January 1—March 31, 1981

B. R. Erdal, W. R. Daniels, and K. Wolfsberg

R. D. Aguilar	S. Maestas
J. N. Albright	A. J. Mitchell
B. P. Bayhurst	D. C. Nelson
D. L. Bish	T. W. Newton
J. D. Blacic	A. E. Ogard
P. L. Bussolini	P. Q. Oliver
F. A. Caporuscio	F. V. Perry
M. R. Cisneros	J. D. Purson
B. M. Crowe	N. A. Raybold
W. R. Daniels	R. S. Rundberg
S. J. DeVilliers	J. J. Simpson
C. J. Duffy	J. R. Smyth
R. R. Geoffrion	D. T. Vaniman
P. M. Halleck	E. N. Vine
T. A. Kelley	R. G. Warren
F. O. Lawrence	K. Wolfsberg

[illegible]

TABLE OF CONTENTS

ABSTRACT	1
I. INTRODUCTION	2
II. WASTE PACKAGE	2
III. NUCLIDE MIGRATION FIELD EXPERIMENTS IN G-TUNNEL - LABORATORY STUDIES	3
A. Preparation of Pretreated Water	3
1. Selection of Groundwater and Rock	3
2. Filtration Method	3
3. Preparation Method	6
B. Batch Sorption Experiments with ^{85}Sr , $^{95\text{m}}\text{Tc}$, ^{137}Cs , ^{133}Ba , ^{141}Ce , and ^{152}Eu	6
1. Matrix Rock	6
2. Fracture Material	6
3. Wafers	10
C. Kinetic Sorption Experiments	10
D. Column Experiments	12
E. Tritium Content of Water in Rock from Hole U12G-RNM8	13
F. Materials Characterization	13
1. X-ray Diffraction Analyses	13
2. Microscopic Examination	13
IV. GEOCHEMISTRY OF TUFF	14
A. Sorption on Samples from Drill Hole USW-G1	14
B. Sorption on Samples from Drill Hole J-13	14
C. Plutonium Isotherm Measurements and Plutonium Chemistry	20
D. Crushed-Rock Column Circulating System	22
E. Crushed-Rock Column Studies	22
F. Solid Core Column Studies (A)	23
G. Solid Core Column Studies (B)	23
H. Effect of Materials for Preparing Wafers on Sorption and Carbon Analyses	26
I. Determination of Fe(II) in Groundwaters	27
J. Analyses of Water from Wells USW-H1 and USW-VH1	27
K. Organic Eh Moderators	28
L. Possible Inorganic Eh Moderators	28
1. Tris(2,2'-bipyridine)osmium(II) Chloride	29
2. Tris(4,4'-dimethyl-2,2'-bipyridine)osmium(II) Chloride	29
3. Tris(4,4'-diphenyl-2,2'-bipyridine)osmium(II) Chloride	31
4. Dichlorobis(2,2'-bipyridine)osmium(III) Chloride	31
5. Dichlorobis(2,2'-bipyridine)osmium(II)	31
6. Ethylenediaminebis(2,2'-bipyridine)osmium(II) Iodide	31

7.	Chloropyridinebis(2,2'-bipyridine)osmium(II) Perchlorate . .	32
8.	Acetylacetonatetobis(2,2'-bipyridine)osmium(II) Chloride . .	32
9.	Tris(orthophenanthroline)osmium(II) Chloride	32
M.	Equipment for Control of Eh	33
N.	Counting Room Software Activities	33
V.	MINERALOGY-PETROLOGY OF TUFF	33
VI.	VOLCANIC HAZARD INVESTIGATIONS	38
A.	Volcanism Studies	38
B.	Basalt Disruption Studies	40
VII.	SITE EVALUATION WORKING GROUP	41
VIII.	ROCK PHYSICS STUDIES	41
A.	Laboratory studies	41
1.	Time-Dependent Deformations	41
2.	Soak Tests	44
B.	Field Studies	45
IX.	QUALITY ASSURANCE	46
A.	Los Alamos National Laboratory	46
B.	U. S. Geological Survey	47
X.	PUBLICATIONS AND ABSTRACTS	48
XI.	ORAL PRESENTATIONS	48
	ACKNOWLEDGMENTS	48
	REFERENCES	48
	APPENDIX A: SORPTIVE PROPERTIES OF YUCCA MOUNTAIN TUFF FROM DRILL HOLE USW-G1	50
	APPENDIX B: CALCULATION OF BREAKTHROUGH CURVES USING THE THOMAS SOLUTION: THE EFFECT OF EQUILIBRIUM ON THE BREAKTHROUGH WITH A LOW NUMBER OF MASS TRANSFER UNITS	55
	APPENDIX C: THE PERFORMANCE OF CRUSHED-ROCK COLUMNS AS CHROMATO- GRAPHIC COLUMNS	61

RESEARCH AND DEVELOPMENT RELATED TO THE NEVADA NUCLEAR
WASTE STORAGE INVESTIGATIONS

January 1 through March 31, 1981

Compiled by

B. R. Erdal, W. R. Daniels, and K. Wolfsberg

Contributors

R. D. Aguilar	S. Maestas
J. N. Albright	A. J. Mitchell
B. P. Bayhurst	D. C. Nelson
D. L. Bish	T. W. Newton
J. D. Blacic	A. E. Ogard
P. L. Bussolini	P. Q. Oliver
F. A. Caporuscio	F. V. Perry
M. R. Cisneros	J. D. Purson
B. M. Crowe	N. A. Raybold
W. R. Daniels	R. S. Rundberg
S. J. DeVilliers	J. J. Simpson
C. J. Duffy	J. R. Smyth
R. R. Geoffrion	D. T. Vaniman
P. M. Halleck	E. N. Vine
T. A. Kelley	R. G. Warren
F. O. Lawrence	K. Wolfsberg

ABSTRACT

This report summarizes the contributions of the Los Alamos National Laboratory to the Nevada Nuclear Waste Storage Investigations for the second quarter of FY-1981.

I. INTRODUCTION

This report summarizes some of the technical contributions from the Los Alamos National Laboratory to the Nevada Nuclear Waste Storage Investigations (NNWSI) project managed by the Nevada Operations Office of the U. S. Department of Energy during the period from January 1 through March 31, 1981. This report is not intended to be a detailed technical document but does indicate the status of some of the investigations being performed at Los Alamos.

II. WASTE PACKAGE (E. N. Vine)

Laboratory work was begun this quarter to study the sorption of the anions pertechnetate and iodide in a tuff environment. The literature was first reviewed for materials with potential anion sorptive capacity. Several of those materials were obtained, and batch experiments were begun for screening at room temperature. Equipment required for waste package studies at elevated temperature and pressure was ordered.

We are using several charcoals and minerals. The minerals are all sulfo-salts of the types A_2BX_3 (bournonite), A_3BX_3 (boulangerite), and ABX_2 (tetrahedrite). There is some discrepancy in the literature as to their ability to sorb TcO_4^- or I^- ; however, experimental conditions were not identical. These minerals, being rare, would probably not be useful themselves as components of the backfill. The experiments are being done instead to try to define a mechanism for removal of technetium or iodide from solution so that an inexpensive substitute can perhaps be synthesized. It seems, for example, that simple sulfide minerals are not effective in the removal of these anions, but that these sulfo-salts are.

The charcoals and minerals were pretreated for several weeks with water from well J-13. The pH of the waters did not change greatly over that time. The pH increased from ~8.15 (for the initial water) to 8.58 for bournonite, to 8.54 for tetrahedrite, and to 8.18 - 8.49 for the charcoals. Only with boulangerite did the pH decrease (to 7.81). Pertechnetate and iodide were added to the pretreated materials and sorption studies are in progress.

III. NUCLIDE MIGRATION EXPERIMENTS IN G-TUNNEL - LABORATORY STUDIES

A. Preparation of Pretreated Water

1. Selection of Groundwater and Rock (K. Wolfsberg, A. J. Mitchell, and S. J. DeVilliers). It is known that the composition of waters from fractures and interstices of the Miocene Tunnel Beds in G-Tunnel, in which the experiment will be performed, is significantly different from the composition of other tuff waters.¹ In order to avoid major chemical reactions during the laboratory and field experiments, it is necessary that the rock and water be reasonably close to equilibrium with the rock. Although there are two seeps in the tunnel incline near the EV-5/HF-23 area, which is near the top of the tunnel beds, it is not known whether this water is in equilibrium with the rock or whether the composition changes on contact with EV-5/HF-23 material.

Crushed matrix and fracture samples taken from the surface of the left rib in the HF-23 area were contacted with waters from Nevada Test Site (NTS) tuffaceous wells 8 and J-13 for varying times and varying proportions of water and rock. The waters were filtered through 0.05- μ m Nuclepore polycarbonate membranes prior to analysis with a plasma-source emission spectrometer. The results (Table I) represent averages for 2- and 4-week contact times. For comparison, the compositions of the well waters and waters from the nearest seeps to the EV-5/HF-23 area are also given. It can be seen that relative proportions of rock and water, rock type, and initial type of water do not significantly affect the final composition. Well J-13 water and matrix rock will be used to prepare water for the initial studies, because of their easy availability; a ratio of 10:1 for water to rock will be used.

2. Filtration Method (R. S. Rundberg, K. Wolfsberg, S. J. DeVilliers, and A. J. Mitchell). Many analytical procedures for water analyses include filtration through 0.45- μ m membrane filters prior to analysis. The filtration of waters through 0.45- μ m Millipore HA filters seems to have been adequate for most of our work with Jackass Flats and Yucca Mountain tuffs, but unusually high apparent concentrations of iron and silicon were noted for the G-Tunnel pretreated waters prepared by this filtration method. Filtration through 0.4- μ m Nuclepore polycarbonate membranes reduced the suspicious concentration significantly, and further filtration through 0.05 μ m, Nuclepore membranes reduced the iron concentration more. The Nuclepore membranes have smaller pore size distributions than the Millipore HA membranes. An example of the

TABLE I
EFFECT OF ROCK AND WATER ON COMPOSITION OF PRETREATED WATER^a

Water	Rock ^b	Water:Rock Proportions	Concentration (mg/l)										
			Mg	Mn	Si	Fe	Ba	V	Ti	Ca	K	Al	Na
Well 8	ff	20:1	0.046	0.089	29	1.8	0.020	0.01	0.11	0.34	6.0	0.041	59
"	ff	10:1	0.032	0.078	32	1.6	0.005	0.01	0.10	0.29	4.5	0.032	64
Well J-13	ff	20:1	0.060	0.090	30	2.0	0.015	0.015	0.13	0.61	6.7	0.020	89
"	ff	10:1	0.024	0.137	34	3.5	0.023	0.012	0.28	0.60	6.1	0.030	90
"	m	20:1	0.041	0.048	29	0.1	0.01	0.012	0.005	0.41	6.1	0.1	88
"	m	10:1	0.036	0.052	30	0.17	0.008	0.015	0.01	0.46	5.9	0.1	92
Well 8	m	10:1	0.030	0.055	30	0.16	0.02	0.012	0.005	0.30	4.8	0.1	61
"	m	5:1	0.03	0.055	30	0.26	0.02	0.010	0.01	0.25	5.4	0.1	68
seep ^c	--	--	0.14	0.09	30	1.0	0.002	0.001	0.13	0.81	3.8	0.4	34
seep ^d	--	--	0.24	0.10	28	2.4	0.002	0.001	0.18	0.38	2.7	1.4	42
Well J-13	--	--	2.4	0.12	31	0.02	0.02	0.017	--	12.6	9.2	0.05	59
Well 8 ^e	--	--	1.1	<0.01	27	<0.01	--	--	--	8.3	3.6	<0.1	31

^a Average value for 2- and 4-wk contacts in air. Filtered through 0.05- μ m Nuclepore membrane.

^b ff = HF-23 fracture fill; m = HF-23 matrix.

^c Middle of incline near EV-5.

^d Lower incline near EV-5.

^e From Ref. 2.

apparent compositions measured after each successive filtration of a water is given in Table II. Even with concentrations of 0.05 to 0.5 mg/l, the concentration of iron far exceeds that which would be expected from the solubility product of ferric hydroxide in pure water in the absence of any complexing. However, it is not practical to filter large quantities of water through membranes with pores smaller than about 0.1 μ m. Furthermore, the rock itself will probably produce fine particles during any experiment.

It should be noted that the tuff of the Tunnel Beds has exhibited a much greater tendency to produce small particles and colloids than any of the tuffs studied in the NNWSI. We shall remain alert to problems that this property may pose.

TABLE II
EFFECT OF FILTRATION ON APPARENT COMPOSITION^a

Element	Concentration (mg/l)		
	0.45- μ m M ^b	0.40- μ m N ^c	0.05- μ m N ^c
Mg	4.0	0.11	0.08
Mn	7.4	0.058	0.021
Si	219.	28.3	27.1
Fe	82.0	1.5	0.6
Sr	0.045	0.000	0.001
Ba	9.0	0.05	0.12
V	0.17	0.005	0.008
Ti	14.	0.09	0.00
Ca	5.4	0.70	0.56
Li	80.	0.059	0.050
K	30.	4.5	4.9
Al	39.	0.7	0.009
Na	102.5	94.1	89.0

^aJ-13 well water contacted with matrix tuff for 3 wk and centrifuged prior to successive filtrations.

^bMillipore HA membrane.

^cNuclepore, polycarbonate membranes.

3. Preparation Method (S. J. DeVilliers, A. J. Mitchell, and K. Wolfsberg).

For the first sets of experiments the waters were prepared by shaking crushed matrix material from the U12G-RNM9 hole (8.1 - 10.0 feet) with well J-13 water in the controlled nitrogen atmosphere (≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide). The pretreated waters were sampled and filtered through 0.05- μm membranes at weekly intervals. The concentrations obtained by analysis with the plasma-source emission spectrometer are given in Table III. It is seen that the waters have essentially reached constant values after 1-wk contact times.

B. Batch Sorption Experiments with ^{85}Sr , $^{95\text{m}}\text{Tc}$, ^{137}Cs , ^{133}Ba , ^{141}Ce , and ^{152}Eu (S. J. DeVilliers, A. J. Mitchell, and K. Wolfsberg)

1. Matrix Rock. Initial batch sorption experiments were performed in the controlled nitrogen atmosphere with ground matrix material from hole U12G-RNM9, 10.8 - 11.9 feet. The core was received "waxed and wrapped." Unfortunately, the colloid problem noted above had not been discovered at the start of the experiment, and the experiment was conducted with tagged groundwater that had been filtered only through 0.45- μm Millipore HA filters. The experiment is being repeated with proper filtration.

Sorption ratios (R_d) from the preliminary experiment, given in Table IV, should be viewed with caution. Nuclides may have sorbed on colloidal particles prior to the experiment. Sorption ratios for cesium, strontium, and barium are high (>1000 ml/g), whereas those for cerium and europium are intermediate. The apparent sorption ratios increase less than a factor of three between 0.5 h and 14 days; however, there is increasing sorption for still longer times. This phenomenon may be caused by sorption on fine particles produced during the experiment.

The unusually high sorption ratios for strontium exhibited by this rock may be related to the exchange of calcium in the water for sodium and potassium, which was observed in the preparation of the waters. The Tunnel Bed tuff has a greater affinity for alkaline earths than other tuffs studied.

2. Fracture Material. Fracture-fill material was obtained from the "waxed and wrapped" core from U12G-RNM9, 7.1 - 8.1 feet. The pulverized material was obtained by grinding the two fracture faces of the core against each other. The pretreated water for these experiments was filtered through 0.05- μm membranes as described above, and the experiments were performed in the controlled nitrogen atmosphere. The results are given in Tables V and VI.

TABLE III
VARIATION OF WATER COMPOSITION WITH PRETREATMENT TIME^a

Contact Time (wk)	Concentration (mg/l)												
	Mg	Mn	Si	Fe	Sr	Ba	V	Ti	Ca	Li	K	Al	Na
1	0.144	0.024	27.4	0.117	0.003	0.318	0.010	0.005	0.666	0.054	8.94	0.019	104.
2	0.047	0.031	34.4	0.395	0.000	0.028	0.011	0.000	0.825	0.042	8.88	0.055	112.
3	0.081	0.021	27.1	0.058	0.001	0.124	0.008	0.000	0.556	0.050	4.91	0.009	89.0
4	0.044	0.036	33.5	0.149	0.000	0.025	0.011	0.000	0.944	0.040	9.13	0.017	109.
5	0.092	0.030	30.7	0.119	0.000	0.028	0.011	0.008	0.469	0.053	8.15	0.011	92.4
6	0.066	0.037	30.2	0.307	0.001	0.016	0.007	0.000	1.03	0.049	9.33	0.041	94.4
7	0.060	0.030	27.3	0.107	0.000	0.006	0.011	0.000	0.447	0.049	5.80	0.003	86.2
8	0.079	0.044	31.8	0.268	0.001	0.017	0.016	0.000	0.982	0.040	11.2	0.043	104.
9	0.119	0.041	29.0	0.209	0.001	0.014	0.015	0.013	0.712	0.058	10.3	0.025	93.7
10	0.048	0.015	30.1	0.040	0.002	0.144	0.020	0.018	0.688	0.071	6.22	0.069	93.5
Average	0.078 (0.010) ^b	0.031 (0.003)	30.1 (0.8)	0.18 (0.04)	0.009 (0.003)	0.072 (0.031)	0.012 (0.001)	0.004 (0.002)	0.73 (0.07)	0.051 (0.003)	8.3 (0.6)	0.029 (0.007)	97. (3.)
	2.4 ^c	0.12	30.7	0.02	0.05	0.02	0.017	--	12.6	0.09	9.2	0.05	59.

^aWell J-13 contacted with HF-23 matrix rock in controlled atmosphere.

^bNumbers in parentheses are standard deviations of the means.

^cWell J-13 water; no contact with solid.

TABLE IV
PRELIMINARY SORPTION RATIOS FOR HF-23 MATRIX^a

Contact Time	R_d (ml/g)				
	Cs	Sr	Ba	Ce	Eu
0.5 h	1 750(1 220) ^b	3 900(1 130)	6 040(2 830)	288(114)	212(84)
1 h	1 450(42)	3 990(110)	5 360(140)	277(5)	215(7)
3 h	2 400(800)	6 040(1 130)	10 300(3 910)	434(146)	339(102)
7 h	3 105(2 180)	8 350(2 620)	11 440(4 190)	391(118)	341(111)
1 day	3 270(2 880)	9 170(6 980)	11 640(10 800)	464(307)	439(279)
2 days	3 420(680)	11 800(1 480)	12 600(1 410)	488(13)	469(26)
14 days	3 400(540)	11 400(560)	15 600 (2 330)	491(102)	449(99)
42 days	10 000(1 700)	48 800(1 270)	27 300(4 670)	823(125)	829(80)
56 days	18 800(10 800)	71 700(28 570)	47 800(30 600)	1 143(504)	1 094(516)

^a R_d values are the averages of two measurements.

^bNumbers in parentheses are standard deviations of the mean.

TABLE V
SORPTION RATIOS FOR FRACTURE-FILL SAMPLES

Time (week)	R_d (mL/g)				
	Cs	Sr	Ba	Ce	Eu
1	10 400(3.7) ^a	1 350(2.7)	20 000(5.3)	240(5.9)	320(5.4)
1	2 100(2.2)	470(2.2)	3 900(2.0)	230(4.2)	280(3.3)
3	13 000(5.8)	1 800(3.9)	21 000(7.5)	380(8.7)	490(8.4)
3	15 000(6.9)	2 500(4.4)	26 000(9.5)	340(10.2)	443(9.9)
4	16 000(8.1)	2 300(5.9)	7 200(4.3)	760(11.9)	870(11.7)
4	13 000(7.5)	2 200(5.8)	7 400(4.1)	490(11.1)	720(10.8)
6	8 300(5.6)	2 400(6.2)	7 600(4.7)	550(8.7)	760(8.3)
6	9 800(5.4)	1 900(6.2)	9 700(5.3)	670(8.4)	1 000(8.0)

^aThe values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; they were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation. These estimated uncertainties were propagated using the rule of change of variables in a moment matrix, assuming independence of the variables.

TABLE VI
SORPTION RATIOS FOR ^{95}mTc ON FRACTURE-FILL SAMPLES

<u>Contact Time (week)</u>	<u>R_d (ml/g)</u>
1	0.0047
3	0.72
3	0.66
4	1.79
4	1.42

Sorption ratios for cesium, barium, cerium, and europium for fracture-fill material are similar to those for the matrix rock, but those for strontium are a factor of two to ten less than those for the matrix rock. Sorption ratios for technetium are small, but may be increasing with time. Because only solution-counting data were used for these technetium values, they are subject to rather large errors. Solids will be assayed for future determinations in order to obtain better values.

3. Wafers. Sorption measurements were performed in air on 13.5-mm diameter wafers prepared from matrix material from core U12G-RNM9, 16.2 - 17.5 feet. The thickness varied from 5 to 9 mm. The wafers were suspended in solutions, which had been passed through 0.05- μm filters, by nylon fishing leader. Sorption ratios, given in Table VII, are comparable in magnitude to those given in Table IV except the values for strontium are much less. There is no obvious correlation with time of contact or thickness of sample. The thickest wafer for the 12-day contact had the largest R_d , but a similar sized wafer for the 27-day contact gave R_d values similar to the others in the experiment. The negative values for technetium are zero and indicate essentially no sorption within the errors of counting solutions only.

C. Kinetic Sorption Experiments (N. A. Raybold and E. N. Vine)

Ten wafers (~1.0 to 1.8 g) of G-Tunnel tuff were contacted for 2 wk with J-13 water that had been pretreated with crushed G-tunnel tuff and then filtered through a 0.05- μm Nuclepore filter. The tuff wafers, suspended on Teflon thread, were then placed into J-13 water, which had been pretreated as described above and which also contained ^{85}Sr , ^{137}Cs , ^{133}Ba , and ^{152}Eu . The wafers were removed for counting at times ranging from 1 h to several weeks.

TABLE VII
SORPTION RATIOS FOR WAFERS

Contact Time (days)	Thickness (mm)	R_d (mℓ/g)					
		Cs	Sr	Ba	Ce	Eu	Tc
6	6.3	5 500(3.2) ^a	370(2.2)	9 600(3.9)	140(5.3)	140(4.7)	-0.58
12	5.6	7 700(3.4)	430(2.1)	14 000(4.3)	280(5.5)	270(4.8)	-0.41
12	8.7	10 000(5.2)	1 300(3.3)	25 000(10.9)	130(7.8)	150(7.4)	-0.12
27	8.3	5 200(3.4)	240(2.2)	11 000(5.2)	330(5.5)	310(4.9)	-0.29

^aSee footnote a, Table V.

Measurements at longer contact times are still in progress. The percent activity sorbed on the wafer vs contact time is given in Table VIII. Even within 1 h most of the ^{85}Sr , ^{137}Cs , and ^{133}Ba activity sorbed on the G-Tunnel wafer. Within 1 day sorption of ^{152}Eu increased from ~7% (1 h) to ~60%. Because this tuff is highly zeolitized (clinoptilolite), the high sorption of strontium, cesium, and barium is expected. Similar studies with pertechnetate and iodide are in progress.

D. Column Experiments (E. N. Vine and N. A. Raybold)

A crushed-rock column of G-Tunnel tuff fracture-fill material was made, and HTO and $^{131}\text{I}^-$ elutions were run. The column was then loaded with $^{99\text{m}}\text{Tc}$, ^{85}Sr , ^{137}Cs , and ^{133}Ba , and the elution of these isotopes is in progress. After elution is complete, the free column volume will be redetermined with HTO or I^- for comparison, because a portion of the crushed G-Tunnel tuff seems to be decreasing in size and gradually passing through the 35- μm frit.

TABLE VIII
PERCENT OF TOTAL ACTIVITY SORBED ON WAFERS^{a,b}

Contact Time (days)	^{85}Sr	^{137}Cs	^{133}Ba	^{152}Eu
0.042	76(3)	74(2)	61(2)	6.8(0.8)
0.125	91(3)	78(4)	64(7)	12.1(0.4)
0.708	92(3)	95(2)	76(3)	41.4(1.4)
0.917	90(1)	90(1)	74(7)	59(5)
1.51	90(2)	96(2)	78(3)	65(5)
2.58	90(1)	91(0.3)	81(3)	67(6)
7.50	92(1)	93(0.5)	83(3)	72(2)
15.50	93(1)	97(3)	85(5)	80(2)
29.50	93(2)	93.5(0.1)	87(4)	79(1)

^aThe percentages given are lower limits because the activity (^{85}Sr , ^{133}Ba , and ^{152}Eu) sorbed on the container walls and the activity sorbed on small fragments of the wafer that broke off and settled on the bottom were not taken into account.

^bThe percentages given are the averages of three or more measurements. The standard deviations of the means are given in parentheses.

A solid core of G-Tunnel tuff (matrix material) was embedded in epoxy. It has been pretreated with well J-13 water for several weeks. A Sage syringe pump quite easily produces water flow through the core. Tritium and iodide elutions will be done soon.

E. Tritium Content of Water in Rock from Hole U12G-RNM8 (W. R. Daniels, R. S. Rundberg, and P. Q. Oliver)

Portions of rock were removed from opposite ends of core U12G-RNM8, 1.0 - 3.4 feet, which had been stored in a plastic bag wrapped with tape. Water was removed from the rock by heating and condensing. The HTO contents were found to be 1.05 and 3.03 nCi/ml at depths of 3.4 and 1.0 feet from the tunnel wall, respectively. Water from rock samples from other depths will be analyzed to determine the relationship between tritium content and depth.

F. Materials Characterization

1. X-Ray Diffraction Analyses (D. L. Bish). X-ray diffraction analyses were performed on the pulverized rock samples used for the sorption studies. In addition, fracture-fill material close to the tunnel rib was examined and found to be virtually indistinguishable from that in the matrix. The results are given in Table IX.

2. Microscopic Examination (C. J. Duffy). Thin sections from both sides of a parting plane in the U12G-RNM9 core have been examined. The mineralogy has not been determined, but the two sides have been found to be distinctly different on a textural basis. A section of side B of U12G-RNM9, 5.9 - 6.4 feet, shows a zone of low porosity, about 3 mm wide, adjacent to the parting plane. The remainder of the section has considerably higher porosity. Section U12G-RNM9, 5.0 - 5.9 feet, side B? (the orientation is not available, but texturally the side resembles side B from 5.9 - 6.4 feet) shows the same low porosity band adjacent to the parting plane. Here the band is about 7 mm wide and shows an increase in shard size away from the parting plane.

Side A of a section of U12G-RNM9, 5.9 - 6.4 feet, shows no regular change in porosity across the section. The porosity is generally lower than in the other sections, although small high-porosity areas are present. The shard size is generally similar to the smaller material of the other sections.

Examination of the tunnel rib in the field indicates that Side B is the lower side of the fracture.

TABLE IX
X-RAY DIFFRACTION ANALYSES

Description	Volume Percent		
	Clinoptilolite	K-feldspar	Illite/Mica
U12G-RNM9, 10.8 - 11.9 feet, matrix	70-90	10-20	5-10
U12G-RNM9, 0.8 - 1.0 feet, fracture fill	60-80	20-40	trace
U12G-RNM9, 7.1 - 8.1 feet, fracture fill	60-80	20-40	trace

IV. GEOCHEMISTRY OF TUFF

A. Sorption on Samples From Drill Hole USW-G1 (S. J. DeVilliers, A. J. Mitchell, E. N. Vine, and K. Wolfsberg)

Measurements of sorption of strontium, cesium, barium, cerium, and europium on an initial set of samples from the USW-G1 hole have been completed. Results of individual determinations are given in Table X, and water analyses determined with the plasma-source emission spectrometer are given in Table XI. The pretreated well J-13 waters were passed through 0.45- μ m Millipore HA filters after 3-wk contacts with the appropriate tuff. The composition of untreated well J-13 water is also given. Details of the work and conclusions are in a status report (Appendix A). In general, the correlations between mineralogy and sorptive behavior noted previously^{3,4} are confirmed, but there are exceptions as noted in Appendix A.

B. Sorption on Samples from Drill Hole J-13 (E. N. Vine and N. A. Raybold)

Preliminary sorption data for 3-wk contact times with ⁸⁵Sr, ¹³⁷Cs, ¹³³Ba, ¹⁴¹Ce, and ¹⁵²Eu on samples JA-26, JA-28, and JA-8 were reported previously.⁵ Sample JA-8 is ~25-50% montmorillonite, 10-20% cristobalite, and 25-50% glass. The JA-26 and JA-28 samples are primarily analcime, quartz, and alkali feldspar. In addition, sample JA-28 contains 2-5% illite/muscovite.

Average sorption and desorption ratios for 3- to 12-wk contact times are given in Table XII. As noted previously,⁵ samples JA-26 and JA-28, which contain analcime in addition to quartz and feldspar, have sorption ratios very similar to those of devitrified, non-zeolitized tuffs. Not surprisingly,

TABLE X
SORPTION AND DESORPTION RATIOS FOR USW-G1 SAMPLES^a

Sample ^b	Contact Time(week)		R _d (mL/g)				
	Sorption	Desorption	Cs	Sr	Ba	Ce	Eu
G1-2233-1	3		13 000(5.5) ^c	40 000(3.9)	200 000(2.3)	830(8.4)	520(7.8)
		6	29 000(10.1)	190 000(14.0)	100 000(14.4)	14 000(13.3)	9 400(12.6)
G1-2233-3	3		11 000(5.2)	55 000(4.1)	210 000(6.8)	1 300(7.9)	900(7.4)
		6	31 000(10.3)	75 000(14.6)	460 000(15.8)	59 000(13.6)	3 800(12.9)
G1-2233-2	6		15 000(5.4)	49 000(4.6)	330 000(9.1)	2 100(8.2)	1 300(7.7)
		3	25 000(9.8)	82 000(13.7)	220 000(13.3)	4 900(12.6)	3 300(12.2)
G1-2233-4	6		14 000(5.2)	50 000(4.6)	260 000(7.2)	1 300(8.0)	870(7.4)
		3	6 500(8.0)	13 000(9.3)	160 000(9.0)	2 200(9.5)	1 700(9.0)
G1-1436-1	3		7 000(3.8)	31 000(3.5)	150 000(4.0)	58 000(10.7)	30 000(7.0)
		6	18 000(9.1)	55 000(12.2)	110 000(11.6)	5 500(11.6)	4 500(11.0)
G1-1436-3	3		7 900(4.0)	36 200(3.7)	140 000(4.0)	62 000(10.2)	32 000(6.7)
		6	29 000(10.0)	100 000(14.8)	300 000(14.8)	5 900(13.1)	4 200(12.5)
G1-1436-2	6		7 400(3.9)	33 000(3.8)	93 000(3.2)	41 000(10.3)	25 000(6.4)
		3	23 000(9.7)	83 000(14.1)	500 000(14.8)	7 200(12.6)	6 100(12.0)
G1-1436-4	6		8 900(4.3)	45 000(4.5)	210 000(5.1)	74 000(11.9)	33 000(7.2)
		3	26 000(10.0)	110 000(14.6)	450 000(14.6)	8 000(13.1)	6 500(12.4)
G1-1982-1	3		1 400(2.5)	430(1.9)	2 500(1.2)	520(4.4)	1 500(3.8)
		6	2 000(7.5)	330(8.4)	3 100(8.0)	5 600(11.7)	6 500(8.4)
G1-1982-3	3		1 400(2.5)	433(1.9)	2 300(1.2)	450(4.4)	1 300(3.6)
		6	2 900(7.4)	340(8.1)	2 600(7.9)	5 900(10.5)	6 100(8.3)
G1-1982-2	6		1 800(2.6)	450(1.9)	3 100(1.2)	640(4.6)	2 000(3.9)
		3	2 100(7.5)	310(8.1)	2 600(8.0)	7 200(11.7)	6 500(8.4)
G1-1982-4	6		1 800(2.6)	450(1.9)	3 200(1.2)	602(4.6)	1 900(3.9)
		3	2 100(7.5)	310(8.1)	2 800(8.0)	9 400(15.5)	800(8.5)
G1-1883-1	3		390(2.2)	58(2.3)	430(1.1)	150(4.1)	170(3.1)
		6	430(7.5)	56(8.0)	420(7.8)	2 100(12.1)	1 500(7.9)

TABLE X (cont.)
SORPTION AND DESORPTION RATIOS FOR USW-G1 SAMPLES^a

Sample ^b	Contact Time(week)		R _d (ml/g)				
	Sorption	Desorption	Cs	Sr	Ba	Ce	Eu
G1-1883-3	3		350(2.2)	60(2.3)	250(1.6)	150(4.0)	170(3.0)
		6	420(7.5)	58(8.0)	440(7.8)	2 000(10.6)	1 300(7.9)
G1-1883-2	6		440(2.2)	57(2.4)	480(1.1)	300(4.2)	330(3.1)
		3	440(7.5)	62(8.0)	460(7.8)	2 300(10.6)	1 300(7.9)
G1-1883-4	6		440(2.2)	58(2.4)	490(1.1)	260(4.2)	300(3.1)
		3	430(7.5)	60(8.0)	450(9.8)	2 200(10.9)	1 300(7.9)
G1-2698-1	3		8 200(4.9)	49 000(4.7)	61 000(4.2)	220(7.5)	180(7.0)
		6	16 000(3.8)	170 000(14.5)	390 000(13.1)	2 400(11.0)	1 900(104)
G1-2698-3	3		7 400(4.5)	39 000(4.3)	56 000(4.0)	169(7.0)	135(6.4)
		6	15 000(8.6)	200 000(14.4)	47 000(12.6)	2 800(10.8)	2 100(10.1)
G1-2698-2	6		8 500(4.9)	43 000(5.4)	77 400(5.0)	270(7.5)	230(7.0)
		3	17 000(9.2)	120 000(14.1)	210 000(12.8)	12 000(11.5)	850(11.1)
G1-2698-4	6		6 600(4.4)	37 000(4.1)	58 000(4.1)	310(6.9)	260(6.3)
		3	20 000(9.7)	350 000(20.0)	62 000(19.1)	1 600(12.3)	1 000(11.9)
G1-1292-1	3		390(2.2)	200(1.9)	1 800(1.2)	54(4.1)	140(3.1)
		6	500(7.4)	110(7.9)	1 400(7.8)	510(8.8)	510(7.8)
G1-1292-3	3		450(2.2)	200(1.9)	2 200(1.2)	79(4.1)	158(3.1)
		6	560(7.5)	120(8.0)	1 700(7.8)	1 200(9.3)	780(7.5)
G1-1292-2	6		500(2.2)	220(2.0)	2 800(1.3)	82(4.1)	160(3.0)
		3	520(7.4)	130(7.9)	15 000(7.9)	94(9.1)	620(7.8)
G1-1292-4	6		380(2.2)	192(2.1)	1 500(1.2)	50(4.1)	100(3.1)
		3	470(7.5)	110(7.9)	1 400(7.8)	610(8.9)	490(7.8)
G1-2363-1	3		1 300(2.2)	170(2.0)	880(1.1)	290(4.1)	1 300(3.5)
		6	1 300(7.4)	160(7.9)	870(7.8)	120 000(100)	450(8.4)
G1-2363-3	3		1 200(2.2)	180(2.0)	830(1.1)	270(4.2)	1 300(3.6)
		6	1 200(7.4)	140(8.0)	800(7.8)	140 000(100)	5 700(9.0)

TABLE X (cont.)
SORPTION AND DESORPTION RATIOS FOR USW-G1 SAMPLES^a

Sample ^b	Contact Time(week)		R _d (mL/g)				
	Sorption	Desorption	Cs	Sr	Ba	Ce	Eu
G1-2363-2	6		1 400(2.2)	170(2.0)	920(1.1)	370(4.6)	1 900(3.7)
		3	1 200(7.4)	150(8.0)	830(7.8)	130 000(100)	6 700(9.7)
G1-2363-4	6		1 400(2.2)	170(2.1)	930(1.1)	310(4.6)	1 600(3.7)
		3	1 200(7.4)	1 400(7.9)	780(7.8)	1 400 000(100)	5 900(9.1)
G1-3116-1	3		7 600(4.1)	2 500(3.5)	116 000(5.4)	89(6.1)	680(5.8)
		6	21 000(9.4)	58 000(13.1)	7 100 000(16.9)	5 600(12.2)	14 000(11.6)
G1-3116-3	3		7 000(4.0)	2 500(3.4)	130 000(5.7)	80(6.0)	660(5.7)
		6	6 200(7.9)	3 100(9.9)	23 000(11.0)	180(4.4)	600(8.9)
G1-3116-2	6		5 500(3.6)	2 200(3.6)	118 000(5.4)	105(5.5)	790(5.1)
		3	8 500(8.2)	32 000(10.4)	190 090(10.5)	3 100(100)	8 900(9.5)
G1-3116-4	6		6 200(3.7)	2 400(3.7)	130 000(6.4)	120(5.6)	900(5.3)
		3	7 900(8.1)	3 500(10.4)	280 000(11.5)	4 200(10.1)	9 400(9.4)
G1-3658-1	3		780(3.5)	1 000(2.6)	870(1.5)	64(5.4)	51(4.9)
		6	1 000(7.8)	1 400(9.4)	1 600(12.9)	680(10.2)	670(8.8)
G1-3658-3	3		820(3.6)	1 400(2.9)	1 200(1.6)	63(5.5)	49(5.1)
		6	1 800(7.3)	350(8.0)	310(7.8)	79(8.1)	70(7.7)
G1-3658-2	6		850(3.7)	1 200(2.9)	1 200(1.5)	147(5.7)	124(5.2)
		3	1 100(7.9)	1 700(9.5)	210(9.0)	1 400(11.6)	1 200(9.1)
G1-3658-4	6		770(3.6)	1 100(2.8)	900(1.5)	126(5.6)	105(5.1)
		3	1 000(7.8)	1 400(9.4)	1 900(8.9)	1 600(11.6)	1 500(9.0)
G1-2289-1	3		1 600(4.9)	1 300(2.8)	7 000(4.2)	4.9(7.2)	27(6.9)
		6	780(11.1)	630(16.9)	5 100(17.1)	44(17.7)	85(14.4)
G1-2289-3	3		1 600(4.8)	1 300(2.9)	5 400(3.7)	4.5(7.2)	17(6.9)
		6	3 600(9.0)	2 100(12.9)	14 000(13.1)	110(12.4)	253(11.9)
G1-2289-2	6		2 000(5.4)	1 700(3.4)	8 300(4.8)	9.4(8.0)	47(7.7)
		3	430(1.5)	440(8.5)	430(8.2)	45(9.0)	65(8.2)

TABLE X (cont.)
SORPTION AND DESORPTION RATIOS FOR USW-G1 SAMPLES^a

Sample ^b	Contact Time(week)		R _d (ml/g)				
	Sorption	Desorption	Cs	Sr	Ba	Ce	Eu
G1-2289-4	6		1 700(3.4)	1 700(3.4)	10 000(5.1)	5.7(7.6)	30(7.3)
		3	5 900(12.1)	2 800(66)	24 000(17.0)	210(16.3)	470(15.7)
G1-2901-1	3		1 400(2.2)	68(2.3)	1 900(1.2)	40 000(100)	195 000(100)
		6	1 400(7.4)	66(7.9)	2 000(7.8)	40 000(100)	200 000(100)
G1-2901-3	3		950(2.2)	66(2.3)	1 200(1.1)	35 000(100)	23 000(28)
		6	1 300(7.4)	67(9.9)	1 900(7.8)	38 000(100)	220 000(100)
G1-2901-2	6		1 400(2.2)	69(2.3)	1 900(1.2)	45 000(100)	210 000(100)
		3	1 400(7.4)	740(7.9)	2 000(7.8)	40 000(100)	200 000(100)
G1-2901-4	6		1 400(2.2)	71(2.6)	1 900(1.2)	49 000(100)	210 000(100)
		3	1 400(7.4)	69(7.9)	2 000(7.8)	37 000(100)	210 000(100)

^aParticle-size distribution <500 μ m.

^bThe G1 indicates that the sample was from USW-G1. The next 4 characters indicate the depth in feet from which the sample was taken. The next number is a sample identification number.

^cThe values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; they were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation. The estimated uncertainties were propagated using the rule of change of variables in a moment matrix, assuming independence of the variables.

TABLE XI
COMPOSITION OF PRETREATED GROUNDWATERS^a

Sample	Concentration (mg/l)												
	Mg	Mn	Si	Fe	Sr	Ba	V	Ti	Ca	Li	K	Al	Na
G1-1292	1.80	0.048	27.2	0.126	0.129	0.674	0.015	0.000	0.394	0.087	6.42	0.559	56.6
G1-1436	0.093	0.036	33.6	0.900	0.002	1.05	0.010	0.074	0.394	0.054	4.08	2.23	85.1
G1-1883	1.27	0.013	28.0	0.048	0.023	0.999	0.006	0.000	9.91	0.073	6.25	0.357	61.2
G1-1982	0.984	0.017	30.8	0.813	0.010	0.520	0.007	0.013	4.86	0.082	5.79	1.37	74.0
G1-2233	0.148	0.029	30.6	0.822	0.001	0.758	0.012	0.054	0.433	0.070	2.08	1.29	85.3
G1-2289	0.359	0.167	42.4	1.33	0.005	0.153	0.022	0.094	0.783	0.116	2.29	2.40	82.8
G1-2363	0.825	0.059	31.6	0.126	0.043	0.947	0.021	0.014	9.75	0.116	4.80	0.515	66.1
G1-2698	0.215	0.072	38.3	1.34	0.004	1.05	0.017	0.109	0.402	0.107	2.64	2.59	82.4
G1-2901	1.46	0.160	34.5	0.217	0.059	0.250	0.015	0.021	17.5	0.121	7.11	1.52	60.9
G1-3116	0.545	0.059	26.9	0.601	0.004	>2	0.027	0.031	1.32	0.075	2.25	1.15	79.2
G1-3658	1.63	0.096	28.2	4.81	0.016	>2	0.036	0.129	0.651	0.175	1.63	4.50	101.
J-13 ^b	2.44	0.12	30.7	0.022	0.052	0.016	0.017	--	12.6	0.090	9.17	0.05	59.1

^aWater from well J-13 treated with ground rock for ~3 weeks and passed through 0.45- μ m Millipore membrane.

^bNo treatment.

TABLE XII
SORPTION RATIOS FOR ADDITIONAL SAMPLES
FROM JACKALS FLATS

Tuff	R_d (ml/g) ^a			
	Sr	Cs	Ba	Eu
JA-8	271(5)	2 740(350)	435(1)	2 130(270)
	311(3)	4 550(430)	480(50)	9 780(2 900)
JA-26	95.3(3.4)	1 730(720)	774(310)	4 210(3740)
	39.3(2.9)	1 580(90)	444(17)	2 880(240)
JA-28	94(20)	1 640(290)	820(50)	2 110(1 000)
	114(2)	2 360(90)	1 160(20)	12 300(500)

^aThe sorption ratio is given on the first line and the desorption ratio on the second line. Numbers in parentheses are the standard deviations of the means.

the sorptive behavior of analcime is quite different from that of clinoptilolite and heulandite.

C. Plutonium Isotherm Measurements and Plutonium Chemistry (W. R. Daniels, F. O. Lawrence, M. R. Cisneros, S. Maestas, and P. Q. Oliver)

Final desorption results from the batch measurements of plutonium sorption ratio dependence on element concentration are listed in Table XIII. The desorptions were carried out for a period of 3 wk (equal to the sorption time).

The average R_d values for the desorptions are 780 ml/g for the YM-22 tuff and 650 ml/g for the YM-49 tuff, with standard deviations of the means of 110 ml/g and 48 ml/g, respectively. The desorption R_d values are higher than the sorption R_d values by factors of two to four, rather than ten as was found before.^{6d} It is possible that the difference may be caused by the shorter total contact time for sorption plus desorption that was used for these isotherm studies (6 wk compared to 15 wk). Except for the highest plutonium concentration, which exhibits the lowest R_d in three of the five groups, there appears to be little correlation between sorption ratio and element concentration in the range studied. There is some tendency toward lower R_d values with

the larger particle size, especially for sample YM-22. When the Freundlich equation⁵ is applied to the desorption data, the parameters given in Table XIV are obtained.

The overall average of n is 0.90 with a standard deviation of 3%. The observed values of n differ somewhat from those obtained from the sorption data, but not in a consistent manner. This may simply be due to the fact that the data are very limited and more data must be collected before drawing any conclusions.

During the last quarter, many experiments have been performed in attempts to prepare plutonium in the +3, +4, +5, and +6 oxidation states and in verification of procedures for separation of oxidation states. All of the experiments are

TABLE XIII
DEPENDENCE OF PLUTONIUM SORPTION RATIO ON CONCENTRATION

Core	Initial Pu Concentration ^a (M)		R _d (ml/g)			
			Sorption		Desorption	
	Added	Actual	<75μm	75-500μm	<75μm	75-500μm
YM-22	1.2 x 10 ⁻¹¹	8.0 x 10 ⁻¹²	60	65	1 100	960
	5.6 x 10 ⁻¹¹	3.0 x 10 ⁻¹¹	63	62	1 200	580
	4.4 x 10 ⁻¹⁰	2.1 x 10 ⁻¹⁰	54	54	990	470
	3.9 x 10 ⁻⁹	1.8 x 10 ⁻⁹	66	41	1 100	920
	3.9 x 10 ⁻⁸	1.0 x 10 ⁻⁸	34	17	280	230
YM-49	1.2 x 10 ⁻¹¹	1.6 x 10 ⁻¹²	170	150	700	670
	5.6 x 10 ⁻¹¹	7.7 x 10 ⁻¹²	160	89	840	790
	4.4 x 10 ⁻¹⁰	1.3 x 10 ⁻¹⁰	130	140	780	590
	3.9 x 10 ⁻⁹	4.3 x 10 ⁻¹⁰	180	220	490	620
	5.4 x 10 ⁻⁸	2.9 x 10 ⁻⁸	270	240	690	340

^aThe plutonium concentrations at 100% yield based on assay of the ²³⁷Pu and ²³⁹Pu solutions are shown as "added." The plutonium concentrations actually present at the start of the batch contacts, given as "actual," are lower because of losses during preparation of the feed solutions.

TABLE XIV
FREUNDLICH ISOTHERM PARAMETERS FOR DESORPTION OF PLUTONIUM

<u>Core</u>	<u>Fraction (μm)</u>	<u>n</u>	<u>k</u>
YM-22	<75	0.84	0.01
	75-500	0.87	0.02
YM-49	<75	0.98	0.36
	75-500	0.92	0.07

directed toward planned batch sorption studies using both oxidized and reduced forms of plutonium.

D. Crushed-Rock Column Circulating Systems (R. D. Aguilar and F. O. Lawrence)

Experiments with circulating columns containing three different types of crushed tuffs have been started with J-13 well water tagged with ^{241}Am tracer. The tuffs (G1-1883, YM-49, and JA-37) were ground and sieved to a 106-250 μm size. The columns hold about 4.5 g of rock, and an initial solution-to-solid ratio of ~ 15 ml/g was used. The groundwater was circulated for 2 weeks to pretreat the rock samples and check out the system. Rock-pretreated groundwaters were tagged with ^{241}Am by the usual evaporation-dissolution procedure.⁶ Circulation of these tagged groundwaters is in progress. Similar, tagged groundwaters are being circulated through systems not containing rock. Aliquots of the aqueous phase will be removed at intervals of 3, 6, and 12 weeks and analyzed. Rock-pretreated groundwaters tagged with ^{237}Pu are scheduled to be circulated through columns now in the pretreatment stage.

E. Crushed-Rock Column Studies (E. N. Vine and N. A. Raybold)

The elution of ^{85}Sr , ^{137}Cs , and ^{133}Ba from columns of crushed tuff from hole USW-G1 cores reported previously² is continuing. Strontium, cesium, and barium have been removed from column G1-1883-A. The R_d values calculated from the data are ~ 20 ml/g for ^{85}Sr , ~ 100 ml/g for ^{137}Cs , and ~ 104 ml/g for ^{133}Ba . These values are 24 to 34% of those obtained by the batch technique. A second G1-1883 column, G1-1883-B, gave an R_d for strontium of ~ 37 ml/g. Cesium and barium have not yet been eluted from that column, which has a volume ~ 7 times that of G1-1883-A. Elution of activity from the other tuff crushed-rock columns is continuing. Insufficient data have been obtained to make estimates of

sorption ratios on those columns (including several new ones started this quarter), except for G1-1292 from which ~41% of the ^{85}Sr has been removed, indicating an $R_d > 106 \text{ ml/g}$. The corresponding batch sorption ratio is 201 ml/g.

Some evaluation of the chromatographic behavior of these columns and theoretical treatment of the experiments is given in Appendixes B and C.

F. Solid Core Column Studies (A) (E. N. Vine and N. A. Raybold)

Ten whole core columns from holes UF25a-1 and USW-G1 are being pretreated with well J-13 water. The tuffs are G1-3116, G1-1436, G1-2901, G1-2233, G1-2289, G1-2854 (2 columns), G1-3658, and YM-30. Most of the columns are 5/8 inch in diameter and ~1.25 to 2 inches in length. A few columns are 0.5 inch in diameter. Water is being pushed through the cores at a low pressure with Sage syringe pumps. Each of the cores was mounted in epoxy, the ends were sawed off, and the epoxy machined so that Bio-Rad Econo-Column fittings could be used. Three of these cores contained filled fractures: G1-2854 (2 columns) and G1-2901.

Four other whole hole USW-G1 cores (1292, 1883, 1982, and 2698) were mounted in a similar manner; however water has not been pushed through these in two weeks.

Pretreating of all the cores will continue until HTO and I^- elutions are run.

G. Solid Core Column Studies (B) (R. S. Rundberg, W. R. Daniels, S. Maestas, and N. A. Raybold)

Tuff samples from the USW-G1 drill hole have been run as columns using a peristaltic pump. These samples have been equilibrated with appropriate pretreated water and have been running for periods as long as three months. Currently, samples are sealed in plexiglass jackets with Buehler epoxy. This method of potting seems to be adequate to provide a jacket which can withstand stress due to the swelling of certain mineral phases, for example, montmorillonite, which occurs when the cores are wet. Previously, glass jackets were used and were found to crack after 4 weeks.

Samples of the G1-1982 and G1-1883 cores from the Prow Pass Member were loaded with spikes of tritium to determine the dispersivity of the rock and the free column volume. These tuffs are from the Prow Pass Member. The tuffs are from a welded, devitrified zone which is free of zeolites (J. R. Smyth, Los Alamos, personal communication, January 1981). The G1-1982 sample, however,

contains a small amount of montmorillonite clay that swelled and disintegrated during equilibration with pretreated water. This left some significant pits (1-2 mm deep) in the ends of the core. The sample G1-1982 material also appears more heterogeneous, having some colored zones that appear to be denser than the surrounding material.

The tritium elutions shown in Figs. 1 and 2 can be fit with a simple dispersion-convection model for a one-dimensional flow field. The Peclet numbers determined by fitting the data were 4 and 10 for samples G1-1982 and G1-1883, respectively. The fluid velocity used in these columns was about 6×10^{-5} cm/s. It should be noted that, for ion exchange (diffusion controlled rates), this velocity, although a factor of 10 higher than the water velocities that may exist in permeable rock at the NTS,⁷ is not fast enough to affect mass transfer (see Appendix C). Furthermore, an additional factor of 10 increase in the fluid velocity may improve column performance by reducing the effect of diffusional broadening without reducing the number of mass transfer units.

A core of sample YM-49, a zeolitized tuff, was encased in epoxy using techniques described in previous reports^{5,6} for use in the high pressure system.⁸ After equilibrating the rock for 4 weeks with pretreated water, the free column volume was determined by tritium elution. (The peak was greatly broadened by diffusion.) The core was then loaded with 1.6×10^5 gamma counts/min of ^{237}Pu and about 10^5 dis/min of ^{239}Pu . The mixture was prepared by drying the tracer and bringing the plutonium into "solution" by shaking with pretreated water. No effort was made to remove particulates from the "solution." In order to achieve flow through the core, it was necessary to increase the pressure to 450 psi from the 200 psi used for the pretreatment, suggesting partial clogging of pores by particulates. A flow rate of 0.7 ml/day was achieved at this pressure, corresponding to a fluid velocity of 6.4×10^{-6} cm/s. This velocity is close to the estimate of Blackennagel and Weiss⁷ of 7×10^{-6} cm/s for flow predominantly through interstitial permeability beneath Pahute Mesa at the NTS. To date (three free column volumes), no activity, that is, <10 counts/min, above background has been observed in the eluate.

Fig. 1. Tuff G1-1883 tritium elution.

Fig. 2. Tuff G1-1982 tritium elution.

H. Effect of Materials for Preparing Wafers on Sorption and Carbon Analyses

(E. N. Vine and N. A. Raybold)

Tuff wafers (~0.75 inch in diameter and 1-2 g) are being used for sorption studies. The preparation of the wafers can involve such materials as isopropyl alcohol, kerosene, Pella oil, or diamond paste. Tests on tuffs from hole USW-G1 to determine the degree of retention of these chemicals are continuing. Desorption measurements with ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , and ^{152}Eu on tuffs G1-2233, G1-1982, G1-1883, and G1-1436 were completed. A summary of the isotopes desorbed and the maximum amount of desorption is given in Table XV.

A number of wafers from tuff G1-1436 were made by sawing in water and then treating with kerosene, Pella oil, or diamond paste. The wafers were then powdered and sent to Dr. Jeffrey L. Means at Battelle Columbus Laboratory in Columbus, Ohio, for analysis of total carbon and total organic carbon. Untreated water from well J-13 and water from the well that was pretreated with YM-38 tuff were also sent for analysis. The results are given in Table XVI.

TABLE XV
EXTENT OF DESORPTION WITH SOLVENTS

<u>Solvent</u>	<u>Isotopes Desorbed</u>	<u>Maximum % Desorbed</u>
IPA ^a	Cs, Ba	0.025
Kerosene	Sr, Cs, Ba	0.081
Pella Oil	Sr, Cs, Ba	0.046

^aIsopropyl alcohol.

TABLE XVI
TOTAL CARBON AND TOTAL ORGANIC CARBON ANALYSES

<u>Sample</u>	<u>Total Carbon</u>	<u>Total Organic Carbon</u>
J-13 water		0.31 ppm
J-13 pretreated water		4.0 ppm
G1-1436/Pella oil	1.17%	0.57%
G1-1436/3- μm diamond paste	0.67%	0.27%
G1-1436/kerosene	0.62%	0.18%
G1-1436 untreated	0.20%	0.10%

Although the organic carbon concentrations in the waters are rather low, the untreated tuff sample contains appreciable organic matter. The nature and extent of the organic content of the tuff in USW-G1 will be investigated in detail. Treatment with Pella oil, diamond paste, or kerosene adds substantially to the organic content.

I. Determination of Fe(II) in Groundwaters (B. P. Bayhurst and S. J. DeVilliers)

The procedure⁶ for the determination of Fe(II) using 4,7-diphenyl-1,10-phenanthroline has been tested using a Hewlett Packard model 8450 UV/VIS spectrophotometer. A spectrophotometer cell with a 5-cm light path should give a detection limit of ~8 ppb for a 50-ml sample, although electronic noise may increase this lower limit. Any Fe(III) present in the water will interfere to a small extent with the Fe(II) determination; however, a correction can be made once the Fe(III) content is known. Total iron can be determined by reducing any Fe(III) to Fe(II) with hydroxylamine and using the method described above or by emission-spectrometric analysis. The Fe(III) content can then be determined by difference; for a significant correction for Fe(III) interference with the Fe(II) measurement, the calculation can be reiterated.

Groundwaters that have been equilibrated with crushed argillite and with tuffs from G-Tunnel and Yucca Mountain at the Nevada Test Site are being analyzed first. Small, suspended particles containing iron would increase the measured iron content of the groundwaters; therefore, supernates after centrifuging and waters filtered through 0.4- or 0.05- μ m Nuclepore membranes are being examined. A comparison will be made between waters prepared in a controlled atmosphere (nitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide) and those prepared in air.

J. Analyses of Water from Wells USW-H1 and USW-VH1 (S. J. DeVilliers, A. J. Mitchell, and K. Wolfsberg)

During February, 1981, water samples from wells USW-H1 on Yucca Mountain and USW-VH1 in Crater Flat were received and analyzed for cations with the plasma-emission spectrometer. Results are given in Table XVII. The composition of the well USW-VH1 water is similar to the tuffaceous, well J-13 water. Water from well USW-H1 is unusual in the low silicon concentration.

TABLE XVII
ANALYSES OF WATERS FROM WELLS USW-H1 AND USW-VH1

Element	Concentration (mg/l)	
	USW-H1	USW-VH1
Mg	0.41	1.94
Mn	0.057	0.032
Si	5.13	24.9
Fe	0.034	0.072
Sr	0.018	0.082
Ba	0.011	0.037
V	0.002	0.009
Ti	--	--
Ca	7.16	10.3
Li	0.074	0.125
K	5.14	4.26
Al	0.003	0.042
Na	74.9	97.1

K. Organic Eh Moderators (B. P. Bayhurst)

Thionine has been investigated as a possible Eh buffer. Although the E_m^7 value of +0.064 V is higher than that of the previously studied⁵ Indigo Carmine, -0.125 V, difficulty has still been encountered in preventing the apparent slow air oxidation of the reduced form. Air oxidation will be eliminated when the system is moved into the newly completed controlled-inert-atmosphere box (Sec. IV.M).

Because pH has been difficult to control, pH buffers are being investigated. Boric acid-borax and tris(hydroxymethyl)aminomethane systems are being used in these preliminary studies.

L. Possible Inorganic Eh Moderators (T. W. Newton and B. P. Bayhurst)

Work has continued on the development of Eh buffers or moderators for use with plutonium and other actinides. Emphasis has been on osmium complexes with formal oxidation potentials below 0.855 V - the value for $Os(2,2'-bipyridine)_3^{2+}$.

A number of complexes have been prepared, purified, and partially characterized. The absorption spectra have been used for identification and for indication of chemical change. Potentiometric titrations have been made to obtain estimates of the oxidation potentials for complexes for which published values are not readily available. Stability with respect to decomposition in water or aqueous solutions has been determined. The results for the individual complexes are discussed below and summarized in Table XVIII.

1. Tris(2,2'-bipyridine)osmium(II) Chloride. This compound was prepared and purified by the method of Fabian, Klassen, and Sonntag¹¹ for comparison with the perchlorate salt prepared previously. It was further purified by recrystallization from a methanol-methyl ethyl ketone mixture during investigation of possible impurities. The air-dried compound corresponds to the heptahydrate; however, the water content can be reduced to 2.5 to 3.0 moles per mole of osmium by heating to 70°C under vacuum. The Os(III) complex was made in solution by oxidation with chlorine or with Ce(IV). Contrary to the observations presented in the previous quarterly report,⁵ the $\text{Os}(\text{bipy})_3^{3+}$ ion is very stable in water or in 7×10^{-4} M H_2SO_4 solutions. It has been observed to persist essentially unchanged for at least 30 days. The decomposition described previously was shown to be due to exposure to light, as suggested by Taube (H. Taube, Stanford University, personal communication, 1981).

2. Tris(4,4'-dimethyl-2,2'-bipyridine)osmium(II) Chloride. This compound was prepared and purified as previously described.¹¹ The spectrum of this preparation agreed with that of a small sample of the compound kindly provided by D. Klassen of McMurtry College. The extinction coefficient at 488 nm, the position of the largest peak between 320 and 600 nm, was found to be $1.42 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. A sample of the material was heated to 70°C under vacuum for 6 h and the equivalent weight, determined as previously described,⁵ was 837 g/mole. This corresponds to about 1.3 moles of water per mole of osmium. The water content of the air-dried material corresponds to 6.5 moles per mole of osmium. A sample of the material was oxidized in water with chlorine to give $\text{Os}(\text{dimebipy})_3^{3+}$. This ion was found to be very stable with respect to decomposition; the spectrum was unchanged after 90 h in water at room temperature or after heating to 90°C for 15 min. However, a 3.5-h exposure to daylight caused a 20% decrease in the absorption peak at 488 nm. Potentiometric titrations of $\text{Os}(\text{dimebipy})_3^{2+}$ and $\text{Os}(\text{bipy})_3^{2+}$ consecutively in the same apparatus showed that the oxidation potential of the methyl substituted complex is

TABLE XVIII
POSSIBLE INORGANIC Eh MODERATORS
SUMMARY OF RESULTS

	Ion ^a	Oxidation Potential (V)	λ_{max} (nm)	Extinction Coefficient (M ⁻¹ cm ⁻¹)	Stability
1.	Os(bipy) ₃ ²⁺	0.885 ^b	480	1.36 x 10 ⁴	good
	Os(bipy) ₃ ³⁺	--	555	6.9 x 10 ²	good
2.	Os(dimebipy) ²⁺	0.694	488	1.42 x 10 ⁴	good
	Os(dimebipy) ³⁺	--	537		good
3.	Os(diphenbipy) ²⁺	0.849	502	2.45 x 10 ⁴	good
	Os(diphenbipy) ³⁺	--	537	6.2 x 10 ³	--
4.	OsCl ₂ (bipy) ₂ ⁺	--	390	--	good
5.	OsCl ₂ (bipy) ₂ ⁰	--	555 ^d	--	--
6.	Os(en)(bipy) ₂ ²⁺	--	505	--	very poor
7.	OsCl(py)(bipy) ₂ ⁺	0.484 ^b	345	1.17 x 10 ⁴	--
	OsCl(py)(bipy) ₂ ²⁺	--	370	5.6 x 10 ³	satisfactory
8.	Os(acac)(bipy) ₂ ⁺	0.153 ^b	--	--	--
9.	Os(phen) ₃ ²⁺	0.877 ^c	427	--	good
	Os(phen) ₃ ³⁺	--	<div style="display: inline-block; vertical-align: middle;"> $\left\{ \begin{array}{l} 375 \\ 455 \end{array} \right.$ </div>	<div style="display: inline-block; vertical-align: middle;"> $\left\{ \begin{array}{l} 7.6 \times 10^3 \\ 1.6 \times 10^3 \end{array} \right.$ </div>	poor

^a(bipy) = 2,2'-bipyridine, (dimebipy) = 4,4'-dimethyl-2,2'-bipyridine, (diphenbipy) = 4,4'-diphenyl-2,2'-bipyridine, (en) = ethylenediamine, (py) = pyridine, (phen) = orthophenanthroline, (acac) = acetylacetonate.

^bReference 9.

^cReference 10.

^dIn chloroform.

191 $\pm$ 2 mV less than for the unsubstituted tris bipyridine complex. These titrations were done in 0.2 M H₂SO₄, using standard Ce(IV) as oxidant. The titration data, cell potential vs ml Ce(IV) added, were fit to the Nernst equation, and the formal potentials were determined by a least-squares procedure. Because the standard oxidation potential for Os(bipy)₃³⁺ is 0.885 V at 25°C (Ref. 9), the potential for the Os(dimebipy)₃^{2+,3+} couple is 0.694 $\pm$ 0.002 V.

3. Tris(4,4'-diphenyl-2,2'-bipyridine)osmium(II) Chloride. This compound was prepared and purified by the general method of Fabian, Klassen, and Sonntag.¹¹ It is relatively insoluble in water and difficulty was encountered in determining the equivalent weight. It was necessary to use Mn(VII) in water rather than Ce(IV) in H₂SO₄ to prevent precipitation during the titration. The molecular weight determined, 1155 $\pm$ 38 g/mole, is in satisfactory agreement with 1186 g/mole, which was calculated for the anhydrous compound. The spectrum was determined between 330 and 600 nm, and the compound was found to be much more intensely colored than Os(bipy)₃²⁺. The extinction coefficient at 502 nm, the location of the largest peak, is 2.45 $\pm$ 10⁴ M⁻¹cm⁻¹. The oxidation potential for Os(diphenbipy)₃²⁺ was determined as described above and found to be about 0.849 $\pm$ 0.002 V, only about 36 mV less than for Os(bipy)₃²⁺. We conclude that the diphenyl substituted complex is so similar to Os(bipy)₃²⁺ itself that further work on its properties is not warranted.

4. Dichlorobis(2,2'-bipyridine)osmium(III) Chloride. This compound was prepared and purified by the method of Buckingham *et al.*¹² Unlike some of the other bis bipyridine complexes (e.g., see Sec. IV.L.6), this compound is quite stable in water at room temperature. The spectrum remained essentially unchanged for at least eight days.

5. Dichlorobis(2,2'-bipyridine)osmium(II). This compound was prepared from the corresponding Os(III) complex (Sec. IV.L.4) by reduction with sodium dithionite according to a published procedure.¹² It is essentially insoluble in water, so this particular Os(II)-Os(III) couple will not be useful for an Eh buffer or moderator. This compound is used, however, as starting material for other preparations.

6. Ethylenediaminebis(2,2'-bipyridine)osmium(II) Iodide. This compound was prepared by Klassen during the few days he was at Los Alamos as a Visiting Staff Member. The method of Buckingham *et al.*¹² was used. This compound is apparently not stable in water even in the dark. A sample was dissolved in water swept with argon, and the absorbances of the various spectral features

were found to increase at approximately 5% per h. Observations during the succeeding five days showed that the spectrum continued to change.

7. Chloropyridinebis(2,2'-bipyridine)osmium(II) Perchlorate. This compound was prepared by refluxing dichlorobis(2,2'-bipyridine)osmium(II) with pyridine in ethylene glycol in a modification of a published method.¹² The perchlorate, rather than the iodide, was precipitated by the use of NaClO_4 rather than NaI . This material, dissolved in methanol, was purified using gel filtration (Sephadex LH-20). An intense green band preceded the brown, product band down the column. The product was precipitated from the methanol solution with ethyl ether and dried under vacuum for about 6 h at 70°-80°C. A sample was analyzed by titration with standard Ce(IV) solution; the equivalent weight was found to be 741 ± 9 g/equivalent. This value is in agreement with that calculated for the monohydrate. The absorption spectrum in water was determined between 310 and 600 nm, and the extinction coefficient of the largest peak at 354 nm was found to be $1.17 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The oxidized species $[\text{OsCl(py)(bipy)}_2]^{2+}$ was prepared in 0.02 M H_2SO_4 by oxidizing the Os(II) complex with Ce(IV) . The most prominent feature in the spectrum of the Os(III) complex is a sharp shoulder at 370 nm with an extinction coefficient of $5.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The substance is at least fairly stable. Its spectrum has been found to remain essentially unchanged for at least 10 days.

8. Acetylacetonatobis(2,2'-bipyridine)osmium(II) Chloride. An attempt to prepare this compound from dichlorobis(2,2'-bipyridine)osmium(II) was not successful. This should be repeated because the compound might prove useful, as its oxidation potential is quite low - reported¹² to be 0.153 V.

9. Tris(orthophenanthroline)osmium(II) Chloride. A small sample of this compound was provided by Professor Klassen. It was oxidized in water with chlorine to make the corresponding Os(III) complex. This complex was heated to 90°C in water for 15 min to check the stability, and it was found that the spectrum had dramatically changed. The stability of Os(phen)_3^{3+} was further checked in 5×10^{-3} M H_2SO_4 at room temperature. A sample of the Os(II) complex was 95% oxidized with Ce(IV) and the spectral changes were followed for 12 days. Large increases in absorbance occurred between 400 and 550 nm. However, when the solution was reduced by adding a small amount of Fe(II) , the spectrum of the original Os(phen)_3^{2+} was restored.

M. Equipment for Control of Eh (A. Ogard)

The Vacuum/Atmospheres, controlled-inert-atmosphere glove box and the Dri-Train purification system are completely installed and tested. Several experiments for producing and measuring low-oxygen fugacity water systems and negative Eh water systems are being installed inside the glove box.

N. Counting Room Software Activities (T. A. Kelley)

Recently, we have been actively pursuing the goal of providing a complete backup to our readout/processor, the PDP-11/60; to this end a high speed link (DMC-11) was installed between the PDP-11/60 and PDP-11/34. The networking software, DECNET, supplied by Digital Equipment Corporation was purchased and installed in both computers. The old 7-track magnetic tape from the old PDP-9 was converted to a 9-track magnetic tape and installed on the PDP-11/34. Our processing software was unified and standardized to work on either machine. The PDP-11/34 now can serve as a complete backup when the PDP-11/60 is down for repairs. DECNET serves as a convenient method of transferring necessary system information from one machine to the other.

V. MINERALOGY-PETROLOGY OF TUFF (B. M. Crowe, D. L. Bish, F. A. Caporuscio, J. D. Purson, J. R. Smyth, and R. G. Warren)

Petrological studies of drill core from exploratory hole USW-G1 in Yucca Mountain are completed; the data are being compiled in a summary report to be issued next quarter. Zeolite and clay alteration zones similar to described zeolite zones in Japan¹³ have been recognized in the stratigraphic section of tuff penetrated in the USW-G1 drill hole. Zone I is the part of the drill hole containing the alteration assemblage smectite clays (dioctahedral Na-K smectite), opal, chalcedony, and authigenic cristobalite. Zone II, which extends from 395 to 955 m below the surface, includes the assemblage alkalic clinoptilolite and mordenite as zeolite phases, and minor clays, which again are dioctahedral Na-K smectites with less than 10 percent illite and quartz predominating over cristobalite. The top of Zone III is placed at about the 955 m level, with the pervasive development of analcime, K-feldspar, and quartz replacing precursor clinoptilolite. Na-K dioctahedral smectites similar to those in Zones I and II are common in the top of Zone III. These smectites are interstratified with less than 15% illite, and preliminary data indicate no clear trend of increasing interstratification with depth.

The first authigenic albite in the core was noted in sample G1-4341 and again in G1-4400 where it has begun to replace coarsely crystalline analcime and grow into and fill cavities and vugs. Authigenic albite was not observed again until below the 1550 m level. However, positive identification in G1-4340 and G1-4400, where it is clearly replacing analcime, would place the top of Zone IV at about 1340 m for purposes of estimating the maximum temperatures to which the rocks were exposed. Authigenic albite in these rocks is nearly pure albite with less than 3 mol.% K-feldspar and no detectable calcium, barium, magnesium, or iron. This is consistent with its growth from a nearly pure sodic analcime.

Below 1550 m, authigenic albite and K-feldspar become the dominant secondary minerals in the nonwelded as well as welded units. These interbedded welded and nonwelded ashflow, airfall, and reworked tuffs have in some cases become so recrystallized that original textures are difficult to recognize in thin sections. Chlorite and celadonite are both common in these lower units and appear to be replacing clays and oxide minerals. Microprobe chemical analysis indicates that some chlorites contain 25 wt.% or more iron (as FeO).

From observation of zeolite zone boundaries it is possible to estimate a maximum paleogeotherm for USW-G1. Based on published work largely by Japanese authors,¹³⁻¹⁷ it is possible to estimate temperatures of zone boundaries. Sodium ion concentrations in pore fluids are estimated to be 200 to 1000 ppm based on well-water compositions between 200 and 500 ppm. This would place the Zone I-II boundary at 40 to 65°C, the Zone II - III boundary at 95 - 105°C, and the Zone III - IV boundary at 130 - 145°C. From these data we obtain an estimated maximum paleogeotherm for USW-G1 substantially above what is currently measured for the drill hole. The lack of zeolites in the current Zone I is evidence that the upper units have never been deeply buried and that temperatures in this zone have never been above about 50°C for any length of time. This may be taken as evidence that Yucca Mountain has remained a relatively stable structural block since emplacement of the Paintbrush Tuff.

The temperatures estimated from zeolite zone boundaries do not agree with the temperatures expected from the degree of interstratification in the smectites. The lack of agreement between zeolite and illite/smectite temperatures suggests that the zeolites and clays formed at separate times through different processes.

The following primary mineralogic features are described below for stratigraphic units of the USW-G1 drill hole: (1) the contents of lithic fragments, phenocrysts, and matrix; (2) the relative proportions of felsic phenocrysts having the largest areas in thin sections; (3) end-member contents of feldspar and barium contents of alkali feldspar determined by electron microprobe analysis; and (4) barium, magnesium, and iron contents of biotite determined by electron microprobe analysis.

The content of lithic fragments is distinct for the middle older, lithic-rich, and lower and middle Tram Tuffs (Table XIX); all contain >10% lithic fragments. Phenocryst contents are distinctly low (<7%) for two units: the ash flow tuff of Calico Hills and the lower part of the Topopah Springs Member (Table XIX).

Many stratigraphic units (Table XIX) can be distinguished by the relative proportion of quartz among those felsic phenocrysts having the largest areas in the thin sections. Units that contain low proportions of quartz (<15%) are the lower older and lithic-rich units of the Tram, lower Bullfrog, Prow Pass, and Topopah Springs Tuffs. The middle and upper older Tram, upper Bullfrog, and bedded/reworked Calico Hills Tuffs contain intermediate proportions of quartz (13-49%); and the Tram Tuff and ash flow tuff of Calico Hills have high proportions of quartz (40-69%). Relative proportions of feldspar are also distinctive for certain units, such as the lithic-rich tuff (alkali feldspar-rich) and the lower older and Topopah Springs Tuff (plagioclase-rich).

Major-element compositions of the alkali feldspar determined by complete microprobe analysis do not vary significantly within most stratigraphic units. Compositional ranges for major elements are narrow and are appreciably greater than the analytical uncertainty only for the Topopah Springs Member. The alkali feldspars in each unit have characteristic median end-member contents, which are represented by the molecular orthoclase (Or) + celsian (Cn) components (potassium and barium end members, respectively) in Table XIX. The ash flow tuff of the Prow Pass Member has alkali feldspar with low Or + Cn content. The alkali feldspars of the Bullfrog and Topopah Springs Tuffs also have relatively low Or + Cn contents. High Or + Cn contents are found for alkali feldspars of the lower older tuff (Tram) and the bedded/reworked tuff of Calico Hills. The median wt.% barium contents of alkali feldspar are high for the lower older tuff and low for most units stratigraphically above the Bullfrog Member.

TABLE XIX

SUMMARY OF CHARACTERISTIC PRIMARY FEATURES FOR STRATIGRAPHIC UNITS BETWEEN
1191- TO 6000-FT DEPTH IN THE USW-G1 DRILL CORE

Unit	Depth Interval ^a (ft)	Number of Thin Sections	Lithic Fragments (%)	Pheno-crysts (%)	% Relative Proportion of Those Felsic Phenocrysts Having the Largest Areas in Thin Sections			Feldspar Compositions					
					Quartz	Alkali Feldspar	Plagio-clase	Alkali Feldspar		Plagioclase		Biotite Compositions	
								Median Or+Cn	Median Wt. % BaO	Dominant An	Range for Most An Contents	Median Molecular Mg/Mg+Fe	Median Wt. % BaO
Lower older tuff	5492-6000	6	4-7 ^b	15-32	0	0-6	94-100	72	3.4	32	26-45	0.62	1.2
Middle older tuff	5330(?) - 5492	2	11-22	18-23	15-44	8-18	48-67	67	0.9	29	15-36	0.58	1.2
Upper older tuff	4940-5330(?)	8	2-8 ^b	14-25	22-49	19-55	19-38	64	0.5	18	15-37	0.55	0.8
Lithic-rich tuff	3946-4940	12	10-21 ^c	7-15	0-12	35-71	22-58	65	0.7	19	16-41	0.58	1.0
Lower tuff of flow breccia	3920-3946	1	7	15	0	0	100	--	--	43	38-50	0.66 ^d	
Lava of flow breccia	3568-3920	4	0	15-26	0	0	100	--	--	61	54-80 ^e	f	---
Lower tuff of Tram	3350(?) - 3522	2	34-37	8-11	40-43	19-37	20-41	67	0.6	37	28-63	0.44	1.0
Middle tuff of Tram	3083-3350(?)	4	20-27	9-15	60-69	13-26	12-27	67	0.5	21	17-41	0.44	1.0
Upper tuff of Tram	2639-3083	8	2-10	11-18	44-68 ^b	17-40	9-25 ^b	67	0.5	21	17-41	0.41 ^g	1.1 ^g
Lower Bullfrog Mbr.	2420(?) - 2639	5	1-5	8-12	5-13	33-52	42-54	61	0.6	15	13-19	0.40	0.3
Upper Bullfrog Mbr.	2173-2420(?)	7	0-3	15-27	13-33	26-40	35-58	61	0.6	15	13-19	0.39	1.3
Bedded/reworded tuff of Prow Pass Mbr.	2152-2173	1	2	17	0	36	64	60	0.4	17	14-20	0.44	1.2
Ash flow tuff of Prow Pass Mbr	1802-2152	5	1-2	9-18	8-15	41-49	41-48	53	0.1	11	8-14	0.42	1.6
Bedded/reworked tuff of Calico Hills	1736-1802	1	3	28	32	15	53	73	1.0	37	24-40	0.46	0.2
Ash flow tuff of Calico Hills	1426-1736	3	1-4	3-6	50-58	17-25	22-26	68	0.2	20	14-23	0.37	0.2
Topopah Springs Mbr (lower part)	1191-1426	5	1-5 ^b	1-3 ^b	1-9 ^b	7-17 ^b	74-91 ^b	57	0.1	16	14-40	0.44	0.2

^aQuery indicates that depth given is accurate to ± 20 ft.

^bExcludes values for a single sample.

^cExcludes values for three samples.

^dMedian for hornblende = 0.69.

^eDominant An = 47, range = 46-52 for microphenocrysts.

^fBiotite rare; median for hornblende = 0.66.

^gExcludes values for two samples.

The plagioclase within each stratigraphic unit has a characteristic dominant composition and a characteristic range beyond which only a few analyses are obtained by electron microprobe, both represented by the molecular anorthite (An) end-member content in Table XIX. The dominant An content of plagioclase is low for ash flow tuff of the Prow Pass Member, and it is also relatively low for the Bullfrog Member. Dominant An contents are high for the bedded or reworked tuff of Calico Hills, the lower older tuff, the lower tuff of the flow breccia, the lowermost portion of the Tram Tuff, and high for the lava of the flow breccia. Ranges in An content of plagioclase are relatively narrow for the Prow Pass, Bullfrog, and lower older Tuffs, and ash flow tuff of Calico Hills. Units with broad and similar ranges in An content are the middle and upper older, lithic-rich, and Tram Tuffs.

The biotite of each stratigraphic unit has a relatively limited range of compositions, as determined by microprobe analysis. Compositions for each unit are represented in Table XIX by the median molecular $Mg/(Mg + Fe)$ ratio. Biotites are richer in magnesium in the flow breccia and the stratigraphically lower units than in the Tram and stratigraphically higher units (Table XIX). The barium contents of the biotite are low in the lower Bullfrog, Calico Hills, and Topopah Springs Tuffs (Table XIX).

Proportions of lithic fragments or phenocrysts and chemical compositions of phenocrysts differ between stratigraphic intervals for relatively few ash flow tuffs units that are not separated by bedded or reworked tuff, such as for the Bullfrog and Tram Tuffs (Table XIX). In contrast, allanite and sphene are abundant for certain depth intervals within stratigraphic units and uncommon or absent within others (Table XX). Sphene is abundant only within the upper portions of the lithic-rich and lower older tuffs, and the lower portion of the upper older tuff (Table XX). It is also present in the lower portion of the lower older tuff and in the middle older tuff, but absent from all other stratigraphic intervals. Allanite is abundant in all intervals where sphene is abundant, and is also abundant in the lower and middle Tram Tuff. These associations suggest that the abundances of sphene and allanite may help to define stratigraphic levels within units at certain points.

TABLE XX

SUMMARY OF THE NUMBER OF ALLANITE AND SPHENE PHENOCRYSTS IN THIN SECTIONS
FOR STRATIGRAPHIC UNITS BETWEEN 1191- TO 6000-FT DEPTH IN THE USW-G1 DRILL CORE

Unit	Depth Interval ^a (ft)	Number of Thin Sections	Total Number of Phenocrysts	
			Allanite	Sphene
Lower older tuff	5800(?) - 6000	2	1	2
	5492-5800(?)	4	22	19
Middle older tuff	5330(?) - 5492	2	1	2
Upper older tuff	5100(?) - 5330(?)	5	32	13
	4940-5100(?)	3	4	0
Lithic-rich tuff	4450(?) - 4940	6	5	0
	3997-4450(?)	6	13	19
Flow breccia	3558-3946	5	0	0
Lower and middle tuff of Tram	3083-3522	6	17	0
Upper tuff of Tram	2639-3083	8	0	0
Lower Bullfrog Member	2420(?) - 2639	5	5	0
Upper Bullfrog Member	2173-2420(?)	7	0	0
Frow Pass Member	1802-2173	6	2	0
Tuff of Calico Hills	1426-1736	4	1	0
Topopah Springs Member (lower part)	1191-1426	5	1	0

^aQuery indicates that depth given is accurate to ± 50 ft.

VI. VOLCANIC HAZARD INVESTIGATIONS (B. M. Crowe, F. V. Perry, and D. T. Vaniman)

A. Volcanism Studies

Geologic mapping and sampling of basaltic rocks continued within the NTS region, the Amargosa Valley south of the NTS, and near Beatty, Nevada. Although basalts very similar to the hawaiites of Crater Flat¹⁸ have been found, there is a great diversity of lava types in the areas surrounding Crater Flat. These diverse lavas include the basaltic andesites and latites of Dome Mountain (8 to 10 Myr) and a mafic basalt series of Nye Canyon (6 to 7 Myr). New geochemical data from the Nye Canyon basalts include basalt types that are the

most primitive basalts yet found in this Plio-Pleistocene volcanic belt of the southcentral Great Basin. The primitive nature of the central of three Nye Canyon basalt intrusions is revealed by its high $Mg/(Mg + Fe)$ ratio (0.69) and its high chromium content (700 ppm). In contrast, the highest known $Mg/(Mg + Fe)$ ratio of any other basalt in the southcentral Great Basin volcanic belt is 0.60, and the highest chromium content found elsewhere is less than 400 ppm. Within the volcanic belt, Nye Canyon basalts may be the only samples which have risen directly from the mantle without appreciable fractionation.

The occurrence of more varied magma types away from Crater Flat is time dependent; the more varied basalt magmas are all older than 5 Myr. Our reconnaissance geochemical studies suggest that a significant mantle metasomatic event occurred about 4 to 5 Myr ago, an event that is recorded in basalt chemistry by a sharp increase in trace element abundances. Table XXI lists lanthanum, samarium, uranium, and thorium contents of basalts older than 5 Myr and younger than 5 Myr in the volcanic belt and illustrates the remarkable increase in trace element abundances for the younger basalts. However, the

TABLE XXI
TRACE ELEMENT CONTENTS^a OF BASALTS OF THE SOUTHCENTRAL
GREAT BASIN VOLCANIC BELT

<u>Basalts Older Than 5 Myr</u>	<u>La</u>	<u>Sm</u>	<u>U</u>	<u>Th</u>
Greenwater Range	27 ± 8	4.2 ± 1.1	0.6 ± 0.3	3.7 ± 2.0
Reveille Range	35 ± 10	6.3 ± 1.5	1.1 ± 0.4	3.1 ± 1.1
Paiute Ridge	33 ± 3	6.2 ± 0.6	1.0 ± 0.1	4.3 ± 0.6
Nye Canyon & other NTS Basalts	36 ± 5	2.6 ± 1.4	0.9 ± 0.2	3.0 ± 1.4
Kiwi Mesa	67 ± 5	7.9 ± 1.0	1.9 ± 0.2	8.0 ± 0.8
<u>Basalts Younger Than 5 Myr</u>				
Crater Flat	100 ± 28	9.6 ± 1.3	2.3 ± 1.4	8.6 ± 3.8
Sleeping Butte	110	12	3.3	12
Greenwaters	83 ± 5	9.7 ± 0.9	1.4 ± 0.3	6.7 ± 0.5
Southern Death Valley	104	10.5	2.0	8.6
Buckboard Mesa	99	9.6	2.6	9.3

^aIn ppm.

correlation of age and trace element content is not perfect. The basalts of Kiwi Mesa, which are presumed to be older than 5 Myr and are currently being dated, are enriched in trace elements. This problem is being pursued in greater detail.

Major element data for basalts of Paiute Ridge and Nye Canyon were completed. Paiute Ridge basalts consist of evolved, high-alkali hawaiites with magnesium values of about 0.50 ppm. Locally, this basalt has formed thick sills. At these localities, in situ differentiation has produced irregular pods and veins of coarse-grained monzonite and syenite. Preliminary modeling of the differentiation mechanism suggests minor fractionation of mafic phases, with volatile transfer of alkalis becoming significant in the latter stages of solidification.

B. Basalt Disruption Studies

Basalt magma paths from mantle derivation through upward migration through the mantle and crust with surface eruption have been examined for impact on consequence studies. The basalt studies suggest magma derivation from mantle peridotite in the depth range of 30 to 90 km. However, numerous variables in the conditions of partial fusion of peridotite preclude detailed prediction of future basalt melt events. Three possible mechanisms are favored for controlling magmatic melt events: 1) mantle stress release in an extensional environment, 2) mantle heterogeneities in thermal conductivity, and 3) mantle metasomatism. Magma ascent rates, estimated assuming Newtonian behavior of basalt melt and low yield strength (300 to $2000 \text{ dyne cm}^{-2}$), indicate rise of magma from mantle depths to surface eruption within periods of days to a week. The lack of major magma chambers at shallow crustal depths for basalts of the NTS region is suggested by the small magma volumes (10^{-1} km^3), the rapid cooling times for basalt dikes, spacing of basalt cinder-cone centers, evidence for elongate fissure feeder systems, and the absence of crustal contamination. Basalt intrusion types are of three forms: 1) radial and concentric dikes within cone complexes, 2) linear feeder dikes that narrow with depth, and 3) sill-like intrusions emplaced during episodes of extension.

Basalt eruption mechanisms are predominantly Strombolian with minor Phreatomagmatic activity. Assuming an eruptive cycle of $2.0 \times 10^{-7} \text{ m}^3$, $0.8 \times 10^7 \text{ m}^3$ would be erupted as pyroclastic activity (cone building) and $1.2 \times 10^7 \text{ m}^3$ as lava, based on past behavior of basalt activity in the NTS

region. Of the volume of pyroclastic debris, about 2.1 percent of the material will be sufficiently fine-grained (<0.06 mm) to be dispersed regionally with prevailing winds.

VII. SITE EVALUATION WORKING GROUP (J. D. Purson)

The Site Evaluation Working Group has begun the process of screening the SW NTS for potential repository locations. A meeting held in Denver to discuss the application of geology, hydrology, and seismology to the process resulted in an unexpectedly large set of data for consideration. The documentation and mapping of these important factors will probably take more time than originally anticipated, but this probably will not be a major problem. The larger quantity of more accurate information should lead to a better decision regarding repository siting.

Personnel involved in geochemical and media studies will be invited to a similar meeting next quarter. Assessment of confidence in the data and integration of subtasks, such as environmental effects, will also be required for a final recommendation.

VIII. ROCK PHYSICS STUDIES

A. Laboratory Studies (P. M. Halleck, J. D. Blacic, and J. N. Albright)

1. Time-Dependent Deformations. Studies of time-dependent deformation are designed to develop a constitutive relation valid over the operational period and decommission phase of a repository. Conventional stress-strain and failure data are unlikely to be useful for prediction of the behavior of hot, wet tuffs for 100 to 1000 years. We are building a unique apparatus to measure mechanical behavior and fluid-flow characteristics for very low strain rates. The resulting data will be used to develop the needed constitutive relations.

A key feature of the time-dependent deformation apparatus at Los Alamos is the ability to maintain a constant true differential stress on the test specimen. This feature is essential if meaningful transient creep and constitutive relations are to be obtained. True stress control is obtained by computer controlled force and strain feedback in which the changing cross-sectional area of the test specimen is accounted for in adjusting the load. Stress can be applied and controlled with a time constant of a few seconds so

that accurate transient strain data can be obtained. The assembled device is shown in Fig. 3.

Either of two pressure vessels may be used with confining pressure capabilities of 69 (shown) or 200 MPa, respectively. Both pressure vessels are externally heated with a maximum temperature capability of 250°C. Temperature gradients along the 5.4 diameter by 12 cm long cylindrical test specimens are typically 2°C or less. The pressure vessels can accommodate up to 50 electrical feed-throughs so that very dense internal instrumentation is possible. We intend to use a combination of strain gauges and internal LVDT transducers for sample strain measurements. A later improvement will be a computer-controlled pressure intensifier that will allow direct volume strain measurement based on oil displacement and very precise pressure control (~0.05 MPa).

Another important and unique feature of our apparatus is the ability to measure water permeability changes in samples while they undergo slow deformation. An important isolation parameter that needs to be evaluated is how groundwater flow around a waste package changes through time. We expect that changes in crack apertures and bulk porosity will change over time due to slow deformations, and these changes will cause water flow rates to vary. The pore pressure system of our device has both a constant flow-through and pressure-pulse-decay capability for permeability measurements.

The duration of the tests is expected to vary from a few days to many weeks. Because of the length of the tests, the matrix of test conditions and tuff types will be divided into initial and follow-on matrices.

Initial:

Bullfrog target horizon

Temperature (T): 100, 200°C

Confining pressure (P_c): 35 MPa

Pore pressure (P_p): 3.5 MPa (10% P_c), 30 MPa (86% P_c)

Stress (S): 100 MPa

In addition, one or more room temperature, uniaxial creep tests will be carried out on G-Tunnel welded tuff to extend the moderately high strain rate data obtained by Sandia National Laboratory.

Data obtained in these tests should help guide conceptual design and preliminary performance models. Later, follow-on tests will be extended to Tram welded tuff and others, depending on programmatic needs. The range of

Fig. 3. Time-dependent deformation apparatus.

test conditions will be broadened so as to obtain the constitutive relations that ultimately will be required for final design and performance models:

T: 50, 150, 250°C
Pc: 20 MPa
Pp: 0, 50, 98% of Pc
S: 25, 50, 75, 150 MPa

2. Soak Tests. The soak tests are designed to produce a large amount of scoping data on potential detrimental effects of exposure to repository conditions on host rocks. The most recent test matrix is shown in Table XXII along with current status of each test. Mechanical test data for unexposed samples have been taken for all except tests 9 and 10.

All tests are now running as shown in Table XXII except tests 7 and 8. Our "high temperature" O-rings, which seal the individual test vessels, survived 200°C for only a few days and decomposed. We are currently evaluating several

TABLE XXII
TEST MATRIX FOR THE SOAK TESTS

Test	Temp (°C)	Confining Pressure (bars)	Pore Pressure (bars)	Duration (mo)	Units Studied ^a	Will be Complete by
1	80	200	50	6	1, 2	15 Apr 81
2	80	100	5	6	1, 2	15 Apr 81
3	120	200	200	6	1, 2	15 Apr 81
4	120	100	5	6	1, 2	15 Apr 81
5	120	200	200	2	1, 2	1 Aug 81
6	120	100	100	2	1, 2	1 Aug 81
7	230	100	100	6	1, 2, 3, 4 ^b	1 Aug 81
8	230	100	100	6	1, 2, 3, 4 ^b	1 Aug 81
9	120	200	200	2	3, 4	Start by 1 June
10	120	100	5	2	3, 4	Start by 1 June

^aKey to tuff units: 1) Topopah Springs (UE25A-1), 2) Calico Hills (UE25A-1), 3) Bullfrog (USW-G1), and 4) Tram (USW-G1).

^bThese tests include both deionized water and water from well J-13.

alternatives to correct this problem. We currently favor a reduction of the test temperature to 180°C and use of Kal-rez O-rings (another high-temperature elastomer). Other possibilities are special EPDM O-rings (expensive and 3 to 4 month lead time) or welding the vessels closed.

The first two tests, 1 and 2, at 80°C are nearly complete and samples should be available for testing in mid-April. The mechanical test results will be available first.

Basic mechanical comparisons (compressive strength, tensile strength, density, and porosity) will be performed for all tests. Mineralogic and petrologic examinations will also be done for all tests. Permeability data will be collected for tests 3 and 6 and thermal properties for tests 1, 4, and 5.

B. Field Studies (D. C. Nelson, T. J. Merson, and W. L. Sibbitt)

Efforts to date have been to scope the At-Depth Test Facility (ADTF) in sufficient detail to obtain an approximate design (Titles I and II) and construction cost estimate and schedule. The ADTF, as currently defined, consists of two phases. The purpose of Phase I (Fig. 4) is to provide the capability to conduct in situ experiments at depth in tuff in Yucca Mountain to identify any features that could possibly disqualify the site for a waste repository. A second function of Phase I, recently included in the program, is to determine if the location is suitable for a Test and Evaluation Facility (TEF). The TEF is a R&D facility that would be constructed at the bottom of the exploratory shaft to store a few hundred canisters of either high-level waste or spent fuel. The purpose of Phase II (Fig. 5) is to conduct design feasibility experiments and evaluate various hydrologic and geologic models, assuming that the site is not selected for a TEF.

Meetings have been held with representatives of U. S. Geological Survey, Sandia National Laboratories, Texas A&M, Re/Spec, Holmes and Narver, Fenix and Scission, Reynolds Electrical and Engineering Company, and DOE/NTSSO to identify the characterization data required for the site, types of experiments to be conducted, related equipment and facilities required to collect these data, the priority of the experiments, and the cost and time required to design and construct the test facilities and perform the experiments. These activities are continuing.

3/19/81

Fig. 4. Conceptual arrangement of the Tuff Exploratory Shaft, Phase I.

IX. QUALITY ASSURANCE (P. L. Bussolini, R. R. Geoffrion, and J. J. Simpson)

A. Los Alamos National Laboratory

The Work Plan and Quality Assurance (QA) Program Plan for the University of Arizona for Matrix Diffusion and Solute Transport Studies of NTS Tuff were written, reviewed, and approved.

The following procedures were reviewed and approved during the quarter:

TWS-CNC7-DP-22, R1 Preparation of Microautoradiographs

Fig. 5. Conceptual arrangement of the Tuff Exploratory Shaft, Phase II.

TWS-CNC7-DP-23, R0 Preparation of Thin Sections for Geologic Material

TWS-G9-DP-24, R0 Alignment of the Siemens Diffractometer

TWS-G7-WP-09, R0 Work Plan for "Creep" Experiments

Compliance of the QA Program was verified through the surveillance activities.

B. U.S. Geological Survey

A Hydrologic Unit Task Procedure and twelve detailed procedures were drafted and reviewed by Los Alamos QA personnel during the quarter. These, excluding two

detailed procedures, were sent to Denver for review, and later eight of these detailed procedures were sent to Denver for approval.

Los Alamos QA personnel represented the U. S. Geological Survey at the January audit at Nevada Operations office.

A meeting was held with W. S. Twenhofel to formalize the detailed procedure format.

X. PUBLICATIONS AND ABSTRACTS

- 1) B. R. Erdal, K. Wolfsberg, J. K. Johnstone, K. L. Erickson, A. M. Friedman, S. Fried, and J. J. Hines, "Nuclide Migration Field Experiments," Los Alamos National Laboratory report LA-8487-MS (1981).
- 2) B. R. Erdal, K. Wolfsberg, D. R. Fortney, J. K. Johnstone, K. L. Erickson, A. M. Friedman, S. Fried, and J. J. Hines, "Nuclide Migration Field Experiments," American Chemical Society 181st National Meeting, Atlanta, GA, March 29 - April 3, 1981 (abstract).
- 3) S. J. DeVilliers and A. J. Mitchell, "How Element Concentration and Solution-to-Solid Ratio Affect the Sorptive Behavior of Geologic Media," American Chemical Society 181st National Meeting, Atlanta, Georgia, March 29 - April 3, 1981 (abstract).

XI. ORAL PRESENTATIONS

- 1) L. D. Tyler and B. R. Erdal, "Evaluation of Tuff as a Host Rock for Geologic Disposal of Nuclear Waste," Waste Management '81 Symposium, February 23-26, 1981, Tucson, Arizona (abstract).

ACKNOWLEDGMENTS

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

REFERENCES

1. A. F. White, H. C. Claassen, and L. V. Benson, "The Effect of Dissolution of Volcanic Glass on the Water Chemistry of a Tuffaceous Aquifer, Ranier Mesa, Nevada," U. S. Geological Survey Water Supply paper 1535-Q (1980).
2. H. C. Claassen, "Water Quality and Physical Characteristics of Nevada Test Site Water-Supply Wells," U. S. Geological Survey report USGS-474-158 (1973).

3. K. Wolfsberg and E. N. Vine, "Correlation of Sorption Properties of Tuff with Mineralogy" in "Evaluation of Tuff as a Medium for a Nuclear Waste Repository: Interim Status Report on the Properties of Tuff," J. K. Johnstone and K. Wolfsberg, Eds., Sandia National Laboratories report SAND80-1464 (1980).
4. E. N. Vine, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, and K. Wolfsberg, "Radionuclide Transport and Retardation in Tuff," in Scientific Basis for Nuclear Waste Management, Vol. III (Plenum, New York, 1981 - in press).
5. K. Wolfsberg and B. R. Erdal, Eds., "Research and Development Related to the Nevada Nuclear Waste Storage Investigation, October 1 - December 31, 1980," Los Alamos National Laboratory report LA-8739-PR (1981).
6. K. Wolfsberg, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, A. J. Mitchell, P. Q. Oliver, N. A. Raybold, R. S. Rundberg, J. L. Thompson, and E. N. Vine, "Sorption-Desorption Studies on Tuff. III. A Continuation of Studies with Samples from Jackass Flats and Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8747-MS (May 1981).
7. R. K. Blankennagel and J. E. Weiss, Jr., "Geohydrology of the Eastern Part of Pahute Mesa, Nevada Test Site, Nye County, Nevada," U. S. Geological Survey professional paper 712-B (1973).
8. E. N. Vine, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, P. Q. Oliver, J. L. Thompson, and K. Wolfsberg, "Sorption-Desorption Studies on Tuff. II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies with Samples from Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8110-MS (January 1980).
9. D. A. Buckingham, F. P. Dwyer, and A. M. Sargeson, "Osmium(III)-Osmium(II) Electrode Potentials. The Effects of Charge, Conjugation, Coordinated Halide, and Substitution in the Ligand," *Inorg. Chem.* 5, 1243 (1966).
10. F. P. Dwyer, N. A. Gibson, and E. C. Gyarmas, "The Redox Potentials of the Tris 2,2'-Dipyridyl OsmiumII/III and the Tris o-phenanthroline Osmium II/III Couples," *J. Proc. Roy. Soc. New South Wales* 84, 80 (1950).
11. R. H. Fabian, D. M. Klassen, and R. W. Sonntag, "Synthesis and Spectroscopic Characterization of Ruthenium and Osmium Complexes with Sterically Hindering Ligands. 3. Tris Complexes of Methyl- and Dimethyl-Substituted 2,2'-Bipyridine and 1,10-Phenanthroline," *Inorg. Chem.* 19, 1977 (1980).
12. D. A. Buckingham, F. P. Dwyer, H. A. Goodwin, and A. M. Sargeson, "Mono- and Bis-(2,2'-Bipyridine) and 1,10-Phenanthroline Chelates of Ruthenium and Osmium," *Australian J. Chem.* 17, 325 (1964).
13. A. Iijima, "Geology of Natural Zeolites and Zeolitic Rocks," in Proc. Fifth International Conference on Zeolites, L. V. C. Rees, Ed. (Heyden, London, 1980), pp. 103-118.

14. A. Iijima, "Effect of Pore Water to Clinoptilolite Analcime Albite Reaction Series," J. Fac. Sci. Univ. Tokyo, Sec II, 19, p. 133-147 (1975).
15. A. Iijima, "Geological Occurrences of Zeolite in Marine Environments," in Natural Zeolites: Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, Eds. (Pergamon Press, Elmsford, New York, 1978), pp. 175-198.
16. A. Iijima and I. Ohwa, "Zeolitic Burial Diagenesis in Creta-tertiary Geosynclinal Deposits of Central Hokkaido, Japan," in Proc. Fifth Int. Conf. Zeolites, L. V. C. Rees, Ed. (Heyden, London, 1980), pp. 139-148.
17. A. Iijima and M. Utada, "Present-day Zeolitic Diagenesis of the Neogene Geosynclinal Deposits in the Niigata Oil Field, Japan", in Molecular Sieve Zeolites, Amer. Chem. Soc. Advances in Chemistry Series, No. 101, pp. 342-349 (1971).
18. D. Vaniman and B. Crowe, "Geology and Petrology of the Basalts of Crater Flat: Applications of Volcanic Risk Assessment for the Nevada Nuclear Waste Storage Investigations," Los Alamos National Laboratory report LA-8845-MS (May 1981).

APPENDIX A

SORPTIVE PROPERTIES OF YUCCA MOUNTAIN TUFF FROM DRILL HOLE USW-G1

S. J. DeVilliers, A. J. Mitchell, E. N. Vine, and K. Wolfsberg

Our assessment of the sorptive properties of tuff was continued with eleven samples from drill hole USW-G1 on Yucca Mountain. Sorption measurements on other cores from the same drill hole are still in progress. The batch technique used was similar to that employed for the determination of sorption ratios for tuff from holes J-13 (Refs. 1 and 3) and UE25a-1 (Refs. 2 and 3). Only one particle size range, 75 to 500 μm , was used because particle size effects were minor in the previous studies.^{1,2} Contact times were 3 and 6 wk, and the solution-to-solid ratio was 20 to 1.

Selection of samples was based on the predominant mineralogy -- mostly glass or clinoptilolite or alkali feldspar, for example. Two cores from the Bullfrog Member of the Crater Flat Tuff and three from the Tram Member of the Crater Flat Tuff were included. (Measurements on additional samples of Tram and Bullfrog are in progress.) A summary of the mineralogy of the samples is given in Table A-I. The summary is based on x-ray diffraction data obtained

TABLE A-I
DESCRIPTION OF TUFF SAMPLES

Sample ^a	Major Component(s) ^b ≥50%	to	Trace Components <5-10%
G1-1292	Glass	cristobalite, alkali feldspar	-----
G1-1436	Clinoptilolite	-----	clay, quartz, alkali feldspar
G1-1883	Alkali feldspar, quartz	-----	clay, mica
G1-1982	Alkali feldspar	-----	quartz, clay
G1-2233	Alkali feldspar	clinoptilolite mica	quartz, clay, mordenite
G1-2289	Clinoptilolite, alkali feldspar	mordenite	quartz, clay
G1-2363	Quartz, alkali feldspar	clay	mica
G1-2698	Clinoptilolite, alkali feldspar	mica	mordenite, clay, quartz
G1-2901	Alkali feldspar	quartz	mica, clay
G1-3116	-----	quartz, alkali feldspar, clinoptilolite, analcime	mica, clay
G1-3658	Clay, alkali feldspar	-----	-----

^aG1 indicates that the sample was from drill hole USW-G1; the number indicates the depth in feet from which the sample was taken.

^bAbundance decreases as entries approach the right side of the table.

by David Bish (Los Alamos National Laboratory, personal communication, February 1981).

The average sorption and desorption ratios for ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , and ^{152}Eu are given on Table A-II. The sorption ratios obtained for plutonium, neptunium, americium, and technetium on some of these cores will be reported later. Results from the USW-G1 core samples confirm the general relationship between sorption ratios and mineralogy, which we have previously noted.^{4,5}

Strontium sorption ratios range from ~ 10 ml/g to $\sim 10^4$ ml/g. The highest R_d values, 10^3 to 10^4 ml/g, were obtained with zeolitized tuffs, as usual. Intermediate values of 10^2 to 10^3 ml/g were found for tuffs containing predominately glass or clay, and values of 10 to 10^2 were obtained on samples containing primarily alkali feldspar, or quartz with small amounts of clay or mica.

The range of sorption ratios of cesium is narrower than that of strontium. The highest values, 10^2 to 10^4 ml/g, also are for zeolitized tuffs with other types of tuffs giving values of 10^2 to 10^3 ml/g. Tuffs containing predominately quartz are the least sorptive.

The correlation between sorption and mineralogy for barium is like that observed for strontium and cesium: high R_d values (10^3 to 10^5 ml/g) on tuffs with zeolites and lower values (10^2 to 10^3 ml/g) for clay-, glass-, quartz-, and cristobalite-containing tuffs.

Of this group of eleven tuffs, the sorptive behavior of sample G1-2289, although it falls into the ranges discussed above, is the most unusual. X-ray diffraction patterns indicated a composition of 30-50% clinoptilolite, 10-20% mordenite, 30-50% alkali feldspar, 5-10% mica, and <5% quartz for this sample. Except for the mordenite, this is quite similar to sample G1-2698 which had 30 to 50% clinoptilolite, 30 to 50% alkali feldspar, 10 to 15% mica, and <5% clay, mordenite, and quartz. However, the sorption ratios are significantly lower on G1-2289: a factor of ~ 4 lower for ^{137}Cs , a factor of ~ 29 lower for ^{85}Sr , and a factor of ~ 9 lower for ^{133}Ba . The sorption behavior of additional cores containing mordenite should be determined. Detailed chemical analyses of the cores studied to date will be made to better understand these results.

The correlations between sorption and mineralogy have been determined only for strontium, cesium, and barium, which probably sorb by ion exchange mechanisms. There is no clear relationship between sorption ratios and

TABLE A-11
AVERAGE SORPTION AND DESORPTION RATIOS^a ON USW-G1 TUFFS
 R_d (mg/g)

Sample ^b	¹³⁷ Cs	⁸⁵ Sr	¹³³ Ba	¹⁴¹ Ce	¹⁵² Eu
G1-2233	13 500(800)	48 500(3 020)	249 000(29 600)	1 380(260)	899(160)
	22 800(5 500)	90 600(37 200)	95 800(44 900)	20 600(13 300)	4 560(170)
G1-1436	7 790(430)	36 300(3 000)	148 000(23 500)	58 400(6 870)	29 900(1 800)
	24 200(2 300)	87 800(12 500)	341 000(88 000)	6 660(60)	5 720(50)
G1-1982	1 620(110)	441(6)	2 770(240)	553(43)	1 660(160)
	2 020(40)	32(1)	2 790(10)	7 000(90)	4 850(1 350)
G1-1883	402(22)	58.4(0.4)	413(55)	212(38)	242(42)
	429(3)	59.1(1.1)	443(8)	2 120(6)	1 370(10)
G1-2698	7 640(430)	41 900(2 600)	63 100(4 900)	242(32)	204(28)
	62 900(4 700)	213 000(50 000)	178 000(81 000)	4 770(2 520)	4 150(300)
G1-1292	429(57)	201(5)	2 090(280)	66(8)	368(214)
	513(18)	117(5)	4 900(3 400)	802(149)	600(66)
G1-2363	1 290(40)	173(1)	893(22)	310(22)	1 520(10)
	1 230(20)	459(310)	819(19)	438 000(31 100)	17 900(13 700)
G1-3116	6 590(460)	2 390(70)	12 400(400)	99(9)	756(55)
	10 800(3 350)	31 100(11 000)	1 890 000(1 730 000)	3 260(1150)	8 160(2 740)
G1-3658	805(19)	1 170(80)	1 020(82)	100(21)	82(19)
	1 240(20)	1 210(300)	988(426)	934(347)	867(316)
G1-2289	1 720(110)	1 480(120)	7 680(970)	6.1(1.1)	30(6)
	541(94)	1 500(570)	10 900(5 300)	102(38)	217(93)
G1-2901	1 280(110)	69(1)	1 700(160)	42 500(3 000)	16 100(4 600)
	1 380(30)	236(168)	2 010(30)	37 900(1 400)	207 000(4 000)

^aThe average sorption ratio is given first, the average desorption ratio second. Numbers in parentheses are standard deviations of the means.

^bSee footnote to Table A-1.

mineralogy for cerium and europium on the USW-G1 cores. This was also observed with samples from J-13 and UE25a-1.^{1,2}

When the additional measurements on the USW-G1 cores are completed and more detailed chemical analyses of the tuffs have been made, the relationship between mineralogy of tuff and sorption ratios will be examined in more detail.

REFERENCES

1. K. Wolfsberg, B. P. Bayhurst, W. R. Daniels, B. M. Crowe, W. R. Daniels, B. R. Erdal, F. O. Lawrence, A. E. Norris, and J. R. Smyth, "Sorption-Desorption Studies on Tuff. I. Initial Studies with samples from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos National Laboratory report LA-7480-MS (April 1979).
2. E. N. Vine, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, P. Q. Oliver, J. L. Thompson, and K. Wolfsberg, "Sorption-Desorption Studies on Tuff. II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies of Samples from Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8110-MS (January 1980).
3. K. Wolfsberg, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, A. J. Mitchell, P. Q. Oliver, N. A. Raybold, R. S. Rundberg, J. L. Thompson, and E. N. Vine, "Sorption-Desorption Studies on Tuff. III. A Continuation of Studies with Samples from Jackass Flats and Yucca Mountain Nevada," Los Alamos National Laboratory report LA-8747-MS (May 1981).
4. K. Wolfsberg and E. N. Vine, "Correlation of Sorption Properties of Tuff with Mineralogy" in "Evaluation of Tuff as a Medium for a Nuclear Waste Repository: Interim Status Report on the Properties of Tuff," J. K. Johnstone and K. Wolfsberg, Eds., Sandia National Laboratories report SAND80-1464 (1980).
5. E. N. Vine, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, and K. Wolfsberg, "Radionuclide Transport and Retardation in Tuff," in Scientific Basis for Nuclear Waste Management, Vol. III (Plenum, New York, 1981 - in press).

APPENDIX B

CALCULATION OF BREAKTHROUGH CURVES USING THE THOMAS SOLUTION:
THE EFFECT OF EQUILIBRIUM ON THE BREAKTHROUGH
WITH A LOW NUMBER OF MASS TRANSFER UNITS

R. S. Rundberg

The existence of slow sorption kinetics has been suggested as a complication in the interpretation of radionuclide migration experiments. To insure that chromatography theory can be correctly applied, it has been recommended (W. L. Kuhn, Battelle Pacific Northwest Laboratories, personal communication, August 1980) that the number of mass transfer units or number of theoretical plates should be greater than 25 or 35, respectively. (If a column is run at speeds which give a lower number of mass transfer units, the apparent K_d will be too low.) It will be shown later (Appendix C), however, that most experiments run at Los Alamos National Laboratory have not been run in the mass-transfer-limited portion of the chromatographic performance curve. Because the mass-transfer rate is dependent on the equilibrium between the carrier ion, sorbed carrier ion, tracer ion, and sorbed tracer ion, calculations were performed to demonstrate this dependence using the Thomas solution.¹

Most calculations of sorption breakthrough curves for elution of ionic tracers from a chromatographic column employ some form of the Rosen solution.² The more general treatment by Thomas,¹ however, takes into account the curved shape of the equilibrium relationship. In many cases, a favorable equilibrium could compensate for the lowering of the apparent K_d by using a column at high fluid velocities. This effect may be especially important in the near-field situation where the radionuclide concentration may be high. Thomas assumed that the rate of adsorption can be represented by an expression for a monovalent ion exchange reaction such as

where

Na-R and Cs-R are the sorbed ions,

c, $q_m - q$, q, $c_o - c$ are the concentrations of the species in the above equilibrium,

q_m is the sorption capacity, and
 c_o is the carrier ion concentration.

The kinetic expression for the forward reaction in the above equilibrium is

$$\rho_B \frac{\partial q}{\partial t} = \kappa a \left[c \left(1 - \frac{q}{q_m} \right) - \frac{1}{K} (c_o - c) \frac{q}{q_m} \right],$$

where

ρ_B is the bulk density,
 κ is the kinetic coefficient,
 a is the interfacial area per unit volume of bed, and
 K is the equilibrium constant.

Solving this equation coupled to the mass balance relationship

$$\frac{\rho_B}{\varepsilon} \frac{\partial q}{\partial t} + v \frac{\partial c}{\partial x} = 0 \quad ,$$

where

ε is the porosity and
 v is the fluid velocity,

substituting

$$\xi = t - \frac{x}{v} \quad ,$$

where x is the column length, and using the appropriate boundary conditions for continuous feed, yields the following solutions:

$$\frac{c}{c_o} = \frac{J(n/K, nT)}{J(n/K, nT) + [1 - J(n, nT/K)] \exp[(1-K^{-1})(n-nT)]} \quad \text{and}$$

$$\frac{q}{q_m} = \frac{1 - J(nT, n/K)}{J(n/K, nT) + [1 - J(n, nT/K)] \exp[(1-K^{-1})(n-nT)]} \quad ,$$

where

$n = \frac{Kax}{v\varepsilon} = \text{dimensionless distance or number of transfer units to position } x,$

$$T = \frac{v\varepsilon c_o t}{q_m \rho_B x} ,$$

$$nT = \frac{Kac_o t}{q_m \rho_B} = \text{dimensionless time},$$

$$J(\alpha, \beta) = 1 - e^{-\beta} \int_0^\alpha e^{-\xi} I_0(2\sqrt{\beta\xi}) d\xi , \text{ and}$$

I_0 is the zero-order modified Bessel function.

A computer program THOMAS was written to calculate breakthrough curves. The J functions were evaluated numerically using Gaussian quadrature. Sixteen-point Gaussian quadrature was found to reproduce exactly the published tables of Vermeulen.³ The resulting curves shown in Figs. B-1 to B-4 for 2 to 25 mass transfer units were calculated with equilibrium constants of 1, 10, and 100. It should be noted that when the breakthrough ($c/c_o = 0.5$) occurs at $T = 1.0$, the following relationship holds.

$$R_f = \frac{K_d \rho_B}{\varepsilon} + 1 ,$$

where

R_f is the retardation factor,

K_d is the distribution coefficient,

ρ_B is the bulk density, and

ε is the porosity.

If T is less than 1.0 at $c/c_o = 0.5$, the following relationship holds

$$R_f = \frac{TK_d \rho_B}{\varepsilon} + 1 .$$

Fig. B-1. Thomas solution breakthrough curves using 25 mass transfer units.

Fig. B-2. Thomas solution breakthrough curves using 10 mass transfer units.

Fig. B-3. Thomas solution breakthrough curves using 5 mass transfer units.

Fig. B-4. Thomas solution breakthrough curves using 2 mass transfer units.

The calculations show that for $K = 1$, the breakthrough begins to arrive early by a few percent at 25 mass transfer units. However, with $K = 10$ the breakthrough does not begin to arrive significantly early until less than five mass transfer units. It is also interesting that increasing the equilibrium constant from 10 to 100 does not significantly improve column performance. A favorable equilibrium, $K > 1$, also sharpens the breakthrough curve, giving an effectively higher number of mass transfer units. This effect could be important in many cases. For example, for YM-22 tuff, the results for sorption capacities, groundwater analyses, and K_d values⁴ give an equilibrium constant of about 20 for cesium. Also, isotherm data⁵ at high transfer concentrations indicate an equilibrium constant of about 17 for cesium on YM-22 tuff. The equilibrium constant for cesium calculated from the sorption capacity, K_d value,⁶ and data from groundwater analyses for JA-18 tuff yield a K of about 120. This may be an important effect for many radionuclides in the near field and, therefore, more measurements of isotherms at high concentrations could prove useful. To put this in perspective, however, for most simple cations, extremely high fluid velocities are required to lower the number of mass transfer units to a level where this effect is important.

REFERENCES

1. H. Thomas, "Heterogeneous Ion Exchange in a Flowing System," J. Amer. Chem. Soc. 66, 1664 (1944).
2. J. B. Rosen, "Kinetics of a Fixed Bed System for Solid Diffusion into Spherical Particles," J. Chem. Phys. 20, 387 (1952).
3. T. Vermeulen, G. Klein, and N. Hiester, "Adsorption and Ion Exchange," in Chemical Engineers' Handbook, 5th Ed., R. H. Perry and C. H. Chilton, Eds. (McGraw-Hill, New York, 1973), Section 16.
4. E. N. Vine, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, P. Q. Oliver, J. L. Thompson, and K. Wolfsberg, "Sorption-Desorption Studies on Tuff. II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies with Samples from Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8110-MS (January 1980).
5. K. Wolfsberg, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, A. J. Mitchell, P. Q. Oliver, N. A. Raybold, R. S. Rundberg, J. L. Thompson, and E. N. Vine, "Sorption-Desorption Studies on Tuff. III. A Continuation of Studies With Samples from Jackass Flats and Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8747-MS (May 1981).

6. K. Wolfsberg, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, B. R. Erdal, F. O. Lawrence, A. E. Norris, and J. R. Smyth, "Sorption-Desorption Studies on Tuff. I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos National report LA-7480-MS (April 1979).

APPENDIX C

THE PERFORMANCE OF CRUSHED-ROCK COLUMNS AS CHROMATOGRAPHIC COLUMNS

R. S. Rundberg and E. N. Vine

Strontium, cesium, barium, and other simple cations should interact with zeolites in geologic media via an ion exchange mechanism. Sorption experiments with argillite by K. Erickson¹ show that the rate of sorption is diffusion controlled. Sorption of strontium, cesium, and barium have been shown to correlate with the mineralogy in tuff.² In addition, the Freundlich isotherms^{3,4} determined for tuffs are consistent with an ion exchange mechanism. To further test this mechanism, the results of experiments with crushed-rock columns were compared with what would be expected from conventional ion exchange, liquid chromatography.

The theoretical plate height in column chromatography is the sum of at least four factors and can be represented by the following equation.⁵

$$H = H_p + H_d + H_s + H_m ,$$

where

H_p is due to dispersion,

H_d is due to molecular diffusion,

H_s is due to mass transfer, sorption-desorption kinetics, and

H_m is due to mass transfer, zone spreading.

The first term, which is due to dispersion, has no velocity dependence and can be represented by the equation

$$H_p = 2\lambda d_p ,$$

where λ is a constant that depends on the packing and d_p is the particle diameter. This contribution to the plate height results in broadening of the chromatographic peak due to the distribution of flow velocities and flow paths. Nonuniform packing of the column will result in a wider distribution of flow velocities and, therefore, broader peaks.

The second term, the molecular diffusion term, is inversely proportional to fluid velocity and, therefore, becomes predominant at slow fluid velocities. This relationship is as follows.

$$H_d = 2\gamma D_m / v \quad ,$$

where

γ is the tortuosity factor,

D_m is the diffusion coefficient in the mobile phase, and

v is the average fluid velocity.

The tortuosity factor is actually inversely proportional to the tortuosity of the flow paths. Spherical beads yield a γ of ~ 0.6 (Ref. 6).

The last two terms are due to the kinetics of sorption and desorption. Since the rate of ion exchange is normally diffusion controlled, these relationships are expressed in terms of the diffusion coefficients of the ions and the geometry of the exchange particles. Both of these terms are directly proportional to the fluid velocity and are as follows.

$$H_s = qrd^2v/D_s \quad ,$$

where

q is a configuration factor,

r is a constant dependent on the relative migration rate,

d is the thickness of the stationary phase, and

D_s is the diffusion coefficient in the stationary phase;

and

$$H_m = \omega d_p^2 v / D_m \quad ,$$

where w is another configuration factor. These equations show that at low fluid velocities the plate height is determined by molecular diffusion and at high fluid velocities by the rate of mass transfer.

The fluid velocities used in most of our crushed-rock column experiments are low enough for the theoretical plate height to be estimated on the basis of longitudinal diffusion alone.

The diffusion coefficients can be calculated from ionic conductivities using the equation by Nernst⁷ for single ion diffusion coefficients at infinite dilution.

$$D_o^i = \frac{RT\Lambda_i}{F^2 |Z_i|}$$

$$= 8.931 \times 10^{-10} T \frac{\Lambda_i}{|Z_i|} ,$$

where

T is the temperature in degrees Kelvin,

Λ_i is the ionic conductivity, and

Z_i is the ionic charge.

The single ion diffusion coefficients were thus calculated from the ionic conductivities⁸ and are given in Table C-I. The theoretical plate heights were then calculated using $\gamma = 0.6$ for the YM54-1 tuff column; as can be seen in Table C-II, the resulting plate heights are too large. The plate heights were also calculated with γ adjusted to give a best fit to the actual plate heights. The calculated theoretical plate heights are large enough to demonstrate that no unusually slow mechanism for sorption is necessary in these cases to explain the data. The calculated plate heights shown in Table C-II can be compared with those in Table C-III. Except for the case of column CS5-2, which was run at a high flow rate, the peak shapes are adequately described by diffusional broadening.

TABLE C-I
DIFFUSION COEFFICIENTS

<u>Cation</u>	<u>Ionic Conductivity</u>	D_o^i <u>(cm²/sec)</u>
Sr ⁺⁺	59.4	7.745×10^{-6}
Cs ⁺	77.3	2.02×10^{-5}
Ba ⁺⁺	63.6	8.32×10^{-6}

TABLE C-II
THEORETICAL PLATE HEIGHTS CALCULATED ON THE
BASIS OF MOLECULAR DIFFUSION ONLY

<u>Cation</u>	<u>YM54-1</u> <u>($\gamma=0.6$)</u>	<u>YM54-1</u> <u>($\gamma=0.17$)</u>	<u>YM54-3</u> <u>($\gamma=0.21$)</u>	<u>YM22B</u> <u>($\gamma=0.35$)</u>	<u>CS5-1</u> <u>($\gamma=0.40$)</u>	<u>CS5-2</u> <u>($\gamma=0.40$)</u>
Sr ⁺⁺	0.14	0.040	0.046	0.032	0.064	0.001
Cs ⁺	0.37	0.104	0.121	0.083	---	---
Ba ⁺⁺	0.15	0.043	0.050	0.034	0.068	0.001

TABLE C-III
CRUSHED-ROCK COLUMN PERFORMANCE

<u>Column</u>	<u>Velocity</u> <u>(cm/sec)</u>	<u>Cation</u>	<u>FWHM/t_o</u>	<u>N_T</u>	<u>N_{mtu}</u>	<u>H</u>
YM22B	1.7×10^{-4}	Sr ⁺⁺	0.57	49	34	0.039
		Cs ⁺	0.56	51	35	0.037
		Ba ⁺⁺	0.72	31	21	0.061
YM54-1	6.6×10^{-5}	Sr ⁺⁺	0.64	39	27	0.038
		Cs ⁺	1.0	16	11	0.094
		Ba ⁺⁺	0.86	22	15	0.069
YM54-3	7.0×10^{-5}	Sr ⁺⁺	0.55	53	37	0.049
		Cs ⁺	0.79	26	18	0.100
		Ba ⁺⁺	0.69	34	24	0.076
CS5-1	9.7×10^{-5}	Sr ⁺⁺	0.75	28	19	0.077
		Ba ⁺⁺	0.65	38	26	0.057
CS5-2	8.8×10^{-3}	Sr ⁺⁺	0.50	64	44	0.056
		Ba ⁺⁺	0.38	110	76	0.033

The performance of chromatographic columns is sometimes expressed in terms of the reduced plate height, h , and the reduced fluid velocity, v :

$$h = H/d_p \quad \text{and}$$

$$v = d_p v/D_m.$$

Surprisingly close agreement was obtained when the reduced plate heights for the two CS5 (Climax Stock granite) crushed-rock columns were compared with the theoretical values for a typically efficient chromatographic column.⁹ The reduced plate height for column CS5-1, assuming a particle diameter of 70 μm (median of the sieve fraction), is 11.0 and the reduced velocity is 0.09. The reduced plate height for column CS5-2 is 8.0 and the reduced velocity is 8.0. These results are within 10% of the theoretical values.⁹ This indicates that, for simple cations, it may be advantageous to run columns at an intermediate fluid velocity near the minimum of the plate-height curve.

REFERENCES

1. K. L. Erickson, "A Fundamental Approach to the Analysis of Radionuclide Transport Resulting from Fluid Flow through Jointed Media," Sandia National Laboratory report SAND80-0457 (1981).
2. E. N. Vine, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, and K. Wolfsberg, "Radionuclide Transport in Tuff," in Scientific Basis for Nuclear Waste Management, Vol. 3 (Plenum Press, New York, 1981 - in press).
3. E. N. Vine, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, P. Q. Oliver, J. L. Thompson, and K. Wolfsberg, "Sorption-Desorption Studies on Tuff. II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies with Samples from Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8110-MS (January 1980).
4. K. Wolfsberg, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, S. Maestas, A. J. Mitchell, P. Q. Oliver, N. A. Raybold, R. S. Rundberg, J. L. Thompson, and E. N. Vine, "Sorption-Desorption Studies on Tuff. III. A Continuation of Studies with Samples from Jackass Flats and Yucca Mountain, Nevada," Los Alamos National Laboratory report LA-8747-MS (May 1981).
5. N. Hadden, F. Baumann, F. MacDonald, M. Munk, R. Stevenson, D. Gere, F. Zamaroni, and R. Majors, Basic Liquid Chromatography (Varian Aerograph, Walnut Creek, California, 1971).

6. J. H. Knox and L. McLaren, "A New Gas Chromatographic Method for Measuring Gaseous Diffusion Coefficients and Obstructive Factors," Anal. Chem. 36, 1477 (1964).
7. W. Nernst, "Zur Kinetik der in Lösung Befindlichen Körper," Z. Physik. Chem. 2, 613 (1888).
8. T. Vermeulen, G. Klein, and N. Hiester, "Adsorption and Ion Exchange," in Chemical Engineers' Handbook, 5th Ed., R. H. Perry and C. H. Chilton, Eds. (McGraw-Hill, New York, 1973), Section 16.
9. J. C. Giddings, Dynamics of Chromatography, Part I. Principles and Theory (Marcel Dekker, New York, 1965).