Geochemistry Studies Pertaining to the G-Tunnel Radionuclide Migration Field Experiment

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RADIONUCLIDE MIGRATION FIELD EXPERIMENT

by

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ABSTRACT

This report presents the results of geochemical studies of Tunnel Bed tuff that were performed by Los Alamos National Laboratory or done at its direction as part of the Nevada Test Site G-Tunnel Radionuclide Migration Field Experiment. A tuff-treated water was prepared and used in laboratory-scale measurements of radionuclide sorption onto crushed Tunnel Bed tuff, pulverized fracture-fill material, tuff wafers, and a solid tuff core. Modelling studies were undertaken to determine the effects of matrix diffusion and unsaturated tuff on the proposed fracture-flow experiments. The initial results of those studies are presented in this report.

I. INTRODUCTION

Los Alamos National Laboratory, Argonne National Laboratory, and Sandia National Laboratories jointly undertook a program to conduct small-scale, at-depth radionuclide migration experiments in G Tunnel at the Nevada Test Site (NTS). The geochemical properties of a particular G-Tunnel formation, Tunnel

Bed 5 tuff, were studied in work directed by Los Alamos to determine whether a successful field migration experiment could be performed in that medium. This report outlines the results of that study.

The major part of this work was devoted to measuring the sorption of radionuclides onto Tunnel Bed tuff. Before these experiments could be undertaken, however, it was necessary to prepare an appropriate water for use in the sorption measurements. The studies related to the preparation of a tuff-treated water that is in approximate equilibrium with the Tunnel Bed tuff are given in this report. The results of batch measurements of radionuclide sorption onto crushed tuff, pulverized fracture-fill material, and wafers are given in Sec. IV. The following section lists the results of column measurements of radionuclide sorption onto pulverized fracture-fill material and onto a solid core of tuff. The next section contains actinide sorption results. The final section of this report discusses the use of two geochemical models to calculate radionuclide sorption during a fracture-flow field experiment. One model emphasizes matrix diffusion effects in a one-dimensional calculation. The second model is more general, but its use for fracture-flow studies is just beginning.

II. TUNNEL BED TUFF CHARACTERIZATION

A. X-Ray Diffraction Analyses

The material used for the sorption studies described in this report is Tunnel Bed 5 tuff. On the whole, the Tunnel Beds consist of medium to massive bedded ash-fall tuff. The tuff is light brown to reddish brown. It is fine to medium grained, and it is generally zeolitized.¹ X-ray diffraction studies were performed on crushed-tuff samples from Tunnel Bed 5. Additional x-ray analyses were performed on fracture-fill material obtained from nearby fractures. The results of these analyses are given in Table I. The fracture-fill material was found to be virtually indistinguishable from the crushed-matrix sample.

B. Thin Section Examinations

Thin sections from both sides of a parting plane in the U12G-RNM9 core were examined microscopically. The mineralogy was not determined, but the two sides were found to be distinctly different on a textural basis. A section of U12G-RNM9, 5.9 to 6.4 ft, Side B, shows a zone of low porosity,

TABLE I
X-RAY DIFFRACTION ANALYSES
OF TUNNEL BED 5 MATERIAL

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

about 3 mm wide, adjacent to the parting plane. The remainder of the section has considerably higher porosity. Side A of a section of U12G-RNM9, 5.9 to 6.4 ft, shows no regular change in porosity across the section. Thus, the porosity of the tuff adjacent to a parting plane exhibited asymmetrical porosity characteristics. An examination of the G-Tunnel location from which the core was taken indicated that Side B is the lower side of the fracture.

C. Measurements of Permeability, Porosity, and Diffusion Coefficients

The permeabilities and porosity of five samples were measured. The permeability was first measured at a low effective confining pressure of 2 to 3 MPa. The confining pressure was raised to a maximum, and a series of measurements was made at successively lower confining pressures. No appreciable changes in permeability were observed as a result of this pressure cycle. The ranges of the individual permeability measurements are listed in Table II. These samples were weighed twice: after the permeability measurements and again after thorough drying. The net mass of water in each sample was used to calculate the porosity of each sample. These results are shown in Table II.

Porosities of Tunnel Bed tuff samples were measured in two other ways. A mercury infusion porosimeter was used to measure porosities caused by pores with diameters $>0.1 \mu\text{m}$. This limit is set by the maximum operating pressure of the porosimeter, which is 1.4 MPa. The results of these measurements are shown in the first column of data in Table III. The other method used to measure porosities is based on measurements of grain densities that are taken

TABLE II
MEASURED PERMEABILITIES AND POROSITIES OF
U12G-RNM9, 5.9 to 6.4 FT, TUFF SAMPLES

<u>Sample^a</u>	<u>Permeability (m²)</u>	<u>Porosity</u>
Side A, Position A	(2 to 8) x 10 ⁻¹⁹	0.39
Side A, Position B	(3 to 6) x 10 ⁻¹⁹	0.39
Side A, Position C	(3 to 9) x 10 ⁻¹⁹	0.31
Side B, Position A	(1 to 4) x 10 ⁻¹⁸	0.39
Side B, Position B	(1 to 3) x 10 ⁻¹⁸	0.37

^aSide A is above the bedding plane; side B is below.

TABLE III
MERCURY INFUSION POROSIMETRY AND GRAIN DENSITY POROSITY DATA

<u>Sample</u>	<u>Porosity (>0.1 μm)</u>	<u>Bulk Density (g/cm³)</u>	<u>Grain Density (g/cm³)</u>	<u>Method^a</u>	<u>Porosity</u>
HF-23 ^b	0.100	1.46	--	--	--
U12G-RNM9 (5.9 to 6.4 ft)	0.147	1.48	2.20 2.21	K W	0.33
U12G-RNM9 (16.2 to 17.5 ft)	0.225	1.31	2.20 2.21	K W	0.40

^aW indicates grain density by water displacement. K indicates grain density by kerosene displacement.

^bFrom the tunnel wall of the HF-23 drift in G-Tunnel near the RNM9 hole.

by the pycnometer technique described in Procedure ASTM D 854-58 (Ref. 2). Two wetting fluids were used: water and kerosene. The results with the two fluids were comparable, as shown in Table III. The sample porosities calculated from the bulk volume measurement are given in the final column of Table III. These values are in the same range as those given in Table II. The pore space in the samples that arises from pore diameters $<0.1 \mu\text{m}$ results in mercury infusion porosimeter measurements that are significantly smaller than the grain density measurements.

Diffusion coefficients were measured for the diffusion of bromide or iodide ions through discs of Tunnel Bed tuffs. The samples were 2.54 cm in diameter and 0.635 cm thick. The ions for these measurements were in solution in tuff-treated Well J-13 water (see Sec. III.A). The results of the diffusion coefficient measurements are given in Table IV. The total porosity, median pore diameter, and α/τ^2 data given in Table IV are for purposes of correlation with the effective diffusion coefficients. Although the median pore diameter measurements are too few to merit a definitive statement about correlation, there appears to be no correlation of the effective diffusion coefficients with total porosity, but the effective diffusion coefficients do show a trend similar to α/τ^2 . The relationship between α/τ^2 , which is called the constrictivity-tortuosity parameter, and the effective diffusion coefficient is given by the equation derived from L. K. Porter et al.³

$$\frac{\alpha}{\tau^2} = \frac{D_e}{D_o \phi_T} ,$$

in which

D_e is the effective diffusion coefficient,

D_o is the aqueous diffusion coefficient,

ϕ_T is the total porosity, and

τ is the same as L_e/L in Ref. 3.

Additional data are required before definite statements about correlative relationships can be made.

TABLE IV
EFFECTIVE DIFFUSION COEFFICIENTS

<u>Sample</u>	<u>Diffusion Species</u>	<u>Effective Diffusion Coefficient</u> (10^{-7} cm ² /s)	<u>Total Porosity</u> (Φ)	<u>Median Pore Diameter</u> (μ m)	<u>α/τ^2</u>
U12G-RNM9 0.8 to 1.0 ft	Br ⁻	4.71 $\pm$ 0.11	0.35	--	0.08
U12G-RNM9 16.2 to 17.5 ft	I ⁻	10.8 $\pm$ 0.03	0.40	0.57	0.16
U12G-RNM9 5.9 to 6.4 ft	Br ⁻	11.3 $\pm$ 0.02	0.33	0.61	0.21

III. WATER PREPARATION AND CHARACTERIZATION

Water to be used both in G-Tunnel field experiments and in laboratory measurements of fracture-flow characteristics with Tunnel Bed tuff should have a composition similiar to that of water equilibrated with the tuff. Otherwise, the water composition will vary during the course of an experiment through interactions with the tuff. These interactions, in the form of dissolution and precipitation reactions, may give rise to misleading interpretations of the experimental results. The investigations described here were undertaken to obtain a supply of water with a composition like that of water equilibrated with Tunnel Bed 5 tuff.

A. Selection of Water and Rock Sources

Water samples were collected from two seeps that occur in the EV-5 area of G Tunnel, near the top of the Tunnel Bed tuff formation, and from two NTS wells (Well 8 and Well J-13) that are located in tuffaceous media. The waters from the seeps and from Well J-13 were filtered through 0.05- μ m Nuclepore polycarbonate filters and analyzed with a plasma-source emission spectrometer. The results are shown in Table V, with US Geological Survey (USGS) analysis results for Well 8 water.⁴

Well 8 and Well J-13 waters were contacted for 2-week and 4-week times with fracture-fill material and Tunnel Bed tuff to determine what the composition of water might be at equilibrium with these G-Tunnel materials. These samples were

filtered through 0.05- μ m Nuclepore filters and analyzed like the water samples described above. The proportions of rock and water were varied, as shown in Table V.

The results of this work indicate that the water from the EV-5 seeps does not appear to be in equilibrium with the Tunnel Bed tuff. Previously published work⁵ showed the striking change in water composition with depth in the per-alkaline tuffs of the Miocene tunnel beds. The sodium concentration in the water increased with depth, and the calcium concentration decreased with depth. Changes like these in water composition apparently require a greater residence time at a given depth than the seep water received for equilibrium to be established. The final composition of water contacted with the fracture fill or tuff matrix in various proportions appears to depend very little or not at all on the initial water source, the rock type, and the relative proportions of rock and water. Consequently, Well J-13 water and matrix rock will be used to prepare water for these studies, because of their ready availability. Water-to-rock proportions of 10:1 will be used.

B. Filtration Effects

Unusually high concentrations of iron and silicon were observed in water that was contacted with Tunnel Bed tuff, then filtered through 0.45- μ m Millipore HA filters before analysis. Consequently, the water was passed through filters with smaller diameter pores to determine whether the analysis results were a function of the pore size. The results of filtering the treated water through 0.45- μ m Millipore filters, 0.4- μ m Nuclepore polycarbonate filters, and 0.05- μ m Nuclepore polycarbonate filters are listed in Table VI. Filtration of the water through 0.05- μ m Nuclepore filters was chosen for all further work because the decrease of element concentrations with pore size (as shown in Table VI) indicates that fine particles of the tuff may be passing through the larger filters. The Tunnel Bed tuff exhibits a much greater tendency to produce small particles and colloids than any of the other NTS tuffs studied to date at Los Alamos.

The concentration of Fe(II) in Well J-13 water was determined in a spectrophotometric procedure that uses 4,7-diphenyl-1,10-phenanthroline as the detection agent. The Well J-13 water had been contacted with Tunnel Bed tuff in a controlled atmosphere of nitrogen in which oxygen was <0.2 ppm and carbon dioxide was <20 ppm. The water was filtered through a 0.05- μ m Nuclepore filter.

TABLE V
WATER COMPOSITIONS

			Concentration (mg/ℓ)										
Water			Mg	Mn	Si	Fe	Ba	V	Ti	Ca	K	Al	Na
			Untreated Water										
Water													
seep ^a			0.14	0.09	30	1.0	0.002	0.001	0.13	0.81	3.8	0.4	34
seep ^b			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 ^c			1.1	<0.01	27	<0.01	--	--	--	8.3	3.6	<0.1	31
			Treated Water ^d										
Water	Rock ^e	Water:Rock Proportions											
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

^aMiddle of incline near EV-5

^bLower incline near EV-5

^cFrom Ref. 4.

^dAverage value for 2-week and 4-week contacts in air. Filtered through 0.05- μ m Nuclepore filters.

^eff = HF-23 fracture fill; m = HF-23 matrix.

TABLE VI
EFFECT OF FILTRATION ON WATER 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 weeks and centrifuged before successive filtrations.

^bMillipore HA membrane.

^cNuclepore polycarbonate membranes.

The Fe(II) concentration was <0.01 mg/l. Therefore, the iron listed in Table II is assumed to be iron either in solution as Fe(III) or associated with particles <0.05 μ m.

C. Effects of Contact Time

An apparatus was constructed for contacting Well J-13 water in ~200-l batches with ~20 kg of crushed Tunnel Bed tuff. The apparatus consists of a 55-gal., polyethylene-lined barrel with an inverted, perforated polyethylene funnel placed inside the barrel. The tuff was placed over the funnel. The Well J-13 water was put into the barrel and circulated with a peristaltic pump, which forced the water down through the funnel, then up through the tuff.

After 28 days of contact, the water was passed through a 0.05- μ m Nuclepore filter, a process that required three 8-hour shifts; then it was transferred to a second barrel containing ~20 kg of fresh crushed tuff. The water was contacted with the second batch of tuff for 24 days. Small aliquots of water were removed at intervals throughout both contact periods to measure water composition. Each aliquot was filtered through a 0.05- μ m Nuclepore filter. A portion of each aliquot was acidified to determine cations and silicon by emission spectroscopy. The results of these measurements are given in Table VII. The unacidified portion of each aliquot was used to measure anions by ion chromatography and acidimetric titration. These results are given in Table VIII. The composition of untreated Well J-13 water is given in each of these two tables for comparison with the other results. The data in the tables indicate that a 7-day contact of Well J-13 water with a single batch of tuff is sufficient to prepare water for use in this experimental program.

The pH of the Well J-13 water varied <0.08 during the treatment with tuff that is described above. The average pH value is 8.32 ± 0.03 .

One measure of the quality of the water composition data, which are shown in Tables VII and VIII, is provided by comparing the cation concentrations with the anion concentrations. The values for the untreated Well J-13 water are 2.85 meq/l for cations and 3.17 meq/l for anions. The average experimental normalities of the tuff-treated water are 3.17 meq/l for cations and 2.86 meq/l for anions. The differences of normalities for cations and anions, 10 and 11% for the untreated and treated water, respectively, are within the range of the 1 to 15% differences typically observed by the USGS in water analyses (see, for example, Ref. 6).

D. Effects of Standing Time and Acidification on Cation Analysis

Experiments were performed to investigate whether the composition of tuff-treated water changes with standing time and whether the addition of acid to the filtered water results in increased stabilization. Well J-13 water that had been contacted with Tunnel Bed tuff and filtered through 0.05- μ m Nuclepore filters was analyzed for cations soon after filtration and again ~4 months later. Some of the filtered water samples were acidified to 0.1 M HNO_3 and analyzed at the same two times. The results are shown in Table IX; the compositions of the waters do not vary significantly with standing time, and acidification does not affect the results significantly.

TABLE VII
ANALYSES OF WELL J-13 WATER TREATED WITH TUNNEL BED TUFF

	Concentration (mg/l)												
	Hg	Mn	Fe	Sr	Ba	V	Ti	Li	K	Al	Na	Si	Ca
Uncontacted ^{a,b} Water	1.8	0.010	0.018	0.04	0.001	0.016	0.013	0.066	5	0.106	45	25	11
Contacted Water (days)													
First contact													
3 ^b	0.031	0.012	0.13	0.001	0.002	0.010	0.008	0.035	2.03	0.040	58.2	26.0	0.47
7	0.044	0.017	0.21	0.002	0.003	0.010	0.008	0.056	2.59	0.057	69.1	30.0	0.68
10	0.042	0.019	0.20	0.002	0.004	0.020	0.015	0.053	2.55	0.056	70.1	29.5	0.70
21	0.031	0.021	0.19	0.002	0.004	0.022	0.012	0.058	2.72	0.046	70.5	28.8	0.59
28	0.035	0.026	0.19	0.001	0.001	0.015	0.013	0.041	2.46	0.043	70.9	29.6	0.64
Second contact													
3	0.029	0.007	0.07	0.001	0.001	0.012	0.007	0.020	2.52	0.031	70.6	28.7	0.66
7	0.031	0.005	0.03	0.000	0.000	0.007	0.006	0.022	2.43	0.031	71.4	28.8	0.63
19	0.024	0.005	0.05	0.001	0.001	0.013	0.020	0.044	2.42	0.025	70.5	29.0	0.53
24	0.028	0.005	0.05	0.000	0.001	0.014	0.019	0.040	2.37	0.026	70.5	27.8	0.68
Mean	0.033	0.013	0.12	0.001	0.002	0.014	0.012	0.042	2.51	0.039	70.4	28.9	0.64
Std. deviation of the sample ^c	0.007	0.009	0.08	0.001	0.002	0.005	0.005	0.014	0.11	0.013	0.7	0.9	0.06
Typical std. dev. of single analysis ^d	0.001	0.002	0.01	--	0.001	0.005	0.003	0.010	0.05	0.001	1.5	0.3	0.1
Limit of detection	0.001	0.002	0.02	--	0.0005	0.01	0.002	0.016	0.05	0.004	3.0	0.05	0.006
Mean concen- tration (mM)	1.36x10 ⁻³	2.4x10 ⁻⁴	2.2x10 ⁻³	1x10 ⁻⁵	1x10 ⁻⁵	2.8x10 ⁻⁴	2.6x10 ⁻⁴	6.0x10 ⁻³	6.4x10 ⁻²	1.5x10 ⁻³	3.06	1.03	1.59x10 ⁻²

^aWater from well J-13, not contacted with Tunnel Bed tuff (listed for comparison).

^bOmitted in mean.

^cA measure of run-to-run analytical precision, assuming that the members in the mean belong to the same sample.

^dWithin-run analytical precision based on three repeat measurements on a sample.

TABLE VIII
COMPOSITION OF WELL J-13 WATER TREATED WITH TUNNEL BED TUFF
AND MEASURED BY ANION CHROMATOGRAPHY AND ACIDIMETRIC TITRATION

	Concentration (mg/l)				
	F	Cl	NO ₃	SO ₄	HCO ₃
Uncontacted Water ^a	2.8	9.4	8.1	23	131
<u>Contacted Water</u>					
<u>(days)</u>					
<u>First contact</u>					
10	2.5	9.2	5.9	17.1	126
28	2.4	9.1	6.4	17.6	120
<u>Second contact</u>					
3	2.3	9.6	6.4	18.1	121
7	2.3	9.7	6.0	18.2	122
Mean	2.38	9.4	6.2	17.8	122
Std. dev. of the sample	0.10	0.3	0.3	0.5	3
Mean concen- tration (mM)	0.125	0.265	0.100	0.185	1.00

^aWater from Well J-13, not contacted with Tunnel Bed tuff (listed for comparison).

E. Tritium Content of Water in Tuff from Core U12G-RNM9

Portions of tuff were removed from opposite ends of core U12G-RNM9, 1.0 to 3.4 ft, which had been stored in a plastic bag that was wrapped with tape. The water was removed from the Tunnel Bed tuff by heating and condensing. The measured tritium concentration was 1.05 and 3.03 nCi/ml at depths of 3.4 and 1.0 ft from the tunnel wall, respectively.

IV. BATCH SORPTION EXPERIMENTS

A. Crushed-Tuff Matrix

Experiments were performed to measure the sorption of radioactive tracers onto crushed Tunnel Bed tuff from tuff-treated Well J-13 water. The Tunnel Bed

TABLE IX

OBSERVED VARIATION IN WATER COMPOSITION WITH STANDING TIME
AND ACID STABILIZATION^a

<u>0.1 N HNO₃ Treatment</u>	<u>Date Analyzed</u>	<u>Mg</u>	<u>Mn</u>	<u>Si</u>	<u>Fe</u>	<u>Sr</u>	<u>Ba</u>	<u>V</u>	<u>Ti</u>	<u>Ca</u>	<u>Li</u>	<u>K</u>	<u>Al</u>	<u>Na</u>
none	2-27-81	0.064	0.046	26.9	0.604	0.002	0.028	0.008	0.003	0.678	0.045	6.22	0.234	94.0
none	6-19-81	0.103	0.024	30.6	0.852	0.005	0.005	0.012	0.034	0.961	0.045	3.96	0.346	92.4
acidified	2-27-81	0.095	0.049	31.0	0.354	0.005	0.107	0.010	0.006	1.40	0.053	6.18	0.207	96.0
acidified	6-19-81	0.137	0.023	35.4	0.815	0.008	0.016	0.016	0.058	1.33	0.050	4.04	0.432	93.6

^aWell J-13 water contacted with Tunnel Bed tuff and filtered through 0.05- μ m Nuclepore filters.

tuff came from G-Tunnel drift HF23, hole U12G-RNM9, 10.8 to 11.9 ft. The tuff was crushed to a particle size $<500\text{ }\mu\text{m}$. The Well J-13 water was treated with Tunnel Bed tuff in the manner described in Sec. III, then filtered through $0.05\text{-}\mu\text{m}$ Nuclepore filters. Batches containing 20 ml water, 1 g crushed tuff, and appropriate tracers were shaken for 2- to 6-week periods under controlled atmosphere conditions (nitrogen with $<0.2\text{ ppm}$ oxygen and $<20\text{ ppm}$ carbon dioxide). The results of these batch sorption measurements, which were performed in duplicate, are reported in Table X in terms of a distribution ratio R_d ; the distribution ratio is defined as the activity per gram of solid divided by the activity per milliliter of solution. The symbol R_d is used for this work to indicate uncertainty concerning the achievement of equilibrium conditions during the experiment. When equilibrium conditions are known to occur or assumed to occur, as in theoretical treatments, the symbol K_d is used for this ratio.

The crushed-tuff samples with the sorbed ^{85}Sr , ^{137}Cs , ^{133}Ba , and ^{152}Eu tracers were contacted with new 20-ml aliquots of tuff-treated Well J-13 water to measure desorption. Contact periods of 3 and 6 weeks were used for these measurements, which were done under controlled atmosphere conditions, as were the sorption measurements. The results are given in Table XI.

A comparison of the results in Tables X and XI indicates that the R_d values for a given tracer approach an equilibrium value with time both in sorption and in desorption experiments. The reproducibility of duplicate determinations is poor, particularly in the desorption measurements. These types of measurements have been performed at Los Alamos with tuffs from other sources. The reproducibility of results from duplicate determinations with Tunnel Bed tuff is poorer than for any of the other tuffs studied. This poor reproducibility may be related to the fine particles that are unique to this tuff.

B. Crushed Fracture-Fill Material

An experiment like those described in Sec. IV.A was performed to measure sorption onto material that had filled a naturally occurring fracture in Tunnel Bed tuff. This experiment was undertaken to determine whether fracture-fill material displayed radionuclide sorption characteristics that were significantly different from those shown by the crushed-tuff matrix material used in the other batch experiments.

TABLE X
AVERAGE R_d VALUES FOR SORPTION OF RADIONUCLIDES
ONTO TUNNEL BED TUFF

<u>Tracer</u>	<u>Valence</u>	<u>Contact Time (weeks)</u>	<u>R_d (ml/g)</u>	<u>Standard Deviation of Mean</u>
^{22}Na	I	2	180	11
		4	194	6
^{54}Mn	II	2	2 050	330
		4	480	260
^{75}Se	IV	2	1.9	0.5
		4	1.6	0.1
^{85}Sr	II	3	41 000	2 000
		6	48 000	6 000
^{113}Sn	II	3	380	130
^{137}Cs	I	3	15 600	400
		6	12 000	1 000
^{133}Ba	II	3	6 300	700
		6	4 600	500
^{152}Eu	III	3	590	40
		6	510	100

The fracture-fill material for this experiment lined a natural fracture that was observed in the "waxed and wrapped" core from U12G-RNM9, 7.1 to 8.1 ft. The fracture-fill material was pulverized by grinding the two faces of the core against each other, but it was not sieved. This batch sorption experiment was performed in a controlled atmosphere (nitrogen with <0.2 ppm oxygen and <20 ppm

TABLE XI
AVERAGE R_d VALUES FOR DESORPTION OF RADIONUCLIDES FROM TUNNEL BED TUFF

<u>Tracer</u>	<u>Contact Time (weeks)</u>	<u>R_d (ml/g)</u>	<u>Standard Deviation of Mean</u>
^{85}Sr	3	96 000	8 000
	6	51 000	10 000
^{133}Ba	3	19 000	4 000
	6	4 400	200
^{137}Cs	3	25 000	4 000
	6	13 000	5 000
^{152}Eu	3	4 100	300
	6	1 600	800

carbon dioxide) with Well J-13 water that had been treated with Tunnel Bed tuff and filtered through 0.05- μm Nuclepore filters. The results are given in Table XII.

A comparison of the data in Table XII with those in Table X for the same tracers and contact times shows that the R_d values for cesium and europium are in reasonable agreement, but the sorption of strontium onto crushed-tuff matrix yields R_d values about 20 times those obtained with fracture-fill material, and the R_d values for barium are two to four times greater for sorption onto fracture-fill material. The reasons for these observations are not known. One would expect from the data given in Table I that the sorption characteristics of crushed-tuff matrix and fracture-fill material would be about the same.

C. Wafers

Batch sorption measurements were performed with Tunnel Bed tuff in the form of wafers suspended from nylon lines in solutions containing radioactive tracers. The water containing the tracers was the customary Well J-13 water, which had been contacted with Tunnel Bed tuff and filtered through 0.05- μm filters. This batch sorption method was investigated to see if the resulting R_d values might

TABLE XII
SORPTION RATIOS FOR FRACTURE-FILL SAMPLES^a

Time (weeks)	R_d (ml/g)					
	Cs	Sr	Ba	Ce	Eu	Tc
1	10 400(3.7)	1 350(2.7)	20 000(5.3)	240(5.9)	320(5.4)	0.0047
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)	0.72
3	15 000(6.9)	2 500(4.4)	26 000(9.5)	340(10.2)	443(9.9)	0.66
4	16 000(8.1)	2 300(5.9)	7 200(4.3)	760(11.9)	870(11.7)	1.79
4	13 000(7.5)	2 200(5.8)	7 400(4.1)	490(11.1)	720(10.8)	1.42
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 (in per cent) for a single measurement of the R_d values; 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.

be more appropriate for predicting radionuclide transport in the case of a waste nuclide repository breach than would the R_d values measured with crushed-tuff matrix samples.

One set of experiments was performed to determine the effects of different wafer thicknesses and different contact times. The wafers were prepared with matrix material from core U12G-RNM9, 16.2 to 17.5 ft. The thicknesses of these 13.5-mm-diam wafers varied from 5 to 9 mm. Sorption measurements were performed in air with varying contact times (see Table XIII). The R_d values in Table XIII are comparable in magnitude to those in Table XII, but the strontium R_d values are much lower than those in Table X. There is no obvious correlation of wafer R_d values with wafer thickness or time of contact.

A second set of wafers, 17 mm in diameter and 2 ± 0.5 mm thick, was used to determine the amount of activity in a tracer solution that was sorbed onto the wafer as a function of contact time. The contact times varied from 10 seconds to 119 days. The wafers were soaked for 2 weeks in the customary tuff-treated and filtered Well J-13 water before the start of the sorption experiments. Then the wafers were suspended from Teflon thread in the tuff-treated Well J-13 water that contained ^{85}Sr , ^{137}Cs , ^{133}Ba , and ^{152}Eu tracers in one set of measurements and $^{95}\text{Tc}^m$ or ^{131}I in another set. The results of the $^{95}\text{Tc}^m$ and ^{131}I sorption measurements are given in Table XIV. If the $^{95}\text{Tc}^m$ had diffused into all the water remaining in the wafer after its 2-week soak, 1.8% of the technetium should have been detected with the wafer. The datum for 916 hours in Table XIV shows that 1.3% of the total technetium activity was measured, which indicates that equilibrium was not reached by that time. The iodine sorption experiments were terminated after 777 hours, because the ^{131}I had decayed to ~6% of its initial activity. This small amount of activity resulted in poor counting statistics. The observed iodine sorption of 1.51% at 777 hours is too poor a value to be significantly different from 1.27%, which is the ^{131}I equilibrium value that would be observed if the ^{131}I had diffused into all the water in the wafer after its 2-week soak. One can conclude from these measurements that there is no evidence for the sorption of $^{95}\text{Tc}^m$ or ^{131}I ions onto the Tunnel Bed tuff wafers.

The results of the measurements of cation sorption onto the Tunnel Bed tuff wafers are given in Tables XV and XVI. The rapid sorption of strontium, cesium, and barium onto these wafers (shown in Table XV) is what one might expect for this zeolitized tuff. The R_d values for wafer sorption times of

TABLE XIII
SORPTION RATIOS FOR WAFERS

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

^aThe values in parentheses are the standard deviations (in per cent) for a single measurement of the R_d values; 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 XIV
PERCENTAGE OF TOTAL ACTIVITY SORBED ON WAFERS

<u>Time (hours)</u>	<u>$^{95}\text{Tc}^m$</u>	<u>Time (hours)</u>	<u>^{131}I</u>
0.5	0.56 (0.05) ^a	0.5	0.60 (0.02)
1.5	0.86 (0.04)	1.4	0.82 (0.01)
4.0	0.98 (0.02)	18	0.99 (0.01)
8.0	1.01 (0.02)	44	1.03 (0.01)
80	1.11 (0.01)	164	1.05 (0.01)
120	1.14 (0.02)	349	1.14 (0.01)
258.5	1.14 (0.01)	541	1.21 (0.01)
408	1.18 (0.02)	777	1.51
916	1.26 (0.02)		

^aValues in parentheses are standard deviations of the means.

22 to 2850 hours are shown in Table XVI. When the data in Table XVI are compared with those in Table XIII, one can note that for similar sorption times, the strontium sorption in Table XVI is ten times greater than that shown in Table XIII. The cesium and barium data in Table XVI are factors of 2 to 6 lower than those in Table XIII, but the europium data in the two tables are similar. The data in Table XVI, like the other data, show no obvious correlation of R_d with contact time or sample size, although at the longer contact times in Table XVI, there does seem to be a decrease in the R_d value with an increase in sample size. The reasons for the differences in R_d values between Tables XVI and XIII are not known.

V. COLUMN SORPTION STUDIES

A. Crushed Fracture-Fill Column

The sorption characteristics of ^{85}Sr , $^{95}\text{Tc}^m$, ^{137}Cs , ^{133}Ba , and ^{152}Eu were studied in an experiment in which the tracers were loaded in a small spike onto a column of crushed Tunnel Bed tuff material, then eluted with tuff-treated Well J-13 water. The column length is 5.0 cm, the diameter is 0.5 cm, and

TABLE XV
CATION SORPTION DATA FOR TUNNEL BED TUFF WAFERS

Time (hours)	Total Activity Sorbed ^a (%)			
	Sr	Cs	Ba	Eu
2.78×10^{-3}	0.75	1.22	0.75	0
8.33×10^{-3}	2.40	3.92	2.15	0.44
1.67×10^{-2}	4.14	7.13	3.82	1.52
2.50×10^{-2}	6.46	11.0	5.81	2.57
3.33×10^{-2}	8.63	14.6	7.14	3.08
8.33×10^{-2}	13.3	23.0	11.5	5.16
2.50×10^{-1}	34.3	53.7	25.5	9.62
2.20×10^1	99.5	99.0	97.8	72.6
3.65×10^1	99.2	99.0	95.6	79.9
6.20×10^1	99.6	99.1	97.8	70.9
3.72×10^2	99.8	99.1	99.0	93.6
7.08×10^2	99.9	99.3	99.4	94.0
2.03×10^2	99.9	99.2	99.2	96.1
2.85×10^3	99.9	99.2	99.2	96.8

^aThe per cent of activity sorbed from 2.78×10^{-3} to 2.5×10^{-1} hours was calculated by comparing the activity on the wafer with the total activity added. The remaining values were calculated from the activity remaining in solution compared to the original activity in solution.

the volume is 0.982 cm^3 . The material used in this column was fracture-fill material (described in Sec. IV) that was crushed to the range of 38 to $106 \text{ }\mu\text{m}$. The measured free-column volume was 0.699 ml with ^{131}I and 0.689 ml with tritiated water; both tracers were added to Well J-13 water that had been treated with Tunnel Bed tuff and filtered through $0.05\text{-}\mu\text{m}$ Nuclepore filters. The density of the fracture-fill material in the column was 0.91 g/cm^3 , and the porosity was 0.71.

TABLE XVI
SORPTION RATIOS FOR TUNNEL BED TUFF WAFERS

Wafer (g)	Time (hours)	R_d (mℓ/g)			
		Sr	Cs	Ba	Eu
1.34	22	3 500	1 900	440	90
1.37		4 200		500	31
1.41		3 600	2 300	470	45
0.97	36.5	2 700	2 600	300	130
1.41		3 000	2 000	450	42
1.78		2 500	1 900	360	84
1.11	62	4 900	2 000	710	42
0.97	372	13 000		1 800	360
1.41		8 300		3 400	190
1.78		9 600	2 800	2 400	320
1.34	708	13 000		1 900	260
1.37		19 000	3 000	4 000	230
1.41		18 000			370
0.97	2 034	13 000	3 800	6 400	680
1.11		8 900	5 800	3 400	520
1.41		4 600	1 900	1 500	390
1.78		3 800	1 700	1 400	330
0.97	2 847	11 000	4 300	6 500	1 800
1.11		13 000	5 300	3 100	620
1.41		4 900	2 000	1 600	440
1.78		5 400	1 600	1 500	320

The tracers were loaded onto the column, and the flow rate was established at 0.015 mℓ/hour, which is equivalent to 9.5 m/year. Only technetium and europium were eluted from the column before the experiment was terminated after 241 days, although small amounts of barium were observed in the eluate occasionally. The technetium was removed in one peak, which contained >96% of the $^{95}\text{Tc}^m$ loaded. The R_d for technetium corresponds to 0.84 mℓ/g, which falls within the range of measured batch sorption ratios for the Tunnel Bed tuff.

Approximately 4% of the europium was removed from the column; the R_d for europium calculated from this effluent observation is 2.3 ml/g.

The crushed fracture-fill column was sectioned and counted to measure the distances that the remaining activities had traveled from the loading point. The remaining europium had moved 8 to 21% of the distance through the column. The europium sorption ratios are 988 to 2560 ml/g, from this observation. Batch measurements gave R_d values of 280 to 1000 ml/g, a range that overlaps the values calculated for the europium that remained on the column. The europium that was eluted during the column experiment may have been in the form of a colloid. Such rapid elution of a fraction of the europium has been observed on other crushed-rock columns.⁷ Very small amounts of the barium were observed in the eluate, but 84% of the ^{133}Ba was detected in the column section closest to the loading point. That section also contained 78% of the ^{85}Sr and 75% of the ^{137}Cs . The remaining strontium, cesium, and barium was detected in the section adjacent to the first section. The column was not sampled in small enough sections to measure the strontium, cesium, or barium concentrations. Hence, the R_d values could not be calculated.

The crushed fracture-fill material from the Tunnel Bed tuff that was used in this column performed differently than any other material used in similar crushed rock column studies at Los Alamos.⁷ Those other materials have included tuff from other sources, granite, and argillite. As the elution progressed in the column with the crushed fracture-fill material from the Tunnel Bed tuff, the eluate became cloudy. The volume of the column material decreased with time, as the material in the column apparently broke apart. The elution process then removed fine particles.

B. Solid Core Column

A solid core of Tunnel Bed tuff was coated with epoxy to form a column. A detailed description of the core is given in Table XVII. A syringe pump was used to force tuff-treated Well J-13 water through the core for several weeks. The column was loaded with ^{85}Sr , ^{137}Cs , and ^{133}Ba . Well J-13 water containing tritiated water (HTO), $^{95}\text{Tc}^m$, and ^{131}I was used to elute the column until the radioactivity was equal to that of the initial traced solution. At that time untraced water was used to continue the elution. The R_d value calculated for $^{95}\text{Tc}^m$ from this elution was 0.16 ml/g. Although technetium sorption was not found on wafers, batch measurements on fracture-fill samples did give sorption ratios ≤ 1.8 .

TABLE XVII
TUNNEL BED SOLID-CORE COLUMN

Diameter	
rock	1.67 cm
rock + epoxy	1.75 cm
Length	2.60 cm
Density	
rock	1.25 g/cm ³
epoxy	1.16 g/cm ³
rock + epoxy	1.24 g/cm ³
Flow rate	0.031 ml/hour
	1.81 x 10 ⁻⁵ cm/second
	5.7 m/year
Free-column volume	
HTO	1.09 ml
I ⁻	1.39 ml
average	1.24 ml
Porosity	0.218
Total volume eluted	268 ml

After approximately 1 year the elution was stopped, and the distribution of activity remaining in the core was measured. The column was sampled by rubbing the damp core on tared pieces of silicon carbide paper. After they dried, the papers were reweighed to determine the amount of rock (and epoxy coating) removed in each sample. Sample sizes ranged from 12.8 to 40.9 mg, which is equivalent to the removal of ~43 to 137 μ m per sample. Fifty-three samples were taken, which removed a total of 0.45 cm. This detailed sampling gives a good indication of the extent of migration of the isotopes studied. The sample size, location in the column, and per cent of the total activity loaded in each sample are given in Table XVIII. When the average distance that each isotope moved through the column was plotted against each of the totals of strontium, cesium, and barium activity, the point within the column where 50% of the total activity had moved was determined. One-half of the strontium had

TABLE XVIII
DATA FROM SECTIONING OF SOLID-CORE COLUMN

Average Distance Through Column (%)	Core Sampled (%)	⁸⁵ Sr Removed (%)	¹³⁷ Cs Removed (%)	¹³³ Ba Removed (%)
0.091	0.183	1.39	2.02	3.91
0.284	0.202	1.93	2.17	4.92
0.521	0.273	2.91	4.31	10.7
0.803	0.291	2.80	4.85	11.3
1.08	0.258	2.30	4.43	9.97
1.32	0.219	2.33	3.38	7.50
1.54	0.223	2.27	2.92	6.21
1.75	0.198	1.47	2.06	3.72
1.93	0.165	0.94	1.82	3.44
2.13	0.231	1.72	2.72	4.62
2.44	0.284	2.68	3.90	6.02
2.71	0.259	1.93	3.14	4.25
2.96	0.231	2.81	3.61	3.74
3.22	0.264	2.56	3.27	4.37
3.48	0.256	2.63	2.52	2.57
3.74	0.258	1.80	2.74	2.41
4.01	0.282	2.96	4.08	3.07
4.29	0.291	2.31	2.11	1.18
4.58	0.291	2.46	2.32	1.30
4.87	0.287	2.45	3.31	1.36
5.17	0.308	2.26	3.12	1.00
5.49	0.343	3.30	2.77	0.79
5.81	0.291	2.55	2.69	0.51
6.19	0.456	3.80	3.37	0.51
6.60	0.362	2.68	2.83	0.32
6.92	0.289	1.84	1.86	0.10
7.20	0.275	2.54	1.62	0.11
7.45	0.218	1.99	1.24	0.07
7.48	0.253	1.00	1.20	
7.97	0.314	3.02	2.13	

TABLE XVIII (cont)

Average Distance Through Column (%)	Core Sampled (%)	^{35}Sr Removed (%)	^{137}Cs Removed (%)	^{133}Ba Removed (%)
8.30	0.347	1.74	1.30	
8.63	0.317	1.44	1.49	
8.93	0.296	2.15	1.07	
9.24	0.333	1.82	1.32	
9.56	0.352	2.36	1.37	
9.98	0.446	2.18	1.28	
10.5	0.518	2.18	1.03	
10.9	0.427	1.94	1.05	
11.4	0.527	2.03	0.73	
11.9	0.369	2.11	0.54	
12.2	0.393	2.02	0.53	
12.6	0.405	1.55	0.34	
13.1	0.436		0.37	
13.5	0.468	2.25	0.28	
13.9	0.400	1.65	0.25	
14.3	0.345		0.18	
14.7	0.366		0.19	
15.0	0.380		0.16	
15.4	0.410		0.12	
15.8	0.367		0.09	
16.2	0.421			
16.7	0.432			
17.1	0.481			
Remaining core		2.79	0.59	

moved 5.5% of the way through the column, indicating 4873 ml would be required to remove 50% of the ^{85}Sr . One-half of the cesium and barium had moved 3.74 to 3.86% and 1.35 to 1.56%, respectively. Therefore, 17 200 to 19 800 ml would be needed to remove 50% of the ^{133}Ba , and 6900 to 7200 ml would be needed to remove 50% of the ^{137}Cs . The sorption ratios calculated from the solid-core data are 690 ml/g for ^{85}Sr , ~1000 ml/g for ^{137}Cs , and 2600 ml/g for ^{133}Ba . The ranges of sorption ratios for strontium, cesium, and barium sorbed onto the same tuff in the form of wafers are quite large: 430 to 19 000 ml/g for ^{85}Sr , 1600 to 10 000 ml/g for ^{137}Cs , and 360 to 25 000 ml/g for ^{133}Ba . The R_d values for ^{85}Sr and ^{133}Ba , calculated from the solid core elution, fall within the range of measured wafer values. The R_d value for ^{137}Cs appears to be somewhat higher when measured by the wafer sorption technique. The very large ranges of sorption ratios on the Tunnel Bed tuff, measured by a variety of techniques on both crushed and intact material, make comparisons difficult. Such a large variability in experimental results from a single sample of tuff has not been found for other tuffs, such as those from Yucca Mountain and Well J-13 in Jackass Flats. The reasons for the large variations in the sorption studies on the Tunnel Bed tuffs from G-Tunnel are unknown.

VI. ACTINIDE SORPTION MEASUREMENTS

A. Uranium Sorption

Uranium sorption onto crushed Tunnel Bed tuff was measured as a function of the pH of the initial solution. The initial pH values were adjusted with hydrochloric acid or sodium hydroxide solutions. The tuff was from core U12G-RNM9, and the material was crushed to a particle size <355 μm . Both sorption and desorption R_d values were measured, and the contact times for each were 6 days. The tracer was uranyl nitrate with normal isotopic composition. After conclusion of the experiments, the uranium concentrations were assayed by neutron activation followed by delayed-neutron counting.

The results of this experiment are given in Table XIX. The variation in sorption ratios with pH may be the result of differences in the species of uranium present. For example, D. Langmuir⁸ reports the stability of a variety of uranium species at 10^{-2} atm CO_2 , ranging from UO_2^{2+} in acid solution through a series of neutral and anionic complexes to $\text{UO}_2(\text{CO}_3)_4^{4-}$ in the pH range investigated in this study.

TABLE XIX
U(VI) pH-ADJUSTED SORPTION RATIOS ON U12G-RNM9 CRUSHED TUFF

pH Value		R _d (ml/g)	
<u>Original</u>	<u>Final</u>	<u>Sorption</u>	<u>Desorption</u>
4.0	7.1	405	
4.0	6.3		2 400
6.0	7.8	137	
6.0	7.3		1 050
7.0	8.6	36	
7.0	8.6		83
8.0	8.7	18	
8.0	8.6		51
10.0	9.1	9	
10.0	8.8		43

B. Neptunium, Plutonium, and Americium Sorption

A series of sorption ratios measurements was undertaken to compare the results obtained when different experimental techniques were used with identical tuff samples and actinide tracer solutions. The tracers were contacted with the crushed tuff in two ways: (1) by using the conventional batch technique, in which the tuff and the tracer solution are shaken together in a closed bottle and (2) by using a pump to recirculate the tracer solution through a column of tuff, which is essentially a batch contact system without physical movement of the tuff. The two were compared to see if the physical contact of the tuff particles with each other during shaking in a batch experiment might produce finer particles that would give different sorption ratios than those obtained from a circulating system in which the tuff did not move.

The Tunnel Bed tuff used for these measurements came from core U12G-RNM9, 8.1 to 10.0 ft, crushed to 106 to 250 μm . The contact times were 3, 6, 9, and 12 weeks for sorption and 12, 9, 6, and 3 weeks for desorption, unless otherwise noted in the data tables. The tracer concentrations that were used were 1.6×10^{-11} M for neptunium, 4.8×10^{-12} M for plutonium, and 9.2×10^{-8} M for americium.

The sorption ratios for the circulating and batch comparisons are shown in Table XX. Contrary to expectations, the R_d value for sorption is higher both for plutonium and for americium in the circulating system than in the batch system. The reason for this observation is not known.

Another comparison was made between R_d values for neptunium measured in a batch system in air and those measured in a similar batch system in a controlled atmosphere. The data for this comparison are shown in Table XXI. The exclusion of oxygen and carbon dioxide resulted in higher R_d values both for sorption and for desorption than when they were measured in air.

TABLE XX
COMPARISON OF SORPTION RATIOS FROM CIRCULATING SYSTEM AND BATCH EXPERIMENTS

Tracer	R_d (ml/g)			
	Circulating System ^a		Batch ^a	
	Sorption	Desorption	Sorption	Desorption
Neptunium ^b	34 (2)	51 (3)	36 (2)	60 (3)
Plutonium ^c	820 (140)		300 (90)	
Americium ^d	3 100 (700)		800 (50)	

^aValues of duplicate analyses are given, with the standard deviations of the means in parentheses.

^bNeptunium batch measurements are for 3-week and 6-week contact times only.

^cPlutonium measurements did not include 9-week contact times, and the initial contact time for the circulating system was 4 weeks.

^dAmericium measurements for circulating system include 3-week and 6-week contact times only.

TABLE XXI
COMPARISON OF NEPTUNIUM BATCH SORPTION MEASUREMENTS
MADE IN AIR AND IN A CONTROLLED ATMOSPHERE^a

R_d (ml/g)			
Sorption		Desorption	
Air	CA	Air	CA
36(2)	71(4)	60(3)	100(3)

^aThe controlled atmosphere (CA) is nitrogen, <0.2 ppm oxygen, and <20 ppm carbon dioxide. The values in parentheses are the absolute-value standard deviations of the means.

VII. CALCULATIONS OF RADIONUCLIDE MIGRATION IN FRACTURED TUFF

These geochemical studies were part of a program to determine the extent of radionuclide migration during groundwater flow through a fracture in Tunnel Bed tuff. Therefore, theoretical studies of the consequences of groundwater flow through a fracture are of interest for this work. The results from two types of calculations are given in this section. The first type is based on a one-dimensional model of fracture flow plus matrix diffusion, and the second type of calculation includes velocity dispersion and porous flow in a three-dimensional tuff matrix.

A. One-Dimensional Fracture Flow with Matrix Diffusion

The importance of matrix diffusion during groundwater flow through a fracture in tuff was investigated in the following model study. The analytical solution for radionuclide transport of this type has been given by I. Neretnieks.⁹

Diffusion in the tuff matrix can be described by the following equation:

$$\frac{\partial C_p}{\partial t} = D_{app} \frac{\partial^2 C_p}{\partial z^2} - \lambda C_p \quad ,$$

in which

C_p = concentration of the radionuclide in the water in pores,

t = time,

$$D_{app} = \frac{D_{eff}}{K_d \rho} ,$$

$$D_{eff} = \varepsilon_p \frac{\alpha}{\tau^2} D^i ,$$

ε_p = matrix porosity,

α = constrictivity of the pores,

τ = tortuosity of the pores,

D^i = ionic diffusion coefficient,

$K_d \rho$ = volumetric sorption ratio, equal to $\varepsilon_p + (1-\varepsilon_p) K_d' \rho_s$,

K_d' = distribution coefficient,

ρ_s = density of the solid,

z = distance into the matrix from the fracture surface, and

λ = radioactive decay constant.

Sorption and convection are given by

$$\frac{\partial C_f}{\partial t} + U_f \frac{\partial C_f}{\partial x} = \frac{D_{eff}}{b} \frac{\partial C_p}{\partial z} \bigg|_{z=0} - \lambda C_f ,$$

in which the symbols not defined previously are

C_f = concentration of the radionuclide in the water in fissures,

U_f = water velocity,

x = distance along the fracture, and

b = half-width of the fracture.

The solution to these equations with the appropriate boundary and initial conditions for a concentration step of duration Δt is

$$\frac{C_p}{C_o} = e^{-\lambda t} \left(\operatorname{erfc} \left\{ \frac{G}{[t_w - (t_o + t)]^{1/2}} \right\} - \operatorname{erfc} \left\{ \frac{G}{[t - (t_w + t_o + \Delta t)]^{1/2}} \right\} \right),$$

in which

$$G = \left\{ \left[D_{\text{eff}} + \frac{1}{2} \frac{U_f(2b)z}{x} \right] / 2b(D_{\text{app}})^{1/2} \right\} t_w,$$

t_w = the time required for the water to reach x , and

t_o = the initial time.

The nominal parameter values chosen for use in these calculations are shown in Table XXII. These values were derived from the measured properties of Tunnel Bed tuff. The ionic diffusion coefficient value corresponds to that of strontium. This value is intermediate between the ionic diffusivities of most monovalent and divalent ions. Fissure apertures from 10 to 100 μm and flow velocities (U_f) from 1 to 100 m/day were used in the calculations.

Figure 1 shows the activity profile for a nonsorbing tracer, $K_d' = 0$, with a flow rate of 1 m/day after 300 days. Although the water has traveled 300 m, the activity has traveled only 9 cm. This result is caused by the loss of tracer to the rock matrix. In Fig. 2, tracer is shown to have penetrated far beyond 1 cm. This apparent retardation occurs because the concentration gradient is highest and the diffusion fastest at the tracer front; therefore, the activity in the leading edge is lost to the matrix until the concentration in the matrix builds up. Figures 3 to 6 show similar profiles at fluid velocities of 10 and 100 m/day. At 100 m/day the tracer begins to exit the 1-m fracture in 0.3 days, and at 10 m/day the tracer front ($C/C_o = 0.5$) moves 10 cm in 3 days.

Figures 7, 8, and 9 show the surface profile for sorbing tracers with a fluid velocity of 100 m/day. Tracers having K_d values $\leq 1000 \text{ ml/g}$ will move more

TABLE XXII
PHYSICAL PARAMETERS USED FOR MATRIX DIFFUSION
CALCULATIONS WITH TUNNEL BED TUFF

Parameter	Symbol	Value
Density	ρ	1.6 g/cm ³
Matrix porosity	ε_p	0.30
Constrictivity/tortuosity	α/τ^2	0.10
Ionic diffusion coefficient	D^i	$7.74 \times 10^{-10} \text{ m}^2/\text{s}$
Effective diffusion coefficient	D_{eff}	$2.71 \times 10^{-11} \text{ m}^2/\text{s}$

Fig. 1. Concentration profile on the fracture surface ($z = 0$).

Fig. 2. Concentration profile in the rock matrix ($x = 0.1 \text{ m}$).

Fig. 3. Concentration profile on the fracture surface ($z = 0$).

Fig. 4. Concentration profile in the rock matrix ($x = 0.1$ m).

Fig. 5. Concentration profile on the fracture surface ($z = 0$).

Fig. 6. Concentration profile in the rock matrix ($x = 0.1$ m).

Fig. 7. Concentration profile on the fracture surface ($z = 0$).

Fig. 8. Concentration profile on the fracture surface ($z = 0$).

Fig. 9. Concentration profile on the fracture surface ($z = 0$).

than 10 cm in 30 days. Figure 10 shows the effect of having a 100- μm fissure aperture. A larger aperture would make it possible to use tracers with much higher K_d values or to use slower fluid velocities. However, the latter may be the only option available if equipment design limits the flow rates that can be introduced into the fracture.

Some interesting relationships are evident in these calculations. (1) To a first approximation, the distance that a given tracer travels in some fixed time interval depends on the flow rate, independent of the aperture. (2) The distance that a given tracer travels in a fixed time interval varies as the square root of the K_d value for a fixed fluid velocity.

B. TRACR3D

A computer code named TRACR3D is being used to model transient air, water, and tracer flow in tuff in a three-dimensional geometry. This code incorporates such transport mechanisms as advection, molecular diffusion, and capillary action. Some of the results from the first calculation with this code are shown

Fig. 10. Concentration profile on the fracture surface ($z = 0$).

in Figs. 11-13. The problem is that of calculating tracer flow in a fracture when the tracer is injected into the fracture from a single borehole and is collected at eight sampling holes regularly spaced in a circular pattern 2 m from the injection point. The geometry of the problem is shown in Fig. 11, with the parameter values that were used. Symmetry reduces the calculation to that of flow in the 22.5° wedge that is shown.

The pressure distribution that would evolve in the horizontal fracture and in the tuff above it following 90 days of water injection is shown in Fig. 12. The plot shows pressure contours on a vertical-plane slice through the axis of the borehole at an angle of 0° from the front face shown in Fig. 11. The pressure drops rapidly because of the strong radial divergence. Figure 13 displays water saturation after 90 days in the same plane as Fig. 12. Water inflow remained virtually constant at 1.1 l/day. The plot shows that the matrix is saturated only to a radius of 1 m and a height of several centimeters. Capillary action has smeared the saturation front.

Additional calculations will be performed to help guide the experimental fracture-flow nuclide migration program.

VIII. CONCLUSIONS

This laboratory study of Tunnel Bed 5 tuff was undertaken to measure geochemical properties pertinent for a radionuclide migration field experiment. The tuff occurs as a bedded ash fall. The x-ray diffraction studies showed that the tuff consists of 60 to 90% zeolitized material. The porosity was measured in the range 0.31 to 0.40. The median pore diameter is approximately 0.6 μm . The permeability of this tuff ranges from 1×10^{-18} to $9 \times 10^{-19} \text{ m}^2$.

The sorption characteristics of radioactive tracers were measured in experiments with crushed tuff, with tuff in the form of wafers, and with solid cores of tuff. The water used in these sorption determinations was NTS Well J-13 water that had been contacted with Tunnel Bed 5 tuff for a week, then filtered through 0.05- μm Nuclepore polycarbonate filters. Use of a filter with this small pore size was necessary to eliminate the fine particles that Tunnel Bed 5 tuff produced when contacted with water. The sorption ratio data from all the experiments can be generalized by grouping the tracers used into three categories: (1) tracers with high sorption ratios: ^{85}Sr , ^{137}Cs , and ^{133}Ba ; (2) tracers with intermediate sorption ratios: ^{54}Mn , ^{113}Sn , ^{152}Eu , and ^{237}Pu ; and (3) tracers with low sorption ratios: ^{75}Se , ^{95}Tc , ^{131}I , ^{238}U , and ^{235}Np . These results are about what one would expect for a zeolitized tuff.

Fig. 11. Cylindrical geometry used in three-dimensional flow calculations.

Fig. 12. Pressure contours 90 days after start of water injection.

Fig. 13. Water saturation contours 90 days after start of water injection.

What was unexpected in the results of these laboratory measurements was the poor reproducibility of the data in comparison to sorption ratio measurements with other tuffs. The poor reproducibility may be related to the tendency of the Miocene tunnel bed tuff to form fine particles when contacted with water. The order of magnitude differences in sorption ratios for some of the results in similar experiments are otherwise inexplicable.

These laboratory studies indicate that Tunnel Bed 5 tuff would be of questionable suitability for a fracture-flow nuclide migration field experiment. The primary purpose for the field experiment is to validate computer models of radionuclide sorption under fracture-flow conditions. Field tests that would be as irreproducible as these laboratory studies would be of limited use in providing experimental verification of model predictions.

Theoretical studies of the consequences of groundwater flow through a fracture were undertaken with two computer codes. A one-dimensional calculation of fracture flow plus matrix diffusion indicated that, to a first approximation, the distance that a given tracer travels in a fixed time interval depends on the flow rate, but not the size of the fracture aperture. Furthermore, the distance that a tracer travels in a fixed time interval varies as the square root of the K_d value for a fixed fluid velocity. The first results, from a three-dimensional calculation for a material saturated only to 85% with groundwater, showed the difficulty of performing a fracture-flow experiment because of capillary action, which resulted in adsorption of the water in the fracture.

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