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Progress Report

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

July 1—September 30, 1980

University of California

LOS ALAMOS SCIENTIFIC LABORATORY

Post Office Box 1663 Los Alamos, New Mexico 87545

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Compiled by

K. Wolfsberg, B. R. Erdal, and B. M. Crowe

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ABSTRACT

Sorption of americium and plutonium was measured in a controlled, oxygen-free atmosphere and in air on a series of tuff samples. Sorption of plutonium was greater in the controlled atmosphere than in air. Sorption of both elements is higher on zeolitized tuff than devitrified tuff. Sorption of strontium, cesium, barium, cerium, and europium is being measured on tuff samples of mineralogies not previously studied, and samples from the USW-G1 drill hole have been selected for study. Work on the dependence of the sorption ratio on element concentration (barium and europium) and on solution-to-solid ratios is reported. Progress on controlling Eh and making Eh measurements is presented. Some tuff-water systems exhibit reduced or negative Eh values under oxygen-free conditions. Development of a method for encasing cores for flow studies is discussed.

Field geologic mapping is being conducted in the Lunar Crater volcanic field of central Nevada. Volcanic rocks of the field have been divided into three units based on the degree of erosional modification of primary volcanic features. Two new megacryst-bearing localities have been discovered in the volcanic field. Eruptive centers of the field are concentrated along north-northeast-trending en-echelon fissures within a central axial rift and along ring-fracture zones

of old cauldron complexes. Crater Flat, adjacent to the NTS region, was the site of repeated eruptions of hawaiite magma of small volume (10^7 to 10^8 m³). Preliminary data suggest a decline in volume and time interval between successive hawaiite eruptions.

Mineralogy-petrology studies are being conducted on core samples from the USW-G1 exploration hole in Yucca Mountain. Zeolite heating tests of core samples from UE25a-1 show density, volume, and weight changes that correlate with alteration of mineral assemblages. Hydrogen-deuterium ratios in water evolved from a clinoptilolite specimen from Yucca Mountain have been measured.

Jacket seals leaked during the first attempt at high temperature exposure in the hydrothermal soak tests. Revised seals using temperature-cured epoxy are being developed. Data from strength tests for various types of tuff conducted at ambient pressure and 400°C for 16 h are presented. A densely welded specimen showed a 40 percent reduction in strength. A new creep apparatus is being assembled. A literature review has been completed concerning the state of knowledge of slow creep for rocks under anticipated repository conditions.

Progress on the Tuff Facility Design and in Quality Assurance is reported.

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 U.S. Department of Energy during the period from July 1 through September 30, 1980. This report is not intended to be a detailed technical document but does indicate the status of the several investigations being performed at Los Alamos.

II. GEOCHEMISTRY OF TUFF

A. Sorption of Plutonium and Americium in a Controlled Atmosphere and in Air

A series of batch measurements of the sorptive behavior of plutonium and americium under both controlled atmosphere (nitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide) and air using Yucca Mountain tuffs has been completed. The results are summarized in Table I. Sorption ratios (R_d) were averaged over contact times of 3, 6, and 12 weeks, corresponding desorption times of 12, 9, and 3 weeks, and particle sizes of <75 and 75-500 μm . The numbers in parentheses

TABLE I
AVERAGE SORPTION RATIOS (ml/g) FOR Am AND Pu

Tracer	Core	Sorption		Desorption	
		Air	CA ^a	Air	CA
²⁴¹ Am	YM-22	4 000 (1200)	1 400 (210)	4 600 (990)	3 700 (830)
²⁴¹ Am	YM-38	5 500 (1100)	5 600 (950)	9 500 (1300)	14 000 (2100)
²⁴¹ Am	YM-54	590 (200)	1 000 (210)	600 (45)	2 500 (380)
²³⁷ Pu	YM-22	140 (38)	220 (46)	1 400 (95)	1 600 (330)
²³⁷ Pu	YM-38	250 (83)	800 (87)	2 000 (490)	>2 200
²³⁷ Pu	YM-54	84 (17)	120 (29)	670 (35)	1 300 (190)

^aControlled atmosphere (nitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide)

indicate the standard deviations of the means for the six values which were averaged for each experiment.

Several observations can be made concerning the results. The zeolitized YM-38 tuff consistently exhibits greater sorption ratios for both americium and plutonium than the two devitrified tuffs, YM-22 and YM-54. Americium sorption is greater than plutonium sorption. The sorption of plutonium on all three tuffs is greater under controlled-atmosphere conditions than in air. Such a change with change in atmosphere is not surprising considering the known speciation effects of plutonium. Americium sorption under controlled-atmosphere conditions is the same or higher for YM-38 and YM-54 but may be less for YM-22 than in air. As reported previously¹ americium has also exhibited a tendency toward large variations in behavior when experimental conditions are changed. This, also, is probably due to speciation effects even though the oxidation state remains unchanged. The differences with change in atmosphere may be attributable to the somewhat reducing nature of the tuff-groundwater systems (recent observations in the controlled atmosphere). Within the experimental uncertainties, particle-size effects appear to be minimal, as, for the most part, do changes with contact time. Any observed contact-time effects resulted in the expected increase in sorption ratio with increasing time. In general, the sorption of americium and plutonium on tuff is intermediate to high with some sorption ratios on the zeolitized tuff being very high.

B. Sorption on Samples from Hole J-13

Preliminary sorption ratios have been obtained for 3-week batch sorption measurements with ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , and ^{152}Eu for tuffs JA-8, JA-26 and JA-28. The R_d values are summarized in Table II. The x-ray diffraction data indicate that JA-8 is ~25-50% glass; JA-26 is ~30-50% analcime, 30-50% quartz, and 10-20% alkali feldspar; core JA-28 is similar to JA-26 with an additional 2-5% illite/muscovite.

C. Samples from Drill Hole USW-G1

Cores from drill hole USW-G1 have been selected for geochemical studies: G1-1292, G1-1436, G1-1883, G1-1982, G1-2083, G1-2233, G1-2289, G1-2698, G1-2901, G1-3116, and G1-3658; the number after the "G1" designation indicates the depth in feet. Other samples will be chosen after the measurements on the first set are underway. Solid cores have been made for flow studies, and the remaining material has been ground for rock-groundwater equilibrations, for batch studies, and for crushed rock columns. The cores selected include three from Bullfrog II and at least one of each type of tuff composed primarily of zeolite, glass, clay, feldspar and quartz, or feldspar and cristobalite.

D. Rock-Water Equilibrations

Because all of the tuffaceous J-13 well water used in the tuff sorption studies is pretreated with crushed tuff before use, we are investigating the dependence of water composition on exposure time to the tuff. Water pretreated with YM-30 tuff (clinoptilolite, quartz, cristobalite, feldspar) was sampled at 42 days, 51 days, 256 days and 301 days, and JA-13 water pretreated with J-26 tuff (see Sec. II.B) was sampled at 14 days, 52 days, and 112 days. Analyses have not yet been performed.

E. Dependence of the Sorption Ratio on the Element Concentration

Batch sorption determinations have been performed with strontium, cesium, barium, and europium for YM-22 (devitrified) and YM-38 (zeolitized) tuffs (two particle-size ranges). Traced solutions of nuclides at several different element concentrations have been contacted with the solid samples for three weeks at ambient temperature. The results for strontium and cesium have been previously reported.² Studies with barium are now complete, and europium studies have been completed for YM-22 but not for YM-38. Treatment of the data was discussed in Ref. 2. A linear relationship was not found for barium

TABLE II
SORPTION RATIOS ON ADDITIONAL TUFF SAMPLES^a

	R_d (ml/g)				
	<u>Sr</u>	<u>Cs</u>	<u>Ba</u>	<u>Ce</u>	<u>Eu</u>
JA-26	34.5	487	209	385	118
JA-28	111	1 234	720	1 350	1 170
JA-8	305	1 963	358	—	1 710

^aThree-week contact time.

and europium isotherms. Although straight lines were obtained for log-log sorption isotherm plots for strontium and cesium,² a simple Freundlich isotherm does not entirely describe the barium and europium data. Values for the parameters of the Freundlich equations, obtained by least-square fits, are given in Table III. The fitted values for n (see footnote in Table III) are all near unity. This indicates that the sorption ratios should be somewhat independent of concentration, as is observed. Values of n less than one indicate possible saturation of sorption sites at higher concentrations, and values greater than one indicate possible precipitation at higher concentrations.

F. Dependence of the Sorption Ratio on the Solution-to-Solid Ratio

Tuff YM-38 (zeolitized) is being used to study the effect of varying the solution-to-solid ratio in batch determinations of sorption ratios. The normal ratio for most of our batch determinations has been 20:1. The results for 3-week contact times are given in Table IV. The 6-week experiments are still in progress. The sorption ratios for cesium and strontium for this tuff sample are rather constant over the solution-to-solid ratios studied. On the other hand, the sorption ratios for barium, cerium, and europium increase considerably as the solution-to-solid ratio increases from 5:1 to 30:1.

G. Redox Potentials

Investigations of measuring and controlling the oxidation-reduction potential of rock-groundwater systems are continuing. Either gold or platinum electrodes, referenced to a standard calomel electrode, are used; the E_h values relative to the normal hydrogen electrode (NHE) are reported. A study of the use of hydroxylamine as a reducing agent was made. Solutions were

TABLE III
FREUNDLICH ISOTHERM PARAMETERS^a

<u>Tuff</u>	<u>Fraction (μm)</u>	<u>Element</u>	<u>n</u>	<u>-log (k)</u>
YM-22	<75	Ba	0.83	1.34
		Eu	1.12	-1.20
	75-500	Ba	0.82	1.57
		Eu	0.92	0.46
YM-38	<75	Ba	1.0	-2.41
	75-500	Ba	1.1	-2.5

^aFreundlich isotherm, $y = kc^n$, where y is the concentration on the solid in moles/g and c is the concentration in solution in moles/l.

sparged with nitrogen for approximately 4 h to remove most of the oxygen prior to placing them into the controlled-atmosphere enclosure. The Eh was measured as a function of pH in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$. An approximately linear correlation was found: $\text{Eh (pH 7)} \approx +120 \text{ mV}$ and $\text{Eh (pH 10.8)} \approx -130 \text{ mV}$. Experiments in the controlled atmosphere ($\leq 0.2 \text{ ppm oxygen}$, $\leq 20 \text{ ppm carbon dioxide}$) led to almost constant pH (9.38 ± 0.1) and Eh ($-14 \pm 4 \text{ mV}$) values. Values at near-equilibrium conditions showed the following Eh values as a function of hydroxylamine hydrochloride concentration:

<u>$\text{NH}_2\text{OH}\cdot\text{HCl}$ Molarity</u>	<u>Eh (mV)</u>
0.023	-12
0.0047	+17
0.00095	+58

Measurements of Eh on unpoised systems are difficult to interpret. A weak signal can be undetectable because of electrical noise in the system. Measurements of both aerated and oxygen-free groundwaters in the absence or presence of many of the samples studied (Climax Stock granite, Eleana argillite, and some of the tuffs) have mostly shown positive potentials. However, mixtures of pulverized YM-54 (devitrified) or YM-38 (zeolitized) tuff samples and water from well J-13 that have been pretreated in the controlled atmosphere for more than one year show slightly lower Eh values, -20 to -140 mV, compared to the values of +300 to +350 mV for aerated solutions at pH values of about 8.

TABLE IV
SORPTION RATIOS AS A FUNCTION OF SOLUTION-TO-SOLID RATIO^a

Sample	Fraction (μm)	Ratio (ml:g)	R_d (ml/g)				
			Cs	Sr	Ba	Ce	Eu
YM-38	<75	5:1	5 970 (11.7)	2 770 (5.4)	11 000 (5.1)	1 330 (17.3)	2 700 (17.7)
		10:1	5 760 (7.5)	2 790 (3.4)	60 000 (9.6)	6 390 (13.1)	9 070 (13.2)
		30:1	7 980 (3.4)	3 610 (2.2)	81 500 (3.6)	9 070 (6.0)	9 700 (5.4)
	75-500	5:1	3 660 (10.6)	2 040 (4.9)	7 410 (5.1)	2 560 (17.2)	3 060 (16.3)
		10:1	5 750 (7.0)	2 840 (3.3)	48 000 (7.2)	7 230 (13.0)	6 780 (11.3)
		30:1	5 540 (3.2)	2 770 (2.1)	54 200 (3.1)	16 000 (5.8)	10 400 (4.9)

^aFor YM-38 tuff, ambient conditions, and three week contact times. Values in parentheses are the standard deviations of the mean (in percent).

A potentiostat will be used to achieve various selected potentials. A Teflon potentiostat cell, 3.6 cm in diameter and 7.5 cm in height, similar to those of Harrar³ and Rai et al.⁴ has been fabricated. The working electrode is a 3.3-cm-diameter cylinder of 52 mesh platinum gauze isolated in a glass cell with a porous Vycor frit making contact with the solution. A salt bridge contains a calomel reference electrode. Inlet and outlet tubes for inert-gas sparging and a sample port with stopper are included.

For long-term experiments a method will be needed to maintain the desired potential after it is reached using a potentiostat. A study will be made of the use of Eh buffers or moderators for this purpose. Possible inorganic Eh moderators were discussed by T. W. Newton.⁵ Ottaway⁶ discusses organic redox indicators in the applicable range. The symbol E_m^7 is defined as the formal potential at pH 7. The formal potential, E'_0 , is the potential of a solution containing equal concentrations (not necessarily molar) of the oxidized and reduced species under specified conditions of the other electrolytes; E'_0 applies at pH = 0. Table V lists possible organic indicators with the corresponding E_m^7 values and pH range under which they can be investigated.

If it is determined that a buffer is reversible and does not interfere with sorption, then the method will be applied for studying sorption of elements such as plutonium, uranium, technetium, and neptunium under both controlled-atmosphere and controlled-Eh conditions.

H. Crushed Tuff Columns

The only crushed rock column completed since the last progress report² was a fast-flow YM-38 (#3) column loaded with ¹³⁷Cs. Fifty percent of the activity was removed in 7680 ml, giving an " R_d " of >21 900 ml/g, compared to a batch R_d of 8 600 ml/g. No peak was obtained in the elution.

Petrographic analyses were performed on tuff from an earlier YM-38 (#1) column and a JA-32 (#1) column, both before and after elution. No change in YM-38 was observed, but there was a slight alteration of feldspar in the JA-32 tuff.

I. Radionuclide Sorption Studies Using Solid Rock Cores

In earlier sorption experiments conducted with rock cores there were indications that a part of the flow path of the water was along the interface between the core and the Teflon sleeve around the core. For example, higher activity levels were sometimes found on the exterior surfaces of the core than

TABLE V
Eh INDICATORS TO BE INVESTIGATED

	E_m^7 (mV)	pH Range
Induline Scarlet	-299	3.0-8.6
Rosinduline 2G	-281	4.8-11.4
Lissamine Blue BF	-253	1-11
N,N'-dimethyl Viologen	-446 ^a	8.4-13
Indigo Carmine	-125	<9 ^b
Pyocyanine	- 34	1-12

^aPotentials of substituted viologens are independent of pH and follow the simple Nernst equation.

^bSemiquinone is formed above pH 9.

on the interior surfaces of the core slices. Possible routes for this exterior flow were thought to be: (1) leakage along the top surface between the end cap and the core, then down the core sides and (2) flow from within the core to the side surfaces, then down the core sides. Various modifications of the end caps and the spacers between the end caps and the core did not seem to eliminate the leakage problem, so the core and end caps were completely encased in a material impermeable to water. We have used both polyurethane and epoxy resins successfully for this purpose. Groundwater traced with ²³³U is being used to examine the activity profiles, i.e., flow patterns for water movement through encased cores.

Thus far the technique of sealing cores and end caps together appears to be an improvement over the previously used Teflon sleeve method for the following reasons: (1) there is no longer concern about flow down the outside surface of the rock core, and (2) there is no need to apply a confining pressure (although this may be done if water must be pumped at pressures in excess of about 500 psi). The Buehler epoxy resin used does not appear to compete strongly with the rock for radionuclide sorption, at least for many elements of current interest. There are still some problems associated with epoxy coated cores, however. Most significantly, a reliable means for introducing the radionuclide into the core must be developed. A factor which complicates studying the effect of different introduction methods is that the flow pattern

of water through the core seems to vary widely with different cores. It will also be necessary to run some long-term experiments to determine the stability of the coating with time.

III. VOLCANISM STUDIES

Detailed studies of volcanism in the south-central Great Basin are being conducted to assess the impact of volcanic risk on siting a waste repository in the Nevada Test Site area. This summary describes ongoing work during the reporting period.

Geologic mapping and petrologic studies are underway in the Lunar Crater volcanic field located in central Nevada. This field is the northernmost volcanic field of a Neogene volcanic belt extending from southern Death Valley through the Nevada Test Site to central Nevada. Volcanic rocks of the field were divided into three major units based upon the degree of erosional modification of primary lava flow features and the degradation of associated cinder cones. Magnetic polarity determinations of the younger two units are consistently normal, indicating they are probably younger than 700 000 y. Magnetic determinations of both normal and reversed polarity were noted for the older volcanic cycle.

Major differences in phenocryst assemblages were noted for each of the mapped volcanic units. The youngest volcanic unit includes two previously described nodule- and megacryst-bearing localities, the Black Rock summit and Easy Chair centers. Two new megacryst-bearing localities were discovered within the field; one is located about 7 km north of the Black Rock Summit cone, and a second is located directly north-northeast of Lunar Crater. Eruptive centers at several localities provide evidence of the possible importance of shallow-level fractionation of one or more magma systems prior to disruption by the younger volcanic systems. From oldest to youngest, the volcanics range from phenocryst poor, to moderately olivine and clinopyroxene porphyritic, to abundantly olivine porphyritic in the northern part of the volcanic field.

Cinder-cone and lava-flow centers are concentrated along a north-northeast trending, axial-rift zone that cuts the central part of the Pancake Range. Individual cones and cone clusters are elongate in a north-northeast direction and aligned along en-echelon fissures or subrifts within the central axial

rift. Scattered cones and lava-flow centers occur along the ring-fracture zone of the Lunar Lake caldera.⁷

Petrologic studies have been completed for the basalts of Crater Flat, including detailed petrography and major- and trace-element analyses. This work is described in a summary paper by C. T. Vaniman and B. M. Crowe, entitled "Geology and Petrology of the Basalts of Crater Flat: Applications to Volcanic Risk Assessment for the Nevada Nuclear Waste Storage Investigation." This report will be issued in the fall of 1980. Crater Flat has been the site of three volcanic cycles within the last 3.7 Myr. Compositional studies indicate that each cycle has approximately similar hawaiite composition. Magma volumes are relatively small (0.01 to 0.1 km³) for each cycle and the number of individual centers per cycle is always less than 10. Limited data suggest a decline in the total volume and time interval between eruptions for successive cycles. These conclusions, which have important applications to probability calculations and magma disruption effects, will be tested by studies of basaltic volcanism within the NTS region.

IV. MINERALOGY-PETROLOGY

A. Mineralogy-Petrology Studies

Mineralogy and petrology studies are being conducted to characterize the tuff that forms Yucca Mountain. Data from the characterization are used to assist in correlation of sorptive and thermomechanical properties of tuff to understand their petrologic controls, and to aid in site characterization.

Many (157) samples of tuff were selected from the USW-G1 drill hole core stored at the U. S. Geological Survey Core Library, Mercury, Nevada. The samples were chosen to represent the range of lithologic types of tuff including cooling unit variations (degree of welding, crystallization, and alteration) within the stratigraphic section. Sampled stratigraphic units include the Tiva Canyon and Topopah Springs Members of the Paintbrush Tuff, Bedded Tuff of Calico Hills, the Prow Pass and Bullfrog Members of the Crater Flat Tuff, and a sequence of predominantly ash-flow deposits of uncertain stratigraphic assignment in the lower part of the drill hole section.

The x-ray diffraction patterns have been obtained for 90 samples and petrographic analyses are in preparation for 42 of these samples. Results of this work will be described in the next progress report.

B. Heating Tests

Laboratory heating tests of various lithologic types of tuff at atmospheric pressure have been undertaken in support of the hydrothermal soak test investigations. Heating tests on tuff with variable alteration mineral assemblages (primarily zeolites) show behavior that correlates with mineralogy (Appendix A). The weight and volume of the samples were monitored after heating in dry air. Three samples of roughly equal bulk densities, but differing mineral abundances, showed different behavior. A clinoptilolite-rich sample (60-90%) showed the greatest weight and volume loss; an analcime-rich sample (60-90%) showed an intermediate weight loss and near-zero volume change; and a glassy specimen showed a volume increase and small weight loss.

The dehydration of a core sample from the UE25a-1 hole with a high percentage of clinoptilolite was investigated as a function of time at approximately 100°C (Appendix B). No further changes in weight, volume, or density were observed after eight hours indicating that hydration equilibrium had been reached. Rehydration of the sample was achieved by exposure to a water-saturated atmosphere at 92°C. Final weight and volume slightly exceeded the initial values, which were in equilibrium with laboratory air. The X-ray analyses of heated specimens indicate that weight and volume changes with dehydration are due to shrinkage of the unit cell of clinoptilolite.

Hydrogen-deuterium ratios in water from a clinoptilolite specimen from Yucca Mountain (UE25a-1) have been measured. Preliminary results show fractionation trends that may be of use in monitoring zeolite dehydration and pore-water migration in and around a repository. An informal report of results is currently in preparation and will be summarized in the next quarterly report.

V. ROCK PHYSICS STUDIES

Hydrothermal soak tests are designed to explore effects of exposure to repository conditions on physical and mineralogic characteristics of tuffs. Samples are exposed to a range of temperature, pressure, and pore pressure conditions for periods up to six months. Mineralogy, tensile and compressive strength, density, porosity, permeability, thermal expansion, and thermal conductivity measurements are taken before and after exposure.

The first attempt has been made for high temperature exposure. However, a jacket seal failed after only 36 h which has resulted in a delay in the

experiment. An attempt will be made to eliminate the leakage by use of temperature-cured epoxy. An extra temperature cycle will then be applied to the specimen. The effects of this extra cycle will be determined by supplementary testing and mineralogic examination.

We have completed a preliminary short-term test simulating thermal runaway. Samples of 6 tuffs, varying in degree of welding, were exposed to 400°C temperatures at ambient pressure for 16 h. Strength was measured by the point load test, an indirect method related to the Brazil test. Average failure loads were compared with similar data for unheated specimens. The samples studied were: (1) B-1, a nonwelded tuff of the Bandelier formation, Los Alamos, NM, (2) B-2, a welded Bandelier tuff, (3) Tbf-1, a nonwelded tuff from the Bullfrog formation, type locality at Lathrop Wells, NV, (4) Tbf-2, partially welded Bullfrog, (5) Tbf-3, partially welded Bullfrog, (6) Tbf-4, densely welded Bullfrog. The results of these tests are shown in Fig. 1. The changes are not statistically significant, except possibly for Tbf-4. These samples show about 40% reduction in strength. Further study may be in order.

Creep tests are designed to establish constitutive relations necessary to extrapolate to strain rates of 10^{-12} sec⁻¹ or less. Such rates may lead to a 0.3% deformation in the 100-year expected operational period of a repository (current guideline, Mine Design Study Working Group) which could, in turn, lead to tunnel failure and fracture permeability increase. The program includes the design and fabrication of a new, unique apparatus for measurement of creep response in tuff under the expected hot, moist, high pressure repository conditions and development of relationships describing the response. The assembly of the new apparatus is about one-half completed. A literature review of slow creep in rocks under hot, wet conditions has been presented to the Mine Design Study Working Group (MIDESWG). Preliminary conclusions for the effect of slow creep on a repository in tuff are summarized below:

- (1) Strain rates of as little as 1.6×10^{-12} sec⁻¹ could lead to repository failure during the 100-year operational period.
- (2) No constitutive relations are currently available to allow extrapolation to these low strain rates.
- (3) Few data are available to evaluate the effects of temperature or moisture on creep in rock. Available data indicate decreases in time-to-failure of two to four orders of magnitude due solely to the presence of water. Increases in temperature also decrease time to failure.

Fig. 1. Failure loads before and after heating treatment; see text for explanation of symbols.

- (4) It is therefore necessary to perform sufficient experiments on tuff under hot, wet conditions to define constitutive relations necessary to evaluate creep strain rates as low as $10^{-12} \text{ sec}^{-1}$.

VI. TUFF FACILITY DESIGN

Based on discussions with DOE/NV and DOE/NTS personnel concerning the federal budget cycle, environmental considerations, and land use permit for the Tuff Test Facility (TTF), a work plan was prepared describing the various project activities that must be completed for the construction of the TTF. Discussions were also held with Fenix and Scisson, Inc. on drilling and mining capabilities, limitations, and operational experiences at the NTS.

The MIDESWG has identified a number of in situ experiments required to obtain data for characterizing the tuff medium. The size and configuration of the underground portion of the TTF will be determined by the requirements of these in situ experiments. Although it will be some time before the experiments are fully defined, efforts have begun for preparing a first draft of the TTF functional criteria and conceptual design.

A draft paper was prepared stating the need and justification for constructing the TTF on an accelerated schedule so that needed design information will be available in time to support the Title I design of the proposed waste repository. The paper also made some suggestions for accelerating the TTF construction schedule.

VII. NUCLIDE MIGRATION FIELD EXPERIMENTS

A draft of the following report has been prepared: B. R. Erdal and K. Wolfsberg (Los Alamos) J. K. Johnstone and K. L. Erickson (SNL), and A. M. Friedman and J. J. Hines (ANL), "A Joint Project of the Los Alamos National Laboratory, Sandia National Laboratory, and Argonne National Laboratory for Nuclide Migration, Field Experiments: Program Plan," Los Alamos National Laboratory report LA-8487-MS (draft).

The material in this report was presented at a peer review at the Nevada Operations Office on August 18 and 19, 1980. The comments of the reviewers are being considered in preparation of the final version of the program plan.

Investigations of the preparation of water suitable for the experiment are in progress. Water from NTS Wells 8 and J-13 and from G-tunnel seeps are being contacted with various tuff samples from the tunnel for varying times. The waters are being analyzed before and after contact with G-tunnel materials. The tritium concentration of waters from the two seeps near the HF-23 location in G-tunnel were 4 and 9 nCi/ml.

VIII. QUALITY ASSURANCE

Implementation of the Quality Assurance program at Los Alamos was continued. The following work plans and procedures were approved and distributed this quarter:

- (1) Procedure for Preparation of Fused Beads for Electron Microprobe Analysis of Rock Powders, TWS-G9-DP-19, RO.
- (2) Procedure for Sample Preparation: Rock Powders, TWS-G9-DP-20, RO.
- (3) Work Plan for the Tuff Test Facility, TWS-WX4-WP-08, RO.
- (4) Surface Area Measurements Via Ethylene Glycol. TWS-CNC11-DP-18, RO.

The following procedure is currently in draft form and is being reviewed: Design Control Procedure for the Tuff Test Facility.

A proving ring for creep tests as performed by Rock Mechanics Group G-7 was brought into the calibration system.

Quality Assurance personnel attended the Headquarters Review Meeting in Las Vegas, Nevada on August 4 and 5, 1980.

IX. PUBLICATIONS AND ABSTRACTS

W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver, "Sorption of Am and Pu on Various Geologic Media under Reduced-Oxygen Conditions," American Chemical Society regional meeting, 1980, New Orleans, Louisiana, December 10-13.

J. R. Smyth, J. L. Thompson, and K. Wolfsberg, "Microautoradiographic Studies of the Sorption of U and Am on Natural Rock Samples," Radioactive Waste Management 1, 13 (1980).

X. ORAL PRESENTATIONS

B. R. Erdal, "Tuff Investigations - Geochemistry," NNWSI Annual Review, Las Vegas, Nevada, August 6, 1980.

B. R. Erdal, "Nuclide Migration Field Experiments," NNWSI Annual Review, Las Vegas, Nevada, August 6, 1980.

B. M. Crowe and D. T. Vaniman, "Volcanism Studies," poster session at NNWSI Annual Review, Nevada Test Site, August 7, 1980.

B. R. Erdal, "Nuclide Migration Field Experiments," Program Plan Peer Review, Las Vegas, Nevada, August 22, 1980.

S. J. DeVilliers, B. P. Bayhurst, W. R. Daniels, F. O. Lawrence, E. N. Vine, and K. Wolfsberg, "Sorptive Properties of Tuff," American Chemical Society National meeting, August 24-29, 1980, Las Vegas, Nevada.

B. R. Erdal, "Nuclide Migration Field Experiments," K₂/K Workshop, Whiteshell Nuclear Research Establishment, Pinawa, Canada, September 22, 1980.

J. R. Smyth, "Zeolite Thermal Stability Studies," NNWSI Task 2 Peer Review, Las Vegas, Nevada, September 26-28, 1980.

B. M. Crowe, "Volcanic Hazard Studies," NNWSI Task 2 Peer Review, Las Vegas, Nevada, September 26-28, 1980.

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The efforts of S. K. Kelly and L. M. Mitchell in typing of drafts and the final copy is greatly appreciated.

REFERENCES

1. E. N. Vine, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, P. Q. Oliver, J. L. Thompson, and K. Wolfsberg, "Sorption-Desorption Studies on Tuff II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies with Samples from Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8110-MS (1980).
2. K. Wolfsberg, B. R. Erdal, and J. R. Smyth, Eds., "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1 - June 30, 1980," Los Alamos National Laboratory progress report LA-8471-PR (1980).
3. J. E. Harrar, "Techniques, Apparatus, and Analytical Application of Controlled-Potential Coulometry," in Electroanalytical Chemistry, Vol. 8, Allen V. Bard, Ed. (Marcel Dekker, Inc., New York, 1975), pp. 1-167.
4. D. Rai, R. J. Serne, D. A. Moore, and R. W. Stromatt, "Electron Transfer Method of Controlling Eh During Adsorption of Multivalent Elements by Geologic Media," Battelle Pacific Northwest Laboratory report PNL-SA-6766 (1978).
5. B. R. Erdal, Ed., "Laboratory Studies of Radionuclide Distributions Between Selected Groundwater and Geologic Media, April 1 - June 30, 1980," Los Alamos National Laboratory progress report LA-8472-PR (1980).
6. J. M. Ottaway, "Oxidation Reduction Indicators of $E' < 0.76$ Volt," in Indicators, Edmond Bishop, Ed. (Pergamon Press, Oxford, 1972), pp. 469-529.
7. E. B. Ekren, W. D. Quinlivan, R. P. Snyder, and F. J. Kleinhamper, "Stratigraphy Structure and Geologic History of the Lunar Lake Caldera of Northern Nye County, Nevada," J. Res. U.S. Geol. Survey 2, 599 (1974).

APPENDIX A

EFFECTS OF MINERALOGY ON WEIGHT AND VOLUME CHANGES IN SELECTED TUFF SAMPLES ON HEATING TO 400°C

F. A. Caporuscio and J. R. Smyth

I. PURPOSE

To record density changes in tuff samples of various mineralogies at different temperatures.

II. SAMPLE DESCRIPTION

- JA-5 Tiva Canyon Member, Paintbrush Tuff. Welded, vitric tuff. Phenocrysts are primarily quartz and sanidine.
- JA-26 Prow Pass Member, Crater Flat Tuff. Nonwelded, zeolitized (analclime) ash-flow tuff. Phenocrysts are quartz, plagioclase, and K-spar.
- YM-40 Bedded tuff of Calico Hills. Altered, nonwelded vitric tuff. Zeolitized with Na + K-rich clinoptilolite. Phenocrysts are quartz, sanidine, and plagioclase.
- B Central portion of Bandelier Tuff. Nonwelded, nonzeolitized, ash-flow tuff with large pumice fragments and moderate amount of lithic fragments.

III. PROCEDURE

Cores (approximately 1-inch diameter and 1½-inch length) of each sample were cut and weighed three times to the nearest 0.001 g. The diameter and length of each core were also measured three times to 0.01 inch. Volumes and densities were calculated using these values.

Each core was heated in a temperature-controlled muffle furnace ($\pm 1^\circ\text{C}$) for a period of 48 h (± 15 min); weight, length, and diameter were redetermined as above for temperatures of 100, 200, 300, and 400°C to yield volume and density as a function of temperature (Table A-I). Changes in the measured and calculated properties between 25 and 400°C are given in Table A-II.

IV. CONCLUSIONS

Experimental results (see Figs. A-1, A-2, and A-3) indicate a range in thermomechanical properties for tuff samples that depend primarily upon the nature and proportion of zeolite minerals present. Density decreases in the zeolite-free JA-5 and B cores were similar and are due primarily to volume increases upon heating because weight changes were negligible. The density decrease in sample JA-26, however, was due to weight loss coupled with negligible volume change. Weight loss in JA-26 is attributed to water loss from analclime in the tuff. The density decrease of sample YM-40 is due to a fractional weight loss that is much greater than the fractional volume loss. The relatively high weight loss is also due to dehydration of the zeolite phase

(clinoptilolite) present in YM-40. Not only was all loosely bound water driven off, but minor amounts of tightly bound water may have also been driven out of the clinoptilolite. The volume decrease in YM-40 is probably due to contraction of the clinoptilolite unit cell upon heating.

APPENDIX B
HYDRATION AND DEHYDRATION OF A CLINOPTILOLITE-RICH CORE
FROM YUCCA MOUNTAIN

F. A. Caporuscio and J. R. Smyth

I. PURPOSE

To determine the rate of density change in a clinoptilolite-rich core sample of Yucca Mountain tuff upon hydration followed by constant temperature.

II. SAMPLE

YM-38: altered, zeolitized, nonwelded, vitric tuff. The zeolites have a median ($\text{Ca} \cong \text{Na} + \text{K}$) clinoptilolite composition. The phenocrysts are quartz, plagioclase, and sanidine.

III. PROCEDURE

Measurements were made for a core of YM-38 tuff approximately 2 cm in length and 2.5 cm in diameter. The sample core was weighed to 0.001 and measured for both length and diameter to 0.01 of an inch; these measurements were repeated three times prior to the test. Average values were then used to calculate volume and density for the sample. These measurements were also performed after each run was completed.

The core was placed in a water-filled dessicator for 48 h at 91°C and the density of the core was remeasured. The hydrated sample was then maintained at a constant temperature of approximately 95°C ($\pm 3^\circ$) in a drying oven. The density of the core was remeasured after 0.5, 1, 2, 3, 8, 16, and 32 h (± 10 min). Following the 32 h dehydration, the core was returned to the dessicator for 48 hours at 92°C for rehydration.

TABLE A-I
WEIGHTS, VOLUMES, AND DENSITIES OF SAMPLES USED FOR HEATER EXPERIMENTS^a

Temp. (°C)	JA-5			JA-26			YM-40			B		
	Wt.	V	ρ	Wt.	V	ρ	Wt.	V	ρ	Wt.	V	ρ
25	33.3860	15.3882	2.1696	26.4739	14.7298	1.7973	25.0519	15.2242	1.6455	21.8645	15.2348	1.4352
100	33.3217	15.3716	2.1677	26.3844	14.7281	1.7914	23.9593	15.2202	1.5742	21.8574	15.2797	1.4305
200	33.2956	15.3861	2.1640	25.9479	14.7472	1.7595	23.0969	15.1210	1.5275	21.8428	15.3407	1.4238
300	33.2876	15.4644	2.1525	25.5573	14.7382	1.7341	22.6973	15.0639	1.5067	21.8313	15.4192	1.4159
400	33.2842	15.5318	2.1430	25.5327	14.7206	1.7345	22.5898	14.9995	1.5060	21.8284	15.3845	1.4189
500	33.2799	15.6081	2.1322	25.4888	14.7245	1.7310	22.5045	14.9524	1.5051	21.8261	15.3788	1.4192

^aV is volume and ρ is density.

TABLE A-II
CHANGES IN PROPERTIES, 25° to 400°C OF SAMPLES USED FOR HEATER EXPERIMENTS^a

	JA-5	JA-26	YM-40	B
Wt. (g)	-0.1061	-0.9851	-2.5474	-0.0384
h (cm)	+0.0290	-0.0043	-0.0094	+0.0094
r (cm)	+0.0030	+0.0007	-0.0094	+0.0040
V (cm ³)	+0.2199	-0.0053	-0.2718	+0.1440
ρ (g/cm ³)	-0.0374	-0.0663	-0.1404	0.0160

^ah is height, r is radius, V is volume, and ρ is density.

Fig. A-1. Cumulative percent weight loss for tuff samples of various mineralogies.

Fig. A-2. Cumulative percent volume change on heating for tuff samples.

Fig. A-3. Cumulative percent density change on heating for tuff samples.

IV. RESULTS

Complete results are presented in Table B-I and Fig. B-1. During the initial hydration run, sample YM-38 exhibited similar increases in weight (6.15%) and in density (5.72%). Subsequent heating resulted in a weight loss of 9.00% and a density decrease of 8.14%. Weight and density parameters show little variation between the 16 and 32 h runs, possibly indicating approach to hydration equilibrium during this time. After rehydration the density was 3.04% lower than that following the first hydration.

V. CONCLUSIONS

The 6.15 wt-% gain during the initial hydration test indicates that the zeolite in the YM-38 tuff core was not fully hydrated before this experiment began. The experiment shows that significant weight and volume changes in clinoptilolite tuff can occur below 100°C with changes in the partial pressure

TABLE B-I
AVERAGE VOLUME AND DENSITY FOR YM-38 MAINTAINED AT 91-95°C

<u>Time(h)^a</u>	<u>Weight(g)</u>	<u>V(cm³)</u>	<u>Density(g/cm³)</u>
BH	18.6257	10.2077	1.8247
H	19.7703	10.2490	1.9290
0.5	19.2063	10.2590	1.8721
1.0	18.8235	10.2814	1.8308
2.0	18.5134	10.2028	1.8018
3.0	18.3237	10.1698	1.8018
8.0 ^b	18.0710	10.1823	1.7747
16.0	18.0709	10.1689	1.7771
32.0	17.9906	10.1526	1.7720
RH	19.2272	10.2798	1.8704

^aBH is before hydration, H is after hydration, and RH is rehydration after 32 h at 95°C.

^bOut of sequence.

of water. Because such changes may critically affect the groundwater flow regime in the vicinity of a waste repository, it is important to continue the investigation of equilibrium reactions between zeolite and groundwater under low-temperature (<100°C) conditions.

The volume of the core (Fig. B-1) generally decreased as the time of heating was increased. In order to avoid the rapid re-equilibration with atmospheric moisture, measurements were made while the samples were still warm. Although thermal expansion is known to be small relative to volume changes due to hydration, the small initial volume increase may simply reflect thermal expansion. After one hour of heating the shrinkage of the clinoptilolite unit cell (determined by X-ray analysis) upon dehydration becomes dominant and produces a net volume decrease.

After rehydration the sample exhibited lower weight and density and a larger volume relative to the initial hydration run. The weight loss following rehydration may be due to non-reversible dehydration. The volume increase following rehydration may be due to slight thermal expansion or to fractures

Fig. B-1. Cumulative changes in density, volume, and weight for clinoptilolite tuff sample YM-38 heated at 95°C as a function of time. Initial values (BH) are for the shelf-dried specimen, and final values (RH) are after rehydration.

introduced by shrinkage of clinoptilolite by dehydration. More tests are required to determine if there are residual non-reversible hydration-dehydration effects in this zeolitized tuff.