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Informal Report

Sorption-Desorption Studies on Tuff

I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada

University of California

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CONTENTS

SORPTION-DESORPTION STUDIES ON TUFF

I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada

by

K. Wolfsberg, B. P. Bayhurst, B. M. Crowe,
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ABSTRACT

Distribution coefficients were determined for sorption-desorption of radionuclides between each of three different types of tuff from drill hole J-13 at the Nevada Test Site and water from that well. The measurements were performed under atmospheric conditions at 22°C and 70°C. Sorption ratios vary greatly with lithologic variety of tuff. A tuff high in zeolite minerals has high sorption ratios (in decreasing order) for Eu, Ba, Cs, and Am and intermediate ratios for Sr and Pu. A tuff high in glass shows very high ratios for Ba, Sr, and Cs, intermediate values for Am and Pu, and low values for Ce and Eu. A devitrified tuff similar mineralogically to a microgranite exhibits intermediate values for Ba, Cs, Am, and Pu and low values for Eu, Ce, and Sr. Values for Ru are low, and those for Mo, Sb, and I are very low or zero for the three types.

SUMMARY

The most important barrier to the movement of dissolved radionuclides by ground water in geologic systems is retardation due to interaction between the radionuclides and the geologic medium. This report summarizes investigations of the behavior of various radionuclides with three types of tuff from drill hole J-13 in Jackass Flats at the Nevada Test Site.

A batch technique was used for sorption and desorption measurements. One-gram quantities of crushed and sieved rock were equilibrated for at least two weeks with water from well J-13. Water to be traced with radionuclides was similarly pre-equilibrated for each type of tuff with crushed but unsieved rock.

Evaporated radionuclides were dissolved in this water. Twenty-milliliter portions of the traced water were shaken with the pre-equilibrated rock samples for various times. The mixture was separated by four separate centrifugings at 16 000 rpm, and the solutions were analyzed for radioactivity. Since there was loss of some of the nuclides to the containers in which the samples were shaken, it was necessary to assay the solid to obtain realistic values for those nuclides. The residues from the sorption experiments that contained sorbed nuclides were used for desorption experiments with the same technique.

Particle size ranges of 106 to 150 μm and 355 to 500 μm were used at ambient (22°C) and elevated (70°C) temperatures. Contact times ranged from ~7 to ~100 days, with an average sorption time of 30 days and an average desorption time of 38 days. The elements studied were Sr, Mo, Ru, Sb, I, Cs, Ba, Ce(III), Eu(III), Pu, and Am. The measurements were performed under atmospheric conditions.

The sorption ratio (R_d = activity per g solid/activity per mL solution) for a given radionuclide, lithologic variety of tuff, and temperature increases slowly with time. Phenomena such as interaction of rock surfaces with water, surface alteration, and diffusion into minerals might explain this observation. Sorption ratios for Ce and Eu are significantly higher when measured in desorption experiments than from the sorption experiments; ion-exchange alone cannot explain the sorption of those elements.

Sorption ratios increase with temperature. The differences in sorption ratios for the two particle-size ranges are relatively small, indicating that sorption on tuff occurs in a regime much smaller than the surface of the sieved particles.

Sorption ratios vary for the three types of tuff. We arbitrarily assign R_d values of about 0, 20, 100, 600, and 10 000 mL/g to lower boundaries of the classifications "very low," "low," "intermediate," "high," and "very high," respectively. These correspond to the following percentages of a nuclide sorbed from ground water under our experimental conditions: 0%, 50%, 83%, 97%, and 99.8%, respectively. In the following discussion classifications are given for ambient temperature. For 70°C some sorption ratios are one grade higher.

A tuff sample that is high in zeolites and that contains no glass exhibits intermediate sorption ratios for Sr and Pu and high ratios for Cs, Ba, Eu, and Am. A sample containing mostly fresh glass has very high sorption ratios for the mono- and divalent ions of Sr, Cs, and Ba, intermediate ratios for Am and Pu, *and low ones for Ce and Eu. A partially welded, devitrified tuff sample (like a microgranite) shows low values for Sr, Ce, and Eu, and intermediate values for for Cs, Ba, Pu, and Am. The vastly different mineralogy of these three types of tuff is probably responsible for the large variation. More work may make it possible to predict sorption ratios from the mineralogy of samples of tuff.*

Sorption ratios for I, Sb, Mo, and U, which are anionic or form soluble complexes, are very low or zero. Those for Ru are low.

Sorption ratios for Pu and Am are very dependent on the method of preparing the solutions containing these elements.

I. INTRODUCTION

The suitability of tuff for the isolation of radioactive waste is being investigated as part of the Nevada Nuclear Waste Storage Investigations. Tuff is a general name applied to pyroclastic rocks composed of particles fragmented and ejected during volcanic eruptions. Samples of tuff may exhibit a wide range of properties depending on their cooling and alteration history. Many of their properties are discussed in Ref. 1. It is known that zeolites, which are present in some types of tuff, present frameworks for retaining many cations.[2]

A necessary consideration for any geologic repository is the possible dissolution of radionuclides from the waste and subsequent transport to the biosphere by ground water. Sorption of radionuclides by the rock can be a significant factor in retarding such transport. Thus, it is necessary to have an understanding of the mechanisms and phenomenology of the sorption-desorption behavior of the radionuclides that are biologically hazardous. Such knowledge will contribute to the prediction of the fate of the radionuclides during the length of time required for the waste to decay to safe levels.

This report presents the results of initial laboratory investigations of the sorptive properties of tuff with a variety of lithologic types of tuff that were obtained from a drill hole at the Nevada Test Site (NTS). Although this study is being conducted primarily as part of the evaluation of the feasability of tuff as a waste-isolation medium, the data will also provide input to a large, general sorption-desorption data bank[3] needed for a variety of representative geologic media.

The parameter most commonly used for describing equilibrium sorption-desorption ion-exchange reactions is the distribution coefficient, K_d (see, for example, Ref. 4). K_d is defined as the concentration per gram of a species on a solid phase divided by its concentration per milliliter in the liquid phase at equilibrium. This parameter is being used to describe the sorption behavior of radionuclides in geologic systems, (see, for example, Refs. 5 and 6) even though equilibrium may not have been established. It is used widely in transport assessments.[3]

II. GEOLOGIC MATERIAL PROPERTIES

The tuff samples were obtained from drill hole J-13[7,8] located in Jackass Flats, Nevada. Water used in these studies came from this well.[7,9,10]

A. Mineralogy.

The three tuff types chosen for these studies came from depths of 433 m (JA-18), 772 m (JA-32), and 1 066 m (JA-37). The sample designations JA-18, JA-32 and JA-37 will be used throughout this report.

Sample JA-18 was obtained from the basal part of the Topapah Spring Member of the Paintbrush Tuff. The sample is a partially welded, vitric lithic ash-flow tuff. Pumice fragments show compaction while shard fragments are only slightly deformed, and delicate, bubble-wall textures are well preserved. Individual shards are oxidized and are pale brown in color. They are composed of largely unaltered glass fringed by a yellow, fibrous phase. Shard interiors are largely isotropic with only a very weak birefringence. The matrix of the tuff consists of a granular, light orange-brown phase that is probably an alteration product of fine-grained ash. Mineralogically, the tuff is a crystal poor rhyolite with trace amounts of sanidine, plagioclase, biotite, quartz, opaque minerals, and relatively abundant lithic fragments.

Sample JA-32 was obtained from the Bullfrog Member of the Crater Flat Tuff. It is a partially welded, devitrified, ash-flow tuff. Pumice fragments and shards are strongly deformed and the rock is partially welded and approaches dense welding. Both pumice fragments and shards are completely devitrified, and devitrification products are largely confined to fragment interiors. Mineralogically, the tuff contains primary amounts of sanidine, quartz, and plagioclase, with trace amounts of biotite and opaque phases.

Sample JA-37 was obtained from an unnamed unit stratigraphically underlying the Bullfrog Member of the Crater Flat Tuff. It may be an unrecognized unit of the Crater Flat Tuff; however, stratigraphic equivalents have not been recognized from surface geologic mapping. JA-37 is a zeolited ash-flow tuff. Pumice fragments appear to show slight compaction although shard fragments (where recognizable) appear undeformed. Glass fragments are completely altered to granular phases (zeolites). Mineralogically, the tuff is relatively crystal rich, containing over 12 percent (total phenocrysts) of sanidine, plagioclase and quartz.

The following detailed mineralogic-petrologic description of the samples is taken from Heiken and Bevier.[8] The results of their modal analyses are given in Table I.

TABLE I

PETROGRAPHIC MODAL ANALYSES OF SAMPLES

	Modes (Volume Percent)		
	JA-18	JA-32	JA-37
Phase			
Sanidine	0.6	3.3	3.0
Plagioclase	0.3	3.0	8.3
Biotite	0.3	1.0	0.3
Quartz	0.3	5.0	Tr
Opaque Min.	0.3	0.3	Tr
Lithic fragments	11.9	Tr	11.0
Glass			
Pale brown pyroclasts	26.9		
Colorless pumice	10.0		
Lt. orange-brown matrix	49.1		
Authigenic Phases			
Pale brown, finely crystalline		59.3	67.7
Colorless, finely crystalline		23.3	6.3
Calcite			0.7
Yellow-green, fibrous			0.3
Coarse, colorless vug filling	0.3		0.3
Spherulitic vug fill		3.7	
Void space		1.0	1.7
No. of points	300	300	300

Sample JA-18. (Depth - 433 m. Vitric-lithic tuff).

a. Description:

This tuff is composed mainly of slightly altered angular pyroclasts with low vesicularity and highly vesicular pumice pyroclasts. The glass of the angular pyroclasts is altered to a pale peach color, with thin colorless rims (colorless, fibrous phases). Pumice pyroclasts appear to be unaltered. Only traces of phenocrysts are present.

Cavities are filled with a colorless, granular phase.

b. Microprobe analyses:

Phenocrysts: K-feldspar.
Sanidine (Or_{65}).
Glass: See Table II.

c. X-ray diffraction (whole rock): glass, trace of heulandite.

Sample JA-32. (Depth 772 m. Crystal tuff).

a. Description:

This welded tuff is similar in most respects to sample JA-31 (see Ref. 8). Both authigenic phases (light brown, finely crystalline and medium crystalline,

TABLE II
MICROPROBE ANALYSIS OF JA-18 GLASS
Weight Percent

Oxide	Pale brown pyroclasts			Light orange-brown matrix		
BaO	0.00	.02	0.00	0.00	.02	0.00
$FeO+Fe_2O_3$	.73	.73	.83	.17	.35	.78
MnO	.07	.05	.06	.02	.01	.88
Na_2O	3.33	3.37	3.36	3.39	3.71	2.84
Al_2O_3	12.01	12.07	12.03	9.91	10.39	10.18
SiO_2	74.21	74.36	74.90	81.29	79.43	79.66
K_2O	5.78	5.73	5.86	2.59	2.59	3.11
CaO	.40	.42	.35	1.01	1.15	1.20
TOTAL	96.55	96.78	97.42	98.40	97.70	97.89
XH_2O	3.0	3.0	2.0	1.5	2.0	2.0

Identification: Rhyolite glass

colorless) are mixed, forming a homogeneous mosaic. Vug fillings, consisting of coarse, colorless phases are mainly concentrated within cracks.

b. Microprobe analyses:

Phenocrysts: Plagioclase (An_{28}).

Feldspar--sanidine (Or_{66}).

Authigenic phases: See Table III.

c. X-ray diffraction (whole rock): albite/sanidine, analcite, quartz, erionite.

Sample JA-37. (Depth - 1 066 m. Lithic tuff).

a. Description:

This tuff is composed of unwelded relict, 60-µm to 1-mm long, highly vesicular shards. Eleven percent of the rock is composed of altered lithic fragments, a few tens of micrometers to ten millimeters long. Included among the lithic fragments are andesite and older welded tuffs.

TABLE III
MICROPROBE ANALYSES OF JA-32
Authigenic phases

Oxide	Weight Percent: Pale brown, finely crystalline				Spherulitic vug fill	
BaO	0.02	0.02	0.00	0.09	0.25	0.16
Na_2O	1.63	1.08	0.12	0.06	5.41	5.90
Al_2O_3	1.10	1.61	0.45	0.32	17.91	18.32
SiO_2	76.44	90.78	94.74	97.94	59.29	62.56
K_2O	3.38	5.37	0.07	0.05	5.72	4.92
CaO	0.08	0.07	0.02	0.01	0.27	0.43
TOTAL	82.64	98.92	95.4	98.5	88.8	92.29
H_2O	16.0	-	-	-	11.0	7.0
Tentative identification	Mostly zeolite and SiO_2	Mix, mostly SiO_2	Mix, mostly SiO_2	SiO_2	Erionite	Erionite

The glass has been replaced by microcrystalline (2-5 μm) granular phases that range in color from pale brown to colorless. Voids between shards have been filled with pale brown, granular (<2 μm diameter) phases that exhibit low birefringence and calcite.

b. Microprobe analyses:

Phenocrysts: Plagioclase--range from An_{18} to An_{42}. Some of the feldspars may be xenocrysts; not surprising in a tuff rich in lithic fragments.

K-feldspar--Sanidine (Or_{87}).

Authigenic phases: SiO_2--Authigenic quartz or cristobalite (very fine grained). See Table IV.

c. X-ray diffraction (whole rock): quartz, clinoptilolite, sanidine, montmorillonite, calcite.

TABLE IV

MICROPROBE ANALYSIS OF PALE BROWN, FINELY CRYSTALINE PHASE OF JA-37

Oxide	Weight Percent
BaO	.37
FeO	.69
MnO	0.00
Na_2O	.47
Al_2O_3	14.29
SiO_2	61.56
K_2O	7.74
CaO	.46
TOTAL	85.62
XH_2O	15.00

Identification: Clinoptilolite

The samples were reduced in size with hammers, with a Braun Chipmunk apparatus, and finally with a pulverizer having the plates set to produce a maximum grain size of about 1 mm. Each material was graded by use of Tyler sieves (ASTM E-11 specification) into the following size fractions: >500 μm, 355-500 μm, 250-355 μm, 180-250 μm, 150-180 μm, 106-150 μm and <106 μm. The 106 150 μm and 355-500 μm fractions were selected for subsequent use in these sorption studies. The fractions were washed briefly with deionized water to remove dust, dried in air, pumped on in a vacuum desiccator containing Drierite for one hour, and dried in the desiccator for two days.

B. Cation Exchange Capacity

The cation exchange capacity (CEC) of each of the 106-150 μm and 355-500 μm fractions selected for study was measured using both cesium and strontium. The measurement was made[11] by shaking weighed 100-mg portions of the solids with 20 mℓ of ~0.5 M CsCl (pH = 8.2) or ~0.5 M $SrAc_2$ (pH = 8.5) in deionized water for 8-14 days. The solutions were spiked with ^{137}Cs and ^{85}Sr, respectively, and the cation concentrations were determined by atomic absorption spectrophotometry. After the appropriate contact time the phases were separated by centrifugation, the solids were washed briefly with water, and were counted with a NaI(Tl) detector to ascertain the amount of strontium or cesium that had exchanged. The results from these measurements, given in Table V, are based on duplicate analyses

TABLE V
CATION EXCHANGE CAPACITY AND SIEVE ANALYSIS

Sample	Mesh Size (μm)	Cation Exchange Capacity (meq/100g) Cs	Sr	Particle Size Distributions (μm) Range	Median	Semi-inter-quartile Range
JA-18	106-150	75	48	106-210	137	12
JA-18	355-500	80	44	300-595	426	38
JA-32	106-150	2	2	90-210	127	15
JA-32	355-500	2	3	300-595	449	30
JA-37	106-150	17	63	106-210	128	14
JA-37	355-500	18	30	300-595	439	36

that agree within 20%. The CEC values for the JA-32 samples are low as might be expected from the similarity of this rock to granite.[12] Those for cesium on the JA-37 samples are in the same range as the CEC values for argillite[13] and alluvium.[11] The CEC values for strontium on the JA-37 samples and for both cations on the JA-18 samples are large as has been observed for the clay bentonite.[11] The difference between the CEC values for Cs and Sr on the JA-37 sample may be related to the presence of calcite in this rock. There is no great dependence of the CEC on particle size, indicating that the internal area of the particles must play a major role in sorption for tuff.

C. Size Distribution Analysis

The size distributions of the particles in the selected fractions were measured by screening techniques.[14] For the range data, the sizes of the smallest screens through which 100% of the material passed were not recorded. However, the screen size listed in Table V as the upper bound for each sample is the size immediately larger than the size recorded as having collected the largest particles in a sample. The median values in Table V were calculated by linear interpolation between screen size data that most closely bracketed the median mass. Similarly, the upper and lower quartile values were calculated by linear interpolation between the screen data that immediately bracketed the 75% and 25% mass values, respectively. The semi-interquartile range as defined by Cramer[15] is a measure of the dispersion of the particle size distribution.

D. Surface Areas

The surface area of the fractions has been determined by two different techniques, the BET method[16] and the ethylene glycol method.[17, 18, 19] The values are summarized in Table VI. The BET method employed nitrogen as the absorbate.[14] The equilibrium ethylene glycol procedure[17, 18] consists of wetting a dried and weighed sample of calcium saturated material with glycol. This is then followed by equilibration in an evacuated desiccator containing an anhydrous calcium chloride-ethylene glycol solvate. The equilibration is repeated until the weights become constant. This presumably indicates that only a monolayer remains.

E. Ground Water Properties

Water was obtained from well J-13 in December 1978. Waters pre-equilibrated with the appropriate tuff were used in most of the sorption measurements. They

TABLE VI
SURFACE AREA MEASUREMENTS

Sample	Mesh Size (μm)	Surface Area (m^2/g) BET	Glycol
JA-18	106-150	7.54	31
JA-18	355-500	6.55	46
JA-32	106-150	3.28	8
JA-32	355-500	2.62	9
JA-37	106-150	9.97	94,115
JA-37	355-500	7.60	131

were prepared by contacting J-13 water for at least two weeks with ground material that had not been sieved, the solution volume to solid ratio was 20 (v/w). The phases were separated by centrifugation at 7 000 rpm and then by filtration through a 0.45 μm Nuclepore filter paper. This procedure was used for preparation of waters pre-equilibrated at ambient temperature (22 ± 2°C) and at elevated temperature (70 ± 1°C). Fresh water was used with the same rock phase in all subsequent batches. Selected batches of the water were sent to the U. S. Geological Survey for analysis, and the results are given in Table VII. Several analyses were also performed at Los Alamos by atomic absorption spectroscopy for calcium, magnesium, potassium, and sodium; these results agreed with those in Table VII within ~10%.

The J-13 water had a pH value of ~7.3 when it was pumped from the well. The pH gradually changed to ~8.4 over a period of two to three months in Los Alamos in a bottle with open space above the liquid. The pH tended to rise to values of 8.5-8.6 while stirring or shaking. Waters equilibrated with JA-18, JA-32, and JA-37 samples assumed pH values of 8.28, 8.63, and 8.32, respectively, at 22°C and values of 8.26, 8.49, and 8.42, respectively, at 70°C.

F. Mineralogic Changes

The samples of ground tuff used for preparing the pre-equilibrated ground water (Section E) were analyzed[20] before and after about 90 days of this treatment by powder x-ray diffraction analysis to look for mineralogic changes due

TABLE VII

WATER ANALYSES

	J-13 Well		JA-18[a]			JA-32			JA-37		
	12/77	4/78	I,22°	III,22°	I,70°	I,22°	III,22°	I,70°	I,22°	III,22°	I,70°
	mg/ℓ										
Barium	0.200	0.200	0.300	0.300	0.300	0.300	0.300	0.300	0.300	0.200	0.300
Calcium	13.	13.	5.8	7.0	2.0	7.2	13.	4.0	8.9	13.	5.2
Iron	0.0	0.0	4.8	3.8	0.82	0.5	0.16	0.05	0.04	0.05	0.02
Lithium	0.05	0.05	0.06	0.05	0.05	0.06	0.05	0.05	0.06	0.05	0.05
Magnesium	2.0	2.0	0.01	0.2	0.0	0.8	1.9	0.2	0.9	1.6	0.3
Potassium	4.7	4.7	6.9	6.9	10.	6.0	5.5	6.0	8.6	6.2	5.6
Sodium	47.	50.	60.	55.	61.	60.	49.	62.	65.	52.	64.
Strontium	0.06	0.04	0.00	0.01	0.00	0.05	0.05	0.03	0.10	0.17	0.70
Bicarbonate	130.	130.	130.	130.	130.	130.	130.	130.	160.	150.	140.
Carbonate	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
Chloride	7.7	7.5	7.7	7.4	7.6	7.8	7.3	7.6	7.5	7.2	7.6
Fluoride	1.7	1.7	1.9	2.2	2.1	1.7	2.3	1.8	2.3	2.2	2.4
Sulfate	21.	20.	24.	21.	21.	21.	19.	20.	19.	19.	20.
	meq/ℓ										
Total Cations	2.98	3.10	3.08	2.94	3.01	3.19	3.08	3.07	3.57	3.30	2.94
Total Anions	2.88	2.85	2.95	2.90	2.89	2.88	2.85	2.86	3.11	3.17	2.90

[a] I,22° stands for J-13 water equilibrated with JA-18 tuff, first equilibration at 22°C.

to hydrothermal alteration during our experiments. No change in the x-ray pattern was observed for sample JA-32. A small increase (<5%) in the clay montmorillonite was observed for sample JA-37, and a slight increase (<1%) in the zeolite clinoptilolite was observed for sample JA-18.

III. SORPTION OF STRONTIUM, CESIUM, BARIUM, CERIUM, AND EUROPIUM

A. Measurement Techniques

1. Preparation of Traced Solutions

The traced waters were prepared using the pre-equilibrated waters described previously and the following commercially available, carrier-free or high-specific-activity radionuclides: ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce (except for the JA-37 experiments), and ^{152}Eu. The appropriate volumes of tracers needed for a set of measurements were evaporated to dryness in a washed polyethylene tube overnight on a steam bath. Concentrated hydrochloric acid was added, and the mixture was taken dry again in order to convert the salts to chlorides. The appropriate volume and type of pre-equilibrated ground water was added, and the mixture was stirred for ~1 hr. The mixture was centrifuged for one hour at 16 000 rpm, followed by filtration through a 0.45 μm Nuclepore filter. The resulting tracer solution was used for the sorption measurements within 0.5 day. An aliquot of this final solution was used for assay (Section 4) of the initial activity of each of the tracers in the solution. This aliquot was acidified with hydrochloric acid before counting in order to stabilize the solution. During the tracer preparation, no cesium, strontium, or barium was lost, but about 50% of the cerium and europium was lost on the filter.

The activities and elemental concentrations of the tracers are given in Table VIII. The concentrations are based only on the specific activities provided by the suppliers. Additional amounts may be naturally present in the pre-equilibrated waters; these will be measured in the future by neutron activation analyses.

2. Sorption Measurements

Batch sorption experiments were performed by shaking weighed one-gram quantities of the crushed rock with 20 mℓ of untraced, pre-equilibrated water for a period of two weeks at ambient temperature (22°C) or 70°C, as appropriate. The samples were contained in stoppered 40-mℓ polyethylene centrifuge tubes at

TABLE VIII

ACTIVITIES OF TRACED WATER AND ELEMENTAL CONCENTRATIONS[a]

	^{85}Sr		^{133}Ba		^{137}Cs		^{141}Ce		^{152}Eu	
	µCi/mℓ	M	µCi/mℓ	M	µCi/mℓ	M	µCi/mℓ	M	µCi/mℓ	M
JA-18 (22°)	0.028	1.1×10^{-6}	0.048	4.4×10^{-8}	0.15	1.1×10^{-8}	0.095	1.1×10^{-6}	0.25	6.2×10^{-7}
JA-18 (70°)	0.026	1.0×10^{-6}	0.054	5.0×10^{-8}	0.16	1.2×10^{-8}	0.072	8.5×10^{-7}	0.11	2.9×10^{-7}
JA-32 (22°)	0.032	1.2×10^{-6}	0.052	4.8×10^{-8}	0.016	1.2×10^{-9}	0.065	7.7×10^{-7}	0.22	5.5×10^{-7}
JA-32 (70°)	0.032	1.2×10^{-6}	0.052	4.8×10^{-8}	0.021	1.6×10^{-9}	0.084	9.9×10^{-7}	0.25	6.2×10^{-7}
JA-37 (22°)	0.022	8.8×10^{-7}	0.064	6.0×10^{-8}	1.9	1.4×10^{-7}	---	---	0.133	3.3×10^{-7}
JA-37 (70°)	0.017	6.5×10^{-7}	0.054	5.0×10^{-8}	0.51	3.9×10^{-8}	---	---	0.039	9.7×10^{-8}

[a]Elemental concentrations are only those added with tracer.

ambient temperature or in screw-cap polypropylene tubes at elevated temperature. All tubes were washed with deionized water prior to use. The phases were separated by centrifuging at 16 000 rpm for one hour. It was assumed[11,12,13] for the calculations that 1 mℓ of this solution remained with the solid. Twenty milliliters of the tagged pre-equilibrated water was then added, the solid sample was dispersed with vigorous shaking, and the mixture was agitated gently for a given time. Contact times varied from 6 to 71 days. The shaking rates were 200 oscillations per minute for the ambient temperature studies, and 80 oscillations per minute for the 70°C samples. A water-bath shaker was used for the latter studies. At the end of the shaking period, the aqueous phase was separated from the solids by four centrifugings, each in a new polyethylene centrifuge tube, each for one hour at 16 000 rpm. An aliquot of the final solution was removed and placed in a standard scintillation counting polyvial. This solution was acidified with hydrochloric acid, and it was then assayed for the remaining activities. The pH values of the solutions before and after contact with the rock were also recorded.

All solutions remaining from the sorption measurements, including the solution used for radioactivity assay, have been stored for future measurement of the final concentration of the major cations. These analyses will be performed using a multichannel, direct reading emission spectrograph utilizing a direct-current, argon-plasma excitation source. The procedures for these analyses are being developed on a Spectrometrics, Inc., model 3 spectrograph.

The same sorption procedure was also performed using a tube that did not have a solid phase present. This control sample was used only to indicate if any of the radionuclides were likely to be removed by the container. In most cases (Section 5), the strontium, cesium, and barium remained essentially completely in solution. However, not all of the cerium and europium remained in solution. We feel that the amount of sorption on the container will vary, depending on whether or not solid material is present, because these elements appear to sorb on any available surface. Therefore, the presence of a solid phase will tend to reduce the fraction of the activity sorbed on the container.

In order to determine the amount of activity of Eu and Ce remaining with the solid phase, whether due to sorption, precipitation, centrifugation of a colloid with the solid, or by some other mechanism, a fraction (~5%) of the solid was removed for radioactivity assay. The solid phase was well mixed prior to sample removal. The fraction of the solid removed was determined from the activities of ^{137}Cs, ^{133}Ba, and ^{85}Sr in the solid aliquot, in the depleted solution, and in the initial solution. This method is reasonable because Cs, Sr, and Ba did not sorb on the container walls. An initial estimate was made by weighing the sample.

3. Desorption Measurements

Desorption measurements were made for samples previously used for the sorption measurements. The assay of the activity on the solid was done as described earlier. Twenty milliliters of untagged, pre-equilibrated water were used for each measurement. The same procedure that was used in the sorption measurements was used for separation of the phases and for radioactivity assay. Desorption contact times varied from 10 to 101 days.

4. Assay of Radioactivity

The samples were counted on an ultra-low-background mount, 95-cm^3, 18.5%, calibrated, coaxial Ge(Li) detector. The 4096 channel spectra were recorded in a multichannel analyzer connected to a PDP-9 computer, where they were analyzed on-line by RAYGUN, a gamma-ray spectroscopy program.[21] This program is designed for use on a minicomputer, and it includes spectral interpretation. Its operation involves: 1) a search for background and peak (non-background) regions; 2) a preliminary peak search in the nonbackground regions; 3) construction of a step function under the peak(s) in each region; 4) construction of an underlying continuum by smoothing the background together with the step functions; 5) a search for peak regions and peaks with stricter criteria; 6) determination of peak positions and areas, and correction for photopeak efficiency; if a multiplet is encountered, separation of the peaks by using peak shape information; 7) a search of the appropriate gamma-ray branching ratio library to find those nuclides represented by gamma rays that appear to be in the spectrum, eliminating those that are not plausible; 8) set up an interference matrix $[A_{ij}]$, where A_{ij} = branching ratio for i^{th} peak indentified corresponding to j^{th} nuclide identified; 9) by a least-squares iteration determine a solution to

$$Y_i = \sum_j A_{ij} X_j \qquad (1)$$

where Y_i = observed intensity of i^{th} peak and X_j = disintegration rate for j^{th} nuclide; 10) correction of the disintegration rate observed for each radionuclide at the counting time to a specified time; 11) performance of an error analysis;

and (12) output of the results in suitable form. A minimum of two counts, separated by at least one day, were taken for each sample. The results from the RAYGUN analyses for each count were simply averaged prior to use.

In general, samples were counted long enough so that the standard deviations of the activities were less than 3%. In the case of ^{133}Ba for the JA-32 samples where $R_d > 20\,000$, the uncertainty was 15 to 20%.

5. Control Samples and Container Effects

The control samples generally indicated that strontium, cesium, and barium remained in solution. Aliquots of the control solutions were withdrawn for counting immediately after the contact period and again after the centrifugations. Table IX gives comparisons of the activities in the control samples with that of the original feed for the ambient temperature experiments with JA-32 samples. It is seen that for Ce and Eu a large fraction of the activity is lost on centrifugation.

TABLE IX

FRACTION OF ACTIVITY REMAINING IN CONTROL SOLUTIONS[a]

Time(days)	Sr	Cs	Ba	Ce	Eu
		Before Centrifugation			
9.6	1.02	1.01	0.99	1.03	0.90
21.0	1.00	1.00	0.98	0.94	0.97
33.9	1.03	1.03	0.94	0.92	0.95
55.0	0.97	0.98	0.91	0.92	0.84
		After Centrifugation			
9.6	1.02	1.02	0.92	0.16	0.36
21.0	1.03	1.03	0.90	0.13	0.32
33.9	1.00	0.99	0.89	0.17	0.38
55.0	0.95	0.92	0.79	0.21	0.39

[a]For sorption experiments with JA-32 blank controls at ambient temperature.

The total activity accounted for between the solid and the solution for the JA-32 samples, assuming an average value of 1.00 for Sr, Cs, and Ba, is given in Table X. Again, some of the Ce and Eu is lost; however, there is no apparent correlation with the losses in the control samples. The amount of sorption on the container may depend on the presence or absence of solids since these nuclides may sorb on any surface. The presence of solids could reduce the fraction sorbed on the container.

Similar effects were observed for the other control samples and actual samples, but the numbers are not tabulated in this report. It is evident that the distribution of Ce and Eu cannot be obtained from analyses of the solution phases and the control samples alone.

6. Calculations

The equilibrium distribution coefficient, K_d, for the distribution of activity between the two phases is conventionally defined as:

$$K_d = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}} . \qquad (2)$$

Under many conditions, it is not known whether equilibrium is achieved for the types of measurements reported here. However, the distribution of activities between the phases is measured, and throughout this report the resulting value is called the sorption ratio, R_d, which is otherwise identical to K_d, but does not imply equilibrium.

TABLE X

FRACTION OF ACTIVITY ACCOUNTED FOR IN SOLID PLUS SOLUTION[a]

Time(days)	Sr	Cs	Ba	Ce	Eu
9.6	1.02	1.00	0.98	0.62	0.76
21.0	1.01	1.21	1.04	0.56	0.88
33.9	0.92	1.05	1.01	0.50	0.77
55.0	0.82	1.23	0.95	0.31	0.48

[a]For sorption experiments with JA-32 samples.

For Sr, Cs, and Ba (and also I, Ru, Sb, and Mo) it was possible to obtain the distribution of activities between the solids and solutions by measurements of aliquots of the solution before and after the sorption experiments. The fraction of the activity, f, remaining in the liquid phase after contact with the solid is determined. Eq. 2 then becomes

$$R_d = \left(\frac{1-f}{f}\right)\left(\frac{m\ell \text{ of solution}}{\text{g of solid}}\right) . \qquad (3)$$

For the desorption experiments with Sr, Cs, and Ba tracers, Eq. 3 was also applied. Corrections were applied for the activity left in solution in the sorption experiment on an earlier desorption experiment, and for the amount of solid removed in the earlier experiment. It was again assumed that 1 mℓ of solution from the earlier experiment remained with the solid.

For Ce and Eu, the activity of the solid phase was used, and Eq. 2 was applied. Although the solids were weighed and counted in approximately the same geometry as the solutions, an exact correction for the entire solid sample in the solution geometry was applied. This factor was obtained for each experiment by comparing the activities of the Sr, Cs, and Ba tracers, for which no wall-sorption effects are assumed, in the solids with those expected from the measurements of solutions alone. This correction was usually less than 10%. The distribution coefficients for the desorption experiments were calculated similarly, taking into account the factors discussed for Sr, Cs, and Ba.

Error analysis was not performed in these calculations. Known errors in the sorption experiments due to counting, weighing, and pipetting uncertainties as well as that due to the assumption of the volume of liquid left with the solid in the previous operation should have contributed to an overall uncertainty of $\leq$10%, generally. For the sorption experiments with Ce and Eu tracers and the experiments with ^{133}Ba on the JA-32 samples, the uncertainties may be as high as 20%.

B. Results and Conclusions

The results of the sorption and desorption determinations for the three types of tuff at the two temperatures are given in Tables XI through XVI. The first three digits of an experiment number are the same for sorption and desorption experiments with the same sample. For example, experiment 5252 was a desorption experiment using the solid remaining from sorption experiment 5250.

TABLE XI

SORPTION RATIOS FOR JA-18 AT 22°C

Experiment	Time (days)	R_d (mℓ/g) Sr	Cs	Ba	Ce	Eu
355-500 µm						
	Sorption					
5250	12.7	8 850	10 300	2 340	20	14
5260	22.6	6 460	10 000	3 260	26	18
5270	44.6	5 820	18 900	7 150	41	26
5280	74.6	16 100	18 800	7 150	70	37
	Desorption					
5252	22.0	12 900	16 000	8 600	36	30
5262	37.9	5 540	16 600	22 800	110	74
5264	101.0	16 300	15 100	33 800	131	144
106-150 µm						
	Sorption					
5090	12.7	11 300	11 700	3 120	26	14
5100	22.6	12 600	13 400	4 510	46	30
5110	40.6	18 300	17 200	4 700	43	32
5120	74.6	21 600	19 500	6 620	78	66
	Desorption					
5092	22.0	21 200	21 600	24 300	116	116
5102	37.9	5 800	18 000	38 200	247	214
5104	101.0	13 700	15 400	40 000	437	353

TABLE XII

SORPTION RATIOS FOR JA-18 AT 70°C

Experiment	Time (days)	R_d (mℓ/g) Sr	Cs	Ba	Ce	Eu
355-500 μm						
	Sorption					
5170	11.6	19 400	20 600	34 500	40	61
5180	19.6	14 700	18 100	40 300	45	62
5190	32.6	22 200	18 700	75 100	41	76
5200	60.3	4 300[a]	19 000	61 100	42	89
	Desorption					
5172	12.6	22 200	21 500	90 800	237	442
5182	19.7	24 000	20 800	67 000	116	262
5192	42.0	17 100	21 300	150 000	223	504
5174	100.0	18 600	25 900	168 000	304	836
106-150 μm						
	Sorption					
5010	11.6	12 600	12 900	23 200	40	63
5020	19.6	22 200	21 000	29 400	36	76
5030	32.6	15 200	16 000	64 100	46	110
5040	60.3	4 700[a]	17 000	64 400	51	128
	Desorption					
5012	12.6	22 300	14 200	69 700	159	283
5022	19.7	30 400	16 600	105 000	350	776
5032	42.0	18 000	16 900	104 000	226	675
5014	100.0	16 700	16 800	107 000	552	---

[a]Not included in averages in Table XVII.

TABLE XIII

SORPTION RATIOS FOR JA-32 AT 22°C

Experi-ment	Time (days)	R_d (mℓ/g) Sr	Cs	Ba	Ce	Eu
355-500 µm						
	Sorption					
5570	9.6	50	105	263	66	48
5580	21.0	52	116	311	90	92
5590	33.9	56	137	368	90	88
5600	55.0	71	120	523	107	121
	Desorption					
5572	12.6	55	198	357	668	608
5582	26.8	52	153	388	489	602
5592	39.6	58	197	557	242	571
5602	80.6	72	175	695	641	783
106-150 µm						
	Sorption					
5410	9.6	48	118	372	43	51
5420	21.0	50	121	369	53	69
5430	33.9	72	125	421	48	73
5440	55.0	55	141	435	160	187
	Desorption					
5412	12.6	48	168	420	1 280	1 570
5422	26.8	41	229	439	344	597
5432	39.6	50	134	562	309	740
5442	80.6	50	147	514	243	1 300

TABLE XIV

SORPTION RATIOS FOR JA-32 AT 70°C

Experiment	Time (days)	R_d (mℓ/g) Sr	Cs	Ba	Ce	Eu
355-500 μm						
	Sorption					
5330	6.6	93	82	900	51	93
5340	13.6	106	85	1 040	61	132
5350	26.6	109	100	1 140	132	380
5360	52.6	144	101	1 570	174	134
	Desorption					
5332	11.6	80	89	1 050	750	1 730
5344	23.7	80	96	950	310	890
5334	20.9	107	99	1 610	1 140	1 070
5352	39.9	123	108	1 790	670	3 150
5362	15.8	70	102	1 210	800	3 970
106-150 μm						
	Sorption					
5490	6.6	82	82	563	53	118
5500	13.6	92	87	662	64	181
5510	26.6	121	118	940	64	217
5520	52.6	158	121	1 280	67	239
	Desorption					
5492	11.6	80	108	710	363	880
5504	23.7	113	104	940	602	1 530
5494	20.9	115	133	970	715	1 320
5512	39.9	144	127	1 270	584	1 600
5522	15.8	93	120	1 070	459	1 980

TABLE XV

SORPTION RATIOS FOR JA-37 AT 22°C

Experiment	Time (days)	R_d (mℓ/g) Sr	Cs	Ba	Eu
355-500 μm					
	Sorption				
5890	11.7	261	704	603	4 130
5900	21.7	250	485	659	4 010
5910	35.7	341	649	826	6 380
5920	70.7	259	747	757	6 880
	Desorption				
5892	13.0	303	880	835	6 010
5904	24.8	320	800	865	14 000
5894	26.8	277	952	893	6 740
5912	39.9	351	966	1 077	18 000
5906	87.3	322	1 100	994	18 300
105-150 μm					
	Sorption				
5730	11.7	298	525	696	2 090
5740	21.7	285	492	746	7 590
5750	35.7	256	505	712	7 260
5760	70.7	347	779	1 040	9 450
	Desorption				
5732	13.0	318	644	813	3 940
5744	24.8	351	804	1 010	7 720
7534	26.8	292	601	746	15 600
5752	39.9	265	716	905	16 700
5745	87.3	318	1 022	1 050	24 000

TABLE XVI

SORPTION RATIOS FOR JA-37 AT 70°C

Experiment	Time (Days)	R_d (mℓ/g)			
		Sr	Cs	Ba	Eu
355-500 µm					
	Sorption				
5810	5.6	655	1 140	1 650	2 060
5820	12.6	793	1 270	2 420	4 420
5830	24.6	1 010	1 350	3 430	4 510
5840	50.6	1 540	1 620	6 600	5 500
	Desorption				
5812	14.0	900	1 340	2 490	7 560
5822	21.6	1 130	4 730	4 420	12 000
5814	19.7	822	1 530	2 960	11 400
5832	40.7	1 520	1 790	6 290	18 600
5842	20.9	1 530	1 790	5 860	18 200
5824	89.3	1 780	4 430	9 920	12 600
106-150 µm					
	Sorption				
5650	5.6	772	1 060	2 000	3 950
5680	12.6	815	1 320	2 490	4 130
5660	24.6	1 210	1 380	4 150	4 000
5670	50.6	1 630	1 790	6 600	5 230
	Desorption				
5652	14.0	1 030	1 230	3 340	9 730
5682	21.6	1 200	4 580	4 760	7 660
5654	19.7	946	1 580	3 530	19 400
5662	40.7	1 870	1 530	7 560	16 900
5672	20.9	1 390	1 390	7 450	12 800
5684	89.3	1 930	5 840	12 000	23 900

The results are also plotted as a function of time in Figs. 1-28.

Although the times for desorption listed in the tables are for desorption alone, the sorption ratios for desorption are plotted at times representing the sum of the sorption plus desorption times. The values tend to fall on a smoother plot this way. There may be a slow interaction of tuff surfaces with the water, alteration of the surfaces, or diffusion of the ions into the minerals. Although most sorption ratios from the desorption experiments are slightly higher than those from the sorption experiments, those for Ce and Eu are usually much higher. This may indicate that Ce and Eu do not sorb by an ion-exchange mechanism or that there are non-sorbing species in the original mixture.

Average sorption ratios for (1) sorption, (2) desorption, and (3) both sorption and desorption were calculated from the results of each type of tuff at each temperature for (1) each particle size, and (2) for both particle sizes. Although it is recognized that the sorption ratios for different times and different conditions do not strictly belong to the same statistical population, the standard deviation of the population, σ_{pop}, was calculated for each set. This value is instructive in comparing the averages. The results of these calculations are given in Tables XVII through XXII. From these tables and figures we conclude that there are no major particle size effects for the tuff samples studied. In addition, the differences in the sorption and desorption values are no greater than the range of the experimental values for Sr, Cs, and, in most cases, Ba. Thus, the average values for these elements for all measurements can be used for modeling and screening purposes. Recommended average values are given in Section VI.

The measured pH values of the traced ground waters before (feed) and after the experiments and for the controls are given in Table XXIII. After shaking, most of the pH values fell into the 8.5 to 8.7 range.

Specific differences in the sorption ratios for the three types of tuff will be discussed in Section VI.

IV. SORPTION OF IODINE, MOLYBDENUM, RUTHENIUM, AND ANTIMONY

A. Measurement Techniques

The traced ground water was prepared by the same method as in Ref. 11. A tuff sample from Area 7 of the Nevada Test Site containing volatile fission products from an underground nuclear explosion was shaken with J-13 water for

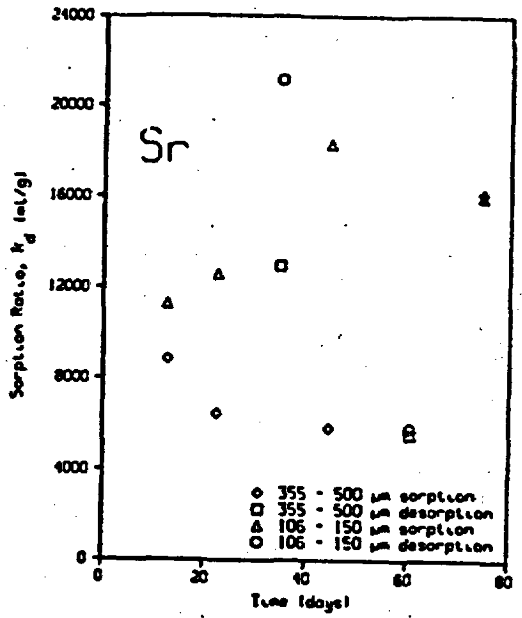

Fig. 1.
Sorption ratios for ^{85}Sr on sample JA-18 at 22°C.

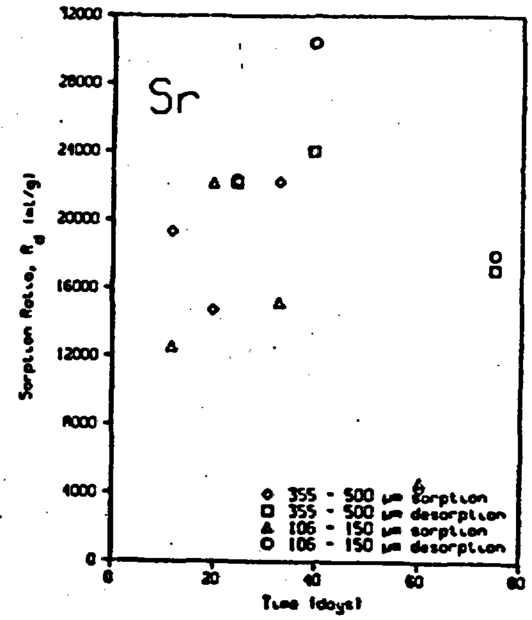

Fig. 2.
Sorption ratios for ^{85}Sr on sample JA-18 at 70°C.

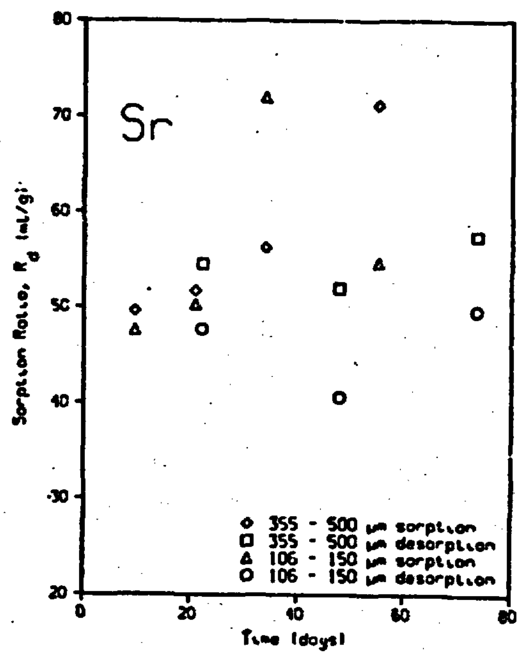

Fig. 3.
Sorption ratios for ^{85}Sr on sample JA-32 at 22°C.

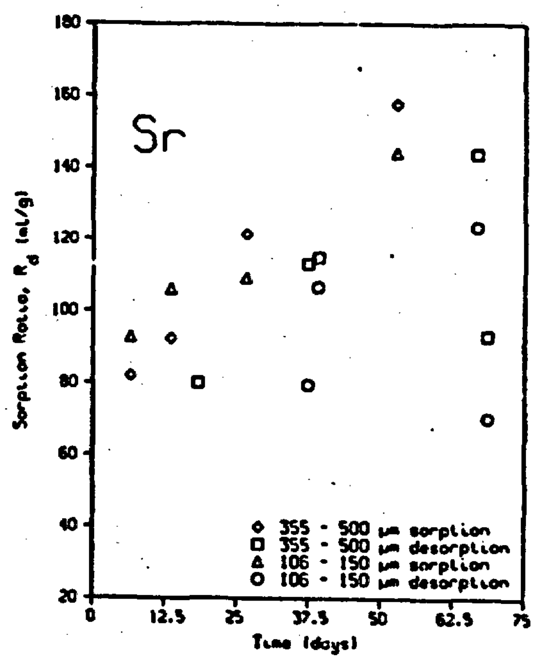

Fig. 4.
Sorption ratios for ^{85}Sr on sample JA-32 at 70°C.

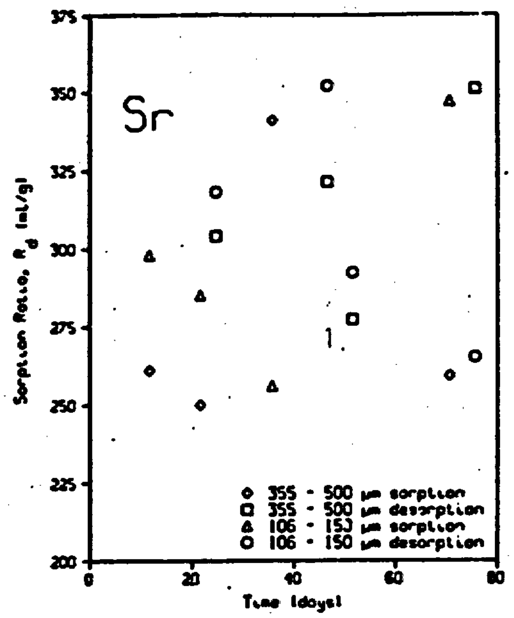

Fig. 5.
Sorption ratios for ^{85}Sr on sample JA-37 at 22°C.

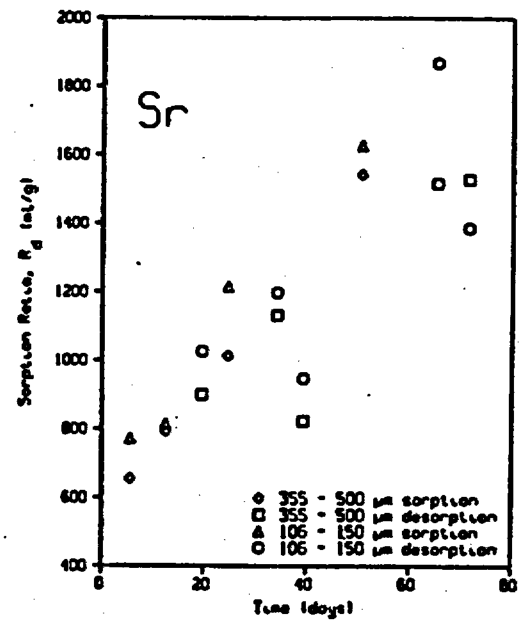

Fig. 6.
Sorption ratios for ^{85}Sr on sample JA-37 at 70°C.

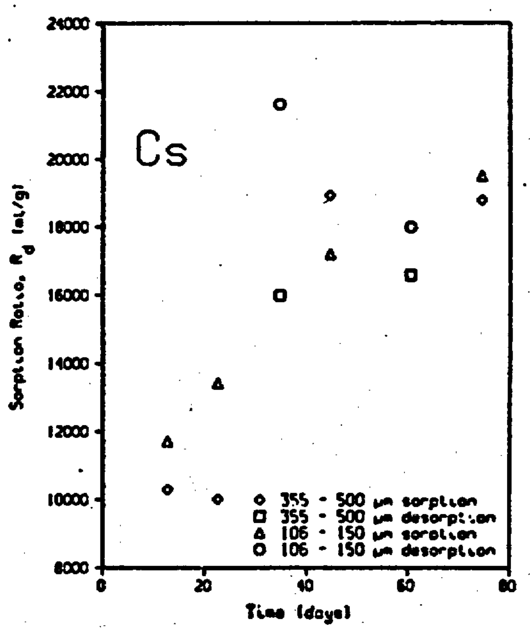

Fig. 7.
Sorption ratios for ^{137}Cs on sample JA-18 at 22°C.

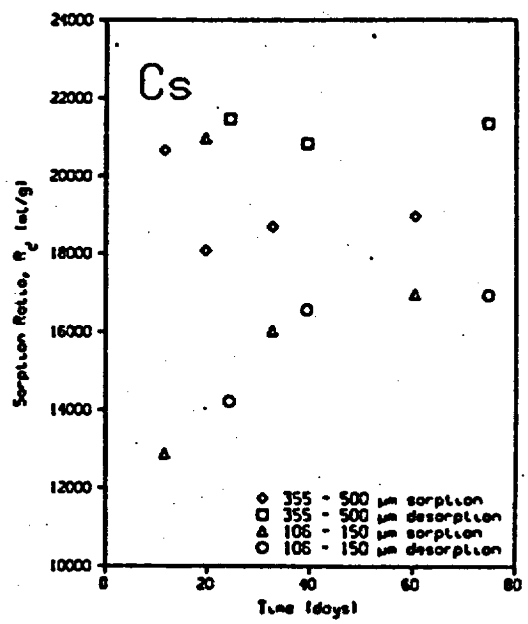

Fig. 8.
Sorption ratios for ^{137}Cs on sample JA-18 at 70°C.

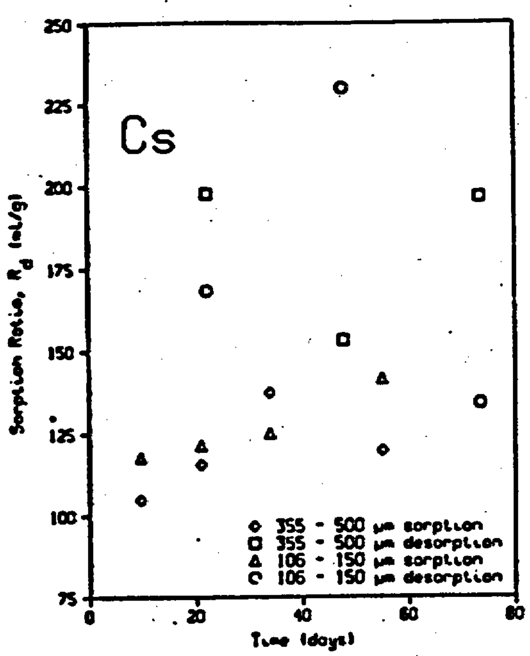

Fig. 9.
Sorption ratios for ^{137}Cs on sample JA-32 at 22°C.

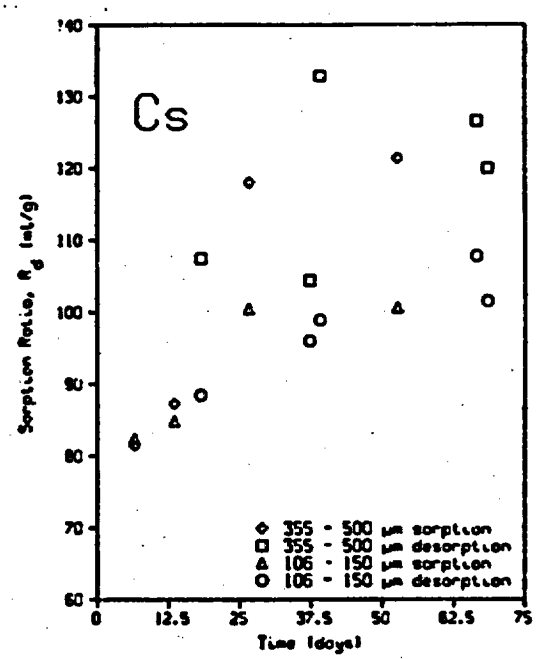

Fig. 10.
Sorption ratios for ^{137}Cs on sample JA-32 at 70°C.

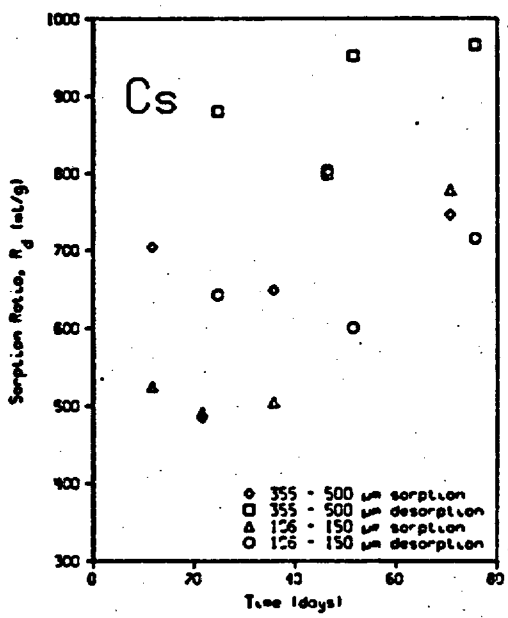

Fig. 11.
Sorption ratios for ^{137}Cs on sample JA-37 at 22°C.

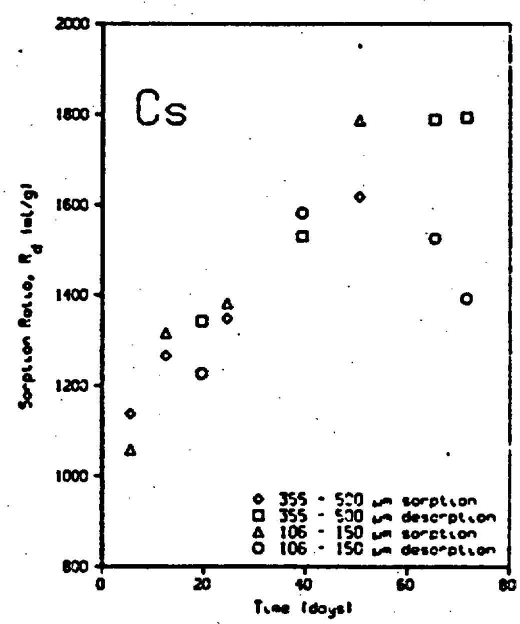

Fig. 12.
Sorption ratios for ^{137}Cs on sample JA-37 at 70°C.

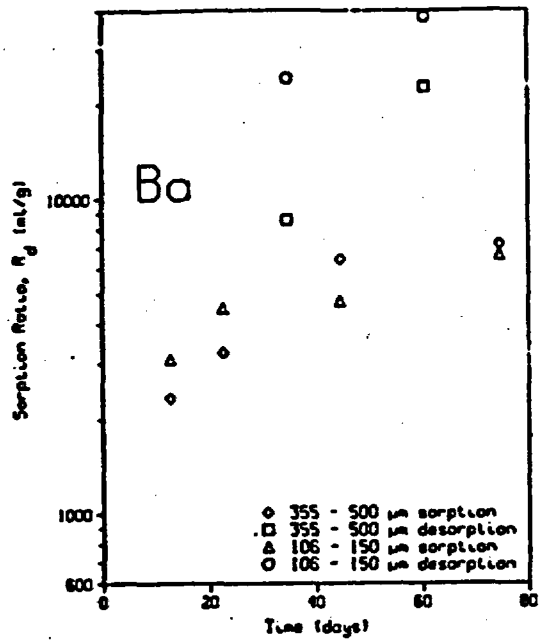

Fig. 13.
Sorption ratios for ^{133}Ba on sample JA-18 at 22°C.

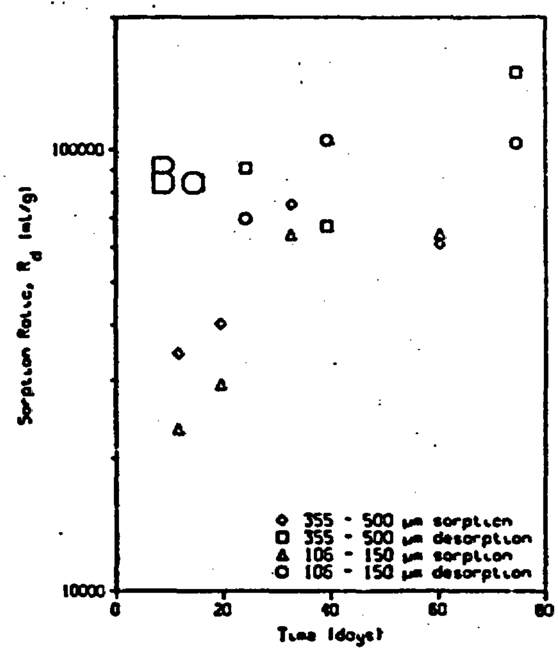

Fig. 14.
Sorption ratios for ^{133}Ba on sample JA-18 at 70°C.

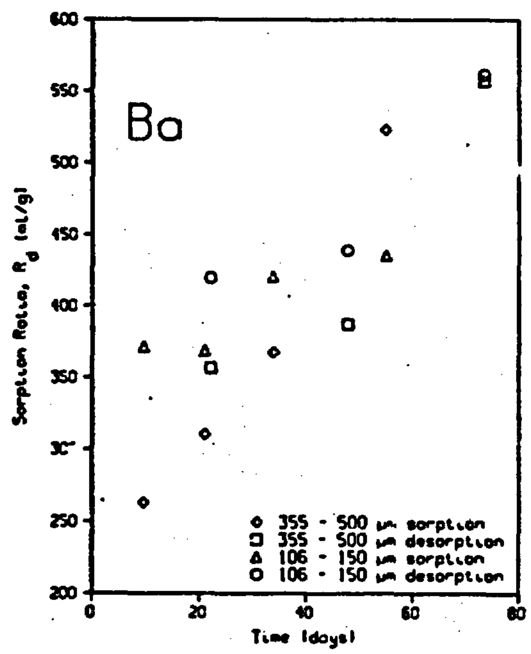

Fig. 15.
Sorption ratios for ^{133}Ba on sample JA-32 at 22°C.

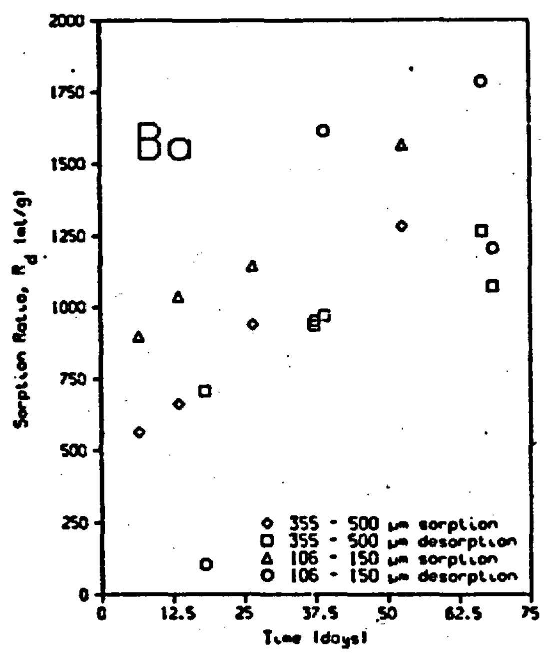

Fig. 16.
Sorption ratios for ^{133}Ba on sample JA-32 at 70°C.

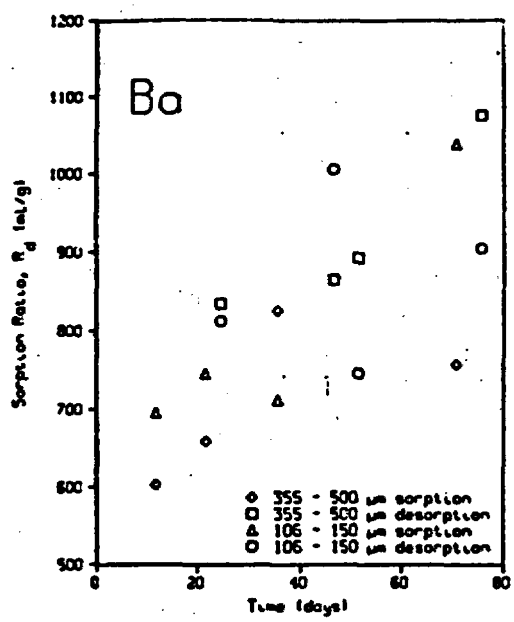

Fig. 17.
Sorption ratios for ^{133}Ba on sample JA-37 at 22°C.

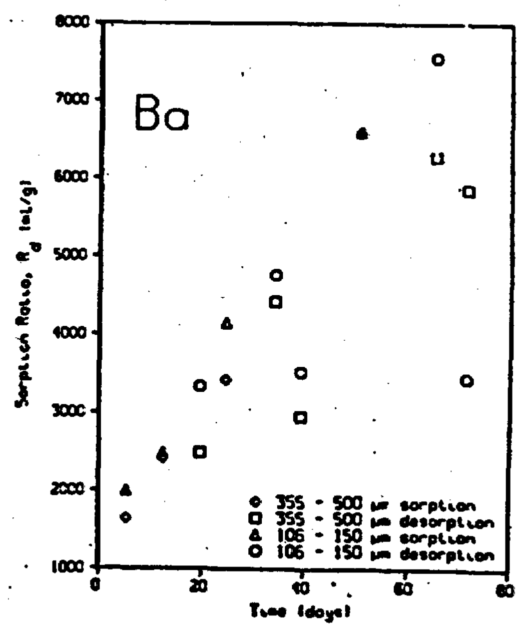

Fig. 18.
Sorption ratios for ^{133}Ba on sample JA-37 at 70°C.

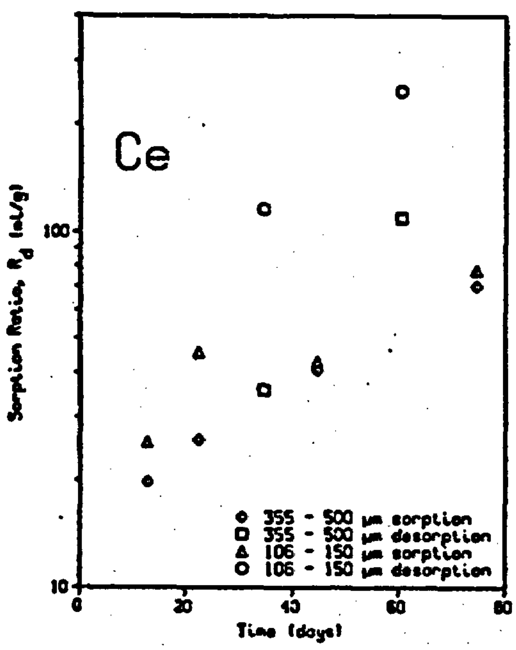

Fig. 19.
Sorption ratios for ^{141}Ce on sample JA-18 at 22°C.

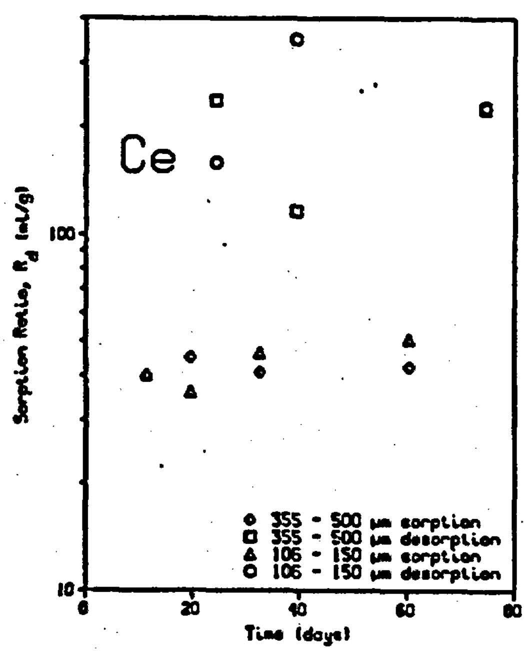

Fig. 20.
Sorption ratios for ^{141}Ce on sample JA-18 at 70°C.

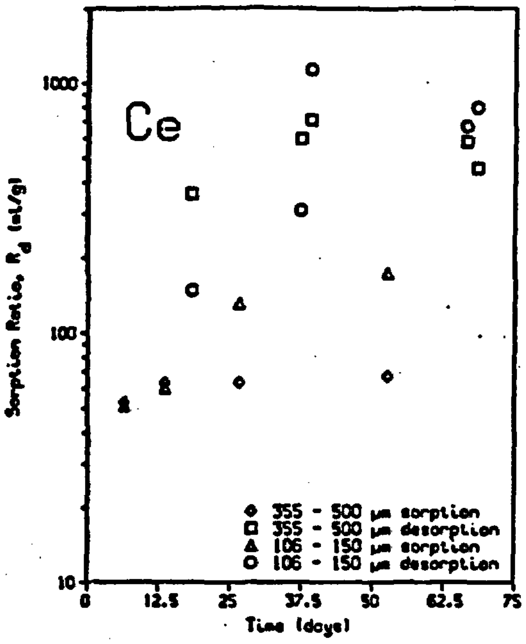

Fig. 21.
Sorption ratios for ^{141}Ce on sample JA-32 at 22°C.

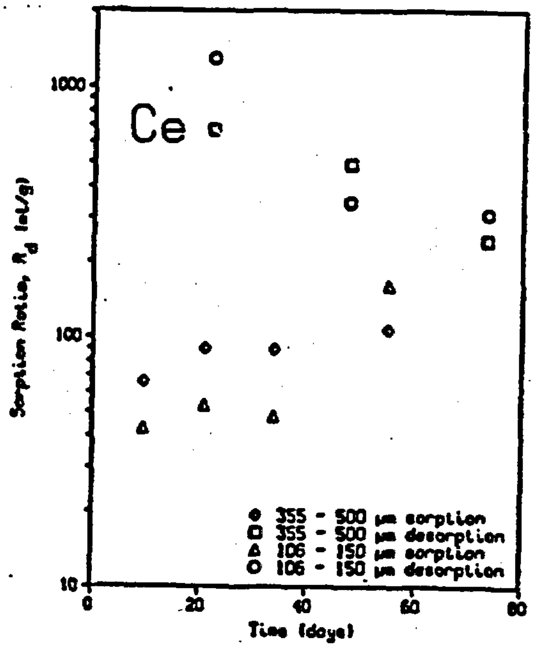

Fig. 22.
Sorption ratios for ^{141}Ce on sample JA-32 at 70°C.

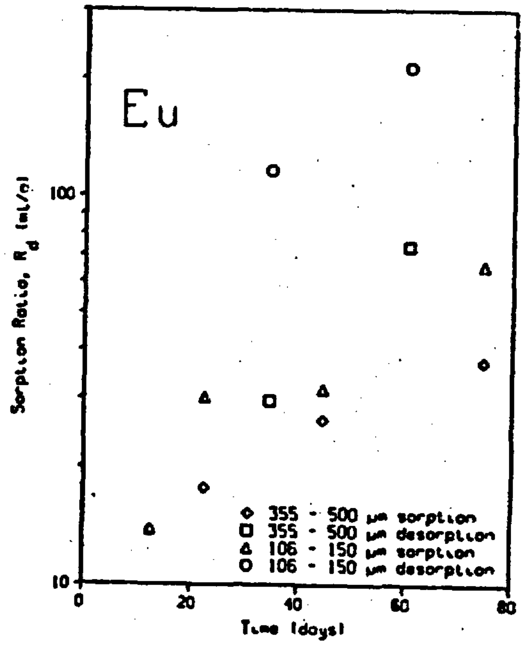

Fig. 23.
Sorption ratios for ^{152}Eu on sample JA-18 at 22°C.

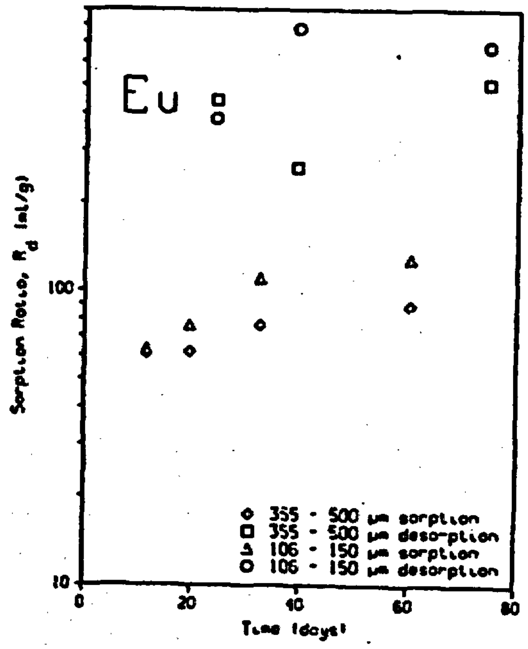

Fig. 24.
Sorption ratios for ^{152}Eu on sample JA-18 at 70°C.

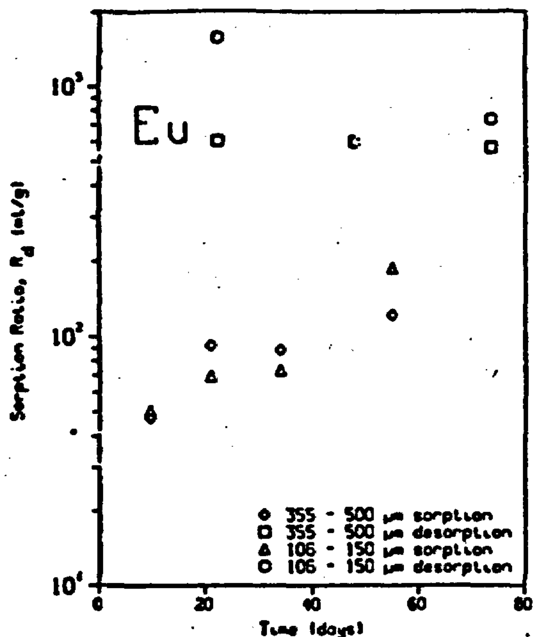

Fig. 25.
Sorption ratios for ^{152}Eu on sample JA-32 at 22°C.

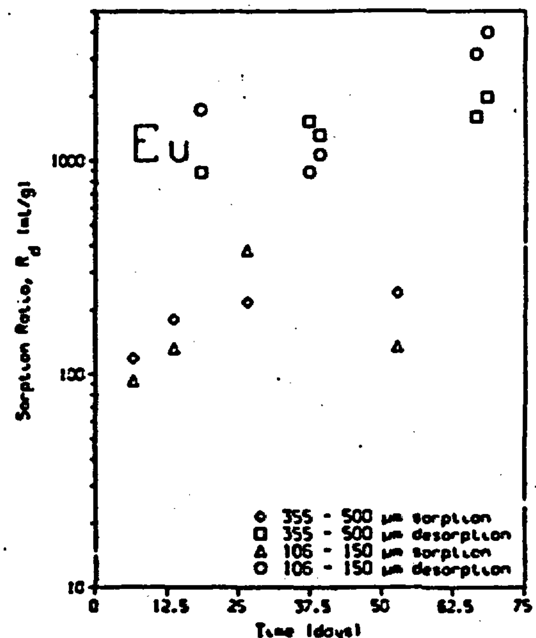

Fig. 26.
Sorption ratios for ^{152}Eu on sample JA-32 at 70°C.

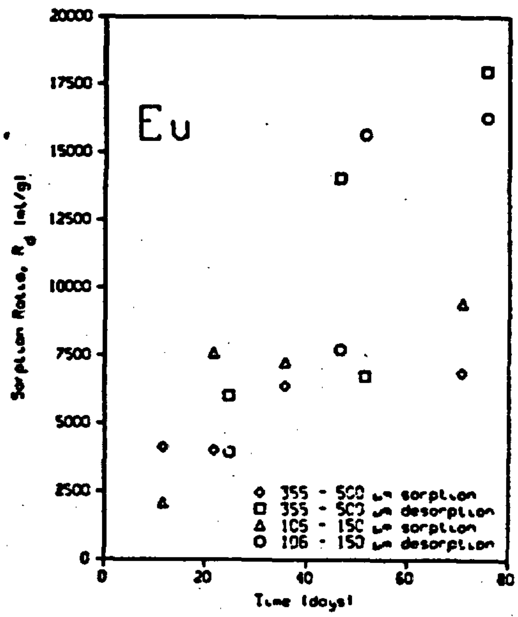

Fig. 27.
Sorption ratios for ^{152}Eu on sample JA-37 at 22°C.

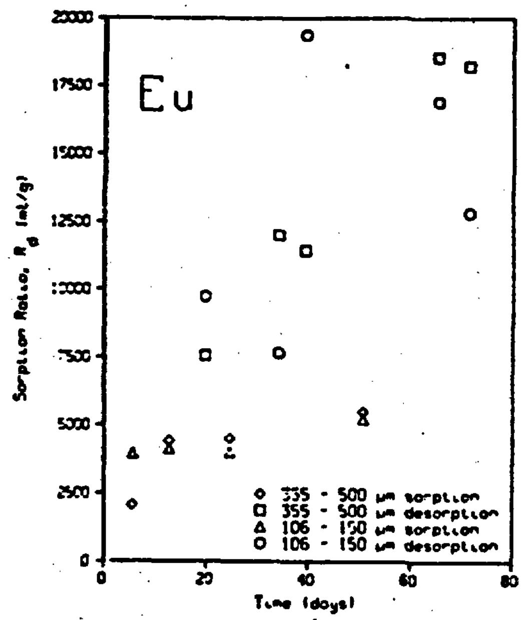

Fig. 28.
Sorption ratios for ^{152}Eu on sample JA-37 at 70°C.

TABLE XVII

AVERAGE SORPTION RATIOS FOR JA-18 AT 22°C[a,b,c]

	R_d(mℓ/g)				
	Sr	Cs	Ba	Ce	Eu
355-500 µm, sorption, av	9 000	14 500	4 800	40	24
σ_{pop}	5 000	5 000	2 000	20	10
355-500 µm, desorption, av	11 000	14 900	15 000	90	80
σ_{pop}	6 000	800	6 000	50	60
355-500 µm, both, av	10 000	15 000	*	*	*
σ_{pop}	5 000	4 000			
106-150 µm, sorption, av	16 000	14 000	4 700	50	40
σ_{pop}	5 000	3 000	1 500	20	20
106-150 µm, desorption, av	14 000	18 000	34 000	270	220
σ_{pop}	8 000	3 000	9 000	160	120
106-150 µm, both, av	15 000	17 000	*	*	*
σ_{pop}	6 000	4 000			
All, sorption, av			4 800	40	30
σ_{pop}			2 000	20	20
All, desorption, av			30 000	180	150
σ_{pop}			10 000	140	100
All, both, av	13 000	16 000	*	*	*
σ_{pop}	6 000	4 000			

[a]Average sorption time, 39 days.

[b]Average desorption, 54 days.

[c]A * symbol indicates that the values for sorption and desorption differ by more than ~σ. A ? symbol after an entry indicates that the difference is close to σ. These symbols also apply for Tables XVIII through XXII.

TABLE XVIII

AVERAGE SORPTION RATIOS FOR JA-18 AT 70°C[a,b,c]

	R_d(mℓ/g)				
	Sr	Cs	Ba	Ce	Eu
355-500 µm, sorption, av	19 000	19 000	50 000	42	72
σ_{pop}	4 000	1 000	20 000	2	13
355-500 µm, desorption, av	20 000	22 000	120 000	220	500
σ_{pop}	3 000	2 000	50 000	80	200
355-500 µm, both, av	20 000	21 000	*	*	*
σ_{pop}	3 000	2 000			
106-150 µm, sorption, av	17 000	17 000	50 000	43	90
σ_{pop}	5 000	3 000	20 000	6	30
106-150 µm, desorption, av	22 000	16 000	100 000	320	600
σ_{pop}	6 000	1 000	20 000	170	300
106-150 µm, both, av	20 000	16 000	*	*	*
σ_{pop}	6 000	2 000			
All, sorption, av			50 000	43	80
σ_{pop}			20 000	5	20
All, desorption, av			110 000	270	500
σ_{pop}			40 000	130	200
All, both, av	20 000	19 000	80 000?	*	*
σ_{pop}	5 000	3 000	40 000		

[a]Average sorption time, 31 days.

[b]Average desorption time, 40 days.

[c]See footnote c of Table XVII.

TABLE XIX

AVERAGE SORPTION RATIOS FOR JA-32 AT 22°C[a,b,c]

	R_d (mℓ/g)				
	Sr	Cs	Ba	Ce	Eu
355-500 μm, sorption, av	57	120	370	90	90
σ_{pop}	10	13	110	20	30
355-500 μm, desorption, av	59	180	500	510	640
σ_{pop}	9	20	160	200	100
355-500 μm, both, av	58	150	430	*	*
σ_{pop}	9	40	150		
106-150 μm, sorption, av	56	126	400	80	95
σ_{pop}	11	10	30	60	60
106-150 μm, desorption, av	47	170	480	300	1 100
σ_{pop}	4	40	70	50	500
106-150 μm, both, av	52	150	440	*	*
σ_{pop}	9	40	70		
All, sorption, av				80	90
σ_{pop}				40	50
All, desorption, av				400	900
σ_{pop}				20	400
All, both, av	55	150	440	*	*
σ_{pop}	9	40	110		

[a]Average sorption time, 30 days.

[b]Average desorption time, 40 days.

[c]See footnote c of Table XVII.

TABLE XX

AVERAGE SORPTION RATIOS FOR JA-32 AT 70°C[a,b,c]

	R_d (mℓ/g)				
	Sr	Cs	Ba	Ce	Eu
355-500 μm, sorption, av	113	92	1 200	100	180
σ_{pop}	22	10	300	60	130
355-500 μm, desorption, av	92	99	1 300	700	2 200
σ_{pop}	2	7	300	300	1 300
355-500 μm, both, av	101	96	1 250	*	*
σ_{pop}	24	9	300		
106-150 μm, sorption, av	90	102	860	60	190
σ_{pop}	60	20	300	6	50
106-150 μm. desorption, av	102	118	990	540	1 500
σ_{pop}	24	12	200	140	400
106-150 μm, both, av	111	111	930	*	
σ_{pop}	27	17	250		
All, sorption, av				80	190
σ_{pop}				40	90
All desorption, av				600	1 800
σ_{pop}				200	1 000
All, both, av	106	103	1 100	*	*
σ_{pop}	2	16	300		

[a]Average sorption time 25 days.
[b]Average desorption time 22 days.
[c]See footnote c of Table XVII.

TABLE XXI

AVERAGE SORPTION RATIOS FOR JA-37 AT 22°C[a,b,c]

	R_d (mℓ/g)			
	Sr	Cs	Ba	Eu
355-500 μm, sorption, av	280	650	710	5 400
σ_{pop}	40	110	100	1 500
355-500 μm, desorption, av	310	940	930	13 000
σ_{pop}	30	110	100	6 000
355-500 μm, both, av	300	810	830	9 400?
σ_{pop}	40	190	150	6 000
106-150 μm, sorption, av	300	580	800	7 000
σ_{pop}	40	140	160	3 000
106-150 μm, desorption, av	310	760	900	13 000
σ_{pop}	30	170	130	8 000
106-150 μm, both, av	300	680	860	10 500
σ_{pop}	30	170	150	7 000
All, sorption, av				6 000
σ_{pop}				2 000
All, desorption, av				13 000
σ_{pop}				7 000
All, both, av	300	740	850	9 900
σ_{pop}	35	190	140	6 000

[a] Average sorption time, 35 days.

[b] Average desorption time, 38 days.

[c] See footnote c of Table XVII.

TABLE XXII

AVERAGE SORPTION RATIOS FOR JA-37 AT 70°C[a,b,c]

	R_d (mℓ/g)			
	Sr	Cs	Ba	Eu
355-500 µm, sorption, av	1 000	1 300	3 500	4 100
σ_{pop}	400	200	2 000	1 500
355-500 µm, desorption, av	1 300	2 600	5 300	13 000
σ_{pop}	400	1 500	2 700	4 000
355-500 µm, both, av	1 200	2 100	4 600	*
σ_{pop}	400	1 300	2 500	
106-150 µm, sorption, av	1 100	1 400	3 800	4 300
σ_{pop}	400	300	2 000	600
106-150 µm, desorption, av	1 400	2 700	6 400	15 000
σ_{pop}	400	2 000	3 300	6 000
106-155 µm, both, av	1 300	2 200?	5 400	*
σ_{pop}	400	1 600	3 000	
All, sorption, av		1 400	3 700	4 200
σ_{pop}		200	2 000	600
All, desorption, av		2 600	5 900	1 400
σ_{pop}		1 700	3 000	6 000
All, both, av	1 200	2 100?	5 000	*
σ_{pop}	400	1 400	2 700	

[a]Average desorption time, 34 days.

[b]Average desorption time, 34 days.

[c]See footnote c of Table XVII.

TABLE XXIII

pH VALUES AFTER EXPERIMENTS

JA-18				JA-32				JA-37			
22°		70°		22°		70°		22°		70°	
ID	pH	ID	pH	ID	pH	ID	pH	ID	pH	ID	pH
Feed	8.48	Feed	8.31	Feed	8.74	Feed	8.53	Feed	8.45	Feed	8.55
5250	8.69	5170	8.51	5570	8.77	5330	8.64	5890	8.71	5810	8.70
5260	8.71	5180	8.60	5580	8.70	5340	8.59	5900	8.70	5820	8.63
5270	8.62	5190	8.67	5590	8.67	5350	8.59	5910	8.65	5830	8.58
5280	8.57	5200	8.67	5600	8.63	5360	8.79	5920	8.67	5840	8.56
5252	8.56	5172	8.54	5572	8.64	5332	8.65	5872	8.67	5812	8.52
5262	8.54	5182	8.54	5582	8.53	5344	8.71	5904	8.67	5822	8.56
5264	8.54	5192	8.67	5592	8.45	5334	8.48	5894	8.63	5814	8.48
		5174	8.65	5602	8.60	5352	8.48	5912	8.48	5832	8.53
5090	8.70					5362	8.57	5406	8.63	5842	8.56
5700	8.71	5010	8.58	5410	8.73					5824	8.46
51,0	8.57	5020	8.64	5420	8.80	5490	8.56	5730	8.74		
5720	8.51	5030	8.60	5430	8.66	5500	8.60	5740	8.77	5650	8.73
5092	8.52	5040	8.61	5440	8.65	5510	8.60	5750	8.79	5680	8.54
5102	8.54	5012	8.63	5412	8.62	5520	8.86	5760	8.66	5660	8.61
5104	8.52	5022	8.55	5422	8.56	5492	8.64	5732	8.71	5670	8.47
		5032	8.55	5432	8.41	5504	8.65	5744	8.63	5652	8.38
Controls:		5014	8.71	5442	8.65	5494	8.48	5734	8.64	5682	8.58
5250	8.64					5512	8.45	5752	8.64	5654	8.41
5260	8.72	Controls:		Controls:		5522	8.59	5745	8.68	5662	8.50
5270	8.59	5170	8.59	5570	8.71					5672	8.40
5280	8.66	5180	8.61	5580	8.69	Controls:		Controls:		5684	8.50
		5190	8.77	5590	8.64	5330	8.34	5890	8.55		
		5200	8.67	5600	8.56	5240	8.30	5900	8.60	Controls:	
						5350	8.40	5910	8.58	5810	8.75
						5360	8.76	5920	8.62	5820	8.66
										5830	8.60
										5840	8.55

[a]Feed pH value is for before the experiments.

two days. The centrifuged solution contained mostly ^{131}I and detectable amounts of ^{99}Mo, $^{103,106}Ru$, and $^{124,125,126}Sb$. The solution was added to a tube containing ^{137}Cs tracer prepared as in Section III.A.1, and the final traced ground water was centrifuged, filtered, and assayed as in that section. The ^{137}Cs tracer was added because it was not known whether any of the other tracers in this experiment would sorb on the container walls. The same tagged solution was used with the three tuff types. It had not been pre-equilibrated with solids in the laboratory. The specific activities and concentrations are given in Table XXIV.

Only the 355-500 μm fractions of the tuffs were investigated, and the sorption contact times at 22°C were 20 and 27 days. Since there was almost no sorption, desorption experiments were not performed.

The blank controls indicated that >98% of the I, Sb, and Ru was recovered. Therefore, these elements do not sorb on polyethyelene or form centrifugable species under the conditions of the experiment, and analysis of the solutions was sufficient for the actual sorption determinations. R_d values were calculated according to Eq. 3.

Results for ^{106}Ru, ^{125}Sb, and ^{126}Sb were not used because of poor counting statistics. Only ^{103}Ru and ^{124}Sb were used for Ru and Sb. Molybdenum-99 results

TABLE XXIV
ACTIVITIES OF ^{131}I-TRACED GROUND WATER

Nuclide	μCi/mℓ	M[a]
^{99}Mo	1.4×10^{-5}	1.3×10^{-14}
^{103}Ru	1.3×10^{-4}	2.6×10^{-12}
^{124}Sb	1.5×10^{-4}	6.1×10^{-12}
^{126}Sb	9.5×10^{-6}	2.6×10^{-13}
^{131}I	8.5×10^{-3}	1.2×10^{-13}
^{137}Cs	7.5×10^{-2}	5.7×10^{-9}

[a]Concentration calculated for carrier-free nuclides.

TABLE XXV

SORPTION RATIOS FOR I, Mo, Ru, AND Sb[a]

R_d(mℓ/g)

Experiment	Time (days)	Cs	I	Mo	Ru	Sb
JA-18						
5310	19.8	10 900	-1.5	4.3	67.	-0.9
5320	26.8	9 200	-0.5		32.	0.2
Ave.		10 000	-1.0	4.3	50.	-0.3
JA-32						
5630	19.8	130	0.35	8.2	88.	0.12
5640	26.8	126	-0.20		44.	-0.88
Ave.		130	0.1		70.	-0.4
JA-37						
5850	19.8	1 360	-0.9	9.7	66.5	0.5
5940	26.8	1 450	-0.2		64.5	0.1
Ave.		1 400	-0.6		65.	0.3

[a]All experiments with non-prequilibrated water at 22°C with 355- to 500-μm iff. mesh tuff.

had ~10% uncertainties for the 20-day times, but the nuclide was essentially not detectable for the 27-day experiments.

B. Results and Conclusions

The results of the sorption measurements are given in Table XXV. Within experimental uncertainties there was no sorption of I and Sb ($f > 0.98$) for any of the tuff samples. The sorption ratios for I and Sb are, therefore, zero. Species of I were not determined in this study. In a previous study[11] I was present mostly as I^- and IO_3^-.

Only 15 to 30 percent of the Mo sorbed in 20 days, and the R_d values for the three tuffs are less than 10.

Twenty to forty percent of the Ru sorbed giving sorption ratios between 50 and 70 mℓ/g.

The Cs sorption ratios given in Table XXV for samples JA-18 and JA-32 agree well with those determined previously with pre-equilibrated ground water (Section III, Tables XI and XIII). However, the Cs sorption ratios for sample JA-37 were almost a factor of three higher for these experiments than for the previous ones (Table XV). The difference may be due to the difference in the compositions of the pre-equilibrated and non-equilibrated waters (Table VII).

Initial and final pH values, which are essentially 8.5, are given in Table XXVI.

V. SORPTION OF PLUTONIUM AND AMERICIUM

A. Measurement Techniques

1. Preparation of Tagged Solutions

The traced waters used in these studies were prepared using the pre-equilibrated water described in Section II.E, isotopically pure ^{241}Am tracer obtained from Oak Ridge National Laboratory, ^{239}Pu tracer (weapons grade) from Los Alamos Scientific Laboratory, and ^{237}Pu tracer obtained from Argonne National Laboratory. Tracer purities were checked by both alpha and gamma spectroscopy. The specific activities of the tracers were measured by alpha and gamma counting: ^{241}Am = 7.23×10^8 dpm/mℓ, ^{239}Pu = 2.5×10^9 dpm/mℓ, $^{237}Pu \sim 4.2 \times 10^6$ dpm/mℓ at feed preparation time. Feed solutions were usually prepared to contain $\sim 2 \times 10^6$ dpm/mℓ of ^{241}Am, and/or $\sim 3 \times 10^5$ dpm/mℓ of ^{239}Pu, or $\sim 2.4 \times 10^3$ dpm/mℓ ^{237}Pu at 100% yield of tracer, which was generally not the case (see below). These correspond to mass concentrations of $\sim 1 \times 10^{-6}$ M Am, $\sim 1 \times 10^{-5}$ M Pu when ^{239}Pu

TABLE XXVI

pH VALUES AFTER EXPERIMENTS

JA-18 ID	JA-18 pH	JA-32 ID	JA-32 pH	JA-37 ID	JA-37 pH
Feed	8.50	Feed	8.50	Feed	8.50
5310	8.50	5630	8.55	5850	8.45
5320	8.47	5640	8.47	5940	8.48

was used, and ~4 X 10^{-13} M Pu when ^{237}Pu was used. Stock tracer solutions were 3 M HCl, and in most cases an attempt was made to hold the chloride added to feed solutions constant at ~0.010 M by adding the same total volume of tracer and 3 M HCl. A limited number of samples were prepared with reduced amounts (~1/10 concentrations) of ^{241}Am tracer and/or chloride to examine the effects of such changes. (Essentially no differences were observed within the limited accuracy of the results.) The ^{237}Pu tracer was treated with $NaNO_2$ so that the Pu was in the IV oxidation state at the beginning. This step resulted in the addition of ~10^{-4} M sodium ion to the feed solutions containing ^{237}Pu. The feed solution that was prepared by adding tracer solution directly to the ground water and then re-adjusting the pH to the original value by adding NaOH solution had about 10^{-2} M sodium ion added.

Several batches of traced feed of sufficient volume to contact a predetermined number of crushed-rock samples, aliquot for concentration determination, and measure the pH value were prepared. For each preparation, the desired amount(s) of tracer solution(s) was evaporated at room temperature, in air, in a polypropylene tube. The dried activity was then contacted several times with 20-mℓ volumes of ground water for periods varying from a few minutes to a final overnight contact. After each contact the tube was centrifuged for one hour at 12 000 rpm, and the aqueous phase was added to a large polyethylene bottle. Contacts were continued until no significant decrease in γ-ray activity in the tube was observed. Generally three contacts were made. Ground water was added to the bulk of the feed solution in the bottle to give a volume ~20 mℓ less than the desired final volume. This bulk solution was then shaken overnight at the same time the final contact was being made in the original tube. The next day the tube was centrifuged, and the solution was added to the bottle. Water was added to give the desired final volume, and the bottle was shaken for at least one hour. The solution was then centrifuged for one hour at ≥6000 rpm and transferred to a new bottle. Within one hour, an aliquot was taken and acidified for later assay of the initial concentration of each tracer, and 20-mℓ portions were added to crushed-rock samples in polypropylene tubes and to empty tubes for use as "controls." The pH value of the remaining solution was then measured. The feed solutions were not filtered because earlier experiments suggested that major fractions of the Am and Pu activities remain on the filters. The yields of tracer in the feed solutions ranged from 5 to 70%, with an average of 34% for six solutions, for water pre-equilibrated at room temperature and from 7 to 50%, with an average of 26%, for six solutions for water pre-treated at 70°C. On the average, the corresponding concentrations were ~10^{-7} M Am and 10^{-6} M Pu when ^{239}Pu was used. The yield of tracer in the one b tch of feed solution containing ^{237}Pu was 43%, giving a concentration of ~2 X 10^{-13} M Pu.

One traced feed solution was prepared by adding 3 M HCl tracer solutions of ^{241}Am and ^{239}Pu to ground water and adjusting the pH to its original value with NaOH solution. The feed was centrifuged and aliquoted before use. The ^{241}Am yield was roughly 18% (~2 X 10^{-7} M). If the ^{239}Pu yield was the same, the Pu concentration was ~2 X 10^{-6} M.

2. Sorption Measurements

Crushed rock from cores JA-18, JA-32, and JA-37 was again used for sorption studies at both ambient (22 ± 2°C) and elevated (70 ± 1°C) temperatures. The material was pre-treated by shaking weighed one-gram quantities with 20-mℓ portions of water from well J-13 for periods of at least two weeks. The samples were contained in pre-washed, capped 40-mℓ polypropylene tubes. The phases were separated by centrifuging at 12 000 rpm for one hour. The weight of the solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pre-equilibration.

Twenty-milliliter portions of traced feed solution of known pH value were added to the tubes containing crushed rock. The solids were dispersed by vigorous shaking, and the mixtures were agitated gently for selected times: 1, 2, 4, and 8 weeks. The shaking rates were 200 oscillations per minute for the ambient temperature samples and 80 oscillations per minute for the 70°C samples.

At the end of a shaking period, the aqueous phases were separated from the solids by four centrifugings, each in a new tube, for one hour at 12 000 rpm. Aliquots of the final solutions were taken for pH measurements, gross gamma counting, and gamma spectroscopy. The solid phases were left in the tubes and counted directly. Since this procedure resulted in the counting of any activity sorbed on the walls of the container, many of the solid samples were carefully removed from the tubes, and the tubes were checked for residual activity. In general, less than 2% of the activity remained; this could be attributed almost entirely to a slight solid residue. Therefore, the activity sorbed on the walls is considered negligible.

The comments in Section III.A.5 concerning "control" samples with traced aqueous phase but no solid are applicable here. Such samples run with Pu and

Am showed much higher wall sorption on the tubes when no solid was present.

Desorption experiments were performed by adding pre-equilibrated ground water to the solid phases from the sorption experiments and continuing as for the sorption experiments.

3. Assay of Radioactivity

Two gamma counting arrangements were used in these experiments. In one, used for ^{241}Am, both liquid and solid samples were observed with a calibrated, 23%, coaxial Ge(Li) detector. The 1024-channel spectra were recorded in an analyzer which is connected to a PDP-9 computer. A minimum of two counts were taken for each sample, and the 60-KeV photopeak of ^{241}Am was integrated. Counting standards were prepared using known amounts of ^{241}Am in the same geometries and conditions as the experimental samples.

Samples containing only a single gamma-ray emitter (^{241}Am with or without ^{239}Pu, or ^{237}Pu) were also counted on a NaI(Tl) detector utilizing a single-channel analyzer and a scaler. Counting standards were prepared as described above.

Plutonium-239 was determined radiochemically[22] after sample dissolution. To date, analyses have been completed for only a few samples.

4. Calculations

Since both solid and liquid phases were counted directly for ^{241}Am and ^{237}Pu, or analyzed directly for ^{239}Pu, the distribution ratio (see Section III.A.6) can be calculated directly from Eq. 2. The activities in the control tubes were not used in the calculations. Examination of the tubes used for the sorption measurements indicate that the container effect (<2%) can be neglected.

B. Results and Conclusions

The results for the distribution ratio measurements for ambient temperature conditions are given in Tables XXVII, XXVIII, and XXIX while those for 70°C are given in Table XXX. Radiochemical analyses for ^{239}Pu have not been completed for most samples. Desorption measurements are also still in progress. The initial and final pH values are also listed in the tables. The R_d values are shown graphically in Figs. 29-34. Mean sorption values for dried tracer preparations for all contact times are given in Table XXXI.

Several general conclusions can be made for the Pu and Am results: At least qualitatively a decrease in particle size is accompanied by a small increase in sorption ratio. The R_d values increase slightly with increasing temperature. A factor of 10^7 change in Pu concentration (~1×10^{-6} M for ^{239}Pu and ~2×10^{-13} M for ^{237}Pu) made no significant difference in the R_d value within the accuracy of the measurements. The most significant difference in R_d values came from the change in method of preparation of traced feed (see Tables XXVIII and XXIX); however, it should be emphasized that, for the measurements where the feed was prepared by adding an acid tracer solution and then re-adjusting the pH values, only a single such feed solution was used. These measurements will be repeated.

TABLE XXVII

Am and Pu SORPTION RATIOS, SAMPLE JA-18, AMBIENT TEMPERATURE

Fraction (μm)	Tracer Preparation Method	Sorption Time (days)	Desorption Time (days)	R_d(mℓ/g) Am	R_d(mℓ/g) Pu	pH Initial	pH Final
106-150	dried	7.0		200	170[a]	---	8.19
		7.0		250		---	8.29
			14	270	160[a]	8.30	---
		7.6		96	70[a]	8.56	7.43
		7.6		310		---	7.52
		14.6		86		8.56	8.42
		14.6		310		---	8.29
		28.6		120		8.56	8.55
		28.6		360		---	8.60
		56.6		57		8.56	8.36
		56.6		85		---	8.57
		13.8			110[b]	8.38	8.30
			13.7		710[b]	8.43	8.51
		28.9			120[b]	8.38	8.41
			14.0		450[b]	8.44	8.56
		55.7			220[b]	8.38	8.42

[a]Approximately 10^{-6} M ^{239}Pu in feed solution.
[b]Approximately 10^{-13} M ^{237}Pu in feed solution.

Definitive conclusions cannot be made for the relationship of the desorption measurements to the sorption measurements.

TABLE XXVIII

Am and Pu SORPTION RATIOS, SAMPLE JA-32, AMBIENT TEMPERATURE

Fraction (μm)	Tracer Preparation Method[a]	Sorption Time (days)	Desorption Time (days)	R_d (mℓ/g) Am	Pu	pH Initial	Final
106-150	dried	7.6		110		8.50	7.60
		14.6		110	110	8.50	8.60
		28.6		140		8.50	8.63
		28.6		230		8.50	8.63
		56.6		79		8.50	8.64
	pH adjust	7		1 600	1 200	7.92	8.26
		14		1 000	1 800	7.92	8.19
		28		1 100		7.92	8.32
			14	2 100	920	8.30	---
355-500	pH adjust	7		890	1 000	7.92	8.19
		14		640		7.92	7.94
			14	920	580	8.30	---
		28		490	820	7.92	8.23

[a]It is emphasized that the "pH adjust" method data are based on a single feed solution preparation; data are given for comparison to indicate variation with preparation method. These experiments will be repeated.

TABLE XXIX

Am and Pu SORPTION RATIOS, SAMPLE JA-37, AMBIENT TEMPERATURE

Fraction (μm)	Tracer Preparation Method[a]	Sorption Time (days)	Desorption Time (days)	R_d(mℓ/g) Am	Pu	pH Initial	Final
106-150	dried	7.6		430	390	8.64	7.53
		14.6		365		8.64	8.52
		28.6		430	180	8.64	8.67
		28.6		1 500		8.64	8.62
		56.6		640		8.64	8.56
	pH adjust	7		7 200	7 200	7.92	8.53
		14		5 200		7.92	8.23
			14	2 700	890	8.30	---
		28		7 500	12 000	7.92	7.94
			14	5 200	1 600	8.30	---
355-500	pH adjust	7		3 700	5 400	7.92	8.38
		14		2 800	7 200	7.92	8.19
		28		3 800		7.92	8.29
			14	5 800	670	8.30	---

[a]See footnote to Table XXVIII.

TABLE XXX

Am and Pu SORPTION RATIOS, SAMPLES JA-18, 32 and 37, 106-150 μm, 70°C

Core Sample	Tracer Preparation Method	Sorption Time (days)	R_d(mℓ/g) Am	R_d(mℓ/g) Pu	pH Initial	pH Final
JA-18	dried	7.6	220		---	7.19
		7.6	190		---	7.32
		14.6	190		---	7.57
		14.6	170		---	8.08
		28.6	290		---	8.61
		28.6	150		---	8.62
		28.6	340		8.60	---
		28.6	370		8.57	8.50
		56.6	300		---	---
		56.6	76		---	---
JA-32	dried	7.6	120		8.46	7.33
		14.6	160		8.46	8.14
		28.6	130		8.46	8.57
		56.6	46		8.46	---
JA-37	dried	7.6	520		8.58	7.33
		14.6	680		8.58	8.06
		14.6	2 100		8.58	8.18
		28.6	960		8.58	8.67
		56.6	800		8.58	---
		56.6	730		8.58	8.52

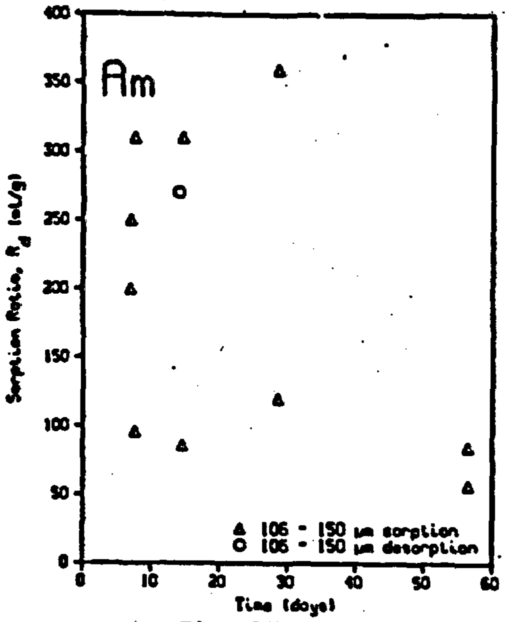

Fig. 29.

Sorption ratios for ^{241}Am on sample JA-18 at 22°C.

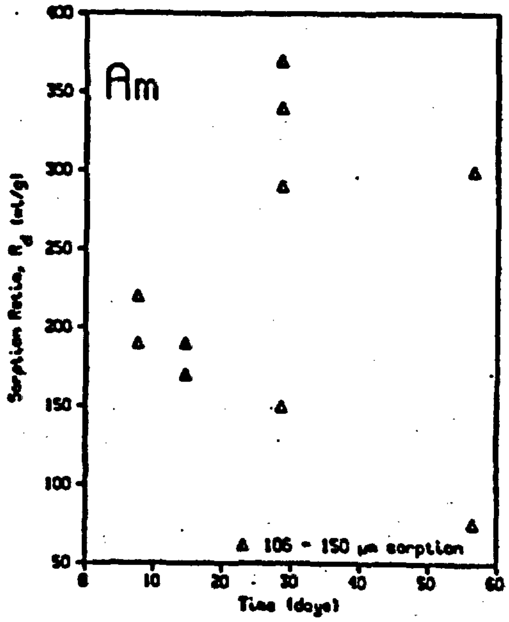

Fig. 30.

Sorption ratios for ^{241}Am on sample JA-18 at 70°C.

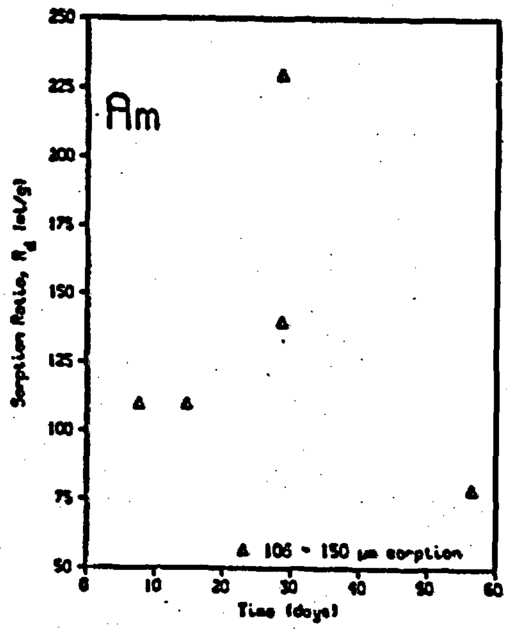

Fig. 31.

Sorption ratios for ^{241}Am on sample JA-32 at 22°C.

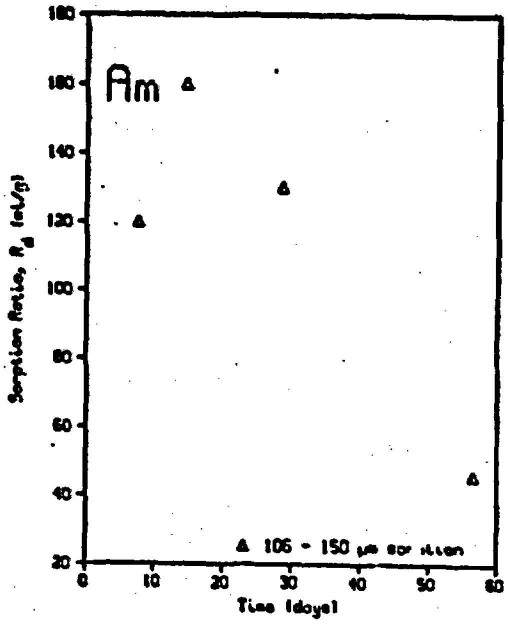

Fig. 32.

Sorption ratios for ^{241}Am on sample JA-32 at 70°C.

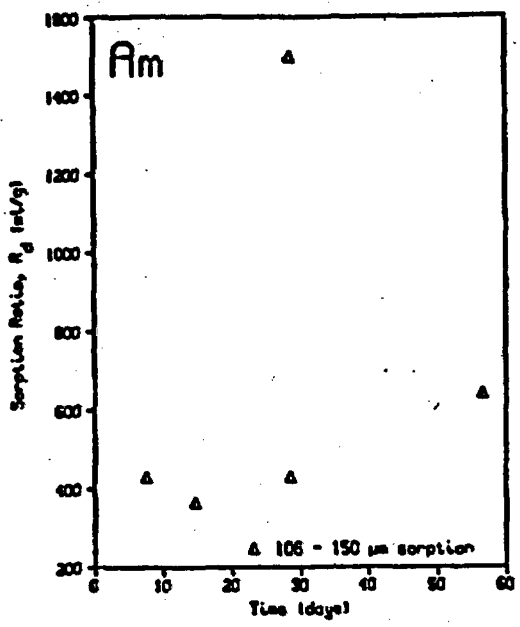

Fig. 33.
Sorption ratios for ^{241}Am on sample JA-37 at 22°C.

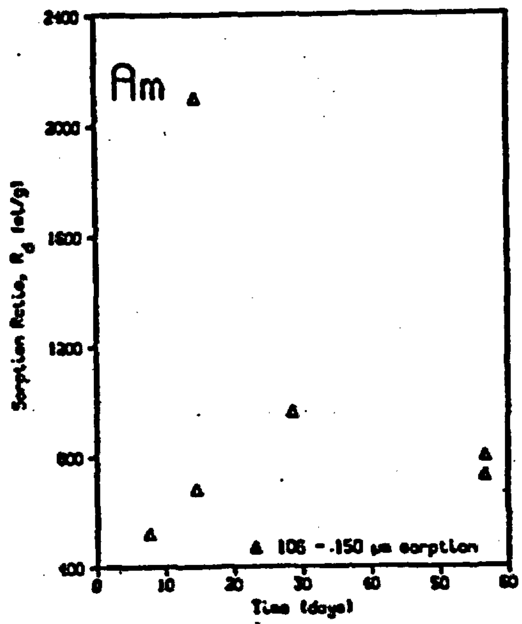

Fig. 34.
Sorption ratios for ^{241}Am on Sample JA-37 at 70°C.

TABLE XXXI

MEAN SORPTION RATIOS FOR Am AND Pu[a]

Element	Core	Temp	R_d(mℓ/g)	σ(pop)
Am	JA-18	22	190	43
	JA-18	70	220	35
	JA-32	22	120	32
	JA-32	70	110	34
	JA-37	22	600	190
	JA-37	70	910	260
Pu	JA-18	22	140	50
	JA-32	22	~110	
	JA-37	22	~280	

[a]Sorption ratios listed are based on dried traced feed preparation and are averages of 1, 2, 4, and 8 week contact times.

VI. CONCLUSIONS

The average sorption ratios determined in this work are summarized in Table XXXII. In addition, preliminary sorption values for U(VI) are <10 mℓ/g for all three tuffs.

It is seen that sorption ratios at 70°C are generally greater than at 20°C. The difference in the behavior of the three tuff samples is quite marked. Sample JA-18, which contains unaltered glass and only a trace of zeolite, has very high sorption ratios for mono- and divalent ions of Sr, Cs, and Ba while the ratios for Am are intermediate and those for Ce and Eu are low. Sample JA-37, which is high in zeolites and contains no glass, has high sorption ratios

TABLE XXXII

AVERAGE SORPTION RATIOS

R_d (mℓ/g)

	JA-18		JA-32		JA-37	
	22°C	70°C	22°C	70°C	22°C	70°C
Sr[a]	13 000	20 000	55	106	300	1 200
Mo, Sorption	4		8		10	
Ru, Sorption	50		70		65	
Sb, Sorption	0		0		0	
I, Sorption	0		0		0	
Cs[a]	6 000	19 000	150	103	740	2 100
Ba[a]		80 000	440	1 100	850	5 000
Ba, Sorption	4 800	50 000				
Ba, Desorption	30 000	110 000				
Ce, Sorption	40	43	80	80		
Ce, Desorption	180	320	400	600		
Eu, Sorption	30	43	90	190	6 000	4 200
Eu, Desorption	150	270	800	1 800	13 000	14 000
Pu, Sorption	140		~110		~280	
Am, Sorption	190	220	120	110	600	910

[a]For sorption and desorption.

for Cs, Ba, and Eu and intermediate ones for Sr and Pu. Sorption ratios for sample JA-32, which is like a microgranite and which contains no glass or zeolites, are low or moderate, similar to those found for Climax Stock granite.[12] The very high sorption ratios for Sr, Cs, and Ba might be associated with the presence of glass and the generally high sorption ratios for Sr, Cs, Ba, Ce, Eu, and Am might be associated with zeolites.

The elements I, Sb, Mo, and U(VI) are anionic or form soluble complexes under the conditions of these experiments. Their sorption ratios on the three tuffs are very low or zero.

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REFERENCES

1. J. R. Smyth, B. M. Crowe, and P. M. Halleck, "An Evaluation of the Storage of Radioactive Waste within Silicic Pyroclantic Rocks," to be published in Environmental Geology.

2. E. W. Vaughan, "Properties of Natural Zeolites," in Natural Zeolites, Occurrence, Properties, Use, L. B. Sand and F. A. Mumpton, eds., Pergamon Press, New York (1978), p. 353.

3. J. F. Relyea, D. Rai, and R. J. Serne, "Interaction of Waste Radionuclides with Geomedia: Program Approach and Progress," to be published in the Symposium on Science Underlying Radioactive Waste Management, Materials Research Society, Boston, November 28-December 1, 1978.

4. E. R. Thomkins and S. W. Mayer, "Ion Exchange as a Separations Method III. Equilibrium Studies of the Reactions of Rare Earth Complexes with Synthetic Ion Exchange Resins," J. Am. Chem. Soc. 69, 2859 (1947); "Ion Exchange as a Separations Method IV. Theoretical Analysis of The Column Separations Progress," J. Am. Chem. Soc. 69, 2866 (1947).

5. G. H. Higgins, "Evaluation of the Ground-Water Contaminants Hazard from Underground Nuclear Explosions," J. Geophys. Res. 64, 1509 (1959).

6. D. H. Lester, G. Jansen, and H. C. Burkholder, "Migration of Radionuclide Chains Through an Absorbing Medium," in Adsorption and Ion Exchange, I. Zwiebel and N. H. Sweed, Eds. (AIChE Symposium Series 152, No. 71, New York, 1975) 202-213.

7. H. C. Classen, "Water Quality and Physical Characteristics of Nevada Test Site Water-Supply Wells," U. S. Geological Survey report USGS-474-158 (1973).

8. G. H. Heiken and M. L. Bevier, "Petrology of Tuff Units from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos Scientific Laboratory report LA-7563-MS, (February 1979).

9. S. L. Schoff and J. E. Moore, "Chemistry and Movement of Ground Water, Nevada Test Site," U. S. Geological Survey Report TEI-838 (1964).

10. R. A. Young, "Water Supply for the Nuclear Rocket Development Station at the U. S. Atomic Energy Commission's Nevada Test Site," Geological Survey Water-Supply paper 1938 (1972).

11. K. Wolfsberg, "Sorption-Desorption Studies of Nevada Test Site Alluvium and Leaching Studies of Nuclear Test Debris," Los Alamos Scientific Laboratory report LA-7216-MS (April 1978).

12. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, C. J. Duffy, F. O. Lawrence, S. Maestas, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Granite," Los Alamos Scientific Laboratory report LA-7456-MS, (February 1979).

13. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Argillite," Los Alamos Scientific Laboratory report LA-7455-MS, (March 1979).

14. R. E. Honnell, Los Alamos Scientific Laboratory, personal communication, 1978.

15. H. Cramer, Mathematical Methods of Statistics (Princeton University Press, 1946), p. 181.

16. S. Brunauer, P. H. Emmett, and R. Teller, "Adsorption of Gases in Multimolecular Layers," J. Am. Chem. Soc. 60, 309 (1938).

17. R. S. Dyal and S. B. Hendricks, "Total Surface of Clays in Polar Liquids as a Characteristic Index," Soil Sci. 69, 421 (1950).

18. C. A. Bower and J. O. Goertzen, "Surface Area of Soils and Clays by an Equilibrium Ethylene Glycol Method," Soil Sci. 87, 289 (1959).

19. B. L. McNeal, "Effect of Exchangeable Cations on Glycol Retention by Clay Minerals," Soil Sci. 97, 96 (1964).

20. R. W. Charles, Los Alamos Scientific Laboratory, personal communication, April 1978.

21. R. Gunnick, Lawrence Livermore Laboratory, B. R. Erdal and T. R. Kelley, Los Alamos Scientific Laboratory, personal communication, 1978.

22. Radiochemistry Group CNC-11, "Collected Radiochemical Procedures," Los Alamos Scientific Laboratory report LA-1721, 4th Ed. (April 1975).

☆U.S. Government Printing Office: 1979 – 677-013/81