

892

**LA-9793-PR**  
**Progress Report**

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

*Research and Development Related to  
the Nevada Nuclear Waste Storage  
Investigations*

*January 1—March 31, 1983*

**Los Alamos** Los Alamos National Laboratory  
Los Alamos, New Mexico 87545

The four most recent reports in this series, unclassified, are LA-9327-PR, LA-9484-PR, LA-9577-PR, and LA-9666-PR.

This report was prepared by the Los Alamos National Laboratory as part of the Nevada Nuclear Waste Storage Investigations managed by the Nevada Operations Office of the US Department of Energy. Based upon their applicability to the investigations, some results from the Radionuclide Migration Project, managed by the Nevada Operations Office of the US Department of Energy, are included in this report.

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

# Research and Development Related to the Nevada Nuclear Waste Storage Investigations

January 1—March 31, 1983

Compiled by  
K. Wolfsberg, D. T. Vaniman, and A. E. Ogard

## Contributors

B. P. Bayhurst	S. S. Levy
H. W. Bentley*	T. J. Merson
D. L. Bish	C. W. Myers
J. D. Blacic	D. C. Nelson
D. E. Broxton	T. W. Newton
F. M. Byers, Jr.	A. E. Norris
F. A. Caporuscio	P. Q. Oliver
B. A. Carlos	D. M. Roy**
M. R. Cisneros	V. L. Rundberg
B. M. Crowe	R. E. Semarge
W. R. Daniels	B. E. Sheetz**
C. J. Duffy	H. E. Simpson
S. D. Francis	J. L. Thompson†
R. R. Geoffrion	D. T. Vaniman
R. C. Gooley	R. J. Vidale
J. P. Hong	P. L. Wanek
J. F. Kerrisk	S. W. White
S. D. Knight	K. Wolfsberg
F. O. Lawrence	D. A. York

\*Hydro Geo Chem Inc., 744 N. Country Club, Tucson, AZ 85718.

\*\*Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

† Department of Chemistry, Idaho State University, Pocatello, ID 83209.

## CONTENTS

ABSTRACT . . . . .	1
EXECUTIVE SUMMARY . . . . .	2
I. INTRODUCTION . . . . .	9
II. FIELD MIGRATION EXPERIMENTS . . . . .	9
A. Field Site . . . . .	9
B. Development and Characterization of Groundwater Tracers . . . . .	13
III. GEOCHEMISTRY OF TUFF . . . . .	16
A. Plutonium Chemistry in Near-Neutral Solutions . . . . .	16
B. Preliminary Assessment of Important Radionuclide Species and Available Thermodynamic Data . . . . .	18
C. Natural Chemical Analogues . . . . .	25
D. Permeability, Porosity, and Hydrothermal Reactions . . . . .	26
E. Plutonium Sorption from a Flowing Solution . . . . .	27
F. Sorption Experiments with Strontium, Cesium, Barium, Europium, and Technetium . . . . .	29
G. Sorption Experiments with Americium, Plutonium, and Neptunium . . . . .	33
H. Other Sorption Experiments . . . . .	33
I. Chlorine-36 Analyses of Groundwater . . . . .	33
IV. MINERALOGY-PETROLOGY OF TUFF . . . . .	36
A. Zeolite Origins . . . . .	36
B. Horizons of Zeolitization . . . . .	36
V. VOLCANISM STUDIES . . . . .	40
VI. ROCK PHYSICS . . . . .	42
VII. SHAFT AND BOREHOLE SEALING . . . . .	44
VIII. EXPLORATORY SHAFT . . . . .	45
A. Design . . . . .	45
B. Test Plan . . . . .	47
IX. QUALITY ASSURANCE . . . . .	49
A. Los Alamos . . . . .	49
B. US Geological Survey . . . . .	50
REFERENCES . . . . .	50

RESEARCH AND DEVELOPMENT RELATED TO THE NEVADA NUCLEAR  
WASTE STORAGE INVESTIGATIONS

January 1--March 31, 1983

Compiled by

K. Wolfsberg, D. T. Vaniman, and A. E. Ogard

Contributors

B. P. Bayhurst	S. S. Levy
H. W. Bentley	T. J. Merson
D. L. Bish	C. W. Myers
J. D. Blacic	D. C. Nelson
D. E. Broxton	T. W. Newton
F. M. Byers, Jr.	A. E. Norris
F. A. Caporuscio	P. Q. Oliver
B. A. Carlos	D. M. Roy
M. R. Cisneros	V. L. Rundberg
B. M. Crowe	R. E. Semarge
W. R. Daniels	B. E. Sheetz
C. J. Duffy	H. E. Simpson
S. D. Francis	J. L. Thompson
R. R. Geoffrion	D. T. Vaniman
R. C. Gooley	R. J. Vidale
J. P. Hong	P. L. Wanek
J. F. Kerrisk	S. W. White
S. D. Knight	K. Wolfsberg
F. O. Lawrence	D. A. York

ABSTRACT

This report summarizes the contribution of the Los Alamos National Laboratory to the Nevada Nuclear Waste Storage Investigations for the second quarter of FY 1983.

## EXECUTIVE SUMMARY

### NUCLIDE MIGRATION FIELD EXPERIMENTS IN TUFF

Computer transport-code estimates of radionuclide retardation in the geologic media surrounding a nuclear waste repository will require validation by field experiments to ensure that extrapolations from laboratory measurements are meaningful. A 400-ft horizontal hole was cored in the Topopah Spring tuff exposure on the eastern slope of Fran Ridge at the Nevada Test Site (NTS); this exploration was undertaken to help locate a suitable site in which to conduct nuclide migration field experiments in tuff. The coring proved to be much more difficult than anticipated; it required a total of 68 work shifts. Use of air as the drill bit lubricant was given up after 185 ft. Of the 60 396 gal. of water and detergent that was used for the remainder of the coring, most remained in the formation. Sluffing caused various difficulties, some of which were alleviated by casing the hole to 240 ft with HCQ drill rods. A three-arm caliper tool could be run only to 290 ft, and a TV camera could not pass through the casing. Examination of the core revealed 22 fractures per linear meter and a calculated 59 fractures per unit cubic meter for the coring interval from 209 to 388 ft. These numbers corroborate the highly fractured character of moderately to densely welded Topopah Spring tuff that was observed in the examination of core from Drill Hole USW GU-3. Calcium carbonate deposits were observed as fill material in fractures throughout the 400 ft of Fran Ridge core. However, calcium carbonate in the form of caliche was not observed beyond 83 ft, a measurement that corresponds to a vertical depth of 22 ft beneath the ground surface at the drilling site. Beyond 100 ft, manganese oxides and siliceous minerals filled most of the fractures that did not contain carbonate. X-ray diffraction techniques determined that the siliceous fill in a fracture at 266 ft contained 88% tridymite and 12% quartz. The core was free of lithophysae, except for a few incipient lithophysae in some flattened pumice inclusions between 266.5 and 272 ft. A detailed report of this coring activity and the resulting observations is in preparation.

Nonsorbing tracers are required in experiments that investigate diffusion as a retardation mechanism and also in those that measure retardation by

sorption. The use of such tracers will be especially important in field experiments that address these phenomena; Los Alamos is now characterizing such tracers in the laboratory. The characteristics of these groundwater tracers are (1) usability and detectability at low concentrations in natural waters, (2) little or no sorption, (3) noninterference with sorption or diffusion of other elements, and (4) different diffusion characteristics in various groundwater tracers. The analytical method being developed allows for determination of five different fluorobenzoates at levels of 0.2 mg/l and simultaneous use of fluorobenzoates and bromide.

#### GEOCHEMISTRY OF TUFF

Data from calculations of the activity of various radionuclides in light-water reactor fuel and waste and from the recent Environmental Protection Agency (EPA) proposed standards for disposal of spent fuel and high-level waste have been combined to assess the relative importance of radionuclides in the waste forms that might ultimately be stored at a Yucca Mountain repository. The thermodynamic data base in the EQ3/6 code will be updated according to the priority established by this assessment. Several elements (americium, cesium, strontium, plutonium, curium, and samarium) exist in large quantities relative to the proposed EPA limits. Thermodynamic data (solubility, complex formations, and redox) are available in the EQ3/6 thermodynamic code for cesium, strontium, and plutonium; some data for americium, curium, and samarium can be obtained from existing compilations. Data for these elements, as well as for others that must be considered, will be obtained wherever possible and tested for consistency, using EQ3/6.

By examining natural analogues that have formed over long periods of time, it is possible to obtain data for predicting the effect of a thermal pulse at Yucca Mountain and for validating chemical models. Preliminary investigation of hot spring localities has been completed, and two conclusions were drawn. (1) Dissolution by flowing warm water leaves a very porous and friable rock; few alteration products seem to remain in place. (2) Highly acid environments tend to evolve in an unsaturated zone if pyrite is present in the tuff.

Measurements of permeability, pore compressibility, storage capacity, and porosity have been made on a sample of the Topopah Spring Member. These

measurements are necessary to model waste-element movement from fractures into the tuff matrix, both by diffusion and in response to the matric potential. These data provide for the first time an opportunity to assess the degree to which porosity is decreased by confining pressure. There may be a reduction of 10 to 20% in the porosity of the tuffs at the repository horizon.

Work has been done to provide complete fluid analysis for the gold bag hydrothermal experiments that address the stability of sorptive phases. Complete characterization of the fluid is critical when extracting thermodynamic data for clinoptilolite and mordenite from this type of experiment.

Previous studies carried out at Los Alamos for the sorption of plutonium on tuff have shown that the sorption ratio  $R_d$  is ~100 ml/g. These studies used batch techniques in which the dissolved plutonium and crushed tuff were in contact for 3- to 12-week periods. Recently, column experiments have been conducted in which the plutonium solution is passed through the crushed tuff in the relatively short contact time of a few hours. Under these conditions, an appreciable fraction of the plutonium showed little or no sorption; plutonium was eluted from the column at almost the same time as the solvent front, which was monitored with tritiated water. This observation may be quite important for nuclear waste management because it implies that there is some mechanism, perhaps kinetics or colloid formation, by which plutonium species might move farther from a repository than would be anticipated on the basis of batch sorption coefficients.

Batch sorption experiments address many of the parameters involved in retardation of waste elements by sorption. Samples from the USW G-2 hole were selected for investigating the sorptive behavior of mordenite, glass, calcite, and analcime. Samples from Drill Hole USW GU-3 were from the unsaturated zone and were similar to those in the proposed repository unit. Mordenite appears to sorb strontium, cesium, and barium well. Calcite has very high sorption ratios for europium, americium, and plutonium. Experiments with other hazardous waste elements are under way.

The cosmogenically produced  $^{36}\text{Cl}$  (half-life  $3.01 \times 10^5$  years) can be used to date old waters and infer water velocities; both are necessary information when assessing transport of waste elements. Water from the alluvial aquifer (Well 5B) in Frenchman Flat gave a  $^{36}\text{Cl}$  date of modern water, whereas that from the 2840- to 2870-ft interval in Well UE-25b#1 gave a  $^{36}\text{Cl}$ -to-total chlorine ratio that suggests an age of  $\sim 3 \times 10^5$  years. This older age may be

real or the result of dilution from a number of chloride sources introduced into the ground during testing of the well. More work with  $^{36}\text{Cl}$  is required to further evaluate such ages.

#### MINERALOGY-PETROLOGY

Estimates have been made of the total amount of sorptive zeolites (heulandite, clinoptilolite, and mordenite) between a repository in the Topopah Spring unit and the static water level. These estimates are based on four commonly zeolitized intervals that can be traced across the exploration block at Yucca Mountain. Analysis of these intervals indicates that the thicknesses of sorptive zeolite, normalized to 100% zeolite, range from 24 to 78 m along vertical pathways between a potential repository and the static water level.

#### VOLCANISM

Basaltic volcanic rocks of the NTS region are divided into three cycles that are based on age and field relations. Basalts of the silicic cycle make up a large-volume, bimodal (basalt-rhyolite) suite formed in the waning stage of the Timber Mountain caldera cycle. The older rift basalts include basalts erupted contemporaneously with the peak of extensional faulting. The younger rift basalts are trace-element enriched and are separated from the older rift basalts by a brief period of no volcanic activity (4 to 6 Myr). A trench cut across the western boundary fault of the Yucca Mountain exploration block revealed a 10-Myr basalt dike emplaced at a shallow level into the fault and fault breccia. The dike has been displaced by subsequent movement along the fault.

#### ROCK PHYSICS

A test matrix was designed for creep testing of nonwelded, zeolitized samples from the tuffaceous beds of Calico Hills. The purpose of the tests is to provide data with which to formulate a preliminary constitutive equation that describes the time-dependent deformation properties of nonwelded tuffs subjected to far-field conditions (for example, for borehole sealing). Test

samples from a single ash-flow unit in Drill Hole USW G-4 were selected, and testing will begin next quarter.

Final results of the "soak" tests were documented. There were significant permanent changes in tensile strength, uniaxial compressive strength, and matrix permeability. However, with a few exceptions, porosity, grain density, and thermal properties were unaffected. Mineralogic and petrologic examinations of the test samples have shown that the reactions involved are the dissolution of silica and feldspar, formation of clays, and possible conversion of clinoptilolite to mordenite. Strength changes are believed to be related to the subtle surface modifications of minerals observed; these changes were probably most active along grain boundaries and fracture surfaces where the catalytic action of water is effective.

#### SHAFT AND BOREHOLE SEALING

The purpose of this task is to evaluate the chemical stability of potential sealing materials in the felsic tuff environment of Yucca Mountain. The process of choosing an appropriate sealant is to identify the reaction products, determine their effects on sealing properties, and minimize the reaction and the reaction rate if the effects are deleterious. A series of laboratory studies already under way will permit observation of rock/sealant reaction in a laboratory setting. Chemical alteration in ancient cement seals in tuff is also being studied. Long-term field studies planned for Yucca Mountain are being done in cooperation with the Materials Testing Laboratory of Pennsylvania State University.

New experiments involve investigating tuff/sealant reactions under unsaturated pore fluid conditions. The object is to determine the chemical reaction taking place in concrete and tuff at a slightly elevated temperature (200°C) on a laboratory time scale; these reactions will help predict the long-term geochemical stability of cement seals in the unsaturated felsic tuff of Yucca Mountain.

The first sealant tested was a concrete containing calcium silicates, aluminates, and ferrites as the major cement phases, a coarse aggregate of Grouse Canyon tuff, a fine aggregate of "NTS Sand #2," and fly ash AD-592-5.

## EXPLORATORY SHAFT

### A. Design

Title I design of both the surface and subsurface Exploratory Shaft (ES) facilities has been completed, and Title II design is nearing completion. Construction of the power line to the NTS boundary is complete, the road to the NTS boundary is nearly complete, and the water line to the NTS boundary has been started. Construction off the NTS is awaiting the execution of a Department of Energy/Bureau of Land Management (DOE/BLM) Cooperative Agreement. Procurement of equipment and buildings has started and the shaft-sinking contract is being written.

### B. Test Plan

Twenty-five proposals for testing in the NNWSI ES were completed this quarter. The proposals, which describe tests to be performed both during shaft construction and in the underground facility, are listed below.

#### Construction phase tests:

- (1) Shaft-wall mapping, photography, and hand specimen sampling
- (2) Large-block sampling and pore water analysis
- (3) Groundwater sampling
- (4) Shaft mechanical testing 1: rock extensometers and pressure cells
- (5) Vertical core drilling from within the shaft
- (6) Lateral drilling at the breakout level
- (7) Overcore testing
- (8) Breakout room testing

#### In situ phase tests:

- (9) Shaft mechanical testing 2: multiple-point borehole extensometers
- (10) Drift-wall mapping
- (11) Radial borehole testing from within shaft
- (12) Lateral core drilling from drifts
- (13) Sampling and testing intact fractures
- (14) Bulk permeability test
- (15) Infiltration test
- (16) Hydrologic testing/Calico Hills
- (17) Waste package testing

- (18) Drift and pillar deformation test
- (19) Enhanced heater block testing
- (20) Canister scale heater testing
- (21) Borehole and drift seal testing
- (22) Diffusion test
- (23) Fracture transport test
- (24) Horizontal emplacement hole drilling test
- (25) Integrated data system proposal

The sequence of testing during shaft construction was formulated, and the ES testing input to the Site Characterization Report was also completed. Requirements and specifications for services and materials to be provided by the shaft construction subcontractor were identified. Lack of effective technology for air drilling underground continues to be a concern.

#### QUALITY ASSURANCE

##### A. Los Alamos

An internal audit was performed of the Los Alamos Group ESS-2 instrumentation laboratory.

Five new detailed procedures were prepared, and three existing procedures were revised.

A quality assurance (QA) training session was presented to all NNWSI personnel. The QA staff prepared a "Quality Assurance Program for Exploratory Shaft Participant Organizations."

Records for Nuclide Migration Field Experiments were transmitted to the records center.

##### B. USGS

An internal audit was performed on the Denver records system.

Six new procedures were approved, and one existing procedure was revised and approved. The Procurement Procedure was sent to Denver for approval.

The DOE performed an audit of the Drill Hole USW G-4 QA records.

## I. INTRODUCTION

This report summarizes some of the technical contributions from the Los Alamos National Laboratory to the Nevada Nuclear Waste Storage Investigations (NNWSI) project managed by the Nevada Operations Office of the US DOE during the period from January 1 through March 31, 1983. The report is not a detailed technical document but does indicate the status of the investigations being performed at Los Alamos.

## II. FIELD MIGRATION EXPERIMENTS

### A. Field Site (A. E. Norris, F. M. Byers, B. M. Crowe, S. D. Francis, J. P. Hong, T. J. Merson, R. E. Semarge, and S. W. White)

In 1980 a program was initiated to address the question of whether accurate models of radionuclide transport through fractures in tuff could be formulated and validated with field migration experiments. This validation would demonstrate the understanding of nuclide transport processes that is vital to licensing a nuclear waste repository. The field work for this program concentrated initially on the bedding planes of Miocene tunnel bed 5 tuff in G-Tunnel at the NTS. The bedding planes proved to be no more hydrologically conductive than the adjacent tuff. Therefore, in 1982 a search began for a more suitable site for this field experiment. The search concentrated on exposures of Topopah Spring and Calico Hills tuffs because it is in these tuffs, above the static water level in Yucca Mountain, that a nuclear-waste repository might be sited. The most accessible of the potential sites for these field experiments is located on the eastern slope of Fran Ridge, just east of Yucca Mountain. Horizontal coring at this Fran Ridge location was performed this quarter as part of the nuclide migration field experiment siting study.

The specifications for the coring included two 400-ft horizontal holes separated by a vertical distance of ~20 ft. This 400-ft horizontal depth was chosen for sampling the Topopah Spring tuff because the distance is similar to the maximum penetration of a proposed adit that would not require continuous forced air circulation. The two holes, one above the other, were to provide the possibility of measuring hydrologic conductivity between the holes through expected vertical fractures. Continuous coring was requested to provide

material that could be examined for fracture frequency, fracture-fill materials, and lithophysal content of the tuff. Finally, the holes were to be drilled with air, if possible, to avoid injecting liquids into the formation.

Drilling at the Fran Ridge site commenced on December 10, 1982. The task proved to be much more difficult than expected; 68 work shifts were required to complete one 400-ft hole. For two reasons the second hole was not even started. First, the budget for both holes was completely expended to core the first hole to depth. Second, air drilling of the first hole was terminated after 185 ft because of excessive bit wear, slow rate of drilling, vibrations along the drill string, and poor core recovery. The remaining 215 ft was drilled with 1438 barrels (60 396 gal.) of water and detergent, most of which remained in the formation because of poor returns. A second hole would have required drilling with water and detergent, too. The resulting contamination of the formation could have been a great detriment to future experiments and could have outweighed the gains from hydrologic conductivity measurements. Therefore, the requirement for the second 400-ft hole was rescinded.

Part of the difficulty associated with drilling the one 400-ft hole arose from the nature of the Topopah Spring tuff. This material has a Mohs scale hardness of 7; even diamond drill bits do not penetrate such hard material easily. Another difficult characteristic of the formation was its tendency to sluff. As a result, drill bits and other parts of the drill string jammed in the drill hole and were lost at various times. About 20% of the drilling shifts was spent simply cleaning the hole or fishing for lost drill string parts. At a depth of 240 ft, the hole size was reduced from 3.937 to 3.032 in. This reduction permitted the use of the original HCQ rods as casing to overcome the worst of the sluffing problems. An added benefit was the great improvement in the quality of core recovered beyond 240 ft; core recovery increased ~50 to 90%.

The hole was completed during the last shift on January 29, 1983. A Birdwell three-arm caliper tool was used to log the hole on January 30, but the maximum depth attained even after a final hole cleaning was 290 ft. An attempt to use a Westech TV camera in the hole was unsuccessful because the clearance inside the HCQ drill rods was insufficient to permit this logging tool to penetrate beyond the 94-ft depth. The camera encountered dirty water within the HCQ drill rods at 45 ft, which indicated that the hole did not have

sufficient upward slope to permit drainage. After this logging activity, the hole was capped; the HQC drill rods were left in place to a depth of 240 ft.

Each piece of recovered core, except for those that were wrapped and waxed, was examined for fractures, fracture-fill mineralization, and lithophysal content. The core recovered from between 209 and 388 ft was complete enough to justify fracture frequency analyses. The results are shown in Table I. The fractures per unit cubic meter  $F_c$  were calculated from the observed linear fracture frequency  $F_m$  and the acute angle A between the core axis and the fracture according to the formula

$$F_c = (\sin A)^{-1} \cdot F_m \quad (1)$$

Application of Eq. (1) (taken from Ref. 1) converts all fractures to a hypothetical set normal to the core axis, which should be representative of the number of fractures that would be measured along any diameter within a unit cubic meter sphere. The mean number of fractures per unit cubic meter (59 for the Fran Ridge Core) can be compared with the 42 fractures per unit cubic meter for Topopah Spring tuff, which was calculated from USW GU-3 core.<sup>1</sup> The USW G-3/GU-3 data show that the moderately to densely welded tuff of the Topopah Spring Member has almost twice as many fractures per unit cubic meter as the next most fractured tuff at Yucca Mountain. The Fran Ridge core data substantiate the highly fractured character of the Topopah Spring Member.

The following observations were made concerning the fracture-fill materials. Fractures at 17, 131, and 155 ft contain breccia, which indicates that these fractures may be parts of fault systems. Calcium carbonate deposits fill fractures throughout the 400-ft core. However, calcium carbonate in the form of caliche was not observed beyond 83 ft. The slope of the ground surface at the Fran Ridge drilling site is ~15°. An 83-ft horizontal distance in the drill hole corresponds to a vertical depth of 22 ft beneath the ground surface. This appears to be the limit of surface water effects. A sample of calcium carbonate fill from a fracture at 285 ft was analyzed by x-ray diffraction techniques; the fill is 99% calcite and 1% quartz. Manganese oxides and siliceous minerals fill most of the fractures beyond 100 ft that do not contain calcium carbonate. The x-ray diffraction techniques determined that the siliceous fill in a fracture at 266 ft contains 88% tridymite and 12% quartz.

TABLE I  
 FRACTURE FREQUENCIES IN UE-25h#1 CORE

<u>Interval (ft)</u>	<u>Fractures/ Linear Meter</u>	<u>Fractures/ Unit Cubic Meter</u>
209.0 - 216.0	21	50
221.0 - 224.5	22	51
224.5 - 232.0	24	68
232.0 - 237.0	16	43
240.0 - 244.7	24	92
245.0 - 249.0	16	48
249.0 - 253.0	16	50
253.0 - 259.0	19	75
259.0 - 263.5	19	56
263.5 - 266.5	21	70
266.6 - 272.0	23	60
272.0 - 275.0	13	40
275.0 - 282.0	21	70
282.0 - 286.0	30	108
286.0 - 293.0	21	68
293.0 - 299.0	24	57
299.0 - 305.0	18	48
307.0 - 312.0	21	42
312.0 - 318.0	24	41
318.0 - 323.0	29	58
333.0 - 337.0	19	46
337.0 - 343.0	17	40
343.0 - 350.0	31	62
350.0 - 355.0	17	50
355.0 - 363.0	24	92
363.0 - 368.0	24	49
368.0 - 372.0	29	82
372.0 - 378.0	26	59
378.0 - 388.0	15	29
Mean	22	59

The lithophysal content of the core was used to determine how closely the Topopah Spring exposure at the Fran Ridge drill site would resemble the lithophysae-free tuff in the exploratory shaft (ES) target unit. The only indication of lithophysae anywhere in the Fran Ridge core was in the interval from 266.5 to 272 ft. The tuff contained several flattened pumice inclusions as much as 5 cm long. A few of these pumice inclusions showed incipient lithophysal cavities with vapor phase crystals. Thus, the horizontal drilling at Fran Ridge was in lithophysae-free tuff. A survey of the drill site indicated that this lithophysae-free tuff is interbedded between lithophysae-bearing strata of Topopah Spring tuff. Similar interbedding of lithophysae-free tuff within lithophysae-bearing strata has not been characterized either in the Topopah Spring Member at Busted Butte or in any of the Yucca Mountain vertical cores.

A detailed report of all the information gained from this horizontal coring activity at Fran Ridge is in preparation. Some hydraulic measurements are also being made in support of field experiments in the unsaturated zone (Sec. III.E).

#### B. Development and Characterization of Groundwater Tracers (P. L. Wanek)

The analytical techniques that are needed to detect and identify several potential water tracers are being studied. One class of tracer compound being considered is fluorinated benzoic acid salts. The analysis parameters for their measurement by high-performance liquid chromatography (HPLC) were varied for optimum sensitivity and resolution.

To maximize a compound's sensitivity to detection, it is necessary to determine the wavelength at which maximum specific absorption for a particular compound takes place. Although the Spectra-Physics program UVSCAN was designed to identify absorption maxima, it was unable to find the region of maximum UV absorption of the fluorobenzoates as determined by a Hewlett-Packard UV-VIS scanning spectrophotometer. Figure 1, a plot of a typical fluorobenzoate UV-VIS scan, illustrates that the area of maximum UV absorption below 260 nm does not have a base line that can be resolved by the UVSCAN computer program and therefore is not identified by using the program. From UV-VIS spectrophotometer data and trial chromatographs that used several different wavelengths between 200 and 235 nm, it was determined that a 225-nm

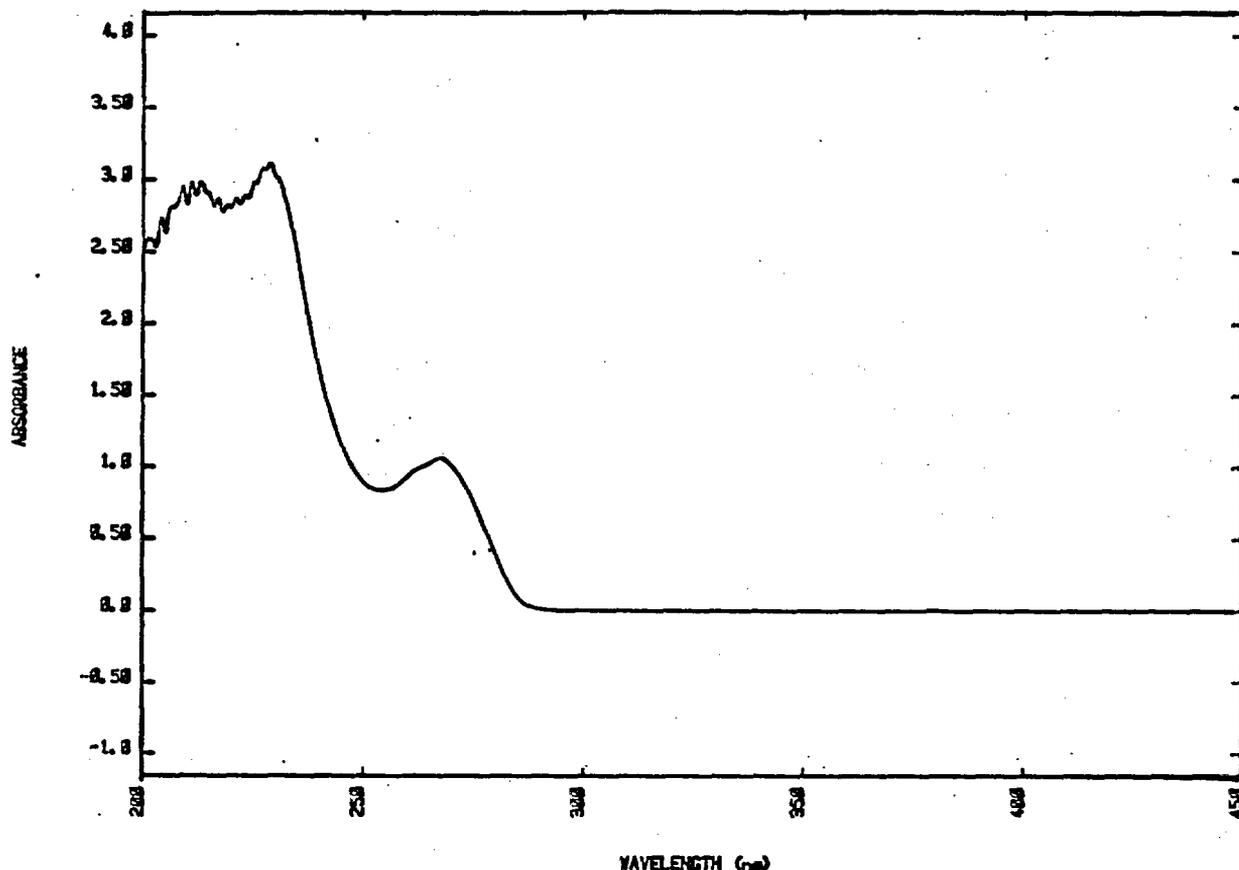


Fig. 1. Example of UV absorbance of a fluorobenzoic acid salt, sodium ortho-fluorobenzoate, relative to excitation wavelength. (Absorbance units-to-salt concentration ratio was not determined.)

wavelength would be optimum for all fluorobenzoate compounds prepared, except trifluoro-ortho-toluate. This takes into account the relative concentration of fluorobenzoates and the background nitrate, which also absorbs at 225 nm and is normally present in waters such as Well J-13 water. It also appears that the nitrate peak, rather than interfering with the tracer compounds, actually provides an internal marker from which relative retention times on the HPLC column can be calculated.

To optimize resolution, various solvent conditions were employed and spectra were obtained using 225 nm as the monitoring wavelength. The six fluorobenzoate salts originally prepared were ortho-fluorobenzoate (OFB), meta-fluorobenzoate (MFB), para-fluorobenzoate (PaFB), pentafluorobenzoate (PFB), 3-trifluoromethylbenzoate (TFMB), and a-a-a-trifluoro-o-toluate (TFOT). Best resolution of a mixture was obtained by eliminating MFB and thereby using

only five salts simultaneously. A mixture of 33% methanol and 67% 0.01 M phosphate buffer ( $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ , pH 5.5) was used for separation on a reverse-phase octadecyl (Alltech Association C-18) column with a flow rate of 1.5 ml/minute. Under these conditions, TFMB had the weakest (broad) peak at the end of the elution series. Great difficulties with base-line drift were encountered at high sensitivity settings (at a range of <0.01 absorbance units). For fluorobenzoate concentration levels below 0.2 mg/l, detection under routine conditions seemed unreliable. Sensitivity could possibly be enhanced by increasing the sample size per injection. (A 10- $\mu\text{l}$  sample size was used in these experiments, but larger volume loops are now being used.)

In rock, the diffusion character of anions such as bromide or thiocyanate is thought to be different from that of compounds such as fluorobenzoate salts; therefore, the simultaneous use of the two types of compounds in a water tracer experiment could be advantageous. Several analytical techniques were investigated before a successful method was found.

The UV-VIS spectrophotometer scans of sodium bromide and sodium thiocyanate solutions determined that neither compound was sensitive to UV excitation much above 200 nm; therefore, neither can be monitored well from an HPLC column effluent by a UV detector, which is the best detection method for the fluorobenzoate compounds. Because both strongly anionic and fluorobenzoate compounds can be separated on an anion exchange column, the use of such a column with a combination of detectors, for example, UV and conductivity or electrochemical, could possibly provide data for both tracer types at low concentration levels. The combination of a Partisil-10 SAX (strong anion exchange) column with a Wescan conductivity detector was tried for samples containing bromide or thiocyanate ions. The eluent used was 0.1 M  $\text{KH}_2\text{PO}_4$ ; no significant peaks were visible above the background conductivity of this buffer.

Because both bromide and thiocyanate ions should be detectable at low concentrations with an electrochemical (EC) detector, a combination of the anion column, UV detector, and EC detector was investigated. A phosphate eluent could not be used because of precipitation problems with the silver electrode of the EC detector. The anion column put restraints on the workable pH range (2.0 to 7.5), so an acetate buffer system was tried with no positive results. Finally, a Dionex "fast-run" anion column, which is not pH-limited, was installed on the HPLC; the UV detector and the EC detector were used. The

standard Dionex anion eluent (0.003 M  $\text{NaHCO}_3$ , 0.0024 M  $\text{Na}_2\text{CO}_3$ ) was used. A 100- $\mu\text{l}$  sample injection loop was also installed to provide a lower detection threshold. With this combination, a mixture of 0.8 mg/l pentafluorobenzoate and 0.5 mg/l bromide was easily detected in Well J-13 water that contained 8 to 9 mg/l nitrate. The minimum detection limits for PFB and bromide have not yet been determined.

### III. GEOCHEMISTRY OF TUFF

#### A. Plutonium Chemistry in Near-Neutral Solutions (T. W. Newton and V. L. Rundberg)

Attempts to understand the chemistry of dilute solutions of Pu(IV) in near-neutral solutions are limited by the available analytical methods. Methods based on the colored redox reagents ceric sulfate, ceric perchlorate, and Os(II) complexes such as  $\text{Os}(\text{dimethylbipyridine})_3^{2+}$  are being developed, as are ion exchange methods that use both organic and inorganic materials.

Los Alamos continues to study ion exchange methods based on zirconium phosphate. Results obtained using a commercial material, BioRad ZP-100A, were not very satisfactory, so at the suggestion of N. Trautmann (Institut für Kernchemie der Universität Mainz), Los Alamos now uses the preparation BioRad ZP-1. The procedure is similar to that described in a previous report;<sup>2</sup> the column of ion exchange material is 4 mm in diameter x 100 mm long. Samples are pipetted onto the top of the column and eluted with 2-ml portions of HCl of increasing concentration. The 2-ml elutriates are dried at about 200°C and are alpha-counted.

The ZP-1 preparation is better than ZP-100A for separating plutonium oxidation states; however, Los Alamos results are not in complete agreement with those communicated by Trautmann et al. For example, most of the Los Alamos Pu(III) sample is eluted with 0.2 and 0.3 M HCl, but ~30% of the plutonium requires 2 M HCl containing 0.05 M hydroquinone and 6 and 9 M HCl. This contrasts with the results at Mainz where the Pu(III) was not eluted until 1.2 M HCl was used. At Los Alamos, however, Pu(III) undergoes some sort of chemical reaction when in contact with ZP-1. The Pu(III) was placed on a ZP-1 column and allowed to stand for 5 hours before elution was started. About 38% as much plutonium was eluted when 0.2 and 0.3 M HCl was used and two

times as much when 2 M HCl containing hydroquinone was used, as was observed in a parallel experiment in which elution was started immediately.

Los Alamos results with Pu(IV) are similar to the Mainz results in that most of the plutonium is eluted by using 2 M HCl that contains a reducing agent such as hydroquinone. In addition, ~25% of the Pu(IV) sample was eluted using 0.3 and 0.5 M HCl. This suggests a possible Pu(III) impurity in the Pu(IV), which must be confirmed.

The Pu(V) is readily eluted from ZP-1 by using 0.05 M HCl, but most of a sample of the Pu(IV) polymer remains on the column even when 12 M HCl is used. The group at Mainz has not yet reported results on these species.

Experiments with equimolar mixtures of Pu(III) and Pu(V) indicate that repropportionation can occur in contact with ZP-1. When the pH of the mixture was 4.3 at the time it was placed on the column, the elution pattern showed the presence of ~47% Pu(IV). In a companion experiment in which the starting solution had a pH of 1.4, only ~20% Pu(IV) was indicated. The concentrations of Pu(III) and Pu(V) in the original mixture were  $2 \times 10^{-6}$  M--small enough that homogeneous repropportionation is completely negligible.

To extend the work reported in a previous quarterly report,<sup>2</sup> experiments have been performed using ion exchange to characterize the products of Pu(IV) reactions at low concentrations.

The Pu(IV) in 3 M HCl was diluted to give a solution  $4.2 \times 10^{-6}$  in plutonium with a pH of 3.0. After about 17 hours, a sample was analyzed using ZP-1 as described above. The elution pattern was consistent with about 27% Pu(III), 27% Pu(V), 27% Pu(IV), and 14% polymer. However, another portion of the same solution did not react with Os(II), which indicates that ordinary monomeric Pu(IV) was not present. It was also noted that 84% of the plutonium present reacts rapidly with ceric sulfate; this indicates the presence of Pu(III) and/or Pu(V) because neither Pu(IV) nor the polymer reacts rapidly with this reagent. At present, the discrepancy between the ion exchange results and the Ce(IV) results is not understood.

In other experiments, Pu(IV) in 3 M HCl was diluted to give  $2.5 \times 10^{-7}$  M plutonium in solutions with pH 3.1 and 6.7. Samples of these mixtures were analyzed using columns of BioRad AG 50W-X2 resin that were modified by treatment with  $H_2O_2$ . The elution patterns were compared; reaction at pH 3.1 gave a product that eluted much as Pu(IV) does, even though the monomeric form was not present. An additional sample taken after 8 days at room temperature

essentially the same elution pattern. The immediate product of reaction at pH 6.7 was determined using a sample taken 2 minutes after the initial dilution. The results were compared with those from the previous sample: only one-third as much of the plutonium was eluted like Pu(IV), whereas nearly 40% behaved as polymer does. A sample taken after ~24 hours showed that ~20% of the plutonium had been lost to the walls and 65% was in a form not eluted with 12 M HCl (polymer). Another sample of the 24-hour mixture was centrifuged for 2 hours at 38 000 g. Samples of the centrifugate were analyzed by alpha counting. The concentration of "soluble" plutonium was found to be  $3 \times 10^{-8}$  M, which indicates that 88% of the original plutonium had been removed. A sample of the centrifugate was analyzed as before, and the elution pattern indicated that the "soluble" plutonium is primarily Pu(V) or Pu(VI). These results are in good agreement with those of Rai and Swanson,<sup>3</sup> whose data indicate that the solubility of flocculated polymer is  $2.7 \times 10^{-8}$  M at pH 6.7 and that the principal oxidation state is Pu(V) or Pu(VI).

#### B. Preliminary Assessment of Important Radionuclide Species and Available Thermodynamic Data (J. F. Kerrisk)

A variety of waste types ultimately could be stored at a Yucca Mountain repository. Depending on whether spent fuel or waste from reprocessed fuel is stored, the actual waste form can have a significant effect on the inventory of certain radionuclides and how they might leach from the waste if water entered the repository. To provide some preliminary guidance for thermodynamic (solubility, speciation, and oxidation-reduction) data collected for geochemical modeling, existing calculations of radionuclide inventories in spent light-water reactor (LWR) fuel and waste have been reviewed and compared with proposed EPA limits on radionuclide release. A preliminary review of available thermodynamic data in the EQ3/6 data base and from other sources has been done for elements with important radionuclides.

1. Radionuclide Inventories and EPA Limits. Early studies of waste management facilities estimated the total activity in fuel and waste that will be stored in repositories. One such study at Oak Ridge National Laboratory listed radionuclide inventories from LWR fuel as a function of time after irradiation.<sup>4</sup> These calculations ran to 3 years for fuel and to 1000 years for waste. The EPA has recently published proposed environmental standards

for management and disposal of spent fuel and high-level waste;<sup>5</sup> release limits were proposed for some specific radionuclides, and general release limits were proposed for other alpha-emitting and nonalpha-emitting radionuclides.

Table II lists data for radionuclide inventories and the EPA release limits both for radionuclides specifically mentioned in the proposed standards and for other long-lived radionuclides. The data are for wastes generated from reprocessing spent LWR fuel and for decay times of 10, 100, and 1000 years (assuming total release at these times). It is assumed that the waste contains all fission products, 0.5% of the uranium and plutonium in the spent fuel, and all other actinides in the spent fuel. Fuel burnup was 33 000 MWD/MTEH (megawatt days/metric ton of heavy metal) at a power of 30 MW/MTEH. Table II also shows the ratio of the waste content to the EPA release limit for the various radionuclides. Large values of this ratio indicate that these radionuclides must be well isolated from the environment; values <1 indicate that the total quantity of radionuclides in the waste is less than the EPA release limit.

If spent fuel instead of processed waste is stored, the data listed in Table II would still apply for most radionuclides except those of uranium and plutonium. Activities and activity-to-EPA-limit ratios for radionuclides of uranium and plutonium can be obtained by multiplying the corresponding values in Table II by 200.

Fuel-element cladding and reactor internal parts also contribute radioactive waste, and data for both are also available for an LWR.<sup>4</sup> Long-lived radioactive isotopes are mostly from the elements cobalt, nickel, iron, zirconium, and niobium. No review of data for these five elements was included here because it is uncertain whether they will be part of the waste. The proposed EPA standards mention only spent reactor fuel and transuranic wastes.<sup>5</sup>

2. Radionuclide Thermodynamic Data. Thermodynamic data relating to solubility, speciation, and oxidation-reduction are available for many of the elements listed in Table II. The data, as collected and used, apply to all isotopes of a given element.

TABLE II  
LWR PROCESSED WASTE DATA

Nuclide	Half-Life (years)	EPA Release Limit <sup>a</sup> (Ci/1000 MTHM)	LWR Processed Waste <sup>b</sup> (Ci/1000 MTHM)			Waste Content-to-EPA-Limit Ratio		
			10 Years	100 Years	1000 Years	10 Years	100 Years	1000 Years
241Am	460	10	$1.8 \times 10^5$	$1.6 \times 10^5$	$4.2 \times 10^4$	$1.8 \times 10^4$	$1.6 \times 10^4$	$4.2 \times 10^3$
243Am	$8 \times 10^3$	4	$1.7 \times 10^4$	$1.7 \times 10^4$	$1.6 \times 10^4$	$4.3 \times 10^3$	$4.3 \times 10^3$	$4.0 \times 10^3$
14C	$5.7 \times 10^3$	200	N.A. <sup>c</sup>	N.A.	N.A.	—	—	—
135Cs	$3 \times 10^6$	2000	290	290	290	$1.5 \times 10^{-1}$	$1.5 \times 10^{-1}$	$1.5 \times 10^{-1}$
137Cs	30	500	$9.5 \times 10^7$	$1.1 \times 10^7$	$1.0 \times 10^{-2}$	$1.9 \times 10^5$	$2.2 \times 10^4$	$2.0 \times 10^{-5}$
237Np	$2 \times 10^6$	20	540	540	570	27	27	29
238Pu	86	400	$1.0 \times 10^5$	$5.2 \times 10^4$	130	250	130	$3.3 \times 10^{-1}$
239Pu	$2 \times 10^4$	100	$1.7 \times 10^3$	$1.7 \times 10^3$	$2.1 \times 10^3$	17	17	21
240Pu	$6.6 \times 10^3$	100	$4.5 \times 10^3$	$8.9 \times 10^3$	$8.2 \times 10^3$	45	89	82
242Pu	$4 \times 10^5$	100	6.8	6.9	7.1	$6.8 \times 10^{-2}$	$6.9 \times 10^{-2}$	$7.1 \times 10^{-2}$
226Ra	$1.6 \times 10^3$	3	N.A.	N.A.	N.A.	—	—	—
90Sr	28	80	$6.0 \times 10^7$	$6.6 \times 10^6$	$1.5 \times 10^{-3}$	$7.5 \times 10^5$	$8.3 \times 10^4$	$1.9 \times 10^{-5}$
99Tc	$2 \times 10^5$	$1 \times 10^4$	$1.4 \times 10^4$	$1.4 \times 10^4$	$1.4 \times 10^4$	1.4	1.4	1.4
126Sn	$1 \times 10^5$	80	550	550	550	6.9	6.9	6.9
79Se	$7 \times 10^4$	500	390	390	390	$7.8 \times 10^{-1}$	$7.8 \times 10^{-1}$	$7.8 \times 10^{-1}$
87Rb	$5 \times 10^{10}$	500	$2.0 \times 10^{-2}$	$2.0 \times 10^{-2}$	$2.0 \times 10^{-2}$	$4.0 \times 10^{-5}$	$4.0 \times 10^{-5}$	$4.0 \times 10^{-5}$
93Zr	$1.5 \times 10^6$	500	$1.9 \times 10^3$	$1.9 \times 10^3$	$1.9 \times 10^3$	3.8	3.8	3.8
129I	$2 \times 10^7$	500	38	38	38	$7.6 \times 10^{-2}$	$7.6 \times 10^{-2}$	$7.6 \times 10^{-2}$
151Sm	90	500	$1.1 \times 10^6$	$5.2 \times 10^5$	400	$2.2 \times 10^3$	$1.0 \times 10^3$	$8.0 \times 10^{-1}$
236U	$2 \times 10^7$	10	1.3	1.3	1.5	$1.3 \times 10^{-1}$	$1.3 \times 10^{-1}$	$1.5 \times 10^{-1}$
238U	$4.5 \times 10^9$	10	1.6	1.6	1.6	$1.6 \times 10^{-1}$	$1.6 \times 10^{-1}$	$1.6 \times 10^{-1}$
241Pu	13	10	$3.4 \times 10^5$	$2.8 \times 10^3$	-0	$3.4 \times 10^4$	280	-0
242Am	150	10	$3.9 \times 10^3$	$2.6 \times 10^3$	42	390	260	4.2
243Cm	32	10	$3.3 \times 10^3$	460	-0	330	46	-0
244Cm	18	10	$1.7 \times 10^6$	$5.5 \times 10^4$	-0	$1.7 \times 10^5$	$5.5 \times 10^3$	-0

<sup>a</sup>Data from Ref. 5.

<sup>b</sup>Data from Ref. 4.

<sup>c</sup>Data not available in Ref. 4.

### Uranium

Several recent reviews of uranium thermodynamics are available.<sup>6-13</sup> Uranium data in the EQ3/6 data base are mostly from the review of Langmuir<sup>6</sup> and have not been updated for about 3 years. They probably should be reviewed, but except for any role carbonate might play in determining uranium solubility at Yucca Mountain, this is not a high-priority item.

### Plutonium

Thermodynamic data on plutonium have been recently reviewed also.<sup>7-11,13,14</sup> The data in the EQ3/6 data base are from the review of Lemire and Tremaine.<sup>7</sup> Questions have been raised concerning the stability of Pu(IV)-carbonate complexes; these questions must be answered experimentally.<sup>15</sup> Other questions will undoubtedly surface as calculations are compared with experiments or as new data are reported for plutonium.

### Americium

There are no data for americium in the EQ3/6 data base at this time. Some thermodynamic data have been measured and some were estimated for this element.<sup>8,9,11,16</sup> Americium probably forms carbonate complexes, which may be important in determining its solubility at Yucca Mountain. Considering the importance of some americium isotopes (Table II) and the uncertainty of the americium data base, work on this element should be given a high priority. (Research is now under way at the Technical University of Munich, West Germany.)\*

### Neptunium

There are no data for neptunium in the EQ3/6 data base. The neptunium thermodynamic data base is as uncertain as the americium data base; some experimental data and some estimates are available.<sup>8-11,13</sup> Carbonate may also be important with neptunium. Only one neptunium isotope appears in Table II; it does not appear to be quite as important as americium.

---

\*From information provided by J. I. Kim, Technical University of Munich, Munich, West Germany.

### Curium

There are no data for curium in the EQ3/6 data base. Fewer thermodynamic data were found for curium in recent reviews than for americium or neptunium.<sup>8,9,11</sup> The two curium isotopes shown in Table II have relatively short half-lives and may not require long-term isolation.<sup>5</sup>

### Carbon

No estimates of the inventory of  $^{14}\text{C}$  were found in Ref. 4. With the exception of organics, which appear to exist in relatively small quantities in Yucca Mountain water, the only soluble carbon species should be carbonate. The chemistry of carbonate is relatively well known and is included in the EQ3/6 data base. Gaseous species containing carbon (for example,  $\text{CO}_2$  and  $\text{CH}_4$ ) must also be considered.

### Cesium

Data for two cesium complexes are in the EQ3/6 data base. Cesium, like the other alkali metals, does not form strong complexes or highly insoluble solids; thus, solubility and speciation may not be important in limiting cesium transport. The formation constant for one of the cesium complexes in the EQ3/6 data base ( $\text{CsCl}^\ominus$ ) differs significantly from the data in other compilations;<sup>8,9,12</sup> this discrepancy should be investigated.

### Radium

No data for radium are in the EQ3/6 data base. Also, no estimates of the inventory of  $^{226}\text{Ra}$  in spent fuel or waste were found in Ref. 4. The isotope  $^{226}\text{Ra}$  is part of the  $^{238}\text{U}$  decay chain. Once the decay chain is in equilibrium, the activity of  $^{226}\text{Ra}$  will be the same as  $^{238}\text{U}$  in spent fuel; that is, ~320 Ci/1000 MTHM. This would give a ratio of waste content to EPA limit of ~100 for  $^{226}\text{Ra}$ . However, because of the long half-life of its precursors, a period of  $10^5$  years is required for  $^{226}\text{Ra}$  to become equal to  $^{243}\text{Am}$ . One reference to thermodynamic data for radium species was found,<sup>8</sup> and further data might be estimated because of the similarity with the chemistry of barium.

### Strontium

Some data for strontium complexes and solids are in the EQ3/6 data base. Numerous compilations containing strontium thermodynamic data also

exist.<sup>8,9,13</sup> The isotope  $^{90}\text{Sr}$  has a relatively short half-life and may only be important during the early history of a repository. In Yucca Mountain water, strontium solubility may be limited by strontianite ( $\text{SrCO}_3$ ); a recent comparison of the data for strontianite in the EQ3/6 data base with other data sources indicates that the EQ3/6 data may be based on older measurements. A review of strontium thermodynamic data is under way.

#### Technetium

There are no data for technetium in the EQ3/6 data base. A number of compilations do list technetium thermodynamic data.<sup>8,9,13</sup> The inventory of  $^{99}\text{Tc}$  is not large compared to the EPA limit.

#### Tin

There are no data for tin in the EQ3/6 data base; however, thermodynamic data are available in a number of compilations.<sup>8,9,12,13</sup> From Table II, it appears that  $^{126}\text{Sn}$  is a moderately important isotope.

#### Selenium

There are no data for selenium in the EQ3/6 data base; however, thermodynamic data exist in a number of compilations.<sup>8,12</sup> Selenium, unlike most of the other radionuclides, should normally exist as an oxyanion in aqueous solution. Thus, its complexes with other cations in Yucca Mountain should be investigated. The inventory of radioactive selenium in spent fuel and waste is small compared to the EPA limit (Table II); therefore, work on this element may be given a lower priority.

#### Rubidium

There are no data for rubidium in the EQ3/6 data base; however, some thermodynamic data exist in compilations.<sup>8,12</sup> Like cesium, rubidium does not form strong complexes or highly insoluble solids. The activity of  $^{87}\text{Rb}$  is quite low because of its long half-life (Table II). Work on rubidium may be given low priority.

#### Zirconium

There are no data for zirconium in the EQ3/6 data base; however, some thermodynamic data exist in compilations.<sup>8,9,12</sup> Based on the activity of  $^{93}\text{Zr}$

and the EPA limit, work on zirconium should be given about the same priority as that for technetium and tin.

### Iodine

There are no data on iodine in EQ3/6; however, some thermodynamic data exist on iodide and iodate species.<sup>8,12</sup> Considering the low activity of <sup>129</sup>I in waste, work on this element may be given a low priority (Table II).

### Samarium

There are no data on samarium in the EQ3/6 data base; however, some thermodynamic data exist in compilations.<sup>8,9,12</sup> The isotope <sup>151</sup>Sm has a relatively short half-life and a high activity early in the life of a repository. In this respect, it is similar to cesium and strontium.

**3. Conclusions.** Based on the previous discussions and the data in Table II, the following priorities are proposed for collecting thermodynamic data to be used in geochemical modeling and for use of these data in preliminary sensitivity analyses.

- (1) Americium - add data to EQ3/6 data base and use for sensitivity analyses.
- (2) Neptunium and curium - add data to EQ3/6 data base and use for sensitivity analyses.
- (3) Carbon and radium - determine the importance of carbon and radium isotopes and rank them in this priority list.
- (4) Strontium and cesium - review existing EQ3/6 data and modify as needed.
- (5) Samarium - add data to EQ3/6 data base and use for sensitivity analyses.
- (6) Uranium and plutonium - continue review of existing EQ3/6 data.
- (7) Technetium, tin, and zirconium - add data to EQ3/6 data base and use for sensitivity analyses.
- (8) Selenium, rubidium, and iodine - add data to EQ3/6 data base and use for sensitivity analyses.

Collection and review of data for other species that may be important for general water chemistry at Yucca Mountain (manganese, zeolites, or clays, for example) must be combined with the above priorities. If radionuclides from cladding and reactor internal parts must be considered as well, work on those elements will be necessary.

### C. Natural Chemical Analogues (R. J. Vidale)

Data that will be useful for predicting the effect of a thermal pulse on the tuffs at Yucca Mountain and for validating chemical models can be obtained by examining natural analogues that have formed over long periods of time. Such natural analogues include: (1) mineral phase assemblages and water compositions of appropriate hot springs, (2) rock core taken at the north end of Yucca Mountain in the hydrothermally altered tuff, (3) samples of NTS tuff in the unsaturated zone that have been altered by the intrusion of a hot diabase dike, and (4) core and water data from boreholes in appropriate geothermal regions where good temperature logs are available. Investigation of the first group of analogues is nearly completed.

Four hot-spring localities have been sampled: (1) Bailey Hot Springs, Beatty, Nevada, (2) Steamboat Springs, Nevada, (3) three hot springs in the ring-fracture zone of the Valles Caldera in the Jemez Mountains, New Mexico, and (4) Sou Hot Springs (also known as Seven Devils Hot Springs) in Dixie Valley, Nevada. The spring water has been analyzed and mineral phase assemblages have been determined for 29 samples. The common minerals present are quartz, cristobalite, alkali feldspar, calcite, and mica. These are the original high-temperature phases of the volcanic tuff. The low-temperature alteration phases, such as clays and zeolites, have moved out of the rock and left it porous and friable. Extensive fine-grained clayey deposits were noted near the springs and will be sampled in New Mexico.

Alteration minerals typical of extremely acid environments were found at Bailey Hot Springs and Steamboat Springs. Such environments are known to exist in the vapor-dominated upper regions of hot-spring systems where atmospheric oxygen has moved down into the pore space in the upper strata. The oxidation of pyrite under these warm, oxygen-rich conditions produces pH values as low as 1 or 2.

It is important to consider possible degradation of the structural strength of Yucca Mountain tuff in regions where a flow (or trickle) of warm water might occur and cause the rock to become porous and friable, like the rock found in the hot springs. It is also important to note the amount of pyrite present in the rock where it is exposed to air in the warm near-field region of the repository and, if necessary, prevent the formation of a highly acid environment.

D. Permeability, Porosity, and Hydrothermal Reactions (C. J. Duffy)

The permeability, storage capacity, pore compressibility, and porosity have been measured on a sample of the Topopah Spring Member from Busted Butte. Solution analysis techniques have been developed for water samples from the gold bag hydrothermal experiments.

Hydraulic measurements on the Busted Butte sample are important for a variety of reasons, particularly in unsaturated tuff. Permeability will determine the rate at which water would be pulled out of a saturated fracture into the tuff matrix in response to the matric potential. This is important for understanding both infiltration of rain water into Yucca Mountain and the possible uptake of waste-element-bearing solutions by the tuff matrix. The porosity is particularly important for understanding the diffusion of waste elements into the pore space of the tuff matrix.

Measurements of permeability, storage capacity, and pore compressibility are made as a function of effective confining pressure. Porosity is measured on unconfined samples. By measuring pore compressibility and storage capacity, it is possible to determine the effect of confining pressure on porosity. The measurements made this quarter indicate that confining pressure in Yucca Mountain might lead to a reduction in the porosity that is as high as 10 to 20% for this particular rock. Additional experiments are under way to make these measurements more precise.

Gold bag hydrothermal experiments are directed toward understanding groundwater chemistry and mineral stability in Yucca Mountain (most particularly in the case of zeolites). At this time there are no measured thermodynamic data for the zeolites clinoptilolite and mordenite. It may be possible to obtain such data from calculations involving the measured equilibrium composition of solution and zeolite. Work this quarter has focused primarily on determining fluid composition. It appears that the necessary

cation concentration measurements that reflect the actual composition of the fluid at pressure and temperature can be made; however, carbonate analyses are difficult because of carbon dioxide exchange between the solution and the atmosphere in which the analysis takes place.

These experiments are particularly important for determining the parameters that control zeolite stability, particularly clinoptilolite, in Yucca Mountain. Field observations indicate that the transformation of clinoptilolite to analcime plus quartz may be an important reaction in Yucca Mountain. It has been generally assumed that this reaction is temperature controlled. An alternate explanation is that clinoptilolite stability is largely controlled by the silica activity and that high silica activity favors clinoptilolite stability. High silica activity, and therefore the presence of clinoptilolite, would be caused by the presence of metastable silica phases such as glass or cristobalite. Low silica activity, and hence the stability of analcime or alkali feldspar, would be caused by quartz crystallization. This explanation is supported by the observation that clinoptilolite in Yucca Mountain generally exists with cristobalite, whereas analcime coexists with quartz.

The fluid analysis of a 150°C gold bag experiment with a clinoptilolite-bearing tuff from the upper Calico Hills tends to support this view; the solution contained 470 mg/l  $\text{SiO}_2$ , which is well above the ~160 mg/l that would indicate equilibrium with quartz.

E. Plutonium Sorption from a Flowing Solution (J. L. Thompson, P. Q. Oliver, and W. R. Daniels)

The tuff used in these experiments, G-1-1292 from the Topopah Spring Member, is 80 to 90% glass, 10 to 20% alkali feldspar, and 5 to 10% cristobalite. The tuff was crushed and sieved, and the 75- to 150- $\mu\text{m}$  fraction was retained. The tuff was contained in plastic columns 5 cm long and 1  $\text{cm}^3$  in volume. Flow rates were 0.15 to 0.025 ml/hour, which corresponds to about 100 to 17 m/year. Although the overall flow rate is slow, nothing can be said about the flow rate through the tuff particles inside the column because the flow paths may be around the crushed particles. The solution was introduced in a continual feed mode through a plastic syringe controlled by a Sage pump, and the effluent was collected dropwise with a fraction collector or in

weighed vials. Tritiated water was employed to monitor the transport of the solvent through the columns. Plutonium and tritium activities were measured by liquid scintillation counting. The plutonium feed solution was prepared by air-drying an acid solution, redissolving it in filtered, rock-equilibrated groundwater, and then filtering the solution through a 0.05- $\mu$ m Nuclepore filter to remove any colloids or particulates. The pH of the solution was ~8.3. Part of the solution and part of the tuff were used in batch sorption experiments that were run simultaneously with the column experiments.

At a flow rate of 0.15 ml/hour, the plutonium elution was not delayed relative to that of tritiated water. At flow rates of 0.074, 0.041, and 0.025 ml/hour, the plutonium was eluted slightly after the tritiated water ( $R_f = 1.5$ ). The activity of the eluted plutonium was 40 to 60% that of the feed solution. When the columns were flushed to remove the sorbed radionuclides, the tritium came off completely, whereas the low-activity plutonium formed a long elution "tail". During the course of the flow experiments, the specific activity of the feed solution was periodically checked; it decreased ~20% during the 4-day period. Acid rinses of the syringe indicated that some plutonium had adhered to the walls of this container. The  $R_d$  sorption ratio of the same crushed tuff, as determined by the batch methodology after a 3-week contact period, was 160 ml/g.

The columns behaved normally with respect to tritiated water; consistent breakthrough volumes resulted from the duplicated columns, repeated runs on the same column, and runs with different flow velocities. The plutonium feed solution gave an  $R_d$  sorption ratio consistent with previous determinations on tuffs of similar composition. The remarkable result was that although some plutonium sorbed on the columns, 40 to 60% did not. Had the plutonium sorbed on the column to the extent predicted on the basis of the batch-determined  $R_d$ , the retention factor  $R_f$  from the column experiment would have been several hundred, not 1.5. Four possible explanations for our experimental observations are that: (1) even at this slow flow rate, most of the flow is around the particles and diffusion into the matrix is slow; (2) the plutonium species in the feed solution require an appreciable contact period (>1 day but <3 weeks) to be sorbed; that is, there is a kinetic aspect to the sorption process; (3) a portion of the plutonium species in the new feed solution does not sorb; however, this would require that speciation changes occurring over a period of days produce products that do sorb strongly; or (4) some plutonium

was sorbed on particulate matter and was washed out from the column. Future experiments may lead to a better understanding of plutonium sorption from a flowing solution.

#### F. Sorption Experiments with Strontium, Cesium, Barium, Europium, and Technetium (S. D. Knight)

Batch sorption measurements with  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{133}\text{Ba}$ ,  $^{152}\text{Eu}$ , and  $^{95}\text{Tc}^{\text{m}}$  and tuff samples from Drill Holes USW G-2 and USW GU-3 were performed. The samples listed in Table III were selected because they have a high abundance of alkali feldspar, calcite, mordenite, quartz, and analcime--minerals whose sorptive behavior has not been fully characterized. This sorptive behavior must be known in order to predict retardation of radionuclides along the flow path. Some of the samples are from the unsaturated zone, an area from which few samples have been studied.

Results available to date are given in Tables IV and V; further results will be presented in the next quarterly report.

In preliminary observations, sorption ratios for strontium, cesium, and barium are high for sample G-2-1952, which contains mordenite. Sorption of europium is highest on sample G-2-723, which is high in calcite. Sorption ratios for technetium are essentially zero for all samples. Some of the ratios for desorption are less than those for sorption. (This is not a frequent observation.) Europium, as usual, does not desorb as readily.

In an additional set of experiments performed concurrently, the samples were shaken with the 40-ml centrifuge tubes in a horizontal position rather than the vertical position normally used. This is a minor improvement to the technique; horizontal shaking should provide more efficient mixing and will be used where possible and been studied.

The results from the two methods of shaking are in agreement for the 6-week contact periods. The rate of reaching a constant value with the new method is still to be determined. It is expected that equilibrium will be reached in a shorter time, thus shortening the experiment periods.

TABLE III  
X-RAY DIFFRACTION ANALYSIS OF SAMPLES FROM USW G3 AND GU-3<sup>a</sup>

Sample	Depth (m)	Abundance (%)										
		Saeco- tite	Mica	Clino- ptilolite	Mordenite	Anat- cine	Quartz	Cristo- balite	Tridy- mite	Alkali Feldspar	Calcite	Glass
USW G-2-547	166.7	5-15	<5					5-15		10-20		40-60
USW G-2-723	220.4	5-15	<5					<5		5-10	30-50	15-30
USW G-2-1952	595.0		<5	5-10	40-60		10-20	10-20		10-20		
USW G-2-3933	1198.8	10-20				20-40	20-40			20-40	5-10	
USW GU3-430.5	131.2							10-15	2-6	75-85		
USW GU3-1302.4	397.0	1-3					2-6	10-15		35-45		30-60

<sup>a</sup>Data for the USW G-2 samples are taken from Ref. 17. Data for USW GU-3 samples that are near the samples studied in this section are taken from Ref. 18. The actual USW GU-3 samples that were studied will also be analyzed.

TABLE IV  
SORPTION RATIOS FOR STRONTIUM, TECHNETIUM, CESIUM,  
BARIUM, AND EUROPIUM ON SEVERAL USW G-2 SAMPLES

Sample	Type <sup>a</sup>	Element	R <sub>d</sub> (mg/g)		Average <sup>b</sup>
			Experimental	Average <sup>b</sup>	
USW G-2-347	Sorption	Sr	256	275	265 (10)
"	"	Tc	0.031	-0.056	0
"	"	Cs	11 900	14 800	13 300 (1 500)
"	"	Ba	3 460	3 520	3 490 (30)
"	"	Eu	360	414	390 (30)
"	Desorption	Sr	217	195	206 (11)
"	"	Tc	0	0	0
"	"	Cs	9 450	8 360	8 900 (550)
"	"	Ba	3 069	2 740	2 900 (170)
"	"	Eu	1 070	2 330	1 700 (630)
USW G-2-723	Sorption	Sr	326	248	290 (40)
"	"	Tc	0.020	-0.008	0
"	"	Cs	4 620	3 530	4 080 (550)
"	"	Ba	3 930	3 080	3 500 (430)
"	"	Eu	>10 000	>10 000	>10 000
"	Desorption	Sr	326	332	330 (4)
"	"	Tc	0	0	0
"	"	Cs	4 280	4 276	4 280 (4)
"	"	Ba	4 200	4 217	4 210 (10)
"	"	Eu	>10 000	>10 000	>10 000
USW G-2-1952	Sorption	Sr	1 940	2 560	2 200 (350)
"	"	Tc	-0.039	+0.022	0
"	"	Cs	61 300	63 400	63 300 (1 100)
"	"	Ba	21 500	28 700	25 000 (3 700)
"	"	Eu	75	103	89 (14)
"	Desorption	Sr	4 390	4 080	4 200 (180)
"	"	Tc	0	0	0
"	"	Cs	47 070	44 650	46 000 (1 400)
"	"	Ba	46 050	34 400	40 000 (6 000)
"	"	Eu	1 770	1 470	1 600 (200)
USW G-2-3933	Sorption	Sr	192	299	240 (60)
"	"	Tc	0.042	0.167	0.1 (0.06)
"	"	Cs	1 580	3 490	2 500 (1 000)
"	"	Ba	1 240	2 220	1 700 (500)
"	"	Eu	687	2 230	1 500 (700)
"	Desorption	Sr	117	164	140 (24)
"	"	Tc	0	0	0
"	"	Cs	1 105	1 750	1 400 (350)
"	"	Ba	905	1 300	1 100 (200)
"	"	Eu	1 950	4 060	3 000 (1 100)

<sup>a</sup>Six-week periods for both sorption and desorption experiments.

<sup>b</sup>Numbers in parentheses are standard deviations of the means. Fraction size for all samples was <500 μm.

TABLE V  
 SORPTION RATIOS FOR STRONTIUM, TECHNETIUM, CESIUM, BARIUM  
 AND EUROPIUM ON SEVERAL USW GU-3 SAMPLES

Sample	Sorption Time (weeks)	Shaking Position	Element	$R_d$ (mR/g)		
				Experimental		Average <sup>a</sup>
USW GU-3-433	6	Horizontal	Sr	56	66	61 (6)
"	"	"	Tc	0.05	-0.004	0
"	"	"	Cs	613	651	630 (20)
"	"	"	Ba	708	912	810 (100)
"	"	"	Eu	86	113	100 (14)
"	"	Vertical	Sr	31.6	28.2	30 (2)
"	"	"	Tc	0.05	0.1	0.07 (0.02)
"	"	"	Cs	436	370	400 (40)
"	"	"	Ba	392	290	340 (50)
"	"	"	Eu	55	82	68 (14)
USW GU-3-1301	"	Horizontal	Sr	25	40	32 (8)
"	"	"	Tc	0.04	0.03	0.03 (0.004)
"	"	"	Cs	125	195	160 (35)
"	"	"	Ba	512	629	570 (60)
"	"	"	Eu	64	87	75 (12)
"	"	Vertical	Sr	23	25	24 (1)
"	"	"	Tc	0.03	0.05	0.04 (0.01)
"	"	"	Cs	109	135	120 (15)
"	"	"	Ba	370	460	420 (50)
"	"	"	Eu	31	44	38 (7)

<sup>a</sup>Numbers in parentheses are standard deviations of the means.

## G. Sorption Experiments with Americium, Plutonium, and Neptunium

(F. O. Lawrence and M. R. Cisneros)

Batch sorption measurements have been made using USW G-2 cores (see previous section) and americium-, plutonium-, and neptunium-traced groundwaters. Measurements are being made on three USW GU-3 cores. Only one core in this series, USW G-2-1952, has been investigated with neptunium tracer. The neptunium was prepared from that produced at the Los Alamos Van de Graaff accelerator in 1982. Since that time, some neptunium tracer has become available from Argonne National Laboratory; it is expected to arrive shortly and will be used in batch studies with the USW GU-3 cores.

In the batch studies performed with USW GU-3 cores, the configuration and temperature are varied during the sorption measurements. Duplicate sets are agitated either horizontally, vertically at room temperature, or vertically in a water bath heated to 85°C. The plutonium batch studies will also include investigations to determine whether plutonium in traced feed solutions and sorption samples acts in a cationic or anionic manner.

Sorption ratios for USW G-2 cores and actinide-traced feeds are listed in Table VI.

Very high sorption ratios are observed for americium and plutonium for sample G-2-723, the sample containing calcite (Table III). Relatively low values are observed for all three elements for sample G-2-1952 (mordenite). These two trends were also observed for europium in the previous section.

The results from the two shaking methods agree.

## H. Other Sorption Experiments (B. P. Bayhurst)

Experiments with uranium and selenium were begun on 14 tuff samples selected for representative variations in mineralogy. The experiments with radium were delayed because the  $^{226}\text{Ra}$  was not delivered until mid-March.

## I. Chlorine-36 Analyses of Groundwater (K. Wolfsberg, H. W. Bentley, and P. L. Wanek)

The nuclide  $^{36}\text{Cl}$  (half-life  $3.01 \times 10^5$  year) is a useful tool for dating old groundwater and inferring rates of underground water movement of both

TABLE VI  
PRELIMINARY BATCH SORPTION VALUES FOR AMERICIUM, PLUTONIUM,  
AND NEPTUNIUM ON SELECTED USW G-2 CORES UNDER AMBIENT CONDITIONS

Core	Isotope	$R_d$ Values (ml/g)	
		Experimental	Average <sup>a</sup> of Duplicate Measurements
USW G-2-547	<sup>241</sup> Am	13 000	13 000 (110)
		13 000	
USW G-2-723	<sup>241</sup> Am	930 000	890 000 (49 000)
		840 000	
USW G-2-1952	<sup>241</sup> Am	1 800	1 800 (70)
		1 700	
		1 700 <sup>b</sup>	1 600 (80)
		1 500 <sup>b</sup>	
USW G-2-3933	<sup>241</sup> Am	7 000	6 600 (370)
		6 200	
USW G-2-1952	<sup>235</sup> Np	2.7	2.7 (0.1)
		2.65	
USW G-2-547	<sup>239</sup> Pu	960	1 200 (200)
		1 400	
USW G-2-723	<sup>239</sup> Pu	>10 000	>10 000
		>10 000	
USW G-2-1952	<sup>239</sup> Pu	77	83 (6)
		88	
		57 <sup>b</sup>	59 (2)
		61 <sup>b</sup>	
USW G-2-3933	<sup>239</sup> Pu	1 500	1 600 (50)
		1 600	

<sup>a</sup>The values in parentheses are the standard deviations of the means.

<sup>b</sup>Rock/water contacts were made using a vertical position for the container. All others were made using a horizontal position.

recent and long time spans.<sup>19</sup> It is produced cosmogenically, and normal ratios of  $^{36}\text{Cl}$  to total chlorine ( $^{35}\text{Cl} + ^{37}\text{Cl}$ ) of  $(600 \pm 100) \times 10^{-15}$  are expected for new meteoritic waters recharging the area around the NTS. Indeed, a ratio of  $634 \times 10^{-15}$  was observed in water from Well 5B, which samples the alluvial aquifer at a depth of 229 to 274 ft in Frenchman Flat. The laboratory blank for reagent NaCl is  $1 \times 10^{-15}$ .

A sample of water taken from the packed off interval in Well UE-25b#1 between 2840 and 2870 ft (Ref. 18) gave a ratio of  $370 \times 10^{-15}$ . This single measurement could suggest an age of  $3 \times 10^5$  years, which is significantly older than the  $^{14}\text{C}$  age dates\* ( $9 \times 10^3$  to  $2 \times 10^4$  years) for waters from a number of wells in the area. The older apparent  $^{36}\text{Cl}$  value may be real, may be caused by mixing the meteoric water with older residual chloride, or may be the result of additional dissolution of chlorine containing no  $^{36}\text{Cl}$ . The latter may be attributable to chlorine from the lithium chloride that is used to tag drilling fluids or to the chlorine added to test a packer. Analyses done during the pumping of the well<sup>18</sup> did not show a factor-of-2 variation in the chloride concentration.

More  $^{36}\text{Cl}$  analyses are planned to obtain information on the ages of waters in the area. These ages will be used to predict rates, volumes, and directions of water movement—all factors that are required to assess the possible transport of waste elements. A large global "pulse" of  $^{36}\text{Cl}$  was deposited between 1953 and 1964 from nuclear weapons testing in oceanic areas.<sup>20,21</sup> This pulse produced  $^{36}\text{Cl}$ -to-total chlorine ratios that are orders of magnitude higher than natural ratios. Bentley and Phillips\*\* have found the high  $^{36}\text{Cl}$  concentrations ~2 m below the surface in alluvium near Socorro, New Mexico. Measuring such profiles of the pulse is a potential help in measuring the infiltration ratio of recent waters; Los Alamos is exploring the possibility of applying this technique for NNWSI. The infiltration rate could help predict water movement in the unsaturated zone and estimate the transport rates of waste elements.

---

\* Taken from December 1982 draft of the NNWSI Site Characterization Report, Chapter 5, to be published by US DOE, Nevada Operations Office.

\*\* Information obtained from H. W. Bentley (Hydro Geo Chem, Inc., 744 North Country Club, Tucson, AZ 85716) and F. M. Phillips (New Mexico Institute of Technology, Socorro, NM 87801).

IV. MINERALOGY-PETROLOGY OF TUFF (D. L. Bish, D. E. Broxton, F. M. Byers, Jr., F. A. Caporuscio, B. A. Carlos, R. C. Gooley, S. S. Levy, R. E. Semarge, and D. T. Vaniman)

Final drafts were prepared for petrology reports on Drill Holes USW G-3 and GU-3 (Ref. 22) and USW H-3, H-4, and H-5 (Ref. 23). The major conclusions, summarized here, concern the nature and origin of zeolitized horizons at Yucca Mountain and the range of variability within horizons that provide major zeolite barriers against waste-element migration.

A. Zeolite Origins

The combined study of zeolitized samples from USW H-3, H-4, and H-5 (Ref. 23) suggests three episodes of zeolitization in the upper Crater Flat Tuff and overlying units. The earliest episode was shallow burial diagenesis of the tuff of Calico Hills and the upper Crater Flat Tuff before emplacement of the overlying Paintbrush Tuff. Evidence for this event is found in geopetal opal deposits that are parallel to bedding and occur between this earliest zeolite development and later zeolite growth. The second episode involved crystallization of heulandite and smectites during late-stage devitrification of the lower vitrophyre in the Topopah Spring unit. A third episode of zeolitization occurred after the Paintbrush Tuff and older units of Yucca Mountain were displaced downward to the east. At present, there is no evidence to correlate variability in zeolite composition with cycles of zeolite origin; depth rather than time of origin appears to be the controlling factor in zeolite composition.

B. Horizons of Zeolitization

The report on the petrology of USW G-3 and GU-3 (Ref. 22) points out the significant variation in alteration between samples from USW G-3/GU-3 and drill cores from farther north. This variation is most evident in the type and occurrence of zeolitization. The type of sorptive zeolitization in USW G-3/GU-3 is virtually restricted to clinoptilolite, with only rare development of mordenite in fractures; yet mordenite is common in drill cores to the north. The occurrence of zeolitization in USW G-3/GU-3 is very sparse above

the basal Prow Pass Member of the Crater Flat Tuff, whereas the overlying tuff of Calico Hills and the nonwelded to poorly welded base of the Topopah Spring unit are heavily zeolitized in drill cores to the north. Until the samples from USW G-3/GU-3 were available, there was reason to assume that the section of Calico Hills/basal Topopah Spring tuffs was a widespread and reliable zeolitized barrier against waste-element migration from any location higher in the Topopah Spring unit. Although this is not the case, it can be shown that thick, sorptive zeolite zones occur across the unsaturated zone pathways that lead away from the host rock throughout the exploration block at Yucca Mountain.

Data revealing the total amount of zeolites along pathways away from a repository in the Topopah Spring unit are needed to predict overall geochemical retardation at Yucca Mountain. In the saturated zone, these pathways are still poorly defined. In the unsaturated zone, however, it is reasonable to assume that the direction of transport is primarily downward, and it is possible now to assess the extent and composition of major zeolite barriers that would occur between a repository in the Topopah Spring unit and the static water level.

Table VII summarizes the data collected to date on zeolitization in four major intervals or horizons beneath the exploration block at Yucca Mountain. It is possible to identify commonly zeolitized intervals underlying the exploration block at Yucca Mountain. These four commonly zeolitized intervals are listed below.

Interval I: the zeolite- and clay-rich zone that commonly occurs at the top of the lower Topopah Spring vitrophyre. Zeolitization here may be a result of alteration concentrated along the devitrification front at the top of the vitrophyre. This is an interval where heulandite (isostructural with clinoptilolite but with lower thermal stability) occurs. This interval tends to be very thin (<3 m) except in UE-25a#1, where it passes directly into Interval II.

Interval II: the relatively thick zeolitized zone that may occur in the bedded, nonwelded, and poorly welded tuffs (and in some cases the lower vitrophyre) that form the base of the Topopah Spring unit and in the underlying tuff of Calico Hills. In this interval clinoptilolite predominates, although mordenite may also occur. An important aspect of this interval is its lateral inconsistency. It is completely vitric and unzeolitized in USW

TABLE VII  
COMMONLY ZEOLITIZED INTERVALS AT YUCCA MOUNTAIN<sup>a</sup>

	USW G-1 SWL=577 m deep	UK-25a#1 UK-25b#1H SWL=471 m deep	USW H-4 SWL=519 m deep	USW H-5 SWL=704 m deep	USW H-3 SWL=754 m deep	USW G-3 USW GU-3 SWL=754 m deep
<u>Interval I:</u> above the lower Topopah Spring vitrophyre	depth: 392 m  15% cpt	depth: 385 m  7% cpt	no samples	depth: 508 m  10% cpt	no samples	depth: 364 m  trace cpt
<u>Interval II:</u> base of the Topopah Spring unit, tuff of Calico Hills	depths: 427 to 565 m (138 m thick)  52% (+17) cpt	depths: 404 to 556 m (152 m thick)  67% (+6) cpt 17% (+20) mord	depths: 400 to 489 m (89 m thick)  63% (+13) cpt 8% (+12) mord	depths: 584 to 594 m (10 m thick)  37% cpt	VITRIC (nonzeolitized)	VITRIC (nonzeolitized)
<u>Interval III:</u> between the Prow Pass and Bullfrog units	depths: 622 to 706 m (84 m thick)  45% (+12) cpt 18% (+18) mord	depths: 636 to 710 m (74 m thick)  60% cpt and mord	no samples	depths: 655 to 689 m (34 m thick)  60% cpt	depths: 518 to 610 m (92 m thick)  68% cpt	depths: 571 to 614 m (43 m thick)  58% (+8) cpt
<u>Interval IV:</u> between the Bullfrog and Tran units	depths: 779 to 822 m (43 m thick)  37% (+6) cpt 15% (+11) mord	depths: 863 to 890 m (27 m thick)  4% (+4) cpt 16% (+10) mord	no samples	no samples	depths: 732 to 760 m (28 m thick)  52% (+17) cpt 18% (+13) mord	depths: 786 to 822 m (36 m thick)  36% (+8) cpt

<sup>a</sup>cpt = clinoptilolite and heulandite; mord = mordenite; and SWL = static water level.

GU-3 and in USW H-3; elsewhere, it is a zone of zeolitization that ranges from 9 m thick in USW H-5 to ~150 m thick in UE-25a#1. These large ranges in thickness indicate that this interval is thin or absent along the crest of Yucca Mountain but thickens dramatically downdip to the east and toward Drill Hole Wash.

Interval III: the poorly welded and bedded tuffs that occur between the Frow Pass and Bullfrog Members of the Crater Flat Tuff. This is another interval, like Interval II, in which clinoptilolite predominates, although mordenite may also occur. This interval is relatively thick (34 to 91 m) in all drill cores, although it occurs below the static water level at Drill Hole Wash (USW G-1 and UE-25a#1) and at the eastern edge of the exploration block (USW H-4).

Interval IV: the poorly welded and bedded tuffs that occur between the Bullfrog and Tram Members of the Crater Flat Tuff. Clinoptilolite is typically abundant in this interval, although mordenite predominates in one drill core (UE-25a#1). This interval varies in thickness from 27 to 44 m and occurs above the static water level only at the southern end of the exploration block (USW H-3 and USW G-3/GU-3).

Using these four intervals, it is possible to evaluate the zeolite abundance between a potential repository in the Topopah Spring unit and the underlying static water level for each of the six localities listed in Table VII. As a first approximation, one can calculate the cumulate equivalent thickness of 100% zeolite between a repository horizon in the Topopah Spring unit and the static water level:

$$T_z = \sum_1 (\text{per cent zeolite in interval } i) \cdot (\text{thickness of interval } i) ,$$

where  $T_z$  is the equivalent thickness of 100% zeolite (mordenite or clinoptilolite-heulandite) summed over each interval or portion of an interval down to the static water level. Interval I is not included in the summation because this interval is very thin and is still poorly constrained between drill holes. The equivalent thicknesses of 100% zeolite are summarized in Table VIII.

The data in Table VIII are preliminary and very approximate. Zeolite abundances can vary greatly within intervals, with standard deviations of

-10 to 35% in the clinoptilolite-heulandite estimates and often more than 100% in the mordenite estimates. However, within these errors, the cumulative abundance of zeolite between a repository in the Topopah Spring unit and the static water level remains typically equivalent to a column several tens of meters thick. This is a very simple treatment of a complex mineralogic and petrologic environment; nevertheless, it places the scale of zeolitization in proper perspective for pathways away from a repository in the unsaturated zone at Yucca Mountain.

#### V. VOLCANISM STUDIES (B. M. Crowe)

The purpose of volcanism studies in NNWSI is to assess the hazards of future volcanism with respect to disruption of a high-level waste repository in southern Nevada. Work on this project is almost complete; the conclusions are now being incorporated in papers for outside publication.

The date when the compositional switch from silicic volcanism to basaltic volcanism began is difficult to identify with certainty in the NTS region. Ekren et al.<sup>24</sup> place this event at sometime before 16 Myr for areas north of the NTS region. Christiansen and Lipman<sup>25</sup> argue that this transition started early in the Timber Mountain-Oasis Valley caldera (TM-OV) cycle. This argument is based on three lines of evidence: (1) the presence of high-silica rhyolite (75 to 79% SiO<sub>2</sub>) ash-flow sheets of composition similar to that of rhyolite in bimodal associations; (2) the local occurrence of basalt interbedded with ash-flow sheets around the caldera complexes; however, although these basalts are present locally, they are rare in outcrops and drill holes; and (3) the small volume of rocks of intermediate composition. Whatever the exact timing of this transition, basaltic volcanism became well established during the waning cycle of TM-OV volcanism. Accordingly, a cycle of basaltic volcanism has been identified that is closely related to silicic volcanism, and in many cases (perhaps most) it forms a bimodal basalt-rhyolite association. The basalts of this association are called the basalts of the silicic cycle (BSC). They are identified by a variety of characteristics, none of which is, by itself, unique. First, there is a close association, in location and time, with the silicic volcanic centers. Second, the BSC were generally large-volume eruptions (>3 km<sup>3</sup>), and their surface outcrops form major topographic features (shields or lava mesas). Third, the BSC exhibit a wide

TABLE VIII  
 THICKNESS OF 100% ZEOLITE ( $T_z$ ) BETWEEN A POTENTIAL REPOSITORY  
 IN THE TOPOPAH SPRING UNIT AND THE STATIC WATER LEVEL

Drill Hole	Equivalent Thickness <sup>a</sup> (m)
USW G-1	72 cpt
UE-25a#1/UE-25b#1H	44 cpt 11 mord
USW H-4	56 cpt 7 mord
USW H-5	24 cpt
USW H-3	74 cpt 4 mord
USW GU-3/USW G-3	38 cpt

<sup>a</sup> cpt = clinoptilolite and heulandite; mord = mordenite; expressed in meters of 100% zeolite.

range of composition (basalt to basaltic andesite or latite), a much wider range than other, younger basalt cycles. As defined, the BSC range in age from 12 to ~8.5 Myr, with a notable peak in occurrence at 10 Myr.

The second recognized cycle of basalts in the region is the older rift basalts (ORB). They are called rift basalts because of their structural association with active extensional faulting. The ORB are separate in location and time from the silicic volcanic centers. They occur either at sites well removed from the silicic centers or are younger than and cannot be related in time to the silicic magmatic suite. The ORB comprise small-volume (<1-km<sup>3</sup>), isolated centers that are widely scattered throughout the NTS region. They were erupted along or closely follow extensional faults, and field evidence suggests that they commonly were erupted contemporaneously with faulting. The ORB range in age from 9.1 to 6.3 Myr.

The third and youngest cycle of basalt volcanism is the younger rift basalts (YRB). These basalts are separated from the ORB on the basis of a

distinct age gap. Despite careful dating of almost all known basalts in the NTS region, no basalts have been found in the range of ~4 to 6 Myr. Thus, the YRB are defined to include all basalts younger than 4 Myr that followed this brief volcanic hiatus. They are very similar in volume and occurrence to the ORB, but their sites of activity are structurally controlled by a different set of faults. More important, their trace element compositions are significantly different from those of the ORB. The YRB range in age from 3.7 to 0.3 Myr.

Field work was conducted in several areas. A new trench was cut along the major boundary fault at the northwest end of the exploration block. This trench exposed the 10-Myr basalt dike called the dike of Yucca Mountain. Contrary to evidence from other outcrops, it is noted that the dike here has been affected by faulting. The dike on the east side of the west-dipping fault plane is completely bounded by faults, and there has been considerable tectonic brecciation of the dike. The west side of the fault consists of tectonic breccia of the Tiva Canyon Member, which has been locally sintered by intrusion of scoriaceous basalt apparently intruded into near-surface fault rubble at or slightly above the depth of magma fragmentation. This western side is a higher structural level of exposure of the fault than the eastern side, and the two sides have been juxtaposed by normal faulting that postdates dike emplacement.

Basalt samples for isotopic studies of lead were obtained from three new sites because previously collected samples are too altered for study. The new samples include the basalts of Black Cone, EMAD, and Nye Canyon.

The volcanic rocks of the southern Death Valley region were examined with L. Wright (Pennsylvania State University) and B. Troxel (University of California, Davis). They have recognized three sequences of volcanic rocks, the uppermost being a bimodal suite of basalt and rhyolite that is part of the Death Valley-Pancake Range volcanic belt.

## VI. ROCK PHYSICS (J. A. Blacic)

A test matrix was designed for creep testing of nonwelded, zeolitized samples from the tuffaceous beds of Calico Hills. The purpose of the tests is to provide data with which to formulate a preliminary constitutive equation that describes the time-dependent deformation properties of nonwelded tuffs

subjected to far-field conditions (for example, for borehole sealing). Samples will be subjected to a time-invariant stress ranging from 50 to 90% of the short-time, uniaxial compressive strength of Calico Hills tuff and temperatures over the range 25 to 75°C. Confining pressure will be held constant at 20 MPa. Both dry and water saturated, drained conditions will be used. Test samples from a single ash-flow unit in Drill Hole USW G-4 were selected, and testing will begin next quarter. Results will be presented in terms of time to failure and critical volume strain at failure as a function of stress and temperature.

Final results of the "soak" tests were documented.<sup>26</sup> Test samples from the Topopah Spring, tuffaceous beds of Calico Hills, Bullfrog, and Tram stratigraphic units were subjected to hydrothermal conditions similar to those expected in the near field of a repository in tuff for times varying from 2 to 6 months. A range of mechanical and thermal properties was measured at ambient conditions before and after the hydrothermal exposure. There were significant permanent changes in tensile strength, uniaxial compressive strength, and matrix permeability. However, with a few exceptions, porosity, grain density, and thermal properties appeared to be unaffected. Mineralogic and petrologic examination of the test samples has established the operation of slow reactions involving the dissolution of silica and feldspar, formation of clays, and possible conversion of clinoptilolite to mordenite. However, it was not possible to establish one-to-one correlations of the minute mineralogic changes with physical property changes. Strength changes are believed to be related to the subtle surface modifications of minerals observed; these changes were probably most active along grain boundaries and fracture surfaces where the catalytic action of water is effective. It thus appears that significant changes in tuff mechanical properties may be expected over time from hydrothermal alteration, possibly without correlated significant changes in mineralogy or thermal properties. It is not clear if the rates of strength reduction implied by the tests can be extrapolated to long times, but possible significant impact of these processes on operational and containment performance should be evaluated.

## VII. SHAFT AND BOREHOLE SEALING (R. J. Vidale, B. E. Sheetz, and D. M. Roy)

New experiments are being run to investigate tuff/sealant reactions under unsaturated pore fluid conditions. Photomosaics of disks made from concrete containing tuff aggregate were prepared. Their texture, chemical composition, and phase composition before reaction were documented. The disks were then suspended in an autoclave at 200°C, 225 psi, and 50% fill of water. The first sample was removed after 28 days and is now being examined for changes in microstructure, chemical composition of the solid and the water, and phase composition of the solid. These examinations will determine the chemical reaction taking place in concrete and tuff at slightly elevated temperature on a laboratory time scale; this reaction data will help predict the long-term geochemical stability of cement seals in the unsaturated felsic tuff of Yucca Mountain.

The lithophysae-free zone of the Topopah Spring formation at Yucca Mountain is now the probable target horizon for location of the waste repository. The characterizations of the Topopah Spring and the Grouse Canyon tuff from G-tunnel that were used for our preliminary experiments showed the two tuffs are significantly different mineralogically and chemically.<sup>2</sup> The lithophysae-free zone of the lower Topopah Spring formation at Fran Ridge was sampled, and the rock was delivered to the laboratory.

Water from Well J-13 has been delivered to the laboratory for use in further experiments. The J-13 well has been thoroughly flushed of drilling impurities; the water now comes from the Topopah Spring formation as well as other units because the Topopah Spring formation is below the top of the water table at that site. At the moment, this water is the best approximation of pore water composition at the probable repository site.

The first sealant tested was a concrete containing calcium silicates, aluminates, and ferrites as the major cement phases; a coarse aggregate of Grouse Canyon tuff; a fine aggregate of "NTS Sand #2;" and fly ash AD-592-5. Analyses of the sand and fly ash<sup>2</sup> showed that large quantities of potentially reactive substances such as dolomite, calcite, calcium oxide, and hematite are present. It is important to change to Topopah Spring tuff for the coarse aggregate and to use sand and fly ash that are chemically simpler and more compatible with the tuff of the coarse aggregate and the surrounding rock. The new cement mixture #82-22 has been designed and prepared with Topopah

Spring tuff as aggregate. It is silica rich and contains purer sand, fly ash, and silica fume than does the previous mixture. Its composition should be more easily reproducible, and it should be less chemically reactive with the felsic tuff.

#### VIII. EXPLORATORY SHAFT (D. C. Nelson, D. A. York, and C. W. Myers)

##### A. Design

The detailed logic network for the ES design, procurement, construction, and construction phase testing was completed. The initial logic was developed by representatives of Los Alamos groups WX-4 and ESS-1 with the assistance of members of the Project Management Support Group of Sandia National Laboratories. The logic was reviewed and modified by those other organizations that will be performing the work; that is, DOE/NV, DOE/NTSSO, H&N, F&S, and REECo. The activity durations were then estimated by the appropriate performing organizations. The target date of October 3, 1983, for the start of shaft sinking was added to the network and the logic calculations were performed. Negative slack paths (schedule overruns) occurred with the primary power system, the water supply system, the emergency power generators, and the headframe. The worst critical path had slack of -21.4 weeks. This is not an unusual occurrence for the first network calculation. It only signifies that the first plan, the preferred plan, will not work. Alternative plans have reduced the slack to approximately zero. Since the logic network was developed, two monthly updates have been conducted. Although the rate of turnaround in updating the network has not been entirely satisfactory, the network indicated the project problems and focused attention on solutions to these problems.

On February 3 and 4, 1983, the ES Test Plan Committee developed new criteria that were incorporated into the Title II design. These criteria include (1) a revised shaft depth, (2) a new breakout procedure, and (3) a new layout for the underground openings. On March 10 and 11, 1983, the ES Test Plan committee met to review the test proposal drafts and to replan the construction phase testing on the existing logic network. Adequate detail on the support required from the shaft-sinking subcontractor for the construction phase testing was not provided at this meeting. REECo requested written

response by March 17, 1983, but received very little. Los Alamos personnel are attempting to obtain this information from the test proposals, though the test proposals have not yet been approved and funded. Another meeting of the committee is planned for April 20 and 21, 1983, when the logic network for the in situ testing will be developed.

On January 13, 1983, the formal Title I design review meeting was held for both surface and subsurface ES facilities. Title II design had already started. The meeting on February 17, 1983, was devoted mostly to solving schedule problems and reporting project status. It was reported that the specifications for the headframe, skips, cage, wire rope, and shaft guides have been completed, reviewed, and approved. REECO reported that procurement of these critical-path items had started.

At the March 17, 1983, ES Project Review Meeting, it was reported that Title II design was nearing completion. Phase I of the Title II design of the water system was completed, and construction of the ~6 miles of water line has started. Phase II of the water system design is expected to be completed by April 1, 1983. Construction of the ES site access road is now complete up to the NTS boundary (except for the addition of oil and chips). Construction of the power line from the Canyon Substation to the NTS boundary is completed. All work located off the NTS is awaiting the issuance of the documents "Finding of No Significant Impact" and "Cooperative Agreement between DOE and the Bureau of Land Management." The Title II site plan and profile drawings were submitted by H&N for review. Structural and mechanical drawings of the hoist house were also completed. Bids have been received for the shop and warehouse buildings. Title II design of the subsurface facilities was submitted by F&S for review. This included drawings and specifications for all equipment and construction for the shaft collar, the shaft, and underground openings. Review of the Title II design of the ES subsurface facilities is in progress and is expected to be completed by March 28, 1983. REECO is writing the contract for the shaft sinking, and it is hoped that approval of the contract's technical specifications will be received by April 15, 1983. A bidders' conference for the shaft-sinking contract is planned for the week of May 23, 1983.

The Nuclear Waste Policy Act of 1982 contains certain requirements that may delay the start of the ES construction by 3 to 4 months.

Sandia National Laboratories representatives have requested that a second breakout be constructed. This issue has not been resolved but could have a significant effect on the ES schedule and cost.

A consulting contract with Stearns-Roger, Inc., Denver, Colorado, has been approved; they have been requested to review portions of the ES design.

#### B. Test Plan

Work by the Exploratory Shaft Test Plan Committee accelerated this quarter. The approach for developing the test plan was restructured into a two-step process. First, test proposals will be developed for approval-in-concept by TPOs and WMPO management. Second, approved test proposals will be integrated into an NNWSI ES Test Plan. The test proposals were to be completed March 24, 1983; this deadline was met and was the major accomplishment of the test plan committee during the quarter. The test plan itself is to be completed by August 1983.

Construction phase tests and in situ phase tests currently proposed for the NNWSI ES are listed below. Testing for site characterization at Yucca Mountain will be performed not only in the drifts, rooms, and alcoves of the underground facility but also within the shaft proper. Tests in the shaft will examine fractures, groundwater compositions, and groundwater ages between the surface and the target unit and slightly below the target unit. This information is necessary for evaluating groundwater flux in the Yucca Mountain unsaturated zone. In addition, deformation of the rock mass around the shaft, which is caused by shaft construction, will be measured. Shaft sinking by conventional mining (rather than drilling) will prevent contamination of the test areas in the underground facility by drilling fluids; it will also permit thorough characterization of the geologic and hydrologic conditions in the unsaturated zone above and, to a limited extent, below the target unit. Limited at-depth testing (that is, testing to define optimum excavation methods and sealing techniques and to refine and confirm repository engineering and design) will be performed.

The following are the tests proposed for the NNWSI Exploratory Shaft.

#### Construction phase tests:

- (1) Shaft-wall mapping, photography, and hand specimen sampling
- (2) Large-block sampling and pore water analysis

- (3) Groundwater sampling
- (4) Shaft mechanical testing 1: rock extensometers and pressure cells
- (5) Vertical core drilling from within the shaft
- (6) Lateral drilling at the breakout level
- (7) Overcore testing
- (8) Breakout room testing

In situ phase tests:

- (9) Shaft mechanical testing 2: multiple-point borehole extensometers
- (10) Drift-wall mapping
- (11) Radial borehole testing from within shaft
- (12) Lateral core drilling from drifts
- (13) Sampling and testing intact fractures
- (14) Bulk permeability test
- (15) Infiltration test
- (16) Hydrologic testing/Calico Hills
- (17) Waste package testing
- (18) Drift and pillar deformation test
- (19) Enhanced heater block testing
- (20) Canister scale heater testing
- (21) Borehole and drift seal testing
- (22) Diffusion test
- (23) Fracture transport test
- (24) Horizontal emplacement hole drilling test
- (25) Integrated data system proposal

Construction phase tests have been designed and sequenced to provide required information and minimize standby time during mining operations.

- Step 1. Mine shaft to top of target unit interval
- Step 2. Explore target unit interval
- Step 3. Mine shaft to breakout within target unit
- Step 4. Explore target unit at the breakout level
- Step 5. Mine muck pocket and landing at breakout level
- Step 6. Mine shaft to total depth

[Shaft contractor dismissed]

Step 7. Measure in situ stress at breakout level

Step 8. Construct and instrument the breakout room

In situ phase testing in the target unit will begin after drift mining, except for the drift and pillar deformation tests, which will begin during drift mining.

The test plan committee also developed and supplied to REECO the requirements and specifications for services and materials that must be provided by the shaft-sinking contractor to support certain construction phase tests. This work is continuing. The committee responded to a request to evaluate the impact of performing in situ tests at two levels.

The ability to air drill laterally from the underground workings continues to be a problem; if the difficulty is not resolved, it will probably eliminate the bulk permeability test and infiltration test and might have an impact on several others. A test of lateral drilling technology at Fran Ridge is being considered.

#### IX. QUALITY ASSURANCE (R. R. Geoffrion and H. E. Simpson)

##### A. Los Alamos

New procedures prepared this quarter by QA personnel include Clay Mineral Separation for X-Ray Diffraction Analysis, Personnel Certification for Los Alamos NNWSI, Geochemical Transport Modeling Work Plan, Quality Assurance Program for Exploratory Shaft Participants, and Design Control Procedure (Exploratory Shaft). Three existing documents were revised this quarter: Quality Assurance Program Plan for Los Alamos NNWSI, Design Review Procedure (Exploratory Shaft), and Design Control Procedure (Exploratory Shaft). A draft of the Integrated Data System and the drawings and specifications for ES electrical equipment and power lines were reviewed.

An updated list of Los Alamos NNWSI participants was prepared. The QA staff presented training sessions (on January 31 and February 11) for those participants; the sessions covered the technical review of publications, calibration of measuring and test equipment, and procurement procedures.

An audit of the Los Alamos Group ESS-2 instrumentation laboratory was performed and closed out. Records for nuclide migration field experiments (1979-1982) were assembled and shipped to the NNWSI records repository.

#### B. US Geological Survey

An internal audit of the USGS Denver records was performed and closed out by the Los Alamos QA staff.

Changes were made to the Procurement Procedure, and the original was given to the project coordinator for approval. The following six new procedures were approved this quarter: Teleseismic P-residual Study of the Tectonic Environment, Geologic Mapping, Subsurface Investigations, Stratigraphic Studies, Structural Geology Investigations, and Geologic Support Activities. The Earthquake Location Procedure was revised and approved.

Test equipment for hydrology and geophysical measurements was calibrated and labeled.

#### ACKNOWLEDGMENTS

The following Los Alamos National Laboratory personnel are acknowledged for their efforts: D. A. Mann (technical assistance); P. A. Elder, M. E. Lark, and S. Lermuseaux (sample counting and gamma-spectra analyses); and L. M. Mitchell (typing of drafts and final manuscript).

#### REFERENCES

1. R. B. Scott, R. W. Spengler, S. Diehl, A. R. Lappin, and M. P. Chornack, "Geologic Character of Tuffs in the Unsaturated Zone at Yucca Mountain, Southern Nevada," in The Role of the Unsaturated Zone in Radioactive and Hazardous Waste Disposal (Ann Arbor Science, Ann Arbor, Michigan, 1982).
2. A. E. Ogard, W. R. Daniels, and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, October 1--December 31, 1982," Los Alamos National Laboratory report LA-9666-PR (May 1983).
3. D. Rai and J. L. Swanson, "Properties of Plutonium(IV) Polymer of Environmental Importance," Nucl. Technol. 54, 107 (1981).
4. "Siting of Fuel Reprocessing Plants and Waste Management Facilities," Oak Ridge National Laboratory report ORNL-4451 (July 1970).

5. Environmental Protection Agency, "Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level, and Transuranic Radioactive Wastes," Federal Register 47, No. 250, 58196-58206 (1982).
6. D. Langmuir, "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits," *Geochim. Cosmochim. Acta* 42, 547-569 (1978).
7. R. J. Lemire and P. R. Tremaine, "Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C," *J. Chem. Eng. Data* 25, 361-370 (1980).
8. L. V. Benson and L. S. Teague, "A Tabulation of Thermodynamic Data for Chemical Reactions Involving 58 Elements Common to Radioactive Waste Package Systems," Lawrence Berkeley Laboratory report LBL-11448 (August 1980).
9. S. L. Phillips, "Hydrolysis and Formation Constants at 25°C," Lawrence Berkeley Laboratory report LBL-14313 (May 1982).
10. B. Allard, H. Kipatsi, and J. O. Liljenzin, "Expected Species of Uranium, Neptunium, and Plutonium in Neutral Aqueous Solutions," *J. Inorg. Nucl. Chem.* 42, 1015-1027 (1980).
11. B. Allard, "Solubilities of Actinides in Neutral or Basic Solutions," in *Actinides in Perspective*, N. M. Edelstein, Ed. (Pergamon, New York, 1982).
12. D. R. Turner, M. Whitfield, and A. G. Dickson, "The Equilibrium Speciation of Dissolved Components in Freshwater and Seawater at 25°C and 1 atm Pressure," *Geochim. Cosmochim. Acta* 45, 855-881 (1981).
13. D. Rai and R. J. Serne, "Solid Phases and Solution Species of Different Elements in Geologic Environments," Battelle Pacific Northwest Laboratory report PNL-2651 (March 1978).
14. D. Rai and R. J. Serne, "Plutonium Activities in Soil Solutions and the Stability and Formation of Selected Plutonium Minerals," *J. Environ. Qual.* 6, 89-95 (1977).
15. K. Wolfsberg, W. R. Daniels, B. R. Erdal, and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1--June 30, 1982," Los Alamos National Laboratory report LA-9484-PR (October 1982).
16. G. Bidoglio, "Characterization of Am (III) Complexes with Bicarbonate and Carbonate Ions at Groundwater Concentration Levels," *Radiochem. Radioanal. Lett.* 53, 45-60 (1982).
17. K. Wolfsberg, W. R. Daniels, D. T. Vaniman, and B. R. Erdal, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, October 1--December 31, 1981," Los Alamos National Laboratory report LA-9225-PR (April 1982).

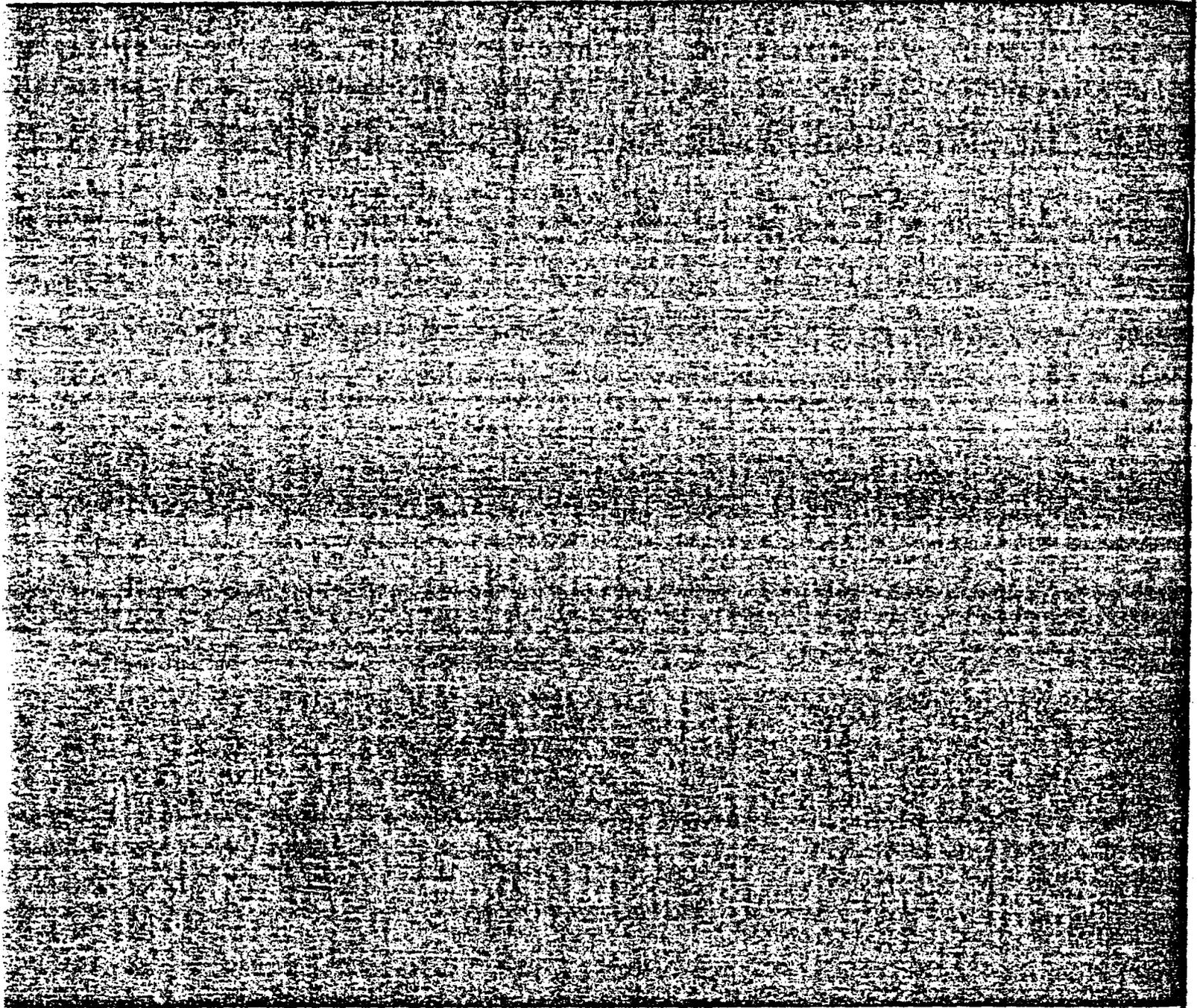
18. W. R. Daniels, B. R. Erdal, and D. T. Vaniman, Comps., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, July 1--September 30, 1982," Los Alamos National Laboratory report LA-9577-PR (March 1983).
19. H. W. Bentley and S. N. Davis, "Application of AMS to Hydrology," in "Symposium on Accelerator Mass Spectrometry," Argonne National Laboratory report ANL/PHY-81-1 (1981), pp. 193-205.
20. D. Elmore, L. E. Tubbs, D. Newman, X. Z. Ma, R. Finkel, K. Nishizumi, J. Beer, H. Oeschger, and M. Andree, "<sup>36</sup>Cl Bomb Pulse Measured in a Shallow Ice Core from Dye 3, Greenland," *Nature* 300, 735 (1982).
21. H. W. Bentley, F. M. Phillips, S. N. Davis, S. Gifford, D. Elmore, L. E. Tubbs, and H. E. Gove, "Thermonuclear <sup>36</sup>Cl Pulse in Natural Water," *Nature* 300, 737 (1982).
22. D. Vaniman, D. Bish, D. Broxton, F. Byers, G. Heikens, B. Carlos, E. Semarge, F. Caporuscio, and R. Gooley, "Variations in Authigenic Mineralogy and Sorptive Zeolite Abundance at Yucca Mountain, Nevada, Based on Studies of Drill Core USW GU-3 and G-3," Los Alamos National Laboratory report LA-9707-MS (in preparation).
23. S. S. Levy, "Petrology of Samples from Drill Holes USW-H3, -H4, and -H5, Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-9706-MS (in preparation).
24. E. B. Ekren, R. E. Anderson, L. L. Rogers, and D. L. Noble, "Geology of the Nellis Air Force Base Bombing and Gunnery Range, Nye County, Nevada," US Geol. Survey professional paper 651 (1971).
25. R. L. Christiansen and P. W. Lipman, "Cenozoic Volcanism and Plate Tectonic Evolution of the Western United States--Pt. II, Late Cenozoic," *Philos. Trans. R. Soc. London, Ser. A* 271, 249-284 (1972).
26. J. D. Blacic, Ed., "Effects of Long-Term Exposure of Tuffs to High-Level Nuclear Waste-Repository Conditions: Final Report," Los Alamos National Laboratory report LA-9330-MS (in preparation).

Printed in the United States of America  
Available from  
National Technical Information Service  
US Department of Commerce  
5285 Port Royal Road  
Springfield, VA 22161

Microfiche (A01)

<u>Page Range</u>	<u>NTIS Price Code</u>						
001-025	A02	151-175	A08	301-325	A14	451-475	A20
026-050	A03	176-200	A09	326-350	A15	476-500	A21
051-075	A04	201-225	A10	351-375	A16	501-525	A22
076-100	A05	226-250	A11	376-400	A17	526-550	A23
101-125	A06	251-275	A12	401-425	A18	551-575	A24
126-150	A07	276-300	A13	426-450	A19	576-600	A25
						601-up*	A99

\*Contact NTIS for a price quote.



Los Alamos