LA-9666-PR Progress Report

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Research and Development Related to the Nevada Nuclear Waste Storage Investigations

October 1-December 31, 1982

LOS Alamos National Laboratory Los Alamos, New Mexico 87545 The four most recent reports in this series, unclassified, are LA-9225-PR, LA-9327-PR, LA-9484-PR, and LA-9577-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.

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October 1—December 31, 1982

Compiled by A. E. Ogard, W. R. Daniels, and D. T. Vaniman

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RESEARCH AND DEVELOPMENT RELATED TO THE NEVADA NUCLEAR WASTE STORAGE INVESTIGATIONS

October 1 - December 31, 1982

Compiled by

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ABSTRACT

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

EXECUTIVE SUMMARY

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 Department of Energy (DOE) during the period from October 1 through December 31, 1982. The report is not a detailed technical document but does indicate the status of some of the investigations being performed at Los Alamos.

NUCLIDE MIGRATION FIELD EXPERIMENTS IN TUFF

Field migration experiments will be undertaken to evaluate the adequacy of laboratory-scale nuclide migration experiments that describe the actual migration and retardation processes in Yucca Mountain tuffs. In addition, if the experiments are planned appropriately, the field experiments can be used in the process of validating geochemical performance models for the tuffs of Yucca Mountain.

The effort to find a suitable site for nuclide migration field experiments in tuff continued this quarter. Surveys were made of the surface characteristics of the Topopah Spring tuff that outcrops at two locations on Busted Butte, at the Nevada Test Site (NTS); these surveys showed that the tuff there more closely resembles the tuff expected at the Topopah Spring tuff target horizon in the Exploratory Shaft than does the Topopah Spring tuff at Fran Ridge, which was selected previously for horizontal coring.

The primary emphasis in the field work now is to secure cores from two nearly horizontal drill holes at Fran Ridge. The cores will be used to determine the depth behind the surface to which weathering effects extend and to measure the fracture characteristics of the Topopah Spring tuff to a distance of 400 ft from the surface. The fracture data (spacing, aperture size, and nature of fill material) will be used both for modeling purposes and for designing the diffusion and fracture-flow experiments. The first of the two horizontal holes has been started.

In preparation for future field experiments, further studies were made to optimize the analysis parameters for separating and detecting fluorinated benzoates, which are potential groundwater tracers.

GEOCHEMISTRY OF TUFF

The chemistry of the groundwater in Yucca Mountain is important for several reasons. (1) The speciation of nuclear wastes that may dissolve in the groundwater will largely be controlled by the groundwater chemistry. The speciation in turn will affect the precipitation reactions, complexing, and other retardation mechanisms. (2) The corrosion rate of the waste package is greatly affected by the groundwater composition. (3) The definition of water flow paths can be aided by a knowledge of the groundwater chemistry.

As another step in creating a data base, groundwaters from Wells USW-H6 and USW-G4 at Yucca Mountain have been sampled and analyzed. Two different methods of sampling were used, each yielding somewhat different results. The results must be used with caution until further experiments clarify these differences.

In continuing efforts to more fully describe the in situ composition of the groundwater, the possible field use of carbon dioxide gas-sensing electrodes, bromide ion-selective electrodes, and ammonia gas-sensing electrodes is being investigated.

Microbiological entities in groundwaters can conceivably alter the composition of the groundwater, resulting in changes in the speciation of waste elements in the groundwater. Two organic materials, a detergent and a polymer, are introduced into the tuffs of Yucca Mountain during the drilling of geologic and hydrologic boreholes. There are experiments to study whether these organics can support the growth of microbiological entities and under what conditions.

Transport of radioactive material through geologic media by particulate flow may be a significant mechanism for dispersing hazardous material from the repository. One type of particulate that may be present is the polymers or colloids of the radioactive waste materials themselves. Therefore, the conditions of formation and the solubility properties of plutonium polymers are being investigated.

Permeability and porosity measurements are necessary to interpret field tests and design laboratory experiments. These measurements also provide a data base for modeling flow in fractures and in the near field. The matrix permeability of two samples of tuff from the Topopah Spring Member have been measured. Results of the permeability measurements are low, in the range of 10^{-18} to 10^{-19} m².

Sorption of radioactive waste elements on minerals in tuff is one of the most important retardation mechanisms in Yucca Mountain tuffs. The majority of available data on the sorptive properties of tuff comes from batch or static laboratory measurements; these are valid results for an equilibrium system. Batch sorption measurements are made continually on tuffs of the unsaturated zones. Sorption experiments have also been initiated for the hazardous waste elements radium and selenium, which have not yet been studied.

Water from various wells and from a particular strata in one well at the NTS has been sampled and analyzed in a continuing program aimed at understanding water chemistry and geochemistry in the vicinity of Yucca Mountain. As part of an evaluation of the analytical results, calculations have been made using the EQ3/6 equilibrium program. These calculations use the analytical data as input; they produce a distribution of species among the various ions and complexes in solution, a list of supersaturated minerals, and a list of the identity and quantity of minerals that would precipitate if the water were at equilibrium. This information is very useful for understanding water chemistry of individual wells and the relation between water chemistry and the minerals observed at the well site. Results from calculations for samples taken from the 28-day pumping test of Well UE25b-1 (Bullfrog Member) and from integral samples from Wells J-13, USW-H4, USW-H5, and UE29a-2 are described.

A large imbalance in the electrical neutrality shown in these calculations resulted in a reexamination of sampling and storage techniques used for the groundwater. This in turn resulted in a second analysis of the groundwaters. The results of the second analysis have a small imbalance in electrical neutrality and illustrate the importance of continually using geochemical and transport models to check the validity and usefulness of the experimental data.

The study of geothermal sites in felsic tuffs like those of Yucca Mountain is being proposed as a natural chemical analogue for mineral alteration and nuclide transport in the tuffs in the near-field thermal gradient of the waste repository. Felsic volcanic tuffs consist of glass particles, mineral phases formed at high temperatures, and alteration mineral phases that are forming slowly through geologic time from the glass and high-temperature minerals. Placing a heat source, such as a repository, in the tuff accelerates and changes the alteration process. In addition, a heat source imposes a temperature gradient. Groundwater or downward-percolating water moving in that temperature gradient will leach, transport, and deposit material over long

periods of time. Warm spring systems are natural analogues for these processes and can be used to extrapolate experimental data from laboratory times of days and months to the hundreds of years that may be required to isolate waste in the presence of the thermal gradient.

Three warm springs in the ring-fracture zone of the Valles Caldera in the Jemez Mountains of New Mexico were sampled. The water composition of warm springs in the ring-fracture zone is known to be very similar to that of Well J-13 at NTS, and the bulk chemical composition of the rock is close to that of the Yucca Mountain tuffs. Warm spring localitites in Nevada with a high probability of appropriate alteration were chosen by combining geothermal resource maps of Nevada with geologic maps, published reports, and theses to find springs with the right water, rocks, and temperatures. Water samples and sequences of rock samples from the two best localities were taken for further analysis.

MINERALOGY-PETROLOGY OF TUFF

Mineralogic and petrologic studies for Drill Hole USW-G3/GU3 were completed this quarter, and a report is in preparation. Some conditions revealed in core from Drill Hole USW-G3/GU3 are unexpectedly different from those in USW-G1, USW-G2, and UE25a-1 in the northern part of the exploration block. The main differences are the vitric character of the Calico Hills and the lesser degree of alteration and secondary-mineral development in USW-G3/GU3. Mineralogy-petrology results from boreholes USW-G1, USW-G2, and UE25a-1 had suggested that the Calico Hills was the thickest and most extensively zeolitized unit within the exploration block. The Calico Hills in USW-G3/GU3 is, however, vitric without the extensive zeolitization observed in the other boreholes. Thus, the Calico Hills appears to be extensively zeolitized in the northern part of the exploration block and vitric in the southern part. The transition from vitric to zeolitized tuff appears to occur near or slightly north of USW-H5 and USW-H4. In addition, the Calico Hills in USW-G3/GU3 is thinner than in USW-G1, USW-G2, and UE25a-1, probably because of distance from the source. The Calico Hills in USW-G3/GU3 also contains a slightly different phenocryst assemblage from that observed in cores from other drill holes.

Drill Core USW-G3/GU3 shows much less alteration and secondary-mineral development than core from other drill holes. Tuff units above the water table in USW-G3/GU3 are more vitric (that is, less altered), which suggests that

the units were not beneath the water table for any extended period following their emplacement. Tuff units below the water table in USW-G3/GU3 have less clay, less calcite, no barite, no authigenic albite, no mordenite, and scarce pyrite. Key minerals such as clinoptilolite, analcime, tridymite, and cristobalite appear at greater depths in USW-G3/GU3 than in boreholes in the northern part of the exploration block. The transition from calcium-rich, magnesiumrich heulandites to potassium-rich clinoptilolites to sodium-rich clinoptilolite with increasing depth, which was observed in boreholes in the northern part of the exploration block, is suppressed in USW-G3/GU3. The transition from sorptive smectites to illite, which occurs at about 3400 ft in USW-G2, was not encountered in USW-G3/GU3. Rather, the transition appears to be about 20% complete in the lower part of USW-G3/GU3. Moreover, clay minerals in USW-G3/ GU3 have not been subjected to the same high temperatures as those in USW-G2.

VOLCANISM STUDIES

Rift basalts in the NTS region show uniform composition for the last 8 Myr. Basalts of the silicic cycle, however, show diversity in composition. Basalts of Black Mountain are strongly alkaline, and basalts of Skull Mountain are subalkaline but have considerable compositional overlap with the rift basalts. Field sampling of NTS basalts for isotope analyses will continue in a cooperative project with S. Simkin at UCLA.

ROCK PHYSICS STUDIES

Results of rock physics studies reported this quarter indicate that near-field conditions should cause slow change in tensile and compressive strengths, porosity, matrix permeability, and mineralogy in some tuff types but little or no changes in thermal properties. An experimental program was designed to perform creep tests using Calico Hills samples.

SHAFT/BOREHOLE SEALING

The purpose of the shaft and borehole sealing project is to evaluate the chemical stability of sealing material in the felsic tuff environment of Yucca Mountain. Any sealing material will react with the rock at some rate because the sealant and rock will be chemically different and because volcanic tuff contains tiny, highly reactive mineral and glass particles. The object in choosing an appropriate sealant is to identify the reaction products, determine their effect on the physical and chemical properties of the seals, and minimize reaction and reaction rates if the effects are deleterious. A series of laboratory studies has been planned to observe test-rock/sealant reactions in a laboratory setting. The work will be done in cooperation with the Materials Testing Laboratory of Pennsylvania State University.

In the geochemistry program, reports on materials currently under consideration for sealing tuffs and other geologic media have been reviewed. The initial choices for rock and cement samples and the major initial cement additives have been analyzed. A survey of the relevant thermodynamic information on the combined tuff/sealant system is underway. Ancient cement seals in volcanic tuff are being examined, and initial experimental tests are underway to study accelerated tuff/sealant reactions in agitated vessels at temperatures ranging from 200 to 25°C.

EXPLORATORY SHAFT

The DOE/NV decided to sink (mine) the Exploratory Shaft, rather than drill the shaft. The mined shaft will be nominally 14 ft in diameter and 1600 ft deep with a 12-in.-thick concrete liner. Title I design of surface and subsurface facilities was nearing completion at the end of the quarter.

Planned construction-phase tests for the Exploratory Shaft include mapping and photographing the shaft-wall, sampling large blocks of tuff, collecting groundwater samples, measuring groundwater flow rates, installing rod extensometers, installing multipoint extensometers, drilling laterally into the target unit, and measuring the overcore. Results will be used as input for the breakout decision and Site Characterization Report. Work on the in situ phase tests continues.

QUALITY ASSURANCE

All Los Alamos quality assurance plans and procedures for the NNWSI were reviewed and revised, and a loose-leaf manual was distributed to project participants at Los Alamos. This manual will be revised and updated on a continuing basis. The drilling and coring program for the horizontal holes was reviewed, and criteria were agreed upon by all participants.

Quality assurance requirements for the Exploratory Shaft are being developed in collaboration with DOE/NV.

The Los Alamos quality assurance manager was assigned to a national committee charged with the task of adapting existing national quality assurance standards for nuclear facilities (ANSI/ASME NQA-1) to the specific requirements of waste management.

Additional quality assurance procedures are being developed. A quality assurance indoctrination and training program was held for personnel at the US Geological Survey, Menlo Park, California.

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 Department of Energy (DOE) during the period from October 1 through December 31, 1982. The report is not a detailed technical document but does indicate the status of some of the investigations being performed at Los Alamos.

II. FIELD MIGRATION EXPERIMENTS

A. Field Site (A. E. Norris, B. M. Crowe, and T. J. Merson)

The effort to find a suitable site for nuclide migration field experiments in tuff continued this quarter. Surveys were made of the surface characteristics of Topopah Spring tuff that outcrops at two locations on Busted Butte at the Nevada Test Site (NTS); these surveys showed that the tuff there more closely resembles the tuff expected at the Topopah Spring tuff target horizon in the Exploratory Shaft (ES) than does the Topopah Spring tuff at Fran Ridge, which was selected previously for horizontal coring. The primary difference between the tuffs of Busted Butte and Fran Ridge is the lithophysae-free character of Busted Butte tuffs and its known relationship to the underlying vitrophyre; the outcropping at Fran Ridge is an unknown distance above the vitrophyre and is not necessarily lithophysae free. However, the cost of developing either site at Busted Butte would be significantly greater than developing the Fran Ridge site for these field experiments because the access roads and power line extensions to either Busted Butte location would be longer than those to the Fran Ridge site.

The primary emphasis of the field work now is to secure cores from two nearly horizontal drill holes at Fran Ridge. The cores will be used to determine the depth behind the surface to which weathering effects extend and to measure the fracture characteristics of the Topopah Spring tuff to a distance of 400 ft from the surface. The fracture data (spacing, aperture size, and nature of fill material) will be used both for modeling purposes and for design of the diffusion and fracture-flow experiments.

The first of the two horizontal holes has been started. At the time of shutdown for the holidays, the hole had been drilled and cored ~150 ft into Yucca Mountain, using only dry air as the lubricant. There have been

problems with drill stem vibration, low life span of the drill bit, and poor-quality cores. Presumably, the vibrations of the drill stem cause the cores to be extremely broken up, which makes it difficult to get a fracturespacing count on the cores.

An 80-kg piece of Topopah Spring tuff was collected at Busted Butte and shipped to Los Alamos for laboratory studies. Material from this piece is being measured for permeability and porosity. The composition of Well J-13 water that has been shaken for 2 weeks with crushed material from this tuff will be determined. Water tracer and radioactive-waste tracer experiments also in progress will be used for diffusion and fracture-flow sorption measurements.

The TRACR3D code is used to define feasible fracture-flow experiment designs. Preliminary data from the Busted Butte tuff permeability measurements indicate that the calculations with 1- μ D permeability are reasonable. The primary difficulty in designing a good field experiment is the complete lack of data about the range of fracture apertures that is likely to be encountered in Topopah Spring tuff. Calculations of water flow are very sensitive to the value of this parameter. The data from the horizontal coring at Fran Ridge are necessary to set limits for the experimental design calculations.

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

Further studies were made to optimize the analysis parameters for separating and detecting fluorinated benzoates, which are potential groundwater tracers. Because the laboratory environment probably represents the best case situation for analysis of these compounds, experiments were performed to assess the reproducibility of the tracer characteristics on a day-to-day basis and their optimum response under routine analysis conditions. Individual compounds in Well J-13 water were analyzed. Solvent proportions were varied in an attempt to increase resolution of the mixtures. It appears that five of six compounds investigated could possibly be used simultaneously in a tracer experiment; however, adding the sixth compound causes considerable problems in resolution.

Using the Spectra-Physics program "UVSCAN" will permit selection of a monitoring wavelength to obtain maximum sensitivity. Preliminary runs have been made using this system, but the results have not been evaluated.

Some literature concerning applications of tracers in a field situation has been reviewed in an attempt to understand their behavior, sorption and dilution effects, etc. It appears that if a comparatively small volume of

tracer solution were injected, one could expect that dilution in the rock formation might mandate analytical detection limits in the part-per-billion range. If dilution were a function of distance between the point of injection and the point of sampling, it is conceivable that an experiment involving only a short travel path for the tracer could allow detection limits several orders of magnitude higher, in the part-per-million range. It now appears that, for the fluorobenzoate compounds studied, part-per-billion sensitivity would require some sort of enhancement, whether by concentration of the sample, derivatization for fluorescence detection, gas chromatography, or some other means.

III. GEOCHEMISTRY OF TUFF

A. Groundwater Chemistry (A. E. Ogard, R. A. Aguilar, A. J. Mitchell, and P. L. Wanek)

Water samples from Wells USW-H6 and USW-G4 at Yucca Mountain have been collected for chemical analysis. Each sample was anaerobically collected, filtered through a 0.05- μ m Nuclepore membrane, and sent to Los Alamos for chemical analysis. The electrode measurements were made in the field. Results from sampling USW-H6 are given in Table I. These results must be used with caution because the water exiting the pump continued to foam; obviously the water still contained drilling detergent at levels >0.2 mg/ ℓ and was not pure formation water. Results from USW-G4 are not complete at this time.

The at-depth samples from Well USW-H4, described in an earlier report,¹ have been analyzed and the results are reported in Table II. The sample numbers reflect the depth in Well USW-H4 from which the sample was taken by wire-line sampling (for example, sample H4-2060 was taken from 2060-ft depth).

B. Analytical Techniques for Groundwater Analysis (P. L. Wanek)

Investigations were made of several potential field methods that are used to analyze selected chemical components of water samples. Comparisons were then made of the accuracy and reproducibility of these field methods and of established laboratory methods.

Because the waters of the Yucca Mountain region of Nevada are characterized by a sodium bicarbonate system, it might be advantageous to be able to measure directly the contribution of free carbon dioxide to the bicarbonate component, especially where access to deep well waters is possible. Therefore, an Orion carbon dioxide gas-sensing electrode was tested; it has a potential capability

TABLE I

COMPOSITION OF GROUNDWATER FROM WELL USW-H6

Analyses	by PES ^a Concen-	Analyse	es by IC ^b Concen-	
Element	(mg/l)	Anion	(mg/l)	Other Data
Mg	0.223	F	4.1	pH = 7.7
Mn	0.042	c1 ⁻	7.7	$Eh = 394 \text{ mV vs H}_2$
Si	20.0	N0_2	N.D. ^C	$[0_2] = 5.7 \text{ mg/l}$
Fe	0.119	ро <mark>3</mark> -	N.D.	$[s^{2}] < 10^{-9} M$
Sr	0.009	NO ₃	5.3	Alkalinity = 2.76 meg/
Ba	0.039	so_4^{2-}	27.5	Total CO ₂ = 3.2 millimole/&
v	0.016	Br	N.D.	"free" (calc.) CO ₂ = 19 mg/l
Ti	0.015			
Ca	5.48			
Li	0.101			
К	2.09			
A1	0.116			
Na	73.9			

^aPlasma emission spectroscopy.

^bIon chromatography.

^CNot detected.

	Concentration (mg/l)												
Sample	Mg	Mn	Si	Fe	Sr	Ba	V	<u> </u>	Ca	Li	<u> </u>	<u>A1</u>	Na
H4-2060	0.348	0.091	11.3	0.054	0.019	<0.002	<0.009	<0.007	8.0	0.262	4.07	0.036	114.3
-2240	0.209	0.096	26.4	0.168	0.016	0.004	11	11	7.3	0.338	3.46	0.035	107.1
-2365	0.227	0.084	26.5	0.196	0.014	0.008	††	11	8.3	0.398	3.44	0.056	109.2
-2600	0.252	0.127	25.3	0.863	0.024	0.011	11	11	12.4	0.374	3.22	0.051	105.1
-2850	0.143	<0.006	26.4	0.011	0.010	<0.002	11	11	3.9	0.328	3.79	0.055	99.7
-2980	0.251	0.081	25.9	<0.05	0.016	0.006	**	**	12.8	0.265	3.49	0.075	92.2
-3400	0.219	0.084	25.4	0.160	0.028	0.007	**	**	11.4	0.260	3.24	0.085	92.8
-3875	0.157	0.086	26.0	<0.05	0.031	0.006	**	**	7.7	0.210	3.30	0.062	97.6
	F	<u>c1</u>	NO ⁻ 2	P04	NO ₃	$\frac{so_4^{2-}}{4}$	Br	<u>s</u> ^{2-^a}	0 ₂	Alk	рН ^b	Eh ^a	
H4-2060	5.4	7.6	<0.1	N.D. ^C	N.D.	32.0	<0.1	-373	0.1	2.957	8.7	-160	
-2240	4.2	7.8	N.D.	**	11	24.4	tt	-423	<0.1	2.686	8.6	-158	
-2365	3.3	7.3	N.D.	11	11	25.0	**	-434	0.1	2.746	8.6	-190	
-2600	3.0	7.6	2.7	**	11	24.8	**	-400	<0.1	2.703	8.4	-177	

27.6

25.5

24.2

24.1

**

**

11

11

-403

-347

-404

-393

<0.1

<0.1

<0.1

~0.12

2.226

2.458

2.526

2.417

9.6

8.6

8.7

8.6

-191

-160

-171

-159

Ι

AT-DEPTH SAMPLES IN WELL USW-H4

^aMillivolts vs H₂.

-2850 4.4

-2980 2.8

-3400 2.9

-3875 2.7

 $^{\rm b}$ Measured at Los Alamos; loss of CO₂ is likely.

N.D.

2.5

1.0

2.3

8.8

7.3

7.1

7.0

N.D.

**

11

<0.1

0.24

1.3

<0.5

<0.5

^CNot detected.

Ι3

to perform measurements in a flow-through, "anaerobic" system. In the normal operating mode, the electrode measures total carbonic species; a citrate buffer, which converts any bicarbonate or carbonate to carbon dioxide by lowering the solution pH to ~5.0, is added to the sample. The gas diffuses through the membrane, changing the electrical potential of the inner electrode solution. This change is monitored on a pH/millivolt meter.

Because no recently collected field samples were available for experiments, Well J-13 water was used. The water samples were of two types: water that had been collected in a tightly stoppered glass bottle with no air access and, for comparison, similar water that had been exposed to air. Total carbonic species $(C_{\rm T})$ were measured, using the procedure in the Orion manual.

The electrode was standardized with standard Orion bicarbonate solutions. Measurements were then made on the Well J-13 water samples. Acidimetric titrations on the same samples determined total alkalinity and bicarbonate for comparison. On the air-exposed sample, the pH was 8.2, the total carbon dioxide was 2.8 x 10⁻⁴ millimole/ ℓ , and alkalinity was 2.62 meq/ ℓ . On the airtight sample, the pH was 6.8, and the total carbon dioxide was 2.3 x 10⁻⁴ millimole/ ℓ (\pm /-0.04). The titration was aborted; apparently the automatic titrator program did not allow enough equilibration time between acid additions to ameliorate the effects of the carbon dioxide concentration. When the same sample was left exposed to air overnight, a value of 2.05 meq/ ℓ alkalinity was obtained, which corresponds to a calculated C_T of 2.01 x 10⁻⁴ millimole/ ℓ .

Other measurements on Well J-13 water were done, in which the free carbon dioxide was measured in the solution before adding the buffer; citrate buffer was added after a maximum carbon dioxide measurement was made, and the total carbon dioxide was obtained. Bicarbonate concentration calculated by difference was 1.8 millimole/ ℓ (108 mg/ ℓ).

Comparisons of the distributions of carbonic species in the Well J-13 samples obtained by electrode and by titration were made by calculating the missing components from Table I of the ASTM Standard Method D-513C.² This table, derived from dissociation constants, describes the fractional components of the bicarbonate/carbonate system that are present at any given pH. The ratio of measured free carbon dioxide to measured total carbon dioxide in many cases corresponded, according to Ref. 2, to a pH value that was lower than any actually measured. The total carbon dioxide values obtained by the electrode were within in a few per cent of the C_T calculated from the titration data. Measured pH values of these Well J-13 samples varied from 6.8 to near 8.5; the titrated alkalinity values ranged from 2.0 to 2.7 meq/2.

These results again seem to point out the importance of immediate, on-site measurements of pH, temperature, and possibly the carbon dioxide concentrations as well, if the system is to be well described. Some measurements on fresh samples would help verify the usefulness of the carbon dioxide electrode as an analytical tool for water chemistry in the field.

An attempt to get even closer to the native-state water characterization by measuring carbon dioxide in a flow-through system was not successful. A peristalic pump was used to pump supposedly equal amounts of sample water and diluted citrate buffer, which were mixed in a "Y" connection, to a flow-through cap in the electrode. The meter readings of carbon dioxide concentration continuously increased with time, and no stable concentration was ever determined.

A very useful tool for field tests is a titration assembly made by Hach. With slight modifications in the setup and by using a weak sulfuric acid cartridge (0.16 meq/ml), values of alkalinity were obtained that deviated <1% from the calculated value of a standard solution and <2% from the automatic titration values for a Well J-13 sample. The Hach method is simple to perform but requires more time to complete than does the automatic titration as it is presently programmed. It is completely portable, requiring only a ring stand and pH meter in addition to the digital titration wheel.

Another potential field method tested was the determination of bromide by ion-selective electrode. This was of interest because it could possibly be used to process large numbers of samples in a short time if sodium bromide were used as a water tracer. The electrode gave linear response to ~0.4 mg/ ℓ bromide. Values in this range can be determined directly in the "concentration" mode of a specific ion meter. For values between 0.2 and 0.4 mg/ ℓ bromide, a calibration curve or known addition methods must be employed. Values below 0.2 mg/ ℓ seem unreliable. These limits are within the range of the limits detectable by ion chromatography using the conductivity detector. The electrode has the advantage of speed, simplicity, and portability. For lower concentration limits, it seems advisable to run selected samples by ion chromatography using the electrochemical detector.

An ammonia gas-sensing electrode was obtained, and a few selected groundwater samples from Nevada were analyzed to investigate the possibility that some combined nitrogen could be present in the form of ammonia, especially in those samples where nitrite was found or in samples that were obtained from a deoxygenated environment. The response of the ammonia electrode appeared to be linear to ~0.04 mg/l as nitrogen, which corresponds to 0.05 mg/l as ammonia. Selected samples of water from Wells J-13 and UE25b-1 at Beatty, Nevada, and G Tunnel at NTS showed no ammonia concentrations above background level. In addition, a sample of Well H-4 water, collected in a Vacutainer and not exposed to air, was found by the Technicon Autoanalyzer method to have <0.05 mg/l ammonia. Therefore, nitrogen in its fully reduced form does not seem to be present in significant concentration in the Nevada groundwaters tested.

<u>C.</u> Plutonium Chemistry in Near-Neutral Solutions (T. W. Newton and V. L. Rundberg)

Adaption of ion exchange techniques to determine Pu(IV) polymer and the various oxidation states of plutonium has continued. Use of H_2O_2 -modified BioRad AG50 X-2 resin^{*} and BioRad Zirconium Phosphate^{**} has been extended to more dilute solutions than the 3 x 10⁻⁵ M solutions previously tested.³ The exchange columns and procedures were the same as those used before. The lower concentrations were in the range from 3 x 10⁻⁷ M to 2 x 10⁻⁶ M, so the entire 2-ml portions of eluent were alpha-counted after evaporating to dryness on Pyrex planchets 4.5 cm in diameter. The elution patterns obtained were similar to those reported previously; this result suggests that the method is limited by counting accuracy rather than by chemical behavior on the ion exchange material.

The Pu(IV) polymer used in the previous experiments and in those described above was several months old, had been prepared to be 8 x 10^{-3} M Pu in 0.05 M HCl, and had been purified by ion exchange. Because the history of the polymer might affect its properties, it was important to compare the results from experiments using the aged polymer with those using fresh polymer prepared in more dilute solution: 10^{-5} Pu and 10^{-3} M HCl. Ion exchange results from using

^{*}As recommended by J. C. Sullivan, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.

^{**}As recommended by H. Gehmecker, Institut für Kernchime der Universität Mainz, D6500 Mainz, West Germany.

the latter preparation showed significant elution with 3 and 6 M HCl and were similar to results for monomeric Pu(IV). However, the amount of monomeric Pu(IV) in the preparation was shown to be only ~2%, based on reaction with Os(II).

To investigate this problem further, 4×10^{-4} M polymer was prepared in 0.01 M HCl. These concentrations were chosen so that changes in the absorption spectrum, as well as changes in the elution behavior could be followed. Concentrated Pu(IV) stock in 3 M HCl was diluted appropriately, and samples for ion exchange were taken at various times. The fraction of the total plutonium eluted with 3 M HCl decreased with time, from 63% by 0.09 hour to 21% by 24 hours. During this same period, the fraction requiring 12 M HCl for elution increased from 32 to 72%, and the characteristic absorption spectrum of the Pu(IV) polymer developed. During the first 0.6 hour, 69% of the total change at 645 nm [loss of Pu(IV)] and 40% of the change at 613 nm (growth of polymer) occurred. These results are to be compared with 50% of the total change in the elution fractions during the same period. Even after 24 hours, when the characteristic polymer spectrum was fully developed, 20% of the total plutonium was eluted by using 3 M HCl. This is contrasted with 3.5% for the purified, aged polymer. This result illustrates the fact that freshly prepared dilute polymer and aged, more concentrated polymer can have different properties even though the absorption spectra are very similar.

In an additional experiment that used essentially the same plutonium and acid concentrations, Os(II) was used to estimate the amount of unreacted Pu(IV) monomer as a function of time. The results showed that, in contrast to the experiments discussed above, in this case ~80% of the monomer had disappeared within the first 0.01 hour.

Further experiments were performed to elucidate the changes that occur in freshly prepared polymer suspensions. Plutonium(IV) in 3 M HCl was diluted to give 2 x 10^{-4} M Pu in 0.01 M acid, and polymerization was allowed to proceed. Changes were monitored by taking samples periodically for treatment with excess Ce(IV) perchlorate in one experiment and excess Os(II) tris-dimethyl-bipyridine in another. Table III shows the concentrations used as well as the times required for reaction with monomeric Pu(IV), as determined in separate experiments.

Absorbance vs time for the Ce(IV) samples at the 830.5-nm Pu(VI) peak showed rapid initial increases caused primarily by unreacted Pu(IV) monomer in

TABLE III

REACTION BETWEEN MONOMERIC Pu(IV) AND Ce(IV) OR Os(II)

Reactant	Concentration (M)	Pu(IV) (M)	Acid	Plutonium Product	Time ^a (minutes)
Ce(IV) perchlorate	8.2×10^{-4}	6.5×10^{-5}	0.1 M HC10 ₄	Pu(VI)	<u><</u> 1
Os(II) tris- dimethylbypyridine	1.2×10^{-5}	4.2×10^{-6}	0.1 M HC1	Pu(III)	<u><</u> 0.75

^aApproximate time for 99% completion.

the polymerizing mixture, followed by a much slower reaction with a component of the polymer. Aged polymer treated in the same way showed essentially no rapid reaction caused by monomeric Pu(IV), but it did show a similar slow reaction.

The absorption of the Os(II) samples at the 488-nm Os(II) peak showed an initial rapid decrease followed by much slower reactions. In the early stages of polymerization, at least two slow reactions were observed, but near the end only one such reaction was evident.

The apparent rates of disappearance of monomeric Pu(IV), based on the initial rapid reaction with either Ce(IV) or Os(II), were the same within ~20% and corresponded to 50% complete in about 0.05 hour.

The results discussed above suggest that polymerization is a complicated process with different components forming (and possibly disappearing) at different rates. Thus, it will be important to extend characterization experiments such as these to as small concentrations as possible to make reliable predictions concerning the nature of the polymeric species in environmental solutions.

Equilibrium data for the Pu(IV) polymer are lacking. In an attempt to remedy this lack, the reaction

$$\frac{1}{n}(PuO_2 \times mH_2O)_n + PuO_2^{2+} = 2PuO_2^{+} + mH_2O , \qquad (1)$$

where the first substance in the equation is the Pu(IV) polymer, was investigated. The equilibrium constant for this reaction is important because, with other thermodynamic data, it can provide a value for the dissociation reaction

$$\frac{1}{n}(PuO_2 \times mH_2O)_n + 4H^+ = Pu^{4+} + (2 + m)H_2O$$

which is closely related to the solubility equilibrium of the hydrous oxide.

In earlier experiments (Ref. 4), 239 Pu was used; the rate of reaction (1) was somewhat slower than the alpha reduction rate of Pu0₂²⁺,

$$PuO_2^{2+} + {}^{1}_{2}H_2O \stackrel{\alpha}{=} PuO_2^{+} + H^{+} + 0.25 O_2 \qquad (2)$$

,

The data indicated that apparent equilibrium in reaction (1) was reached somewhere between 16 and 20 days and that the apparent equilibrium constant is approximately $(3.7 \pm 0.7)10^{-5}$ M at pH 3.

These experiments have now been repeated using 242 Pu to decrease the rate of reaction (2) and increase the relative importance of reaction (1). Three experimental mixtures were prepared using 242 Pu and were sealed into 10-cm absorption cells. The absorbances at the principal Pu(VI) peak (830.5 nm) were determined periodically over 213 days. At the end of this time the cells were opened, and the sum of the Pu(V) and Pu(VI) concentration was determined using the reaction with excess Ce(IV) perchlorate. It was shown earlier that Pu(IV) polymer reacts only slowly with this reagent. The experimental results are summarized in Table IV.

The rate of disappearance of Pu(VI) by reaction (2) in the absence of polymer (B in Table IV) was essentially constant and was 0.11% of the total plutonium per day. This is to be compared with 1.25%/day for the analogous ²⁴⁹Pu experiment.⁴

In the presence of polymer (A in Table IV), the average loss of Pu(VI) by reaction (2) can be estimated $(5.00-2.61-0.71)10^{-5}/213 = 7.9 \times 10^{-8}$ M/day or 0.054%/day, based on the total plutonium present. This reduction is about one-half of that observed in the absence of polymer, indicating that polymeric plutonium is less effective than monomeric plutonium in promoting alpha reduction.

	Concentrations		
		$(M \times 10^5)$	
	A Polymer + Pu(VI)	B Pu(VI) Only	C Polymer Only
Pu(VI) initial	5.0	5.0	0
Polymer initial	9.5	0	9.5
Pu(VI) 213 days	2.61	3.81	0.04
Total soluble Plutonium	5.71	4.97 ± 0.05	0.61
Pu(V) from Polymer	0.71	0	0.61

TABLE IV THE 242 Pu(VI) - 242 Pu(IV) POLYMER REACTION IN 0.002 M HClO₄

The average rate of formation of Pu(V) from the polymer (A in Table IV) amounts to 0.7 x $10^{-5}/213 = 3.3 \times 10^{-8}$ M/day. In the analogous experiment using 239 Pu, the rate was 0.48 x $10^{-5}/30 = 1.6 \times 10^{-7}$ M/day. This shows that the rate of reaction (1) is strongly influenced by the alpha particle selfirradiation. This is consistent with the observation that the average rate of formation of Pu(V) or other species capable of rapid reaction with Ce(IV), in the absence of Pu(VI) (C in Table IV), is 85% of that observed in the presence of Pu(VI).

The key assumption required to obtain an equilibrium constant from the data is that reaction (1) is at equilibrium when its net rate is zero, that is, when the observed rate equals the alpha reduction rate. An additional assumption is that the alpha reduction rate remains constant during the course of the reaction, as it does in the absence of polymer. However, because the rate of reaction (1) depends much more strongly on the radiation level than on the Pu(VI) concentration, the key assumption appears quite uncertain. Thus, the value for the equilibrium constant for reaction (1), based on the 239 Pu data⁴ or the similar value that could be obtained from the 242 Pu data, should not be trusted. The conclusion is that the purely chemical rate of reaction (1) is so small that a reliable equilibrium constant cannot be determined.

D. Matrix Permeability and Porosity of Unsaturated Tuffs (C. Duffy)

The matrix permeability of two samples of tuff from the Topopah Spring Member have been measured. Sample USW-GU3 (765.5- to 765.9-m depth) is from the likely repository horizon. The other sample is from the surface at Busted Butte. The USW-GU3 sample has a permeability of ~1.5 x 10^{-18} m² at 24 and 100°C. Preliminary measurements on the Busted Butte sample give permeabilities in the range of 3 to 5 x 10^{-19} m² at room temperature. Detailed modeling is needed to assess the proportion of matrix vs fracture flow; however, if these formations become saturated, it seems probable that at the low permeabilities, matrix flow would be quite small. This, however, should not be taken as proof that matrix flow is not important to waste-element retardation. Small amounts of matrix flow may be quite important because of the large amount of surface area that would be exposed for sorption compared to that exposed by fracture flow.

Porosity was also measured on the USW-GU3 sample. A value of 13.5% was observed. This result emphasizes again that these rocks, despite their low permeability, have considerable porosity into which waste elements may diffuse, even in the absence of matrix flow.

E. Microbiological Activity at Yucca Mountain (L. E. Hersman)

Successive transfers of those organisms first isolated on detergent or polymer media have been performed. Initially, five different bacterial species were isolated on the detergent medium, and four were isolated on the polymer medium. Following several transfers, it appears that one, perhaps two, species growing on both the detergent and polymer media may not survive. This can be explained, in part, by nutrient transfer. After a series of transfers, less and less of the original medium (soil) is transferred with the organisms. If the organisms are unable to use the detergent or polymer as a substrate, then as a result of dilution, less of the original media is available for growth. A second possibility is that improper growth conditions have been maintained, thereby allowing only marginal growth of these organisms.

From old, discarded incubation flasks of detergent and polymer media, an algal species has been isolated. To date, two transfers have been performed, each resulting in vigorous growth of the algae. Although algal contamination in subsurface systems should not pose a significant problem (because of the absence of light), these results are interesting because they demonstrate that the polymer can serve as a growth medium for algae, bacteria, and fungi-three of the four major groups of organisms found in the microbial world, the fourth being protozoa. Obviously, growth on the polymer is not limited to a few specialized bacteria but, rather, is available to a broad range of microorganisms with diverse nutrient requirements.

Shaker flasks of detergent and polymer media have been innoculated with a selected species of each nutrient: one isolated from detergent medium and one isolated from polymer medium. These media have been incubated at 25°C for 3 weeks and will be used as a source of innoculum for the Warburg oxygen-uptake manometers. An incubator is being constructed that not only maintains the proper temperature (± 0.2 °C) but also provides a shaking motion to ensure that oxygen depletion does not occur. The Warburg flasks will be filled with 10 ml of either detergent or polymer media, innoculated with the appropriate microorganisms, and incubated at 25°C while oxygen-use rates are being determined. These experiments should provide information relevant to oxygen depletion in the areas of Yucca Mountain where polymer and/or detergent drilling fluids have been introduced.

F. Sorption on Tuff (W. R. Daniels, F. O. Lawrence, B. P. Bayhurst, S. D. Knight, and M. R. Cisneros)

Batch sorption measurements were started this quarter to determine the sorptive properties of some USW-G2 and USW-GU3 tuff samples. Four USW-G2 tuff samples were selected for their special mineralogic composition. Each one of these four samples is rather high in one of the following constituents: glass, calcite, mordenite, or analcime. The USW-GU3 samples were selected from several horizons and were to include different mineralogic compositions. The radionuclides chosen were 85 Sr, 137 Cs, 133 Ba, 152 Eu, and 95 Tc^m; the measurements for all five are run concurrently, and samples are counted on germanium-lithium counters.

The USW-G2 tuff samples were in contact with the solutions of radionuclides for 6 weeks. The solids and solutions were separated after centrifugation and counting has begun on both. Desorption measurements have been started on these samples, and sorption ratios determined from these experiments will be included in the next quarterly report.

Sorption measurements on USW-GU3 samples are also in progress and contact time again will be 6 weeks. Both vertical and horizontal positions have been used for shaking samples; results from the two methods will be compared to observe any possible differences in the sorptive behavior of tuff. During this quarter, the 235 Np that was produced by irradiation of a 235 U target at the Los Alamos Van de Graaff accelerator was separated from the target solution. This process is necessary because neptunium tracer is no longer prepared by Argonne National Laboratory. A small amount of 235 Np was made in this initial attempt.

Batch samples have also been started using a number of USW-G2 cores with americium and the recently prepared 235 Np. Plutonium-239 will be used shortly with batch samples of the same cores. The USW-G2 cores used in this recent set of experiments are: USW-G2-547, which is from the Pah Canyon Member and is richest in glass; USW-G2-723, which is also from the Pah Canyon Member but is rich in calcite; USW-G2-1952, which is from Calico Hills and is rich in mordenite; and finally, USW-G2-3933, which is from the lower Tram Member and is high in analcime.

Plans are being made to study the sorption characteristics of uranium and selenium in USW-GU3 and USW-G1 cores of selected mineralogies. Preliminary tests have been started to determine if experiments with the two elements can be run together. A 75 Se tracer sample will go to Omega West Reactor and the delayed neutron counting facility to ensure that the gamma background will not interfere with the determination of uranium.

The decay of 238 U and 234 U present in high-level waste or spent fuel will produce 226 Ra over very long time periods; therefore, radium has a high ranking in the hazards index for underground disposal. Preliminary experiments to measure 226 Ra sorption coefficients by the batch method have been started. Because of the 226 Ra daughter, 222 Rn gas, and its subsequent decay products, much care must be exercised in handling sample tubes and counting containers. All manipulations required in the determination will be carried out in a glove box under negative pressure until the samples are sealed in counting containers. Sample and counting containers are being tested with neon and a leak detector.

The plan now is to count ²²⁶Ra with its decay chain through ²¹⁰Pb approximately at equilibrium. The solution from the sorption experiment will be counted on a germanium-lithium detector in a thin-windowed, stainless steel container in which the fill hole is sealed with an O-ring valve.

Barium-133 sorption coefficients will be measured in the same or a parallel experiment. If the radium results follow trends shown by barium, it could be assumed that the much more easily determined barium sorption characteristics are adequate for radium predictions.

G. The EQ3/6 Calculations for Various NTS Well Samples (J. F. Kerrisk)

1. Introduction. Water from various wells and from a particular strata in one well at the NTS has been sampled and analyzed in a continuing program aimed at understanding water chemistry and geochemistry in the vicinity of Yucca Mountain. As part of an evaluation of the analytical results, calculations have been done with the EQ3/6 chemical equilibrium program.⁵ These calculations use the analytical data as input; they produce a distribution of species among the various ions and complexes in solution, a list of supersaturated minerals, and a list of the identity and quantity of minerals that would precipitate if the water were at equilibrium. This information is very useful for understanding water chemistry of individual wells and the relation between water chemistry and the minerals observed at the well site. This section describes some results from calculations for samples taken from the 28-day pumping test of Well UE25b-1 (Bullfrog Member) and for integral samples from Wells J-13, USW-H4, USW-H5, and UE29a-2.

2. Description of Calculations. Analytical data are available on recent water samples from five wells at NTS.³ The largest amount of data is from the 28-day pumping test of Well UE25b-1 (June 23 through July 20, 1982). For this test, packers were used to isolate a particular depth so that water was taken only from the Bullfrog Member tuff. Total concentrations were measured for fluoride, chloride, bromide, nitrate, nitrite, sulfate, phosphate, lithium, sodium, potassium, magnesium, calcium, strontium, barium, aluminum, silicon, manganese, iron, vanadium, and titanium. Two sets of data for sodium are presented: glass-contained acidified samples and plastic-contained nonacidified samples. Measurements of pH, Eh with a platinum electrode, dissolved oxygen, detergent content, titration alkalinity (to pH = 4.5), and water temperature were also made. Bromide and lithium were not considered in the calculation because data for these ions and their complexes are not currently available in the EQ3/6 data base; total concentrations of both species were quite small (bromide <0.4 mg/ ℓ and lithium <0.3 mg/ ℓ). Phosphate, titanium, and vanadium were at or below detection limits in this water and were also ignored in the calculations. The detergent content of the water was not used as data for the calculation but was considered in the interpretation of the results.

The standard EQ3/6 data base contains only a limited number of manganese species and no data on nitrite. Manganese has been found in all the water analyses from the isolated Bullfrog Member in Well UE25b-1;³ it may be a factor in controlling the redox state of the water. Thermodynamic data for 13 aqueous complexes and 16 minerals containing manganese have been collected and added to the EQ3/6 data base for these calculations. These data cover the common manganese complexes and minerals in the II, III, IV, VI, and VII oxidation states. Thermodynamic data for nitrite have also been added to the EQ3/6 data base; with both total nitrate and nitrite concentrations measured, the Eh of the nitrate/nitrite redox couple can be calculated and compared with the Eh measured with a platinum electrode.

For the Well UE25b-1 pumping test, one or more water samples were analyzed for anions, pH, alkalinity, and dissolved oxygen on each day of the test. Only one cation analysis was available per day. Ten samples were chosen for use in the calculations; they ranged from day 7 through day 28. When more than one analytical result was available for a given day, the first sample analyzed that day was used in the calculations.

Integral water samples, that is, samples from no specific formation in the well, have recently been collected from four other wells at NTS (J-13, USW-H4, USW-H5, and UE29a-2). Analytical data for these samples are similar to those for Well UE25b-1, except that a few of the minor cations were not reported. The EQ3/6 calculations were also similar. Only one set of analytical data was available from each well.

For all the calculations, the measured pH, Eh, temperature, and total concentrations of all the species considered were used as input data. The program uses Eh to distribute species involved in redox reactions among the various oxidation states in the data base if no further information is available. This was done for the S^{2-}/SO_4^{2-} , Mn^{2+}/Mn^{3+} , and Fe^{2+}/Fe^{3+} redox couples. Measured data on dissolved oxygen were used to calculate Eh for the $H_2O/O_2(g)$ couple. Where no dissolved oxygen was detected, a value of 0.01 mg/ ℓ was assumed. There are three oxidation states of nitrogen available in EQ3/6: ammonium ion, nitrite, and nitrate. Measured data for total nitrite and nitrate contents were used to calculate Eh for the NO_2^-/NO_3^- couple. Where no nitrite was detected, a value of 0.01 mg/ ℓ was assumed in the oxidation states of not total nitrite and nitrate contents were used to calculate Eh for the NO_2^-/NO_3^- couple. Where no nitrite was detected, a value of 0.01 mg/ ℓ was assumed. Analyses for ammonium ion were not performed; ammonium ion and ammonium complexes were not considered in these calculations.

Real solutions are electrically neutral; however, errors in analytical measurements or the presence of analyzed species usually result in some cation/ anion imbalance when actual data are used for equilibrium calculations. This imbalance can be ignored, or as is often done, the total concentration of one of the major species can be adjusted to achieve electrical balance. The major cation in the waters considered here is sodium and the major anion is carbonate (mostly present as HCO_3). The analytical data for all of the UE25b-1 samples and most of the other data showed a relatively large electrical imbalance if the sodium analyses from the glass-contained acidified samples were used. Calculations were done in which both sodium and carbonate total concentrations were adjusted to achieve electrical balance. In reality, titration alkalinity rather than total carbonate was measured. These two quantities are related, depending on the pH and concentrations of other species that can accept \mathbf{H}^{T} during the titration. The EQ3/6 code has the capability to accept titration alkalinity as input data and calculate total carbonate. This feature was used for these calculations.

3. Well UE25b-1 Results.

a. Glass-Contained Acidified Samples. Ten samples from day 7 through day 28 of the pumping test were used in the calculations. The analytical data for all samples showed a relatively large electrical imbalance, with total cations 15 to 30% greater than total anions. If total carbonate is varied to achieve electrical balance for these samples, the calculated alkalinity is greater than the observed alkalinity. Figure 1 shows the observed alkalinity as well as a plot of calculated alkalinity and calculated total carbonate obtained in this manner as a function of time. Up to about day 20, there is a relatively constant difference between calculated and observed alkalinity; at later times, the difference increases. The reason for the low alkalinity observed on day 21 is unknown.

The increase in calculated alkalinity and calculated total carbonate that is associated with increasing electrical imbalance beyond day 20 is related to an increase in sodium. This is evident in Fig. 2, where total sodium content is plotted as a function of time. Although there is considerable scatter, after day 20 there is 10 to 15% more sodium found than at earlier times. Similar plots for two other ions, calcium in Fig. 3 and chloride in Fig. 4, may show real variations with time, but they are too small to be significant and are not related to the changing electrical imbalance. Another way of



Fig. 1. Alkalinity and total carbonate for samples from Well UE25b-1.



Fig. 2. Total sodium content for samples from Well UE25b-1.



Fig. 3. Total calcium content for samples from Well UE25b-1.



Fig. 4. Total chloride content for samples from Well UE25b-1.

showing the relation between the electrical imbalance and total sodium is presented in Fig. 5, where the difference between calculated and observed alkalinity is plotted as a function of total sodium content. Larger sodium content is related to a larger electrical imbalance, as measured by the difference in calculated and observed alkalinity. The one data point well above the line is from day 21--the day when low alkalinity was observed (see Fig. 1).

Another way to perform the calculations is to assume that the observed alkalinity represents the carbonate content of the water and vary the total sodium content to achieve electrical balance. Figure 6 shows the calculated total sodium content obtained in this manner compared with the observed total sodium. The calculated total sodium content is well below the observed level; the increase in electrical imbalance beyond day 20 can also be seen in Fig. 6.

If the electrical imbalance problem with these samples has one single cause, the most likely possibilities are that the titration alkalinity is too low, that the total sodium is too high, or that another anion, not reported in the analysis, is present. If another anion is present, it was not detected by the alkalinity titration; therefore, it would be an anion of a relatively strong acid. Most of the inorganic anions that fit this description (Cl⁻, Br⁻, SO²₄, and NO₃) have been determined in separate analyses. There are organic anions that qualify, such as those from alkylbenzene sulfonic acids that may be contained in the detergents that are used during drilling. However, the quantity that would be required to achieve electrical balance would be on the order of 100 mg/ ℓ . This is well into a concentration range where observable frothing would occur.⁶ Measured detergent contents were in the range of a few milligrams per liter early in the test, but after day 10 they decreased to below 0.1 mg/ ℓ .³ Thus, contamination by enough detergent to cause the electrical imbalance is not reasonable.

<u>b.</u> Plastic-Contained Nonacidified Samples. Because there appears to be a direct relationship between the electrical imbalance and the total sodium content in glass-contained acidified samples, groundwater samples from Well UE25b-1 kept in plastic bottles were analyzed. It was thought that the HNO₃ used to stabilize the cations might also be leaching sodium from the KIMAX volumetric flasks. The results were reported but not discussed in an earlier



Fig. 5. Relationship between electrical imbalance and total sodium content for samples from Well UE25b-1.



Fig. 6. Observed and calculated sodium content for samples from Well UE25b-1.

report.³ Figure 7 is a plot of total sodium content as a function of time for both sets of sodium data compared with calculated sodium content; the glasscontained acidified samples are labeled original data and the plastic-contained samples are labeled new data. Agreement between the plastic-contained nonacidified sample data and the calculated results is much better and is within 10% for most of the data. Sample procedures for groundwater will now be changed; acidified samples will only be contained in plastic.

There are three measures of the redox state of the water samples: the measured Eh, the dissolved oxygen content, and the nitrite-nitrate ratio. Figure 8 shows the Eh calculated from the dissolved oxygen content and from the nitrite-nitrate ratio compared with the Eh measured by a platinum electrode. Before day 20, the dissolved oxygen content used for the calculation is approximately the detection limit for this quantity because none was detected; thus, the calculated Eh represents an upper limit for this couple early in the test. After day 20, the nitrite content used in the calculation is approximately the detection limit for this couple late in the test. Large differences among values of Eh representing different redox couples are common in natural waters.⁷ The trend of all three redox parameters is toward more oxidizing conditions at later times.

Only total quantities were measured for the species involved in three other redox couples: the $S^{2-}/S0_4^{2-}$ couple, the Mn^{2+}/Mn^{3+} couple, and the Fe²⁺/Fe³⁺ couple. Species were distributed among the available oxidation states for these couples, using the Eh measured with the platinum electrode. Under these conditions (Eh = 0 to 160 mV), essentially all the sulfur in solution would be as sulfate, and essentially all the manganese in solution would be in the +2 oxidation state. These conclusions are based on the assumption that the couples are in equilibrium with the platinum-electrode Eh. Because nonequilibrium conditions are common among redox reactions, the only way to determine the actual distribution of species in various oxidation states is by measurement.⁷

The EQ3 calculations indicate that water from Well UE25b-1 is supersaturated with respect to a large number of minerals (~60); they are mostly aluminosilicate minerals. However, when EQ6 is used to determine the minerals that would precipitate, only quartz, kaolinite, nontronite, and witherite (BaCO₂) are indicated as precipitates for the early samples. All samples with



Fig. 7. Total sodium content of Well UE25b-1 samples.



Fig. 8. Eh for three redox couples for samples from Well UE25b-1.

a measurable dissolved oxygen content also indicated pyrolusite (MnO₂) as a precipitate. This occurs because EQ6 considers only one (equilibrium) redox state for the solution; the equilibrium Eh is determined from the concentrations of the various species that can participate in redox reactions. Dissolved oxygen controls the redox state when it is present in measurable amounts.

4. Other Results. Only one integral analysis was available from each of four other wells at NTS: J-13, USW-H4, USW-H5, and UE29a-2. Table V summarizes some of the measured data and calculated results for these wells. The electrical imbalance (as measured by the difference between the observed and calculated sodium contents when sodium is varied to achieve electrical balance) is about the same magnitude and direction for two of the samples (USW-H4 and USW-H5) as it was for UE25b-1. For the UE29a-2 sample, there is excellent agreement between the calculated and observed sodium content. For the J-13 sample, the total cation content is low; this is in direct contrast to the observed behavior for the other samples. Thus, the consistent pattern of electrical imbalance seen in the UE25b-1 samples was not present in the integral samples from the other four wells.

TABLE V

RESULTS OF CALCULATIONS FROM WELLS J-13, USW-H4, USW-H5, and UE29a-2

	•		
7.2	7.4	7.95	7.3
357	250	353	408
1.96×10^{-3} 2.48 x 10^{-3}	3.66×10^{-3} 3.19 x 10^{-3}	4.05×10^{-3} 2.56 x 10^{-3}	2.21×10^{-3} 2.24×10^{-3}
775 507	763 479	730 454	769 503
() 10	56	0	0
	7.2 357 1.96 x 10 ⁻³ 2.48 x 10 ⁻³ 775 507 () 10 90	7.2 7.4 357 250 1.96 x 10 ⁻³ 2.48 x 10 ⁻³ 3.66 x 10 ⁻³ 3.19 x 10 ⁻³ 775 763 507 479 () 10 56 90 44	7.2 7.4 357 250 353 1.96×10^{-3} 2.48 $\times 10^{-3}$ 3.66 $\times 10^{-3}$ 3.19 $\times 10^{-3}$ 4.05 $\times 10^{-3}$ 2.56 $\times 10^{-3}$ 2.56 $\times 10^{-3}$ 4.05

^aMeasured using a platinum electrode.

^bSodium varied to achieve electrical balance.

The Eh of these four samples (measured with a platinum electrode) is consistently higher than was seen for UE25b-1, as is the dissolved-oxygen content (see Table V). The Eh calculated from the $H_2O/O_2(g)$ couple is similar to the calculated Eh for UE25b-1 because any detectable quantity of dissolved oxygen, even at the detection limit, is large enough to give values of Eh in the 700-mV range. The values of Eh calculated for the NO_2/NO_3 couple must be considered as a lower limit because no nitrite was detected for these samples; a value of 0.01 mg/2, approximately the detection limit, was used for the calculations. For the other three redox couples where only total quantities were measured, the aqueous species distributions calculated from the measured Eh for the S²⁻/ SO₄²⁻ couple and Mn²⁺/Mn³⁺ couple are the same as for UE25b-1; essentially all the sulfur in solution is as sulfate, and essentially all the manganese in solution is in the II oxidation state. For the Fe²⁺/Fe³⁺ couple, the higher Eh for these four samples leads to some iron in the III oxidation state (see Table V).

The EQ6 calculations for samples from Wells J-13, USW-H4, USW-H5, and UE29a-2 indicate that quartz, kaolinite, nontronite, and pyrolusite would precipitate from all four. Witherite, which was indicated as a precipitate for the Well UE25b-1 water, is not indicated here because barium content was not determined for these samples. The sample from Well USW-H5, because of its high pH, also showed muscovite as a precipitate.

5. Summary. The chemical equilibrium computer program EQ3/6 has been used to calculate the state of recent water samples from five NTS wells. The major results of this investigation are listed below.

- (1) The waters from all five wells are generally similar. Sodium is the major cation and carbonate is the major anion (present mostly as HCO₃). Aqueous silica is present in the 60-mg/l range. Other cations present in lesser amounts are calcium, potassium, and magnesium; anions present in lesser amounts are sulfate, chloride, and nitrate. Numerous minor anions and cations were also detected.
- (2) Most of the samples analyzed showed a relatively large electrical imbalance between cations and anions. For the series of samples from Well UE25b-1, there was a relation between the magnitude of the electrical imbalance and the total sodium content. The most likely causes for this imbalance were a low measured titration alkalinity or a high measured total sodium content. Additional results have confirmed that this imbalance is excess sodium leached from the glass KIMAX volumetric flasks by the HNO₃ that was added to stabilize cations.

- (3) The series of samples from Well UE25b-1 were more oxidizing (had a larger Eh) at later times. There were large differences between the solution Eh calculated from the $H_2O/O_2(g)$ couple, from the NO_2^2/NO_3^2 couple, and from the value measured with a platinum electrode. Samples from the other four wells were more oxidizing than were the UE25b-1 samples.
- (4) All the samples were supersaturated with a large number of minerals, mostly aluminosilicate minerals. However, only a few minerals would precipitate if the waters were in equilibrium. They include quartz, kaolinite, nontronite, and witherite (BaCO₃), where barium was determined. In some of the more oxidizing samples, pyrolusite (MnO₂) was also indicated as a precipitate.

H. Transport Code Development (B. J. Travis and R. S. Rundberg)

Efforts on the TRACR3D code development included writing a user's manual for the code, which will be issued as a separate Los Alamos report. 8

I. Natural Chemical Analogues (R. J. Vidale)

The study of geothermal sites in felsic tuffs like those of Yucca Mountain will give essential information on mineral alteration and nuclide transport in the tuffs in the near-field thermal gradient of the waste repository. Felsic volcanic tuffs consist of glass particles, mineral phases formed at high temperatures, and alteration mineral phases that are forming slowly through geologic time from the glass and high-temperature minerals. Placing a heat source, such as a repository, in the tuff accelerates and changes the alteration process. In addition, a heat source imposes a temperature gradient. Groundwater or downward-percolating water moving in that temperature gradient will leach, transport, and deposit material over long periods of time. Warm spring systems are natural analogues for these processes and can be used to extrapolate experimental data from laboratory times of days and months to the hundreds of years that may be required to isolate waste in the presence of the thermal gradient.

The program plan for the study of warm spring analogues includes (1) a literature search for published information on hot-spring localities with appropriate rock and water compositions, (2) acquisition of as much information as possible from the published literature and from workers in the field, (3) investigation of several of the most promising localities, and (4) a modeling effort, integrated with other transport and reaction modeling, to describe the chemical behavior of major and trace elements moving within a temperature gradient in felsic tuff. During this quarter, emphasis has been on part (3) of this plan.

Three warm springs in the ring-fracture zone of the Valles Caldera in the Jemez Mountains of New Mexico were sampled. The water composition of warm springs in the ring-fracture zone is known to be very similar to that of Well J-13 at NTS, and the bulk chemical composition of the rock is close to that of the Yucca Mountain tuffs. The object of the Jemez sampling is to study the long-term natural alteration of a single rock at this water composition as a function of the different spring temperatures.

Warm spring localities in Nevada with a high probability of appropriate alteration were chosen by combining geothermal resource maps of Nevada with geologic maps, published reports, and theses to find springs with the right water, rocks, and temperatures. Nine localities in central Nevada were examined for bedrock exposure and for mineral alteration of the bedrock by the warm springs. Water samples and sequences of rock samples from the two best localities were taken for further analysis.

The initial sampling phase of the warm spring analogue program has now been completed, and water and rock samples are being analyzed. Preliminary data suggest that there are two principal types of alteration observed in these springs, one derived from bicarbonate systems of near-neutral pH and the other from acid sulfate waters. The acid sulfate systems seem to be derived from the oxidation of pyrite in the rock by warm aqueous solutions mixed with air. It may prove important to minimize the amount of pyrite-bearing rock that is exposed to air within the repository to avoid possible formation of acid waters.

IV. MINERALOGY-PETROLOGY STUDIES (B. H. Arney, D. L. Bish, D. E. Broxton,
F. M. Byers, F. A. Caporuscio, R. C. Gooley, G. H. Heiken, S. S. Levy,
C. W. Myers, R. E. Semarge, and D. T. Vaniman)

Mineralogic and petrologic studies of Drill Hole GU3/G3 have been completed. The samples from drill core USW-G3/GU3 differ from previously studied core samples at Yucca Mountain. Data collected from mineralogic and petrologic studies highlight two major points of variation. First, the tuff of Calico Hills has a much more complex primary mineralogy than is observed elsewhere at Yucca Mountain. Second, the degree of alteration and secondary mineral development in drill core USW-G3/GU3 is much less extensive than in drill core samples farther to the north and northeast at Yucca Mountain.

A. Complex Mineralogy of the Tuff of Calico Hills

The tuff of Calico Hills in Drill Hole USW-G3 has several characteristics that distinguish it from its occurrence in other drill holes to the north. Probably the most important difference is the vitric nature of the unit in Drill Hole USW-G3. In previously cored exploratory holes such as J-13, USW-G1, UE25a-1, and USW-G2, the tuff of Calico Hills has always been thoroughly zeolitized. Preliminary stratigraphic logs and x-ray diffraction (XRD) analyses of cuttings from hydrology holes USW-H5, USW-H4, and USW-H3 indicate that the lateral transition from zeolitic to vitric Calico Hills takes place in the vicinity or slightly north of Drill Holes USW-H5 and USW-H4. Until this recent drill hole data became available, the tuff of Calico Hills was considered the thickest, most continuous zeolite bed in the exploratory block. Now it is known to be zeolitic only at the north end of the block.

Another striking feature of the tuff of Calico Hills in Drill Hole USW-G3 is its reduced thickness (147.3 ft; 44.9 m). In the vicinity of Drill Hole Wash the unit is 400 to 500 ft thick, and at Drill Hole USW-G2 it is 947 ft (288 m) thick. The southward thinning of the Calico Hills probably represents thinning away from its source area.

Compared to that in previous drill holes, the modal petrography of phenocrysts in the lower air-fall tuff of drill core USW-G3 is unique and somewhat problematic. In addition to normal "Calico-like" phenocryst assemblages of quartz, plagioclase, sanidine, and biotite, the lower air-fall tuff in drill core USW-G3 has minor amounts of green hornblende, orthopyroxene, and clinopyroxene. Initially, the presence of pyroxenes and hornblende was thought to indicate that the bedded tuff belongs in the Prow Pass or Wahmonie tuffs. However, the abundance and proportion of major phenocryst phases and the compositional ranges of feldspars and biotites strongly suggest an equivalency to lower tuff of Calico Hills subunit tuffs identified in Drill Holes USW-G1 and USW-G2. For example, in drill core USW-G2, the basal ash flow contains 20.9% phenocrysts in the following proportions: plagioclase (50.7%), quartz (25.0%), sanidine (17.7%), and biotite (6.6%). In drill core USW-G3, the basal air-fall tuff contains 21.5% phenocrysts in the following proportions: plagioclase (51.7%), quartz (29.3%), sanidine (12.4%), biotite (3.2%), hornblende (1.6%), opaque oxides (1.3%), orthopyroxene (0.3%), and clinopyroxene (0.1%). Sanidine compositions were found to average Or_{73} in the basal ash flow of drill core USW-G2 and Or_{72} in the basal air fall of drill core USW-G3. Similarities in Mg/Mg+Fe ratios of biotites were also found for basal Calico Hills units of both drill holes (averaging 0.44 in both). In drill core USW-G3, orthopyroxene in the basal Calico Hills is relatively magnesium rich (Mg/Mg+Fe = 0.64). These mineral compositions differ greatly from sanidine (Or_{52}), biotite (Mg/Mg+Fe = 0.55), and orthopyroxene (Mg/Mg+Fe = 0.30) compositions typical of the Prow Pass Member. Despite the presence of somewhat exotic minor phenocrysts, the basal air fall of the tuff of Calico Hills in Drill Hole USW-G3 has many characteristics similar to those of its counterparts elsewhere on Yucca Mountain.

B. Restricted Degree of Alteration and Secondary Mineral Development

Within drill core USW-GU3, and particularly within drill core USW-G3, secondary minerals are less abundant and generally of lower grade (lower temperature of formation) than in drill cores USW-G1 and USW-G2, UE25a-1 and UE25b-1h, or J-13. Work in preparation suggests that core USW-G3/GU3 is also less extensively altered than the samples from core USW-H4, although the degree of alteration in USW-G3/GU3 may be roughly comparable to USW-H5 and USW-H3. Four major differences are described below.

1. Less Alteration within the Exploratory Block. Samples from USW-G3/GU3 tend to be less altered than samples from comparable depths in the northern part of Yucca Mountain. The distributions of primary and alteration phases are summarized in Fig. 9. Whereas the Topopah Spring unit north of Drill Hole Wash contains only an upper and lower vitrophyre, the lowermost 200 ft (61 m) of the Topopah unit in USW-GU3 are vitric, as are the underlying 200 ft that include the tuff of Calico Hills and the upper Prow Pass Member of the Crater Flat Tuff. Aside from the lower Topopah vitrophyre, this vitric material is mostly nonwelded. The preservation of so much vitric rock indicates that these units were not beneath the water table for any extended time following their emplacement. The hydrology hole USW-H5, also at the Yucca Mountain crest and within the exploration block, has abundant glass within the Calico and upper Prow units. Hydrology hole USW-H4, however, at the eastern edge of the exploration block, has abundant glass only at the top of the Calico unit, overlying a thoroughly zeolitized zone. The differences between Drill Holes USW-H5 and USW-H4 may indicate that the present eastward dip of lithostratigraphic units was already well developed at the time of zeolitization.

Alteration beneath the water table is also less extensive at Drill Holes USW-G3/GU3 than in the drill holes in the north of Drill Hole Wash. The vein-filling assemblage calcite-quartz-barite with high matrix calcite concentrations in USW-G2 and the abundant vein-associated pyrite in UE25b-lh are not found in USW-G3/GU3. Calcite concentrations in USW-G3/GU3 are generally <1% at all depths, in contrast to an average >10% in USW-G2 at depths below 3900 ft and in UE25b-lh below 2800 ft. Barite is absent in USW-G3/GU3 and pyrite is scarce (traces only below 3700 ft). The first appearances of key index minerals are also deeper in USW-G3/GU3 than in the drill holes further north. Clinoptilolite appears in abundance at 1827-ft depth (vs ~1300 ft in UE25a-1, 1400 ft in USW-G1, and 1630 ft in USW-G2, discounting probable perched water-table occurrences); analcime appears at 4000-ft depth (vs 3370 ft in UE25a-1, 3100 ft in USW-G1, and 3250 ft in USW-G2). Authigenic albite does not occur at all in USW-G3. These mineral zones are summarized in Fig. 9.

In accordance with the decreased alteration of USW-G3/GU3, those phases that have lower stability ranges persist to greater depth than in the drill holes in the north of Drill Hole Wash. Tridymite is found as deep as 2070 ft in USW-G3, whereas it occurs no deeper than ~320 ft in UE25a-1, 1100 ft in USW-G1, and 900 ft in USW-G2. Cristobalite occurs as deep as 3700 ft in USW-G3 but no deeper than ~1250 ft in UE25a-1, 2800 ft in USW-G1, and 3400 ft in USW-G2.

2. Reduced Clay Abundance in USW-G3/GU3. The USW-G3/GU3 samples have fewer and generally smaller clays (<10 μ m) than do the samples from more northerly drill holes. Clay abundances in upper USW-G3/GU3 average <1%; only a few samples have >10% and they are from bedded zones or fractures. Below 3500 ft, clay abundances of ~10% become common. In contrast, clay abundances of ~10% or more are common throughout UE25a-1/b-1h, USW-G1, and USW-G2. Samples from USW-G3/GU3 also lack the coarse illites that occur in USW-G2 (Fig. 7 of Ref. 9). The limited smectite-to-illite transition in USW-G3/GU3 is discussed in detail in Sec. IV.B.3.

3. Relative Absence of Mordenite in USW-G3/GU3. Detailed XRD studies of USW-G3/GU3 indicate that mordenite is virtually absent from bulk tuff samples (excluding fractures). This is in striking contrast to the data from UE25a-1/b-1h, USW-G1, and USW-G2, where mordenite is an abundant alteration



MINERAL ABUNDANCES DETERMINED BY X-RAY DIFFRACTION DRILL HOLES USW-GU3/G3

Fig. 9. Bulk sample XRD data from drill core USW-G3/GU3.

phase within the tuff matrix. Mordenite does occur in abundance along several fractures in USW-G3/GU3. The patchy distribution of mordenite within this part of the exploration block suggests limitations on its usefulness as a natural sorptive phase, unless flow were totally restricted to fractures.

4. Transition from Calcium, Magnesium-Heulandite in the Topopah Spring Unit to Potassium, Sodium-Clinoptilolite at Depth. Open-channel zeolites such as clinoptilolite/heulandite and mordenite have greater sorptive capacity than zeolites of less open structure (for example, analcime). Among the sorptive zeolites, clinoptilolite and heulandite appear to be the most abundant and are most consistently present in USW-G3/GU3. Heulandite is distinguished from clinoptilolite by its lower short-term thermal stability (it breaks down rapidly at ~250°C); available data from Yucca Mountain indicate that heulandites here have higher calcium and magnesium content and clinoptilolites have more sodium and potassium.

Caporuscio et al.⁹ have noted that the heulandites and clinoptilolites from USW-G2, at the northern end of Yucca Mountain, indicate a transition from calcium-rich, magnesium-rich heulandite above the Topopah unit to potassium-rich clinoptilolite in the Topopah and Calico units (1745- and 2158- to 2430-ft depths) to sodium-rich clinoptilolites in the Prow and Bullfrog units (3067- to 3250- and 3492-ft depths). This trend from calcium-plus-magnesium to potassium enrichment and then to sodium enrichment with increasing depth is typical of zeolite zonations in the NTS region. The data from USW-G1, further south, show a comparable trend, although the various units may have average zeolite compositions that are very different from their compositions at equivalent depths in USW-G2.

In contrast to the data from USW-G1 and USW-G2, the data from Drill Hole USW-G3/GU3 further south at Yucca Mountain suggest that the trend of calciumpotassium-sodium zonation with depth does not occur here. There is a sharp contrast between the calcium-rich, magnesium-rich heulandites at 1195 ft (364.2 m) in the Topopah Spring unit and the potassium-rich, sodium-rich clinoptilolites in the underlying units. However, there is no consistent pattern of compositional variation with depth among the clinoptilolites.

The possible correlation of heulandite thermal stability with calcium content is an item of concern. In addition to the possible correlation between thermal stability and composition, the effects of these variations in large cation types (calcium-magnesium, sodium, or potassium) on sorptive exchange are

yet to be determined. Although the current target zone within the Topopah Spring unit is not zeolitized, zeolites do occur at the top of the lower vitrophyre. Moreover, the presence of zeolites below the target zone may provide an important part of the retardation setting during the isolation period of repository life. For these reasons it is important to understand the sorptive capabilities of those zeolites.

5. Lack of Illite Clay. The transition from expandable to poorly expandable clay is abrupt in USW-G2 and occurs between the Bullfrog and Tram units at ~3500 ft; clays below this depth are potassium-rich, are mostly illites, and have a high interlayer cation content (~1.4 to 1.7). In contrast, the clay data from core USW-G3/GU3 suggest that the transition to illite is <20% complete as deep as 5014 ft (total depth of USW-G3). Interlayer cation contents are correspondingly low, typically 0.7 to 0.8 but never more than 1.3. The XRD data confirm this limited transition to illite (see below).

The clay minerals in USW-G3/GU3 were studied by XRD in an effort to determine the temperature of alteration in the hole and to estimate the expandability and cation exchange capacity of the clays. Data were obtained using <2-µm-size fractions for XRD analysis. Based on computer-simulated XRD patterns of randomly interstratified illite-smectites, the type and amount of interstratification with illite and the thickness of the ethylene glycol-smectite complex can be determined. The thickness of the complex can be related in a general way to smectite layer charge and exchange capacity. The data indicate clay alteration temperatures <40°C. This contrasts sharply with the data from USW-G2, where illites with formation temperatures >235°C occur below 5100 ft.¹⁰ In USW-G3/GU3, the maximum percentage of illite layers interstratified with smectite is 15 to 25%, attained at the bottom of the hole (Fig. 9). The (001) spacings of the smectites in USW-G3/GU3 at room temperature and a given humidity can be used as an indicator of interlayer cation composition. Most smectites have basal (001) spacings of 12 to 14 Å and probably have mixed sodium-calcium interlayers. Spacings between 10 and 12 Å at the bottom of the Tram unit are consistent with mixed potassium-sodium or potassium-calcium smectites. There are no clear trends in the thickness of the ethylene glycol-smectite complex; most smectites in USW-GU3 and USW-G3 have a normal to slightly higher than normal layer charge, although the smectites between 3799.0 and 3847.5 ft have low layer charges. A low layer charge is consistent with a lower cation exchange capacity.

V. VOLCANISM STUDIES (B. M. Crowe, D. T. Vaniman, F. Caporuscio, and W. S. Baldridge)

Geochemical studies are being conducted for the volcanic hazards program, in which the composition patterns of past volcanism are examined to test predictions of future rates of volcanic activity. The studies are divided into major and trace element analyses and isotopic analyses. Selected bivariant major- and trace-element geochemical plots were compiled for the basalts of the NTS region. The rift basalts (RB) show a narrow range of compositional variation on a $Na_20 + K_20$ vs SiO_2 diagram (Fig. 10). This is evidence for the uniformity of basalt compositions in the NTS region for the last 8 Myr. The most variable unit of the RB is the basalt of Buckboard Mesa; all other units closely overlap in composition. Plots of $Na_20 + K_20$ vs SiO_2 for the basalts of the silicic cycle (BSC) with the superimposed RB field illustrate several features (Fig. 11):

(1) there is considerable overlap in composition between the RB and the BSC;

- (2) there is a great diversity of basalt compositions among the BSC;
- (3) the basalts of Black Mountain are the most strongly alkaline suite of the NTS region; and
- (4) the basalt of Skull Mountain is of subalkaline composition.

Plots of samarium vs lanthanum for the RB (Figs. 12 and 13) show that the cycle can be divided into two distinct fields: older RB, which are not enriched with respect to lanthanum and samarium, and younger RB, which are strongly enriched. Overlap for the two cycles occurs only for the 3.7-Myr basalt of Crater Flat. Data from the BSC show a great range in abundance of lanthanum and samarium. Some of the BSC have the lanthanum and samarium contents of the older RB, whereas others overlap in composition with the younger RB; however, the degree of enrichment is not as great for the BSC.

Field sampling of basalts in the NTS region was completed during this quarter; samples were obtained for the isotopic studies that were a cooperative project with S. Semken at UCLA. Samples of the BSC from Dome Mountain were basalts that were mapped as units separate from the basalt of Dome Mountain. The southern and central basalt localities of Nye Canyon were sampled and mapped. Both of these localities are maar volcanoes with a lava lake sequence that filled the crater depression. The walls of the maars (tuff cones) are now largely removed by erosion. Samples were taken from the basalt



Fig. 10. Rift basalts of the NTS region.



Fig. 11. NTS region basalts of the silicic cycle.



Fig. 12. Younger and older rift basalts of the NTS region.



Fig. 13. Lanthanum and samarium compositions of basalts of the silicic cycle of the NTS region. Circles are fields of the younger and older rift basalts from Fig. 12.

of Rocket Wash, a newly recognized RB, and from two pyroxene basalts exposed at the Rocket Wash locality that underlies the Thirsty Canyon Tuff.

VI. ROCK PHYSICS (J. D. Blacic)

A draft of the final report on the effects of simulated repository conditions on the physical and mineralogical properties of Yucca Mountain tuffs was completed.¹¹ In the report it is concluded that significant changes in tensile and compressive strengths, porosity, matrix permeability, and mineralogic content are to be expected in some tuff types in response to the near-field conditions associated with a repository in tuff. These changes will develop slowly over time because of slow mineralogic and structural alteration of the tuffs. It is also concluded that little or no change in thermal properties is expected because no changes were noted after 6-month-long tests.

The results of the above exploratory tests and a preliminary report on creep of welded tuff, also completed this quarter, formed the basis for discussions among Los Alamos and SNL investigators about the need for laboratory measurement of time-dependent strength (creep) of target horizon tuffs. It was concluded that this data is needed for conceptual design and performance modeling of a repository in Topopah Spring tuff and for borehole sealing in the Calico Hills tuff. An experimental program was designed and tests will begin next quarter on the Calico Hills tuff. Additional evaluation is needed to determine the data requirements for Topopah Spring tuff.

VII. SHAFT AND BOREHOLE SEALING (R. J. Vidale)

This study evaluates the chemical stability of sealing material in the felsic tuff environment of Yucca Mountain. Any sealing material will react with the rock at some rate because the sealant and rock will be chemically different and because volcanic tuff contains tiny, highly reactive mineral and glass particles. The object in choosing an appropriate sealant is to identify the reaction products, determine their effect on the physical andc hemical properties of the seals, and minimize reaction and reaction rates if the effects are deleterious. A series of laboratory studies have been planned that will permit observation of test-rock/sealant reactions in a laboratory setting. The work will be done in cooperation with the Materials Testing Laboratory of Pennsylvania State University. The participants in the shaft and borehole sealing program are working together to choose potential sealants that will prove practical from the standpoints of emplacement, physical properties, and chemical properties and that have some historical documentation for satisfactory performance. The initial choice of rock was tuff from the Grouse Canyon Member that is exposed in G tunnel at the NTS. It was anticipated that both sealant and rock would be changed when a specific rock horizon was chosen for the repository.

In the geochemistry program, reports on materials currently under consideration for sealing tuffs and other geologic media have been reviewed. The initial choices for rock and cement samples and the major initial cement additives have been analyzed. A survey of the relevant thermodynamic information on the combined tuff/sealant system is under way. Ancient cement seals in volcanic tuff are being examined, and initial experimental tests are under way to study accelerated tuff/sealant reactions in agitated vessels at temperatures ranging from 200 to 25°C.

The lithophysae-poor zone of the Topopah Spring Member at Yucca Mountain now seems to be the probable target horizon for the waste repository. Characterization of Grouse Canyon tuff aggregate and the relevant part of the Topopah Spring (Table VI) shows that the two are significantly different mineralogically and chemically. It will be advisable to change the rock being used in the studies to the Topopah Spring tuff.

The sealant now being tested is 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 (Table VII) show large quantities of potentially reactive substances such as dolomite, calcite, calcium oxide, and hematite. It will be important to change to Topopah Spring tuff for the coarse aggregate and to consider the use of sand and fly ash that are chemically more simple and more compatible with the tuff of the coarse aggregate and the surrounding rock.

The initial laboratory run, made in a rocking autoclave at 200°C and 1500 psi for 2 weeks, showed extensive reaction within a sample of concrete that contains tuff aggregate. Preliminary analyses show the formation of zeolites and tobermorite and strong leaching by water of alkalis from the concrete. It

TABLE VI

CHARACTERIZATION OF ROCK

Aggregate from G Tunnel (Grouse Canyon Unit)	Minera	l Content (%)
Quartz	23	to 28
Clinoptilolite	8	to 12
Mica	1	to 3
Cristobalite	3	to 7
regate from G Tunnel rouse Canyon Unit) Quartz Clinoptilolite Mica Cristobalite Alkali feldspar <u>dle Topopah Spring Formation</u> Quartz Clinoptilolite Mica Cristobalite Alkali feldspar Montmorillonite	55	to 65
Middle Topopah Spring Formation		
Quartz	10	to 20
Clinoptilolite	unnel Mineral Co it) (%) 23 to 2 e 8 to 2 ar 1 to 2 ar 55 to 6 ing Formation 10 to 2 e - 30 to 2 30 to 2 ar 30 to 2 te 2 to 2	-
Mica		-
Cristobalite	30	to 50
Alkali feldspar	30	to 50
Montmorillonite	2	to 10

TABLE VII £ CHARACTERIZATION OF THE MAJOR ADDITIVES

Minera	1 ((%)	Content
5	to	15
25	to	30
2	to	4%
1	to	3
35	to	40
16	to	20
	Minera 5 25 2 1 35 16	Mineral ((%) 5 to 25 to 2 to 1 to 35 to 16 to

Fly Ash AD-592-5

Quartz, CaO, and hematite About equal proportions Possible MgO

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can be concluded that observable reactions will occur in laboratory studies and that the experimental studies planned for this program should prove feasible.

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

A. Design

A decision was made by DOE/NV to conventionally sink (mine) rather than drill the ES. Following this decision, design criteria (DCL-4) were submitted to DOE/NTSSO to be used by the architect-engineers as the basis for the Title I design of the shaft, underground openings, and related systems. Also, design criteria (DCL-3) for the surface facilities were updated and transmitted to DOE/NTSSO.

Two existing unused hoists (one main and one auxiliary) that will satisfy the requirements of the ES were located at the NTS. The hoists were reserved for that purpose; they will be refurbished at the NTS and recertified for the project. An existing headframe was also located at the NTS; a decision on the suitability of this headframe for the ES is expected very soon. If the decision is affirmative, a detailed structural analysis will be conducted on the headframe.

Design studies have been conducted on the desired shaft diameter and the shaft liner. The inside diameter of the finished shaft will be 12 ft. The shaft-liner options studied were (1) rockbolts and wire mesh, (2) steel sets and lagging, and (3) poured concrete. The last option with a 12-in.-thick liner will be recommended; it will require a mined shaft with a nominal 14-ft diameter.

A draft Work Breakdown Structure for the ES has been developed by DOE/NV. The document includes summary work packages with charge numbers to permit cost summarization. Logic diagrams are being developed for the ES design, procurement, construction, and site evaluation efforts. The diagrams are developed both as detailed diagrams and summary (overview) diagrams. The initial diagram efforts have yielded a date of October 3, 1983, as the start date for sinking the shaft.

Regular project meetings will be held approximately every month to assist in the project management. Three such meetings were held during this quarter. One of the ES project review meetings was held on December 16, 1982, at which time most of the Title I design package (for surface and subsurface facilities) was distributed for comment. The balance of the Title I design package will be completed by January 3, 1983. Also at that time, an updated project construction cost estimate will be completed.

B. Test Plan

The ES test plan includes construction phase tests and in situ phase tests. The construction phase tests include testing in the principal borehole (USW-G4) during shaft construction and during construction of the underground workings. Planning for testing during shaft construction was a major activity this quarter.

The ES is to be sunk by conventional mining. Separate test operations will be performed during shaft sinking for

- shaft-wall mapping and photography,
- collection of large block samples in tuff,
- collection of groundwater samples and measurement of inflow rates, and
- installation of rod extensometers.

After the shaft is completed to total depth and is lined, the internals are installed, and the mining contractor is demobilized, construction phase testing will continue with the following, using platforms within the shaft:

- installation of multipoint extensometers,
- lateral drilling into the target unit, and
- overcore measurements of in situ stress.

Results from these tests will provide needed information on fracture fill, geometry, groundwater in porous and fractures, material properties, rock deformation, and in situ stress. Findings will be used to select the exact breakout level for the underground workings and to assess groundwater flux and other features relevant to the isolation potential at Yucca Mountain.

Test procedures will be prepared before testing. Results from the tests will be analyzed continuously. Interim reports on results will be integrated into a report to be used for the horizon breakout decision. At a later time, final reports on each of the tests will be completed and results included in the Site Characterization Report.

IX. QUALITY ASSURANCE (R. R. Geoffrion)

A. Los Alamos

The Exploratory Shaft Design Control Procedure was reviewed and approved. A meeting was held at DOE/NV to discuss quality assurance (QA) direction for the ES work. A document containing suggested QA requirements for ES participants was prepared and sent to H. Melancon, DOE-NV, at his request.

All Los Alamos NNWSI QA documents were reviewed and revised. A manual of QA procedures was compiled and distributed to Los Alamos NNWSI project personnel. Revisions and additions will be distributed on a continuing basis. A draft version of the Los Alamos NNWSI organization chart was prepared and circulated for comment.

A meeting was held with the Los Alamos technical personnel concerned with the drilling and coring program for the horizontal holes. A drill hole criteria meeting was then held (by conference call) with representatives of all partipants in the project.

A QA review of the plan for on-site roads for the ES (phase 6) was completed.

The Los Alamos QA manager was assigned to a committee whose responsibility it will be to evaluate NQA-1 for applicability to waste management activities. The committee will make recommendations to ANSI/ASME for changes (probably in the form of an addendum to NQA-1) that are appropriate to waste management.

B. US Geological Survey

Denver approvals were obtained on six detailed procedures.

A QA indoctrination and training program for USGS personnel was held in Menlo Park, California.

A data index for NNWSI records was completed, and a surveillance schedule was drafted.

A meeting was held in Denver with QA Overview and USGS Management to close out the latest Overview/DOE-NV audit.

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