 72.3 m, the fracture density is much lower. Successive flows at this depth will be forced to take similar routes each time allowing less time for pores to drain between flows. This may explain why this interval is associated with the smallest increase in ^{14}C activity, even though it is the only depth where flow was directly observed from the video log.

An upper limit on the magnitude of imbibition of fracture flow can be calculated using the tritium data. The results from distilled samples are all close to zero (Fig. 2.8), indicating that the contribution of water to the matrix from each fracture flow is small. The contribution per flow may be smaller still if some portion of the measured tritium is a result of *in situ* production. (*In situ* production should be less than 0.07 TU based on Andrews et al., 1989a.) For the purpose of calculating an upper limit on imbibition, it will be assumed that all the tritium found in pore waters is a result of imbibition of fracture flow with a maximum final concentration of 0.3 TU.

Calculations are made using two simplifying assumptions: (1) the matrix adjacent to a fracture is represented as a box with a constant aqueous volume, and (2) input to the box occurs from fracture flow and from matrix flow with discharge equal to total input (steady state). The average tritium content of water in the box will depend on the initial content of each input water, the relative proportion of water from each source, and the residence time of water in the box:

$$a = \left(\frac{q_M}{q_M + q_F} \right) \left(\frac{\int_0^T a_M e^{-\lambda t} dt}{T} \right) + \left(\frac{q_F}{q_M + q_F} \right) \left(\frac{\int_0^T a_F e^{-\lambda t} dt}{T} \right) \quad (2.1)$$

where a is the radioisotope concentration (or activity) of the whole sample, a_M and a_F are the initial radioisotope concentrations of matrix and fracture flow, respectively, λ is the decay constant ($\ln 2/\text{half-life}$), T is the average residence time of water in the box, and q_M and q_F are the flow rates (volume/time) input to the box from matrix and fracture, respectively.

The solution to Eqn. (2.1) is

$$\alpha = \left(\frac{a_M q_M + a_F q_F}{\lambda T [q_M + q_F]} \right) (1 - e^{-\lambda T}) \quad (2.2)$$

Equation (2.2) can be expressed as a function of the fractional volumes input into the box per unit time by making use of the following relationships:

$$q_M = m V, \quad (2.3)$$

$$q_F = f V, \quad (2.4)$$

and

$$T = \frac{V}{q_M + q_F} \quad (2.5)$$

such that:

$$T = \frac{1}{m + f} \quad (2.6)$$

where V is the volume of the box (static), and m and f are the fractions of water from each source per unit time (time^{-1}) relative to the volume of the box. The sum of m and f cannot exceed one. Substituting Eqns. (2.3) through (2.6) into Eqn. (2.2) and reducing yields:

$$\alpha = \frac{m a_M + f a_F}{\lambda} \left(1 - e^{-\left[\frac{\lambda}{m+f} \right]} \right) \quad (2.7)$$

Recent water imbibing into the matrix from a fracture must increase the total tritium concentration of a pore-water sample by a minimum of about 0.3 TU before it can be recognized. If all the water in the matrix comes from successive fracture flows, m in Eqn. (2.7) is zero. If the initial tritium concentration of fracture flow (a_F) is 6 TU, and the final water (α) is constrained to a maximum of 0.3 TU, f cannot exceed 0.0028. This means a maximum of 0.33% of the volume of the box is replaced with imbibed fracture water each year. The average residence time of water in the box must be at least 358 years (Eqn. (2.6)). Shorter residence times will result in tritium concentrations greater than 0.3 TU.

Input from both fracture and matrix flow allows the annual fracture contribution to be slightly higher as a result of dilution by "dead" matrix water. In this case, a_M will equal zero. Figure 2.9

Figure 2.9 Iso-tritium concentration plots of 0.3 TU for contribution of matrix and fracture flow to a mixing zone of fixed volume vs. average residence time of water in the mixing zone. Contribution is plotted as a fraction of the total volume of water in the mixing zone. The m term is the annual contribution of matrix water (0 TU initial), f is the annual contribution from fracture water (6 TU initial), and *total fracture contribution* is the total volume of water in the mixing zone derived from fracture flow (Eqn. 2.9).

is an iso-concentration plot of 0.3 TU for variable contributions from fracture (6 TU initial) and matrix (0 TU initial). The lines labeled *m* and *f* are the annual fractional contributions to the box, while the line labeled *total fracture contribution* is the fraction of the total volume of the box derived from fracture input. The total fraction is found by solving Eqn. (2.1) for $q_F/(q_M + q_F)$:

$$\frac{q_F}{q_M + q_F} = \frac{a\lambda T - a_m(1 - e^{-\lambda T})}{(a_F - a_m)(1 - e^{-\lambda T})} \quad (2.8)$$

When a_m is equal to zero, Eqn. (2.8) reduces to:

$$\frac{q_F}{q_M + q_F} = \frac{a\lambda T}{a_F(1 - e^{-\lambda T})} \quad (2.9)$$

Longer residence times allow greater total contribution from fracture flow, but smaller annual input. Maximum possible annual input from fracture flow with no increase in tritium above 0.3 TU is about 5% with an unrealistic residence time of one year.

A 358-year residence time for water traveling through a 50 cm section of rock requires an unsaturated hydraulic conductivity of approximately 4×10^{-11} m/s. Unsaturated hydraulic conductivities of samples from the white unit (upper ~30 m) range from 21×10^{-9} to 3.3×10^{-9} m/s for saturations of 0.96 to 0.70, respectively (Rasmussen et al., 1990). No measurements have been made on core from the gray unit, but the porosity is considerably lower (Table 2.1). A two order-of-magnitude decrease in unsaturated hydraulic conductivity is a reasonable possibility.

These calculations suggest that fracture flow contributions are very small on an annual basis, but could be a significant source of pore water over time. At 129.4 and 132.7 m, imbibition may be more significant, but no tritium measurements were made at these depths. The influence of non-steady-state conditions is discussed later in this section.

2.3.1.2 Impact of Fracture Flow on the Distribution of ^{14}C in the Matrix

The previous discussion leads to the second observation that measurements from the fracture zones do not represent anomalous activities on an otherwise monotonically decreasing activity plot. Rather, fracture flows appear to control the ^{14}C distribution by establishing new "initial" conditions wherever they occur. Elevated ^{14}C activities many meters beneath producing fractures indicates that imbibition of water flowing through fractures is a significant source of pore water throughout the sampled unsaturated zone.

2.3.1.3 Observed vs. Anticipated Evidence of Fracture Flow Imbibition

There are several possible reasons why the increase in ^{14}C activity does not always occur

within the predicted zones. At 133.8 m, the predicted zone was a best guess attempt that could simply be off by a small margin. A large interval at this depth is fractured. High neutron and low resistivity readings suggest that water may travel through fractures in any portion of this region. Routes may vary with duration and magnitude of flow events. Larger flows could exceed the capacity of one pathway forcing flow into new channels. Pathways may also change as preferred routes become restricted due to secondary mineralization. The maximum and minimum geophysical responses may reflect an older pathway with a high clay and water content that is no longer a preferential pathway.

The pore water associated with these peak responses could also have been missed. Over half the core from a ten-meter interval at this depth was pulverized by the drilling bit (Appendix A). The core thought to be associated with the maximum neutron readings may have actually been lost. The sampled core could have come from a much less transmissive interval.

At 72.3 m, the above explanations do not fit because flow is limited to a narrow zone, if not to a single fracture. At this depth, smaller-scale lateral fractures or joints may play a role where they intersect the primary fracture. If these fractures transmit water farther away during longer duration flows, or if they transmit water during some flows and not others, the pores in the adjacent matrix may behave like the less saturated matrix described previously. These pores may have greater opportunity to drain between the larger flows. Pores farther away from the primary fracture could then contain greater proportions of recent flows.

The sampling method could also play a role. A single core sample may intersect multiple lateral joints some distance below the primary fracture. This core would contain a greater proportion of recent water because it is encountering it at more than one location.

2.3.1.4 Contribution of Fracture Flow to the Perched Aquifer

The final observation is that the ^{14}C activity of pore water extracted from core from the saturated zone is much higher than that of water pumped from the perched aquifer. Water introduced to the perched aquifer by fractures may result in a localized region with higher ^{14}C activity. Core from this region would reflect that activity. Samples pumped from the aquifer, on the other hand, represent the average composition of water drawn from a large region. Samples were not collected until many borehole volumes had been removed. The aquifer samples in Fig. 2.7 reflect the average ^{14}C activity of perched water drawn from some distance away, while the pore-water samples reflect localized contribution from fracture flow.

The close match between the two points beneath the perched water table is anticipated if the local aquifer is well mixed. Similarity with the data just above the water table (142.7 m) may be evidence of a previous higher elevation of the water table as discussed earlier. Limited water chemistry results do not fit with a well mixed model, however. The total dissolved-solid content of the one sample squeezed from the saturated zone is high relative to the perched aquifer samples (Tables 2.2 and 2.3). Analysis of additional pore-water samples is required to address

Table 2.2 Chemical composition of pore water obtained by uni-axial compression. Each heading refers to the average depth of several composited core samples. Concentrations are given in mg/L.

	8.5 m	11.0 m	12.0 m	15.6 m	21.0 m	152.8 m
pH	7.3*	6.7**	6.8**	7.5*	6.5**	7.5*
HCO ₃	69.9	102.5	102.6	82.7	63.0	121.5
SO ₄	55.9	30.5	70.6	18.8	26.7	34.1
NO ₃	14.2	<0.5	<0.5	9.7	19.1	23.5
PO ₄	5.2	10.5	<0.5	2.2	<0.5	<0.5
Cl	22.6	37.1	40.8	33.7	45.2	46.0
Na	52.9	47.1	58.8	51.2	56.4	47.7
K	2.6	3.5	3.1	2.7	2.8	18.0
Ca	22.3	27.8	35.1	21.9	15.8	35.9
Mg	5.4	4.5	7.4	5.8	4.0	7.1
SiO ₂	37.4	67.4	68.7	43.2	60.3	43.0
TDS	288	331	387	272	293	377
Ch. Bal.	9.7%	7.5%	5.8%	14.7%	6.9%	5.7%

* pH measured on 9/22/94

** pH measured on 8/12/94

Charge balance is calculated according to:

$$Ch. Bal. = \frac{\sum meq_{cations} - \sum meq_{anions}}{\sum meq_{cations} + \sum meq_{anions}} 100\% \quad (2.10)$$

where *meq* is milli-equivalents per liter.

Table 2.3 Chemical Composition of Perched Aquifer Water. Concentrations are given in mg/L. (Br, F and PO₄ were below detection limit of 0.25 mg/L.)

	6/11/93	7/8/93	11/2/93
T (°C)	23	23	22.4
pH	7.2	7.4	7.44
HCO ₃	122.6	121.7	118.3
SO ₄	1.9	1.9	1.9
NO ₃	0.9	1.0	1.3
Cl	4.4	4.0	4.1
Na	22.5	22.1	21.0
K	0.9	0.9	0.9
Ca	20.7	20.6	19.3
Mg	3.8	3.8	3.5
Al	<0.05	<0.05	nd ^b
SiO ₂	51.8	54.8	52.4
DOC	7.3	6.0	5.0
Dissolved O ₂	nd	nd	6.4
TDS	229	231	223
Ch. Bal.	3.5%	3.6%	1.5%

^b nd = no data available

this question adequately. The compression technique used to extract pore water from core samples is described in Davidson (1995).

Boundaries can be placed on the contribution of fracture flow to the local aquifer by using Eqn. (2.8) for both ³H and ¹⁴C. Figure 2.10 shows iso-concentration/activity plots for ³H and ¹⁴C for variable contribution of fracture and aquifer water in a local mixing zone. Input values for the older aquifer water are 0 TU and a ¹⁴C activity of 0.6672 fmc. Input values for water traveling through fractures for Fig. 2.10a are 6 TU and a ¹⁴C activity of 1 fmc. The common solution for the plots is the point where the two lines cross. This occurs at a residence time of 169 years with 47% of the mixing zone derived from flow through nearby fractures. If the tritium concentration of the mixed zone is considered to be below detection, the solution becomes anywhere along the ¹⁴C plot to the right of the ³H curve. As a point of reference, if a value of 0.1 TU is entered for α instead of 0.3, the common solution occurs at a residence time of 572 years with 53% of the mixing zone derived from fracture flow.

The influence of bomb pulse ¹⁴C and ³H will lower each line. Figure 2.10b shows the same plots as Fig. 2.10a with the exception that the α_F input terms are varied over time to

Figure 2.10 Contribution of fracture flow (f , expressed as a percent) to the mixing zone in the perched aquifer beneath DSB-1 versus residence time (T) using Eqn. (2.8) where the mixed water has a ^{14}C activity of 0.816 fmc, and a ^3H concentration of 0.3 TU. Input values for water entering the mixing zone from the aquifer are $a_A(^{14}\text{C}) = 0.667$ fmc and $a_A(^3\text{H}) = 0$ TU. Input values for water entering from fractures for 6a are $a_F(^{14}\text{C}) = 1$ fmc and $a_F(^3\text{H}) = 6$ TU. For 6b, $a_F(^{14}\text{C})$ is set equal to 1 fmc prior to 1955 and then is varied using atmospheric measurements from Burchuladze et al. (1989); $a_F(^3\text{H})$ is set equal to 6 TU prior to 1955 and then is varied using atmospheric measurements compiled by the IAEA.

account for elevated atmospheric radioisotope levels during the past 50 years. The ^{14}C plot is generated using ^{14}C measurements on atmospheric CO_2 and wines from northern Europe (Burchuladze et al., 1989). The ^3H plot is generated using average annualized data compiled by the International Atomic Energy Agency from stations surrounding the Apache Leap (Waco, TX; Flagstaff, AZ; Menlo Park, CA; Santa Maria, CA; and Chihuahua, Mexico). The common solution for these plots pushes the residence time out to 426 years, but the portion of the mixing zone derived from fracture flow remains unchanged at 47%.

The potential contribution to the mixing zone from fracture flows (f) is only slightly sensitive to variations from the assumed pre-1950 ^3H concentration of 6 TU, and ^{14}C activity of 1.0 fmc (the α_F terms). A constant pre-1950 ^3H concentration of 12 TU raises the value of f in Fig. 2.10b to 50% ($T = 553$ yrs.); a ^{14}C activity of 0.95 fmc raises f to 55% ($T = 470$ yrs.). In each case, fracture flows contribute approximately half the water in the mixing zone.

2.3.2 Gas-Phase ^{14}C and ^3H Distribution

Casing in the borehole prevented gas sampling from the upper 54 m with one exception where a 5 m gap near the surface permitted a sample to be collected at a depth of 4.3 m. This sample contained post-bomb ^{14}C activity and may have drawn atmospheric air.

The ^{14}C activity of the first three data points below the casing (69.2, 72.1 and 86.3 m; Fig. 2.7) closely match the activity of the pore-water samples. The slightly lower activity of the pore-water samples fits anticipated error introduced by the distillation technique (Davidson, 1995). Below these points, the match between gas and pore-water activity is much more variable.

The agreement between gas and pore-water samples may be a function of air permeability and pumping history. At 69.2, 72.1 and 86.3 m, air permeability was low compared to deeper intervals (Fig. 2.6). Air drawn from these intervals had to come from pores in the nearby matrix which should be in isotopic equilibrium with water from pores sampled by the core at those depths. At 101.4 and 114.1 m, air permeability was slightly higher. Air samples collected from these intervals represent air some distance away from where the core was collected.

At 130.4, 133.8, and 145.8 m, air permeabilities were quite high due to extensive fracturing. At these depths, most of the air withdrawn came from the fractures, possibly drawn from large distances. Davidson (1995) documents large changes in stable and radioactive carbon as a function of pumping time at 130.4 m. These samples represent air that may have had no physical connection with the pore water sampled from core at these depths. The lowest two points, connected by a broken line, were collected after withdrawing almost 100 m^3 of air (STP) from each interval (Fig. 2.6). Stable carbon isotope data and P_{CO_2} measurements indicate that atmospheric air was drawn at these depths (Davidson, 1995).

Only two tritium samples were collected from formation air (133.8 and 145.8 m; Fig.

2.8). A minimum of 100 ml is required for sensitive tritium analysis. This volume could only be obtained by collecting water vapor continuously during pumping of the most permeable intervals. The resulting samples are composites of all the air withdrawn. Although the match between gas and pore water is close in Fig. 2.8, the air sampled was probably drawn from a large distance away and is not a reliable measurement.

If atmospheric air was incorporated into the lowest CO₂ samples, it may be anticipated that water vapor samples should contain measurable tritium. If atmospheric air was drawn late in the pumping history, high tritium vapor would have been collected during a short period near the end of sampling. After integrating with the rest of the sample, the final tritium concentration could still be below detection. Carbon samples, on the other hand, represent the gas composition at the end of pumping where atmospheric contamination may be high.

Murphy (1995) suggested that ¹⁴C distribution in unsaturated zones in arid to semi-arid climates might be controlled by gas phase diffusion of ¹⁴CO₂. In his model, ¹⁴CO₂ diffusion takes place in response to a decay induced concentration gradient with a final steady-state distribution influenced by exchange with the aqueous phase. Advective flow is limited to barometric effects. If aqueous transport is slow, the activity of pore waters will reflect the time required for ¹⁴CO₂ to diffuse to depth rather than the actual age of the water or air.

Ideally, these phenomena should produce monotonically decreasing ¹⁴C activity with depth. Open fractures could provide a pathway for faster diffusion, resulting in local increases as a borehole intersects these fractures, but it cannot explain post-bomb activity at 129.4 m. Visual observation of water entering the borehole at 72.3 m, and geophysical evidence of increased saturation at this and other depths suggests that water flowing through fractures controls the distribution of radiocarbon in the unsaturated zone rather than gaseous diffusion.

Gas/aqueous equilibrium appears to exist between pore waters and the air sharing those pore spaces, as evidenced by the data from 69 to 86 m. On a slightly larger scale, differences between the ¹⁴C activity in pore waters from adjacent core suggests that physical barriers exist within the formation, or that recent flows have introduced a fresh supply of ¹⁴C that has not yet equilibrated with nearby gas and water. Physical isolation may occur if the imbibition of fracture water results in zones of near saturation.

2.3.3 Impact of Non-Steady-State Conditions

Small-scale annual variability in the frequency and duration of the flow of water through fractures will not significantly alter the results of the steady-state models discussed for pore water or aquifer recharge as long as mean conditions do not change over the course of a few hundred years. Long-term variability on the order of several hundred or more years will have greater impact.

If climate changes result in extremely infrequent, short-duration rainfalls, moisture

content will decrease within the unsaturated zone. Water entering fractures under these conditions will experience increased imbibition. Short-duration flows may not reach the aquifer in significant quantity. Fracture flow could continue to be a primary source of pore water in the unsaturated zone, but subsequent recharge to the aquifer might be through slow percolation through the matrix. The tritium concentration, and, to a lesser extent, the ^{14}C activity of pore water adjacent to a fracture will vary depending on how long ago the last flow occurred. The rate of gaseous diffusion of $^{14}\text{CO}_2$ could also exceed the rate of aqueous transport, shifting the control of the distribution of ^{14}C in the unsaturated zone.

Under wetter conditions than currently observed, water flowing through fractures will be more frequent and possibly of longer duration. Imbibition per flow will decrease as higher saturation in the adjacent matrix restricts additional input, but total contribution to the matrix over time will increase. Higher water content in the unsaturated zone will result in increased matrix flow and shorter pore-water residence times. Pore waters adjacent to a fracture should contain higher ^{14}C activities and ^3H concentrations relative to the current system. Total contribution to the aquifer from matrix flow will increase, but recharge directly from fractures should increase by a larger factor. The result will be a larger fractional contribution to the aquifer from flow through fractures than currently observed. If fractional contribution from fractures flows is already very large, however, the fractional increase under wetter conditions may not be as significant as the increase in the total volume of annual recharge.

2.4 AGE CORRECTIONS

Quantitative corrections for this system are impossible due to the complex history of mixing. Every sample collected potentially represents a mixture of waters of different ages interacting with a gas phase that may have been influenced by previous aqueous mixtures. Analysis of the data is thus limited to the qualitative interpretation offered in the previous sections.

Added factors that could make even qualitative interpretation difficult, such as dissolution of carbonate minerals or oxidation of old organic material, are not significant. Although calcite has been identified in other boreholes at the Apache Leap to the east (Weber and Evans, 1988; Davis et al., 1991, Davidson and Bassett, 1995), no carbonate minerals have been found in DSB-1 core. Carbonate dissolved from wind-blown dust or from minor surface deposits are rapidly equilibrated with soil CO_2 . One sample of surface runoff was measured for ^{14}C and found to have post-bomb activity (Fig. 2.7). Four runoff samples measured for $\delta^{13}\text{C}$ were found to be at or near isotopic equilibrium with soil CO_2 .

Organic carbon was found in the perched aquifer at concentrations of 4 to 7 mg C/L (Table 2.2). Dissolved organic carbon concentrations taken from two saturated soils at the surface were 20 mg/L, indicating a potential gradient. Significant DOC concentrations were also found in pore water from squeezed core, but variable contamination from the compression

system prevented quantitative determination (Davidson, 1995). Oxidation of organic carbon will take place over time, but the rate is slow enough to be of minimal impact. Other sites where the oxidation of organic material is known to contribute significant inorganic carbon to the system generally have decreasing oxygen concentrations with depth, increasing CO₂ concentrations with depth, and/or sub-surface methane production (Wood and Petraitis, 1984; Fritz et al., 1989; Szabo and Kyser, 1990; Keller, 1991). These phenomena were not observed at DSB-1.

One ¹⁴C measurement was made on DOC from the perched aquifer (Fig. 2.7). Organic material percolating through matrix pores is likely to experience retardation relative to DIC. The similar ¹⁴C activities of DOC and DIC samples in the aquifer, however, indicate that the transport of organics to the aquifer is not significantly delayed. This is consistent with the hypothesis that substantial recharge occurs through fractures where the probability of retardation of organic material is greatly reduced.

2.5 GEOCHEMICAL EVOLUTION

2.5.1 Introduction

Radioisotope data indicate a significant percentage of the aquifer beneath DSB-1 is derived from fracture flow. Models simulating the geochemical evolution of water from the surface to the aquifer suggest that the older aquifer water may also be derived largely from recharge through fractures. The results of this investigation are preliminary because of uncertainty in the exact chemical composition of mineral phases and pore waters found in the Apache Leap Tuff. Small pore-water sample volumes prevented multiple analyses for most dissolved species resulting in poor precision and, in some cases, large charge imbalances (Table 2.2). Variation in pH is probably a result of measurement error. Samples measured on the same day have roughly the same value, but the samples measured on 8/12 are significantly different than the samples measured on 9/22. Carbon dioxide partial pressures for these samples, calculated using the chemical equilibrium computer code PHREEQE (Parkhurst et al., 1980), match measured formation CO₂ concentrations much better for the higher pH measurements.

2.5.2 Reaction Pathway Models for the Evolution of Perched Aquifer Chemistry

It is clear from a general comparison of TDS values of pore waters (Table 2.2) and aquifer water (Table 2.3) that dilution of pore water is required if it is a source of water in the aquifer. Some fraction of the aquifer must come from a more dilute source, such as surface runoff (Table 2.4) delivered through fractures. Comparison of individual dissolved species further shows that the aquifer is not a result of pure dilution, nor of simple mixing between surface runoff and any of the pore waters. Reaction with CO₂ and mineral phases must also be considered to account for the chemical composition of aquifer water.

NETPATH (Plummer et al., 1991) is a computer code which simulates changes in the

Table 2.4 Chemical composition of surface runoff. Concentrations are given in mg/L. Sample locations are shown in Fig. 2.1.

	1/18/92 ^a			8/26/92 ^a		
	AQ-U	AQ-M	AQ-L	AQ-U	AQ-M	AQ-L
T (°C)	3.5	7.5	8.5	23.3	27.3	28.1
pH	6.17	5.78	5.75	6.00	5.96	5.50
HCO ₃	4.2	2.3	2.3	3.7	1.9	2.3
SO ₄	17.6	19.4	17.8	16.8	19.0	17.2
Cl	2.8	2.4	2.3	1.8	2.5	2.0
Na	4.0	3.8	3.7	3.7	3.8	3.4
K	1.2	1.0	0.9	1.3	1.7	1.6
Ca	4.9	4.4	3.9	5.9	5.9	5.1
Mg	1.4	1.4	1.3	1.5	1.6	1.3
Al	0.2	0.2	0.2	nd ^b	nd	nd
Fe	0.01	0.06	0.08	nd	nd	nd
SiO ₂	27.6	29.7	29.7	31.4	37.2	38.1
TDS	64	65	62	66	74	71
Ch. Bal.	6.6%	3.8%	3.8%	14.1%	12.2%	9.8%

^a F, Br, NO₃ and PO₄ all below detection limit of 0.25 mg/L

^b nd = no data available

concentration of dissolved aqueous species from an initial water to a final water. Changes are simulated by dissolving primary silicate minerals and CO₂ gas, precipitating secondary minerals, and allowing for evaporation, dilution or mixing with another water.

The DSB-1 system was modeled using average surface runoff and individual pore waters as possible initial source waters. Average surface composition was used because runoff reaching the aquifer will be a composite of many different events. Because the pore-water results are variable and of uncertain quality, individual pore waters were considered as possible sources of aquifer water to evaluate the effect of significantly different initial pore-water compositions. Table 2.5 gives minerals considered for possible dissolution or precipitation in this investigation. Default mineral compositions within NETPATH were used where provided.

There are no significant mineral sources of chloride, sulfate or nitrate in the Apache Leap Tuff. Sulfate and nitrate have anthropogenic sources that contribute to some samples, but increases in chloride must be due to evaporative concentration. Chloride can substitute for OH⁻ in biotite and hornblende, but preliminary compositional analyses suggest that chloride

Table 2.5 Minerals considered for dissolution or precipitation by NETPATH (Plummer et al., 1991).

Mineral	Composition	
plagioclase	An_0 to An_{100}	user defined
biotite	$KMg_3AlSi_3O_{10}(OH)_2$	NETPATH default
hornblende	$CaNa_2Mg_3Al_4Si_6O_{22}(OH)_2$	user defined
CO ₂ gas	CO ₂	---
kaolinite	$Al_2Si_2O_5(OH)_4$	---
chlorite	$Mg_3Al_2Si_3O_{10}(OH)_2 \cdot Mg_2(OH)_6$	NETPATH default
smectite	$K_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 \cdot nH_2O$	user defined
illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	NETPATH default
SiO ₂	SiO ₂	---

substitution is not significant. Even with measurable substitution, there is an insufficient mass of biotite and hornblende present in the Apache Leap Tuff to account for the observed aqueous-chloride concentrations. This is consistent with the findings of an investigation on the loss of halogens from other volcanic rocks by Noble et al. (1967).

In the following models, chloride is brought to the concentration found in the aquifer by mixing low-chloride surface runoff with high-chloride pore waters, and by additional evaporation of the mixed water if necessary. Sulfate and nitrate are altered in proportion to their concentrations in the two initial waters.

NETPATH solutions are not unique. For any set of input minerals and water compositions, there are generally multiple possible solutions. Evaluation to determine the most plausible solutions requires specific knowledge of mineral compositions and abundances in the system being modeled. Table 2.6 gives example solutions for the geochemical evolution of water in the perched aquifer beginning with average surface runoff and a specific pore water, and allowing possible reactions involving the minerals listed in Table 2.5.

The most striking result shown in Table 2.6 is the low contribution from pore water. All three examples limit the contribution of pore water to less than 2%. Trials using each of the remaining pore waters from Table 2.2 produce similar results given the mineral constituents listed in Table 2.5. Maximum contribution from pore water is less than 2.4% for all possible solutions.

The result of varying the Ca/Na content of plagioclase for input in NETPATH is of

Table 2.6 Example NETPATH (Plummer et al., 1991) solutions for the geochemical evolution of perched aquifer water beginning with average surface runoff and a pore water from 15.6 m. Positive and negative signs indicate mmol/L dissolved or precipitated, respectively.

average surface runoff	98.2%	98.2%	98.1%
pore water from 15.6 m	1.8%	1.8%	1.9%
evaporate	1.45X	1.45X	1.43X
plagioclase (An ₃₂)	+0.975	+0.975	+0.889
biotite	+0.532	+0.044	
hornblende			+0.029
CO ₂	+1.881	+1.881	+1.880
chlorite	-0.260		
smectite		-0.207	-0.073
illite	-0.927		
SiO ₂		-1.737	-2.076

interest. The contribution of surface runoff and the evaporation factor in this model are both inversely proportional to the calcium content of plagioclase. Surface runoff contribution and the evaporation factor both decrease with increasing calcium content up to a maximum calcium composition of An₃₆ where the evaporation factor equals one. With no evaporation, the final chloride concentration is reached only by mixing the two initial waters. This allows a maximum contribution of just under 10% from the pore water with the lowest chloride concentration. Calcium content greater than An₃₆ requires higher pore water contribution which elevates chloride above measured aquifer concentrations.

Maximum evaporation factors of 1.8 are observed at plagioclase compositions of An₂₉ with no contribution from pore water. No solutions are found using plagioclase with a Ca content less than An₂₉ for the suite of minerals used in this study. The maximum evaporation factor is determined by the difference between the chloride concentration of surface runoff and the perched aquifer. With no contribution from pore water, surface runoff must be concentrated by a factor of 1.8 to achieve the chloride concentration observed in the aquifer.

Realistic solutions are constrained to a narrow range of plagioclase compositions from An₂₉ to An₃₆. Plagioclase composition in Apache Leap Tuff is reported by Peterson (1961) to be between An₂₂ and An₄₀, in agreement with the findings above. Conclusions from these results are

tentative. The precise range of plagioclase composition producing realistic reaction-pathway solutions will change as the Ca or Na content of other minerals such as hornblende are altered. Further investigation is required to determine the precise composition of minerals present.

The only dissolved species that are not adequately accounted for by the reaction pathway models are nitrate and sulfate. Altering nitrate and sulfate by simple mixing and evaporation results in nitrate concentrations about 4 times too low relative to measured values in the aquifer, and sulfate concentrations about 14 times too high.

Low nitrate is best explained by large variability in individual samples, including the aquifer itself. No nitrate was present during the initial purge of DSB-1, but nitrate appeared in subsequent sampling. The evolution of nitrate cannot be reasonably modeled without greater knowledge of its spatial and temporal sources.

High sulfate in surface runoff is due to dissolution of sulfate minerals deposited on the surface as dry fall from copper smelting. Magma Copper Company operated a smelter 3 Km NW of DSB-1 from 1924 to 1972 (Evans and Rasmussen, 1990). Although the smelter has not operated for over 20 years, the soil still retains significant dry fall from that era. Bassett et al. (1994) documented that the $\delta^{34}\text{S}$ signature of precipitation is altered by dissolution of dry fall resulting in a significant difference between precipitation and runoff. Surface runoff has a $\delta^{34}\text{S}$ ranging from about -4 to +1 ‰, while precipitation is about +8 ‰. (Analytical precision is ± 0.4 ‰.)

A recent source of sulfate at the surface means that the system is not at steady-state with respect to sulfate. Reaction pathway models cannot simulate the changes in the concentration of a dissolved species if the source varies with time. This explains why the large discrepancy exists between measured and modeled sulfate levels.

Sulfur isotope values ($\delta^{34}\text{S}$) from two perched aquifer samples from DSB-1 were 5.8 and 6.7‰. These values are fairly close to that of precipitation, suggesting that most of the water in the aquifer near DSB-1 was recharged prior to 1924. This is consistent with radioisotope data indicating that *annual* recharge through fractures is small. Insufficient time has passed for current surface-runoff sulfate concentrations to have significantly elevated perched water concentrations.

2.6 DSB-1 DATA RELATIVE TO THE REGIONAL SYSTEM

2.6.1 Gaseous Diffusion of $^{14}\text{CO}_2$

Data collected from DSB-1 indicate that the distribution of ^{14}C in the local unsaturated zone is controlled by aqueous fracture flows. Exchange between aqueous and gas phases results in increased gas phase ^{14}C activity where imbibition of fracture flow occurs.

Data from the perched aquifer on a regional scale is sparse. Samples have been collected at two other locations believed to be part of the perched system intersected by DSB-1. Carbon-14 activity from the Oak Flats borehole several kilometers down-gradient east of DSB-1, and from seepage into Magma Mine's Never Sweat haulage tunnel beneath a perched aquifer to the north (Fig. 2.1) have ^{14}C activities of 0.6827 ± 0.0046 and 0.6885 ± 0.0044 , respectively (Bassett et al., 1994). These are essentially the same as the activity measured at DSB-1. Tritium concentrations from Oak Flats and the tunnel, however, are reported as 1.86 ± 0.22 and 1.20 ± 0.41 TU, respectively (Bassett et al., 1994). Tritium is below detection at DSB-1.

The similarity in ^{14}C activity could simply be fortuitous. Aquifer water sampled at the tunnel and Oak Flats may represent a mixture of aquifer water that is older than at DSB-1 with more substantial contribution from recent fracture flow. This could produce a mixed water with ^{14}C activity similar to DSB-1, but with measurable tritium.

A second possibility is that the ^{14}C activity of the regional aquifer is controlled by gaseous diffusion of $^{14}\text{CO}_2$. The DSB-1 borehole is located beneath an ephemeral stream at the bottom of a drainage basin. Fractures transecting the basin are periodically exposed to water under positive pressure initiating fracture flow. Flow events are frequent enough to control the ^{14}C distribution in the unsaturated zone and to significantly increase the ^{14}C activity of the local aquifer.

Away from stream beds, which is most of the surface area of the region, significant fracture flow may be far less common. If gaseous diffusion is more rapid than aqueous flow through the matrix, pore water will take on ^{14}C from the gas phase, as discussed in Section 2.3.2. If gas phase diffusive transport exceeds the flow rate of water through the aquifer, the aquifer will also acquire ^{14}C from the gas phase. The result is an aquifer that has a uniform ^{14}C activity regardless of the actual age of the water so long as formation parameters, and the distance between the surface and the aquifer do not widely vary. Gaseous diffusion of ^3H is irrelevant in this model because the gas to liquid ratio for water under atmospheric conditions is exceedingly small.

Diffusive transport is represented by Fick's second law, modified to include radioactive decay (symbol definitions are given in Table 2.7):

$$\frac{\partial a}{\partial t} = \phi_a D \frac{\partial^2 a_g}{\partial x^2} - \lambda a \quad (2.11)$$

The steady-state solution for constant boundary conditions is (modified from Murphy, 1995) (symbol definitions are given in Table 2.7):

$$a_g = \frac{(a_{atm} e^{QL} - a_{wt})e^{-Qx} + (a_{wt} - a_{atm} e^{-QL})e^{Qx}}{e^{QL} - e^{-QL}} \quad (2.12)$$

Table 2.7 Terms and values used to model gaseous $^{14}\text{CO}_2$ diffusion (modified from Murphy, 1995).

term	definition	value - units
a_g	^{14}C activity of the gas at depth x	
a_{atm}	^{14}C activity of the atmosphere	1
a_{wt}	^{14}C activity at the depth of the water table	0.6672
L	distance between surface and lower boundary	arbitrarily large
x	depth	14800 cm
λ	radioactive decay constant for ^{14}C	$3.831 \times 10^{-12}/\text{sec}$
ϕ_w and ϕ_a	water and air filled porosity, respectively	arbitrary
K_d	ratio of aqueous/gaseous carbon for equivalent volumes	4.18
K_a	ratio of aqueous+adsorbed/aqueous carbon	1 - 6.5
D_o	diffusion coefficient of $^{14}\text{CO}_2$ in air at STP	$0.144 \text{ cm}^2/\text{s}$
T and T_o	measured and standard temperature, respect.	293° K both
P and P_o	measured and standard pressure, respectively	12.4 and 14.7 psi
D	$= D_o (P_o/P)(T/T_o)^{1.823}$	$0.161 \text{ cm}^2/\text{s}$
τ	tortuosity	1 - 2
Q	$= [\lambda (1 + K_a K_d \phi_w / \phi_a) / (D/\tau)]^{1/2}$	

If a large value of L is chosen instead of the depth to the aquifer such that a_g approaches zero at $x < L$, maximum equilibrium ^{14}C activities can be determined at the depth of the aquifer for a range of formation parameters. The measured activity of the aquifer can then be compared with the model to determine if diffusion could realistically produce the observed phenomena. Murphy (in press) proposed setting L equal to the depth of the water table and modifying formation variables to fit observed data, but there is no unsaturated zone data at present from a region where fracture flow does not dominate.

Of the terms in Table 2.7, the most variable or uncertain are tortuosity (τ), the significance of adsorbed carbon (K_a), and the saturation. The K_a term refers to the possibility that a significant reservoir of carbon is adsorbed to mineral surfaces (Striegl, 1988; Striegl and Armstrong, 1990; Davidson, 1995). Saturation is not directly stated in Eqn. (2.12), but the ratio of water to gas filled porosity in the Q term is related to saturation.

A range of values were used for tortuosity, K_a , and saturation (by varying the porosity terms) in Eqn. (2.12) with each result set equal to an activity of 0.6672 at 148 m (14800 cm).

Figure 2.11 plots the resulting relationships between saturation, tortuosity and Ka as iso-activity lines for various Ka values. Figure 2.12 plots calculated saturation in the formation with depth based on gravimetric water content and porosity data (Geddis, 1994; E. Hardin, 1995, written communication). Unidentified measurement bias places the mean saturation at 0.97. If a proportional correction is applied by dividing each value by 1.3, only a few points are left above saturation with a mean of 0.74. This correction is highly speculative, but is useful for a rough assessment of the conditions governing gaseous diffusion. At 70% saturation, diffusive control of the system is plausible for values of Ka ranging up to about 3 (Fig. 2.11).

Measurable tritium concentrations are problematic for this model. Tritium requires an aqueous source of recent water. If recent water is recharged near a sampling well in enough volume to produce measurable tritium, the same water will be a source of modern ^{14}C . This source will supply ^{14}C to the aquifer at a much faster rate than gaseous diffusion. The diffusion model can account for the regional radiocarbon results only if the tritium concentrations are a result of contamination during sampling or handling.

2.6.2 Evidence of Fracture Recharge from Regional ^3H , $\delta^{34}\text{S}$, and Cl/SO_4 Data

If the tritium data from the haulage tunnel and the Oak Flats borehole are accurate, significant modern water has been added to the aquifer through nearby fractures in the last 50 years. Sulfur concentrations and isotopes prove to be useful tools at the ALRS for evaluating the reliability of the tritium data. Surface runoff introduced to the aquifer within the last 50 years should have had elevated sulfate concentrations and decreased $\delta^{34}\text{S}$ values relative to older water residing in the aquifer, as discussed earlier. If enough modern surface water has been introduced to the aquifer to elevate the ^3H concentration of the mixed water above 1 TU, decreases should be observed in the $\delta^{34}\text{S}$ signature, along with increases in the sulfate concentration relative to a conservative species such as chloride.

The Cl/SO_4 ratios for surface runoff within the DSB-1 drainage basin range from 0.11 to 0.16. Ratios observed for runoff in other drainage basins and from Queen Creek just to the north range from about 0.07 to 0.17 (Bassett et al., 1994). The perched aquifer sampled from DSB-1, where tritium concentrations are below detection, has a Cl/SO_4 ratio ranging from 2.11 to 2.32. Aquifer samples with measurable tritium resulting from larger recent contributions of surface runoff should have Cl/SO_4 ratios and $\delta^{34}\text{S}$ values intermediate between surface runoff and the aquifer at DSB-1.

Water seeping into the tunnel beneath the aquifer to the north has Cl/SO_4 ratios ranging from 0.38 to 0.88 and $\delta^{34}\text{S}$ values ranging from approximately 2 to 4 ‰ (Bassett et al., 1994; sample locations T-CB1 and T-CB2). Both indicators are intermediate, suggesting that the measured tritium concentration of 1.20 TU is plausible. The ^3H , $\delta^{34}\text{S}$, and Cl/SO_4 data at this location all indicate that modern surface runoff has been introduced to the aquifer in significant quantity.

Figure 2.11 Iso- ^{14}C activity plots (activity = 0.6672 fmc) at a depth of 148 m using Eqn. (2.12) with saturation and tortuosity as independent variables for several values of Ka (Ka is the ratio of aqueous plus adsorbed inorganic carbon relative to aqueous carbon alone).

Figure 2.12 Uncorrected, calculated saturation of DSB-1 core based on gravimetric water content and porosity measurements (Geddis, 1994; Hardin, 1995, written communication). The mean is shown as a dashed line at 0.97. The dotted line at 1.0 is the maximum saturation physically possible.

Results from the first perched aquifer encountered at the Oak Flat borehole are less definitive. The Cl/SO₄ ratios for the two samples collected are 1.2 and 2.4. The $\delta^{34}\text{S}$ of the only sample analyzed is approximately 7 ‰ (Bassett et al., 1994). These values, with the exception of the first Cl/SO₄ ratio, are very similar to DSB-1, suggesting that contribution to the aquifer from modern surface runoff is low here relative to where the aquifer overlies the tunnel. The measured tritium concentration of 1.86 TU from the Oak Flat borehole is thus suspect and should be verified with additional sampling.

2.7 SUMMARY

Radioisotope measurements and geochemical modeling indicate that the perched aquifer is recharged primarily by surface runoff delivered through fractures. Isotopic data from the saturated zone beneath DSB-1 suggest the presence of a local mixing zone with equivalent contributions from the aquifer and from nearby fractures. Aquifer water flowing into this region also appears to originate from fracture flows. Preliminary reaction pathway modeling, considering surface runoff and pore waters sampled from the white unit as possible sources of aquifer water, limit the contribution from pore water to less than 10%. Actual contribution may be considerably less.

Data from the unsaturated zone at DSB-1 identify at least four fracture sets conducting water. Water was visually observed entering the borehole at 72 m, and matrix pore water collected from a fracture zone near the water table contained post-bomb ¹⁴C. Intervals at 47 and 101 m also contained anomalously high ¹⁴C activity in association with suspected water-bearing fracture zones.

It is surmized that near saturation of the matrix immediately surrounding fractures limits the imbibition of flowing water and encourages transport to greater depth. Fracture water entering the matrix is mixed with water from previous flows resulting in a composite of young and old water. Annualized contribution to the matrix from fractures in most cases is small based on tritium concentrations, but may be the primary source of matrix water over time. The influence of fracture-flow imbibition can be observed in the ¹⁴C activity of pore waters many meters below producing fracture zones.

Carbon-14 distribution beneath ephemeral streams appears to be controlled by the magnitude and frequency of fracture flows. Carbon-14 in formation air samples from most depths follow the same trends as ¹⁴C in pore water demonstrating active exchange between the two phases.

Processes governing the distribution away from sources of concentrated surface runoff are uncertain. Gaseous diffusion of ¹⁴CO₂ is capable of generating the observed ¹⁴C activity of the regional perched aquifer if there is not a faster pathway for ¹⁴C replenishment. Tritium, $\delta^{34}\text{S}$ and Cl/SO₄ data from water seeping into the haulage tunnel beneath the perched aquifer indicate

that fracture flow also provides the fastest pathway at this site. At the Oak Flat borehole, the reported ^3H level is high, but it is not substantiated by the $\delta^{34}\text{S}$ or Cl/SO_4 data.

2.8 APPENDIX A: CORE RECOVERY

Table A.1 Core recovery from DSB-1. Negative numbers in the "Lost" column mean the core recovered was greater in length than the distance drilled. This can happen when core lost from one run is recovered on the following pass. Depth measurements are linear distance along borehole. Recovery documentation did not begin until 30.69 m.

Start (m)	End (m)	Distance Drilled (m)	Core Recovered (m)	Core Lost (m)
30.69	33.68	2.99	2.74	0.24
33.68	36.64	2.96	3.11	-0.15
36.64	39.74	3.11	3.14	-0.03
39.74	42.91	3.17	3.11	0.06
42.91	45.81	2.90	3.11	-0.21
45.81	49.10	3.29	3.14	0.15
49.10	52.30	3.20	2.96	0.24
52.30	55.17	2.86	3.14	-0.27
55.17	58.24	3.08	3.14	-0.06
58.24	61.44	3.20	?	?
61.44	64.16	2.71	2.59	0.12
64.16	67.36	2.99	3.08	-0.09
67.36	70.50	3.14	3.14	0.00
70.50	73.58	3.08	3.14	-0.06
73.58	76.74	3.17	3.08	0.09
76.74	79.64	2.90	2.93	-0.03
79.64	82.72	3.08	3.05	0.03
82.72	85.74	3.02	3.14	-0.12
85.74	88.88	3.14	2.96	0.18
88.88	91.89	3.02	3.14	-0.12
91.89	94.97	3.08	3.08	0.00
94.97	98.11	3.14	3.14	0.00
98.11	100.98	2.86	2.77	0.09
100.98	104.02	3.05	2.80	0.24
104.02	106.80	2.77	3.08	-0.30
106.80	107.92	1.13	1.28	-0.15
107.92	110.70	2.77	2.50	0.27
110.70	113.78	3.08	3.11	-0.03
113.78	116.82	3.05	3.02	0.03
116.82	119.87	3.05	2.96	0.09
119.87	122.92	3.05	3.11	-0.06
122.92	125.97	3.05	2.96	0.09
125.97	129.02	3.05	3.05	0.00
129.02	132.06	3.05	3.14	-0.09
132.06	135.11	3.05	3.11	-0.06
135.11	138.16	3.05	2.96	0.09

Table A.1 - *Continued*

Start (m)	End (m)	Distance Drilled (m)	Core Recovered (m)	Core Lost (m)
138.16	141.21	3.05	2.96	0.09
141.21	144.25	3.05	2.96	0.09
144.25	147.30	3.05	2.96	0.09
147.30	150.35	3.05	2.93	0.12
150.35	153.40	3.05	3.05	0.00
153.40	156.45	3.05	3.05	0.00
156.45	157.63	1.19	1.28	-0.09
157.63	159.80	2.16	2.22	-0.06
159.80	162.51	2.71	2.44	0.27
162.51	165.68	3.17	2.19	0.98
165.68	168.09	2.41	2.59	-0.18
168.09	171.05	2.96	2.74	0.21
171.05	172.02	0.98	0.61	0.37
172.02	174.98	2.96	0.85	2.10
174.98	176.17	1.19	0.79	0.40
176.17	176.65	0.49	0.49	0.00
176.65	178.09	1.43	1.01	0.43
178.09	180.83	2.74	0.98	1.77
180.83	180.98	0.15	0.00	0.15
180.98	181.13	0.15	0.27	-0.12
181.13	182.66	1.52	1.31	0.21
182.66	183.57	0.91	0.82	0.09
183.57	184.88	1.31	0.98	0.34
184.88	186.53	1.65	1.92	-0.27
186.53	188.08	1.55	1.43	0.12
188.08	190.28	2.19	1.31	0.88
190.28	191.16	0.88	0.70	0.18
191.16	191.95	0.79	0.73	0.06
191.95	192.69	0.73	0.76	-0.03
192.69	195.58	2.90	1.83	1.07
195.58	196.37	0.79	0.82	-0.03
196.37	197.29	0.91	0.76	0.15
197.29	197.44	0.79	0.15	0.00
197.44	198.51	0.91	0.98	0.09
198.51	199.12	0.15	0.55	0.06
199.12	199.15	1.07	0.03	0.00
199.15	201.80	0.61	2.41	0.24

Table A.1 - *Continued*

SUMMARY		
Depths Along Borehole (m)	Vertical Depths (m)	Percent Recovery
2.4 - 30.5	1.7 - 22.6	100 (estimated)
30.5 - 50	22.6 - 36.8	98.6
50 - 75	36.8 - 56.2	101.1
75 - 100	56.2 - 76.0	99.9
100 - 125	76.0 - 95.9	99.3
125 - 150	95.9 - 115.7	98.6
150 - 175	115.7 - 135.5	85.4
175 - 201.8	135.5 - 156.8	78.4
Total core lost		10.0 m
Total Recovery		95.0%

2.9 APPENDIX B: ISOTOPE DATA

Stable carbon isotope analyses were performed by the Isotope Geochemistry Lab in the Geosciences Department at The University of Arizona.

Table B.1 $\delta^{13}\text{C}$ of pore water obtained by uni-axial compression.

Depth (m)	$\delta^{13}\text{C}$ (‰)
11.0	-13.7
12.0	-14.9
21.0	-18.5

Table B.2 $\delta^{13}\text{C}$ of pore water obtained by vacuum distillation.

Depth (m)	$\delta^{13}\text{C}$ (‰)
9.0	-27.6
15.0	-21.7
20.5	-22.0
39.9	-35.7
42.2	-30.6
47.1	-24.8
69.3	-35.6
72.3	-25.2
86.0	-25.8
101.8	-22.0
102.5	-25.7
114.6	-19.2
129.4	-23.3
132.7	-25.8
133.8	-21.5
142.7	-26.3
150.0	-29.6
155.4	-24.2

Table B.3 $\delta^{13}\text{C}$ of formation air. Days identified at 130.4 m indicate how long the interval was pumped before sampling.

Depth (m)	$\delta^{13}\text{C}$ (‰)
4.3	-21.2
69.2	-21.8
72.1	-22.3
86.3	-22.2
101.4	-21.4
114.1	-21.4
130.4 (open hole)	-21.6
130.4 (1 day)	-21.6
130.4 (2 days)	-21.9
130.4 (3 days)	-21.2
130.4 (5 days)	-20.5
133.8	-20.4
145.8	-18.0

Table B.4 $\delta^{13}\text{C}$ of perched water.

Sample Date	$\delta^{13}\text{C}$ (‰)
6/11/93	-16.7
7/8/93	-16.9

Table B.5 $\delta^{13}\text{C}$ of surface runoff. Sampling locations are shown in Fig. 2.1.

Sample ID/Date	$\delta^{13}\text{C}$ (‰)
AQ-U 1/18/92	-17.9
AQ-L 1/18/92	-17.3
AQ-U 8/26/92	-18.9
AQ-L 8/26/92	-19.9

Table B.6 $\delta^{13}\text{C}$ of soil CO_2 collected during different seasons at various locations on the Apache Leap. Sample locations are shown in Fig. 2.1.

Sample ID	11/4/91	1/18/92	4/23/92	9/1/92
SG-C	-20.0		-19.3	
SG-L	-22.0	-18.2	-20.2	-22.1
SG-L		-20.3	-19.8	
SG-MN				-21.6
SG-MS	-18.1	-21.7	-20.4	
SG-U		-20.0	-22.0	-19.9
SG-U		-19.0		
SG-LNB	-20.3			
SG-CON	-20.9			

Carbon-14 analyses were performed by the AMS (accelerator mass spectrometer) facility (funded by NSF) in the Physics Department at The University of Arizona.

Table B.7 ^{14}C activity of pore water obtained by uni-axial compression.

Depth (m)	Fraction Modern Carbon	1σ
11.0	0.8740	± 0.0054
12.0	0.8594	± 0.0057
21.0	0.8754	± 0.0054

Table B.8 ^{14}C activity of pore water obtained by vacuum distillation.

Depth (m)	Fraction Modern Carbon	1σ
7.8	0.8899	± 0.0054
9.0	0.8555	± 0.0055
15.0	0.8173	± 0.0055
20.5	0.8934	± 0.0054
39.9	0.8075	± 0.0097
42.2	0.7430	± 0.0048
47.1	0.8421	± 0.0070
69.3	0.8749	± 0.0054
72.3	0.8495	± 0.0066
86.0	0.8794	± 0.0057
101.8	0.9339	± 0.0110
102.5	0.8504	± 0.0055
114.6	0.8144	± 0.0070
129.4	1.0248	± 0.0064
132.7	0.9946	± 0.0062
133.8	0.7426	± 0.0053
142.7	0.8089	± 0.0058
150.0	0.8130	± 0.0055
155.4	0.8196	± 0.0098

Table B.9 ^{14}C activity of formation air. Days identified at 130.4 m indicate how long the interval was pumped before sampling.

Depth (m)	Fraction Modern Carbon	1 σ
4.3	1.0209	± 0.0064
69.2	0.9059	± 0.0056
72.1	0.8745	± 0.0057
86.3	0.9018	± 0.0058
101.4	0.8028	± 0.0053
114.1	0.7814	± 0.0052
130.4 (open hole)	0.9236	± 0.0059
130.4 (2 days)	0.6613	± 0.0047
130.4 (5 days)	0.7235	± 0.0050
133.8	0.7016	± 0.0085
145.8	0.7286	± 0.0047

Table B.10 ^{14}C activity of perched water.

Sample Date	Fraction Modern Carbon	1 σ
6/11/93	0.6648	± 0.0065
7/8/93	0.6709	± 0.0053
11/2/93	0.6635	± 0.0066
11/2/93 (DOC)	0.6430	± 0.0137

Table B.11 ^{14}C activity of surface runoff. Sampling location is shown in Fig. 2.1.

Sample ID/Date	Fraction Modern Carbon	1 σ
AQ-M 8/26/92	1.1759	± 0.0073

Tritium analyses were performed by the Tritium Lab at the University of Miami.

Table B.12 Tritium concentration of pore water obtained by vacuum distillation.

Depth (m)	TU	1 σ
42.2	0.19	± 0.12
47.1	0.03	± 0.07
69.3	0.00	± 0.13
72.3	0.28	± 0.08
101.8	0.13	± 0.08
133.8	0.13	± 0.12
142.7	0.00	± 0.08
150.0	0.14	± 0.12

Table B.13 Tritium concentration of formation air.

Depth (m)	TU	1 σ
133.8	0.08	± 0.06
145.8	0.00	± 0.06

Table B.14 Tritium concentration of perched water.

Sample ID	TU	1 σ
6/11/93	0.00	± 0.09
7/8/93	0.00	± 0.09

3. REPORT ON URANIUM FRACTIONATION IN SURFACE, VADOSE ZONE AND PERCHED WATERS AT THE ALRS

by E.L. Hardin and R.L. Bassett

3.1 INTRODUCTION

The $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) in vadose zone and perched waters at Apache Leap is much greater than 1 (Fig. 3.1, Table 3.2) which can be attributed to radioactive decay effects since chemical behavior of the isotopes is similar. If chemical fractionation of dissolved uranium isotopes were significant in nature it would be evident from the ratio of $^{235}\text{U}/^{238}\text{U}$, but this ratio is constant to within about two significant digits.

Table 3.1 Predominant modes of decay for the series from ^{238}U through ^{234}U .

Nuclide	Approximate Decay Energy (MeV)	Dominant Emissions	Mean Lifetime
^{238}U	4.2	α	6.46×10^9 yr
^{234}Th	0.2	β^- (& γ)	34.8 d
^{234}Pa	0.5	β^-	1.69 min
^{234}U	4.7	α	3.58×10^5 yr

Fractionation of ^{234}U could be attributed either to some direct effect of radioactive decay, or to the chemical properties of the intermediates ^{234}Th and ^{234}Pa . Since ^{234}U is enriched rather than depleted in groundwater, the relative insolubility of Th and Pa does not seem to have an important role. Rather, some other process concentrates ^{234}U in the mobile phase.

Groundwater $^{234}\text{U}/^{238}\text{U}$ fractionation has been widely reported for 30 yr and explanations are based on the energetic alpha-decay of ^{238}U . Conservation of momentum requires that the ^{234}Th daughter atom is recoiled with an energy of 72 keV. Two basic mechanisms have been proposed: (1) direct recoil of ^{234}Th and subsequent daughters into solution, and (2) transformation of the daughter ^{234}U into a form that is more easily solubilized than ^{238}U . The relative importance of these mechanisms and the implications for natural U transport have not been examined in felsic tuffs nor for vadose zone vs. perched aquifer conditions. Clearly, if direct recoil contributes significantly to fractionation then this implies strong partitioning and retardation of U.

The following sections comprise a report of work in progress. Investigations have

Figure 3.1 Schematic of sampling locations at the ALRS, for uranium geochemical investigations. (The symbol nomenclature matches Table 3.2.)

Table 3.2 Uranium in surface, vadose zone, and perched waters at the ALRS. (Symbol nomenclature follows accompanying figure.) Error estimates are based on internal precision (i.e. between-sample variability for duplicated analyses).

Symbol	Sample	Depth (m)	U _{tot} (ppt)	Mass U (ng) ¹	Activity
SW	Watershed Runoff (AQ-M, 1/18/92)	0	23±2 (N=3) ⁽²⁾		
SW	Watershed Runoff (AQ-M, 8/26/93)	0	40±7 (N=3) ⁽²⁾		
SW	Watershed Runoff (DSB ³ , creek 8/31/94)	0	28±1 (N=2) ⁽²⁾	>40 (N=2)	1.43 ±0.007
FW6	Fracture #6 (8/31/94)	2	117 ⁽¹⁾	155	1.94 ±0.005
FW20	Fracture #20 (8/31/94)	2	138 ⁽¹⁾	195	2.09 ±0.005
MW6	Squeezed Pore Water (DSB ³ core from 6 m)	4	45 ⁽¹⁾	1.0	1.93 ±0.048
MW13	Squeezed Pore Water (DSB core from 13 m)	9	389 ⁽¹⁾	23.7	2.15 ±0.011
MW22	Squeezed Pore Water (DSB core from 22 m)	15	198 ⁽¹⁾	10.6	2.08 ±0.015
PW	Perched Water (DSB ³ , purged, 6/11/93)	~140	241 ⁽²⁾		
PW	Perched Water (DSB, purged, 7/18/93)	~140	212±1 ⁽²⁾	>80 (N=2)	6.235 ±0.002
PW	Perched Water (DSB, purged, 11/2/93)	~140	232 ⁽²⁾		
PWT	Perched Water (mine tunnel, CP-4, 9/14/90)	~200	602 ⁽²⁾		
PWT	Perched Water (mine tunnel, 7920', 9/14/90)	~200	740 ⁽²⁾		
PWT	Perched Water (mine tunnel, CP-1, 7/29/93)	~200	672 ⁽²⁾	>200 (N=2)	5.311 ±0.002
PWOF	Perched Aquifer (Oak Flat borehole, 4/4/90)	~100	741 ⁽²⁾		

⁽¹⁾ Analyzed by TIMS, ⁽²⁾ Analyzed by ICP/MS, ³ Deep Slant Borehole

improved understanding of the spatial distribution and mechanisms for ^{234}U fractionation in the vadose zone and perched aquifer at Apache Leap. Further studies are underway emphasizing current methods for sample collection and U analysis, to test a conceptual model for fractionation and to evaluate implications of this for transport of natural U.

3.2 PRELIMINARY RESULTS FROM THE ALRS

The Apache Leap Tuff was sampled along a generalized flow path including an ephemeral stream, fracture zones near the surface, vadose zone matrix pore water, the underlying perched aquifer, and a point where the aquifer discharges into a mine tunnel (Fig. 3.1, Table 3.2). Total uranium concentration and U isotopes were measured on filtered, acidified samples using inductively coupled plasma/mass spectrometry (ICP/MS) and thermal ionization mass spectrometry (TIMS). The circumstances of sample collection were as follows:

- ◆ Surface water samples were collected at a point upstream from the deep slant borehole (DSB) a few days after summer and winter rainfall/runoff events.
- ◆ Fracture water samples were collected from shallow borings a few days after a summer rainfall/runoff event.
- ◆ Pore water was collected by squeezing preserved tuff cores in a consolidation cell in the manner of Peters et al. (1992). Pore water yield declined with more densely welded tuff, and the intervals reported in Table 3.2 were selected for production.
- ◆ Perched water was pumped from the DSB on 3 separate occasions with purging prior to sample collection (Davidson, 1995).
- ◆ Perched water discharge in the mine was sampled from a constantly producing fracture.

A uranium blank of approximately 0.18 ng was obtained for core squeezing by repeatedly soaking critical components of the apparatus in Type 1 water in a manner simulating the collection of one sample of the type used for isotopic analysis. Chemical separation was performed in a clean room using reagents which had been double sub-boiling distilled (Seastar Chemicals). The blank can be attributed mostly to the core consolidation apparatus, in which pore water contacted stainless steel endcaps for a few hours during the squeezing of each core sample. This statement is based on a process blank and previous results with the chemical procedure of Goldstein et al. (1989).

Values reported in Table 3.2 for total U and $^{234}\text{U}/^{238}\text{U}$ are similar to other studies of ground waters from felsic tuffs. Zielinski and Rosholt (1978) reported U concentrations from 0.5 to >7 ppb for tuffaceous aquifers on the Nevada Test Site, with $^{234}\text{U}/^{238}\text{U}$ activity ratios in the range 3 to 5. Stuckless et al. (1991) summarized $^{234}\text{U}/^{238}\text{U}$ data for groundwater from the tuff

and valley fill aquifers near Yucca Mountain, where activity ratios in the range 2 to 5 are common. Ludwig et al. (1993) reported $^{234}\text{U}/^{238}\text{U}$ activity ratios between 2.4 and 7 for springs and wells throughout the southern Great Basin.

3.3 FRACTIONATION MECHANISMS

Extensive literature exists on $^{234}\text{U}/^{238}\text{U}$ fractionation giving rise to four general proposed mechanisms as summarized by Petit et al. (1985a):

- ◆ Direct recoil of daughter ^{234}Th into solution as the result of ^{238}U decay (Kigoshi, 1971). Thorium ions in solution are rapidly hydrolyzed to Th(IV) and may be adsorbed to mineral surfaces, but can readily return to solution after beta-decay to $^{234}\text{U(VI)}$.
- ◆ Selective leaching of ^{234}U from recoil damage tracks (e.g. Fleischer and Raabe, 1978). The track provides access to the daughter nuclide, and solubilization may proceed more or less rapidly depending on whether the release mechanism is surface controlled.
- ◆ Enhanced diffusion of daughter nuclides along recoil damage tracks produced by ^{238}U decay (Kigoshi, 1971). Published studies do not distinguish this proposed mechanism from selective leaching.
- ◆ Solubility differentiation by auto-oxidation of ^{234}U to U(VI) while relatively insoluble $^{238}\text{U(IV)}$ predominates in primary minerals (Rosholt et al., 1963). Recoiled ^{234}Th may be oxidized to $^{234}\text{Th(IV)}$ during stopping, or by subsequent hydrolysis, followed by beta-decay to $^{234}\text{U(VI)}$.

In the discussion that follows leaching, track diffusion, and auto-oxidation mechanisms are lumped together under the term selective leaching. The proposed mechanisms overlap, since each emphasizes a different but interdependent aspect of the same physio-chemical process.

3.3.1 Direct Recoil

Direct recoil was observed in vitro by Kigoshi (1971) who monitored ingrowth of dissolved ^{234}Th in a suspension containing natural zircon sand with ^{238}U as an impurity. Observation of ^{234}U buildup is infeasible because of its long lifetime. As a consequence, buildup of ^{234}U over thousands of years may be useful in understanding U transport in natural systems.

Direct recoil fractionation has been observed as a consequence of decreasing redox potential along flow paths in regional aquifers in Texas (Kronfeld, 1974; Cowart, 1980), Canada (Ivanovich et al., 1991), and elsewhere (Osmond and Cowart, 1992). Groundwater activity ratios

of 5 to > 12 have been attributed to this mechanism using supporting data that include modern redox conditions and local accumulation of secondary U. Fractionation ($AR > 10$) in ancient sedimentary brines from Israel was attributed to direct recoil (Kronfeld et al., 1975) but other such brines are much less fractionated (Kraemer and Kharaka, 1986) possibly because elevated temperature accelerates isotopic exchange (Osmond and Cowart, 1992).

To better understand the effects of U sorption and isotopic exchange on the perched water activity ratio at Apache Leap, consider the aquifer a well-mixed reservoir ("box") with constant inflow and outflow, and inflow that has constant U concentration and activity ratio (Fig. 3.2). The resulting lumped parameter model has the form:

$$\frac{dC_{238}}{dt} = \frac{1}{T} (C_{238} - C_{238,0}) - \frac{\rho_b}{\theta\rho_w} k(KC_{238} - S_{238}) - \lambda_{238} C_{238} \quad (3.1)$$

$$\frac{dC_{234}}{dt} = \frac{1}{T} (C_{234} - C_{234,0}) - \frac{\rho_b}{\theta\rho_w} k(KC_{234} - S_{234}) - \lambda_{234} C_{234} + \frac{\rho_b}{\theta\rho_w} f\lambda_{238} S_{238} \quad (3.2)$$

$$\frac{dS_{238}}{dt} = k(KC_{238} - S_{238}) - \lambda_{238} S_{238} \quad (3.3)$$

$$\frac{dS_{234}}{dt} = k(KC_{234} - S_{234}) - \lambda_{234} S_{234} + (1-f)\lambda_{238} S_{238} \quad (3.4)$$

where:

- C = mobile phase concentration (mass/mass; subscript 0 denotes inflow)
- S = immobile phase concentration (mass/mass; subscript 0 denotes inflow)
- k = first-order rate constant for sorption/desorption (sec^{-1})
- K = phase partition coefficient (mass/mass)
- T = residence time (assumed to be 1000 yr)
- λ = decay constants for ^{234}U and ^{238}U
- f = efficiency of direct recoil (assumed to be 0.5)

and:

$$\frac{\rho_b}{\theta\rho_w} = 40 \quad (\text{rock:water mass ratio}) \quad (3.5)$$

Direct Recoil Model for U-234 Fractionation

Figure 3.2 Schematic of lumped parameter model for direct recoil, e.g. in a perched aquifer.

This model is used to examine the effects of k and K on the steady state groundwater activity ratio. It has no limitation on availability of sorption sites, and ignores interaction between sorbed species. The effect of isotopic exchange is approximated by sorption/desorption rate constant k , which is reasonable if there is strong isotopic disequilibrium between the phases. Use of the model does not depend critically on the value for recoil efficiency.

The model was cast as a set of time-dependent, fully implicit finite difference equations. For initial conditions the system was assumed to be in chemical and isotopic equilibrium with the inflow, with $AR=3$ to represent recharge. Radioactive decay was initiated at $t=0$ and the model was stepped through several hundred time increments to 10^6 yr, which is several half-lives of ^{234}U . This solution method is unconditionally stable and yields accurate results for large times (Press et al., 1989).

Steady state $^{234}\text{U}/^{238}\text{U}$ activity ratios ($AR_{4/8}$) are plotted against the partition coefficient and rate constant in Fig. 3.3, for a perched water residence time of 10^3 yr. These figures show that fractionated groundwater is associated with rather sharp (order of magnitude) threshold behaviors of k and K . Ignoring inflow and outflow, and neglecting decay of ^{234}U , buildup of ^{234}U in the mobile phase requires the rate of ^{234}U gain from direct recoil to exceed the rate of loss to sorption:

$$f\lambda_{238} S_{238} > k(KC_{234} - S_{234}) \approx kKC_{234} \quad (3.6)$$

or rearranging:

$$k < f\lambda_{238} S_{238} / KC_{234} \approx f\lambda_{238} KC_{238} / KC_{234} = f\lambda_{234} / AR_{4/8} \approx 10^{-14} \text{ sec}^{-1} \quad (3.7)$$

assuming $AR_{4/8} = 6$ and that ^{238}U is at sorptive equilibrium. (In this model ^{238}U is initially in sorptive equilibrium and remains so because the decay rate is the same in both phases.)

The small magnitude estimated for k may be interpreted as irreversible U sorption relative to the residence time of groundwater in the perched aquifer. Also, for fractionation to approach that observed in the perched water requires $K > 100$ (expressed as a whole-rock value). If the sorbent comprises a small mass fraction then the mineral-specific partition coefficient must be on the order of 10^4 or greater. Such values have been observed for ferrihydrite in the laboratory without competing ions, and with complexes limited to uranyl-carbonato species (Waite et al., 1994; Hsi and Langmuir, 1985). Such data have limited applicability but they do show that ferrihydrite, Mn-oxide, and possibly Ti-oxide are more likely substrates for significant fractionation by direct recoil than clays (Ames et al., 1983; Langmuir, 1978).

Laboratory studies of U adsorption to ferrihydrite have been done at higher U

Figure 3.3 (upper) $^{234}\text{U}/^{238}\text{U}$ activity ratio vs. U partition coefficient for different values of the first order sorption rate constant. (lower) Activity ratio vs. constant for different values of the U partition coefficient.

concentrations than exist in situ so the measured partition coefficients include weaker, more readily reversible binding sites. The probable existence of reversible sites in situ means that isotopic exchange is ongoing at some unknown rate, but the effect is limited by the amount of U adsorbed on them. Ho and Doern (1985) studied desorption of U from a hematite suspension by successive washings with electrolyte at constant pH. These results demonstrated multiple types of sites as proposed by Benjamin and Leckie (1981) and showed that U was most irreversibly adsorbed at the lowest solution concentrations. Irreversibility at the laboratory time scale was inferred for adsorbed U concentrations of at least ~ 1 mg U/g sorbent. From the "box" model discussed above this is orders of magnitude greater than what is needed to explain the observed ^{234}U fractionation, using reasonable values for C_{238} and K.

Another important aspect of possible sorbents is that they must be stable over the long times needed for ^{234}U to build up from direct recoil. As pointed out by Petit et al. (1985a) direct recoil from primary minerals requires unrealistically low etch rates for those minerals, in order for significant excess ^{234}U to build up in solution. This is another reason for positing secondary minerals such as ferrihydrite and Mn-oxides as stable substrates for direct recoil.

In summary, within the limitations of the model used, direct recoil can produce the observed increase in fractionation from recharging fracture waters (AR~2) to the perched aquifer (AR~6) at Apache Leap. There must be sufficient capacity for sorption that is effectively irreversible, and the sorbent must be stable on a time scale related to the groundwater residence time and the lifetime of ^{234}U . Laboratory studies show that among secondary minerals typical of felsic tuff, precipitated ferrihydrite, Mn-oxides, and possibly Ti-oxide are the best prospects as substrates for direct recoil.

3.3.2 Selective Leaching

Fleischer (1980; 1982) described a series of experiments in which ^{235}U atoms were recoiled by alpha-decay of a $^{239}\text{PuO}_2$ source, and captured by polished mineral surfaces. The mineral samples were exposed to aqueous solutions, then analyzed for residual ^{235}U by the induced fission track method. Data for the fraction of ^{235}U removed were "noisy" but served to illustrate selective leaching (quartz) and dependence of leach rate on pH (muscovite). Selective leaching has also been produced in vitro using uraninite (Eyal and Fleischer, 1985), Pb-ion implanted minerals (Petit et al., 1985b), and Stripa granite (Andrews et al., 1989b). For published studies using natural materials the $^{234}\text{U}/^{238}\text{U}$ activity ratio ranges from near unity to as high as 2 for Stripa granite.

Implantation experiments using heavy ions accelerated to energy levels comparable to ^{234}Th recoils from ^{238}U decay show that damage tracks in solids are on the order of 200 Å deep (Dran et al., 1980). Layers of implanted heavy ions have been observed directly using ion beam techniques and the ions tend to be concentrated at the end of their range (Dran et al., 1984). Recoil stopping of heavy particles involves mostly momentum exchange between colliding nuclei. Damage is caused by displacement of lattice atoms and is long lasting in insulating materials

(Matzke, 1982). By contrast, stopping of the 4.2 MeV alpha particle emitted by ^{238}U takes place mainly by ionization that tends to heal, and the energy is dispersed over a much longer track ($\sim 20\ \mu\text{m}$). Thus the alpha particle produces only a fraction of the damage caused by the recoil atom, and it is dispersed over a much greater volume.

Selective leaching is inherently an incongruent mechanism, and the extent of ^{234}U fractionation depends on the incongruity of dissolution. Congruently dissolving mineral phases that contain U tend to dilute the excess ^{234}U derived from incongruent dissolution. Petit et al. (1985a) argued that any selective leaching process is subject to this effect given the U content and etching rates of common minerals. In other words, attributing fractionation to selective leaching of recoil daughters implies unrealistically low rates of congruent dissolution for all U bearing minerals (e.g. less than $10^{-13}\ \text{m/yr}$). Even if minerals such as quartz and feldspar contain only trace amounts of U, such low dissolution rates constrain their dissolution rates and thus constrain the rate of whole rock dissolution to unrealistic levels.

This bounding argument was extended by Petit et al. (1985) to all types of leaching and track diffusion, by analogy to the hydrated gel layer that builds up on the surface of incongruently dissolving glasses, and retards but does not fundamentally alter the isotopic composition of released U as long as the mobilities of ^{234}U and ^{238}U are the same in the gel layer and in solution. This may not be so as discussed below for the auto-oxidation mechanism. Petit et al. (1985a) also evaluated direct recoil from dissolving primary U bearing minerals but did not consider more stable secondary minerals. To summarize their analysis, the selective leaching mechanism must be consistent with the rate of whole rock weathering which may be on the order of $10^{-6}\ \text{m/yr}$. The principle applies wherever whole rock dissolution is active, and down gradient to the extent that a significant portion of the U in groundwater comes from whole rock dissolution.

Some type of selective leaching does occur as demonstrated by activity ratios for short residence time waters from Apache Leap and elsewhere. Petit et al. (1985a) state that restricted solubility (mobility) of ^{238}U vs. ^{234}U is a more likely cause for fractionation than selection based on incongruity. The aqueous solubility of U(IV) is orders of magnitude lower than U(VI) especially in the presence of carbonate and with low concentration of vanadium (uranyl vanadates may precipitate at low U levels).

To evaluate whether fractionation is caused by auto-oxidation of parent $^{238}\text{U(IV)}$ to $^{234}\text{U(VI)}$ first consider the fate of recoiled ^{234}Th . Alpha-decay of $^{238}\text{U(IV)}$ produces a formal valence of Th^{+2} which stabilizes at Th^{+4} due to hydrolysis in solution, or interaction with neighboring oxygen atoms in most geologic materials (Regil et al., 1989). From known lattice displacement energies it can be calculated that up to 1500 atoms are displaced along the track (e.g. Lindhard and Scharff, 1961). Recoiled ^{234}Th is heavy and likely to stop near light atoms such as oxygen, due to low-energy collisions that tend to form oxygen Frenkel pairs (interstitial-vacancy pairs). Oxidation to Th(IV) is likely under such conditions. Subsequent beta-decay produces $^{234}\text{Pa(V)}$ in its most stable valence state, then $^{234}\text{U(VI)}$. In support of this model Regil

et al. (1989) discussed "hot atom" experiments on solid uranium compounds, which showed that in U(IV) compounds a large proportion of α -recoils produce U(VI) if the compounds contain oxygen, but not if they contain a reducing species or no oxygen.

Once $^{234}\text{U(VI)}$ forms as an interstitial species, fractionation may take place with congruent dissolution. The restricted solubility of primary $^{238}\text{U(IV)}$ enhances the $^{234}\text{U}/^{238}\text{U}$ AR in solution. Solubility of U(VI) vs. U(IV) species ranges over at least 3 orders of magnitude, so it is reasonable to question why the overwhelming majority of activity ratios observed in nature are less than 12. The answer may lie in the combined effects of congruent dissolution rate (relative to the production rate of ^{234}U in dissolving minerals) and the availability of oxygen. With increasing congruent dissolution rate the activity ratio of released U converges to unity, being limited by the rate of ^{234}U production. The highest rates of congruent dissolution are likely near the surface where recharge waters are fresh, and waters tend to be oxygenated. Conversely, ^{234}U fractionation is greatest where dissolution rates are slower and/or oxygen fugacity is lower. Overall production of U(VI) in solution is greater in the near-surface oxygenated environment, with the result that much of the mobile U in groundwater dissolves in a less fractionating environment. Extending this idea, when highly fractionated ($\text{AR} > 5$) groundwater is encountered it is reasonable to question whether the total U dissolved by recharging waters in the near-surface environment is somehow limited, or alternatively whether direct recoil is the cause of the high activity ratios, because sorption of near-surface dissolved U is necessary to eliminate excess ^{238}U .

Selective leaching is inferred when residence time is brief compared to the ^{234}U lifetime, and on this basis activity ratios up to ~ 5 have been attributed to selective leaching (Osmond and Cowart, 1992). For higher activity ratios it may be difficult to discern the contributions of selective leaching and direct recoil without other hydrogeologic data (Andrews et al., 1989b). In summary, the bounding analysis of Petit et al. (1985a) has identified problems with selective leaching mechanisms based on incongruency and diffusion. The auto-oxidation mechanism is based on experimentally verified "hot atom" behavior and mobility dependence on valence.

3.4 FRACTIONATION AT APACHE LEAP

Either mechanism could operate in the Apache Leap Tuff to some extent. Selective leaching apparently occurs near the surface in soils and fracture zones, as indicated by short residence time and from the relation between total U and $^{234}\text{U}/^{238}\text{U}$ for surface and fracture waters. A mixing plot of $^{234}\text{U}/^{238}\text{U}$ vs. inverse concentration of total U, based on preliminary data (Fig. 3.4), suggests that the near-surface fractionation process differs fundamentally from that deeper in the formation. Surface and near-surface (≤ 15 m) waters all lie on a trend that does not include the perched water. The concentration of total U in near-surface waters approaches that of the perched water but the AR remains low.

A mixing line connecting near-surface fracture waters with the DSB perched water would imply an end member of highly fractionated water at depth (Fig. 3.4). If the sampled fracture

Figure 3.4 Mixing plot of $^{234}\text{U}/^{238}\text{U}$ activity ratios vs. inverse concentration of total uranium, for water samples from the ALRS.

waters are representative of recharge, then a mixing-type model implies that whatever process produces the excess ^{234}U in perched water may be capable of producing activity ratios far in excess of the observed value of ~ 6 . This degree of fractionation has been associated only with direct recoil processes in the literature.

Representative chemical analyses (Table 3.3) show that the perched water is somewhat more dilute than "squeezed" pore waters yet with significantly higher $^{234}\text{U}/^{238}\text{U}$ (Table 3.2). Perched water is evidently diluted by rapid recharge, which evidently originates in near-surface fractures with AR ~ 2 . For perched water ^{234}U to result from mixing of rapid recharge with matrix flow would require matrix pore water with AR $\gg 6$. From pore water samples analyzed so far there is no evidence for this.

The "gray" tuff unit (Fig. 3.1) has a matrix saturated hydraulic conductivity on the order of 0.1 mm/yr whereas the hydraulic conductivity of the fracture network could be 10^3 times greater depending on saturation. Thus the residence time of water in the fractures of the vadose zone or perched aquifer could be significantly less than for the tuff matrix. This translates to much higher water:rock ratio for recharge pathways, and waters which are pumped from the perched zone.

Dissolution processes tend to be more congruent with increased water:rock ratio, as fresher waters remove more dissolution products such as silica. For this reason and those given above, auto-oxidation seems most likely among proposed selective leaching mechanisms to account for perched water fractionation. Perched water in the DSB has dissolved oxygen at 6 ppm and the temperature is within a few degrees of the average surface temperature (Davidson, 1995) so these are not causes of differential fractionation. A lower rate of dissolution may be an important factor contributing to fractionation in the perched water, distinguished from deep vadose zone pore water by relatively short residence time on the order of 3 kyr (Davidson, 1995).

The alternative mechanism to explain perched water fractionation is direct recoil. Secondary minerals cause repartitioning of uranium to the immobile phase, with subsequent recoil of daughters into solution. Although they provided no strong evidence, Zielinski and Rosholt (1978) proposed this effect for oxidizing waters from tuffaceous aquifers, whereby repartitioning of uranium was associated with "...secondary oxides of iron, manganese, and titanium which form as alteration rims or collect in areas most accessible to water such as micro fissures."

Oxide precipitates are found as matrix constituents and fracture lining minerals in the Apache Leap Tuff sampled by the DSB. Variation of whole rock composition and magnetic susceptibility suggest that oxidative alteration has accumulated near the surface, along fractures, and in the perched aquifer (Figs. 3.5 and 3.6).

Table 3.3 Representative chemical analyses for surface water, pore water, and perched water at the ALRS (mg/L).

Location	Date	Temp. (C)	pH (field)	HCO ₃ (titration)	SO ₄	NO ₃	PO ₄	Cl	Na	K	Ca	Mg	SiO ₂	Charge % Bal.
Watershed Runoff (AQ-M) ^{1,6}	1/18/92	7.5	5.78	2.3	19.4	bd ²	bd ³	2.4	3.8	1.0	4.4	1.4	na ⁵	3.8 %
Watershed Runoff (AQ-M) ^{1,6}	8/26/93	27.3	5.96	1.9	19.0	bd ²	bd ³	2.5	3.8	1.7	5.9	1.6	na ⁵	12.2 %
Pore Water (AQ-15M-A) ⁸	squeezed 6-7/94	24 (lab)	6.7 (lab)	102.5 (TIC) ⁴	30.5	bd ²	10.5	37.1	47.1	3.5	27.8	4.5	67.4	7.5 %
Perched Water (DSB, purged) ⁷	7/8/93	23	7.4	121.7	1.9	1.0	bd ³	4.0	22.1	0.9	20.6	3.8	54.8	3.6 %
Mine Tunnel (CB-1) ¹	2/27/90	24.0	8.0	138.2	16.6	2.6	bd ³	6.7	21.0	0.82	29.2	5.2	62	0.3 %

¹ source: Bassett et al. (1994). ² below 0.5 mg/L. ³ below 0.25 mg/L. ⁴ from total inorganic carbon with TIC/TC analyzer.

⁵ not analyzed. ⁶ below 0.25 mg/L in F and Br; and 0.2 mg/L in Al. ⁷ 6.0 mg/L dissolved organic carbon; below 0.25 mg/L in F and Br; below 0.05 mg/L in Al

⁸ source: Davidson (1995). ⁹ Charge balance = 100% $\{[\Sigma \text{ cations}(\text{eq}) - \Sigma \text{ anions}(\text{eq})] / \Sigma \text{ all ions}(\text{eq})\}$

Figure 3.5 Magnetic susceptibility normalized by total Fe, from chemical analysis of cuttings and core samples, plotted vs. true depth for both the DSB and the nearby VOB.

Figure 3.6 (left) Magnetic susceptibility from laboratory measurements and the EM39 induction log, for the VOB. (right) Total Mn and Ti from chemical analysis of cuttings and core samples, including data for both boreholes plotted against depth.

4. GEOPHYSICAL STUDIES

by E.L. Hardin and R.L. Bassett

4.1 INTRODUCTION

Geophysical activities were undertaken as part of a multi disciplinary project to investigate site characterization methods that could be applied at Yucca Mountain, Nevada, possible site of a future geologic repository for high-level radioactive waste. Geophysical logs were used to look for evidence of fracture flow in the unsaturated zone, and to guide spatial sampling for geochemical studies. Laboratory data from cores and cuttings were used to better interpret these logs.

4.2 DATA DESCRIPTION

The deep slant borehole (DSB) and the vertical observation borehole (VOB) were drilled at the Apache Leap Research Site operated by the University in central Arizona. The Apache Leap Tuff at this location is thick, mostly devitrified and partly to densely welded (Peterson, 1968). Summary descriptions of the DSB and VOB are as follows:

- ◆ The DSB plunges $\sim 45^\circ$ perpendicular to the strike of widely spaced, high-angle fractures. Single-shot deviation measurements made at distances of 182, 252 and 393 ft. from the surface show that the deviation decreases from 45° to $\sim 37.5^\circ$ at depth. The DSB has a total length of 660 ft. and is dry above a perched water table at approximately 624 ft. (483 ft. true vertical depth). It was fully diamond-cored, and the upper third was reamed and cased. The diameter telescopes from 6 in. to 4.52" and 3.98" in the lower unreamed sections. Drilling was done with compressed air to limit contamination of core samples and the formation. Cores were recovered by wireline in 10-ft. runs, inspected and sealed in Protec Core packaging.
- ◆ The VOB is an uncased, vertical drillhole collared 50 ft. from the DSB at the surface. It has a total depth of 560 ft. and is dry above the perched water table at 488 ft. (Same as the depth to perched water depth in the DSB, to the accuracy of the deviation survey.) The diameter of the VOB is 6 in., and it was drilled with compressed air using a tri-cone rotary bit. Cuttings samples were collected every 10 ft. and stored in cloth bags.

Both boreholes were collared in the more porous upper "white" unit and drilled into the more densely welded "gray" unit below, within what may be a single cooling unit of the Apache Leap Tuff (nomenclature of Peterson, 1968).

4.3 GEOPHYSICAL LOG SUMMARY

A suite of geophysical logs was acquired from the DSB including:

- ◆ Nuclear logs: dual-detector neutron, γ - γ density, and natural- γ (USGS).
- ◆ Electrical logs: Geonics EM-39 induction/susceptibility.
- ◆ Borehole television: COLOG, Inc.

Acoustic and galvanic resistivity methods could not be used with dry hole conditions. Also, the minimum hole diameter (~ 10 cm) limited the project to slim-hole tools. At this writing only the EM-39 electrical induction log was acquired for the VOB.

4.3.1 Nuclear Logs

A Comprobe dual detector neutron tool was used with a 3.16 Ci source, owned and operated by the U.S. Geological Survey (USGS). This is a mandrel tool which ran along the lower side of the borehole. The ratio of near to far ^3He detector count rates is sensitive to scattering (near) and capture (far) properties of hydrogen present as water, and so responds to volumetric moisture content but was uncalibrated (Fig. 4.1). Other elements in the tuff (e.g. Si, Ca) may capture more thermal neutrons than hydrogen, so changes in mineralogy/petrology could appear as moisture changes. The neutron count ratio is offset by the presence of water in the borehole at the perched water table (Fig. 4.1).

The γ - γ density tool was also built by Comprobe and operated by the USGS. This mandrel tool was decentralized by a single caliper arm, with the tool weight maintaining its position approximately along the lower side of the hole. It was calibrated in the field with half-blocks of Mg and Al metals, and the logarithm of far:near detector count ratio was interpolated between these limits to obtain formation density (Serra, 1984). The density log was nearly unaffected at the perched water table. Log response at fracture zones is probably associated with borehole rugosity, i.e. where rock fragments broke away from the borewall during drilling.

The natural- γ tool was built and operated by the USGS. The activity log is nearly uniform except for statistical counting noise approximated by the square root of the count rate (Fig. 4.2). Uniform natural gamma activity overall is consistent with five whole-rock uranium and thorium analyses of intact samples distributed over the length of the DSB. Total U and Th concentrations of 3.0 ± 0.1 ppm and 10.4 ± 0.6 ppm, respectively, were obtained (between-sample standard deviations). Lower activity above ~230 ft. corresponds with the density trend in Fig. 4.1, associated with the greater porosity of the "white" tuff unit.

4.3.2 Induction Logs

Induction logs were acquired approximately 2, 4, 6, 8, and 20 months after drilling. Most

Figure 4.1 Density and neutron logs for the DSB Logs have been smoothed using a running average.

Figure 4.2 Natural gamma activity log from the deep slant borehole.

logging was done with a Geonics EM-39 owned and operated by the University of Arizona. The EM-39 sonde was fitted with a PVC plastic sheath to protect from abrasion in the angled borehole. The system had been calibrated previously by the manufacturer, and was periodically rechecked in a reference borehole at another site.

The EM-39 is a 3-coil type instrument that is nulled at the surface just prior to use. As formation resistivity exceeds 100 Ω -m formation-induced signals in the receiver coil become very small, approaching the magnitude of the instrument null signal. The quality of the null adjustment determines the maximum resistivity that can be reported by the system. Drift of the instrument null can be expected during logging, as seen from a crossplot of successive EM-39 logging runs (Fig. 4.3) that exhibits appreciable drift for resistivity greater than ~ 200 Ω -m.

The DSB was logged with the EM-39 from about 245 ft. near the bottom of the steel casing, to the cable limit of about 590 ft (Fig. 4.4). Lower resistivity at greater depth corresponds to a trend toward wetter conditions in the neutron log (Fig. 4.1). In addition there are spikes which correlate between the logs. Repeat logging of the DSB produced similar results in the most conductive intervals but deviated considerably in resistive zones.

The VOB was logged from 20 to 560 ft. with detection of lower resistivity at intervals which were noticeably wetter during drilling (Fig. 4.5). Comparison of induction logs from the VOB and DSB (converted to true depth) shows that the VOB has lower resistivity overall but does not intersect the feature observed in the DSB below true depth of 430 ft.

The EM-39 produces an in-phase signal proportional to formation magnetic susceptibility, which is directly related to magnetite, ilmenite, and other ferrimagnetic minerals that are relatively abundant in felsic tuffs. In-phase response is reported as a percentage of the primary transmitter signal. Figure 4.6 shows that there is substantial variation in the abundance of magnetic minerals (assuming that the geometrical distribution of mineral grains is reasonably uniform). The lower limit of detected susceptibility is related to drift of the null adjustment, just as for resistivity, but log features were replicated by repeat logging.

4.3.3 Borehole Television

A black-and-white high-resolution television survey was conducted by COLOG, Inc. The video provided digital depth indication, and the vertical direction was plainly evident from slight vertical offset in the centralizing springs. Fracture traces in the upper 2/3 of the borehole are widely spaced, either high-angle or subhorizontal. Nearly all fracture indications from nuclear and induction logs are associated with observed fractures in the television log, but many fractures are visible that are not indicated by the other logs, similar to what is found with the borehole acoustic viewer in fluid-filled boreholes (Keys, 1987; Paillet, 1991). In the lower 1/3 of the DSB rock texture appears more disturbed and fractures more frequent. Below 480 ft. much of the rock is disturbed so that feature orientation is not readily discernible.

Figure 4.3 Crossplots of same-day successive logs of the deep slant borehole with the EM-39 induction tool. Both the resistivity (upper) and in-phase (lower) are examined for repeatability.

Figure 4.4 Geonics EM-39 induction log for the deep slant borehole (10/5/94 A). Both quadrature (resistivity) and in-phase (susceptibility) components are shown.

Figure 4.5 Comparison of EM-39 resistivity logs for the vertical observation borehole and the deep slant borehole (recomputed to vertical depth).

Figure 4.6 Magnetic susceptibility of core and pulverized rubble samples, plotted with the EM-39 in-phase response, vs. true depth.

4.4 PETROPHYSICAL MEASUREMENTS

4.4.1 Bulk Density and Volumetric Moisture Content

Moisture content was determined gravimetrically using two series of DSB core samples:

- ◆ G-series cores (53) were initially weighed in the field, then analyzed later in the laboratory in Tucson (A.M. Geddis, written communication).
- ◆ P-series cores (49) were preserved using the Protec-Core wrapping system, stored in the laboratory for 9 months, then analyzed.

Cores were placed in a 105°C convective oven for drying. Most water loss occurred in the first 48 hr, but change of up to 0.1% of total weight per day continued after the third day. By the final weighing the rate of drying diminished to less than 0.1% per day.

Bulk volume was measured for the G-series cores by volumetric immersion in water. The P-series cores were measured gravimetrically by resaturating, then suspending in a beaker of deionized water on an analytical balance. Small buoyancy changes during the first 5 minutes were extrapolated back to zero time. This is more precise than the volumetric method because of the inherent precision of the balance.

Wet bulk density values computed from initial or "preserved state" weights were in the range 2.2 to 2.4 g/cm³ for the "white" tuff unit, and 2.4 to 2.5 g/cm³ for the "gray" unit. These values are in reasonable agreement with the density log (Fig. 4.7). In open hole the density log is roughly 3% low which may be attributed to the effects of partial water saturation and the use of metals with low atomic number as calibration materials (Serra, 1984).

Volumetric moisture data for the P- and G-series cores are plotted with the neutron log against depth in Fig. 4.8. Overall similarity between the series indicates small moisture losses during delayed handling of the P-cores. Increased moisture content in the upper ~200 ft. corresponds to the more porous "white" tuff unit exposed at the surface. Data from the interval between 200 ft. and 300 ft. are grouped between 6% and 7.5%, but scatter increases below 300 ft. suggesting a transition in formation conditions.

Volumetric moisture data for approximately 100 core samples are plotted against neutron log ratio values interpolated at the same depths in Fig. 4.9. Comparison of data groups shows a trend in neutron log response, if the most porous samples from the "white" tuff unit are ignored. As the porosity increases to around 15% or more, there is probably diminished capture of thermal neutrons by mineral elements such as Si or Ca, which reduces the near:far count ratio.

4.4.2 Porosity and Apparent Saturation

After moisture analysis the P-cores were stored, then dried again and resaturated. The

Figure 4.7 Wet bulk density for P-cores which were preserved for laboratory analysis. Plotted with the density log for comparison.

Figure 4.8 Volumetric moisture content vs. depth for the P- and G-series cores, plotted with the uncalibrated near:far neutron count ratio log.

Figure 4.9 Crossplot of neutron log values vs. volumetric moisture content of cores. The log was smoothed and resampled at core depths.

weight change from resaturation was used to estimate porosity assuming full saturation. Cores selected for resaturation were from the "gray" tuff unit interval from which induction logs were acquired. They were placed upright in a vacuum vessel and evacuated for 24 hr. Deionized water was introduced from below, and saturation proceeded for at least 72 hr under vacuum (water vapor). Cores were then towel dried and weighed.

The effect of saturation time was studied for a few representative cores by monitoring weight change during repeated cycles of evacuation and saturation. It can be expected that partial resaturation will occur with this procedure as shown from scatter in the resulting grain density values for 30 P-cores (Fig. 4.10). Assuming that grain density is uniform, the scatter in solid phase evident from Fig. 4.10 (about 1% of total volume) is exactly the scatter in void volume measured by this procedure.

Initial saturation of the P-cores was investigated by comparing initial volumetric moisture content (based on bulk volume from gravimetric immersion) with porosity from resaturation. Resulting values for apparent saturation are plotted against depth in Fig. 4.11. Values as high as 1.15 apparent saturation again indicate porosity underestimation by up to 1% of total volume. (Assuming cores were fully saturated initially, with true porosity of 7%.) In summary, for the "gray" tuff unit porosity varies from 5 to 8% and nearly all P-cores tested had initial saturation of at least 80% even allowing for porosity underestimation. The data of Fig. 4.11 also show spatial variability in porosity (more than the measurement error) measured on core samples taken from a few feet apart.

4.4.3 Electrical Resistivity and Induced Polarization

The 49 P-cores were selected to include replicate samples of a few spikes and other features of the induction and neutron logs. As each core package was unsealed in the lab, samples were brushed, weighed, and kept in plastic containers until electrical measurements were made. Resistivity measurements were made to investigate the performance of the EM-39 system for formation resistivity above 100 Ω -m.

Induced polarization (IP) occurs when geologic media have limited capacity to conduct sustained electric current, and charge carriers build up at compositional interfaces. This produces a charging effect commonly associated with sulfide minerals, partial saturation, and also with the fine pore structure and solution interface phenomena characteristic of clay bearing rocks. IP (or chargeability, in units of mV/V) is also directly related to resistivity because current path restriction becomes less important with higher saturation or lower pore fluid resistivity.

Resistivity and time-domain IP measurements were made with high-precision voltmeters under computer control. Chargeability was computed from voltage decay after a direct current was rapidly turned off. The core holder for electrical measurements was the same design used by Thornburg (1990), but the porous plates were redesigned with electrodes inlaid into the sides facing the sample instead of the electrolyte reservoir. This way the measured core resistance did

Figure 4.10 Grain density vs. porosity for P- and G-series cores. Bulk volume and solid volume were measured differently for the series as noted.

Figure 4.11 Porosity and apparent initial saturation, for P-cores from the "gray" tuff unit. Neutron log peaks (e.g. at 325 and 370 ft.) are discussed in the text.

not require correction for resistance of the porous plates. About 1 mL of paste mixed from water and silica flour was used between each electrode and the sample for electrical contact. The resistance of the paste layers was on the order of 50 Ω , which was smaller and easier to control than the resistance of porous plates, with the disadvantage that a small amount (< 1 mL) of fluid bled from the paste into the sample. For IP measurements the silver electrodes were prepared in the manner described by Geddes and Baker (1975). The resulting AgCl patina reduced background noise to an equivalent chargeability of about 0.5 mV/V in dilute saline.

Core measurements indicate that much of the section sampled by the DSB is more resistive than 200 Ω -m but less resistive than indicated by the EM-39 log (Fig. 4.6). There is qualitative agreement where replicate sets of core measurements compare with spikes in the log (e.g. at 410 and 535 ft.). Chargeability data show that the IP effect is of limited magnitude, suggesting that clays are sparsely distributed. In summary, the EM-39 resistivity agreed with laboratory values for resistivity less than $\sim$ 100 Ω -m, provided semi-quantitative information for higher resistivity to roughly 200 Ω -m, and qualitative location information for features with resistivity above that.

4.4.4 Pore Water Resistivity

Core resistivity values plotted in Fig. 4.12 show that when selected cores were measured again after drying and resaturating with deionized water, they were more resistive because of pore water depletion in dissolved ions. Pore water resistivity in partially saturated media is difficult to measure, and only a few samples were acquired by core squeezing (Davidson, 1995). The available data were of two types: direct measurements on small samples diluted to 4 mL with Type 1 deionized water, and inferred values calculated from major ion analyses for squeezed pore water using WATEQ4F (Ball and Nordstrom, 1990). These are summarized in Table 4.1. All of these values lie within a relatively narrow range, compared to the observed range of natural waters. Comparison between values may not be justified as indicated by the discrepancy in near-replicate samples AQ15m-A and -B. Redistribution of moisture within a Protec-Core package before "squeezing," and variation in the duration of "squeezing" tests are possible causes for variability.

Application of pore water resistivity values is further complicated because pore water samples were not obtained throughout much of the DSB due to the difficulty of "squeezing" more densely welded tuff samples. In addition, using pore resistivity to evaluate the relation between resistivity and saturation is problematic because pore water composition very likely changes as the samples are dewatered.

4.4.5 Magnetic Susceptibility

Petrographic examination of the Apache Leap tuff was reported by Peterson (1961). The proportions of phenocrysts in the "white" and "gray" units were reported as 41.0 and 42.7%, respectively. Of these the proportions identified as magnetite were 3.4 and 2.9%, giving mass

Figure 4.12 Resistivity (left) and induced polarization or chargeability (right) measured on preserved P-cores, including data for cores that were dried and resaturated. The EM-39 resistivity log for the deep slant borehole is also plotted.

Table 4.1 Measured and calculated pore water resistivity from squeezed pore water samples from the DSB.

Sample	Approx. DSB Core Depth (ft)	Calc. TDS (ppm)	Calc. Sp. Cond. ($\mu\text{S}/\text{cm}$)	Meas. Sp. Cond. ($\mu\text{S}/\text{cm}$)	Comment
AQ12m	39	288	386		
AQ15m-A	50	331	385		A & B from separate cores
AQ15m-B	50	387	500		
AQ22m	72	272	356		
AQ29m	95	296	377		
AQ197m	646	377	502		perched aquifer
Composite 1	56			480	diluted 1:1 for measurement
Composite 2	582			455	diluted 1:2 for measurement

fractions of about 0.5 to 1%. This is approximate because of variability associated with formation characterization using thin sections, and because hornblende was reported in similar abundance. However, the levels reported by Peterson are great enough that the susceptibility of the Apache Leap tuff should be readily measurable.

Rock susceptibility depends also on the size, aspect ratio, and orientation of magnetite grains. In addition, oxidative weathering converts reduced-Fe or -Mn minerals to nonmagnetic species. Susceptibility was measured on intact cores, core fragments, and drill cuttings to evaluate the in-phase response of the EM-39, the variability of which was in turn evaluated for information on possible weathering processes. For the DSB a series of 70 samples was prepared including intact dry cores and rubble from core drilling, which was pulverized and poured into plastic sample bottles the same size as cores. For the VOB drill cuttings were sampled in the field, subsampled with a splitter, then poured into plastic sample bottles. Samples were analyzed in a computer-controlled susceptibility bridge calibrated against a sample bottle filled with reagent-grade MnO_2 powder.

The effects of classification caused by pouring samples into bottles were investigated using multiple bottles subsampled from the same pulverized core. The effect of possible anisotropy in whole cores vs. isotropy assumed for granular samples was investigated by

measuring intact cores and adjacent cores which had been pulverized. No significant differences could be attributed to sample preparation or anisotropy effects.

Features in the EM-39 in-phase logs for the DSB and VOB are well matched by sample susceptibility data (Fig. 4.6). Susceptibility is generally greater in the VOB than the DSB, possibly because the DSB transects a rock mass that has accumulated more oxidative weathering. Cuttings from the VOB match the log better than core samples from the DSB, possibly because only competent rock is recovered by coring and it tends to be less weathered. The interval from 410 to 440 ft. (true depth, Fig. 4.6) in the DSB has similar susceptibility to the VOB and is probably relatively unweathered.

4.5 RELATIONSHIPS AMONG ELECTRICAL PROPERTIES, VOLUMETRIC MOISTURE, SATURATION, AND CLAY CONTENT

A crossplot of neutron vs. EM-39 resistivity (Fig. 4.13) in the DSB can be interpreted in terms of resistivity vs. saturation for the "gray" tuff unit. Taking the slope of the frontier of points below 100 Ω -m, the neutron ratio changes from 0.7 to 1.2 while resistivity varies roughly 10-fold. Core measurements showed that the porosity in this interval varies between about 5 and 8%, and the lowest saturation encountered in core samples was around 80%. Assigning the neutron ratio change to a saturation range from 80 to 100%, gives a power law relationship between saturation and resistivity.

Thornburg (1990) examined resistivity-saturation relations for 12 cores from the "white" tuff unit, fitting the data using the classical power law expression (e.g. Keller and Frischknecht, 1966)

$$\frac{R}{R_{\text{sat}}} \propto S^{-n} \quad (4.1)$$

with an average value of $n=0.67$. For petroleum reservoir rocks $n=2$ is often used, but using either value a 20% change in saturation does not produce a 10-fold change in resistivity.

The effects of pore fluid resistivity and porosity have been neglected so far in this discussion. The observed decrease of resistivity is definitely associated with increased moisture content because it corresponds to a trend on the neutron log. Decreasing pore water resistivity could also be a factor, except the range of pore water resistivity observed with core squeezing is insufficient to account for changes in resistivity. A similar argument can be used to limit the effect of porosity variation using Archie's Law, Thornburg's (1990) data for the "white" tuff unit, and the distribution of porosity observed in core samples (Fig. 4.11).

This discussion leads to recognition that porosity, saturation, and pore fluid resistivity effects are small, and even taken together do not readily account for the observed range of resistivity in the DSB. A possible explanation is lithology change in the lower part of the

Figure 4.13 Crossplot of neutron log count ratio vs. EM-39 resistivity. Each log was "bin-averaged" by averaging all values within each 1-ft. interval.

borehole, such as secondary mineralization which lowers resistivity but is not readily sampled in the core and therefore is not represented in porosity or saturation data. This is consistent with borehole television images in which the lower part of the DSB appears altered. The existence of sampling bias is indicated from:

- ◆ Core losses which increased significantly in the lower part of the DSB (Fig. 4.14).
- ◆ The neutron log trend below about 480 ft. (distance from collar) in the DSB which is not indicated by volumetric moisture measurements on cores (Fig. 4.8).

Secondary alteration is not apparent in the VOB for which the EM-39 induction log indicates only 2-fold variation of resistivity in the "gray" tuff unit, with a gradual trend toward lower resistivity with depth. Electrical properties therefore indicate that the DSB samples lateral variation that may be associated with secondary processes.

4.6 EVIDENCE FOR MOISTURE MOVEMENT ALONG FRACTURES

Neutron, density, and induction logs in the DSB respond systematically at small features of a few meters or less, suggesting that these are fractures with higher moisture content, lower resistivity, and borehole rugosity (Figs. 4.1 and 4.4). In addition these features are readily correlated with discrete fractures or fracture zones evident from borehole television. Significantly, some of these log features are broad relative to the thin-bed responses of the logs, indicating that water is moving in fracture zones.

The shape of some log features also suggests moisture movement. The neutron log (Fig. 4.8) and to a lesser extent the EM-39 resistivity log (Fig. 4.5) exhibit tailing on the downhole side of several spikes, which is pronounced at 325 and 385 ft. in the DSB (distance from collar). This suggests that matrix imbibition favors the downward side of these zones, or possibly that water flowed into the angled borehole wetting the downward side to which the neutron log is most sensitive. In either case moisture movement along fractures is inferred.

4.7 MAGNETIC SUSCEPTIBILITY AND THE EXTENT OF WEATHERING

A key question concerning the DSB and VOB susceptibility profiles is whether their features resulted from primary ash flow structure or low temperature alteration from hydrogeologic causes. Weathering of a significant portion of distributed magnetite requires access by pore water to the rock matrix. Minerals such as plagioclase would be weathered resulting in the precipitation of silica and possibly smectite, in addition to ferric oxide hydrates. Susceptibility decrease could therefore be associated with lower resistivity. Comparing EM-39 resistivity and in-phase response logs (Fig. 4.4) shows that at spikes where susceptibility is least, resistivity is also lowest. Crossplots of EM-39 resistivity vs. in-phase response (not shown) show

Figure 4.14 Core loss data from drilling logs. For each core run, core loss (gain) is the difference between distance drilled and core footage recovered.

weak correlation ($r=0.3$ to 0.6) particularly in the "gray" tuff unit, for both the DSB and VOB. Crosstalk between in-phase and out-of-phase signals can be expected with the EM-39, but the magnitude is small as indicated by signal separation at spikes where only one signal responds. Thus the observed correlation could be the result of weathering.

The DSB and VOB are collared close together in the bed of an ephemeral stream. Magnetic susceptibility in the "white" tuff unit beneath the stream bed is relatively low, increasing with depth. This variation is common to both boreholes, and could also be the result of syngenetic vapor-phase alteration. In the "gray" tuff unit below about 250 ft (true depth) the DSB and VOB data deviate significantly, with both the in-phase log and susceptibility measurements showing about twice as much susceptibility response in the VOB. Such variation over distances less than the cooling unit thickness indicates that secondary processes are more active in the vicinity of the DSB. In addition the absence of low susceptibility spikes in the DSB log suggests that this part of the rock mass has been more extensively altered than near the VOB. Logs and laboratory measurements for both boreholes show diminished susceptibility below the perched water table.

4.8 SUMMARY OF FORMATION CONDITIONS

In the "white" tuff unit from the surface down to about 200 ft. (true depth) porosity decreases gradually from approximately 20% to about 6% with a corresponding increase in resistivity. There are several wet fractures in this interval but not all fractures present are wet. Low susceptibility in the "white" unit indicates pervasive oxidation of ferromagnetic minerals, assuming the elemental composition of the tuff sheet is relatively uniform. From 200 to 300 ft. (true depth) in the DSB porosity is nearly constant and saturation is 80% or more. There are a few wet fractures with evidence of moisture movement. This zone corresponds to the upper part of the "gray" tuff unit identified by Peterson (1961; 1968).

From 300 ft. down to the perched water table, resistivity gradually decreases in the VOB with low resistivity, low susceptibility spikes at fracture intersections. At a true depth of about 350 ft. in the DSB the moisture content increases and the resistivity decreases sharply, along a trend which is probably associated with increasing abundance of secondary mineralization. The same trend does not appear in the VOB. Below 350 ft. (true depth) in the DSB fractures occur as increasingly thick zones, and are less well represented in the core. Within fracture zones the rock texture is disturbed, with alteration products evident from borehole television. Based on this information and the discrepancy between the boreholes, it is likely that the DSB penetrates a broad, laterally discontinuous feature such as a fault or major fracture zone below 350 ft. (true depth).

Magnetic susceptibility fluctuates in both boreholes for roughly 50 ft. above the current perched water table near 485 ft. (true depth). Low susceptibility spikes are closely associated with fractures, and conditions in or near the perched aquifer may also favor magnetite

weathering. The perched water table could have been 50 ft. higher in the geologic past, particularly during colder Pleistocene conditions. More recently, the perched water table may have been drawn down by dewatering of the nearby Magma mine since construction of shaft #9 in 1972.

5. WATER BUDGET CALCULATIONS

by E.G. Woodhouse, R.L. Bassett, W.J. Shuttleworth, and D.L. Thompson

5.1 INTRODUCTION

The purpose of this research is to measure how much water is available for infiltration, to potentially recharge a perched water table, in a fractured, welded tuff. Infiltration is measured as a component of the water budget, where precipitation into a watershed is balanced by runoff, evapotranspiration, and infiltration. In terms of infiltration, the water budget is expressed as follows:

$$I = P - R - E \quad (5.1)$$

where I = infiltration, P = precipitation, R = runoff, and E = evapotranspiration. This equation assumes no net groundwater flow into or out of the basin, and no change in surface water storage over time. These assumptions are valid for many watersheds, including the one used for this investigation.

Precipitation, runoff, and evapotranspiration can all be measured directly, which enables a relatively precise value for infiltration to be determined. Precipitation is measured with recording rain gages; spatial variability can be estimated from measurements from several gages placed throughout the watershed. Runoff is measured with flumes at the outlet of the watershed; more than one size flume is needed to record different volumes of flow.

Evapotranspiration is a value that is frequently estimated based on temperature, relative humidity, and land cover typical of an area. However, a more precise value can be determined using direct measurements and the theory of the energy budget. In the energy budget, net incoming solar radiation is balanced by energy used to heat the air (sensible heat flux), energy to heat the soil and rocks (soil heat flux), and energy used to evaporate water from the ground and vegetation (latent heat flux). The latent heat flux divided by the latent heat of vaporization gives a measurement of evapotranspiration over a given time and area. Thus, evapotranspiration in terms of the energy budget is expressed as:

$$E = \frac{L_e}{\lambda} \quad (5.2)$$

where

$$L_e = R_n - H - G \quad (5.3)$$

E = evapotranspiration, L_e = latent heat flux, λ = latent heat of vaporization, R_n = net incoming solar radiation, H = sensible heat flux, and G = soil heat flux. The latent heat flux can be calculated directly from measurements of a temperature and relative humidity gradient between two elevations, soil and rock temperatures and temperature changes, and net radiation, using a Bowen ratio system, which will be described in detail in a later section.

To acquire all the necessary measurements, a weather station was set up in the 514,000 m² watershed containing the deep slant borehole at the Apache Leap Research Site (ALRS) in Superior, Arizona (Fig. 2.1). The site is in south-central Arizona, at the western edge of a mountainous region covering the central and eastern part of the state. The high point of the watershed occurs at the top of a steep slope rising sharply to the east of the town of Superior, approximately 560 m below. Total relief within the watershed is 125 m. The drainage basin has steep, rocky sides with sparse vegetation, and the main channel curves around from a northeastern exposure in the upper third, to an eastern exposure in the central part, and back to a northeastern exposure in the bottom quarter. Vegetation is primarily scrub oak and manzanita, with acacia near the main drainage, and prickly pear, yucca, and agave cacti on the edges.

The location for installing the weather sensors was chosen in an attempt to represent the average conditions in an area that exhibits mostly extremes. The weather station is approximately midway both lengthwise across the drainage and along the watershed, but slightly closer to the bottom, for access purposes. The area immediately surrounding the station contains both bare rock, sandy soil, and vegetation, so a mixed cover is monitored. A 6-m high tower was installed to place the instruments above the local vegetation, but not so high as to be above the local climatic conditions. Away from this weather station, a second recording precipitation gage was installed at the highest point of the watershed, and flumes were installed at the outlet.

5.2 DATA ACQUISITION

5.2.1 Precipitation

Precipitation measurements are obtained from two recording rain gages placed at ground level, one at the main weather station and one at the top of the watershed. The gages record tenths of millimeters of precipitation by a mechanism that tips to one side, sending an electronic pulse to the data logger, every time 0.1 mm is collected. They can be calibrated by adjusting the tipping mechanism.

5.2.2 Runoff

Runoff out of the watershed is recorded by two flumes installed at the channel outlet. A large flume records discharges greater than 0.0057 m³/s, and a small flume records discharges up to 0.0057 m³/s.

5.2.3 Evapotranspiration

Evapotranspiration is measured as a component of the energy budget, the parameters of which are measured with a Bowen ratio system. An "off-the-shelf" Bowen ratio system manufactured by Campbell Scientific, Inc. (CSI) was set up at the main weather station in the watershed.

5.2.3.1 Theory of the Bowen Ratio System

Within a few meters of the earth's surface, the water vapor flux and heat flux can be expressed as:

$$E = k_v \frac{\partial q}{\partial z} \quad (5.4)$$

and

$$H = \rho c_p k_H \frac{\partial T}{\partial z} \quad (5.5)$$

respectively, where

E = water vapor flux ($\text{kg/m}^2\text{s}$)

H = heat flux (W/m^2)

q = vapor density (kg/m^3)

ρ = air density (kg/m^3)

c_p = specific heat of air ($\text{kJ/kg}^\circ\text{C}$)

T = temperature ($^\circ\text{C}$)

z = vertical height above surface (m)

k_v = eddy diffusivity for vapor (m^2/s)

k_H = eddy diffusivity for heat (m^2/s)

By applying the universal gas law to Eqn. (5.4) and using the latent heat of vaporization, the latent heat flux is obtained in terms of vapor pressure:

$$L_e = \frac{\lambda \rho \epsilon k_v \partial e}{p \partial z} \quad (5.6)$$

where: L_e = latent heat flux (W/m^2)

λ = latent heat of vaporization (kJ/kg)

ϵ = ratio of molecular weight of water to the molecular weight of air

e = vapor pressure (kPa)

p = atmospheric pressure (kPa)

In practice, finite gradients are measured, and an effective eddy diffusivity is assumed over the vertical gradient:

$$L_e = \frac{\lambda \rho \epsilon k_v (e_1 - e_2)}{p (z_1 - z_2)} \quad (5.7)$$

$$H = \frac{\rho c_p k_H (T_1 - T_2)}{(z_1 - z_2)} \quad (5.8)$$

In general, k_v and k_H are unknown, but can be assumed to be equal.

The Bowen ratio is the ratio of H to L_e :

$$\beta = \text{Bowen ratio} = \frac{p c_p (T_1 - T_2)}{\lambda \epsilon (e_1 - e_2)} \quad (5.9)$$

where the ratio $(p c_p)/(\lambda \epsilon)$ is the psychrometric constant.

The surface energy budget is given by:

$$R_n = G + H + L_e \quad (5.10)$$

where

R_n = net radiation for the surface (W/m^2)

G = soil heat flux (W/m^2)

Substituting $L_e \beta$ for H in Eqn. (5.10) and solving for L_e yields:

$$L_e = \frac{R_n - G}{1 + \beta} \quad (5.11)$$

The Bowen ratio system gives β in Eqn. (5.11) by measuring temperature and relative humidity (RH) at two heights; RH is then converted to vapor pressure. Temperature is measured with thermocouples; RH is measured with a single cooled mirror dew point hygrometer. R_n is measured with a net radiometer; G is measured from soil heat flux plates, and soil and rock

temperature thermocouples buried at depth in the soil or rock. L_e is then used to solve for total evapotranspiration. (Theory from CSI, 1993.)

5.2.3.2 Mechanics and Components of the Bowen Ratio System

5.2.3.2.1 Acquisition of Data

Figure 5.1 shows a diagrammatic sketch of the Bowen ratio system used at the ALRS. All of the sensors are wired to a CR10 datalogger mounted on a 6-m high tower, which also holds other weather monitoring instruments, including two 1.5-m long "arms" with some of the sensors. The datalogger is kept in a weatherproof box which also contains a dew point hygrometer used to measure the vapor pressure gradient. The datalogger and hygrometer are powered by a single deep cycle marine battery which is recharged by a 51-watt solar panel. Measurements are made in intervals of 1 or 10 seconds, and 20-minute averages are recorded.

The temperature gradient is measured every second by 75 μm diameter chromel-constantine thermocouples located at the end of each arm. The distance between the arms can be adjusted within the limits of the tower height; at ALRS the arms are approximately 4 m apart. The thermocouples each have two parallel junctions to minimize loss of data. A differential voltage is measured by the datalogger due to the difference in temperature between the two arms; resolution of the datalogger is 0.006°C.

The vapor pressure gradient is measured through the difference in relative humidity between the two arms. Filtered air-intake ports are located midway out the arms, and a pump ducts the air to 2-liter buffering containers (Fig. 5.2). The air from the different heights is then ducted alternately to a common dew point sensor, minimizing instrument error. The air is buffered in temporary storage to minimize any possible impact of the fact that the two heights are sampled at slightly different times. Air is ducted from a given arm for two minutes, during which time measurements are made every second, before switching to the other arm. Thirty seconds are allowed to elapse immediately following the switch to allow complete exchange of air. The average values for each arm are then recorded at the end of every 20 minutes.

The dew point humidity sensor consists of a small mirror with an electronic cooler and thermometer over which the sample is drawn, together with a light source and light detector capable of measuring the amount of light reflected by the mirror. As the air is being blown over the mirror, it is cooled; the mirror mists over when the temperature is low enough to saturate the air in contact with the mirror, thereby altering its reflectivity. When this occurs, the thermometer records the dew point. This process is repeated to give a time series of samples of dew point temperatures. The vapor pressure is calculated from the dew point at a given temperature through well-established empirical functions. The measured dew point will be affected (usually raised) by dust that provides nucleation sites on the mirror; for this reason, the air is carefully filtered at the intake point, and the mirror is periodically cleaned. Small contamination of the mirror should still provide good data, however, because both upper and lower measurements are

Figure 5.1 Schematic diagram of Apache Leap Research Site automatic weather station.

Figure 5.2 Vapor Measurement System

made on the same mirror, and only the absolute difference is of interest.

Net incoming solar radiation is measured by a net radiometer mounted on a separate pole away from the main tower, to minimize interference from tower instruments and components. The net radiometer is placed over an area of mixed ground cover, including bare rock, soil, and vegetation, to record an average value. Previous studies made at a weather station in similar desert conditions close to Tucson showed that one net radiometer mounted somewhat higher over mixed cover gives essentially the same value as separate net radiometers close to the ground, one over vegetation and one over bare ground, assuming 40 to 70% bare ground.

Soil heat flux is measured by a combination of two soil heat flux plates and four parallel thermocouples (Fig. 5.3). The soil heat flux plates are buried 8 cm below the surface, one beneath a bush, and one under bare soil. The soil thermocouples are located above the plates at 6 cm and 2 cm depth, and are wired together to yield an average temperature in the soil above the heat flux plates. The heat flux at the surface is calculated by adding the heat flux at depth to the energy stored in the layer above the plates. To calculate the energy stored, the change in soil temperature over the averaging period is multiplied by the soil heat capacity. The soil heat capacity is a function of the soil bulk density, the specific heat of dry soil, the soil water content, and the specific heat of water. The bulk density and water content are not only site-specific, but will vary according to site conditions. Therefore, soil samples were collected from the site under different conditions to be used for the calculations; at each time, several samples were collected and an average value is used for the calculations.

Rock heat flux is measured at the site by four parallel thermocouples that record an average rock temperature and the change in temperature over the averaging period. The four thermocouples were installed horizontally into a rock face at depths of 8, 6, 4, and 2 cm below the surface of the rock, which rose approximately 12 cm above the surrounding soil (Fig. 5.3). To install the thermocouples, holes were drilled into the rock, and the thermocouples were coated with silicone sealant mixed with rock dust and pushed into the hole at least 2 cm beyond the opening on the outside. The sealant plugged the opening around the wires. Rock heat flux is a function of the thermal conductivity of the rock; such measurements have been made of Apache Leap tuff in the past (Todd Rasmussen, unpublished data) and were used for these calculations.

5.2.3.2.2 Calibration and Maintenance

Most of the sensors arrive calibrated by the manufacturer, and frequent calibration of the sensors is not part of regular maintenance. The temperature and vapor pressure measurements are compared to data from the combination temperature/relative humidity probe also mounted on the tower, however, and the net radiometer measurements are compared to pyranometer measurements for comparable (though lower magnitude) signals. The manufacturers for the net radiometer and soil heat flux plates do recommend that the instruments be returned for a yearly recalibration. The system is set up so it can run for two weeks without maintenance.

Figure 5.3 Soil and Rock Heat Measurements at the ALRS Automatic Weather Station.

5.2.3.3 Additional Weather Data

Several additional instruments have been installed on the main weather tower as part of the collection of a complete set of weather data. All instruments are tied into the common CR10 datalogger powered by a deep-cycle marine battery recharged by the solar panel. Additional measurements include wind direction and speed, and the standard deviation of each; and, as previously mentioned, total incoming solar radiation, and temperature and relative humidity independent of the Bowen ratio system. All measurements are made every 10 seconds, and an average is recorded every 20 minutes.

5.3 DATA MANIPULATION AND ANALYSIS

5.3.1 Precipitation Data

Both of the recording rain gages collect data regarding rainfall intensity, hourly totals, and daily totals. For the purpose of calculating a water budget, only the total rainfall over a given time period is required. The average of the total rainfall from each of the recording locations is used in calculation of the water budget. This average amount is multiplied by the surface area of the basin to obtain a quantity of rainfall for the basin. Additional semi-quantitative studies are currently underway using 13 nonrecording wedge-type rain gages scattered throughout the basin; results are not yet available, however preliminary review of these data suggests that the locations of the two recording gages tend to receive average basin-wide rainfall amounts.

5.3.2 Runoff Data

Head in the flume is converted to flow rate according to established relationships for the specific types of flumes (Field Manual for Research in Agricultural Hydrology, 1979). Field calibration measurements of head vs. discharge were made to confirm and slightly modify the established relationships, to develop functional relationships for each flume. Total runoff for a specified period of time is determined by using a Riemann sum technique.

5.3.3 Evapotranspiration Data

5.3.3.1 Calculation of Fluxes from Raw Data

Soil and rock heat fluxes, and the latent heat flux are calculated from the Bowen ratio system measurements; net radiation is measured directly, and the sensible heat flux is determined to be the remainder of the value of net radiation after the other fluxes are subtracted.

5.3.3.1.1 Soil Heat Flux

To calculate the soil heat flux, the average of the two soil heat flux plates (open and shaded) is first calculated using an arithmetic average. Next, the energy stored above the heat flux plates is calculated. Values for soil bulk density and moisture content must be input at this point. The equation used to calculate energy storage is:

$$S = \frac{dT_s}{T * D * BD * (CS + W * CW)} \quad (5.12)$$

where:

- S = energy stored (W/m²)
- dT_s = change in soil temperature (°C)
- T = output interval (1200 seconds)
- D = depth to flux plates (0.08 m)
- BD = soil bulk density (kg/m³)
- CS = specific heat of dry soil (estimated to be 840 J/kg°C)
- W = soil water content (kg H₂O/kg soil)
- CW = specific heat of water (4190 J/kg°C)

Soil heat flux, G_s, is then the sum of S and the average heat flux, F (CSI, 1993).

5.3.3.1.2 Rock Heat Flux

To calculate the rock heat flux, the following equation is used:

$$Gr = \frac{\sqrt{2} T_a k_s}{D} \sin \left[\frac{2\pi}{P} (t - \phi) + \frac{2\pi}{8} \right] \quad (5.13)$$

where:

- Gr = rock heat flux (W/m²)
- T_a = amplitude of the sine wave in the surface temperature of the rock
- k_s = thermal conductivity of the rock (J/ms°C)
- D = damping depth of the rock (cm)
- P = period (24 hours)
- t = time of day (hours)
- φ = phase shift (hours)

The amplitude and phase shift of the sine wave in the surface temperature of the rock are

determined by fitting a sine curve to the plot of rock temperature versus time at the average depth of the thermocouples (5 cm), and then correcting the values to the surface. A thermal conductivity value was obtained from previous studies of the Apache Leap tuff. Damping depth is calculated from the equation:

$$D = \left(\frac{86400 \alpha}{\pi} \right)^{0.5} \quad (5.14)$$

where:

$$\alpha = \text{thermal diffusivity of the rock} = \frac{k_s}{\rho C} \quad (5.15)$$

with:

ρ = density of the rock (kg/m³)
 C = specific heat of the rock (J/kg°C)

Density and specific heat values were also obtained from previous studies of the Apache Leap tuff. Values of 1.95 J/ms°C thermal conductivity, 2180 kg/m³ density, and 800 J/kg°C specific heat give a thermal diffusivity of 1.12 m²/s and a damping depth of 17 cm.

To correct the amplitude of the sine wave at depth to the surface,

$$T_a = \frac{T'_a}{\exp\left(-\frac{z}{D}\right)} \quad (5.16)$$

where T'_a = amplitude from the fitted sine wave at depth.

The phase shift at depth is corrected to the surface by:

$$\phi = \phi' - \left(\frac{24z}{2\pi D} \right) \quad (5.17)$$

where ϕ' = phase shift from the fitted sine wave at depth.

A total soil/rock heat flux G is calculated as the arithmetic average of the soil and rock heat fluxes, assuming approximately 50% each soil and rock coverage.

5.3.3.1.3 Latent Heat Flux

The latent heat flux is calculated from the Bowen ratio, given by:

$$\beta = \frac{P * CP * dT}{0.622 * EW * dq} \quad (5.18)$$

where:

β = Bowen ratio

P = atmospheric pressure (kPa)

CP = specific heat of air (1.01 kJ/kg°C)

dT = temperature gradient between arms (°C)

EW = latent heat of vaporization (2470 kJ/kg)

dq = vapor pressure gradient between arms (kPa)

(note: 0.622 is the ratio of the molecular weight of water to the molecular weight of dry air)

The latent heat flux, as described in the Theory section, is calculated from:

$$L_e = \frac{R_n - G}{1 + \beta} \quad (\text{all units W/m}^2) \quad (5.19)$$

5.3.3.1.4 Sensible Heat Flux

The sensible heat flux is calculated once all other fluxes have been determined:

$$H = R_n - G - L_e \quad (\text{all units W/m}^2) \quad (5.20)$$

5.3.3.2 Filtering Out Bad Data

Bad data occurs under two conditions, one relating to the operation of the Bowen ratio system, and the other relating to the ambient weather conditions. Whenever the Bowen ratio system is recalibrated and cleaned (approximately once every 2 weeks), the hygrometer must be turned off. Before this occurs, all data collected up to that point is averaged and saved, and flagged so that it is identified as not a complete 20-minute record. In the processing of data, these incomplete periods are not used, and instead, values for parameters from the time periods prior and subsequent to that time are used to interpolate values for the missing time periods.

A review of the equations for the Bowen ratio and latent heat flux shows that the Bowen ratio is undefined for $dq = 0$, and that latent heat flux is undefined when the Bowen ratio = -1. The Bowen ratio calculation could theoretically be expected to break down in the morning and evening when $R_n - G$ approaches zero. Early plotting of the unprocessed data indicated poor results for some distance on either side of $dq = 0$ and $\beta = -1$, so in the data processing programs, corrections are made to account for these circumstances, and are noted with the use of flags. When $|dq| < 0.005$, L_e is set to 0 and one flag is set. When $|1 + \beta| < 0.4$, another flag is set, and the value is interpolated according to previously calculated values. In the early plotted data, negative L_e would occasionally occur, which is not usually expected in a climate as dry as this area. In some cases, however, relative humidity did get high, which would support a negative L_e . Therefore, the processing programs leave L_e as is when the relative humidity is higher than 80%, but flags it. For negative L_e when relative humidity is less than 80%, L_e is set to zero, and flagged differently.

5.3.3.3 Calculation of Evapotranspiration from Latent Heat Flux

Evapotranspiration can be calculated simply by dividing the latent heat flux by the latent heat of vaporization. This depth of water is then multiplied by the area of the watershed to obtain a rate of evapotranspiration. The rate can then be used to calculate the volume of water lost to the atmosphere over a given time period, for use in the water budget.

5.4 RESULTS

5.4.1 Storm Fluxes

Figures 5.4 and 5.5 show the raw data collected from noon on January 3, 1995 through January 7, 1995, when a winter frontal storm passed through the site. During this time, the rain gages recorded an average of 16.6 mm rain over the basin for a total volume of 8532 m³ of water. Passage of the storm is reflected in many of the sensors: relative humidity and vapor pressure were high during times of precipitation, while net radiation and incoming solar radiation were both significantly reduced, resulting in lowered daytime air temperatures. Wind speed increased after the rain stopped and the sky began to clear. The soil heat experienced a sharp negative flux, most likely as water moved through the soil and wetted one side of the heat flux plate before the other. Soil and rock temperatures remained relatively constant once the ground became saturated.

Figure 5.6 shows the energy budget for a typical winter frontal storm day. Not surprisingly, evaporation is not high during conditions of cold, moist air; an average rate of 0.115 mm/day was calculated from the Bowen ratio data, translating to 177 m³ over the watershed.

The large and small flumes recorded a total of 7873 m³ runoff out of the watershed

Figure 5.4 Apache Leap Research Site data, January 3-7, 1995.

Figure 5.5 Apache Leap Research Site data, January 3-7, 1995.

Figure 5.6 Energy budget for typical ALRS storm.

following the storm. Figure 5.7 shows the water budget for this period; evaporation was assumed to be a constant average daily value. Water budget calculations yielded just 482 m³ of water, or 6% of the total precipitation entering the watershed, for infiltration into the ground. The small fraction of water available for infiltration was not surprising in this situation, as the watershed had received approximately 10 mm rain in the 10-day period preceding this storm, and the weather had remained cold and moist during the entire period. The surface of the rocks in the watershed is characterized by extensive pits and depressions which have been observed to hold a considerable amount of water following a rain event. In the January 3-7 storm, however, these depressions would have already been filled by the previous rains; in addition, the soil and rocks were already saturated by that time. Therefore, most of the water entering the watershed would be expected to exit as runoff.

Data from precipitation events in the watershed following extended dry periods indicate that a far smaller portion of the water leaves the area as runoff. Preliminary calculations suggest that as much as 65% of the total precipitation is not accounted for by evapotranspiration or runoff, although the fraction stored in depressions at the surface has not yet been determined. These data indicate that the timing of the storm, as well as its duration and intensity, will have a significant effect on the distribution of water within the watershed.

5.4.2 Yearly Fluxes

Figure 5.8 shows the solar, net, and soil heat fluxes for the year March 1994 to March 1995, along with the average daily temperature during that time. The data clearly show a seasonal cycle, with maximum temperatures and fluxes occurring in the warm, dry summer months. Figure 5.9 shows additional weather data for that time, including wind speed, relative humidity, and precipitation. These data were used to run an off-line Biosphere-Atmosphere Transfer Scheme (BATS) model (Dickinson et al., 1993), which predicts evapotranspiration using the data and additional calibration parameters based on soil and vegetation characteristics. The BATS model used for these calculations was calibrated to a semi-arid desert site near Tucson that is similar, but not identical, to ALRS. Figure 5.10 shows the evapotranspiration predicted by the BATS model, compared to the precipitation measured at the site. Clearly, evapotranspiration is driven by water availability, rather than the seasonal radiation cycle. For this 12-month period, the total rainfall in the watershed was 424 mm; the total evapotranspiration predicted by the model was 379 mm, or 89% of the precipitation. Measured evapotranspiration was not available for this entire time period to compare to the modeled data due to malfunctions in the Bowen ratio system during extreme weather. Furthermore, runoff data for the year were not available to complete the budget and estimate infiltration over the longer term. However, the large quantity of modeled evapotranspiration suggests that it accounts for the most significant portion of precipitation.

Water Budget for ALRS Storm, January 4 - 7, 1995

Figure 5.7 Water budget for ALRS storm, January 4-7, 1995.

Figure 5.8 Apache Leap Research Site fluxes, March 1994 - March 1995.

Figure 5.9 Apache Leap Research Site data, March 1994 - March 1995.

Figure 5.10 BATS evaporation and precipitation data, March 1994 - March 1995.

6. RAPID ESTIMATE OF SOLID VOLUME IN LARGE TUFF CORES USING A GAS PYCNOMETER

by A.M. Geddis, A.G.-Guzman, and R.L. Bassett

6.1 INTRODUCTION

A thermally-insulated, rigid-volume gas pycnometer system has been developed. The pycnometer chambers have been machined from solid PVC cylinders. Two chambers confine dry high-purity helium at different pressures. A thick-walled design ensures minimal heat exchange with the surrounding environment and a constant volume system, while expansion takes place between the chambers. The internal energy of the gas is assumed constant over the expansion. The ideal gas law is used to estimate the volume of solid material sealed in one of the chambers. Temperature is monitored continuously, and incorporated into the calculation of solid volume. Temperature variation between measurements is less than ± 0.05 °C. The data are used to compute grain density for oven dried Apache Leap tuff core samples. The measured volume of solid and the sample bulk volume are used to estimate porosity and bulk density. Intrinsic permeability was estimated from the porosity and measured pore surface area, and is compared to in-situ measurements by the air-permeability method. The gas pycnometer accommodates large core samples (0.25 m length x 0.11 m diameter), and can measure solid volume greater than 220 cm³ with less than 1% error.

6.1.1 Solid Volume in Porous Material

The solid volume of a **regularly** shaped solid object (cube, sphere, right circular cylinder, etc.) can be calculated from direct measurements of the object. The solid volume is equivalent to the bulk volume for most regular solid shapes. If the mass of this object is measured its bulk density is calculated as mass per volume. The solid volume of an **irregularly** shaped solid object (broken core sample, coffee cup, etc.) is more difficult to measure. An indirect measurement is needed to estimate the solid volume. For example: A known amount of liquid can be displaced by immersing the irregular object. The solid volume is not necessarily equivalent to the bulk volume in this case. The bulk volume is loosely defined as the volume enclosed by a surface covering the irregular shape. In the case of a coffee cup, the bulk volume would be much greater than the solid volume. The irregular object's bulk density can also be calculated from the ratio of its mass to bulk volume. Various terms such as material, skeletal, particle, or grain density are used to describe the ratio of mass to solid volume; all of which represent the density of the solid volume fraction of the bulk volume of an irregularly shaped object.

Porous objects can be considered as highly irregular solid shapes. For a liquid displacement method to accurately estimate a porous sample's solid volume the fluid would have to permeate all of the pore space. If the material has a low permeability it may take a long time

for the fluid to enter all of the accessible pores. The fluid may never encounter some pores because of trapped air, pore throat restrictions, or sealed voids, all of which would be incorrectly interpreted as part of the solid volume. Further, the liquid may react with surfaces or hygroscopic minerals causing them to increase their volume by swelling. A gas pycnometer is a device that has been used for many years to measure the solid volume of solid and porous material. Sample materials have ranged from aerogel foam to diamonds to lunar materials (Cadenhead and Stetter, 1975). The pycnometry method requires that the object be placed in a gas tight vessel, such that imposed gas pressure changes can be measured precisely. In the method presented here, the pressure and temperature of dry high purity helium is measured before and after the imposed pressure change. Helium is able to enter much smaller pores than a permeating fluid such as water. The ideal gas law is used to compare the measured pressure changes against known volumes. This comparison is used to predict the solid volume of porous Apache Leap tuff core samples. Core samples from the deep slant borehole (G and P series) and the covered site (Y series) have been tested (Site map is given in Fig. 2.1).

6.1.2 Estimated Parameters

The ratio of mass to solid volume for oven dry core samples is reported as grain density (ρ_g). The determination of grain density variation in tuff is particularly useful for defining major variations in lithology. Changes in lithology can indicate differences in chemical composition, mineral content, or hydraulic properties, all of which may affect physical flow characteristics of water. The bulk volume of core samples was estimated either by measuring the displaced water volume upon immersion of water-saturated samples, or direct measurement of the dimensions of samples that approximate a right circular cylinder in shape. The difference between bulk volume and solid volume of a core sample is its porosity (ϕ). In this method the effective, or connected porosity is determined. Porosity variation in tuff yields important information about the material's ability to conduct liquid and gas. The bulk volume measurement also yields an estimate for bulk density (ρ_b), when divided into oven dry mass. An estimate of bulk density aids in describing the distribution of various chemical species in many bulk transport schemes. These three parameters are related mathematically as:

$$\rho_b = \rho_g (1 - \phi) \quad (6.1)$$

The intrinsic permeability (k) of a porous material may be closely related to its porosity. Permeability of the core samples is estimated using an empirical relationship by Kozeny-Carman (de Marsily, 1986, p. 62). The relationship uses powers of porosity and pore surface area in the calculation of permeability, and was established using unconsolidated sediments. Volcanic rock contains vesicular porosity not found in most granular material, and significant error may result when applying the relationship to tuff. Pore surface area for Y2 core has been measured in a previous investigation (Rasmussen, 1990). The Kozeny-Carman permeability is compared to in-situ measurements made in Y2 by the air permeability method (Guzman, 1995).

6.1.3 Previous Work

Many gas pycnometers reported in the literature loose accuracy from improper selection of construction materials; either the material is thermally too conductive, or too flexible (Torstensson and Eriksson, 1936; Stevens, 1938; Kummer and Cooper, 1945; Page, 1947; Russell, 1949). Flexible materials tend to yield error due to deformation of the system, which is assumed to have a constant volume. Rigid materials are required to accurately employ gas pycnometer technology. Instrument error can be minimized if the pycnometer system is operated under isothermal conditions, and low pressures are used. Many investigators do not measure temperature, or assume an isothermal system (De Backer, 1967; Stonestrom and Rubin, 1989). Error resulting from the impact of heat flow on pressure measurement in the system tends to be a random phenomena associated with operation of the instrument in a regime not covered by the calibration. This situation could arise as the result of a misplaced hand, coffee cup, or other heat source. Internal energy of the gas will change as heat is conducted in or out of the system. This will alter the pressure reading in poorly insulated devices. A gas pycnometer made of aluminum has shown a pressure response to the heat of a hand (T.E. Detty, personal communication), which is similar to the response of a constant volume gas thermometer. Several soil science based applications attempt to develop field gas pycnometers (Page, 1947; Russell, 1949; Visser, 1938), which could be exposed to large temperature fluctuations.

The choice of a uniform bulk volume sample size also helps reduce error. This results when the pycnometer is calibrated to respond most accurately over a narrow range of solid volume, as is found in uniform bulk volume samples of similar media. A single point in the middle of this range is checked daily or prior to use. Unfortunately, the uniform bulk volume is usually small, on the order of 100 cm³ or less, and most geologic media are not uniformly porous. The small sample chambers may require precise coring of tuff material, for example. Brittle phenocrysts might be under sampled in an attempt to cut small right circular cylinders. Some investigators use barometric pressure as a reference pressure (Russell, 1949), which is assumed constant from test to test. The resulting error is considered negligible and is typically not corrected for.

Some commercially available pycnometers employ chambers that are sized to bracket selected solid volume ranges (Micromeritics MultiVolume Pycnometer 1305 and the AccuPyc 1330 from Micromeritics Instrument Corp., 1993). The error associated with each range is reported, and the devices are accurate and precise. Beckman Instruments provides the Beckman Air Comparison Pycnometer (Beckman Instr., 1981) that relies on positioning a reference piston to maintain a zero pressure differential pressure between two cylinders. Unfortunately, the largest sample chamber among these devices is only 150 cm³. The pycnometer designed for this study has a sample chamber capacity of 2,300 cm³.

The most thorough analysis published to date appears to be Bielders, et al. (1990). They measure the particle density of volcanic soils with a Beckman Air Comparison Pycnometer. They found that air pycnometry measurements gave larger values for particle density when compared

to helium pycnometry. This was attributed to gas adsorption phenomena and found to be linearly related to the surface area of the soil samples as measured by ethylene glycol monoethyl ether. When air was used the endpoint drifted to lower and lower pressure. The lower pressure implies a smaller solid volume, which in turn would cause the higher particle density value (for a given mass of sample). They tested silica gel desiccant and estimated density as large as 20 g/cm^3 , which is approximately ten times larger than typical values. This is used to identify water vapor as the primary adsorbed gas. Dry high-purity helium (99.995 mole %) was used in the calibration and core testing performed for this study.

6.2 EXPERIMENTAL INSTRUMENTATION

A schematic diagram of the gas pycnometer system with cylinder dimensions and major components is given in Fig. 6.1. The sample chamber (V_2) is approximately 1.5 times the volume of the reservoir chamber (V_1) (i.e. $1.5 V_1 = V_2$). The internal volume of each cylinder is approximately $1,800 \text{ cm}^3$, and $2,700 \text{ cm}^3$ (V_1 and V_2), with the plugs inserted. This volume includes the connecting hardware associated with each chamber. The chambers were machined from solid cylinders of PVC using a lathe in the Chemical Engineering Machine Shop, UAz. The stock material was Geon 8761 PVC (Type I, Grade 1, normal impact, low shear cube compound for pipe extrusion). Precise machining is required only to provide gas tightness as the solid volume measurement is made relative to the ratio V_2/V_1 . The resulting chambers are extremely rigid as required for this application. The cylinders are firmly secured adjacent to one another in a horizontal position. Core samples are placed into the sample chamber lengthwise. The plug of the reservoir chamber is secured in place with evenly torqued bolts and not opened during the period of calibration and core testing for this project. A U-shaped clamp (not shown in Fig. 6.1, see slots on base of sample chamber) is placed over the sample chamber cylinder, and a large acme threaded screw is tightened to approximately 35 foot pounds against a metal plate (also not shown) affixed to the back of the plug.

6.2.1 Thermal Properties of the Pycnometer System

Thermal conductivity of the PVC is reported as $K_T = 1.2 \text{ BTU hr}^{-1} \text{ in}^{-1} \text{ }^\circ\text{F}^{-1} \text{ ft}^{-2}$ (International Plastics Selector, 1980). Typical units for thermal conductivity are $\text{BTU hr}^{-1} \text{ in}^{-1} \text{ }^\circ\text{F}^{-1}$ or $\text{W m}^{-1} \text{ }^\circ\text{C}^{-1}$ (Halliday and Resnick, 1981). The value for K_T is actually a heat flux per unit dimension, based on the geometry of a PVC tube (personal communication, Plastics Engineer, B.F. Goodrich). The parameter (K_T) describes the number of BTU's transferred across a tube wall per hour, per inch of tube wall thickness, per $^\circ\text{F}$ temperature differential across the tube wall, per square foot of transfer area. The actual heat loss is found by replacing the unit wall thickness, unit transfer area, and unit temperature gradient, with the actual system conditions, over a given time period. For example, if the tube wall thickness is doubled, the heat loss is reduced by one-half. This implies that heat loss during a 60-second period, from a tube similar to V_2 , with a transfer area of approximately 1.2 ft^2 (0.11 m^2), a 2.0 inch (5.1 cm) wall thickness, and a $1.8 \text{ }^\circ\text{F}$ ($1 \text{ }^\circ\text{C}$) change in temperature established and maintained across the tube wall is

Figure 6.1 Schematic diagram of the gas pycnometer system (dimensions are in centimeters).

approximately 5×10^{-3} BTU's, or 5 Joules. This heat loss is negligible with regard to deviation of the gas from ideal behavior, and the testing chambers are considered to be thermally well insulated from their surroundings.

The linear expansion coefficient of the PVC is $L_E = 5.2 \times 10^{-5}$ cm/cm/°C (International Plastics Selector, 1980). The units are expressed as length of expansion per length of PVC tubing, regardless of wall thickness. The sample chamber is conservatively approximated as a 30 cm long tube. The wall thickness of the tube is 5 cm. For a 0.5 °C change experienced throughout the PVC, the coefficient implies a change in length of 0.001 cm. This translates to a change in volume of about 0.1 cm³ for the sample chamber.

6.2.2 System Leak Testing

The system has been pressure tested many times and is found to leak at an acceptable rate. Gas tightness is attained using double 0.476 cm (3/16") o-rings on each chamber plug (Fig. 6.1). The plastic connecting hose is ½" O.D., 4,000 kPa (600 psi) rated, rigid-wall brake line material, and is kept as short as possible. The hose and its fittings are insulated with expandable spray foam and encased in clear polycarbonate. The connecting hose is assumed not to expand during calibration and core testing, and to be a poor conductor of heat. Access ports are 0.635 cm (¼ inch) holes drilled through the base of each cylinder. These are enlarged and tapped directly into the PVC on the exterior as required (Fig. 6.1). Tank valve stems are used as fill and bleed vents.

Examples of leak tests are provided in Fig. 6.2. Plot (A) illustrates the results of a 24 hour test period during which pressure was increased in both cylinders and the connecting valve was open. The pressure was increased to approximately 10 kPa greater than maximum core testing pressure. Spikes on the temperature traces are artificial +0.25 K markers to indicate midnight during overnight testing. The total system leak rate is very small, on the order of 1.4 Pa/minute. This is calculated as the slope of a line from the first to the last point of the test. Most core tests require about 1 minute to perform and this pressure increment can not be resolved, with the pressure transducers used, during that time. Fig. 6.2, plot (B), represents four overnight tests with the valve closed. One of the cylinders was pressurized and the record of that cylinder's pressure is shown. The other cylinder was left near atmospheric pressure. Each cylinder was pressurized twice for plot (B). The very slow leak rate could be the result of molecular diffusion effects of helium but has not been investigated further.

6.3 GAS PYCNOMETER THEORY AND CALIBRATION

6.3.1 Gas Pycnometer Theory

As was mentioned earlier, gas pycnometry has been used for many years to measure the volume of solid material sealed in a gas tight system. This is accomplished by monitoring imposed pressure changes and solving the ideal gas law. The ideal gas law predicts a constant

Figure 6.2 Leak testing of gas pycnometer system. Spikes on temperature traces are artificial +0.25 K markers indicating midnight during overnight testing. In plot (A) the connecting valve is open; and in plot (B) the valve is closed and each cylinder was pressurized twice.

relationship between pressure, volume, and temperature of a confined gas. This well known law is:

$$PV = nRT \quad (6.2)$$

where:

P = Absolute Pressure [Pa],

V = Volume [m^3],

n = moles of gas,

R = $8.314 \text{ [m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}\text{]}$,

T = Temperature [K].

Gas confined in the pycnometer exists in two different states when temperature and pressure are measured, an initial state and final state. The initial state occurs when the connecting valve is closed (see Fig. 6.1), the reservoir chamber (V_1) pressure has been increased to approximately 2 atmospheres (absolute), while the sample chamber (V_2) is left at atmospheric pressure. The final state is imposed after the connecting valve is opened and the two chambers are allowed to come to equal pressure. The gas in V_1 expands into V_2 . To apply the ideal gas law to this system, internal energy of the gas must be constant over the imposed pressure change. By this it is meant that the system does no work on, and transfers no heat to, its surroundings. Then, according to the first law of thermodynamics, the internal energy remains constant through the change (Ohanian, 1985). If internal energy is not constant the ideal gas law does not hold, and the relationship between pressure, temperature, and volume of the gas is not linear.

Internal energy of a gas is monitored by measuring its temperature. The first law requirements are also met if the temperature is equal at the initial and final states (in a constant volume system). When the valve is opened, however, the moving gas causes the temperature in the system to change. In poorly insulated devices this results in a heat flux across system boundaries. If the initial temperature was dependent on ambient conditions then a single test cycle would require a period of time to allow the system to return to the initial (ambient) temperature prior to measurement of the final state. This may not occur for some time, or at all if the ambient temperature conditions are not constant. Heat sources in the immediate environment can also cause the temperature to vary between initial and final states. The pycnometer designed and employed for this report imposes the requirements of the first law on the gas. The system does not change volume between initial and final states, so the gas can not do work on its surroundings. The thick walled construction and insulated connecting tube does not allow any heat to be transferred across system boundaries. Internal energy of the gas remains constant over the change from initial to final states.

There is a temperature change in the system simultaneous with the change from initial to final states. A temperature measurement, therefore, should be incorporated into the ideal gas law to properly describe the volume change of gas. The temperature has not been incorporated into

any previous analysis reported in the literature. The standard method described by Danielson and Sutherland (ASTM, 1986) uses Boyle's law to relate the change in gas volume between initial and final pressure states. In the following analysis the temperature is left in the ideal gas law allowing for a more complete monitoring of system conditions.

As mentioned previously, P_1 is arbitrarily increased to near 2 atmospheres, and P_2 remains at atmospheric pressure. Therefore, the **initial system** can be described as follows. In the reservoir chamber,

$$\frac{P_1 V_1}{T_1} = n_1 R \quad (6.3)$$

and in the sample chamber,

$$\frac{P_2 V_2}{T_2} = n_2 R. \quad (6.4)$$

If the valve between the two chambers is opened, the **final system** can be described as;

$$\frac{P_3 V_3}{T_3} = n_3 R. \quad (6.5)$$

The volume of gas in V_1 expands into a new volume defined as V_3 , which is simply V_1 and V_2 connected, i.e.; $V_3 = V_1 + V_2$. Notice that the amount of gas does not change after the valve is opened, i.e.; $n_1 R + n_2 R = n_3 R$. V_3 is eliminated in Eqn. (6.6) after substituting.

$$\frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2} = \frac{P_3 (V_1 + V_2)}{T_3} \quad (6.6)$$

V_1 and V_2 are not accurately known and need not be determined individually providing the response of the device is calibrated, against their ratio, using precisely known volumes. Solving for V_2/V_1 results in;

$$Ratio = \frac{V_2}{V_1} = \frac{\left(P_3 - \frac{P_1 T_3}{T_1} \right)}{\left(\frac{P_2 T_3}{T_2} - P_3 \right)}. \quad (6.7)$$

T_3 is the temperature of V_3 at P_3 . It is measured separately in both cylinders, and averaged ($T_3 = (T_{1,f} + T_{2,f})/2$). Similarly, P_3 is measured separately in both cylinders and averaged ($P_3 = (P_{1,f} + P_{2,f})/2$). All variables on the right side of Eqn. (6.7) can be measured. This equation is solved over each testing cycle of opening the valve. Each core is tested through approximately 10 cycles. The temperature ratios, T_3/T_1 , and, T_3/T_2 , are typically close to 1.000

± 0.001 (0.1%).

There are a variety of phenomena that take place in the application of gas pycnometry which could cause the pressure and temperature measurements to deviate from the ideal. Expanding and contracting gas causes heat movement from the sample and the system material. There appears to be no way to prevent this and still perform the measurement. Core testing was performed under the same conditions as the calibration in an attempt to minimize the impact of the measurement itself on the result.

The largest source of non-ideal behavior reported in the literature is associated with the adsorption of water vapor by surface active materials, such as clays, that may be found in a sample (Biielders, et. al, 1990). The dry high purity helium used for this report is passed through a Drierite water trap prior to filling the reservoir chamber. The trap and filling hose allow the helium to equilibrate with room temperature after expansion out of the storage cylinder. It is assumed that water vapor effects do not impact the measurement performed for this report. There are several reasons for choosing helium. Most importantly, helium is an inert monatomic gas that closely obeys the ideal gas law (Matheson Gas Data Book, 6th ed., 1980). The helium molecule is small, allowing it to access pores and micro fractures on atomic length scales. Also, the root-mean-squared velocity of a gas is inversely proportional to its mass (Ohanian, 1985). As helium is very light its velocity is very large. The wave of pressure that sweeps through a sample is assumed to equilibrate instantaneously throughout the accessible pore space.

6.3.2 Gas Pycnometer Calibration

Calibration of the gas pycnometer entails altering the internal volume of the system by placing spheres of known volume into the sample chamber. The ratio, V_2/V_1 , is calculated at each volume increment. When core is tested, the ratio is again calculated and the volume of solid is back calculated from the calibration curve. The spheres are actually miniature pool balls manufactured by the Belgian Aramith Co. They are precision ground to perfect spheres (product information sheet), and are made from a cast phenolic resin. The spheres are assumed to have zero connected porosity, as this is a characteristic of solidified phenolic resins, and a low heat capacity (compared to the various metallic materials that were considered for the calibration). The advantage of low heat capacity is rapid thermal equilibrium with the surroundings which decreases any thermal memory.

To generate the calibration curve the sample chamber was opened, one calibration sphere was inserted, and the system was sealed with the U-shaped clamp and screw. The gas pressure in the system was cycled (as discussed above) approximately twenty times for each sphere added to the sample chamber. A total of twenty-two spheres were eventually included in the sample chamber. This represents calibration of the gas pycnometer over a range of approximately 640 cm³. The result is shown in Fig. 6.3. Maximum and minimum solid volume predicted for any sample tested is covered in the calibration range. The average solid volume is near 300 cm³ which occurs in the middle of the range.

Note that the 23 apparent points on Fig. 6.3 represent 469 cycles of the pycnometer. No raw data were excluded or otherwise rejected from this calibration curve. The instrument is believed to respond linearly over the range of laboratory conditions encountered. The calibration curve used for core testing is:

$$\text{Volume of Solid} = -1798.86 \left(\frac{V_2}{V_1} \right) + 2687.14, r^2 = 0.9999 \quad (6.8)$$

Figure 6.4, Plot (A), depicts the difference between measured and predicted sphere volume, as a function of measured sphere volume. Predicted sphere volume is calculated with Eqn. (6.8). There seems to be some diurnal pattern to the error, but no removable trend. Plot (B) shows these errors to be normally distributed about their mean. There does not seem to be a trend in error with solid volume measured, and the error is considered random. One standard deviation is equal to 1.88 cm^3 , which is 1.24 % of the smallest solid volume predicted (151.3 cm^3 for g12b). This percent error decreases to 0.62 % for an average solid volume of 300 cm^3 . The standard deviation is termed the "Std. Err. in VOL Est." in Fig. 6.3. The random error can be decreased by testing a sample through multiple cycles and averaging. The total error is the sum of the instrument error and the random error. The instrument error is a function of the thermistor and pressure sensor calibrations, and the change in volume of the assumed rigid system. The sensors are linear over the range of measurement. The error for the pressure transducer offset was 0.08 kPa, which is 0.08 % of 95 kPa, the minimum pressure used. The error in the thermistor offset was $\pm 0.2 \text{ }^\circ\text{C}$ at 295 K, which equals 0.07%. The system is assumed rigid, so the sum of these three sources of instrument error is 0.15%. The total error, therefore, is estimated at 2.2 cm^3 ($1.88 \text{ cm}^3 + 0.15\%(220 \text{ cm}^3)$) which implies an estimate of solid volume $>220 \text{ cm}^3$ with $<1\%$ error.

6.4 BULK VOLUME ESTIMATION AND GRAVIMETRIC WATER CONTENT

6.4.1 Bulk Volume Estimation

A rather simple device was constructed that connects a buret to a graduated cylinder on a ring stand in order to measure bulk volume. They are mounted vertically, adjacent to one another, and are connected by means of a flexible hose at their base. The inside diameter of the graduated cylinder is approximately $\frac{1}{2}$ inch (1.3 cm) greater than the outside diameter of the core samples. When an object is immersed in the graduated cylinder water rises in both tubes to an equal height. The fine gradations on the buret allow the operator to read the change of water volume to $\pm 0.1 \text{ mL}$ (in the buret). The immersion of one calibration sphere in the graduated cylinder displaces the water in the buret approximately 1.0 mL. An average sphere volume of 28.8 cm^3 was assumed, which corresponds to an instrument error of $\pm 2.88 \text{ cm}^3$ for the apparatus.

Figure 6.3 Gas pycnometer calibration curve. The instrument was cycled 469 times over a three day period. The curve is linear as the ideal gas law would predict.

Figure 6.4 Gas pycnometer calibration error analysis. Plot (A) illustrates measured minus predicted volume of calibration spheres, as a function of measured sphere volume. Plot (B) is a histogram of the error frequency.

After a G series or Y2 series core sample was tested in the gas pycnometer it was soaked in Tucson tap water for several days. The core was assumed to have acquired a saturated rind as a result of the soaking. This was done to reduce the amount of water a core might imbibe while being tested. Core was immersed 5 or 6 times, and the water volume displaced in the buret was recorded each time. The immersion bulk volume estimate is in lieu of developing core saturation procedures for measuring bulk volume with the gas pycnometer. At the pressure of operation entrapped air could affect this measurement if the samples were not completely saturated. In fact, this behavior is required for part of the entrapped air tests performed in the literature (see for example Stonestrom and Rubin, 1989). Sealing the core with any substance that alters the tuff renders it useless for future testing in the pycnometer, or other comparative testing, and was not employed.

An estimate of bulk volume was made for any core sample that closely approximated a right circular cylinder by measuring its length and diameter with a vernier caliper. The error involved in this method is a function of the condition of the core. If a sample is rough or chipped, the estimate is not very accurate. The error is probably similar in magnitude to the immersion method, but has not been quantified. The bulk volume of all the G series and Y2 series core samples was estimated by the immersion method using the bulk volume estimator. This means that cut G series samples had their bulk volume estimated by both methods. Bulk volume of the P series cores was estimated by direct measurement only.

6.4.2 Gravimetric Water Content

The Y2 series core samples were removed from storage and scrubbed lightly with a wire brush while being rinsed under Tucson tap water. Any remaining dust and dirt from drilling, and any loose pieces of tuff material, were removed. This was done to assist in establishing a relatively constant dry weight by removing small bits of material that would eventually fall off over time as a result of handling. Also, lithologic contrast in the core record is much more evident on the cleaned samples.

Fifty-three samples of tuff were retrieved during the DSB drilling project. They were labeled g1 - g53 (sample g12 broke cleanly into two pieces that were labeled g12a and g12b). The samples were wire brushed (dry) to remove any loose material and weighed within 30 minutes after removal from the base of the borehole. The samples were later dried in an oven and reweighed on the same scale to determine gravimetric water content. Oven drying core involves heating the samples at 105 °C to a constant weight (Gardner, ASTM, 1986). Figure 6.5 shows gravimetric water content for the original 53 G series samples. Gravimetric water content for the core samples was determined using the following equation (Gardner, ASTM, 1986):

$$w = \frac{(Mass_{wet} - Mass_{dry})}{Mass_{dry}} \quad (6.9)$$

Figure 6.5 Gravimetric water content (w) with depth in the DSB. Gravimetric water content after 48 days of drying was slightly less than at 16 days for most samples below the 50 m depth.

The spike in Fig. 6.5 near 65 m was from a sample that was taken immediately below a wet fracture. The fracture aperture was on the order of 20 cm and appeared to contain water washed pebbles at the point where the borehole intersected it. The decrease in gravimetric water content from the surface down to 60 m could be the result of water flowing in the stream bed and infiltration down to that point. The weight of most samples increased an average of 0.6 g between 16 days and 48 days of drying. This results in the calculation of a lower gravimetric water content. An explanation of this anomalous behavior is proposed below. The 16 day data is assumed to be the true gravimetric water content.

After the gravimetric analysis the core samples were rinsed with Tucson tap water while being lightly scrubbed with a wire brush. The core was stored in cardboard core storage boxes. Fourteen additional G series cores, and 42 P series cores were removed from their protective packages after approximately 8 months in storage. Water had condensed on the inside of the protective envelope, and no attempt was made to determine gravimetric water content of these samples. The 14 G series samples were labeled g54 - g67. They were rinsed with Tucson tap water while being scrubbed with a wire brush. The P series core were sampled by E. Hardin for the purpose of resistivity measurements and could not be wetted. The P series samples were dry brushed with a nylon brush. Both of these subsets were taken from envelopes containing cut core, so their shape closely approximates a right circular cylinder. This allows their bulk volume to be estimated by measuring their length and diameter. Several of the original 53 G series samples were also from core that was cut in the field. None of the Y2 series core was cut.

Core testing with the gas pycnometer is performed with the same pressure conditions and in the same temperature range as the calibration. Core samples are sealed in the sample chamber in an identical fashion as described in the calibration section. The core samples are tested through approximately 10 cycles of the pycnometer. The ratio is calculated using Eqn. (6.7), and the solid volume is estimated from Eqn. (6.8), for each cycle. Figure 6.6 shows the ratio estimate for 23 randomly selected G series core samples. The figure indicates that the ratio estimate is fairly constant from cycle to cycle. The cycle number can be thought of as testing time as each trace in the figure required 20-30 mins to generate.

6.5 GRAPHIC RESULTS AND DISCUSSION

6.5.1 Graphic Results

Data from the gas pycnometer testing is reported in Geddis (1994). All parameters are reported with depth along the borehole to coincide with core logs. Conversion to real depth is approximated by depth times $\cos(45^\circ)$. Trends in the estimated parameters with depth are best recognized graphically, and the data is presented in this format on the following pages. The initial parameter calculated is grain density (ρ_g) (g/cm^3), which is the ratio of the oven dry weight of a core sample to the volume of solids estimated by the pycnometer. Figure 6.7 shows the trend in grain density with depth in the DSB. Both the P series and G series are included. The volume of

Figure 6.6 Ratio (V_2/V_1) estimate as a function of cycle number. The 23 G series cores were randomly selected. The ratio estimate shows no trend through a test, and is consistent from cycle to cycle.

Figure 6.7 Grain density with depth in the DSB. Both P and G series are shown.

solid was changed for one core sample (p33). The sample was initially determined to contain 289.7 cm³ of solids, which was increased to 302.6 cm³ after a re-test. The original estimate of grain density for this sample was observed as an anomalous spike point on Fig. 6.7 and the new value more closely agrees with adjacent values.

Bulk density (ρ_b) (g/cm³) is calculated as the ratio of oven dry weight to bulk volume. After determination of grain density and bulk density, porosity ϕ (cm³/cm³) can be calculated using Eqn. (6.1). Figure 6.8 illustrates the trend in porosity and bulk density with depth in the DSB. Both P and G series samples are shown.

Volumetric water content can be calculated from gravimetric water content using Eqn. (6.10):

$$\theta = w \left(\frac{\rho_b}{\rho_w} \right) \quad (6.10)$$

where:

ρ_w = water density (= 1.0 g/cm³).

Figure 6.9 shows volumetric water content with depth in the DSB. The Y2 series core was processed in the same way as the P and G series core. Grain density for the Y2 series core is shown in Fig. 6.10. Porosity and bulk density for Y2 series core is illustrated in Fig. 6.11.

6.5.2 Intrinsic Permeability

An estimate of intrinsic permeability has been made for the core samples. The Kozeny-Carman equation (de Marsily, 1986) is an empirical formulation that relates powers of pore surface area and porosity to permeability. This equation is:

$$k = \frac{\phi^3}{5 S^2 (1 - \phi)^2} \quad (6.11)$$

where:

S = pore surface area per unit volume of solid (cm²/cm³),

k = permeability, (cm²).

The permeability of G and P series core can be found in Geddis, 1994, and was calculated using a mean pore surface area of 3.5 x 10⁴ cm²/g and a grain density of 2.51 g/cm³. This pore surface area is taken from Rasmussen, et al. (1990). The pore surface area is defined as the interfacial area between the wetting fluid and the rock matrix, obtained using the mercury intrusion method. Pore surface area is converted to a volume basis using the average grain density of Y2 core determined with the gas pycnometer (2.61 g/cm³). An average volumetric

Figure 6.8 Porosity and bulk density with depth in the DSB. Both P and G series samples are shown.

Figure 6.9 Volumetric water content with depth in the DSB. This parameter is calculated from gravimetric water content and bulk density of G series core.

Figure 6.10 Grain density with depth in the Y2 borehole.

Figure 6.11 Porosity and bulk density with depth in the Y2 borehole.

pore surface area for Y2 core is $3,321 \text{ cm}^2/\text{cm}^3$, with a standard deviation of $798 \text{ cm}^2/\text{cm}^3$. This was computed by excluding one sample in Rasmussen, 1990 (sample JE). This average value, and porosity determined by the gas pycnometer, was used to calculate the permeability. The intrinsic permeability of borehole Y2 has also been determined in-situ by the air permeability method (Guzman, 1994). The arithmetic average of in-situ tests on 50 cm intervals is compared to the Kozeny-Carman permeability in Fig. 6.12.

6.5.3 Discussion

The grain density illustrated in Fig. 6.7 for the DSB ranges in value from 2.50 to 2.66 g/cm^3 , and there is a trend toward lower grain density with depth. The figure indicates a shift to lower density near the 30 m depth and is associated with a color change in the core record. The maximum difference in adjacent samples is approximately 0.06 g/cm^3 , but averages closer to 0.02 g/cm^3 . The range in grain density for Y2 core (see Fig. 6.10) is much lower. The range is from 2.58 to 2.63 g/cm^3 , and there is a slight increase in grain density with depth. The maximum difference in adjacent samples is approximately 0.03 g/cm^3 (at 20 m), but averages closer to 0.01 g/cm^3 .

The porosity illustrated in Fig. 6.8 for the DSB ranges from $0.21 \text{ cm}^3/\text{cm}^3$ near the surface to $0.02 \text{ cm}^3/\text{cm}^3$ at depth. The porosity averages around $0.05 \text{ cm}^3/\text{cm}^3$ in the lower 2/3 of the borehole. It is this low porosity that is used to explain the extended drying times required for the gravimetric analysis. Figure 6.8 also shows bulk density with depth, in the range from 2.07 to 2.47 g/cm^3 . The parameters show remarkable consistency in trend with depth. The porosity and bulk density for Y2 series samples again shows a smaller range and lower variability from sample to sample. The porosity initially decreases with depth away from the surface and averages $0.19 \text{ cm}^3/\text{cm}^3$ over most of the borehole. Bulk density shows the opposite near surface trend and averages 2.11 g/cm^3 . The Y2 samples were obtained from the same lithologic unit that occurs in the upper 30 m of the DSB. The parameters obtained over those depths in the DSB show close agreement to those obtained from borehole Y2. The proximity and similar elevation of the two wellheads support this finding.

The volumetric water content illustrated in Fig. 6.9 shows a decrease with depth near the surface and a relatively constant (or slightly increasing) value over the lower 2/3 of the borehole. As was mentioned previously in the gravimetric analysis, the spike at 65 m represents a sample obtained immediately below a wet fracture. The fracture aperture (approx. 20 cm) was large enough to contain coarse sand and fine gravel in significant quantities, nearly 0.5 liters was retrieved from the core barrel during drilling. The sediment was remarkably devoid of clay, and some of the larger rock fragments had the rounded appearance of water washed pebbles, recorded at near record levels over most of central Arizona immediately prior to and during the drilling. The stream flowed with water continuously during this time. The decrease in water content with depth away from the surface could, therefore, be interpreted as a wetting front.

The permeabilities compared in Fig. 6.12 for the Y2 series core show interesting

Figure 6.12 Intrinsic permeability with depth in Y2. There appears to be a similar trend between in-situ air permeability estimates (Guzman, 1995), and Koseny-Carmen permeability estimates based on gas pycnometer porosity, in the low permeability range (10^{-17} to $10^{-16} m^2$).

agreement in trend, in the 10^{-17} to 10^{-16} m² range. The much larger permeabilities (from approx. 10^{-15} to 10^{-13} m²) predicted by the in-situ air permeability method are associated with fractured zones (Guzman, personal communication). The porosity and pore surface area based Kozeny-Carman permeability is only applicable to matrix permeability, and is two orders of magnitude less overall. This implies that the air permeability method is a more accurate and conservative estimate of permeability than that of Kozeny-Carman in fractured tuff.

A hypothesis was formulated prior to core testing that there would be some noticeable difference in grain density (and therefore bulk density and porosity) between cut samples and uncut samples in the DSB. The assumption was that weathering and secondary mineralization would alter tuff material adjacent to a fracture face. Most of the G series are uncut samples, many of which were retrieved with obvious natural fractures bounding them, while the P series are all cut samples, representing matrix material away from a fracture. There is no apparent difference in these sub-sets, as is most evident when comparing the P series and the G series in Fig. 6.7.

Also reported in Geddis (1994) is the coefficient of variation (CV) in solid volume for a test sequence (the series of pressure cycles applied to each sample). This parameter is simply the ratio of the standard deviation in solid volume to the average solid volume (multiplied by 100) computed over the number of cycles indicated. The maximum CV in any test sequence was 1.59%, with an average of 0.7 % for all tests.

6.5.4 Re-Tested Core Samples

The pycnometer was used to re-test 22 core samples, and test three additional P- series samples. Most of the re-tested core was selected randomly to cover the length of each borehole. Several samples were selected based on lack of agreement in grain density with adjacent samples. The re-tested data is reported in Geddis (1994). The magnitude of the average difference in solid volume between the original test and the re-test of 21 of these samples is 1.6 cm³, with a standard deviation of 1.3 cm³. The re-tested values were not consistently higher or lower than the original data. The error computed for the calibration of the instrument was 2.2 cm³, and the difference between the two tests is consistent with this. Sample P33 could have had an incorrect original estimate as a result of operator error. The close agreement in solid volume implies acceptable instrument precision.

Also reported with the re-tested core data is the solid volume predicted by excluding the first cycle of each test series, and computing solid volume from the average of the remaining cycles. This was done because it was observed that the first ratio estimate was greater than the second estimate for many of the tests illustrated in Fig. 6.6. In most cases exclusion of the first ratio estimate results in a slightly greater estimate of solid volume, and a slightly lower coefficient of variation for the test. However, there is no physically meaningful difference in the parameters estimated this way, and all cycles of each test were used to calculate solid volume. It is speculated that the first estimate suffers from the effect of opening the system to insert a new

sample. The effect could be the result of water vapor in the laboratory air that enters the system, but is not investigated further.

6.6 CONCLUSIONS

Gas pycnometry is a simple and accurate technique for measuring the solid volume of porous material. It is especially useful when applied to material that has low matrix permeability and low porosity, as helium is able to enter the smallest accessible pores in a short time period. The pycnometer should be constructed with materials that are poor conductors of heat and do not change shape when operating pressures are applied. The pycnometer should be designed such that the sample chamber can accommodate large samples of variable size and shape. The optimal configuration is one in which the sample bulk volume is almost as large as the sample chamber. This is because the relatively constant random error becomes a smaller percent of the estimate as the solid volume increases. The temperature of the system should be measured and incorporated into the analysis. The reasons are that theory requires it, and it is a simple way to monitor system conditions. In this way operation of the instrument in a regime not covered in the calibration is easily recognized. The operation of the instrument could be enhanced with the use of automatic valves and automated data collection. A sample could be inserted into the chamber and an automated sequence initiated that would result in solid volume estimation to specified convergence criteria. This level of automation is used in some of the commercial devices. A calibration could also be performed with water saturated helium, and the device could be used to estimate volume of solid and liquid in a partially saturated core sample. This type of calibration would also be required if the device were used to estimate trapped air. The device is ruggedly constructed and could be employed near hole during drilling to estimate volumetric water content of freshly retrieved samples.

7. FIELD AIR INJECTION EXPERIMENTS

by A.G.-Guzman and Shlomo P. Neuman

To conduct defensible safety analyses of high level radioactive waste repositories in geologic media, it is necessary to reliably model fluid and contaminant transport around such repositories. Not only must models describe flow and transport processes in the geosphere reliably but they must be operational by relying on measurable inputs, and verifiable by generating outputs that can be compared with observations. The potential high level waste repository at Yucca Mountain in Nevada will be located in an unsaturated fractured tuff environment, underlain by a fractured carbonaceous aquifer. Mathematical models of flow and transport in this environment must be based on equations and algorithms which reliably describe multiphase flow and transport in porous-fractured tuffs, must admit measurable flow and transport parameters, and must produce outputs at least partially verifiable in the field. To address the question what constitutes a reliable model of flow and transport in environments similar to those which prevail at Yucca Mountain, and to resolve the issue how one evaluates the corresponding parameters on the basis of appropriate field measurements, the University of Arizona (UA) has been conducting research at the Apache Leap Research Site (ALRS) near Superior, Arizona. The work is sponsored by the US Nuclear Regulatory Commission (NRC) under Contracts NRC-04-90-51 (FIN L1282) and NRC-04-90-052 (FIN L1283).

The UA research at ALRS has several components. This chapter concerns pneumatic permeability tests within inclined shallow boreholes at the site. Issues being investigated include the proper conduct and interpretation of such tests in single boreholes, the extent to which fractured and porous block permeabilities can be identified, the extent to which fracture geometric data can be used to help predict permeabilities, the effects of phenomena such as two-phase flow and inertia (including variations of permeability with pressure and saturation), scale - dependence of the test results, upscaling of the test results to obtain effective permeabilities for larger rock blocks, spatial and directional variability of single-hole air permeabilities, the extent to which single-hole tests results can be used to predict permeability variations between boreholes, corroboration of such predictions by means of cross-hole fluid and tracer tests, and the extent to which air permeabilities are indicative of permeabilities to water. Two phase flow simulations using the code VTOUGH, geostatistical tools, and stochastic models are used in support of the investigation. One question of interest is the role that continuum and discontinuum concepts must play in models of flow and transport in the context of available, or potentially available, data.

The bulk of the experimental data presented in this report is being published concurrently as a NUREG report entitled Validation Studies for Assessing Flow and Transport Through Unsaturated Fractured Rock (Bassett et al., 1994, in print). Here the material is presented in the context of validation issues. Also, new data not available during the preparation of that report is included. The geostatistical analysis encompass all the data available to date.

7.1 EXPERIMENTAL SETUP

There are currently twenty-one 4-in diameter boreholes which vary in depth from about 11 m to about 32 m at the site. These boreholes were drilled in sets of three which are labeled the X-, Y-, Z-, V-, and W-series. The area around the boreholes is covered by a thick plastic liner. Another G-series consists of six boreholes outside the plastic cover. The V- and G- series consist of vertical boreholes; the other boreholes are slanted at a 45° angle. The azimuth of the X and Y slanted boreholes is of 90° (CCW from North), that for the W boreholes 180°, and that of the Z boreholes 270° (Fig. 7.1). Testing to date has centered on borehole Y2 and its neighbors at the center of the experimental site.

Air permeability testing is conducted with a straddle-packer system furnished with rubber glands about 1.68 m in length. The interval between the glands is variable to allow testing at different measurement supports. A permeability test consists of imposing an increasing sequence of flow rates (a minimum of three) each of which is extended until a steady state pressure response is attained. The working definition for steady state is a pressure change of 0.1 cm (Hg) or less within an interval of 30 minutes. A schematic representation of the injection system and its major components is shown in Fig. 7.2. Air pressure, temperature and relative humidity are measured at the surface and at the injection interval. Atmospheric temperature and pressure are also monitored. The flow rate is preset at the surface with the aid of electronic mass flow controllers. The experimental parameters are recorded at a logarithmic time scale, starting at 2 seconds at early time for each flow rate and increasing up to 2 minutes after 90 minutes of observation. All data are recorded automatically and electronically. At the end of an injection sequence, the temperature, pressure, and relative humidity in the interval are allowed to recover to their initial conditions. These recovery data are also monitored. After a test is completed, one has at least seven different sets of data which can be used to determine the air permeability of the rock surrounding the interval; three transient sets during injection, three steady state sets and one recovery set.

The analysis presented here concerns only steady state data. Water capillary displacement affects the transient data to an extent that renders the application of available single-phase interpretation techniques unreliable. The transient data sets should be interpreted in the context of multiphase flow, but we do not at present have the tools to do so. An alternative to analytical analysis of the transient data is their interpretation by numerical inverse procedures as suggested by Finsterle and Pruess (1994). We hope to do so in the future. The following section offers a brief account of the steady state analysis. The interested reader is referred to Guzman (1995) and Bassett et al. (1994) where a more detail description is presented.

7.2 STEADY STATE INTERPRETATION

Hvorslev (1951) and Hsieh et al. (1983) present an analytical expression for the spatial distribution of steady state water pressure around a hydraulic injection test interval which considers the equipotentials to form prolate spheroids. Modified for air, this expression takes

Figure 7.1 Spatial locations of boreholes at the ALRS.

Figure 7.2 Schematic representation of the air injection system.

the form:

$$Q_{sc} = 4 \pi L \frac{k}{\mu} \frac{T_{sc}}{T p_{sc} Z} \frac{p^2 - p_o^2}{\sinh^{-1} \left[\frac{L/2+z}{r} \right] + \sinh^{-1} \left[\frac{L/2-z}{r} \right]} \quad (7.1)$$

where Q_{sc} is the volumetric flow rate at standard conditions, k is air permeability, μ is air viscosity, L is distance between the straddle packers, T is air temperature in the injection interval, p_{sc} is the pressure at standard conditions (1 atm), T_{sc} is the temperature at standard conditions (20°C), Z is air compressibility, p_o is ambient air pressure, p is air pressure in the rock at a radial distance r and vertical distance z from a point at the center of the interval. The pressure in the test interval, p_w , is usually associated with $z=0$ and the borehole radius $r=r_w$. If $L/r_w \gg 1$, flow is predominantly radial and Eqn. (7.1) can be written as:

$$k = Q_{sc} \frac{\mu \ln(L/r_w)}{\pi L (p_w^2 - p_o^2)} \frac{T p_{sc}}{T_{sc}} \quad (7.2)$$

Equation (7.2) has the advantage over standard radial flow equations that it does not require introducing a fictitious radius of influence.

At the ALRS, air injection has to date been conducted on scales (in terms of L) of 0.5 m, 1.0 m, 2.0 m and 3.0 m. As the radius of each borehole is about 0.05 m, the smallest aspect ratio in our test is $L/r_w = 10$. Figure 7.3 shows how the ratio of k^R from the radial flow Eqn. (7.2) and k^P from the prolate spheroidal flow Eqn. (7.1) varies with L when $r_w = 0.05$ m. It follows from this figure that, under our test conditions, calculations resulting from the radial flow Eqn. (7.2) differs from those from Eqn. (7.1) by not more than 0.5%.

Local heterogeneities (layers, lenses, fractures, other) and anisotropy may alter the steady state flow regime around the test interval. When layers or fractures intersect this interval, flow in the rock may be predominantly two-dimensional. If preferential flow channels exist in such layers or fractures, flow in them may be predominantly one-dimensional. Intermediate flow regimes corresponding to non-integer (fractal) dimensions may also develop in some cases (Barker, 1989).

Table 7.1 summarizes the in-situ permeability data available to date as well as local 3-D coordinates. A number of permeability values, resulting from different flow rates and repeated testing, are reported for each interval. There are two sections in this Table, one including the permeability data obtained from tests along borehole Y2 at three different scales of measurement (0.5, 1.0, 2.0 and 3.0 m), and the other summarizing the 1.0-m data for all the other boreholes (X2, V2, W2A, Z2 and Y3).

Figure 7.3 Ratio of apparent permeability estimates from the radial and prolate spheroidal analytical solution.

Table 7.1 Summary of air permeability measurements.

Borehole: Y2		Scale: 3.0 m			
Xo = 20.25 m		Yo = 29.85 m		Zo = -0.34 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmean)
4.08	4.99E-15	5.31E-15	109.16	118.69	-32.90
6.37	7.23E-16	8.51E-16	116.99	125.25	-34.78
9.37	9.11E-16	1.23E-15	111.96	115.93	-34.47
12.37	1.93E-15	2.37E-15	110.15	130.28	-33.77
15.37	2.06E-14	2.87E-14	107.64	68.16	-31.33
18.37	3.01E-15	3.29E-15	114.09	75.94	-33.39
21.37	6.94E-16	1.19E-15	103.97	119.82	-34.60
24.37	8.47E-16	9.21E-16	114.50	128.70	-34.66
27.37	1.42E-16	1.74E-16	120.71	138.74	-36.38

Borehole: Y2		Scale: 2.0 m			
Xo = 20.25 m		Yo = 29.85 m		Zo = -0.34 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmean)
3.00	4.04E-15	6.89E-15	67.52	84.49	-32.88
4.00	3.12E-15	5.32E-15	68.09	89.12	-33.13
6.10	3.66E-16	8.10E-16	84.03	167.46	-35.15
8.10	4.61E-17	1.86E-16	121.81	141.98	-36.92
10.10	7.97E-16	1.77E-15	72.35	122.85	-34.37
12.10	1.03E-15	2.26E-15	71.16	112.96	-34.12
14.10	1.43E-15	2.21E-15	73.26	113.67	-33.96
16.10	2.76E-14	2.91E-14	66.90	70.66	-31.20
18.10	2.00E-15	3.49E-15	69.31	98.76	-33.57
20.10	8.05E-16	1.54E-15	74.14	128.76	-34.43
22.10	6.84E-16	1.40E-15	75.40	133.26	-34.56
24.10	4.66E-16	1.25E-15	72.81	137.98	-34.81
26.10	3.26E-17	1.09E-16	121.33	162.42	-37.36
28.10	9.62E-17	1.33E-16	75.90	136.39	-36.72

Borehole: Y2		Scale: 1.0 m			
Xo = 20.25 m		Yo = 29.85 m		Zo = -0.34 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmn)
3.07	9.541E-15	9.850E-15	71.92	86.32	-32.27
4.05	2.236E-15	2.722E-15	107.85	120.51	-33.63
5.03	6.068E-16	7.071E-16	122.65	136.55	-34.96
6.01	1.175E-15	1.233E-15	99.13	119.36	-34.35
6.99	1.800E-16	2.502E-16	115.43	175.05	-36.08
7.97	2.171E-16	2.936E-16	139.47	154.91	-35.90
8.95	3.864E-16	5.302E-16	113.60	135.17	-35.32
9.93	1.907E-15	2.197E-15	93.01	128.17	-33.82
10.91	1.636E-15	2.010E-15	96.91	129.32	-33.94
11.89	2.941E-15	3.197E-15	84.54	116.84	-33.42
12.87	2.050E-15	2.315E-15	95.87	131.20	-33.76
13.85	2.011E-15	2.269E-15	91.88	132.20	-33.78
14.83	2.649E-15	2.850E-15	86.43	90.13	-33.53
15.81	4.516E-14	4.943E-14	71.03	67.74	-30.68
16.79	4.665E-14	4.856E-14	67.23	67.85	-30.68
17.77	5.525E-15	5.687E-15	72.23	90.06	-32.81
18.75	3.356E-15	3.598E-15	79.46	114.35	-33.29
19.73	1.905E-15	2.042E-15	93.15	128.41	-33.86
20.71	4.621E-16	5.560E-16	136.56	149.34	-35.21
21.69	8.692E-16	1.176E-15	90.38	119.27	-34.52
22.67	1.151E-15	1.479E-15	85.02	124.61	-34.27
23.65	1.339E-15	1.565E-15	82.35	122.11	-34.17
24.63	1.970E-16	3.478E-16	91.68	126.82	-35.84
25.61	4.718E-17	8.815E-17	129.41	164.01	-37.23
26.59	9.005E-17	1.666E-16	102.29	104.53	-36.59
27.57	1.043E-16	1.401E-16	101.64	127.41	-36.64
28.55	5.627E-17	7.454E-17	128.03	144.61	-37.27
29.00	5.781E-17	7.956E-17	117.92	128.74	-37.22

Table 7.1 Summary of air permeability measurements (continued).

Borehole: Y2		Scale: 0.5 m			
Xo = 20.25 m		Yo = 29.85 m		Zo = -0.34 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmean)
2.83	1.56E-15	2.25E-15	94.95	124.00	-33.91
3.33	1.47E-14	1.62E-14	92.58	71.54	-31.80
3.83	2.89E-15	3.48E-15	92.93	113.38	-33.38
4.33	5.62E-16	7.16E-16	132.53	147.24	-34.99
4.83	3.10E-16	4.27E-16	111.06	126.81	-35.55
5.33	8.00E-16	9.81E-16	109.96	130.31	-34.66
5.83	1.74E-15	1.88E-15	93.14	132.58	-33.95
6.33	1.11E-16	1.67E-16	142.60	139.36	-36.53
6.83	7.46E-17	9.75E-17	167.40	172.89	-37.00
7.33	2.81E-16	3.52E-16	115.59	149.08	-35.70
7.83	1.26E-16	1.71E-16	135.36	148.68	-36.46
8.33	1.73E-16	2.56E-16	120.60	137.56	-36.10
8.83	2.19E-16	3.45E-16	126.35	150.48	-35.83
9.23	4.47E-16	4.47E-16	135.55	135.55	-35.34
9.74	2.25E-15	2.87E-15	84.36	132.13	-33.61
10.33	5.91E-16	9.26E-16	92.65	123.30	-34.84
10.83	1.31E-15	1.92E-15	82.81	132.04	-34.08
11.33	1.61E-15	2.27E-15	82.14	132.79	-33.89
11.83	2.92E-15	3.30E-15	78.09	125.76	-33.41
12.23	2.43E-15	2.87E-15	77.00	132.08	-33.57
12.83	9.23E-16	1.24E-15	91.99	132.17	-34.47
13.33	1.33E-15	1.99E-15	84.97	139.63	-34.05
13.83	1.54E-15	2.00E-15	82.62	139.46	-33.98
14.33	1.57E-15	2.22E-15	82.46	133.99	-33.92
14.83	2.99E-15	3.42E-15	78.07	126.99	-33.38
15.33	2.62E-15	3.17E-15	79.46	130.68	-33.48
15.83	3.28E-15	3.88E-15	80.82	129.09	-33.27
16.33	7.19E-14	8.18E-14	70.07	87.64	-30.20
16.83	3.19E-15	4.73E-15	111.50	132.84	-33.18
17.33	3.05E-15	3.75E-15	78.00	128.34	-33.32
17.83	4.45E-15	5.60E-15	74.34	114.58	-32.93
18.33	4.01E-15	5.12E-15	75.26	117.07	-33.03
18.83	1.58E-15	2.58E-15	82.33	137.76	-33.84
19.33	8.93E-16	1.25E-15	100.09	135.94	-34.48
19.83	1.92E-15	2.51E-15	79.81	128.18	-33.75
20.33	3.16E-16	4.55E-16	103.70	124.24	-35.51
20.83	3.02E-16	4.26E-16	100.66	131.70	-35.56
21.33	6.08E-16	1.01E-15	87.75	124.85	-34.78
21.83	6.38E-16	8.59E-16	91.10	114.61	-34.84
22.33	5.59E-16	1.01E-15	86.69	138.33	-34.82
22.83	1.42E-15	1.55E-15	88.15	125.30	-34.14
23.33	1.60E-15	1.89E-15	77.11	125.03	-33.99
23.83	6.98E-16	9.13E-16	98.77	129.48	-34.76
24.33	4.13E-16	5.31E-16	109.60	144.78	-35.30
24.83	1.81E-16	2.27E-16	121.26	144.80	-36.14
25.33	8.47E-17	8.53E-17	162.41	163.39	-37.00
25.83	7.14E-17	8.57E-17	152.64	160.71	-37.09
26.33	9.21E-17	1.07E-16	138.53	146.93	-36.85
26.83	1.57E-16	2.07E-16	113.68	139.35	-36.25
27.33	1.55E-16	2.16E-16	114.50	138.95	-36.24
27.83	1.13E-16	1.25E-16	128.13	142.38	-36.67
28.33	4.41E-17	5.36E-17	157.10	172.84	-37.56
28.83	7.55E-17	1.10E-16	126.02	146.50	-36.93
29.23	9.14E-17	1.16E-16	123.51	146.11	-36.81

Table 7.1 Summary of air permeability measurements (continued).

Borehole: X2		Scale: 1.0 m			
Xo = 19.88 m		Yo = 24.99 m		Zo = -0.05 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmean)
2.51	1.76E-15	4.35E-15	72.61	94.88	-33.52
3.49	2.79E-14	3.39E-14	67.55	73.71	-31.11
4.47	1.35E-15	1.96E-15	108.68	139.83	-34.05
5.45	1.08E-15	2.84E-15	78.86	114.84	-33.98
6.43	1.93E-16	2.65E-16	113.80	131.06	-36.03
7.41	1.64E-16	2.43E-16	128.51	143.98	-36.15
8.39	1.38E-15	2.30E-15	95.47	126.05	-33.96
9.37	7.51E-16	1.26E-15	114.84	133.21	-34.57
10.35	1.10E-15	1.65E-15	109.11	131.59	-34.24
11.33	8.22E-14	9.05E-14	67.36	68.45	-30.08
12.31	1.77E-15	2.43E-15	117.29	131.70	-33.81
13.29	4.47E-16	1.04E-15	83.73	117.84	-34.92
14.27	1.57E-15	3.06E-15	86.66	121.00	-33.75
15.25	1.37E-15	4.22E-15	78.65	86.45	-33.66
16.23	1.72E-15	3.21E-15	85.31	118.98	-33.69
17.21	7.15E-16	1.57E-15	94.70	137.92	-34.48
18.19	8.21E-16	1.96E-15	79.82	120.39	-34.30
19.17	1.38E-15	2.15E-15	82.21	116.74	-33.99
20.15	3.61E-16	7.83E-16	88.35	137.87	-35.17
21.13	1.15E-16	3.05E-16	100.00	123.07	-36.21
22.11	1.80E-16	6.84E-16	100.02	137.75	-35.59
23.09	1.54E-15	3.97E-15	77.40	108.46	-33.63
24.07	7.71E-17	1.18E-16	121.84	134.52	-36.89
24.00	2.18E-17	7.08E-17	108.61	124.95	-37.78
25.00	3.27E-17	1.85E-16	96.49	198.81	-37.09
26.00	5.82E-17	3.00E-16	84.53	177.16	-36.56
27.00	1.43E-16	2.73E-16	77.88	158.14	-36.16
28.00	1.35E-16	2.86E-16	78.56	163.75	-36.17
29.00	1.14E-16	2.59E-16	80.39	157.98	-36.30
30.00	5.46E-17	1.53E-16	94.09	159.62	-36.93

Table 7.1 Summary of air permeability measurements (continued).

Borehole: W2A		Scale: 1.0 m			
Xo = 36.80 m		Yo = 13.20 m		Zo = -0.00 m	
L(m)	Kmin	Kmax	Pmin	Pmax	ln(kmean)
2.75	5.26E-15	1.12E-14	71.83	149.17	-32.50
2.55	7.03E-15	1.16E-14	82.32	147.01	-32.34
3.53	1.46E-16	1.34E-15	88.13	170.40	-35.36
4.53	7.13E-17	1.96E-16	126.83	159.57	-36.67
5.53	8.76E-17	1.50E-16	152.36	162.09	-36.70
6.53	1.63E-16	6.66E-16	97.46	138.73	-35.65
7.53	1.85E-16	1.17E-15	93.88	159.21	-35.30
7.55	6.54E-17	1.40E-15	82.24	165.44	-35.73
8.53	5.11E-16	5.21E-15	87.07	172.06	-34.05
9.53	9.82E-16	5.44E-15	77.74	168.85	-33.70
10.53	1.35E-16	2.92E-16	128.69	155.20	-36.16
11.55	1.50E-16	5.88E-16	99.33	179.45	-35.75
12.55	1.24E-16	2.81E-16	104.18	164.98	-36.22
13.55	1.62E-16	1.01E-15	79.21	153.22	-35.45
14.55	3.53E-16	1.23E-15	72.46	154.66	-34.95
15.55	5.75E-16	2.44E-15	69.95	132.00	-34.37
16.55	2.97E-15	4.21E-15	67.52	109.11	-33.28
17.55	2.10E-15	3.90E-15	71.43	91.96	-33.49
18.55	2.97E-15	5.83E-15	69.69	98.92	-33.11
19.55	3.63E-16	1.33E-15	72.34	167.14	-34.90
20.55	1.18E-15	1.98E-15	67.18	142.99	-34.12
21.55	9.98E-16	1.98E-15	66.89	142.91	-34.20
22.55	3.78E-16	1.09E-15	69.37	162.52	-34.98
23.55	2.88E-16	7.76E-16	71.93	158.63	-35.29
25.55	2.02E-16	3.88E-15	79.55	112.12	-34.66
26.55	2.43E-16	3.73E-16	70.69	92.97	-35.74
27.55	2.14E-16	4.15E-16	71.06	177.35	-35.75
28.55	1.78E-16	4.66E-16	71.96	169.03	-35.79
23.70	4.00E-16	9.01E-16	70.09	176.72	-35.05
24.90	2.29E-15	4.18E-15	66.32	109.14	-33.41
25.90	2.86E-16	5.30E-16	69.42	101.28	-35.48

Borehole: V2		Scale: 1.0 m			
Xo = 36.00 m		Yo = 28.10 m		Zo = -0.00 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmean)
2.37	8.79E-18	4.15E-17	117.18	167.00	-38.50
3.38	3.12E-17	3.64E-17	158.07	162.82	-37.93
4.37	4.87E-17	7.14E-17	144.41	164.08	-37.37
5.37	5.85E-17	9.25E-17	118.82	132.81	-37.15
6.37	5.59E-17	1.06E-16	126.40	141.09	-37.11
7.37	8.98E-17	2.28E-16	107.69	122.70	-36.48
8.37	3.21E-14	3.69E-14	66.67	72.10	-31.00
9.37	4.47E-16	2.94E-15	88.88	114.83	-34.40
10.37	1.29E-15	2.03E-15	96.71	114.63	-34.06
11.37	1.40E-15	5.78E-15	78.13	93.76	-33.49
12.37	7.67E-16	9.72E-16	103.25	119.88	-34.69
16.37	2.83E-16	6.36E-16	84.89	130.65	-35.40
17.37	6.55E-17	9.27E-17	129.03	147.76	-37.09
18.37	1.08E-16	2.00E-16	108.81	142.68	-36.45
19.37	8.58E-17	1.42E-16	117.32	155.73	-36.74
20.37	7.77E-17	1.94E-16	121.54	145.05	-36.64
21.37	7.45E-17	1.30E-16	123.11	151.72	-36.86
22.37	4.66E-16	7.85E-16	72.35	114.15	-35.04
23.37	2.65E-17	2.65E-17	186.46	186.46	-38.17
24.37	1.99E-17	1.99E-17	156.65	156.65	-38.46
25.37	1.33E-17	1.33E-17	169.66	169.66	-38.86

Table 7.1 Summary of air permeability measurements (continued).

Borehole: Z2		Scale: 1.0 m			
Xo = 30.58 m		Yo = 34.99 m		Zo = -0.21 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmean)
2.58	3.94E-16	4.92E-16	159.14	167.07	-35.36
3.58	1.23E-16	4.68E-16	104.92	148.29	-35.97
4.56	1.48E-16	5.95E-16	99.35	144.57	-35.75
5.56	1.26E-16	5.87E-16	103.89	145.22	-35.84
6.56	8.92E-17	3.26E-16	115.84	171.48	-36.31
7.56	1.01E-16	2.74E-16	111.30	167.31	-36.34
8.56	1.80E-16	4.59E-16	93.90	170.61	-35.79
9.56	1.26E-14	1.41E-14	70.57	81.14	-31.95
10.56	7.22E-15	1.02E-14	73.83	86.62	-32.39
11.56	5.63E-15	6.64E-15	84.88	95.59	-32.73
12.56	1.25E-14	1.38E-14	74.98	81.52	-31.96
13.56	5.12E-14	5.28E-14	68.24	70.49	-30.59
14.56	3.07E-15	6.69E-15	73.42	95.52	-33.03
15.56	1.17E-15	3.42E-15	84.01	116.89	-33.85
16.53	4.05E-16	2.17E-15	74.59	139.36	-34.60
17.53	1.79E-16	2.34E-16	135.94	148.20	-36.13
18.53	7.25E-14	7.76E-14	67.56	70.04	-30.22
19.53	1.42E-16	5.05E-16	100.74	143.61	-35.86
20.53	2.88E-17	3.76E-17	156.40	162.78	-37.95
21.53	2.54E-17	2.54E-17	164.67	164.67	-38.21
22.53	3.72E-14	4.09E-14	69.46	79.69	-30.88
23.53	8.18E-17	2.72E-16	102.86	168.67	-36.44
24.53	7.19E-17	2.91E-16	111.71	180.22	-36.47
25.53	4.96E-17	1.30E-16	125.93	171.88	-37.06
26.53	1.29E-16	3.32E-15	85.26	94.25	-34.96
27.53	1.33E-15	5.83E-15	69.83	167.41	-33.51
28.53	2.53E-15	9.56E-15	68.10	157.82	-32.95
29.53	2.20E-15	5.77E-15	68.22	155.33	-33.27

Table 7.1 Summary of air permeability measurements (continued).

Borehole: Y3		Scale: 1.0 m			
Xo = 10.22 m		Yo = 29.68 m		Zo = -0.32 m	
L(m)	Kmin	Kmax	Pmin	Pmax	Ln(Kmean)
2.55	4.63E-14	5.15E-14	68.57	71.25	-30.65
3.55	5.03E-15	7.73E-15	86.74	169.46	-32.71
4.55	1.19E-14	2.62E-14	67.09	128.16	-31.67
5.55	1.72E-15	9.51E-15	72.84	170.95	-33.14
6.55	3.79E-16	2.98E-15	80.81	167.96	-34.48
7.55	9.30E-16	7.56E-15	69.97	171.82	-33.56
8.55	1.36E-15	8.56E-15	70.63	163.13	-33.31
9.55	3.40E-15	6.69E-15	66.86	95.45	-32.98
10.55	8.55E-15	1.37E-14	71.30	173.95	-32.16
11.55	5.60E-16	6.59E-15	75.48	95.78	-33.89
12.55	6.15E-16	1.83E-14	74.77	150.24	-33.33
11.55	8.38E-15	1.41E-14	119.84	163.89	-32.15
13.55	3.69E-16	2.80E-15	70.51	162.75	-34.52
14.55	3.64E-16	2.63E-15	69.03	167.35	-34.56
15.55	4.81E-16	2.65E-15	70.49	166.65	-34.42
16.55	6.04E-16	1.82E-15	75.48	191.92	-34.49
17.55	4.75E-17	3.49E-16	126.05	178.28	-36.59
18.55	1.00E-17	3.29E-17	143.09	168.65	-38.55
19.55	3.77E-17	6.94E-17	132.60	147.23	-37.51
20.55	2.16E-16	1.13E-15	71.29	146.02	-35.25
21.55	9.99E-18	9.99E-18	168.44	168.44	-39.14
22.55	7.31E-18	7.31E-18	162.65	162.65	-39.46
23.55	6.76E-16	2.02E-15	67.90	166.30	-34.38
24.55	1.06E-16	3.05E-16	98.37	142.42	-36.26
25.55	2.01E-17	2.01E-17	177.52	177.52	-38.45
26.55	5.38E-17	1.04E-16	121.28	188.01	-37.13
27.55	3.24E-17	3.24E-17	146.96	146.96	-37.97
28.55	3.92E-17	3.92E-17	135.12	135.12	-37.78
29.55	7.68E-17	2.27E-16	107.76	169.57	-36.56
30.55	9.97E-17	2.98E-16	100.16	160.42	-36.30
31.55	4.03E-17	1.03E-16	133.92	188.94	-37.28
32.55	7.89E-16	1.42E-15	68.89	212.09	-34.48
33.55	7.56E-16	1.08E-15	76.71	160.22	-34.64
34.55	2.13E-16	2.28E-16	90.61	170.14	-36.05
35.55	1.47E-16	2.20E-16	93.80	161.20	-36.25
36.55	1.58E-17	1.58E-17	233.16	233.16	-38.69
37.55	1.27E-17	1.27E-17	221.37	221.37	-38.91

7.3 PRESSURE DEPENDENCE

When Eqn. (7.1) or (7.2) apply, knowledge of the flow rate, pressure and temperature in the test interval allow computing k . In multiple flow rate tests such as ours, one can compute a k for each flow rate. Under viscous flow and under a single phase flow regime, application of Eqn. (7.2) results in a number of k -estimates which differ from each other due to experimental error (white noise). In most of our tests, however, such k values either decrease (Fig. 7.4a) or increase (Fig. 7.4b) consistently with increasing mean pressure (the arithmetic average of p_w and p_o). In other words, our tests indicate that in-situ air permeability as obtained by means of Eqn. (7.2) is non-unique, depending strongly on the applied mean pressure. This kind of permeability increase was observed by Wentworth (1944) during gas flow through thin cracks in lava rock. He attributed the phenomenon to an enhancement of permeability due to gas adsorption on the rock surfaces. Estes and Fulton (1956) observed a similar enhancement in permeability when studying slip phenomena in sandstone and limestone cores. They attributed the increase in permeability with flow rate to experimental difficulties at higher liquid saturations due to redistribution of the liquid phase within the cores. Montazer (1982) briefly mentioned the possible effects of moisture on his permeability measurements. We suspect that the enhancement of permeability observed by these authors, and by us in numerous intervals at the ALRS, may be attributed to displacement of water, which partially blocks air movement, by air. Other mechanisms such as rock deformation, leakage around the packers, or gas diffusion and adsorption are in our view less likely to act as the primary causes of this consistent phenomenon at the ALRS. That two-phase flow causes k to increase is strongly supported by our numerical experiments, described in detail in Guzman (1995). These experiments also reproduce the behavior observed in Fig. 7.5, where the pressure during a constant flow rate injection test first increases to a maximum and then decreases slowly toward a steady state value.

Other behavior which suggests two-phase flow effects, and is reproduced well by our numerical experiments, is that observed during two types of specially designed field experiments. In the first type, air was injected at a step-wise increasing sequence of flow rates followed by a step-wise decreasing sequence back to the initial value. In the second type, air injection started at a very low flow rate and increased gradually to the maximum allowed by our equipment (20 slpm, standard liters per minute). In both types of experiments, the total air pressure at the injection interval was kept at less than 250 KPa. Figure 7.6 shows the results of two experiments of the first type completed in boreholes Y2 and X2 at measurement supports of 0.5 m and 1.0 m. The arrows indicate directions of change in the flow rate and mean pressure. For example, the test depicted in Fig. 7.6a consisted of the following flow rate sequence: 500, 750, 1000, 1200, 750 and 500 sccm (standard cubic centimeter per minute). It is seen that equilibrium pressures during flow rate increase are consistently larger than those during flow rate decrease. On the other hand, air permeabilities are smaller during flow rate and mean pressure increase than during their decrease. This hysteretic behavior is commonly observed during laboratory determinations of non-wetting phase relative permeability (Anderson, 1987) and has the following simple two-phase flow explanation. When dry air is injected into the medium, some water evaporates and some is forced out of larger voids (due to capillary pressure re-equilibration) into smaller voids.

Figure 7.4 Changes of apparent permeability as a function of pressure. (a) Inertial flow effects. (b) Two-phase flow effects.

INJECTION TEST
Y2-JH5
08-20-91

Figure 7.5 Non-monotonic change of pressure response during an air injection test.

Figure 7.6 Hysteretic behavior of apparent permeability as a function of injection rate.

Increasing flow rate, and consequently increasing air pressure, results in higher capillary pressure which in turn produces a larger pore space to be occupied by air and thereby in an enhancement of air permeability. This physical behavior is analogous to that relied upon by the Hassler (1952) method to determine relative permeabilities for rock cores in the laboratory. When the flow sequence is reversed and the resulting mean air pressure decreases; the capillary pressure decreases and some water moves back toward the borehole. Some of it, however, remains in vapor phase, and some has difficulty returning from small to larger voids due to the ink-bottle effect and differences between receding and advancing capillary angles. Hence the void volume available for air flow is larger than it was during the drying portion of the test, requiring lesser pressure to maintain a given flow rate, and resulting in a larger apparent permeability. Similar behavior is depicted by retention curves where drainage and imbibition data are available (Rhodes, 1993, Fig. 2.3).

The second type of test was designed to span as large a pressure and permeability range as allowed by the field equipment, aiming to determine the critical air entry pressure at which water movement (drainage) starts to occur. Pressure responses for two of these tests are depicted in Fig. 7.7. As shown in this figure, the tests consisted of twelve flow rates in 1-m injection intervals along boreholes Z2 and W2A. The pressure stabilizes "rapidly" (within 100 to 200 minutes) at low flow rates, but takes significantly longer to stabilize at higher flow rates. Whereas, at small injection rates the pressure increases monotonically toward a stable value, at larger flow rates the pressure first increases to a maximum and then decreases monotonically to a steady value. Based on calculated changes of permeability, it appears that drainage occurs at all pressure levels but resistance to drainage varies in a nonlinear fashion, frustrating our attempts to establish a unique air entry value for a given borehole interval. Numerical simulations (Guzman, 1994) closely reproduce the observed two-phase behavior supporting our contention that the observed permeability changes are the result of capillary displacement of water by air.

Minimum and maximum permeability values in Table 7.1 correspond to those obtained during multiple injection rates and repeated testing. In general, apparent air permeability increases with increasing pressure (injection rate), but, there are some "high-permeability" intervals for which it decreases with increasing pressure (injection rate). We attribute this decrease in permeability to inertial flow effects resulting from high pore flow velocities (Guzman, 1995). Due to the pressure dependence of measured permeability, sample statistics are reported for mid-range permeability values (average of minimum and maximum k) for each interval. Table 7.2 includes the corresponding sample statistics for all available data.

7.4 SCALE DEPENDENCE

A basic assumption behind the concept of flow and transport through porous media is that the partial differential equations used to describe these processes apply on some macroscopic scale. The precise magnitude of this scale is rarely, if ever, specified or mentioned. Though the dependence of permeability on the scale of measurement is often recognized, evidence for such scale dependence is usually circumstantial. Studies by Cushman (1984) and

Figure 7.7 Pressure response during a multi-step injection test.

Table 7.2 Summary statistics of steady state permeability data in m².

Borehole ID	Scale of Measurement (m)	Number of Samples	<i>k</i>			<i>ln k</i>		
			Mean (10 ⁻¹⁵)	Median (10 ⁻¹⁵)	Variance (10 ⁻³⁰)	Mean	Median	Variance
Y2	0.5	54	3.01	0.85	110.2	-34.76	-34.71	2.25
	1	28	5	1.38	147.9	-34.47	-34.22	3.07
	2	13	3.39	1.17	57.6	-34.63	-34.43	2.78
	3	9	3.27	0.90	37.0	-34.46	-34.78	2.12
X2	1	30	4.95	1.08	266.9	-34.83	-34.52	2.93
Z2	1	28	8.38	0.86	313.5	-34.51	-35.16	4.96
W2A	1	31	1.73	0.74	5	-34.84	-35.05	1.37
V2	1	21	2.12	0.11	55.8	-36.28	-36.74	3.78
Y3	1	23	6.06	1.68	109.7	-34.47	-34.36	5.5
All	1	161	4.72	0.87	154.5	-34.85	-34.9	3.71

Desbarats and Bachu (1994) underline the need for additional research on the effect of measurement support on the spatial statistics of environmental data.

Our systematic measurement of k at the ALRS on four different scales (measurement supports) provides a unique opportunity to observe the variation of permeability with such scale. Table 7.2 shows that the arithmetic mean of k increases from $3.01 \times 10^{-15} \text{ m}^2$ at the 0.5-m scale to $5.0 \times 10^{-15} \text{ m}^2$ at the 1.0-m scale, then drops somewhat at the 2.0-m scale, and then further decreases at the 3.0 m scale for borehole Y2. As the flow is predominantly radial in all four cases, one would expect the arithmetic averages to be independent of measurement support. We attribute the increase in mean k from 0.5- to 1.0-m scales partly to sampling error and partly to the nested semivariogram structure observed in borehole Y2; a theoretical explanation of this phenomenon can be found in a recent paper by Neuman (1994). This author indicates that when the log permeability behaves as a multi-scale random process (see Section 7.6) the effective permeability varies as a power of the measurement scale. We believe that the subsequent drop in mean k from 1.0 m to 2.0 m, and then to 3.0 m scales is an artifact of the small sample at the 2.0 and 3.0 m scale; theoretically we expect mean k to either stabilize or to continue increasing with the length of the support. The sample size decreases from 54 at 0.5 m to 28 at 1.0 m to 13 at 2.0 m to 9 at 3.0 m test intervals.

Theoretically, the variance of k should decrease as the support length increases. Instead, it increases from 0.5 to 1.0 m scales, then decreases. A similar increase in variance is reported by Desbarats and Bachu (1994) when comparing core-scale permeability data to those obtained from drill-stem test measurements. However, we again suspect that part of this is due to the small size of our data sets, especially at the 1.0, 2.0 and 3.0 m scales in borehole Y2.

Existing stochastic theories of flow and transport in heterogeneous media rely heavily on a knowledge of the mean and variance of log permeabilities. It is clear from our data that both the mean and the variance of $\ln k$ may vary with the scale of measurement in a way which may or may not be theoretically predictable by these theories. This emphasizes the need to perform site characterization on a wide range of well-defined scales of measurements, both in terms of support (size of rock sample tested) and in terms of correlation distanced between supports to reveal semivariogram structures such as the nested forms discussed in the next section.

To study further the relationship between our measurements at different scales, and to verify further that flow in our tests is predominantly radial, we computed spatial weighted averages of the 0.5- and 1.0-meter permeability data over test intervals of 1.0 and 3.0 m. We then compared these local spatial averages, arithmetic and geometric, with k values actually measured at the 1.0 and 3.0-m scales. The actual distance between the straddle-packers corresponding to the "1.0-meter scale" was 0.98 m. Weighting was performed according to

$$k_a = \sum_{i=1}^n \frac{l_i}{L} k_i \quad \text{and} \quad (7.3)$$

$$k_g = \prod_1^n (k_i)^{l_i/L} \quad \text{where} \quad L = \sum_1^n l_i \quad (7.4)$$

l_i being the portion of the particular interval completely contained within a larger interval L , k_a and k_g being the arithmetic and geometric averages, respectively. Three upscaled estimates were obtained in this way; 3-meter values based on 0.5- and 1.0-meter data, and 1-meter values based on 0.5-meter data. We found that arithmetic averages provide better estimates than geometric averages, the latter generally underestimating the measured values. Both averages under predict the measurements at high permeabilities, but the arithmetic averages do so to a lesser extent than do the geometric means. The fact that the arithmetic averages produce better estimates supports our earlier contention that flow during the straddle-packer injection tests at the ALRS is predominantly radial.

7.5 SPATIAL VARIABILITY AND STATISTICAL ANALYSIS

The spatial variability of apparent air permeability measured at four different scales is shown in Figs. 7.8 to 7.11. The data are presented in the form of rectangles which delineate depth intervals and ranges of computed permeabilities. Also shown are the minimum (dashed curve) and maximum (solid curve) pressures applied during each test. In general, there is no indication of a systematic trend as a function of depth. However, a pseudo-periodic behavior becomes more prominent as the scale of measurement is reduced. Even for data at the 0.5-m scale, there does not seem to be a direct correlation between fracture occurrence and permeability in borehole Y2 though high permeabilities are expected to be associated with some degree of fracturing. We conclude that a visual identification of open fractures is a poor predictor of permeability, which must therefore be measured directly by means of pneumatic (or hydraulic) tests.

Boreholes X2, Z2, W2A, V2 and Y3 have been completely tested at a scale of 1 m. Permeabilities as function of pressure and position along these boreholes are shown in Figs. 7.12 through 7.16, respectively. Again a poor correlation is found between fracture traces and the permeability estimates in boreholes X2, Z2 and Y3. Permeability estimates along borehole W2A, vary with pressure over wider ranges than do those in the other boreholes. These larger changes may be the result of either the effect of the plastic cover on the natural distribution of moisture along the rock profile (around boreholes X2, Y2, Z2, V2 and Y3) or the spatial variability of the fluid retention properties of the rock. We believe that the effect of the plastic cover, rather than spatial variation in rock properties, is responsible for the observed changes. The effect of seasonal variability on moisture distribution, and in turn on apparent "in-situ" permeability, needs to be studied further.

The statistics of log-transformed permeability estimates ($\ln k$) in different boreholes and the corresponding histograms are summarized in Figs. 7.17 to 7.19. These statistics correspond

Figure 7.8 Spatial distribution of apparent permeability along borehole Y2 at a scale of 3.0 m.

Figure 7.9 Spatial distribution of apparent permeability along borehole Y2 at a scale of 2.0 m.

Figure 7.10 Spatial distribution of apparent permeability along borehole Y2 at a scale of 1.0 m.

Figure 7.11 Spatial distribution of apparent permeability along borehole Y2 at a scale of 0.5 m.

Figure 7.12 Spatial distribution of apparent permeability along borehole X2 at a scale of 1.0 m.

Figure 7.13 Spatial distribution of apparent permeability along borehole Z2 at a scale of 1.0 m.

Figure 7.14 Spatial distribution of apparent permeability along borehole W2A at a scale of 1.0 m.

Figure 7.15 Spatial distribution of apparent permeability along borehole V2 at a scale of 1.0 m.

Figure 7.16 Spatial distribution of apparent permeability along borehole Y3 at a scale of 1.0 m.

All Boreholes

Mean	-35.0160
Standard Error	0.1550
Median	-34.9810
Mode	-36.5630
Standard Deviation	1.9666
Variance	3.8676
Kurtosis	-0.2083
Skewness	0.1813
Range	9.3770
Minimum	-39.4580
Maximum	-30.0810
Sum	-6127.7948
Count	175.0000
Confidence Level(0.950000)	0.2914

Boreholes Y2, X2 & Y3

Mean	-34.9413
Standard Error	0.2064
Median	-34.5162
Mode	-36.5630
Standard Deviation	2.0115
Variance	4.0460
Kurtosis	-0.1905
Skewness	-0.0065
Range	9.3770
Minimum	-39.4580
Maximum	-30.0810
Sum	-3319.4270
Count	95.0000
Confidence Level(0.950000)	0.4045

Figure 7.17 Summary statistics: (a) composite apparent permeability at 1-m scale, (b) azimuth west, dip 45°.

Borehole Z2

Mean	-34.5124
Standard Error	0.4209
Median	-35.1605
Mode	NA
Standard Deviation	2.2274
Variance	4.9615
Kurtosis	-0.8747
Skewness	0.3442
Range	7.9920
Minimum	-38.2130
Maximum	-30.2210
Sum	-966.3470
Count	28.0000
Confidence Level(0.950000)	0.8250

Borehole W2A

Mean	-34.8433
Standard Error	0.2099
Median	-35.0500
Mode	NA
Standard Deviation	1.1689
Variance	1.3662
Kurtosis	-0.5162
Skewness	0.5193
Range	4.3640
Minimum	-36.7040
Maximum	-32.3400
Sum	-1080.1420
Count	31.0000
Confidence Level(0.950000)	0.4115

Figure 7.18 Summary statistics: (a) azimuth east, dip 45°, (b) azimuth south, dip 45°.

Borehole V2

Mean	-36.2799
Standard Error	0.4242
Median	-36.7428
Mode	NA
Standard Deviation	1.9440
Variance	3.7793
Kurtosis	1.2083
Skewness	1.0528
Range	7.8613
Minimum	-38.8619
Maximum	-31.0006
Sum	-761.8788
Count	21.0000
Confidence Level(0.950000)	0.8315

Figure 7.19 Summary statistics: (a) vertical direction.

to the mid-range log-transformed permeability, $(\ln k_{max} + \ln k_{min})/2$. The statistics of the complete (composite) data set including permeabilities from four directions (Fig. 7.17a) show that the resulting histogram is relatively symmetric (skewness = 0.153), with the mean close to the median, and a flat distribution (kurtosis = -0.142), Hann (1977). Histograms for the particular directions and boreholes are not as well defined as the composite histogram, due to the smaller size of these samples.

7.6 GEOSTATISTICAL ANALYSIS

To date, one hundred and sixty five (165) one-meter intervals have been tested along six holes oriented along four different directions at the ALRS. These data provide a unique opportunity to study the three-dimensional spatial structure of air permeability. Here we present a brief summary of the geostatistical analyses (Guzman, 1995) together with sample semivariograms of $\ln k$ from borehole Y2 at four measurement scales. The geostatistical analysis is performed on the log transformed mid-range permeability data.

A three-dimensional omni-directional semivariogram for the available 1-m scale data is presented in Fig. 7.20. Semivariogram values corresponding to lags with less than 40 pairs were deemed unreliable and are not included in this figure (shading of particular semivariogram values is a function of the number of pairs). This semivariogram shows an echelon structure indicative of a nested hierarchy of processes acting at different scales. The first correlation structure has a sill of 1.2 and a range of about 3.0 m. The second structure shows a sill of 3.8 and a range of about 12.0 m. The sill and range for the third structure remain undefined due to the relatively small size of the sampling domain (40 m x 25 m x 35 m). Possible explanations for these correlation structures are; (1) the lower plateau (or sill) is associated with rock matrix and small discontinuous fractures whereas the higher sill is representative of more conductive better connected fractures prevalent at intermediate scale, (2) different deposition sequences during the formation of the tuff may result in heterogeneities within the rock mass, (3) a combination of effects from fracture and matrix heterogeneity on the overall physical characteristics of the rock mass.

Multiscale continua behavior has been reported in the soil literature by Burrough (1983), in the petroleum literature by Hewett (1986), and in the hydrologic literature by Grindrod and Impey (1992) and Desbarats and Bachu (1994). They like others, have associated it with fractal behavior, a concept used by Neuman (1990, 1993, 1994) to explain the scale dependence of dispersivities and hydraulic conductivities. An upcoming paragraph deals with the application of this theory to the available air permeability data from the ALRS.

Semivariograms corresponding to 0.5, 1.0, 2.0, and 3.0 m test intervals in borehole Y2 are shown in Fig. 7.21. As there are only nine data points at the 2.0 and 3.0 m scales, these sample semivariograms are relatively ill defined. The semivariograms corresponding to 0.5 m and 1.0 m test intervals reveal well defined structures (Fig. 7.21c and d). Both show two distinct plateaus, suggesting (again) the presence of a multiscale (nested) correlation structure.

Figure 7.20 Three-dimensional omni-directional semivariogram of $\ln k$ at 1-m scale.

Figure 7.21 Semivariograms of $\ln k$ along Y2: (a) 3-m scale, (b) 2-m scale, (c) 1-m scale, and (d) 0.5-m scale.

The structure with the lower sill exhibits a correlation scale (range) of about 6.0 m, the other about 11.0 m.

Semivariograms of $\ln k$ at 1.0 m scale in the directions W, E, and S at a 45° and 90° dip are shown in Fig. 7.22. These semivariograms seem to involve elements of a nested structure and pseudo-periodicity. The nugget component for all our semivariograms is surprisingly small. We tentatively attribute the differences among these directional semivariograms largely to sampling errors (the 1.0 m samples are relatively small).

The observed nested structure in Figs. 7.20 and 7.21a is similar to that discussed by Neuman (1990, 1993, 1994) in connection with his scaling theory. According to this theory, the variance (sill) and correlation scale (range) of log permeabilities tend to increase consistently with separation distance. They are associated with a power-law semivariogram:

$$\gamma(s) = c s^{2w} \quad (7.5)$$

where s is separation distance, c is a constant, and w is the Hurst coefficient. Large values of $w(>0.5)$ correspond to smoothly varying log permeability fields whose spatial increments are positively correlated (persistent), $w = 0.5$, to fields with uncorrelated increments (pure Brownian process), $0 < w < 0.5$ to noisy fields with negatively correlated (antipersistent) increments. Equation (7.5) implies that the log permeability field is self-affine with a fractal dimension $D = E + 1 - w$, where E is the topological dimension. As such, the log permeability field lacks either a finite correlation scale or a finite variance. Neuman (1990, 1993) predicted on the basis of apparent dispersivities from tracer tests, and verified on the basis of permeabilities and transmissivities from hydraulic tests (Neuman, 1994), that the Hurst coefficient w tends toward 0.25 as sample size increases. Whereas the data quoted by Neuman span scales from 0.1 m to 45 km, Desbarats and Bachu (1994) have recently reported $w = 0.22$ for log transmissivities in a sequence of sands and shales for scales up to 100 km.

Figure 7.23 shows a log-log semivariogram of the available three-dimensional data from ALRS at 1 m scale. Also shown is a power law model fitted to the data by weighed least squares. The latter is a straight line with half slope $w = 0.30$. This is remarkably close to the generalized value of $w = 0.25$ predicted by Neuman. When we pool all available air permeability data from the ALRS (Fig. 7.24) including 54 on the 0.5 m scale, 175 on the 1.0 m scale, and 86 on the 3.0 m scale, a Hurst coefficient of $w = 0.29$ is obtained. These semivariograms excludes points with fewer than 40 pairs. The 3-m data set used in this calculation was obtained by Rasmussen et al. (1990).

Whereas the power law does not reproduce details of the nested structures in Fig. 7.20, it nevertheless captures the multiscale trend of the data. As pointed out by Neuman (1990, 1993, 1994) deviations around this model are due in part to the fact that log permeability is often not

3-D Directional Semi-variograms

Mid-Range $\ln k$

Figure 7.22 Directional semivariograms of $\ln k$: (a) azimuth west, dip 45° , (b) azimuth east, dip 45° , (c) azimuth south, dip 45° , (d) vertical direction.

Power Semi-Variogram for ALTS 1-m Scale $\ln(k)$ Data

Figure 7.23 Log-log semivariogram of $\ln k$ at the 1-m scale.

Power Semi-Variogram for ALTS Pooled $\ln(k)$ Data

Figure 7.24 Log-log semivariogram of $\ln k$ of the pooled data from the 0.5-, 1.0-, 2.0- and 3.0-m scales.

self-similar at the local scale but rather exhibits a nested, echelon structure. Each echelon in such a structure represents some discrete, statistically homogeneous geologic unit or feature. Only when the effect of enough such units and/or features is superimposed does the generalized power reveals itself.

The fact that our air permeability data are amenable to a consistent geostatistical analysis suggests to us that the air permeability data from ALRS behave, for all practical purposes, as if they represented a multiscale continuum. A continuum representation has been found adequate for log permeabilities from various other fractured rock sites including granites at Oracle, Arizona, Stripa and Finnsjon in Sweden, and Fanay-Augeres in France (Neuman, 1987, 1990; Kostner, 1993; Ando, 1994). This supports an earlier conclusion by Neuman (1987, 1990) that one can often treat the permeability of fractured rocks as a random (stochastic) field defined over a (possibly multiscale) continuum.

7.7 DISCUSSION

Based on an extensive data set consisting of steady state apparent air permeability values, we have reached the following conclusions. The apparent air permeability from straddle-packer tests is a strong function of the applied pressure. Changes in air permeability with pressure are due to two-phase flow and, in some cases to inertial flow. Computer simulations confirmed the two-phase flow explanation. Upscaling of the apparent permeability is accomplished best via weighted arithmetic averaging.

Geostatistical and statistical analyses indicate that the apparent permeability data from ALRS behave as a stochastic multiscale continuum with an echelon and power-law (fractal) structure. The latter is associated with a Hurst coefficient $w = 0.29$ to 0.30 which is remarkably close to the generalized value $w = 0.25$ predicted by Neuman (1990, 1994). Additional permeability tests spanning larger rock volumes at the ALRS would help to determine whether the seemingly fractal behavior extends beyond the scales already tested.

Our results strongly suggest that site characterizations must be based on hydrogeologic data collected on a spectrum of scales relevant to performance assessment. They further point out the need to consider two-phase flow and inertia effects in the interpretation of air injection tests. The transient part of these tests may hold the key to site evaluation of functional relationships between rock permeability, fluid pressure and saturation. We believe the inverse methods hold a promise in this regard, and propose to use them in the context of our ALRS data.

8. TASK IV: WORKSHOPS ON FRACTURE FLOW AND TRANSPORT

by R.L. Bassett

Workshop VII was organized by The University of Arizona, Center for Nuclear Waste Regulatory Analysis, and the U.S. Nuclear Regulatory Commission and was convened in Phoenix, Arizona in January 1991. More than 70 scientists attended, giving presentations and participating in the open discussions. A field trip was conducted to the Apache Leap Tuff Site at which time technical presentations were made by the students, faculty, and staff of The University of Arizona. A description of the technical program and speakers is given in Table 8.1. The workshop was highly successful and future workshops were recommended.

Technical presentations addressed the several specific topics in a format which allowed for much more discussion. Abstracts were not required, and scientists were encouraged to bring their latest research. The discussions were excellent and this open format will be used in the future meetings.

Table 8.1

EVANS WORKSHOP VII

Flow and Transport through Unsaturated Fractured Rock

MONDAY, Jan. 30, 1995: TRAVEL DAY		
TUESDAY, Jan. 31, 1995		
8:00 am - 2:00 pm	TOPIC 1: Characterization of Fractured Rock Properties	
8:00	Mr. T.J. Nicholson <i>NRC</i>	INTRODUCTION
8:30	Dr. James L. Conca <i>WSU Tri-Cities</i>	Determination of Unsaturated Transport Parameters in Whole Rock Using the UFA Method
9:00	Dr. Sitakanta Mohanty <i>CNWRA</i>	Preliminary Investigation of Mechanical-Hydrological Coupled Processes Using a Single Rock Joint
9:30	Dr. Joe Rousseau <i>USGS</i>	Results of Prototype Borehole Instrumentation at the Hydrologic Research Facility, Area 25, Nevada Test Site and Preliminary Results of Borehole Monitoring at Yucca Mountain, Nevada
10:00	BREAK	
10:30	Dr. Yvonne Tsang <i>LBNL</i>	Characterizing Flow and Transport in Fracture Rocks - A Stochastic Continuum Approach
11:00	Dr. Bill Murphy and Dr. Ron Green <i>CNWRA</i>	Report on Pena Blanca
11:30	DISCUSSION	
12:00	LUNCH	
1:00	Dr. Amado Guzman <i>UofAZ - HWR</i>	Spatial Structure of Air Permeability on the Apache Leap Tuff Site (ALTS)
1:30	Dr. Gary LeCain <i>USGS</i>	USGS Air Permeability Testing Program at Yucca Mountain, Nevada

TUESDAY, Jan. 31, 1995		
2:00 p.m. - 3:00 p.m.	TOPIC 2: Geophysical Methods of Fracture Detection	
2:00	Dr. Larry Myers <i>LBNL</i>	Detection of Fractures by Seismic Methods
2:30	DISCUSSION	
3:00 - 5:30	POSTER SESSION	

WEDNESDAY, Feb. 1, 1995: FIELD DAY

THURSDAY, Feb. 2, 1995		
8:00 am - 12:00 pm	TOPIC 3: Infiltration in Arid Environments	
8:00	Dr. Mike Sully <i>REECO, Inc.</i>	ET Measurements in Frenchman Basin at the NTS
8:30	Dr. Lorraine Flint <i>Foothill Engr. Consult.</i>	Shallow Infiltration and Initiation of Fracture Flow
9:00	Dr. Bridget Scanlon <i>UofTX - BEG</i>	Controls of Subsurface Flow in an Arid Setting including Evaluation of Preferred Pathways
9:30	Dr. Stuart Stothoff <i>CNWRA</i>	Effects of Alluvium Depth of Time-Averaged Infiltration
10:00	BREAK	
10:30	Dr. Scott Tyler <i>DRI</i>	
11:00	DISCUSSION	
12:00	LUNCH	
1:30 pm - 5:00 pm	TOPIC 4: Perched Zone Studies (Investigations)	
1:30	Dr. Randy L. Bassett <i>UofAZ - HWR</i>	Simulation of Focused Flow Using Coupled Hydrologic-Geochemical Models

THURSDAY, Feb. 2, 1995		
2:00	Dr. John Stuckless <i>USGS</i>	Strontium and Uranium Isotopic characterization of UZ-14 Perched Water
2:30	Dr. June Fabryka-Martin <i>LBNL</i>	Proposed Resolution of Discrepancies in Radiometric Age Dates for Yucca Mountain Waters
3:00	Dr. Jay Quade <i>UofAZ - Geosciences</i>	Geologic Records and Isotope Geochemistry of Perched Volcanic Springs, Southern Nevada
3:30	Dr. Ross Batzoglou	Testing an Alternative Conceptual Model of Groundwater Flow at Yucca Mountain
4:00	DISCUSSION	
4:30 - 5:30	POSTER SESSION	

FRIDAY, Feb. 3, 1995		
8:00 am - 12:00 pm	TOPIC 5: Critical Data Needs	
8:00	Dr. Gordon Wittmeyer <i>CNWSA</i>	Optimal Sampling Design for Predicting Flow in Unsaturated Soils
8:30	Dr. Gudmundur Bodvarsson <i>LBNL</i>	Development of a Three-Dimensional Model of Moisture, Gas and Heat Flow at Yucca Mountain, Nevada
9:00	Dr. Shlomo P. Neuman <i>UofAZ - HWR</i>	Dependence of Process Equations and Parameters on Data
9:30	DISCUSSION	
10:00	BREAK	
10:30	Dr. Chin-Fu Tsang <i>LBNL</i>	A Discussion of Data Needs, Predictive Calculations and Conceptual Models
11:00	Dr. Dwayne Chesnut <i>LLNL</i>	Effects of Site Scale Heterogeneity on Radionuclide Transport
11:30	DISCUSSION	
12:00	ADJOURN WORKSHOP	

EVANS WORKSHOP VII

Flow and Transport through Unsaturated Fractured Rock

**January 31 - February 3, 1995
Phoenix, Arizona**

FIELD TRIP TO APACHE LEAP RESEARCH SITE

FEBRUARY 1, 1995

ITINERARY

8:00	Assemble at the Radisson Hotel Main Entrance
8:30	Depart Hotel for Field Site
10:00	Stop 1 - Arrive Magma Copper Company - "Never Sweat Tunnel"
10:30	Stop 2 - Queen Creek Monitoring Site
11:15	Arrive at Covered Site and Deep Slant Borehole Site
11:30	Stop 3 - Covered Borehole Site
12:30	Lunch
1:30	Stop 4 - Deep Slant Borehole/Flume/Gas Sampling
2:30	Stop 5 - Weather Station/Bowen Ratio
3:30	Depart Apache Leap Field Site for Phoenix
4:45	Arrive Radisson Hotel

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T.J. Nicholson, NRC Project Manager

11. ABSTRACT (200 words or less)

This is a final technical report for a project of the U.S. Nuclear Regulatory Commission (sponsored contract NRC-04-090-051) with The University of Arizona. The contract was an optional extension for the period July 12, 1994 to May 31, 1995. The project manager is Thomas J. Nicholson, Office of Nuclear Regulatory Research. The objectives of this contract are to examine hypotheses and test alternative conceptual models concerning unsaturated flow and transport through fractured rock and to design and execute confirmatory field and laboratory experiments to test these hypothesis and conceptual models at the Apache Leap Research Site near Superior, Arizona.

Each chapter in this progress report summarizes research related to a specific set of objectives and can be read and interpreted as a separate entity. The tasks include detection and characterization of historical rapid flow through fractured rock and the relationship to perched water systems using environmental isotopic tracers of ^3H and ^{14}C , fluid and rock derived $^{234}\text{U}/^{238}\text{U}$ measurements, and geophysical data. The water balance in a small watershed at the ALRS demonstrates the methods of accounting for ET, and estimating the quantity of water available for infiltration through fracture networks. Grain density measurements are now possible for core-sized samples using a newly designed gas pycnometer. The distribution and magnitude of air permeability measurements have been done in a three-dimensional setting and the subsequent geostatistical analysis is presented. Electronic data sets of the data presented here are available from the authors; more detailed discussion and analyses are available in the referenced technical publications.

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