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Laboratory Studies of Radionuclide Distributions Between Selected Ground Waters and Geologic Media

October 1—December 31, 1978

Compiled by

B. R. Erdal

Contributors

B. P. Bayhurst

G. E. Bentley

I. Binder

W. R. Daniels

S. J. DeVilliers

B. R. Erdal

F. O. Lawrence

E. N. Vine

K. Wolfsberg

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BETWEEN SELECTED GROUND WATERS AND GEOLOGIC MEDIA

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ABSTRACT

The Los Alamos Scientific Laboratory contribution to the Waste Isolation Safety Assessment Program, Task 4, for the first quarter of FY-79 mostly involved uranium, plutonium, and americium batch sorption studies needed to extend or complete the data bases for argillite, tuff, and granite. Initial efforts have been made to develop the equipment and procedures for performing migration rate studies on crushed, consolidated, and fractured rock, and for performing measurements under controlled atmosphere conditions. Several additional analytical procedures to be utilized for chemical characterization have been developed, and several additional ethylene glycol surface area measurements have been completed.

I. INTRODUCTION

The Los Alamos Scientific Laboratory (LASL) contribution to the Waste Isolation Safety Assessment Program (WISAP), Task 4, for FY-79 has four principal objectives. The first is to perform migration rate studies using three different types of columns: 1) crushed rock; 2) whole cores; and 3) cores containing natural fractures. The effects of atmospheric conditions and flow rate will be investigated and attempts to model the column behavior will also be made. Second, the batch sorption methodology developed in FY-78 will be used for studies under controlled atmosphere conditions. The results from the batch studies will be used as guidelines for the migration rate studies. Third, the microautoradiographic technique currently utilized at LASL will be used for studies of the sorption of additional radionuclides on polished or ground surfaces of mineral grains and for identification of the specific adsorbing surface in natural (nonpulverized) systems. Finally, studies of the chemistry of several radionuclides in the $\text{pH} \approx 8$ solutions that frequently occur in natural environments will be initiated. It is also important to develop procedures for preparing certain chemical species and for characterizing the species present.

All of these studies will be limited to three geologic types - granite, argillite, and tuff - usually from, but not limited to, the Nevada Test Site (NTS). Natural ground waters or waters having a chemical composition related to the phreatic water will be used for all studies. Detailed analytical and mineralogical analyses of all materials will be made.

II. PROGRESS REPORTED PREVIOUSLY

The results obtained by the LASL program since its beginning in September 1977, have been summarized in several reports.¹⁻⁵ Proper methods for performing batch sorption measurements have been developed. These methods have been applied to studies of the sorption behavior of various radionuclides on alluvium, granite, argillite, and tuff. The effects of particle size, surface area, contact time, and temperature, under atmospheric conditions, have been investigated for Sr, Tc(VII), Cs, Ba, Ce(III), Eu(III), U(VI), Pu, and Am. The effects of these parameters vary significantly with the element and medium under investigation, as do the absolute values of the sorption ratios.

A microautoradiographic technique was developed⁵ to identify the sorption sites for U and Am on ground and polished surfaces of petrographic thin sections of the four media studied. Most of the sorption took place in the clay and zeolite phases.

Equipment for measuring the permeability and porosity of consolidated rocks and rocks containing natural fractures was developed and utilized.

III. ACTIVITIES DURING THE REPORTING PERIOD

The majority of the activity during the first quarter of FY-79 involved those batch sorption studies needed to extend the current data bases for argillite and tuff. The final results for Pu and Am sorption on granite have been calculated and incorporated in the final draft of the report.² Some work has been started to assess the variability of sorption behavior on tuff samples. Initial efforts have been made on the development of equipment and procedures for performing migration rate studies on crushed, consolidated, and fractured material. Similarly, development of equipment for performing controlled atmosphere measurements has been started. Several ethylene glycol surface area measurements have been completed. Several additional analytical procedures to be utilized for chemical characterization of the systems have been developed. Finally, preparation of publications, presentation of reports at national meetings, preparation of data for the WISAP Task-4 data base, etc., have involved some effort.

A. Sorption of Plutonium and Americium on Argillite

W. R. Daniels
F. O. Lawrence

The measurement of the sorption behavior of americium and plutonium on argillite under atmospheric conditions involved geologic materials and ground waters described earlier.³

1. Measurement Techniques.

a. Preparation of Tagged Solutions. Most of the traced waters used in these studies were prepared using the pre-equilibrated synthetic ground water described in Ref. 3, ²³⁷Pu tracer produced at Argonne National Laboratory under contract with Battelle (PNL), and isotopically pure ²⁴¹Am tracer obtained from Oak Ridge National Laboratory. (Feed solutions were prepared so as to contain $\approx 10^{-12}$ M Pu or $\approx 10^{-6}$ M Am at 100% yield of tracer in water; actual concentrations can be calculated from the yields given in Table I). Stock tracer solutions were in 3 M HCl, which resulted in an added chloride concentration of $< 10^{-2}$ M. The ²³⁷Pu tracer was treated with NaNO₂ so that the Pu was in the IV oxidation state at the beginning. This step resulted in the addition of $\approx 10^{-4}$ M sodium into the feed solutions containing plutonium. In general, feed solutions were prepared by the drying technique described in Sec. III. B.1.a.

Some samples were run using one of two feed solutions containing both ^{241}Am and ^{239}Pu , partially in order to examine the effect of a large change in Pu concentration. (The concentration at 100% yield would have been $\approx 10^{-6}$ M Am and $\approx 10^{-12}$ M Pu; actual concentrations can be estimated using the data in Table I). One such feed solution was prepared by drying the tracer, and one was prepared by adding the tracer solution directly to the water and then readjusting the pH to its original value by adding NaOH solution. The latter experiment was considered worthwhile because of the large differences in sorption observed with tuffs and dried or pH-adjusted feed solutions.⁴

In order to examine the difference in apparent sorption resulting from filtering the feed solutions, solutions were centrifuged for one hour at 12 000 rpm (28 000 g) and then portions were used in the batch experiments both before and after filtering through a 0.4- μm Nuclepore filter (all plastic parts). The filters always retained activity which had not been removed by centrifuging. The tracer yields in the feed solutions were determined by gamma-counting aliquots and are given in Table I.

TABLE I
TRACER YIELDS IN FEED SOLUTIONS

Tracer	Temperature(°C)	Yield (%)	
		Unfiltered	Filtered
^{237}Pu	22	54	48
^{237}Pu	70	30	6
^{241}Am	22	38	22
^{241}Am	70	42	15
$^{241}\text{Am} + ^{239}\text{Pu}$	22	11 ^b	0.2 ^b
$^{241}\text{Am} + ^{239}\text{Pu}^a$	22	19 ^b	0.4 ^b

^aTracer was not dried; pH readjusted with NaOH.

^bAm yield; other experiments indicate that the Pu yield was probably approximately the same, at least for the unfiltered solutions.

b. Sorption Measurements. Crushed rock from cores 1 (548 m) and 2 (717 m) from the Eleana formation at the NTS were used for batch sorption studies at both ambient ($22 \pm 2^\circ\text{C}$) and elevated ($70 \pm 1^\circ\text{C}$) temperatures. Three particle sizes

were used: 106-150, 150-180, and 355-500 μm . The material was pretreated by shaking weighed one-gram quantities with 20-ml portions of synthetic ground water for periods of at least two weeks. The samples were contained in pre-washed, capped 40-ml polypropylene tubes. The phases were separated by centrifuging at 12 000 rpm for one hour. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after pre-equilibration.

Twenty-ml 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 weeks. The shaking rates were 200 oscillations per minute for the ambient temperature samples and 80 oscillations per minute for the 70°C samples.

At the end of a shaking period, the aqueous phases were separated from the solids by centrifuging, usually four times, each time transferring the water to a new tube, for one hour at 12 000 rpm (28 000 g). Usually the final solution was aliquoted and the remainder was then passed through a 0.4- μm Nuclepore filter, sometimes twice, and aliquoted again, in order to observe the effect of filtering on the observed sorption ratio.

A number of rock-water mixtures were transferred to clean tubes before the first centrifuging. The original tubes were then checked for activity in order to determine the gamma activity sorbed on the walls. This was found to be negligible (2% of total input activity). All other solid phases were left in the original tubes and counted directly after centrifuging.

Earlier comments²⁻⁴ concerning the use of "control" samples with traced aqueous phase but no solid are applicable here. The activity in the control samples was found to sorb on the walls much more readily than when rock was also present.

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

c. Assay of Radioactivity. Solid samples were normally gamma-counted for ²⁴¹Am or ²³⁷Pu on a NaI(Tl) detector utilizing a single-channel analyzer and a scaler. Counting standards were prepared using known amounts of ²⁴¹Am or ²³⁷Pu in the same geometries and conditions as the experimental samples.

Liquid samples were usually gamma-counted with a NaI well counter (Packard Auto-gamma Scintillation Spectrometer). Standards were prepared in the appropriate geometry.

^{239}Pu will be determined radiochemically⁶ after sample dissolution.

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

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

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

2. Results and Conclusions. Contact times of 1, 2, and 4 weeks have been completed, and desorption experiments have been completed on some ^{237}Pu -traced samples. Gamma counting is essentially completed for both solid and liquid phases from the above samples. Data analysis is in progress.

Tentative general conclusions which can be made include: Very little Am or Pu sorbs on the container walls when crushed argillite is present. Sorption of Am and Pu on argillite is high, probably 10^4 ml/g or greater. Filtering the output solution helps remove any trace of remaining solid, which would have a large effect at these high R_d values with very little activity in the final solution. However, filtering may well remove soluble, noncentrifugable but filterable species that should be considered as nonsorbed and therefore transportable in groundwater. Some final solutions were filtered twice, which would give information concerning the sorption on the filter membrane or equipment if the effects mentioned above could be distinguished.

When the data are processed, information should be available for the partition of Pu and Am between ground water and argillite concerning variations with core sample (mineralogy), contact time, particle size, surface area, temperature, Pu concentration, filtering of input and final solutions, method of tracer preparation, and sorption or desorption.

B. Sorption of Plutonium and Americium on Tuff

W. R. Daniels
F. O. Lawrence

The measurement of the sorption behavior of americium and plutonium on tuff under atmospheric conditions involved geologic materials and ground waters described earlier.⁴

1. Measurement Techniques.

a. Preparation of Tagged Solutions. The traced waters used in these studies were prepared using the pre-equilibrated waters described earlier,⁴ 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 specific activities of the tracers were measured by alpha and gamma counting: $^{241}\text{Am} = 1.23 \times 10^8$ dpm/ml, $^{239}\text{Pu} = 2.5 \times 10^9$ dpm/ml, $^{237}\text{Pu} \approx 4.2 \times 10^6$ dpm/ml at feed preparation time. Feed solutions were usually prepared so as to contain $\approx 2 \times 10^6$ dpm/ml of ^{241}Am , and/or $\approx 3 \times 10^5$ dpm/ml of ^{239}Pu , or $\approx 2.4 \times 10^3$ dpm/ml ^{237}Pu at 100% yield of tracer, which was generally not the case (see below). (These correspond to mass concentrations of $\approx 1 \times 10^{-6}$ M Am, $\approx 1 \times 10^{-5}$ M Pu when ^{239}Pu was used, and $\approx 4 \times 10^{-13}$ M Pu when ^{237}Pu was used.) Stock tracer solutions were in 3 M HCl and in most cases an attempt was made to hold the chloride added to feed solutions constant at ≈ 0.01 M by adding 3 M HCl when the volume of tracer used was reduced. A limited number of samples were prepared with reduced amounts ($\approx 1/10$ concentrations) of ^{241}Am tracer and/or chloride to examine the effect of such changes. (Essentially no differences were observed within the limited accuracy of the results.) The ^{237}Pu tracer was treated with NaNO_2 so that the Pu was in the IV oxidation state at the beginning. This step resulted in the addition of $\approx 10^{-4}$ M sodium into the feed solutions containing ^{237}Pu . The feed solution, which was prepared by adding tracer solution directly to the ground water, then readjusting the pH to the original value by adding NaOH solution, had about 10^{-2} M sodium ion added.

Several batches of traced feed of sufficient volume to contact a predetermined number of crushed-rock samples, aliquot for concentration determination, and measure the pH value were prepared. For each preparation, the desired amount(s) of tracer solution(s) was evaporated at room temperature, in air, in a polypropylene tube. The dried activity was then contacted several times with 20-ml volumes of ground water for periods varying from a few minutes to a final overnight contact. After each contact the tube was centrifuged for one hour at 12 000 rpm, and the aqueous phase was added to a large polyethylene bottle. Contacts were continued until no significant decrease in γ -ray activity in the tube was observed. Generally three contacts were made. Ground water was added to the bulk of the feed solution in the bottle to give a volume ≈ 20 ml less than

the desired final volume. This bulk solution was then shaken overnight at the same time the final contact was being made in the original tube. The next day the tube was centrifuged, and the solution was added to the bottle. Water was added to give the desired final volume, and the bottle was shaken for at least one hour. The solution was then centrifuged for one hour at ≥ 6000 rpm and transferred to a new bottle. Within one hour, an aliquot was taken and acidified for later assay of the initial concentration of each tracer, and 20-ml portions were added to crushed-rock samples in polypropylene tubes and to empty tubes for use as "controls." The pH value of the remaining solution was then measured. The yields of tracer in the feed solutions ranged from 5 to 70%, with an average of 34% for six solutions, for water pre-equilibrated at room temperature and from 7 to 50%, with an average of 26% for six solutions, for water pretreated at 70°C. On the average, the corresponding concentrations were about 1×10^{-7} M Am and 1×10^{-6} M Pu. The yield of tracer in the one batch of feed solution containing ^{237}Pu was 43%, giving a concentration of $\approx 2 \times 10^{-13}$ M Pu.

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

b. Sorption Measurements. Crushed rock⁴ from cores JA-18, JA-32, and JA-37 was used for sorption studies at both ambient ($22 \pm 2^\circ\text{C}$) and elevated ($70 \pm 1^\circ\text{C}$) temperature. The material was pretreated by shaking weighed one-gram quantities with 20-ml portions of water from well J-13 for periods of at least two weeks. The samples were contained in prewashed, capped 40-ml polypropylene tubes. The phases were separated by centrifuging at 12 000 rpm (28 000 g) 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-ml 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 weeks. The shaking rates were 200 oscillations per minute for the ambient temperature samples and 80 oscillations per minute for the 70°C samples.

At the end of a shaking period, the aqueous phases were separated from the solids by four centrifugings, each in a new tube, for one hour at 12 000 rpm.

Aliquots of the final solutions were taken for pH measurements, gross gamma counting, and gamma spectroscopy. The solid phases were left in the tubes and counted directly. Since this procedure meant that any activity sorbed on the walls of the container was also counted, many of the solid samples were carefully removed from the tubes, and the tubes were checked for residual activity. In general, less than 2% of the total input activity remained; this could be attributed almost entirely to a slight solid residue. Therefore, the activity sorbed on the walls is considered negligible.

The comments concerning "control" samples with a traced aqueous phase but no solid are applicable here.²⁻⁴ Such samples run with Pu and Am showed much higher wall sorption on the tubes when no solid was present.

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

Samples containing only a single gamma-ray emitter (²⁴¹Am with or without ²³⁹Pu, or ²³⁷Pu) were also counted on a NaI(Tl) detector utilizing a single-channel analyzer and a scaler. Counting standards were prepared as described above. ²³⁹Pu was determined radiochemically⁶ after sample dissolution; to date analyses have been completed for only a few samples.

d. Calculations. Since both solid and liquid phases were counted directly for ²⁴¹Am and ²³⁷Pu or analyzed separately for ²³⁹Pu, the sorption ratio 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. Examination of the tubes used for the sorption measurements indicated that the container effect could be neglected ($\leq 2\%$).

2. Results and Conclusions. The results for the distribution ratio measurements for ambient temperature conditions are given in Tables II-IV, while those for 70°C are given in Table V. Radiochemical analyses for ²³⁹Pu have not

been completed for many samples. The experiments with ^{237}Pu are not complete and data from these are not included in the tables. Desorption measurements are also still in progress. The initial and final pH values are also listed in the tables.

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

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

TABLE II
 ^{241}Am and ^{239}Pu SORPTION RATIOS, SAMPLE JA-18, AMBIENT TEMPERATURE

Fraction (μm)	Tracer Prep. Method	Sorption Time (d)	Desorp. Time (d)	R_d (ml/g)		pH	
				Am	Pu	Initial	Final
106-150	dried	7.0	14	200	170		8.19
		7.0		250			8.29
				270	160	8.30	
		7.6		96	70	8.56	7.43
		7.6		310			7.52
		14.6		86		8.56	8.42
		14.6		310			8.29
		28.6		120		8.56	8.55
		28.6		360			8.60
		56.6		57		8.56	8.36
		56.6		85			8.57

C. Sorption of Uranium(VI) on Tuff and Argillite

B. P. Bayhurst

The measurement of the sorption behavior of uranium(VI) on tuff and argillite under atmospheric conditions involved geologic materials and ground waters described in Refs. 3 and 4, respectively. The procedure used for these measurements was described in Ref. 2.

The initial pH values for the tuff measurements were 7.6, 8.1, and 8.4 for JA-18, JA-32, and JA-37, respectively. The estimated U(VI) concentration was $\approx 10^{-7}$ M. The results for the measurements involving tuff are given in Tables VI-VIII.

As expected, uranium(VI) is poorly sorbed 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. There seems to be a tendency toward slightly higher sorption on the finer sieve fractions. There does not seem to be a strong dependence on the mineralogy since all sorption ratios are low, but petrographic analysis⁴ indicates that the samples are rather different.

The U(VI) sorption studies on Eleana argillite have just begun. Four fractions (106-150 μ m, 250-355 μ m, 355-500 μ m, <75 μ m) of CN1, two fractions (<75 μ m, 355-500 μ m) of CS2, and the <75- μ m fractions of CN3 and CN4 are being utilized. The U(VI) concentration is $\approx 4 \times 10^{-7}$ M. The counting and data analysis are in progress.

D. Variability of the Sorption Behavior for Tuff

E. N. Vine
S. J. DeVilliers
K. Wolfsberg

To date we have studied⁴ the sorption behavior of a variety of radionuclides on tuff samples from the Jackass Flats area of the NTS. In order to further assess the variability of this behavior and try to develop a data base of information for predictive purposes specific for tuff, additional tuff samples from a different area at the NTS were obtained for study using the batch technique.

1. Measurement Techniques.

a. Materials. Yucca Mountain tuff cores were obtained from the USGS core library at the NTS. Thirty-five core samples were taken, ranging from 207- to 762-m depths. Experiments to measure batch sorption ratios of five representative cores are now in progress. All cores are being studied by LASL Group G-6 for mineralogy and more of these cores will be used for similar measurement if they look mineralogically interesting. The five cores now in use are described in

TABLE III
 ^{241}Am and ^{239}Pu SORPTION RATIOS, SAMPLE JA-32, AMBIENT TEMPERATURE

Fraction (μm)	Tracer Prep. Method*	Sorption Time (d)	Desorp. Time (d)	R_d (mL/g)		pH	
				Am	Pu	Initial	Final
106-150	dried	7.6		110		8.50	7.60
		14.6		110	110	8.50	8.50
		28.6		140		8.50	8.63
		28.6		230		8.50	8.63
		56.6		79		8.50	8.64
	pH adjust	7		1600	1200	7.92	8.26
		14		1000	1800	7.92	8.19
		28		1100		7.92	8.32
			14	2100	920	8.30	
355-500	pH adjust	7		890	1000	7.92	8.19
		14		640		7.92	7.94
			14	920	580	8.30	
		28		490	820	7.92	8.23

*The "pH adjust" method data are based on a single feed solution preparation; data are given for comparison to indicate variation with preparation method. These experiments will be repeated.

Table IX. Measurements with two of them, YM 22 and YM 49, are being run in duplicate by separate individuals to check on technique.

b. Preparation of Tagged Solutions. J-13 well water⁴ was pre-equilibrated separately with ground material from each Yucca Mountain core. The contact time was 2 weeks with a solution-to-solid ratio of 20 mL/g. The solid was removed from each solution by centrifugation at 6000 rpm followed by filtration through a 0.45- μm Nuclepore filter paper.

Each traced water was prepared using the pre-equilibrated 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 polyethylene tube in a Scientific Products "Temp-Blok Module Heater." Concentrated HCl was added and the mixture was again evaporated to dryness. The appropriate volume of pre-equilibrated ground water was added and the mixture was stirred for 24 hours, after

TABLE IV
 ^{241}Am and ^{239}Pu SORPTION RATIOS, SAMPLE JA-37, AMBIENT TEMPERATURE

Fraction (μm)	Tracer Prep. Method*	Sorption Time (d)	Desorp. Time (d)	R_d (ml/g)		pH	
				Am	Pu	Initial	Final
106-150	dried	7.6		430	390	8.64	7.53
		14.6		365		8.64	8.52
		28.6		430	180	8.64	8.67
		28.6		1500		8.64	8.62
		56.6		640		8.64	8.56
	pH adjust	7		7200	7200	7.92	8.53
		14		5200		7.92	8.53
			14	2700	890	8.30	
		28		7500	12000	7.92	8.23
			14	5200	1600	8.30	
355-500	pH adjust	7		3700	5400	7.92	8.38
		14		2800	7200	7.92	8.19
		28		3800		7.92	8.29
			14	5800	670	8.30	

*See footnote to Table III.

which it was filtered twice through 0.45- μm Nuclepore filter paper. The resulting tracer solution was used within a few hours for the sorption measurements.

c. Measurements. Batch sorption experiments are currently in progress. One-gram quantities of 106- to 500- μm or <106- μm crushed rock were shaken (200 oscillations/minute) with 20 ml of untraced pre-equilibrated water for two weeks. The tubes were then centrifuged at 16 000 rpm (32 000 g) for 1 hour. The weight of solution remaining with the solid phase was obtained by weighing the tube plus solid before and after pre-equilibration. Twenty ml of tagged water was then added. The samples are now being shaken at ambient temperature. They will be removed in January after approximately 20- and 40-day contact times. Concurrently we are also running similar experiments on two types of epoxy: "Barco Bond" and "Eco Bond." Should one of these materials prove to be nonsorptive and stable in the solutions used, it could be used as a "container" for whole cores in subsequent experiments.

TABLE V
 ^{241}Am and ^{239}Pu SORPTION RATIOS, SAMPLES JA-18, -32, and -37, 106-150 μm , 70°C

Core Sample	Tracer Prep. Method*	Sorption Time (d)	R_d (m ℓ /g)		pH	
			Am	Pu	Initial	Final
JA-18	dried	7.6	220			7.19
		7.6	190			7.32
		14.6	190			7.57
		14.6	170			8.08
		28.6	290			8.61
		28.6	150			8.62
		28.6	340		8.60	
		28.6	370		8.57	8.50
		56.6	300			-
		56.6	76			
JA-32	dried	7.6	120		8.46	7.33
		14.6	160		8.46	8.14
		28.6	130		8.46	8.57
		56.6	46		8.46	
JA-37	dried	7.6	520		8.58	7.33
		14.6	680		8.58	8.06
		14.6	2100		8.58	8.18
		28.6	960		8.58	8.67
		56.6	800		8.58	
		56.6	730		8.58	8.52

*See footnote to Table III.

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

Fraction (μm)	Sorption Time (d)	Desorp. Time (d)	R_d (ml/g)*	Final pH
106-150	6.937	19.972	4.9 (37)	7.9
		19.972	13.0	7.9
	13.997		3.5 (49)	7.9
		13.915	11.7	8.1
	20.977		10.6 (21)	7.8
		7.929	43.8	8.0
355-500	6.937		1.6 (95)	8.0
		19.972	9.7	8.2
	13.997		1.4 (99)	8.2
		13.915	6.4	8.3
	20.977		1.3 (110)	8.0
		7.929	6.3	7.9

*The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these 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. The estimated uncertainties in the desorption measurements are all greater than 100%.

2. Results and Conclusions. Since the Yucca Mountain cores were not obtained until mid-November 1978, the batch R_d measurements are still in progress and results are not yet available.

E. Migration Rate Studies

W. R. Daniels
B. R. Erdal

The behavior of radionuclides under the conditions that occur when ground water flow through geologic materials is very complex. Kinetic factors probably play a major role, as do the chemical speciation, the formation of radiocolloids, the temperature, and the mineralogy along the flow path. Therefore, one must study the cumulative effects of all factors influencing the migration rate. The effects of individual variables can then be obtained by parametric studies.

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

<u>Fraction (μm)</u>	<u>Sorption Time (d)</u>	<u>Desorp. Time (d)</u>	<u>R_d (mL/g)</u>	<u>Final pH</u>
106-150	6.937		3.5 (49)	7.6
		19.972	15.4	7.8
	13.977		2.9 (56)	7.8
		13.915	11.9	8.0
	20.977		2.6 (45)	7.6
		7.929	9.6	7.6
355-500	6.937		1.4 (84)	7.7
		19.972	0.2	7.9
	13.997		1.3 (109)	8.1
		13.915	5.4	8.3
	20.977		1.3 (107)	8.3
		7.929	5.2	8.4

*See the footnote to Table VI.

Migration rate studies will be performed using three different types of columns: 1) crushed rock; 2) whole cores; and 3) cores containing natural fractures. Rock-equilibrated waters prepared from naturally occurring ground waters or of composition related to the phreatic water will be used. The studies with crushed-rock columns will be made in order to compare the results to those from the FY-78 batch sorption studies performed on the geologic materials. The effect of atmospheric conditions on the behavior of certain elements will be assessed, as will the effect of flow rate. The behavior of various radionuclides when ground water flows through naturally porous rocks (tuff) and through rocks containing natural fractures (granite) will be studied.

1. Materials Preparation. Sufficient quantities of Climax Stock quartz monzonite ("granite") containing natural fractures have been obtained from the NTS during a recent field trip. A request has also been made to the Atomic Energy of Canada, Ltd. (Tjalle T. Vandergraaf) for similar samples of the White-shell granite.

LASL Group CMB-6 has prepared several cores 2.54 cm in diameter by 1.6 cm long of tuff (8 each), granite (6 each), and argillite (4 each) by a diamond-coring technique. The procedure has recently been used to make seven granite cores

TABLE VIII
U(VI) SORPTION RATIOS, SAMPLE JA-37, AMBIENT TEMPERATURES

<u>Fraction (μm)</u>	<u>Sorption Time (d)</u>	<u>Desorp. Time (d)</u>	<u>R_d (ml/g)*</u>	<u>Final pH</u>
106-150	6.937		4.0 (44)	7.3
		19.972	6.1	7.7
	13.997		4.8 (35)	8.0
		13.915	9.6	8.2
	20.977		5.1 (33)	8.5
		7.929	11.2	8.4
355-500	6.937		2.6 (175)	8.5
		19.972	2.2	8.5
	13.997		4.2 (39)	7.7
		13.915	9.2	7.9
	20.977		4.7 (36)	8.1
		7.929	11.9	8.2

*See the footnote to Table VI.

TABLE IX
DESCRIPTION OF YUCCA MOUNTAIN CORES

<u>CORE</u>	<u>Depth (feet)</u>	<u>General Description</u>
YM 22	847.8-848.8	Purplish-gray, densely welded, tuff, pumice <3cm
YM38	1504.3-1505.5	Pale brown, unwelded tuff
YM 45	1939.0-1930.9	Light gray, pumice-rich vitric tuff, 2% lithics <3mm
YM 48	2113.2-2114.2	Light green-gray, 3-5% lithics <1mm, fracture 60°/vertical, 1mm thick filled with black material
YM 49	2220.0-2221.0	Brown-gray, pumice-rich, poorly welded tuff, pumice <1cm, 2-3% lithics <2mm
YM 54	2491.0-2491.6	Light-gray densely welded pumice-rich vitric tuff, trace lithics

containing natural fractures. These latter cores are being checked for high permeability to ascertain if a crack is present.

Sufficient quantities of the crushed material are currently available. All grinding is now done in a non-iron system using an agate mortar with a 50- or 70-mm agate ball (Tekmar Co., Pulverisette). This system can also be used for grinding under water or in an inert atmosphere. All sieving is done using plastic sieves (Spex Industries, Inc.).

2. Assembly of Column Systems. The equipment for the crushed-column studies is currently being assembled. The rather low flow rates that will be used are delivered by syringe pumps (Sage Instruments, models 220 and 355) or gravity flow. The pumps can deliver as little as about 0.02 ml per hour from a 5 ml syringe at about 1 atmosphere. The systems are constructed entirely of plastic (Teflon or polypropylene) using commercially available columns (Bio-Rad) and HPLC Teflon tubing and connections (Pierce Chemical Co.). These systems are currently being tested.

An apparatus similar to the equipment used in FY-78 for permeability measurements was constructed for use as a high-pressure column apparatus. This may be somewhat of a misnomer because the net difference between the confining pressure and the delivery pressure (which equals the effective pore pressure) is normally in the 50- to 100-psi range. The equipment design is based on that of Brace et al.⁷ as modified by Potter⁸ and is shown schematically in Fig. 1. The right-circular cylindrical core sample is placed in a Teflon sleeve and a porous disk of pressed stainless steel fiber is placed on each end of the sample. Steel cylinders of the same diameter as the sample, with pressure lines attached, are then inserted into the ends of the Teflon cylinder and the assembly is placed in a pressure vessel, which then is pressurized by a miniaturized air-driven hydraulic pump (Haskel, MCP-88). The stainless steel capillary tubing leading to the collecting tube has a 0.048-cm i.d. The delivery pressure is supplied by a metering pump (Altex, model 100A) capable of operation either as a constant-flow metering pump or as a constant-pressure source up to 10^4 psi. It has a minimum metered flow rate of 0.01 ml/min and is pressure limiting within the operating range without shutoff. Currently all tubing is stainless steel rated at 60 000 psi. Two of these systems have been constructed.

3. Porosity Measurements. The system described above for studying high-pressure columns was utilized for some preliminary measurements of connected pore space (i.e., free column volume or effective porosity) of tuff and granite cores.

Fig. 1. Schematic of the high-pressure column apparatus.

The volume of tritiated water required to fill the available pore space of a rock core 2.54 cm in diameter and 1.6 cm thick was measured by liquid scintillation counting. By comparison with the total core volume, the fraction of free space was determined. Three measurements on a tuff core from well J-13 at the NTS, JA-35, Core #3, gave values of 0.233, 0.247, and 0.239 for an average of 0.240 with a spread of $\pm 3\%$. Measurements on two Climax granite cores gave values of 0.0015 for Core #6A and 0.0050 and 0.0081 for two measurements on Core #2A.

The tritiated water method appears to give satisfactory results for the available pore space in tuff and granite. Limited data suggest that measurement

of the low values for granite is less reproducible than for the higher tuff values. The performance of the equipment during these measurements indicates that actual studies of flow through cores can begin soon.

F. Measurements Under Controlled Atmosphere Conditions B. R. Erdal

It is necessary to study radionuclide sorption under conditions that simulate the conditions that occur deep underground. Under these conditions the redox effects of the rocks themselves can become important since, e.g., the fugacity of oxygen will be very low. This is particularly important for those elements, e.g., Pu, Np, Tc, I, that have multiple oxidation states.

The majority of the equipment needed to perform sorption measurements under reduced oxygen conditions or conditions having a specified atmosphere has been received. Installation of the various components is proceeding. The two-station controlled atmosphere box was manufactured by Vacuum/Atmospheres Co. (model DL-002-S-P). The oxygen concentration is being measured by use of a Teledyne trace-oxygen analyzer (model 317-X, special modifications of LASL). The Vacuum/Atmospheres Co. gas purification system (model MO-40-2-H) has not been received. However, controlled atmosphere measurements will soon be started. The boxes will be used for batch measurements, some column measurements, and for preparation of materials under controlled conditions.

G. Materials Characterization B. P. Bayhurs, G. E. Bentley, I. Binder

In order to be able to use the data bank of sorption information for the estimation of the migration behavior of a nuclide in any geologic material and type of water, one must gather the appropriate supporting information for the materials used. A method for rapidly analyzing the ground waters for the major and minor elements is under development. Similarly, a technique for determination of trace constituents of solids and solutions has been developed. Final determinations of surface areas by the ethylene glycol technique have also been completed.

1. Emission Spectrometry. The Spectrometrics Inc. twenty-channel direct-current plasma-source emission spectrometer allows the simultaneous determination, in a liquid sample, of up to twenty preselected elements. The suite of elements to be determined is selected by inserting a cassette into the instrument so that only certain atomic emission wavelengths are permitted to impinge upon the instrument's elements.

Two multielement cassettes are currently operational, and two additional

cassettes are awaiting final vendor check-out and field alignment in the instrument. The operational cassettes are set up for the following elements: 1) Si, Al, Fe, Mg, Ca, K, T, Mn, Au, Ag, Ba, Rb, Sr, Li, V, Ga, and Sn; and 2) Li, K, Na, Mg, Al, Rb, Mo, T, V, Sc, Bi, Pb, Tl, Hg, Cd, Sb, W, and Ga. The cassettes awaiting final setup include the following elements: 1) Li, K, Na, Mg, Al, Si, B, Be, Se, As, Ge, Ga, Zn, Cu, Ni, Co, Sr, and In; and 2) La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Tb, Ho, Er, Tm, Yb, Lu, Hf, Ta, Y, and Ga. If it is desired to determine an element not included in one of the multielement cassettes, it is possible to do so by using a variable single-element cassette.

Limits of detection for most metallic elements, as aqueous standards, are well less than $0.5 \mu\text{g/ml}$, with many elements having limits of detection of less than $0.05 \mu\text{g/ml}$. Early results using aqueous multielement standards indicate that the instrument is easily capable of 10% precision at the 1-mg/ml level. It will be necessary to extensively evaluate interelement and other matrix effects to assure that the results are accurate.

2. Neutron Activation Analysis. All rock-equilibrated waters used for sorption measurements may have significant concentrations of the carriers for each of the tracers studied. A neutron activation analysis technique has been developed to determine these concentrations.

Initially, only one sample of equilibrated Climax Stock water² (batch 4, 70°C) was analyzed. Approximately 375 ml of this water was reduced to solids by a freeze-drying process (VirTis Unitrap II). The weighed solid was loaded into a plastic vial for neutron activation in the thermal column of the Omega West reactor at LASL. The induced activities were measured and identified by means of a calibrated Ge(Li) gamma-ray spectrometer. The results for this single measurement are given in Table X.

The final carrier concentrations due to the tracers² were $1.2 \times 10^{-6} \text{ M (Sr)}$, $1.4 \times 10^{-9} \text{ M (Cs)}$, $2.4 \times 10^{-8} \text{ M (Ba)}$, and $1.3 \times 10^{-6} \text{ M (Ce)}$. Therefore, the ratio of the initial concentrations in the water to that due to the tracer were 0.51(Sr), 0.86(Cs), 27(Ba), and 0.0011(Ce). The concentration due to the tracer dominated for the Ce measurements, while that due to the water dominated for the Ba measurements. The Sr and Cs values are about equal.

3. Ethylene Glycol Surface Area Measurements. Since many sorption ratios are expected to scale with surface area, it is necessary to measure the surface area. Table XI summarizes the measurements performed to date for all materials

studied in the first year of the LASL program. The equilibrium glycol procedure^{9,10} was used. Briefly, this procedure consists of wetting a dried and weighed sample of calcium-saturated material with glycol. This is then followed by equilibration in an evacuated desiccator containing an anhydrous calcium chloride-ethylene glycol solvate. The equilibration is repeated until the weights become constant, presumably indicating that only a monolayer remains.

Generally, the granites or granite-type material⁴ (Jackass Flats tuff JA-18) have low surface areas relative to argillites and tuff. This is presumably due to the high clay/zeolite content in the latter materials, which have considerable internal surface area. The surface areas do not scale strongly with particle size except perhaps for the granites. This is consistent with the observation²⁻⁴ that the amounts of the various minerals in the sieve fractions are relatively constant.

TABLE X
NEUTRON ACTIVATION ANALYSIS

<u>Induced Activity</u>	<u>µg element/ g water</u>	<u>Element Molarity</u>
²⁴ Na	6800	3.0×10^4
⁴² K	2200	5.6×10^5
⁴⁷ Ca	8800	2.1×10^8
⁶⁵ Zn	3.6	5.5×10^8
⁸⁸ Br	1.8	2.2×10^8
⁸⁵ Sr	53	6.1×10^7
⁹⁹ Mo	11	1.2×10^7
¹³⁴ Cs	0.17	1.2×10^9
¹³¹ Ba	88	6.4×10^7
¹⁴¹ Ce	0.19	1.4×10^9

IV. ACTIVITIES PLANNED FOR NEXT QUARTER

The following is a brief outline of some of the activities planned for the period January 1 - March 31, 1979.

A. Batch sorption measurements

1. Finish Pu and Am on argillite and granite
2. Finish U on argillite
3. Finish tuff variability study
4. Start some controlled atmosphere measurements for Pu and Am

TABLE XI
SURFACE AREA MEASUREMENTS

<u>Identification</u>	<u>Core</u>	<u>Fraction (μm)</u>	<u>Treatment*</u>	<u>Surface Area(m^2/g)</u>
Climax granite	5	106-150	W	8
		250-355	W	4
		500-800	W	7
	7	106-150	W	7,11
		250-355	W	3
		500-850	W	3
Westerly granite			U	<1
Eleana argillite	1	106-150	W	50,47
		250-355	W	63
		355-500	W	45,49
		106-150	U	51,48
		355-500	U	64,64
	2	<75	U	75
	3	<75	U	99
	4	<75	U	92
Argillaceous shale NY			U	46
Jackass Flats tuff	18	106-150	W	31
		355-500	W	46
	32	106-150	W	8,8
		355-500	W	9
	37	106-150	W	94,115
		355-500	U	3
Umtanum basalt			U	2
Oolitic limestone			U	32
Alluvium U3BV				560
Bentonite				

*W implies that the samples were briefly washed with distilled water to remove dust; U implies that the sample was not washed with distilled water.

5. Start some controlled atmosphere measurements for Tc
- B. Microautoradiography
 1. Start additional sorption studies on petrographic thin-sections
 - a. Am in a carbon dioxide atmosphere
 - b. Np sorption
 2. Start development of procedure for determining the microstructural distribution of α -emitters on infiltrated rocks
- C. Migration rate studies
 1. Crushed rock columns
 - a. Start studies on granite
 - b. Start studies on tuff
 2. Whole cores
 - a. Start porous flow (tuff) or fracture flow (granite) studies
 - b. Start modification of high-pressure equipment to use Teflon-lined components wherever possible
- D. Materials characterization
 1. Reactant solutions
 - a. Start neutron activation analysis for trace element concentration for starting solutions
 - b. Start emission spectrographic analysis for beginning and ending concentrations of major cations
 2. Solid phases
 - a. Analyze for major elements (LASL Group CMB-6)
 - b. Start analyses for trace elements by neutron activation
 - c. Do the mineralogy/petrology on new materials as they are received (LASL Group G-6)
 - d. Perform additional cation exchange capacity measurements

RECENT PUBLICATIONS, DRAFTS, AND PRESENTATIONS

1. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, C. J. Duffy, F. O. Lawrence, S. Maestas, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Granite," Los Alamos Scientific Laboratory report LA-7456-MS (1979).
2. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Argillite," Los Alamos Scientific Laboratory report LA-7455-MS (1979).

3. K. Wolfsberg, B. P. Bayhurst, W. R. Daniels, B. R. Erdal, F. O. Lawrence, and A. E. Norris, "Sorption-Desorption Studies on Tuff," Los Alamos Scientific Laboratory report LA-7480-MS (1978).
4. J. L. Thompson and K. Wolfsberg, "Applicability of Microautoradiography to Sorption Studies," Los Alamos Scientific Laboratory report LA-7609-MS (1978).
5. B. R. Erdal, W. R. Daniels, D. C. Hoffman, F. O. Lawrence, and K. Wolfsberg, "Sorption and Migration of Radionuclides in Geologic Media," Symposium on Science Underlying Radioactive Waste Management, Materials Research Society, Boston, Massachusetts, Nov. 28 - Dec. 1, 1978.
6. B. R. Erdal, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, D. C. Hoffman, F. O. Lawrence, J. R. Smyth, J. L. Thompson, and K. Wolfsberg, "Laboratory Studies of Radionuclide Transport in Geologic Media," submitted to IAEA Symposium on the Underground Disposal of Radioactive Wastes, Otaniemi, Finland, July 2-6, 1979.
7. B. R. Erdal, R. D. Aguilar, P. Q. Oliver, and B. P. Bayhurst, "Radionuclide Sorption Studies on Granite and Argillite," to be presented at the Joint ACS/CSJ Symposium on Radioactive Waste Disposal, Honolulu, Hawaii, April 1-6, 1979.
8. W. R. Daniels, F. O. Lawrence, P. Q. Oliver, and S. Maestas, "Sorption of Pu and Am on Tuff, Granite, and Argillite," to be presented at the Joint ACS/CSJ Symposium on Radioactive Waste Disposal, Honolulu, Hawaii, April 1-6, 1979.
9. J. R. Smyth, K. Wolfsberg, and J. L. Thompson, "Microautoradiographic Studies of U and Am Sorption on Minerals," to be presented at the Joint ACS/CSJ Symposium on Radioactive Waste Disposal, Honolulu, Hawaii, April 1-6, 1979.
10. K. Wolfsberg, B. P. Bayhurst, B. M. Crowe, W. R. Daniels, B. R. Erdal, D. C. Hoffman, F. O. Lawrence, and J. R. Smyth, "Sorption Properties of Tuffs," to be presented at the Joint ACS/CSJ Symposium on Radioactive Waste Disposal, Honolulu, Hawaii, April 1-6, 1979.

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REFERENCES

1. K. Wolfsberg, "Sorption-Desorption Studies of Nevada Test Site Alluvium and Leaching Studies of Nuclear Test Debris," Los Alamos Scientific Laboratory report LA-7216-MS (1978).
2. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, W. R. Daniels, C. J. Duffy, F. O. Lawrence, S. Maestas, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Granite," Los Alamos Scientific Laboratory report LA-7456-MS (1978).
3. B. R. Erdal, R. D. Aguilar, B. P. Bayhurst, P. Q. Oliver, and K. Wolfsberg, "Sorption-Desorption Studies on Argillite," Los Alamos Scientific Laboratory report LA-7455-MS (1978).
4. K. Wolfsberg, B. P. Bayhurst, W. R. Daniels, B. R. Erdal, F. O. Lawrence, and A. E. Norris, "Sorption-Desorption Studies on Tuff," Los Alamos Scientific Laboratory report LA-7480-MS (1978).
5. J. L. Thompson and K. Wolfsberg, "Applicability of Microautoradiography to Sorption Studies," Los Alamos Scientific Laboratory report LA-7609-MS (1978).
6. J. Kleinberg and H. L. Smith, Eds., "Collected Radiochemical Procedures (Radiochemistry Group CNC-11)," Los Alamos Scientific Laboratory report LA-1721, 4th Ed. (1975).
7. W. R. Brace, J. B. Walsh, and W. T. Frangos, "Permeability of Granite Under High Pressure," J. Geophys. Res. 73, 2225 (1968).
8. J. M. Potter, "Experimental Permeability Studies at Elevated Temperature and Pressure of Granite Rocks," Los Alamos Scientific Laboratory report LA-7224-T (1978).
9. R. S. Dyal and S. B. Hendricks, "Total Surface of Clays in Polar Liquids as a Characteristic Index," Soil Sci. 69, 421 (1950).
10. C. A. Bower and J. O. Goertzen, "Surface Area of Soils and Clays by an Equilibrium Ethylene Glycol Method," Soil Sci. 87, 289 (1959).