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Sorption-Desorption Studies on Tuff

II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies with Samples from Yucca Mountain, Nevada

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SORPTION-DESORPTION STUDIES ON TUFF

II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies with Samples from Yucca Mountain, Nevada

by

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ABSTRACT

Distribution coefficients were determined by a static (batch) technique for sorption-desorption of radionuclides between tuffs from drill holes UE25a#1 and J-13 at the Nevada Test Site and water from well J-13. Measurements were performed under atmospheric and controlled atmosphere conditions. Under atmospheric conditions tuffs high in zeolite minerals had sorption ratios of ~10^3 to 10^4 mℓ/g with Sr, Cs, Ba, Ce, Eu, Am, and Pu. For tuffs similar mineralogically to a microgranite the sorption ratios were ~10^2 to 10^3 mℓ/g. Values for U and Tc were obtained under controlled atmosphere (<0.2 ppm O_2) conditions. Studies were also begun to measure distribution ratios by a dynamic (column) technique. The ratios obtained for the elements studied, Sr, Cs, and Ba, were similar to, although lower than, those obtained by batch methods.

SUMMARY

The investigation of the sorptive properties of tuff at the Nevada Test Site was extended during FY-79 to include samples from drill hole UE25a#1 in Yucca Mountain, as well as samples from drill hole J-13 in Jackass Flats. Sorption of additional elements was determined by a batch technique, and the technique was applied to study the effects of changing atmosphere and water composition. Migration rate studies were performed with columns of crushed

rock, and studies of flow and migration through whole cores and fractured cores were started. Autoradiography was useful in showing the distribution of nuclides in the core studies, in determining the state of aggregation of Am in solution, and in determining sorption sites.

Comparison of the sorption ratios of Sr, Cs, Ba, Ce, and Eu for the Yucca Mountain samples with those for the Jackass Flats samples continues to show favorable sorptive properties of tuff. In fact, the zeolitized tuff samples from Yucca Mountain have significantly higher sorption ratios for Sr, Cs, and Ba than does the zeolitized tuff sample from Jackass Flats. Micrograniteлike devitrified tuff samples from both locations show lower values with Sr, Cs, and Ba. The sorption of Ce and Eu seems to be independent of zeolite content, with some micrograniteлike samples also exhibiting high sorption ratios for these elements. A standard technique was developed for measuring sorption ratios of Pu and Am, which present special problems because of their behavior in solutions at the pH of the groundwaters. The greatest sorption for these elements was observed with a zeolitized tuff.

Batch sorption measurements with Sr, Cs, Ba, Ce, and Eu under a nitrogen atmosphere did not reveal any significantly different behavior than in air with zeolitized or micrograniteлike tuff samples. Technetium and uranium sorb poorly on tuffs both in air and in nitrogen. However, the sorption ratio for Tc is measurably higher under nitrogen.

The composition of groundwater has been shown to be a major factor in sorption. Sorption ratios of Sr, Cs, and Ba are higher in less concentrated solutions than in more concentrated solutions probably because of less competition for available sorption sites. The ratios for Ce and Eu are reversed, which may be due to a greater tendency of Ce and Eu to form radiocolloids.

Measurements of migration rates with columns of crushed material show elution curves similar to those from ion-exchange columns. The distribution coefficients determined by this method are generally less than by the batch method, but in most cases the results agree within a factor of two or three. The differences may be due to kinetic or diffusion effects; however, varying the flow rate through one type of tuff did not show any major effect.

Techniques for studying the transport of radionuclides through whole cores of rock and through cores containing fractures are being developed. Microautoradiography is useful in determining the distribution of nuclides in the cores.

Microautoradiography has also been useful in showing the state of aggregation of Pu and Am species present in groundwater. Solutions used in the sorption determinations contain a broad range of aggregated species (polymers or colloids), while those in the desorption experiments did not, suggesting that large particulates are not removed from the solids during desorption nor are they formed in solutions at that time.

Autoradiographic techniques were also extended to the study of sorption sites of Pu and Np on thin sections of tuff. Plutonium appears to sorb rather indiscriminately (partly as aggregated species) on most rock thin sections with, perhaps, some enhanced sorption on zeolites. Neptunium does not sorb as well as plutonium and generally in aggregated form. Sorption of neptunium is greatest on zeolites, less on feldspars, and least on quartz. Alteration minerals in grain boundaries and fractures exhibit high sorptive properties.

I. INTRODUCTION

If geologic repositories are to be used for the storage of radioactive wastes, their effectiveness must be demonstrated. Intruding groundwater could result in dissolution of radionuclides from the waste and subsequent transport to the biosphere. Retardation due to interactions with the geologic media is the most important factor in retarding such transport, aside from engineered barriers. Thus, it is necessary to understand the mechanisms of transport and sorption-desorption behavior in order to predict the fate of the radionuclides during the time period required for decay to safe levels.

The parameter most commonly used for describing equilibrium sorption-desorption ion-exchange reactions is the distribution coefficient, K_d (see, for example, Ref. 1). K_d is defined as the concentration of a species per gram on the solid phase divided by its concentration per milliliter in the liquid phase at equilibrium. This parameter currently is being used to describe the sorption behavior of radionuclides in geologic systems (see, for example, Refs. 2 and 3), even though equilibrium may not have been established. Throughout this report the sorption ratio is called R_d, which is identical to K_d but does not imply equilibrium.

The suitability of tuff for the isolation of radioactive waste is being studied 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 have a wide range of

properties depending on their cooling and alteration history. Many of the properties are discussed in Ref. 4, and a demonstration of the variation in radiochemical behavior with three types of tuff is given in Ref. 5. This report presents the results of the sorptive properties of tuff obtained from a recent drill hole at the Nevada Test Site (NTS). Additional data (see Ref. 5 for the initial laboratory investigations) for tuff from an older NTS drill hole are also reported.

II. GEOLOGIC MATERIALS PROPERTIES

The tuff samples were obtained primarily from the Yucca Mountain, Nevada exploratory drill hole UE25a#1. Additional samples also came from drill hole J-13, located in Jackass Flats, Nevada. Water used in these studies came from the J-13 well.[6,7,8]

A. Mineralogy

The six Yucca Mountain tuffs used in these studies came from depths of 258 m (YM-22), 459 m (YM-38), 588 m (YM-45), 644 m (YM-48), 678 m (YM-49), and 759 m (YM-54). Tuff samples JA-18, JA-32, and JA-37 from drill hole JA-13 have previously been described.[5,9] The following descriptions of the Yucca Mountain samples are part of a more detailed report,[10] which includes modal and microprobe analyses.

Sample YM-22, a devitrified, densely welded tuff, was obtained from the Topopah Springs Member of the Paintbrush Tuff. The rock consists of relict pumices in a matrix of small shards and vugs (5- to 20-μm diameter) filled with fine crystalline, pale brown to colorless phases. Coarser shards and pumice pyroclasts are zoned, ranging from 10-μm diameter colorless phases along rims to 300-μm diameter phases in the centers. Rare phenocrysts include equant, slightly rounded plagioclase (An_{14-16}), amphibole and biotite replaced by hematite, alkali feldspar, and magnetite. Lithic fragments consist of rounded vitric tuff clasts. The rock is crossed by en echelon, 20- to 150-μm wide fractures which are filled with quartz and parallel the fabric.

Sample YM-38, an altered, nonwelded vitric tuff, was obtained from the Bedded Tuff of Calico Hills. This tuff consists of slightly compacted, 0.5- to 8-mm-long relict pumice pyroclasts. Glass has been replaced by a fine crystalline mixture of authigenic quartz and clinoptilolite. Vesicles and voids are partially to completely filled with tabular, 10- to 30-μm-long crystals of

clinoptilolite. Phenocrysts include plagioclase (An_{15-24}), sanidine (Or_{66}), quartz, and biotite; nearly all are fractured. Lithic fragments from 300-μm to 5-mm-long consist of vitric and crystal-vitric welded tuff clasts.

Sample YM-45, a devitrified, welded, vitric-crystal tuff, was obtained from the Prow Pass Member of the Crater Flat Tuff. It consists of poorly preserved relict pumice pyroclasts, 3- to 4-mm-long, with abundant voids enclosed by very fine (1- to 2-μm-diameter) to fine (10- to 25-μm) grained granular to fibrous colorless phases. Pumice pyroclasts are replaced by a mixture of these fine-grained phases, spherulites, and subhedral to euhedral tabular, colorless crystals up to 100-μm-long. Phenocrysts include resorbed to euhedral plagioclase, sanidine, and biotite. Rare lithic fragments consist of welded *tuff clasts.*

Sample YM-48, an altered, slightly welded vitric tuff, and sample YM-49, a non-welded vitric tuff, like YM-45, were obtained from the Prow Pass Member of the Crater Flat Tuff. Sample YM-48 consists of 1- to 4-mm-long pumice pyroclasts in a matrix of 10-μm- to 0.6-mm-long shards and finely crystalline (<1- to 8-μm-diameter) colorless cementing phases. Pyroclast interiors are still glassy; rims and vesicle walls are altered to a colorless, 3- to 5-μm-long fibrous phase which grows perpendicular to these boundaries. Numerous phenocrysts include plagioclase (An_8), sanidine (Or_{53}), rounded quartz, orthopyroxene, biotite, and magnetite. Randomly oriented 15- to 20-μm-wide fractures are occasionally filled with a zeolite.

Sample YM-49 is similar in many respects to sample YM-48, but the alteration is more advanced. Pyroclasts are completely altered to a colorless, 10- to 15-μm-long fibrous phase. In contrast to sample YM-48, where most pyroclast voids were vesicles, portions of some clasts in sample YM-49 have been dissolved to form vugs. These solution vugs and vesicles are lined or filled with colorless, euhedral tabular, 15- to 25-μm-long crystals of clinoptilolite. Plagioclase (An_{12}) and sanidine (Or_{55}) are the dominant phenocrysts; quartz, magnetite, and biotite are also present. Glomerocrysts up to 2 mm in diameter also occur. Lithic fragments consist of welded tuff clasts up to 3 mm in diameter.

Sample YM-54, a devitrified, welded tuff, is from the Bullfrog Member of the Crater Flat Tuff. In hand specimen this appears to be a welded tuff; however, in thin section no relict pyroclasts have been preserved. There is only a fabric of lenticular zones of coarsely crystalline phases that may have been

welded pyroclasts. Most of the rock consists of colorless to tan, 2- to 20-μm-diameter, alkali feldspar and quartz crystals. Scattered throughout this "matrix" are irregular patches of more coarsely crystalline (150- to 100-μm-diameter) alkali feldspar and quartz grains; the larger of these are sometimes roughly rimmed by spherulites. Phenocrysts include sanidine (Or_{65}) and quartz with quartz overgrowths, oxidized biotite, plagioclase, and magnetite. Xenocrysts of mafic phases altered to phlogopite and hematite also occur.

B. Cation Exchange Capacity

The cation exchange capacities (CEC) of the 106- to 500-μm fractions of the Yucca Mountain cores were measured using both cesium and strontium. The measurements were 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 to 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, and the solids were washed briefly with water and then counted with a NaI(Tl) detector to ascertain the amount of strontium or cesium that had exchanged. The results from these measurements are given in Table I.

The YM-38 core shows a higher CEC which correlates with a larger surface area (see Table II).

TABLE I

CATION EXCHANGE CAPACITIES OF YUCCA MOUNTAIN TUFF

	Cation Exchange Capacity[a] (meq/100g)	
Core	Cs	Sr
YM-22	2	3
YM-38	109	54
YM-45	6	6
YM-43	51	21
YM-49	107	27
YM-54	4	4

[a]The cation exchange values are not final since the exact cesium and strontium concentrations have not been determined.

C. Surface Areas

The surface areas of NTS tuffs have been determined by the ethylene glycol method.[12,13,14] The values are summarized in Table II.

D. Groundwater Properties

1. Preparation of Waters. Water from well J-13 was pretreated with the appropriate tuff. Each water was prepared by contacting J-13 water for at least two weeks at ambient temperature with ground material that had not been sieved. The solution to solid ratio was 20 mℓ/g. The phases were separated by centrifugation at 7 000 rpm (21 000 g's) and then by filtration through a 0.45-μm Nuclepore filter. The same rock phase was used with fresh water to prepare all subsequent batches of pretreated water. Selected batches of the water were sent to the U. S. Geological Survey for analysis; however, the results have not yet been received. Waters treated with the ground tuff samples assumed the pH values given in Table III.

2. Neutron Activation Analysis. Since the waters used for sorption measurements may have significant concentrations of the carriers for each of the tracers studied, an instrumental neutron activation analysis technique has been developed to determine these concentrations.[15] The water samples studied to date are the YM-49 rock pretreated water and the YM-22 rock pretreated water. The results for these waters are given in Tables IV and V.

TABLE II
SURFACE AREA MEASUREMENTS

Sample	Particle size(μm)	Surface Area(m^2/g)
JA-18	106-150	31
JA-32	"	8,8[a]
JA-37	"	94, 115[a]
YM-22	106-500	22
YM-38	"	103
YM-45	"	43
YM-48	"	19

[a]The two values are from separate determinations.

TABLE III

pH OF THE TUFF-PRETREATED WATERS

Sample	pH
YM-22	8.24[a]
YM-38	8.17
YM-45	8.13
YM-48	8.13
YM-49	8.24[a]
YM-54	8.12

[a]This value represents the average pH of waters prepared by two different investigators.

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

A. Measurement Techniques

1. Preparation of Traced Solutions. Six pretreated waters were prepared by shaking water from the J-13 well with ground material from each of the six Yucca Mountain cores. The contact time was 2 wk with a solution to solid ratio of 20 mℓ/g. The solid was removed from each solution by centrifugation at 7 000 rpm followed by filtration through a 0.45-μm Nuclepore filter.

Each traced water was prepared using the pretreated waters and the radionuclides ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu. The tracers needed to prepare each traced solution were evaporated to dryness in a washed polyethylene tube in a Scientific Products "Temp-Blok Module Heater". Concentrated hydrochloric acid was added, and the mixture was again evaporated to dryness. The appropriate volume of pretreated groundwater was added, and the mixture was shaken for 24 h, after which it was filtered twice through a 0.45-μm Nuclepore filter. The resulting tracer solution was used within a few hours for the sorption measurements. An aliquot of this final solution was used for assay of the initial activity of each of the tracers in the solution. This aliquot was acidified with hydrochloric acid before assaying in order to stabilize the solution.

The activities and elemental concentrations for the tracers are given in Table VI. The concentrations are based only on the specific activities provided by the suppliers. Additional amounts may be naturally present in the

TABLE IV

NEUTRON ACTIVATION ANALYSIS, YM-49 WATER[a]

Induced Activity	mg/ℓ[b]	Molarity[b]
^{24}Na	4.0×10^{1}	1.8×10^{-3}
^{47}Ca	1.9×10^{1}	4.7×10^{-4}
^{46}Sc	1.8×10^{-5}	4.0×10^{-10}
^{59}Fe	6.7×10^{-2}	1.2×10^{-6}
^{60}Co	5.1×10^{-5}	8.6×10^{-10}
^{65}Zn	6.7×10^{-3}	1.0×10^{-7}
^{76}As	9.3×10^{-3}	1.2×10^{-7}
^{75}Se	4.8×10^{-4}	6.1×10^{-9}
^{82}Br	8.0×10^{-2}	1.0×10^{-6}
^{86}Rb	8.5×10^{-3}	1.0×10^{-7}
^{85}Sr	5.6×10^{-2}	6.4×10^{-7}
^{99}Mo	2.3×10^{-2}	2.4×10^{-7}
^{103}Ru	3.8×10^{-4}	3.8×10^{-9}
^{124}Sb	1.1×10^{-3}	9.0×10^{-9}
^{134}Cs	2.9×10^{-4}	2.2×10^{-9}
^{131}Ba	1.1×10^{-2}	8.0×10^{-8}
^{140}La	2.7×10^{-4}	1.9×10^{-9}
^{141}Ce	1.3×10^{-3}	9.3×10^{-9}
^{147}Nd	1.2×10^{-3}	8.3×10^{-9}
^{153}Sm	6.3×10^{-4}	4.2×10^{-9}
^{152}Eu	1.2×10^{-5}	7.9×10^{-11}
^{169}Yb	2.5×10^{-5}	1.4×10^{-10}
^{181}Hf	3.8×10^{-5}	2.1×10^{-10}
^{239}Np	8.5×10^{-3}	3.5×10^{-8}

[a] Rock pretreated water.

[b] For the element of the induced activity, except for ^{239}Np, which is for uranium.

TABLE V

NEUTRON ACTIVATION ANALYSIS, YM-22 WATER[a]

Induced Activity	mg/ℓ[b]	Molarity[b]
^{24}Na	2.91×10^{1}	1.3×10^{-3}
^{42}K	3.75×10^{0}	9.6×10^{-5}
^{47}Ca	7.08×10^{0}	1.8×10^{-4}
^{46}Sc	3.43×10^{-6}	7.6×10^{-11}
^{51}Cr	1.06×10^{-3}	2.0×10^{-8}
^{59}Fe	2.15×10^{-2}	3.8×10^{-7}
^{60}Co	2.44×10^{-5}	4.1×10^{-10}
^{65}Zn	2.47×10^{-3}	3.8×10^{-8}
^{76}As	5.85×10^{-3}	7.8×10^{-8}
^{75}Se	3.73×10^{-4}	4.7×10^{-9}
^{82}Br	5.73×10^{-2}	7.2×10^{-7}
^{86}Rb	6.75×10^{-3}	7.9×10^{-8}
^{85}Sr	1.10×10^{-2}	1.3×10^{-7}
^{99}Mo	1.06×10^{-2}	1.1×10^{-7}
^{103}Ru	1.29×10^{-4}	1.3×10^{-9}
^{124}Sb	3.04×10^{-4}	2.5×10^{-9}
^{134}Cs	3.51×10^{-4}	2.6×10^{-9}
^{131}Ba	9.56×10^{-3}	6.9×10^{-8}
^{141}Ce	2.83×10^{-4}	2.0×10^{-9}
^{147}Nd	1.05×10^{-3}	7.3×10^{-9}
^{153}Sm	5.00×10^{-5}	3.3×10^{-10}
^{182}Ta	2.53×10^{-5}	1.4×10^{-10}
^{239}Np	1.12×10^{-3}	4.7×10^{-9}

[a]Rock pretreated water.

[b]See footnote b, Table IV.

TABLE VI

ACTIVITIES OF TRACED WATERS AND ELEMENT CONCENTRATIONS[a]

	^{85}Sr		^{133}Ba		^{137}Cs		^{141}Ce		^{152}Eu	
Water	nCi/mℓ	M	nCi/mℓ	M	nCi/mℓ	M	nCi/mℓ	M	nCi/mℓ	M
YM-22	56	3.8×10^{-8}	17	1.5×10^{-8}	15	1.2×10^{-9}	54	6.8×10^{-7}	19	4.8×10^{-8}
YM-38	54	3.7×10^{-8}	15	1.4×10^{-8}	15	1.3×10^{-9}	89	1.1×10^{-6}	27	6.9×10^{-8}
YM-45	37	2.5×10^{-8}	13	1.2×10^{-8}	12	1.0×10^{-9}	68	8.6×10^{-7}	45	1.1×10^{-7}
YM-48	52	3.6×10^{-8}	14	1.5×10^{-8}	14	1.2×10^{-9}	57	7.3×10^{-7}	19	4.7×10^{-8}
YM-49	56	3.7×10^{-8}	17	1.6×10^{-8}	14	1.2×10^{-9}	22	2.8×10^{-7}	54	1.4×10^{-7}
YM-54	38	2.6×10^{-8}	12	1.1×10^{-8}	20	1.6×10^{-9}	71	9.0×10^{-7}	56	1.4×10^{-7}

[a]Element concentrations include only those added with the tracer.

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 1-g quantities of the crushed rock with 20 mℓ of untraced, pretreated water for a period of two weeks at ambient temperature (22°C). The samples were contained in stoppered 40-mℓ polyethylene centrifuge tubes. All tubes were washed with deionized water prior to use. The phases were separated by centrifuging at 16 000 rpm (32 000 g's) for 1 h and decanting. The volume of solution remaining with the solid was determined by weighing. Twenty milliliters of the tagged pretreated water were then added, the solid sample was dispersed with vigorous shaking, and the mixture was agitated gently for a given time. Contact times were approximately 20 or 40 days. The shaking rate was 200 oscillations per minute. 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, for 1 h 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.

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 the strontium, cesium, and barium remained essentially completely in solution. However, not all of the cerium and europium remained in solution. It was felt that the amount of sorption on the container would vary, depending on whether or not solid material was present, since these elements appear to absorb on any available surface. Therefore, the presence of a solid phase would tend to reduce the fraction of the activity absorbed on the container.

In order to determine the amount of activity remaining with the solid phase, whether due to sorption, precipitation, centrifugation of colloids with the solid, or by some other mechanism, a fraction (5% to 25%) of the solid was removed for radioactivity assay. The solid phase was mixed well prior to sample removal. The fraction of the solid removed was determined both by weighing and from the activity of ^{137}Cs in the solid aliquot and in the initial and final solutions. This method is reasonable since cesium did not absorb on the container walls. The tube was weighed before and after removing the sample.

3. Desorption Measurements. Desorption measurements were made for most of the samples previously used for the sorption measurements. The assay of the activity on the solid was done as described earlier. Twenty milliliters of untagged, pretreated water were used for the measurements where ~5% of the solid had been removed and a fifteen-milliliter volume was used when ~25% of the solid had been removed. This was done in order to keep the solution to solid ratio ~20 mℓ/g. The same procedure that was used in the sorption measurements was used for separation of the phases and for radioactivity assay. Desorption contact times were approximately 20 or 40 days.

4. Assay of Radioactivity. The solution and solid samples were all counted on a calibrated, 14%, coaxial Ge(Li) detector. The two different sample geometries were carefully intercalibrated. The 4096 channel spectra were recorded in multichannel analyzers, which are connected to a common PDP-9 computer, where they were analyzed on-line by RAYGUN, an in-house gamma-ray spectroscopy program. This program is designed for use on a minicomputer and it includes spectral interpretation. Its operation involves: 1) a search for background and peak (nonbackground) regions; 2) a preliminary peak search in the nonbackground regions; 3) construction of a step function under the peaks(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 and 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 the i^{th} peak identified corresponding to the j^{th} nuclide identified; 9) by a least-squares iteration determine a solution to

$$Y_i = \sum_j A_{ij} X_j \quad (X_j \text{ unknown})$$

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

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

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

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.

The following equation was used to calculate the sorption ratios for strontium, cesium, and barium:

$$R_d = \frac{(D \cdot A_f) - A_t}{A_t} \cdot \frac{V}{W} \quad . \qquad (1)$$

where

A_f = the activity per mℓ of a given radionuclide in the tagged water (feed added to the sample),

A_t = the activity per mℓ in the supernatant solution after the required contact time,

W = the weight (grams) of solid material used,

V = the total final volume of supernatant solution, and

D = the dilution factor to take into account the residual solution from the wash that remains with the solid.

The amount of residual solution (V_r) left with the solid material was calculated from the weight increase of the sample plus container (g_r) after the two prewashes, and the measured density (ρ_r) of the solutions used:

$$V_r = g_r/\rho_r \quad .$$

Therefore, for these measurements (20.0 mℓ spike volume)

$$V = 20.0 + V_r$$

and

$$D = 20.0/(20.0 + V_r) \quad .$$

The activities in the control samples were not used in the calculations. However, the results would not be changed since no container effect was observed in these experiments.

The standard deviation for each measurement was obtained from the errors associated with the activity measurements (generally less than 2%), 3% uncertainty assumed for g_r, a 0.5 mg uncertainty in W, and a 0.5% uncertainty in the volumes. The errors were propagated using the rule for change of variables in a moment matrix assuming independence of the variables and Eq. (1).

For the cerium and europium cases, a different calculational method was used. Since a container problem has never been observed for cesium, the sorption ratio for cesium was used as an internal monitor. The activities of cerium or europium and cesium in the solid and solution samples were measured. The sorption ratio is

$$R_d = \frac{A_s}{A_t} \cdot \frac{V}{W} \quad , \qquad (2)$$

where

A_s = activity on the solid.

If a ratio of R_d values is calculated using Eq. (2) one has, after rearrangement,

$$R_{dx} = \frac{\frac{A_{sx}}{A_{sm}}}{\frac{A_{tx}}{A_{tm}}} R_{dm} \quad , \qquad (3)$$

where the x and m refer to the cerium (or europium) and cesium, respectively. This equation was used to calculate the sorption ratio for the cerium (or europium) since the R_d for cesium was calculated using Eq. (1) in the same experiment.

The standard deviation was calculated using the same procedure as previously discussed and Eq. (3).

For the desorption measurements the sorption ratio was again calculated assuming that the cesium did not have an affinity for the container. The activity, A^o_{sm}, of ^{137}Cs on the solid at the beginning of a desorption measurement was calculated using

$$A^o_{sm} = A^o_m (1 - f_m) (1 - f_d),$$

where

A^o_m = the initial ^{137}Cs activity at the beginning of the sorption measurement,

f_m = the fraction of ^{137}Cs activity in remaining solution after the sorption measurement, and

f_d = the fraction of the solid removed from the sample prior to beginning the desorption measurement.

The cesium sorption ratio was then calculated by

$$k_{dm} = \frac{A^o_{sm} - A_{tm} \cdot V}{A_{tm} \cdot V} \cdot \frac{V}{(1 - f_d) W},$$

where

$$V = 15.0 + V_r.*$$

The sorption ratios for all other species in the desorption measurement were then calculated using the sorption ratio for cesium and Eq. (3). An error analysis similar to that described earlier was also performed.

B. Results and Conclusions

The results for the R_d measurements for the 106- to 500-μm fractions of the Yucca Mountain tuffs are given in Table VII, while those obtained for the <106-μm fractions are given in Table VIII. Table IX gives the starting and final pH values of each solution. It is evident from Table VII (YM-22 and

*$V = 20.0 + V_r$ for those measurements where 20 mℓ were used for the desorption studies. (See Section III.A.3).

TABLE VII

SORPTION RATIOS FOR YM TUFFS (106-500-μm FRACTION)

Sample Number	Sorption Time (d)[a]	Desorption Time (d)	R_d(mℓ/g)[b] Cs	Sr	Ba	Ce	Eu
YM-22	19.63		258(2.6)	47.5(2.3)	907(2.8)	1 390(3.9)	1 280(4.3)
			382(2.4)	47.5(2.8)	851(2.3)	1 250(5.3)	1 180(4.8)
		41.63	356(7.6)	58.6(3.3)	655(8.3)	6 060(10.8)	3 350(8.4)
	39.63		270(2.6)	55.2(2.2)	982(2.8)	1 670(4.8)	1 680(4.0)
		20.65	382(7.5)	62.6(8.0)	989(8.2)	8 070(10.8)	3 900(9.1)
	39.63		237(2.4)	48.5(2.8)	855(2.3)	1 130(4.8)	1 410(4.2)
		20.63	356(7.6)	56.7(8.4)	827(8.4)	5 440(13.1)	3 120(8.6)
YM-38	19.63		11 800(6.3)	18 200(4.3)	77 300(9.1)	896(8.9)	2 620(9.0)
	39.63		8 220(3.1)	10 200(2.5)	80 900(10)	624(4.4)	1 520(4.5)
		20.65	13 100(7.7)	21 700(55)	257 000(57)	2 640(53.8)	7 280(54)
YM-45	19.63		481(2.8)	167(2.3)	1 160(2.3)	1 010(5.3)	2 110(5.1)
		41.63	445(7.6)	189(8.4)	1 480(8.4)	7 450(9.4)	7 100(8.4)
	39.63		325(2.7)	175(2.4)	1 410(2.4)	711(5.2)	1 620(4.7)
		20.63	427(7.7)	178(8.6)	1 240(8.6)	4 660(9.7)	6 430(8.7)
YM-48	19.63		14 900(11)	1 800(2.5)	12 000(8.2)	871(16)	1 750(16)
	39.63		22 100(13)	2 500(3.2)	23 000(11)	1 860(19)	2 700(15)
		20.65	30 400(17)	2 910(28)	41 100(32)	12 500(29)	9 330(24)
YM-49	19.63		29 400(17)	2 680(2.8)	25 600(14)	557(25)	1 020(25)
			37 200(11)	2 580(2.5)	30 000(17)	491(17)	1 200(16)
		41.63	37 600(10.0)	4 450(13)	51 100(22)	1 050(13)	1 600
	39.63		35 800(20)	3 790(3.7)	59 200(21)	814(25)	1 510(25)
		20.65	40 000(21.3)	4 440(27)	69 200(31)	1 090(27)	3 080(27)
	39.63		42 600(7.8)	3 820(2.4)	54 000(15)	351(12)	1 020(11)
		20.63	40 100(11)	4 260(14)	75 750(22)	967(14)	1 580(14)
YM-54	19.63		289(2.5)	87.5(2.3)	719(2.3)	178(4.7)	583(4.2)
		41.63	289(7.6)	80.4(8.3)	623(8.2)	1 550(8.6)	2 100(8.1)
	39.63		205(2.5)	80.5(2.6)	586(2.4)	106(4.4)	371(3.7)
		20.63	353(7.7)	84.1(8.4)	640(8.4)	717(8.8)	1 680(8.3)

[a] The two R_d values given for a single time or set of times represent results obtained by two different investigators.

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

TABLE VIII

SORPTION RATIOS FOR YM TUFFS (<106-μm FRACTION)

Sample Number	Sorption Time (d)[a]	Desorption Time (d)	R_d (mℓ/g)[b]				
			Cs	Sr	Ba	Ce	Eu
YM-22	39.63		542(2.8)	66.2(2.2)	1 295(3.1)	1 555(5.2)	1 460(4.7)
		20.65	497(7.5)	74.4(8.0)	1 630(8.4)	4 860(10.8)	3 960(9.2)
YM-38	39.63		5 920(6.7)	7 375(5.0)	39 650(2.0)	954(9.6)	2 645(9.7)
		20.65	13 100(7.8)	17 800(53.5)	115 000(54.3)	4 910(53.5)	10 100(53.5)
YM-45	19.63		738(3.1)	217(2.3)	969(2.1)	539(5.0)	989(4.6)
		41.63	781(7.6)	240(8.5)	1 220(8.5)	4 100(9.1)	5 790(8.5)
	39.63		554(2.8)	218(2.3)	1 240(2.3)	669(5.0)	1 660(4.5)
		20.63	836(7.8)	228(9.1)	1 320(9.1)	6 780(11.0)	9 700(9.4)
YM-48	39.63		6 930(7.4)	1 200(2.5)	10 285(7.5)	2 945(11)	3 075(11)
		20.65	22 800(14.6)	2 430(33.9)	27 200(35.9)	13 100(35.9)	6 840(34.2)
YM-49	19.63		21 900(5.7)	1 520(2.1)	17 000(5.9)	568(8.8)	1 380(8.5)
		41.63	15 400(8.7)	2 380(10.7)	27 800(12.6)	1 380(10.7)	2 190(10.3)
	39.63		8 660(3.9)	1 680(2.2)	9 230(4.7)	529(6.5)	1 340(6.1)
YM-54	19.63		267(2.5)	95.0(2.5)	524(2.2)	113(4.7)	393(4.1)
		41.63	274(7.6)	120(8.4)	688(8.4)	1 000(8.6)	1 930(8.2)
	39.63		227(2.5)	97.1(2.5)	650(2.3)	174(2.3)	703(3.9)
		20.63	324(7.7)	105(8.5)	684(8.5)	689(8.9)	1 660(8.4)

[a,b]See footnotes to Table VII.

TABLE IX

pH VALUES, AMBIENT TEMPERATURE

Sample	Fraction (μm)	Sorption Time (d)[a]	Initial pH	Sorption Final pH	Desorption Final pH
YM-22	106-500	19.63	8.28	8.36	
			8.20	8.46	8.53
		39.63	8.28	8.37	8.25
			8.20	8.49	8.44
	<106	39.63	8.28	8.39	8.23
YM-38	106-500	19.63	8.17	8.45	
		39.63	8.17	8.44	8.31
	<106	39.63	8.17	8.36	8.26
YM-45	106-500	19.63	8.13	8.15	8.45
		39.63	8.13	8.46	8.55
	<106	19.63	8.13	8.48	8.51
		39.63	8.13	8.46	8.53
YM-48	106-500	19.63	8.13	8.51	
		39.63	8.13	8.34	8.36
	<106	29.63	8.13	8.37	8.44
YM-49	106-500	19.63	8.34	8.62	
			8.14	8.46	8.54
		39.63	8.34	8.34	8.36
			8.14	8.46	8.49
	<106	19.63	8.14	8.49	8.45
		39.63	8.14	8.48	8.53
YM-54	106-500	19.63	8.12	8.47	8.52
		39.63	8.12	8.42	8.46
	<106	19.63	8.12	8.46	8.51
		39.63	8.12	8.48	8.50

[a]The two pH values given for a single sorption time represent results obtained by two different investigators.

YM-49 samples) that the sorption ratios determined by different investigators using the same experimental procedures and materials are fairly reproducible. Most values agree to within about 20%.

There is no consistent correlation between the sorption ratios and the particle sizes used in these studies for either the sorption or desorption measurements. For example, the R_d values for strontium, cesium, and barium on YM-38, YM-48, and YM-49 decreased as the sieve fraction size decreased, while the values for the rest of the core samples tended to increase or remain approximately constant with decreasing size. Cerium and europium seem to behave differently. It was thought that fractionation of minerals in the sieving process might explain these results. However, x-ray diffraction analyses indicate no difference in x-ray patterns or intensities (M. L. Sykes, Los Alamos Scientific Laboratory, personal communication). Thus, unless the difference in sorption behavior is due to a relatively minor component which is not resolved by x-ray diffraction, it is unlikely that mineral fractionation can explain these results. A more likely explanation may come from the fact that the smaller fraction (<105-μm) has been ground to particles smaller than natural grain sizes, exposing different surfaces, and perhaps destroying others.

As was observed with three tuffs from Jackass Flats,[5] sorption ratios from the desorption experiments are generally higher than those from the sorption experiments, particularly those for cerium and europium. This probably indicates that cerium and europium do not sorb by ion-exchange or that there are non-sorbing species in the original mixture. The average sorption and desorption ratios for strontium, cesium, barium, cerium, and europium for all measurements are given in Section X. Specific differences in the sorption ratios for the different types of tuff are also discussed in Section X.

It was thought that if an epoxy material was found to be nonsorptive and stable, it might be useful as a "container" for whole core columns. The results of sorption measurements with "Barco Bond" and "Eco Bond" epoxy adhesives are given in Table X. Although the R_d values are generally small, results do indicate that, particularly with cerium and europium, these materials may cause problems if used in sorption measurements with a core.

C. Effects of Groundwater Composition on Sorption Ratios

Since the composition of the groundwater may have a pronounced effect on the sorption ratio for many radionuclides, experiments to assess this

TABLE X

SORPTION RATIOS FOR BARCO BOND AND ECO BOND EPOXYS

Sample	Sorption Time (d)	R_d (mℓ/g)					pH	
		Cs	Sr	Ba	Ce	Eu	Initial	Final
Barco Bond	39.63	0.2	0.3	0.5	7.3	15.5	7.91	8.21
Barco Bond[a]	29.63	15.2	2.2	39.3	23.4	27.3	7.91	8.85
Eco Bond	29.63	2.7	39.4	45.2	261.	300.	7.91	7.03
Eco Bond[a]	39.63	0.02	0.1	1.1	47.0	48.7	7.91	7.81

[a]These samples were pre-equilibrated with J-13 water two weeks before the traced J-13 water was added.

dependence for tuff have been initiated. The compositions of the two solutions being used in the study were selected to represent extremes for the media being studied. While the dependence of the sorption ratio on specific major ion concentrations cannot be determined in these experiments since the concentrations of several ions were varied, the overall effects can be distinguished. The same sieve fraction (250- to 355-μm) was used in all experiments. All measurements were made under atmospheric conditions.

1. Measurement Techniques. The approximate initial compositions of two solutions selected for study are given in Table XI. The dilute solution (labeled Water I) was prepared by adding 2.2 mℓ KCl solution (17.2 mg/mℓ), 13.2 mℓ NaOH solution (4.0 mg/mℓ), and 1.24 mℓ Na_2SO_4 solution (23.9 mg/mℓ) to 74 mg $Ca(OH)_2$ plus 19.2 mg $Mg(OH)_2$. The mixture was diluted to 4.0 ℓ with deionized water and then sparged with carbon dioxide for about 36 h. The solution was next sparged with nitrogen until pH ≅ 8 was reached. It was then allowed to air-equilibrate for 2 d prior to use. The more concentrated solution (labeled Water II) was prepared in a similar manner using 370 mg ($Ca(OH)_2$, 192 mg $Mg(OH)_2$, 2.2 mℓ KCl solution, 17.9 mℓ NaOH solution, 17.3 mℓ Na_2SO_4 solution, and 9.1 mℓ NaCl solution (7.3 mg/mℓ).

The 250- to 355-μm sieve fractions of three tuff samples (JA-18, JA-32, and JA-37) were studied. Weighed 1-g quantities of these materials were pretreated for 2 wk with 20 mℓ of the appropriate water. The phases were then separated by centrifugation at 12 000 rpm (28 000 g's).

TABLE XI
APPROXIMATE INITIAL GROUNDWATER COMPOSITION (mg/ℓ)

Constituent	Water I	Water II
Na	10	50
K	5	5
Ca	10	50
Mg	2	20
SO_4	5	70
Cl	4.5	15

Rock-treated waters were prepared by shaking each of the two waters with the 150-to 355-μm fraction of sample JA-37. A solution-to-solid ratio of 20 mℓ/g was used. The phases were separated by centrifugation at 6 000 rpm (20 000 g's) for 1 h followed by filtration through 0.45-μm Millipore filter membranes.

The ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu tracers were added to these rock-treated waters using the technique described earlier (evaporation to dryness followed by dissolution). The concentrations due to the carrier added with the tracer are given in Table XII.

Each tuff sample was treated with the tagged water by the procedures described earlier (see Section IIIA)) for measuring sorption ratios. All solutions and solids were assayed for radioactivity, and our standard calculation methods were used. Contact times were 4 and 8 wk.

Determination of the actual composition of the waters before and after contact with the rock is in progress.

TABLE XII
ELEMENT CONCENTRATIONS[a]

	Molarity				
Water	Sr	Cs	Ba	Ce	Eu
I	6.2×10^{-8}	5.7×10^{-10}	9.2×10^{-9}	1.3×10^{-8}	7.5×10^{-9}
II	6.8×10^{-8}	1.2×10^{-9}	1.4×10^{-8}	1.8×10^{-8}	3.2×10^{-8}

[a]Element concentrations due to the tracer solutions used.

2. Results. The results from the 28-day and 60-day sorption measurements are given in Table XIII. Representative sorption ratios[5] of the same tuff samples and radionuclides in pretreated J-13 water are given in Table XIV for comparison. Table XV gives the initial and final pH values.

The composition of the groundwaters seems to be a major factor in the R_d value of a particular radionuclide. R_d values of cesium, strontium and barium are higher in the less concentrated solution, as might be expected with fewer ions competing for a site on the rock. For cerium and europium, however, larger R_d values are generally observed for the more concentrated solution, perhaps due to a greater tendency of cerium and europium to form radiocolloids in higher concentrations of SO_4^{-2} ions. The sorption mechanism(s) of cerium and europium seems to be quite different from that of strontium, cesium, and barium, which sorb mainly by ion-exchange. These results indicate the importance of determining both the cation and anion compositions of the groundwaters or solutions used in making R_d measurements.

IV. SORPTION OF TECHNETIUM

A. Measurement Techniques

The sorption of technetium on the 106- to 500-μm fraction of three Yucca Mountain cores YM-22, YM-48, and YM-49 was studied under atmospheric conditions to look for variability of the R_d values with concentration of technetium. Four concentrations of technetium were used: 10^{-3} M, 10^{-6} M, 10^{-9} M, and 10^{-12} M. All traced solutions contained ^{95m}Tc supplied by Argonne National Laboratory. The 10^{-3}, 10^{-6}, and 10^{-9} M solutions also contained ^{99}Tc. Filtration of the technetium solutions prior to use was done with a 0.4-μm Nuclepore filter assembly and polycarbonate membrane since it was found that as much as 25% of the technetium (from the 10^{-3} M solution) was adsorbed on the glass frit of a Millipore filter bed. Preparation of pre-equilibrated waters and samples was done as previously described (see Section II.D.) for Yucca Mountain tuffs. The experiments were run in an identical manner with the 40-d sorption time measurements in the tuff variability study (see Section II.D.and III.A.). After 41-d sorption and 65-d desorption contact times, the aqueous and solid phases were separated by four centrifugings for 1 h at 16 000 rpm each in a new polyethylene tube. The pH values of the solutions were recorded and aliquots of the aqueous and solid phases were taken for counting.

TABLE XIII

THE EFFECT OF GROUNDWATER COMPOSITION ON SORPTION RATIOS (mℓ/g)

Sample	Water	Time(d)	Cs	Sr	Ba	Ce	Eu
JA-18	I	27.63	10 900(13.8)	23 600(9.7)	17 200(7.8)	945(20.4)	130(20.5)
	I	59.63	15 200(7.6)	27 000(7.5)	119 000(12.9)	1 470(11.3)	1 700(10.7)
	II	27.63	743(7.5)	5 030(4.2)	46 400(17.3)	5 200(17.3)	4 560(12.7)
	II	59.63	8 440(4.4)	4 850(3.0)	82 200(7.6)	≧34 200	15 400(10.6)
JA-32	I	27.63	130(4.1)	84.2(2.6)	587(2.5)	2 870(12.6)	1 690(11.2)
	I	59.625	143(3.7)	85.0(2.0)	656(2.1)	≧54 700	4 200(7.6)
	II	27.625	85.2(3.2)	17.9(4.4)	156(1.9)	≧30 300	23 500(31.2)
	II	59.625	73.0(3.3)	17.7(4.4)	182(1.8)	≧45 900	≧61 000
JA-37	I	27.63	1 330(3.5)	415(2.2)	840(1.9)	27 100(20.5)	12 000(9.2)
	I	59.625	1 390(3.6)	385(1.8)	882(1.9)	≧48 400	≧25 600
	II	27.625	844(2.8)	74(2.4)	375(1.8)	≧36 600	12 700(10.0)
	II	59.625	757(2.8)	149(2.4)	339(1.8)	≧33 000	50 900(10.0)

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

TABLE XIV

REPRESENTATIVE SORPTION RATIOS[a]

	R_d(mℓ/g)				
Material	Cs	Sr	Ba	Ce	Eu
JA-18	6 000	13 000	4 800	40	30
JA-32	150	55	440	80	90
JA-37	740	300	850		6 000

[a]See Ref. 5. Measurements were made with water from well J-13.

TABLE XV

pH VALUES

		pH		
Solid	Water	Initial	28-d	60-d
JA-18	II	8.62	8.63	8.63
	I	8.17	8.22	8.40
JA-32	II	8.62	8.54	8.50
	I	8.17	8.20	8.25
JA-37	II	8.62	8.54	8.45
	I	8.17	8.31	8.39

The solution and solid samples were counted on a Ge(Li) detector which had been calibrated for the two sample geometries. The 4096-channel spectra were recorded in a multichannel analyzer connected to a PDP-9 computer where they were analyzed by the gamma-ray analysis code RAYGUN. Each sample was counted at least two times, and the results were averaged. The sorption ratios were calculated directly from:

$$R_d = \frac{\text{Activity in the solid phase per unit mass of solid}}{\text{Activity in solution per unit volume of solution}} .$$

B. Results and Conclusions

The results of the sorption-desorption measurements at ambient temperature are given in Table XVI. Also included in the table are the initial and final pH values of each solution. In all cases the sorption ratios are close to

zero and no concentration effect is observed. The average sorption ratios were 0.30, 0.15 and 0.21 mℓ/g for samples YM-22, YM-48, and YM-49, respectively. Desorption ratios were 4 to 11 times larger: 1.2 mℓ/g for sample YM-22, 1.7 mℓ/g for sample YM-48 and 2.0 for sample YM-49.

TABLE XVI

SORPTION RATIOS FOR TECHNETIUM ON TUFF

Tuff Sample	Tc Concentration(M)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)	pH Initial	pH Final
YM-22	10^{-3}	39.67		0.13	7.99	8.30
			64.99	0.47		
	10^{-6}	39.67		0.17	7.92	8.43
			64.99	1.2		
	10^{-9}	39.67		0.16	7.81	8.29
			64.99	1.9		
	10^{-12}	39.67		0.72	7.89	8.34
			64.99	1.2		
YM-48	10^{-3}	39.67		0.16	8.08	8.08
			64.99	1.5		
	10^{-6}	39.67		0.14	8.03	8.19
			64.99	1.2		
	10^{-9}	39.67		0.11	8.02	8.20
			64.99	2.3		
	10^{-12}	39.67		0.20	8.01	8.14
			64.99	1.6		
YM-49	10^{-3}	39.67		0.16	7.93	8.02
			64.99	1.3		
	10^{-6}	39.67		0.20	8.06	8.21
			64.99	1.5		
	10^{-9}	39.67		0.25	8.07	8.14
			64.99	2.7		
	10^{-12}	39.67		0.23	8.10	8.02
			64.99	2.3		

V. SORPTION OF URANIUM(VI)

A. Measurement Techniques

Measurements of the sorption of uranium on samples JA-18, JA-32 and JA-36 have been made. The ^{237}U used in these measurements was made by the $^{236}U(n,\gamma)$ ^{237}U reaction in the HFIR reactor at the Oak Ridge National Laboratory. The tracer was taken to dryness, diluted with the appropriate groundwater, and filtered through a 0.4-μm Millipore filter. The estimated uranium(VI) concentration was $\sim 10^{-7}$ M. Initial pH values were 7.6, 8.1 and 8.4 (at ambient temperature) and 8.3, 8.5, and 8.4 (at 70°C) for samples samples JA-18, JA-32 and JA-37, respectively.

The assay of the radioactivity was done on a 3 in x 3 in Na(Tl) detector and multichannel analyzer. The activity of the ^{237}U was obtained by integrating the counts in the energy region between 35 and 360 keV. The standard deviation of the assay was assumed to be 5%. Due to the short half-life of ^{237}U, the sorption contact times were 1, 2, and 3 wk, and the desorption contact times were 3, 2, and 1 wk, respectively.

B. Results and Conclusions

The results of the measurements are shown in Tables XVII, XVIII, XIX and XX. As expected, uranium(VI) is sorbed poorly on tuff under the conditions used. This is presumably due to the rather high carbonate concentration in these waters, which would strongly complex the uranyl ion.

Generally, the uranium(VI) sorption ratios at 70°C are several times greater than those measured at ambient temperature. Perhaps this is due to the increased rate of diffusion into solid matrix at higher temperatures. This may also be indicated by the tendency for the amount of sorption to increase somewhat with time and by the observation that the desorption ratios are significantly higher than sorption ratios. It is difficult to correlate the observed sorption ratios with mineralogy. However, the highest values were obtained for the sample having the highest zeolite content (JA-37).

TABLE XVII

U(VI) SORPTION RATIOS, SAMPLE JA-18, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (d)	Desorp. Time (d)	R_d (mℓ/g)[a]	Final pH
106-150	6.94		4.9 (37)	7.9
		19.97	13.0	7.9
	14.00		3.5 (49)	7.9
		13.91	11.7	8.1
	20.98		10.6 (21)	7.8
		7.93	43.8	8.0
355-500	6.94		1.6 (95)	8.0
		19.97	9.7 (95)	8.2
	14.00		1.4 (99)	8.2
		13.91	6.4	8.3
		20.98	1.3 (110)	8.0
		7.93	6.3	7.9

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

TABLE XVIII

U(VI) SORPTION RATIOS, SAMPLE JA-32, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (d)	Desorp. Time (d)	R_d (mℓ/g)	Final pH
106-150	6.94		3.5 (49)	7.6
		19.97	15.4	7.8
	13.98		2.9 (56)	7.8
		13.91	11.9	8.0
	20.98		2.6 (45)	7.6
		7.93	9.6	7.6
355-500	6.94		1.4 (84)	7.7
		19.97	0.2	7.9
	14.00		1.3 (109)	8.1
		13.91	5.4	8.3
	20.98		1.3 (107)	8.3
		7.93	5.2	8.4

[a]See footnote a, Table XVII.

TABLE XIX

U(VI) SORPTION RATIOS, SAMPLE JA-37, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (d)	Desorp. Time (d)	R_d(mℓ/g)[a]	Final pH
106-150	6.94		4.0 (44)	7.3
		19.97	6.1	7.7
	14.00		4.8 (35)	8.0
		13.91	9.6	8.2
	20.98		5.1 (33)	8.5
		7.93	11.2	8.4
355-500	6.94		2.6 (175)	8.5
		19.97	2.2	8.5
	14.00		4.2 (39)	7.7
		13.91	9.2	7.9
	20.98		4.7 (36)	8.1
		7.93	11.9	8.2

[a]See footnote a, Table XVII.

TABLE XX

U(VI) SORPTION RATIOS, 70°C, 355-500 μm FRACTION

Core	Sorption Time (d)	Desorption Time (d)	R_d(mℓ/g)[a]	Final pH
JA-18	6.68		4.2(36.9)	8.33
		20.95	12.9(72.7)	8.30
	13.68		3.6(42.5)	8.26
		13.93	9.5(101)	8.32
	20.68		4.3(30.9)	8.43
		5.40	18.2(51.1)	8.37
JA-32	6.68		9.9(20.2)	8.50
		20.95	22.7(31.5)	8.45
	13.68		10.5(20.0)	8.41
		13.93	19.3(34.4)	8.47
	10.68		14.8(16.0)	8.28
		5.93	19.8(27.2)	8.33
JA-37	6.68		12.9(17.5)	8.35
		20.95	57.9(20.6)	8.36
	13.68		16.8(14.7)	8.32
		13.93	41.6(18.8)	8.39
	20.68		18.5(14.0)	8.49
		5.93	39.5(18.3)	8.36

[a]See footnote a, Table XVII.

VI. SORPTION OF PLUTONIUM AND AMERICIUM

A. Measurement of Sorption Ratios

The measurement of the sorption behavior of americium and plutonium on tuff under atmospheric conditions involved geologic materials and groundwaters described in Ref. 5.

1. Measurement Techniques

a. Preparation of Traced Feed Solutions. The traced waters used in these studies were prepared using the pretreated waters described earlier,[5] 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 produced at Argonne National Laboratory under contract with Battelle (PNL). Tracer purities were checked by both alpha and gamma spectroscopy. The ^{237}Pu tracer was treated with $NaNO_2$ so that the plutonium was in the IV oxidation state at the beginning of the experiments; this resulted in the addition of $\sim 10^{-4}$ M sodium into the feed solutions containing ^{237}Pu. Feed solutions were prepared* by two methods. Most of the solutions for Experiments 1, 2, and 3 were prepared by drying the tracers at room temperature and then dissolving them in the appropriate groundwater. This operation resulted in the addition of $\sim 5 \times 10^{-3}$ M chloride to the feed solutions. In Experiment 4 the traced feed solutions were prepared by adding ^{237}Pu or ^{241}Am tracer solution to the pretreated groundwater and readjusting the pH to the original value by adding NaOH solutions. This step added $\sim 1 \times 10^{-3}$ M sodium and $\sim 5 \times 10^{-3}$ M chloride to the feed solutions. Feed solutions were prepared to contain $\sim 1 \times 10^{-6}$ M americium, $\sim 1 \times 10^{-5}$ M plutonium when ^{239}Pu was used, and $\sim 4 \times 10^{-13}$ M plutonium when ^{237}Pu was used. After allowing for losses during the preparation of the traced feed solution, final concentrations were $\sim 4 \times 10^{-7}$ M americium, $\sim 1 \times 10^{-13}$ M plutonium with ^{237}Pu, and $\sim 4 \times 10^{-7}$ M plutonium with ^{239}Pu, but these varied significantly from one feed solution to another.

b. Sorption Measurements. Crushed rock from cores JA-18, JA-32, and JA-37 was used for sorption studies at both ambient (22° ± 2°C) and elevated (70 ± 1°C) temperatures. The material was pretreated by shaking weighed 1-g quantities with 20-mℓ portions of water from well J-13 for periods of at least two weeks. The samples were contained in prewashed, capped, 40-mℓ

*Additional details are given in Reference 5.

polypropylene tubes. The phases were separated by centrifuging at 12 000 rpm (28 000 g's) for one hour. The weight of the wash 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 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 wk. A few contacts are being continued for ~6 months to examine long-term effects. 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. Solutions were transferred by decanting the first three times and by transferring with a plastic pipet the last time. In Experiment 4 three centrifugings were normally carried out (1, 1, and 2 h), and the solutions were transferred by pipet each time. Extreme care was taken to avoid transferring any particulates from the bottom of the tubes or in surface films. Aliquots of the final solutions were taken for pH measurement, gross gamma counting, and gamma spectroscopy. The solid phases were left in the tubes and counted directly. The activity sorbed on the walls is considered negligible (see Section VI.B.). The comments[5,16,17] concerning control samples with a traced aqueous phase but no solid are applicable here. Such samples run with plutonium and americium showed much higher wall sorption on the containers when no solid was present.

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

c. Assay of Radioactivity. Solid samples were normally gamma-counted for ^{241}Am or ^{237}Pu on a NaI(Tl) detector utilizing a single channel analyzer and a scaler. Liquid samples were usually gamma counted with a NaI well counter (Packard Auto-gamma Scintillation Spectrometer). Both liquid and solid samples were sometimes counted using a calibrated, 23%, coaxial Ge(Li) detector. The 1024-channel spectra were recorded in a multichannel analyzer connected to a PDP-9 computer.

A minimum of two counts were taken for each sample. Counting standards were prepared using known amounts of ^{241}Am or ^{237}Pu in the same geometries and conditions as the experimental samples.

The ^{239}Pu was determined radiochemically[18] after sample dissolution. Some analyses are not yet complete.

d. Calculations. Since both solid and liquid phases were counted directly for ^{241}Am and ^{237}Pu, or analyzed separately for ^{239}Pu, the sorption ratio, R_d, can be calculated directly as:

$$R_d = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}} .$$

The activities in the control tubes were not used in the calculations; container effects are considered negligible.

2. Results and Conclusions. The results to date for the batch measurements of the sorption behavior of ^{241}Am, ^{237}Pu, and ^{239}Pu on tuff under atmospheric conditions are given in Tables XXI through XXV. Data for samples that were contacted for six months and for some samples that were traced with ^{239}Pu are not yet available. The initial and final pH values are also listed in the tables.

The quoted R_d values were calculated from direct counts of the solids and aliquots of the aqueous phases after they were centrifuged but before they were filtered. Average sorption ratios for both "dried" and "pH adjusted" methods of preparing the traced feed solutions are listed in Table XXV. These ratios were averaged over 1-, 2-, 4-, and 8-week contact times, 106- to 150- and 355- to 500-μm particle sizes, and $\sim 10^{-6}$ and $\sim 10^{-13}$ M plutonium concentrations. The errors quoted are the standard deviations of the means.

For comparison purposes, the results for Experiment 4 are presented in Table XXVI. Although more limited in scope, these data are probably more reliable than those from earlier experiments because of an improved experimental technique.

Based primarily on the data of Experiment 4, several general comments can be made for the plutonium and americium results: The sorptive properties tend to vary with the mineralogy; the R_d values are highest for the zeolitized tuff (JA-37). At least qualitatively the americium R_d value for sorption or desorption tends to increase slightly with increasing particle size, while the plutonium value shows a slight decrease. The R_d values show very little increase with longer contact times; the plutonium values tend to increase more than do the americium values. At least for the pH-adjusted feed solutions of Experiment 4, the R_d values for americium sorption tend to increase with

TABLE XXI

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

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d (mℓ/g)		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
1	106-150	dried	7		200	170[a]		8.19
1			7		250			8.29
				14	270	160[a]	8.30	
2			7.6		96	70[a]	8.56	7.43
2			7.6		310			7.52
				59.8	810		8.51	8.58
3			13.8			110[b]	8.38	8.30
				13.7		710[b]	8.43	8.51
2			14.6		86		8.56	8.42
				34.7	440		8.51	8.53
2			14.6		310			8.29
				59.8	710		8.51	8.57
2			28.6		120	81[a]	8.56	8.55
2			28.6		200		8.53	8.58
				34.7	1 200		8.51	8.15
2			28.6		360			8.60
				59.8	790		8.51	8.58
2			28.6		220		8.52	8.60
3			28.9			120[b]	8.38	8.41
				14.0		450[b]	8.44	8.56
3			55.7			220[b]	8.38	8.42
				17.8		97[b]	8.35	8.45
2			56.6		57	68[a]	8.56	8.36
2			56.6		100		8.52	8.57
				34.7	2 000		8.51	8.36
2			56.6		85			8.57
				59.8	2 300		8.51	8.52
2			56.6		85		8.53	8.49
4	106-150	pH adjust	32.9		450		8.55	8.42
				41.8	1 000		8.50	8.59
4			32.9		440		8.55	8.43
				41.8	930		8.50	8.64
4			60.9		420		8.55	8.27
				43.8	950		8.50	8.62
4			61.9		430		8.55	8.44
				44.8	970		8.50	8.65

[a] Approximately 10^{-6} M ^{239}Pu.

[b] Approximately 10^{-13} M ^{237}Pu.

TABLE XXII

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

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d(mℓ/g)		pH	
			Sorp	Desorp	Am	Pu[a]	Initial	Final
2	106-150	dried	7.6		110		8.50	7.60
				34.7	2 800		8.58	8.56
2			14.6		110	110	8.50	8.60
2			28.6		140		8.50	8.63
2			28.6		230		8.50	8.63
				34.7	1 500		8.58	8.34
2			56.6		79		8.50	8.64
1	106-150	pH adjust	7		1 600	1 200	7.92	8.26
1			14		1 000	1 800	7.92	8.19
1			28		1 100		7.92	8.32
				14.0	2 100	920	8.30	
1	355-500	pH adjust	7		890	1 000	7.92	8.19
4			13.0		1 300		8.59	8.49
				47.8	2 100		8.46	8.64
1			14		640		7.92	7.94
				14	920	580	8.30	
4			14.0		1 400		8.59	8.45
				47.8	3 900		8.46	8.69
1			28		490	820	7.92	8.23
4			61.9		1 200		8.59	8.50
				44.8	2 100		8.46	8.67
4			62.9		1 700		8.59	8.52
				47.8	2 600		8.46	8.69

[a] Approximately 10^{-6} M ^{239}Pu.

TABLE XXIII

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

Experiment Number	Fraction (μm)	Tracer prep	Time (d) Sorp	Time (d) Desorp	R_d(mℓ/g) Am	R_d(mℓ/g) Pu	pH Initial	pH Final
2	106-150	dried	7.6		430	390[a]	8.64	7.53
2			14.6		365		8.64	8.52
				34.7	14 000		8.60	8.47
2			28.6		430	180[a]	8.64	8.67
2			28.6		1 500		8.64	8.62
				34.7	21 000		8.60	8.28
2			56.6		640		8.64	8.56
1	106-150	pH adjust	7		7 200	7 200[a]	7.92	8.53
1			14		5 200		7.92	8.23
				14	2 700	890[a]		8.30
4			14.0		11 000		8.60	8.48
				47.8	12 000		8.58	8.64
4			14.7		10 000		8.59	8.44
				47.8	8 900		8.58	8.63
1			28		7 500	12 000[a]	7.92	7.94
				14	5 200	1 600[a]	8.30	
4			27.7			750[b]	8.35	8.33
				40.8		5 300[b]	8.56	8.60
4			27.7			720[b]	8.35	8.33
				40.8		8 600[b]	8.58	8.59
4			33.9		14 000		8.60	8.52
				42.8	11 000		8.58	8.56
4			34.7		14 000		8.59	8.57
				42.8	9 500		8.58	8.55
4			54.7			1 900[b]	8.35	8.30
				43.8		5 500[b]	8.58	8.56
4			60.9		12 000		8.60	8.31
				43.8	12 000		8.58	8.57
4			62.6		11 000		8.59	8.54
				44.8	10 000		8.58	8.59
4			63.6		13 000		8.59	8.56
				47.8	9 700		8.58	8.61
1	355-500	pH adjust	7		3 700	5 400[a]	7.92	8.38
1			14		2 800	7 200[a]	7.92	8.19
1			28		3 800		7.92	8.29
				14	5 800	670[a]	8.30	
4			32.9		12 000		8.60	8.50
				41.8	17 000		8.58	8.58
4			33.9		13 000		8.60	8.51
				42.8	17 000		8.58	8.55
4			60.9		14 000		8.60	8.37
				43.8	18 000		8.58	8.58
4			62.9		12 000		8.60	8.53
				47.8	33 000		8.58	8.60
4			27.7			280[b]	8.38	8.40
				40.8		6 500[b]	8.58	8.61
4			27.7			320[b]	8.38	8.40
				40.8		3 600[b]	8.58	8.59
4			54.7			450[b]	8.38	8.28
				43.8		1 000[b]	8.58	8.59
4			54.7			470[b]	8.38	8.46
				43.8		1 900[b]	8.58	8.56

[a] Approximately 10^{-6} M ^{239}Pu.

[b] Approximately 10^{-13} M ^{237}Pu.

TABLE XXIV

Am AND Pu SORPTION RATIOS, SAMPLES JA-18, -32, and -37, 70°C

Core Sample	Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d(mℓ/g)		pH	
				Sorp	Desorp	Am	Pu[a]	Initial	Final
JA-18	2	106-150	dried	7.6		220			7.19
					33.9	3 100		8.35	8.48
	2			7.6		190			7.32
	2			14.6		190			7.57
					33.9	3 600		8.35	8.42
	2			14.6		170			8.08
	2			28.6		290			8.61
	2			28.6		150			8.62
	2			28.6		340		8.60	
	2			28.6		370		8.57	8.50
	2			56.6		300			
	2			56.6		76			
JA-32	2	106-150	dried	7.6		120		8.46	7.33
	2			14.6		160		8.46	8.14
	2			28.6		130		8.46	8.57
	2			56.6		46		8.46	
JA-37	2	106-150	dried	7.6		520	240	8.58	7.33
	2			14.6		680		8.58	8.06
	2			14.6		2 100		8.58	8.18
	2			28.6		960		8.58	8.67
	2			56.6		800		8.58	
	2			56.6		730		8.58	8.52
JA-37	4	355-500	pH adjust	32.9		32 000		8.37	8.23
					41.7	3 800		8.41	8.59
	4			33.9		48 000		8.37	8.25
					42.7	7 200		8.41	8.46
	4			61.8		19 000		8.37	8.51
					44.7	5 500		8.41	8.58
	4			62.8		37 000		8.37	8.64
					47.8	4 800		8.41	8.58

[a]Approximately 10^{-6} M ^{239}Pu.

TABLE XXV

AVERAGE SORPTION RATIOS[a] (mℓ/g) FOR Am AND Pu

Element	Core	Temp (°C)	Dried		pH Adjusted	
			Sorption	Desorption	Sorption	Desorption
Am	JA-18	22	180 (30)	1 100 (260)	435 (6)	960 (15)
		70	230 (30)	3 400 (300)		
	JA-32	22	130 (30)	2 200 (650)	1 100 (120)	2 300 (310)
		70	110 (30)			
	JA-37	22	670 (210)	17 000 (3 500)	8 800 (1 100)	12 000 (2 000)
		70	970 (240)		34 000 (6 000)	5 300 (720)
Pu	JA-18	22	140 (30)	350 (140)		
	JA-32	22	~110		1 200 (210)	750 ± 170
	JA-37	22	280 (100)		3 300 (1 200)	3 800 (950)

[a]Sorption ratios are given for both "dried" and pH adjusted" methods of preparing the traced feed solutions. They are averaged over 1-, 2-, 4-, and 8-week contact times, 106- to 150- and 355- to 500-μm particle sizes, and $\sim 10^{-6}$ and $\sim 10^{-13}$ M plutonium concentrations. Values in parentheses are the standard deviations of the means (absolute values).

TABLE XXVI

AVERAGE SORPTION RATIOS[a] FOR Am AND ^{237}Pu EXPERIMENT 4 DATA

Element	Core	Temp (°C)	R_d(mℓ/g)	
			Sorption	Desorption
Am	JA-18	22	435 (6)	960 (15)
	JA-32	22	1 400 (110)	2 700 (420)
	JA-37	22	12 000 (500)	14 000 (2 100)
		70	34 000 (6 000)	5 300 (720)
^{237}Pu	JA-37	22	700 (210)	4 600 (1 000)

[a]Sorption ratios are given for the "pH adjusted" method of preparing the traced feed solutions. They are averaged over 1-, 2-, 4-, and 8-week contact times and 106- to 150- and 355- to 500-μm particle sizes. Values in parentheses are the standard deviations of the means (absolute value).

increasing temperature, while those for desorption tend to decrease with increasing temperature. The method of preparing the traced feed solutions appears to have influenced the observed sorption ratios, the "pH adjusted" method giving somewhat higher R_d values than the "dried" method for sorption but approximately the same for desorption. However, the improved procedure used in Experiment 4 (pH adjusted) for centrifuging and transferring solutions after contact may have resulted in the removal of more particulates from solution, which would result in the observation of higher R_d values. Five different feed solutions of ^{241}Am and two of ^{237}Pu were used in Experiment 4 with no observable differences in their behavior for a given element. This indicates that the feed preparation, at least for the pH-adjusted method, is fairly reproducible. For americium, the R_d values were greater for desorption than for sorption, except possibly at 70°C. Comparison of results for ^{239}Pu (~4 x 10^{-7} M) and ^{237}Pu (~1 x 10^{-13} M), at least for "pH adjusted" feed solutions, shows higher sorption R_d values for ^{239}Pu but higher desorption R_d values for ^{237}Pu. Also, for ^{239}Pu the sorption R_d values are greater than the desorption but for ^{237}Pu the desorption R_d values are greater than the sorption.

B. Behavior of Americium and Plutonium in Groundwater.

Although a considerable number of procedural variables were examined during batch sorption experiments with tuff,[5] argillite,[16] and granite,[17] the following discussion is primarily based upon tuff Experiment 4 (see Section VI.A.). In this experiment improvements were made in the method used for separating solid and liquid phases after contact, presumably reducing the amount of particulates present in the aqueous phase and giving more accurate results. A few operations were added to examine container sorption for samples and controls, the fraction of centrifugible species in the controls, the effect of filtering successive portions of the same "after-contact" solution through the same filter membrane, the effects of filtering after-contact solutions through filter membranes with different pore sizes, and the effects of centrifuging after-contact solutions a different number of times and for different durations. A few contacts will be continued for ~6 months to examine long-term effects. The procedure used for phase separation after contact was usually three centrifugings, for 1, 1, and 2 h, at 12 000 rpm (28 000 g's). Extreme care was taken to avoid transferring any particulates from the bottom of the tube or in surface films. The centrifuged solutions were then filtered in various ways.

In some cases, aliquots were taken for counting after each centrifuging and each filtering.

Sorption on container walls during tuff contacts was measured by transferring the contents after contact, without centrifuging, to new tubes and counting the original tubes. Sorption on the container walls when solids were present was measured for twenty-four ^{241}Am and seven ^{237}Pu samples. The amount of activity sorbed on the container, with the possibility of retention of a small amount of solid even after transfer, averaged 2.1% for americium and 2.5% for plutonium. For the controls, container sorption averaged 24% for nine americium solutions at room temperature, 74% for four americium solutions at 70°C, and 16% for two plutonium solutions at room temperature. The amount of plutonium or americium activity remaining on the containers is obviously much lower for the samples than for the controls.

During earlier experiments container sorption for argillite samples was examined in essentially the same way except that the control samples were centrifuged and the aqueous phase was transferred to another tube. The activity observed in a control tube therefore represented the sum of wall sorption and centrifugable species. Sorption on the container walls when solids were present was measured for thirteen ^{241}Am and nine ^{237}Pu samples. The amount of activity sorbed on the container, with the possibility of retention of a small amount of solid even after transfer, averaged 1.2% for americium and 0.6% for plutonium. For the controls, the americium activity remaining with the container averaged 13% for thirteen solutions at ambient temperature and 90% for four solutions at 70°C. For two plutonium controls at each temperature the values were 43% at ambient and 88% at elevated temperature. Again, container sorption was much higher for the controls than for samples containing crushed rock.

The distribution of activity sorbed on the tuff control tubes was investigated. The bottoms of six tubes were washed twice with 2.5-mℓ portions of 3 M HCl; the activity removed was assumed to represent that sorbed on the bottom of the tube. The tubes were then completely washed with two 2.5-mℓ portions of 3 M HCl, and the activity removed from each tube was assumed to represent that sorbed on the walls. The final "clean" tubes were checked by gamma counting. The amounts of activity on the bottom and walls were calculated per unit area; the ratio "bottom" to "walls" varied from 0.3 to 1.1 with an average of 0.7. Results for nine argillite controls gave an average of 1.2 for this ratio.

The activity on both sets of control tubes appears to have been sorbed fairly evenly on the surface.

The above results for container sorption suggest that sorption is dependent on available surface area, so when crushed tuff is present, container sorption is negligible.

For the tuff controls described above, the fraction of centrifugable species was measured by centrifuging the contents of the new tubes after the first transfer, again transferring the liquid, and counting the activity left in the tubes. The average fraction of the activity in the solution after contact which was removed by one 1-h centrifuging was 17% for nine americium controls at room temperature, 37% for four americium controls at 70°C, and 13% for two plutonium controls at room temperature. Since there was a significant amount of centrifugable species in the control solutions, presumably a similar fraction of the activity was also present with the samples where it would have been combined with the crushed rock and counted with the sorbed activity.

Each of three centrifugings (1 h, 1 h, 2 h) removed additional activity from americium solutions after contact and, therefore, would appear to be necessary. (Such measurements were not made with plutonium solutions.)

In an experiment to see if effects related to the filtering process result in a change in the radionuclide concentration of solutions after contact, three ~3-mℓ portions of a solution were passed through the same 0.4-μm polycarbonate membrane. Each portion was aliquoted and counted after passing through the membrane. The averages of the relative concentrations of the solutions after filtering in this way are given for a number of samples in Table XXVII. Filtering successive portions of the same after-contact solution through the same filter membrane does not appear to result in a significant difference in the concentration of plutonium or americium in the solution.

The effects of centrifuging the solutions after contact and then passing them through filters with various pore sizes were examined by counting aliquots of the solution after each step. Data for a number of samples and controls are given in Table XXVIII. Filter sequences used were 1.0-0.4-0.05, 0.4-0.4, and 0.05-0.05 μm. The most recent procedure for centrifuging and transferring after contact gave plutonium solutions from which no additional plutonium was removed by filtering. This was not true for americium, where a factor of two or more of the activity was sometimes removed by filtering the centrifuged solutions, the results varying with the contact temperature. This suggests

TABLE XXVII

EFFECT OF CONSECUTIVE FILTERING OF TRACED SOLUTIONS THROUGH 0.4-μm MEMBRANES

	Ratio of Activity Concentrations of Different Portions	
	Second/First	Third/First
Samples		
^{241}Am		
22°	0.98	0.97
70°	0.97	0.93
Controls		
^{241}Am		
22°	0.94	0.92
70°	0.99	0.98
^{237}Pu		
22°	0.98	0.97

that plutonium does not significantly sorb on polycarbonate filter membranes, at least in the time required for filtering. The activity present in a plutonium solution after it has been centrifuged three times is, therefore, probably the "true" value for calculating sorption ratios. For americium, centrifuging the solution after contact would appear to establish a lower limit to the sorption ratio since crushed rock particles and particulates remaining with the solution would tend to lower the calculated R_d.

In an attempt to clarify the mechanism by which americium is retained on filter membranes, 38 filters from the sequential filterings listed on Table XXVIII were examined by a microautoradiographic technique. Approximately one-half to one-third of each filter membrane was mounted on a glass slide by coating with a thin layer of parlodion (a 2% solution in isopentyl acetate). The slide was then alpha counted to determine the length of exposure time needed (calculated to give ~10^7 total disintegrations) and clamped together with a second slide on which a Kodak AR.10 strippable emulsion had been mounted. It was found that mounting the emulsion directly onto the coated filter made visualization of single tracks very difficult. To get a good adherence of the emulsion on blank glass slides, the slides were first etched with a dilute solution of HF, then dried and coated with a solution of 2% parlodion in

TABLE XXVIII

AVERAGE ACTIVITY REMOVED[a] FROM SOLUTIONS BY CENTRIFUGING AND FILTERING
(in percent)

Treatment	Samples			Controls		
	^{237}Pu	^{241}Am	^{241}Am[b]	^{237}Pu	^{241}Am	^{241}Am[b]
Centrifuge[c] 1 h (2nd)		28	51		14	8
Centrifuge 2 h (3rd)		24	26		6	8
Filter 1.0 μm	0	10		3	28	0
Filter 0.4 μm	0	13		2	26	0
Filter 0.05 μm	0	27		1	28	48
or						
Filter 0.4 μm		22		2	26	6
Filter 0.4 μm		11		-	24	3
or						
Filter 0.05 μm	0	39	70		40	
Filter 0.05 μm	0	21	6		32	

[a]Decreases in activity are in percent of input activity for a given operation removed by that operation.

[b]For 70°C solutions.

[c]All centrifugings were at 12 000 rpm.

isopentyl acetate, dried again and finally coated with a thin gelatin layer by dipping the slide in a water solution containing 0.5% gelatin and 0.06% $KCr(SO_4)_2 \cdot 12H_2O$.

Microautoradiography of the "sorption" membranes showed not only single-alpha tracks but also clusters and stars, indicating the presence of large complex species, polymers, or colloids in the so-called solutions, even after

multiple centrifugings. Some "sorption" solutions were filtered through several membranes with the same or decreasing pore sizes (see Table XXVIII). In general, all of these membranes were found to retain americium in clusters, stars, and single tracks. Americium species in these solutions probably exist in a broad range of particle sizes. In contrast, the "desorption" membrane generally showed only single alpha tracks, suggesting that some americium sorbed on the membranes and that large particulates were not removed from the solids during desorption nor did they form in the aqueous phase during contact. In related work Bert Allard (Chalmers Univeristy, Göteburg, Sweden, personal commumication) observed sorption ratios for Millipore filter paper comparable to those for rock-forming minerals during "batch" sorption experiments with americium in simulated groundwater.

Considering the above results, we have decided to take the conservative approach in calculating americium sorption ratios and use the results from the solutions after they have been centrifuged but not filtered.

It is important to emphasize that the measured sorption ratios for plutonium and americium include effects other than sorption. There may well be differences in the behavior of plutonium or americium even between supposedly identical solutions at pH 8 to 8.5, e.g., in the degree of polymerization and radiocolloid formation, and hydrolysis resulting in variations in species (including charge) and particle size. Grebenshchikova and Davydov[19] reported that the charge on colloidal Pu(IV) species may be either positive (at low pH values) or negative (at high values) and that the isoelectric pH, or point of zero charge, is in the pH region 8.0 to 8.5. Polzer and Miner[20] presented a plot of effective charge (due to hydrolysis) of the americium species vs. pH for a 0.1 M $LiClO_4$ solution. Between pH 8.0 and 8.5 the average effective positive charge per atom of americium varied from ~1.3 to essentially zero. Therefore, large variations in the behavior of both plutonium and americium could be expected in this pH range.

VII. MEASUREMENTS IN CONTROLLED ATMOSPHERE CONDITIONS

A. Controlled Atmosphere Equipment

The equipment needed to perform sorption measurements under reduced oxygen conditions or conditions having a specified atmosphere was installed. The two-station controlled atmosphere boxes were manufactured by Vacuum/Atmospheres Co. (Model DL-002-S-P). The oxygen concentration is measured by use of a

Teledyne trace-oxygen analyzer (Model 317-X, special modifications for LASL). The nitrogen gas is cleaned by a Vacuum/Atmospheres Co. gas purfication system (Model MO-40-2-H). The system works very reliably and the oxygen concentration is <0.2 ppm. The terms "controlled atmosphere" or "anaerobic" in this report refer to a nitrogen atmosphere with <0.2 ppm oxygen.

B. Preparation of Materials

Solid samples of YM-22, YM-38, and YM-54 cores were ground in the controlled atmosphere in a non-iron system using an agate mortar with a 50- or 70-mm agate ball (Tekmar Co, Pulverisette). Each material was graded by use of Tyler sieves (ASTM E-11 specification) into two size fractions, <75 μm and 75 to 500 μm, the entire sample was ground until it passed into one of these fractions. Well J-13 water was used, and the rock-treated waters were prepared by contacting batches of the groundwater, which had been sparged with high purity nitrogen for at least 1 h with pulverized material that had not been sieved. The contact time was at least 2 wk at ambient temperature with a solution volume to solid ratio of 50 mℓ/g. The phases were separated by centrifugation at 7 000 rpm for 1 h followed by filtration through a 0.4-μm Nuclepore filter. All operations were performed in the controlled atmosphere boxes.

The solid samples were also pretreated with the appropriate groundwater by shaking weighed 1-g quantities of the crushed rock with 20 mℓ of the water for a period of two weeks at ambient temperature. The samples were contained in 40-mℓ polypropylene (Oak Ridge) screw-cap centrifuge tubes. All tubes were washed with deionized water prior to use. The phases were separated by centrifuging at 12 000 rpm (18 000 g's) for 1 h. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pretreatment.

C. Sorption of Strontium, Cesium, Barium, Cerium, and Europium

The traced solutions containing ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu were prepared in the controlled atmosphere conditions by adding the appropriate volume of pretreated groundwater to bottles in which the tracers had been evaporated to dryness. The traced waters were shaken for two days before filtration through a 0.45-μm Millipore filter. Sorption measurements were begun within about 0.2 day after filtration. The concentrations of the traced solutions are given in Table XXIX.

TABLE XXIX

ELEMENT CONCENTRATIONS[a] OF TRACED WATERS

Tracer	Water: YM-22	YM-38	YM-54
^{85}Sr	7.9×10^{-8}	8.3×10^{-8}	8.0×10^{-8}
^{137}Cs	2.2×10^{-9}	2.8×10^{-9}	2.8×10^{-9}
^{133}Ba	2.2×10^{-8}	2.2×10^{-8}	1.2×10^{-7}
^{141}Ce	2.2×10^{-8}	6.8×10^{-8}	1.2×10^{-7}
^{152}Eu	2.1×10^{-8}	9.3×10^{-8}	1.5×10^{-7}

[a]Element concentrations given in moles per liter are only those added with the tracer; actual concentrations may be higher.

Batch sorption measurements at ambient temperatures under anaerobic conditions are in progress, with 1-g samples being contacted with 20 mℓ of traced water. Thus far approximately one-third of the samples have been studied (after a three-week contact time). These samples were centrifuged for 1 h at 12 000 rpm and the solid and aqueous phases were separated by pipetting off the liquid into a clean tube. After centrifuging for another hour at 12 000 rpm (18 000 g's) the solutions were pipetted off into a clean tube and centrifuged for 2 h. An aliquot was taken for activity assay, and pH measurements were made on the rest of the solution. A small amount of the solid was transferred to a counting vial for assay. All the handling of the solid and solution samples was done inside the controlled atmosphere box. The samples were assayed for radioactivity using the techniques and methods of calculation described earlier (See Section III.A).

The results from the three week sorption measurements are given in Table XXX. Table XXXI gives the initial and final pH values. Overall, the anaerobic R_d values do not differ significantly from those obtained under normal atmospheric conditions. The R_d values of Sample YM-38, the only zeolite-containing core studied under anaerobic conditions, were one to two orders of magnitude larger than those for the other (non-zeolite) cores. The R_d values of ^{137}Cs, ^{85}Sr, ^{133}Ba, ^{141}Ce, and ^{152}Eu are lower approximately 70% of the time under the controlled atmosphere conditions. (See Tables VII and VIII for the aerobic results.) However, the R_d values for the two atmosphere conditions generally agree within a factor of about two. Only with Ce and Eu on the smaller

TABLE XXX

SORPTION RATIOS FOR YUCCA MOUNTAN TUFFS UNDER CONTROLLED ATMOSPHERE CONDITIONS

Sample	Fraction	Sorption Time(d)	R_d(mℓ/g)[a] ^{137}Cs	^{85}Sr	^{133}Ba	^{141}Ce	^{152}Eu
YM-38	<75μm	20.63	9 490(6.2)	9 090(5.4)	57 000(22.7)	647(9.2)	1 130(8.9)
YM-38	75-500μm	20.63	7 920(5.8)	7 230(5.1)	33 700(13.6)	556(8.7)	841(8.3)
YM-54	<75μm	20.63	362(2.5)	100(2.4)	609(1.7)	147(4.1)	530(3.5)
YM-54	75-500μm	20.63	210(2.4)	76.2(2.4)	367(1.6)	115(4.1)	329(3.4)
YM-22	<75μm	20.63	384(2.5)	72.6(2.6)	664(4.7)	626(4.7)	797(3.8)
YM-22	75-500μm	20.63	203(2.5)	48.3(2.8)	205(1.6)	762(5.4)	711(4.0)

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

TABLE XXXI

pH VALUES, ANAEROBIC MEASUREMENTS

Sample	Fraction	Initial pH	Final pH
YM-38	<75μm	8.63	8.55
YM-38	75-500μm	8.63	8.68
YM-54	<75μm	8.65	8.68
YM-54	75-500μm	8.65	8.69
YM-22	<75μm	8.66	8.42
YM-22	75-500μm	8.66	8.50

fraction of Sample YM-38 do the values differ by as much as a factor of about 9. (R_d's are larger under normal atmospheric conditions.) However, the larger R_d values were obtained for a sorption time of ~6 weeks rather than of 3 weeks. When the 6-week measurements are completed, it is possible that there will be better agreement. The differences may also be due to the absence of carbon dioxide in the controlled atmosphere studies. The anaerobic measurements also give a more consistent relationship between R_d and particle size, with the smaller fraction generally having a higher R_d value.

D. Sorption of Uranium

The ^{237}U tracer was prepared by taking the tracer to dryness, diluting in the controlled atmosphere with the appropriate groundwater and filtering through a 0.4 μm millipore filter. The uranium concentration was ~1.8×10^{-6} M.

The sorption studies under controlled atmosphere conditions at ambient temperature of the three Yucca Mountain cores are complete, and desorption data are being collected. Sorption times ranged from ~6 to ~20 days. Results are given in Table XXXII. All Yucca Mountain tuffs sorbed uranium poorly, but sample YM-38, which contained zeolites, had a significantly higher sorption ratio. The "negative" R_d values indicated for uranium YM-22 are zero within experimental uncertainties. In general, sorption ratios increase with time.

Sorption-desorption studies under normal atmospheric conditions for the same Yucca Mountain cores are under way to determine the effect of oxygen on sorption for uranium.

TABLE XXXII

URANIUM SORPTION ON YUCCA MOUNTAIN CORES UNDER ANAEROBIC CONDITIONS

Sample	Particle Size (Microns)	Time (days)	R_d[a] (mℓ/g)
YM-22	<75	6.75	-0.14(1100)
		13.75	0.90(170)
		20.78	1.2 (140)
	75-500	13.75	-0.17(860)
		20.78	0.81(190)
YM-38	<75	6.7	16.7 (16)
		13.74	19.6 (15)
		20.77	14.4 (17)
	75-500	6.72	10.9 (21)
		13.74	13.8 (18)
		20.77	15.0 (17)
YM-54	<75	6.74	1.0 (150)
		13.76	1.8 (87)
		20.79	2.3 (70)
	75-500	6.74	0.77(200)
		13.79	1.4 (110)
		20.79	1.7 (92)

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

E. Sorption of Technetium

Traced solutions containing ^{95m}Tc at a concentration of $\sim 10^{-12}$ M were added to the solid samples described in Section VII.B. One-third of the experiments, after a contact time of 3 wk, have been completed. The phases were separated by centrifugation at 12 000 rpm for 2 h. The aqueous phase was then centrifuged 2 additional times of 1 h each before an aliquot was taken for counting. After removing a portion of each solid phase (~25%) and weighing, fresh, untraced, pretreated water was added to the remaining solid and desorption studies were begun. These samples, along with two-thirds of the samples from the sorption determination are currently being shaken.

Results for the 3-wk sorption contact time are given in Table XXXIII. A direct comparison of results with those obtained for technetium in air is difficult because only one sample, YM-22, was studied under both sets of conditions, although with slightly different fraction sizes. The average R_d value for sample YM-22 (106 to 500 μm) in air was 0.29 mℓ/g -- not significantly different from 0.40 mℓ/g found under anaerobic conditions for the 75- to 500-μm fraction. The smaller fraction, <75-μm, gave an R_d value ~3.8 mℓ/g. The tuff samples studied under anaerobic conditions had an average sorption R_d ~2.5 mℓ/g (at 21 days for both fractions), while those studied in air averaged ~0.22 mℓ/g for a contact time approximately twice as long. Although there is approximately an order of magnitude difference between the two sets of measurements, all the R_d values are low. Possibly there is a small amount of reducing material present to account for these results. Measurements under controlled

TABLE XXXIII

SORPTION RATIOS OF TECHNETIUM ON YM TUFF. ANAEROBIC CONDITIONS

Sample	Fraction Size(μm)	Sorption Time(d)	R_d (mℓ/g)	pH	
				Initial	Final
YM-22	75-500	20.67	0.4	8.86	8.64
	<75	20.67	3.8	8.86	8.81
YM-38	75-500	20.67	2.6	8.82	8.33
	<75	20.67	3.0	8.82	8.69
YM-54	75-500	20.67	4.7	8.62	8.69
	<75	20.67	0.7	8.62	8.72

atmosphere conditions with longer contact times are in progress, and perhaps a comparison with the R_d values at comparable contact times (~six weeks) will show a greater divergence.

VIII. MIGRATION RATE STUDIES

A. Crushed Rock Columns

1. Measurements. Crushed rock column studies have been made on three types of media from the Nevada Test Site: tuff, argillite and granite. The results of the argillite and granite work are reported here because of the general interest in comparing methods of measuring sorption. The geologic materials chosen were those on which batch R_d measurements had previously been made in order to provide a comparison with results obtained on the columns. The tuff pretreated waters used for infiltration were the same as those previously described in this report for the batch studies. The preparations of waters for the argillite and granite columns were described in Ref. 16 and 17, respectively.

Water delivery rates were controlled by syringe pumps (Sage Instruments, Model 352). Initially the columns, 0.5-cm x 2- to 4-cm (Bio-Rad Econo Columns), were run by gravity flow and the syringe pumps were used only to control the delivery rate of the water to the top of the column. The actual flow rate through the column was not known. A simple, upflow, 0.4- to 0.5-cm x 2-cm column was then developed to maintain a known, steady, flow rate controlled by the Sage pumps. The columns were modified from Bio-Rad Econo Columns by shortening them to ~2 cm, lining with Teflon, and placing polyethylene bed supports and polypropylene Luer fittings on each end.

A summary description of the crushed-rock columns studied and the parameters measured are given in Table XXXIV. Each column was characterized in terms of the total column volume V (the size of the column calculated from column dimensions), the free column volume FCV (measured and used to calculate the effective column porosity), the dry bulk density, the particle size, and the flow rate. Flow rates were determined by weighing the eluate sample delivered in a known time period. Gravity flow columns tended to decrease in flow rate before a steady flow rate was maintained. For example, the YM54#1 and YM-54#3 columns began with flow rates of ~0.08 and ~0.07 mℓ/h and decreased to ~0.04 and ~0.03 mℓ/h, respectively. However, the flow rates of the upward-flow

TABLE XXXIV

CRUSHED ROCK COLUMN DESCRIPTIONS

Geologic Materials	Particle Size, μm	Column Size cm x cm	Porosity	Density g/cm^3	Flow Rate mℓ/h	Type of Flow
Tuff:						
YM-54#1	35-106	1.50 x 0.50	0.793	0.98	0.037	S,G
YM-54#2	35-106	1.50 x 0.50	0.612		0.067	CF,G
YM-54#3	35-106	2.60 x 0.50	0.669		0.033	S,G
YM-38#1	35-106	4.00 x 0.50			0.060	S,G
YM-38#2	106-500	2.12 x 0.40	0.357			S,U
YM-38#3	106-500	2.45 x 0.45	0.390			S,U
JA-32#1	35-106	4.40 x 0.49	0.549	0.89	0.131	S,G
JA-32#2	35-106	2.20 x 0.50	0.678		18.0	CF,G
JA-32#3	35-106	1.80 x 0.50	0.635		0.082	S,U
JA-18	106-150	2.0 x 0.40	0.562			S,U
JA-37	106-150	2.15 x 0.45	0.444			S,U
YM-22	35-106	1.90 x 0.50	0.654	1.16	0.077	S,U
YM-45	106-500	2.10 x 0.40	0.318			S,U
Argillite:						
UE-17#1	180-250	2.40 x 0.45	0.592	1.11	0.053	S,U
UE-17#2	180-250	2.43 x 0.45	0.644	1.18	0.054	S,U
Granite:						
CS#7	35-106	2.10 x 0.50	0.592	1.26	0.045	S,U
CS#5	35-106	2.15 x 0.50	0.597	1.25	0.041	S,U

[a]U = upward, G = gravity, CF = continuous feed, S = spike loading

columns were found to be relatively constant for a given column, syringe, and pump setting. Upward-flow rates ranged from 0.041 to 0.082 mℓ/h. A flow rate of 0.045 ml/h for a 2.1-cm-long column with a free column volume of 0.224 mℓ would correspond to a flow velocity of ~37 m/y.

The free column volumes of approximately one-third of the columns studied were determined by use of both HTO and $^{131}I^-$. In the iodide case, the ^{131}I breakthrough (leading edge) curve and the rinse (trailing edge) were both used. There was essentially no difference in the values obtained with HTO or with $^{131}I^-$, and all measurements for a given column were averaged irrespective of the method used. For example, the FCV for a YM-54 column obtained with iodide (breakthrough) was 0.177 mℓ and with HTO was 0.182 mℓ. On the YM-22 column, the iodide breakthrough method gave 0.249 mℓ and the iodide rinse gave 0.239 mℓ. Another YM-22 column (not yet used or included in Table XXXIII) gave 0.208 mℓ with HTO, 0.205 mℓ by the iodide breakthrough method, and 0.199 mℓ by the water rinse method. The values for the CS-5 and CS-7 granite columns, the UE17#1 and UE17#2 argillite columns, and the JA-18, JA-37 and YM-45 tuff columns were measured using ^{131}I only.

The radionuclides studied were usually added to the column in a minimal (5- to 15-μℓ) volume or "spike." P. Rickert et al. (Argonne National Laboratory) had previously noted a concentration dependence for cesium sorption on limestone, where the R_d value for cesium decreased with increasing concentration. The concentration of cesium in our batch measurements ($\sim 10^{-9}$ M) was $\sim 10^{-3}$ times that of the cesium spike added to two YM-54 columns. Another YM-54 column was, therefore, run with a continuous feed of ^{137}Cs at a concentration comparable to that of the batch measurements in order to determine if the cesium concentration effect also existed for tuff. The radioisotopes used were ^{85}Sr, ^{137}Cs and ^{133}Ba, although studies were begun recently with ^{141}Ce and/or ^{152}Eu (YM-38, YM-45).

In addition to varying the radionuclide loading concentration (of ^{137}Cs) on crushed-core columns, the flow rates were also varied on three JA-32 tuff columns loaded with ^{85}Sr. Flow rates were varied from 0.082 mℓ/h to 18 mℓ/h. Two of these columns were run by gravity flow and the third was run by the upward flow technique.

2. Data Collection and Analysis. Eluate fractions from each column were collected in closed pretared vials. The vials were replaced daily and weighed immediately after removal for the eluate volume determination. At

flow rates of ~0.03 to ~0.08 mℓ/h, this represented ≤1 to 2 mℓ/d. Each sample was diluted to a known volume, sealed and saved for measurement of radioactivity. Samples from a given column were counted with a NaI(Tℓ) detector until some activity was observed. If more than one radioisotope had been placed on the column, all samples, beginning with the one in which activity was first detected, were counted on a Ge(Li) detector, and data was collected and reduced as in Section III.A.4. If only one radioisotope had been added to a column, all eluate fractions were counted with a NaI(Tℓ) detector.

The activity per milliliter of each fraction collected (and of each tracer, if more than one was used), was plotted against the total volume which had been eluted at the time the sample was taken. An example of these plots is given in Fig. 1 (column YM-54#3). A main reason for column studies is that the behavior of a radionuclide can be observed directly as it flows through the rock. The relative velocity of the radionuclide with respect to the groundwater velocity, or the retardation factor, R_f, can then be related to the distribution coefficient or K_d*:

$$R_f = K_d(\rho/\varepsilon) + 1,$$

where:

ρ = density and

ε = porosity = $\frac{FCV}{V}$.

Thus, the total volume eluted that corresponded to the peak of each radioisotope was compared to the free column volume (the volume corresponding to the peak of the $^{131}I^-$ or HTO curve) to obtain the retardation factor and subsequently, the R_d.

Such data can also be represented by a breakthrough curve where the (cumulative) fraction of the total activity is plotted against eluate volume. If the breakthrough curve is symmetrical, the volume where $A/A_T = 0.5$ (that is, where 50% of the activity has been eluded) should correspond to the peak of the elution curve. The elution and breakthrough curves from JA-32#1 column are plotted in Figures 2 and 3.

*Since K_d implies reversible equilibrium and batch studies have shown that equilibrium is not attained in a few weeks or months for many cases, R_d is used throughout this report.

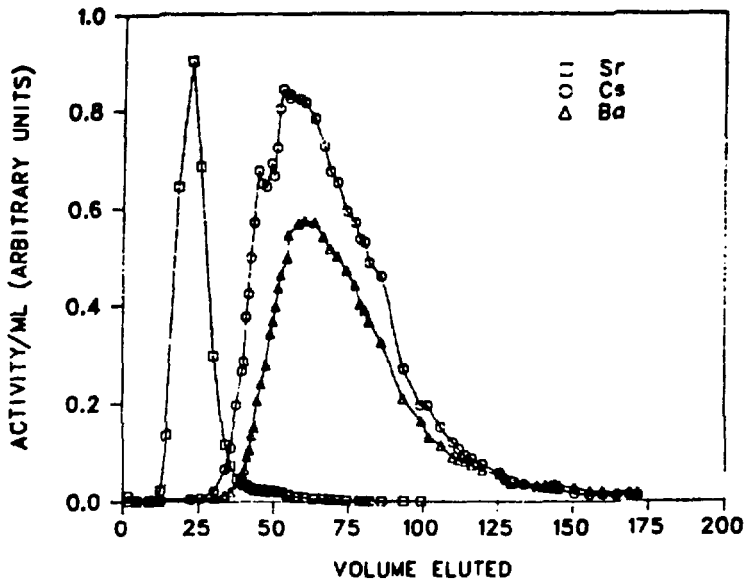

Fig. 1. Elution Curve, Column YM-54#3

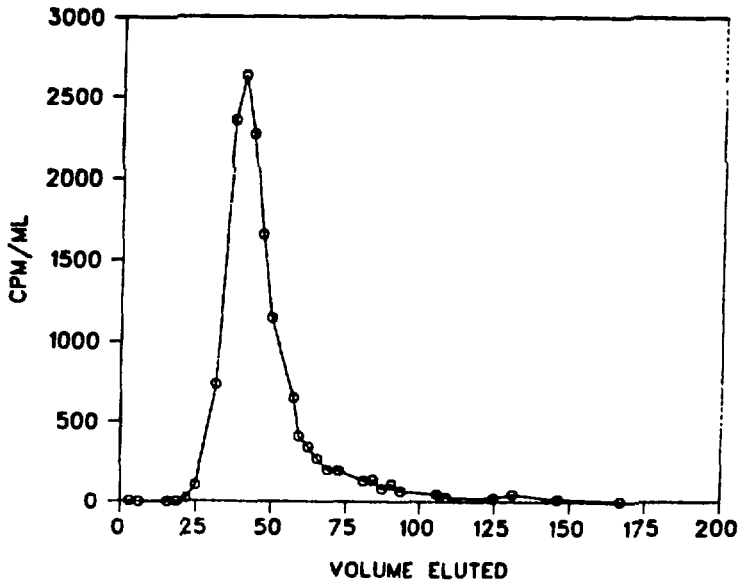

Fig. 2. Elution Curve, Column JA-32#1 with ^{85}Sr

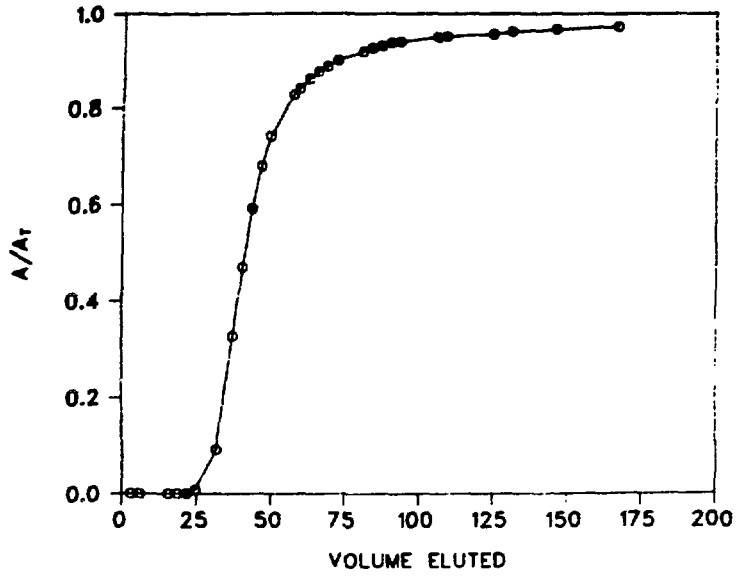

Fig. 3. Breakthrough Curve, Column JA-32#1 with ^{85}Sr

3. Results and Conclusions. The columns for which data are available are those begun initially to develop techniques. Of the seventeen columns which are described in Table XXXIV, ten of the columns are still running, with one or more isotopes yet to be eluted. Thus, the conclusions to date should be considered preliminary. The materials and isotopes chosen initially were those for which batch R_d values were known to be low. The exception, ^{85}Sr on YM-38, where the R_d ~14 000 to 22 000 mℓ/g for sorption-desorption, was begun before the batch measurements had been completed. It is not surprising that no ^{85}Sr has been eluted in ~240 days.

The initial pH of the waters used is given in Table XXXV. There was little or no pH change of the waters due to flow through the columns.

The R_d values which have been calculated from the column data are given in Table XXXVI. The data from batch measurements are also given for comparison. Generally, the peak shapes of the elution curves were symmetric, and fifty percent of the activity eluted corresponded closely to the peak of the elution curve. For example, in Figs. 2 and 3 for ^{85}Sr on column JA-32#1, A/A_T = 0.5 at 41.5 mℓ and the peak of the elution curve was at 39.0 mℓ. For all three JA-32 columns, the average R_d calculated from peak volumes was 41.6 mℓ/g,

TABLE XXXV

pH OF WATERS USED FOR CRUSHED ROCK COLUMN INFILTRATION

Pretreated Water	pH
YM-54	8.12
YM-38	8.17
YM-22	8.24
YM-45	8.13
JA-32	8.10
JA-37	8.17
JA-18	7.76
Argillite	7.90
Granite	7.99

and that from the volumes at A/A_T = 0.5, 43.3 mℓ/g. Since the other columns studied to date also had symmetric peakshapes, the peak volumes were used for convenience to calculate retardation factors. This made it unnecessary to rely on an external standard as a monitor of total activity, A_T, or to wait until all the activity had been eluted from a column to calculate A_T.

Three general conclusions can be drawn from the results:

1) The R_d value from column studies, at least for JA-32 tuff with ^{85}Sr, is independent of flow rate. R_d values of 37 and 35 mℓ/g were obtained for a flow of ~18 mℓ/h (gravity flow) and 0.082 mℓ/h (upward flow), respectively. A value of 52 mℓ/g was obtained for another JA-32#1 (gravity flow) column where the delivery rate was 0.131 mℓ/h. (The actual flow rate, although unknown, was probably on the order of several mℓ/h.) The higher R_d obtained for the JA-32#1 column could be due to the column being twice as long as the other two, although two YM-54 columns which also differed in length by almost a factor of two, gave identical R_d values for ^{85}Sr. Variations in rate constants and distribution coefficients with bed depth have been noted in the literature (see, for example, Ref. 21).

2) The effect of the cesium ion concentration on R_d appears to be negligible for the crushed tuff core studied, YM-54. Two columns where ^{137}Cs was loaded at ~10^{-6} M gave R_d values of 113 and 92 mℓ/g. A third column where the ^{137}Cs concentration was ~10^{-9} M gave an R_d

TABLE XXXVI

COMPARISON OF BATCH R_d AND COLUMN R_d VALUES (mℓ/g)

	Column/Batch[a] (Sorption, Desorption)		
Column	Sr	Cs	Ba
CS-7	15/(18,22)	NA[b]/(328,734)	44/(175,176)
CS-5	8.5/(14,19)	NA/(347,533)	32/(154,155)
YM-54#1	44/(84,82)	92/(247,321)	126/(652,632)
YM-54#2	Not Used	80/(247,321)	Not Used
YM-54#3	44/(84,82)	113/(247,321)	122/(652,632)
YM-22	30/(50,57)	122/(287,365)	335/(899,824)
JA-32#1	52/(56,47)	Not Used	Not Used
JA-32#2	37/(56,47)	Not Used	Not Used
JA-32#3	35/(56,47)	Not Used	Not Used
UE-17#1	43/(138,133)	NA/(1 830,3 110)	NA/(4 270,5 530)
UE-17#2	52/(156,131)	NA/(1 580,3 810)	NA/(4 900,5 600)

[a]The batch sorption-desorption R_d values are the mean (ambient temperature) R_d values from the following sources:

CS (granite) Ref. 17, from fractions 106-150 μm, 250-355 μm, and UE-17 (argillite), Ref. 16, from fractions <75 μm, 106-150 μm, and 355-500 μm for ≦8 weeks.
JA-32 (tuff), Ref. 5, for fraction 106-150 μm for ≦8 weeks (sorption) and ≦11.5 weeks (desorption).
YM-54, -22 (tuff), this report, for fraction ≦106 μm for ≦6 weeks.

[b]NA indicates the experiment is still in progress and results are not yet available.

value of 80 mℓ/g. All three values are approximately three times lower than the R_d obtained by a batch technique.

3) Batch R_d values are greater than column R_d values for all the columns analyzed thus far. The ratios of batch to column R_d values are given in Table XXXVII. The biggest differences are factors ~5, for ^{133}Ba. In most cases the agreement between batch and column determinations is within a factor of 2 to 3. Given the variation in batch R_d measurements themselves, this is fairly good agreement. The flow rates and column sizes used correspond to velocities of $\sim 10^{-4}$ cm/sec or ~30 m/y, which, although not slow by geologic standards, are within a

TABLE XXXVII

R_d(BATCH)/R_d(COLUMN)RATIOS

Column	^{85}Sr	^{137}Cs	^{133}Ba
CS-7	1.3		4.0
CS-5	1.9		4.8
YM-54#1	2.0	3.6	5.1
YM-54#2	-	3.1	-
YM-54#3	2.0	2.5	5.3
YM-22	1.8	2.7	2.6
JA-32#1	1.0	-	-
JA-32#3	1.4	-	-
UE-17#1	3.1	-	-
UE-17#2	2.8	-	-

reasonable range for flow rates in geologic media ($\sim 10^{-7}$ to 10^{-3} cm/sec). The fact that column R_d values (for materials with low R_d) tend to be smaller could, in part, be due to the shorter residence times. Perhaps in batch experiments lasting weeks or months, diffusion contributes significantly in cases of low R_d. This effect would be negligible in a (comparatively short time) column experiment. (In fact a significant difficulty with small crushed core columns -- even given good agreement with batch R_d data -- will be in relating such data, obtained over small distances in short contact times, to long distances and long contact times.)

Since preliminary data indicated that increasing flow rate did not significantly alter results, experiments will be started to look at isotopes having high R_d values on tuff. A column of YM-38#3 loaded with ^{85}Sr (average batch R_d ~18 000) should be eluted in ~38 days at a flow rate of ~3 mℓ/h. It will also be important to measure cerium and europium column R_d data for comparison with batch measurements, since sorption of these elements is apparently not by ion-exchange mechanisms. Such experiments are in progress (YM-38 and YM-45).

B. Whole-Core and Fractured-Core Studies

1. Measurements. Several experiments were performed involving solutions of radionuclides pumped through solid rock cores. The equipment used in these

experiments is shown in Figure 4. The rock, in the form of a polished cylindrical core 15.9 mm high and 25.4 mm in diameter, was encased in a Teflon sleeve fitted with stainless steel end pieces containing 0.48 mm ID delivery tubes. This assembly was contained in a pressure vessel maintained at a "confining pressure", typically ~1 000 psi. Groundwater was forced through the core at a controlled rate and "pumping pressure" significantly lower than the confining pressure. After the core had been flushed, it was removed, and a small volume of high specific activity solution was placed on the top face. The core was again placed in the pressure assembly, and the rate of transport of the radioactive material through the core was determined by monitoring the activity in the eluate.

2. Data Collection and Analysis. Two experiments were conducted with ^{233}U and JA-26 tuff.[9] These experiments were undertaken primarily to develop techniques. After placing the ^{233}U solution on the core and reassembling the pressure apparatus, water was pumped through the core only until appreciable amounts of activity appeared in the eluate. In the first experiment, using

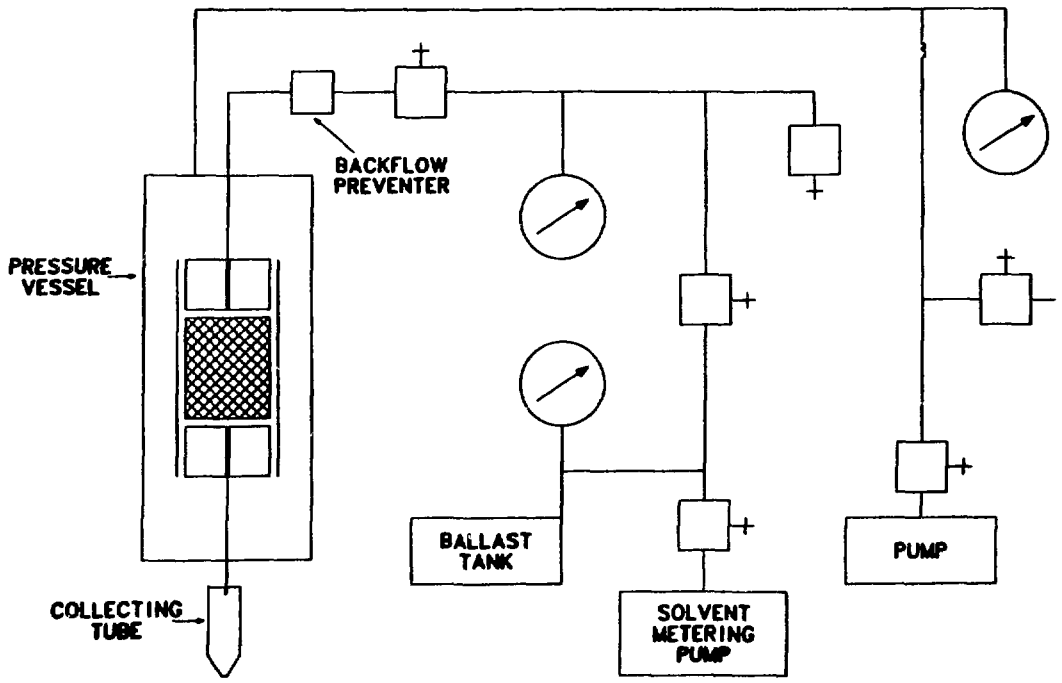

Fig. 4. Schematic of the high-pressure column apparatus.

mixed isotopes of uranium, 4.8 mℓ of effluent passed through the core. In the second, using isotopically pure ^{233}U, 13.4 mℓ of effluent passed through. The pumping rates were 0.35 to 0.7 mℓ/hr. The rock cores were sliced perpendicular to the direction of water flow using a small rock saw (Isomet, Model 11-1180) and were then counted. Sawing the tuff cross-sections thinner than about 1.2 mm tended to dislodge grains. It was necessary to cool and lubricate the saw blade with a liquid which would not dissolve the UO_2^{++} sorbed on the rock. Benzene was found to be satisfactory.

The surface activity on the rock cross-sections was observed using emulsions in one of two ways. In the first technique, a microscope slide coated with Kodak NTB-2 or NTB-3 liquid emulsion (and dried) was placed against the rock until about 10^6 to 10^7 disintegrations had occurred and then was developed using standard procedures. This yielded a transparent slide with the alpha tracks readily visible, but it was difficult to correlate the tracks with their points of origin on the rock with a certainty of better than a few millimeters. Even with the use of a jig constructed to align the rock core and microscope slide it was not possible to improve the registration significantly. A second technique involved coating the emulsion directly on the rock, then exposing and developing it in situ. To insure good adhesion of the emulsion, an undercoating of parlodion and gelatin had to be applied. The liquid emulsions worked better than the strippable emulsion (Kodak AR.10) for this application. With the emulsion developed in place, registry with the underlying surface was no problem, but viewing the tracks was difficult against the opaque background. The tracks could be illuminated with reflected, polarized light, but the underlying minerals could not be seen well. Thus, neither emulsion technique proved to be very useful for identifying specific sorption sites by mineral composition.

Several Climax Stock granite cores were studied with ^{233}U or ^{85}Sr. The results are presented in this report because of general interest in the method and the similarity of granite and welded tuff. About 50 µℓ of ^{85}Sr were placed on the top face of a Climax granite core with a crack running lengthwise through it. Filtered, synthetic granite groundwater was pumped through the core for ~140 days at an average rate of 0.17 mℓ/day. During the first few days the effluent had a specific activity of about 10^3 cpm/mℓ. Then it fell to about 10^2 cpm/mℓ and was more or less constant (correcting for the decay of ^{85}Sr) until elution was stopped. Several cross-sectional slices of this core

were taken and Kodak NTB-3 emulsions were used to locate the ^{85}Sr on the surfaces. The tracks produced in the emulsion were generally dots, and were rather difficult to identify unless they were present in high concentrations. The granite could be cut in very thin slices (≦0.5 mm), and even slices several millimeters thick were translucent. The distribution of activity in the cross-sectional slices through the depth of the core was measured with a NaI detector and is shown in Fig. 5. It appeared that this activity was distributed through the length of the core with a linear concentration gradient.

Another granite core was placed in the pressure apparatus and flushed with filtered synthetic granite water (about 0.7 mℓ) at a pumping pressure of 550 psi and confining pressure of 1 000 psi. Then, about 75 μℓ of isotopically pure ^{233}U solution containing about 7.6 mg of uranium (10^8 dis/min) were applied to the top of the core and pumping was resumed at the same pressures previously used. The flow rate varied from 0.1 to 0.3 mℓ/day. About 60% of the activity was eluted in the first 0.5 mℓ, and about 35% in the next 0.6 mℓ. This effluent was concentrated to about 200 μℓ and reintroduced on the top of the core. Pumping was continued as before until about 0.2 mℓ of effluent was collected and its specific activity began to increase rapidly. The core was removed, and several slices were taken from the top and bottom ends.

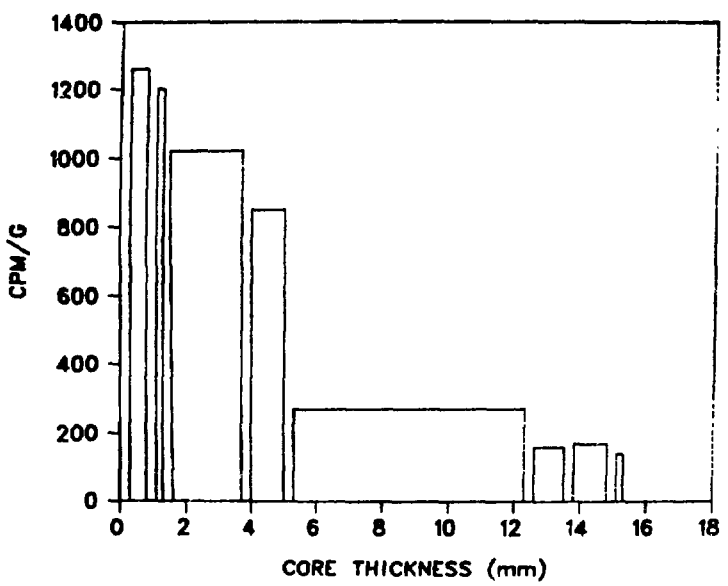

Fig. 5. Distribution of ^{85}Sr in a Climax Stock Granite Core.

A third granite core was selected because it had an apparent fracture plane extending the length of the core. It was then split cleanly along the old fracture. The inner surfaces of the fracture contained a number of small, gold-colored particles which x-ray analysis showed to be iron pyrite. The core sections were recombined, inserted in a Teflon sleeve, and placed in the pressure apparatus. The confining pressure was increased to the point (5 000 psi) where water would not flow through the core under the force of gravity. After flushing with synthetic granite water about 50 μℓ of ^{233}U were dried in the center of the top of the core (several mm from the crack). Pumping of water through the core was resumed after reassembly in the pressure apparatus and pressurization to 5 000 psi. Activity was detected in the first 0.5 mℓ of effluent, so the flow was stopped. Three days later the core was removed, and slices (about 2 to 3 mm thick) were sawed from each end.

3. Results and Conclusions. The flow of uranyl solutions through JA-32 tuff cores resulted in an even distribution of ^{233}U in the core. The ^{233}U activity, which was placed at the center of the top faces of the tuff cores, was found to have spread laterally so that at a depth of about 1 mm there were no obvious concentration gradients across the diameter of the core. It was also observed that a substantial fraction of the activity was still on the top surface when some of it had passed completely through the core. The stainless steel frits in contact with the top and bottom surfaces of the core showed some activity, though the amount relative to the total activity was small for the tuff columns.

The usefulness of autoradiography for identifying minerals at specific sorption sites on the tuff core cross sections was limited since viewing the tracks with reflected polarized light made visualization of the underlying minerals difficult.

Since granite core slices were translucent, microautoradiography was more valuable. It revealed that flow through the "non-cracked" granite core was by means of a very few small cracks, with the majority of the rock mass not coming in contact with the ^{233}U solution. Some sorption by minerals along the path of flow was indicated. An apparent radiocolloid was detected at a site along a crack several millimeters into the core. The top surface of the cracked granite core showed regions of high track density in the middle and along one segment of the crack. At a depth of several millimeters tracks were found only along the large crack and along a small crack branching from the large

crack. The bottom surface of the core had activity distributed fairly uniformly over it. The interior surface of the large crack was difficult to observe with the microscope because of the roughness, but alpha tracks were found over most of the surface. There were several regions of very dense tracks on the surface; however, identification of the sorbing mineral(s) has not yet been made. Thus the flow of uranyl solutions in solid granite cores was confined to small cracks within the core, while for the tuff studied an even distribution was observed. However, with ^{85}Sr on a granite core, after 140 days and a flow rate of ~0.17 mℓ/day, no pattern of high ^{85}Sr concentration in the vicinity of the crack was found; the activity appeared to be distributed throughout the core.

IX. MICROAUTORADIOGRAPHY

Microautoradiography has been employed[22] as an adjunct to other standard techniques for studying the sorption of certain elements on selected rocks. Whereas column or batch methodologies yield information on the sorption of the gross rock, microautoradiography can indicate the specific mineral phase responsible for the sorption. The work described below had three major objectives:

1) to extend autoradiographic sorptive studies on rock thin sections to Pu and Np,
2) to use autoradiography to investigate the sorptive behavior of radionuclides in solid rock cores, and
3) to use autoradiographic techniques with certain beta emitting radionulcides.

A. Alpha Microautoradiography

Techniques previously had been developed for preparing autoradiograms of ^{233}U and ^{241}Am on thin sections of rocks derived from the Nevada Test Site (alluvium, tuff, granite, and argillite).[22] In general, the same techniques were employed with ^{239}Pu and ^{237}Np.

An effort was made to prepare ^{239}Pu solutions of groundwaters with activity levels which would remain constant with time. All water used for these solutions was filtered through 0.4- and 0.05-μm filters, and the solutions were stored in capped Teflon tubes. The original Pu stock solution (in $HClO_4$) was evaporated to dryness, the Pu dissolved in distilled water, taken to

dryness, and redissolved in the groundwater. It was found that Pu would disappear from these solutions in a period of several days, but it could be reproducibly reintroduced (probably in a colloidal form) by placing the Teflon tubes in an ultrasonic bath for a minute. It was suggested that this "colloidal Pu" would settle out on the thin section under the force of gravity, but experiments conducted with droplets of Pu solution hanging suspended from the thin section gave the same activity and sorption on the rock surface as when the droplets were sitting on top of the thin section.

Microautoradiograms were prepared of ^{239}Pu on JA-25 and JA-26 tuff. Only in one thin section of a JA-25 tuff did there seem to be enhanced sorption by a particular mineral, a zeolite. Generally the alpha-track distribution was fairly uniform, with a number of stars present (indicating aggregated species). It appears that Pu sorbs rather indiscriminately on rock thin sections, and even on glass.

Attempts to sorb ^{237}Np on rock thin sections were hampered by the rather low tendency of the Np to sorb (lower than Pu by at least a factor of 10), and by the presence of large amounts of the ^{233}Pa daughter in the radioactive source solution. The ^{233}Pa sorbed strongly on the thin sections, and the beta radiation from this nuclide exposed the emulsions to the point of obscuring the alpha tracks generated by the ^{237}Np. Two procedures were employed to purify the Np: a TTA extraction,[23] and a fluoride precipitation followed by extraction on an ion exchange column.[19] Neither of these procedures gave a very complete separation. Autoradiograms were prepared with JA-26 tuff thin sections using a high specific activity solution (~7 x 10^6 dis/sec/mℓ) with the ^{233}Pa in secular equilibrium with the ^{237}Np. In general the Np seemed to deposit in some aggregated form. Dense clumps of tracks were present on all the thin sections. There is possibly some association of the tracks with specific minerals; analyses of the thin sections is in a preliminary stage. On the JA-25 sample there was much more activity in the zeolitized ground mass than in phenocrysts of quartz and feldspar. Relative sorption on various minerals was observed on a slide of tuffaceous alluvium. The greatest sorption was on zeolites, less on feldspars, and least on quartz. High sorption was also observed in grain boundaries and fractures.

B. Beta Microautoradiography

A number of autoradiograms were prepared using ^{85}Sr, ^{63}Ni, ^{233}Pa, and ^{90}Sr. Kodak AR.10 strippable emulsion, Kodak liquid emulsions NTB-2 and NTB-3, and a film-backed emulsion "Ultrafilm ^{3}H" manufactured by LKB, Rockville, Maryland were utilized. Beta tracks (generally spots) were readily visible at moderate surface densities against a clear background but were difficult or impossible to identify except at very high densities against the mottled backgrounds typical of rock thin sections. Thus it appears that beta autoradiography may be limited in geologic applications to situations in which high resolution is not required and in which rather large track density can be tolerated.

X. CONCLUSIONS

The average sorption ratios determined by batch techniques are given in Table XXXVIII. Also included are values for strontium, cesium, barium, cerium, and europium sorption ratios on Jackass Flats tuffs from Ref. 5. The largest R_d values for strontium, cesium, and barium on Yucca Mountain tuffs were found with zeolite-containing samples YM-38, YM-48 and YM-49. Sample JA-37,[5] also a material high in zeolites, had sorption ratios for these elements lower by a factor of 10 to 100. Very high sorption ratios for the ions of strontium, cesium, and barium were thought[5] to be associated with the presence of glass, since JA-18 contained unaltered glass, and only a trace of zeolites, and had high sorption ratios. No other tuff sample containing glass has been studied to date. The importance of zeolites and/or glass to high sorption ratios of strontium, cesium, and barium on tuff is not yet fully understood. Microgranite-like samples YM-22, YM-45 and YM-54 gave lower R_d values with ^{85}Sr, ^{137}Cs, and ^{133}Ba, as did sample JA-37 which was also like a microgranite. Cerium and europium sorption seemed to be independent of zeolite content. With plutonium and americium the R_d values were highest for the zeolitized tuff (JA-37).

Even under controlled atmosphere conditions technetium and uranium gave low sorption ratios ($\leq$10 mℓ/g). It was thought that perhaps the tuffs would have sufficient potential to reduce TcO_4^- (to TcO_2) and U(VI) (to U(IV)), which would be expected to sorb. Possibly the oxygen concentration of $\leq$0.2 ppm is too high, or perhaps longer sorption times will be required (such measurements are in progress for technetium).

TABLE XXXVIII

REPRESENTATIVE SORPTION RATIOS (mℓ/g)[a]

Element	YM-22	YM-38	YM-45	YM-48	YM-49	YM-54	JA-18[c]	JA-32[c]	JA-37[c]
Cs, Sorption	340	8 600	530	17 000	29 000	250	6 000	150	740
Cs, Desorption	400	13 000	630	27 000	33 000	310		440	
Sr, Sorption	53	12 000	190	1 800	2 700	90	13 000	55	300
Sr, Desorption	63	20 000	200	2 700	3 900	97			
Ba, Sorption	980	66 000	1 200	15 000	33 000	620	4 800	440	850
Ba, Desorption	1 000	190 000	1 300	34 000	51 000	660	30 000		
Ce, Sorption	1 400	830	730	1 900	550	140	40	80	
Ce, Desorption	6 100	3 800	5 700	13 000	1 200	990	180	400	
Eu, Sorption	1 400	2 300	1 600	2 500	1 200	500	30	90	6 000
Eu, Desorption	3 600	8 700	7 300	8 100	2 100	1 800	150	800	13 000
Tc, Sorption	0.3[2.1]	[2.8]		0.2	0.2	[2.7]			
Tc, Desorption	1.2			1.7	2.0				
U, Sorption	[0.5]	[15]				[1.5]	3.9	2.2	4.2
U, Desorption							15	8.0	8.4
Am,[b] Sorption, 22°C							310	620	4 700
70°C							230	110	17 000
Am, Desorption 22°C							1 000	2 300	14 000
70°C							3 400		5 300
Pu,[b] Sorption							140	660	1 800
Pu, Desorption							350	750	3 800

[a]The numbers in brackets are from anoxic measurements. Unless otherwise indicated, all measurements were at ambient temperature.

[b]The combined average sorption ratios for both "dried" and "pH adjusted" methods of traced feed solution preparation are given. See Table XXXIII for separate averages of the two methods.

[c]Values for Cs, Sr, Ba, Ce, and Eu on JA-18, -32 and -37 were taken from Ref. 5.

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