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**Laboratory Studies of Radionuclide Distributions
Between Selected Groundwaters and Geologic Media**

January 1—March 31, 1979

University of California

MASTER

LOS ALAMOS SCIENTIFIC LABORATORY

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Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media

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Compiled by
B. R. Erdal

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LABORATORY STUDIES OF RADIONUCLIDE DISTRIBUTIONS
BETWEEN SELECTED GROUNDWATERS 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 second quarter of FY-79 involved plutonium, americium, and uranium(VI) batch sorption studies on argillite. The behavior of plutonium and americium in aqueous solutions at $\text{pH} \approx 8$ with respect to container sorption, filtering, and centrifuging was also investigated. Studies of the variability of the sorption behavior for tuff were completed. Migration rate studies on crushed and fractured materials were initiated. The development of the systems for performing controlled atmosphere measurements has been completed. Additional chemical analysis have been performed, as were some studies related to microautoradiography. Additional cation exchange capacity and ethylene glycol surface area measurements have also been made.

I. INTRODUCTION

The Los Alamos Scientific Laboratory (LASL) contribution to the Waste Isolation Safety Assessment Program (WISAP), Task 4, in FY-79 has five 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 sorbing surface in natural (nonpulverized) systems. Fourth, studies of the sorption behavior in systems related to salt domes will be performed as requested. Finally, studies of the chemistry of several radionuclides in the $\text{pH} \approx 8$ solutions that frequently occur in natural environments will be initiated.

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 groundwaters or waters having a chemical composition related to the phreatic water will be used for all studies. Detailed analytical and mineralogical analysis 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.¹⁻⁶ 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 specific sorption sites for actinides on ground and polished surfaces of petrographic thin sections.

During the previous quarter, most of the effort involved studies of the partitioning of uranium, plutonium and americium between groundwater and argillite, tuff, and granite. Studies of the variability of sorption ratios for tuff were initiated. Initial efforts were also made to develop the equipment and procedures for performing migration rate studies on crushed material, whole cores, and cores containing natural fractures, and for performing measurements under controlled atmosphere conditions. Additional analytical procedures for chemical characterization were also developed. Appendices A-D give the results of the Controlled Sample Program performed in FY-78.

III. ACTIVITIES DURING THE REPORTING PERIOD

Much of the activity during the second quarter of FY-79 involved those batch sorption studies needed to extend the current data bases for argillite and tuff. Some of the final results for plutonium, americium, and uranium(VI) on argillite have been obtained. The behavior of plutonium and americium in aqueous solutions at $\text{pH} \approx 8$ with respect to container sorption, filtering, and centrifuging was also investigated. Studies of the variability of the sorption behavior for tuff were completed. Migration rate studies on crushed and fractured materials were initiated. The development of the systems for performing controlled atmosphere measurements has been completed. Additional chemical analysis have been performed, as were some studies related to microautoradiography. Additional cation exchange capacity and ethylene glycol surface area measurements have also been made. Finally, preparation of publications, travel, 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, S. Maestas, and P. Q. Oliver)

1. Investigation of the Behavior of Plutonium and Americium in Aqueous Solutions at $\text{pH} \approx 8$.

a. Container Sorption. In an attempt to learn more about the known erratic behavior of plutonium and americium in solutions at $\text{pH} \approx 8$, both container-sorption and filtering effects were studied using samples described in Ref. 6. Container sorption for samples was examined by transferring both aqueous and solid phases after contact to a new tube before centrifuging. The empty polypropylene tubes were then counted for gamma activity. The "control" tubes, i.e., those with traced aqueous phase but no solid, were handled somewhat differently.

They were centrifuged at 12 000 rpm for 1 h, and the aqueous phase was then poured into another tube. The original tubes were then gamma counted. The percentages of the total activity in the solutions before contact that remained on or in the containers after contact for a number of samples and controls are given in Table I. (Contact times for samples and controls were 1, 2, 4, and 8 weeks. There was no correlation between the activity found on the containers and the contact times within this range.) The amount of plutonium or americium activity remaining on the containers used during the contacts is obviously much lower for the samples than for the controls. We conclude from these results that container sorption can be neglected in calculating sorption ratios for plutonium and americium on argillite, at least for polypropylene tubes. (We have some evidence that polycarbonate tubes behave in the same manner.) Any correction based on results from such controls is inappropriate.

At room temperature, a higher fraction of the americium activity remained with the control tubes when the feed solutions had not been filtered before contact and when feed solutions were prepared by pH readjustment rather than by drying the tracer. These effects are probably due to differences in polymer and radiocolloid formation under these conditions.

In future experiments, control solutions will be transferred after contact and before centrifuging, which should more clearly distinguish effects of centrifugable species and sorption on the bottoms of the containers.

The distribution of activity in the control tubes was investigated. The bottoms of some of the original tubes were washed twice with 2.5-ml portions of water. The gamma activity in this water was assumed to approximate the amount of centrifugable species in the original aqueous phase. Since the tubes had been shaken during the contact period, the water washes probably did not remove activity sorbed on the tube during contact. The bottoms of the tubes were then washed twice with 2.5-ml portions of 3 M HCl, and the activity removed in each case 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 the activity sorbed on the walls. The final "clean" tubes were also gamma counted. The distribution of the activity in each tube is shown in Table II. The fraction of centrifugable species was less than 10% in all but two of the tubes.

The areas of the "bottom" and the "walls" of a tube were calculated to be 7.74 and 26.0 cm², respectively, and the appropriate activities were calculated

TABLE I
Pu AND Am INPUT ACTIVITY LEFT WITH CONTAINER AFTER CONTACT^a

Tracer	Samples (%)		Controls (%)	
	22 ^c	70 ^o	22 ^o	70 ^o
²³⁷ Pu	0.46	0.18 ^b	37	78
	0.37	2.2	49	97
	0.16 ^b	1.1		
	0.45			
	0.42 ^b			
	0.35			
²⁴¹ Am	4.4	1.1	17 ^b	89 ^b
	1.1	0.35 ^b	24 ^b	80 ^b
	0.33	0.81	3	94
	0.42	0.58	6	98
	4.1		6	
	1.4		9 ^c	
	0.32		9 ^c	
	0.29 ^b		8 ^c	
	0.22		11 ^c	
			14 ^{c,d}	
			19 ^{c,d}	
			19 ^{c,d}	
			20 ^{c,d}	

^aContact times were 1, 2, 4, and 8 weeks. There was no correlation with contact time within this range.

^bFeed solutions were centrifuged before contact. All others were centrifuged and then filtered (0.4- μ m Nuclepore polycarbonate membrane).

^cPlutonium-239 tracer was also present in the solution.

^dFeed solution was prepared by pH readjustment rather than drying.

TABLE II
DISTRIBUTION OF ACTIVITY IN CONTROL TUBES

Tracer	"Centrifugable" (%)	"Bottom" (%)	"Walls" (%)	Left in tube (%)	"Bottom" "Walls" ^a
²³⁷ Pu	50	10	37	3	0.9
²³⁷ Pu	1	11	76	12	0.5
²³⁷ Pu	6	25	62	7	1.4
²⁴¹ Am	2	44	53	<1	2.8
²⁴¹ Am	8	17	75	<1	0.8
²⁴¹ Am	17	34	49	<1	2.3
²⁴¹ Am	3	19	76	2	0.8
²⁴¹ Am	5	15	79	1	0.6
²⁴¹ Am	7	12	80	<1	0.5

^aRatio of activities per unit area.

per unit area. The ratios of these values are also presented in Table II. The relative activity of "bottom" and "walls" varied considerably, but the amounts per unit area were very roughly the same with the ratios scattering around 1. The activity on the control tubes appears to have been sorbed fairly evenly on the surface. Current results are consistent with earlier observations^{2,3} that sorption is dependent on available surface area, so when crushed argillite is present container sorption is negligible.

b. Filtering

The effects of filtering were investigated by passing tagged feed solutions and solutions after contact with argillite through 0.4- μ m polycarbonate membranes (Nuclepore). Both filtered and unfiltered feed solutions were used to contact the argillite samples and also for control samples. The data are presented in Table III. After contact most aqueous phases were centrifuged four times for 1 h at 12 000 rpm. Within an hour of the last centrifuging, some of these solutions

TABLE III
ACTIVITY REMOVED BY 0.4- μ m MEMBRANE^a (IN PERCENT)

	22°C					70°C				
	<u>ave.</u>	<u>σ(ave)</u>	<u>#^b</u>	<u>highest</u>	<u>lowest</u>	<u>ave.</u>	<u>σ(ave)</u>	<u>#^b</u>	<u>highest</u>	<u>lowest</u>
<u>²³⁷Pu</u>										
Before Contact	9.5		1			79		1		
After Contact-										
Filter 1	77	7	9	94	39 ^d	88	8	5	100	57
Filter 2 ^c	32	15	4	71	6					
Controls	58	5	2	63	54	36	31	2	67	5
<u>²⁴¹Am</u>										
Before Contact	42		1			64		1		
After Contact-										
Filter 1	77	2	17	89	61	98	1	8	99.6	93
Filter 2 ^c	22	7	2	29	15	21		1		
Controls	28	3	13	50	13	94	2	4	99	89

^aNuclepore polycarbonate membrane. All plastic parts.

^bNumber of measurements.

^cPercent of the activity remaining after the first filtering that is removed by the second filter.

^dA single value <0% was omitted as a physical impossibility. This was attributed to counting statistics.

were filtered; in a few cases they were filtered a second time within 1 h of the first. The fractions of the activity removed by filtering are shown in the table.

The Nuclepore filters, which have a uniform pore size of $0.4\ \mu\text{m}$, give a good particle size separation. Activity removed by the first filter may have been on fine dirt particles which remained with the aqueous phase during transfers between centrifugings, or true radiocolloids. The distinction between these two is probably not sharp at intermediate particle sizes. Centrifugable particle sizes will be discussed in the next section. Some solutions were aliquoted at different depths after centrifuging but without transfer or mixing, and the specific activity was observed to vary with depth. Therefore, we clearly have a gradation in particle sizes ranging from large rock particles firmly held at the bottom of a tube after centrifuging to extremely fine particles ("true" radiocolloids) near the surface of the liquid.

For sorption ratio measurements, solutions were transferred and mixed before being aliquoted for counting so that particles in the aqueous phase were representatively sampled. Aliquots were taken with large-tip, large-volume (several mL) plastic pipets. During the transfer there was certainly a possibility, regardless of the care taken, of resuspending fine particles from the surface of the solid phase, as well as of transferring surface films which sometimes exist with argillites. Filtering would have removed particles larger than $0.4\ \mu\text{m}$ regardless of the source.

The possibility of sorption on the polycarbonate filter membranes cannot be eliminated on the basis of the filtering data because sorbable species could be essentially removed by the first filter and not be available for sorption by the second. In fact, some additional activity usually was removed by filtering solutions a second time; this could have been due to sorption or to remaining particulates.

The filtering data for the controls which were centrifuged and then filtered show removal percentages which approach the values for the samples. Since the controls have no solid material, particles being removed are probably polymerized species which were not removed by centrifuging, or at least were resuspended during transfer. Significant amounts of particle sizes $>0.4\ \mu\text{m}$ are apparently present in the controls. Waters used in preparation of the original feeds had been pre-equilibrated with crushed argillite but had been passed through

0.45- μ m Millipore filter before use. Both filtered and non-filtered feeds were used, but the results for both samples and controls did not correlate with that variable.

There is considerable scatter among the sorption ratios calculated from either centrifuged or filtered solutions. There is also considerable scatter in the fraction of the activity removed by filtering. In general, the fraction removed by filtering was somewhat greater at the higher temperature. This was true for the feed solutions before contact, even though the water was not heated during the ≈ 24 h required for preparation of these solutions. The water for the 70°C feed had, of course, been pre-equilibrated with crushed rock at 70°C earlier. It should be emphasized that the observations with feed solutions were limited to two for each nuclide. Each of our sorption ratio determinations is made on a separate sample rather than by withdrawing aliquots of the aqueous phase at intervals, and thus even among replicates the relative amounts of centrifugable/noncentrifugable and filterable/nonfilterable species vary a great deal from sample to sample.

Additional experiments with membranes having smaller pore sizes are planned.

c. Centrifuging

It has been suggested by W. L. Polzer, LASL, that an estimate of the size of particles removed from solution by centrifuging can be made from a form of Stoke's law⁷ for solution viscosity:

$$r^2 = \frac{9 \eta \ln(R_2/R_1)}{8 \pi^2 t N^2 (d_p - d_m)},$$

where r is the radius of a particle with density d_p which will travel the distance between R_1 and R_2 (given as radii from the center of the centrifuge) in a time t at a centrifuge speed of N revolutions per second in a medium with a density d_m and a viscosity η . For $t = 1$ h, $N = 200$ rps, $d_m = 1$ g cm⁻³, $\eta = 0.010$ poise, and assuming $R_1 = 7$ cm (surface of aqueous phase), $R_2 = 11$ cm (bottom of tube), and a particle density of 4 g cm⁻³, particles with a diameter >0.02 μ m would essentially all be removed from the aqueous phase. However, the possible error in the particle density and the fact that tubes rest at an angle in our centrifuge could lead to a significant difference between the calculated and the actual diameter of particles removed. Filtering data suggest that particles >0.4 μ m in diameter were left in the aqueous phase after centrifuging (or were resuspended during solution transfer).

2. Measurement of Sorption Ratios - Results and Conclusions.

Batch measurements of the sorption behavior of ^{241}Am and ^{237}Pu on argillite under atmospheric conditions were started last quarter.⁶ Except for data analysis for the desorption of americium, the work has been completed. The results to date are given in Tables IV, V, and VI. Sorption ratios (R_d) were calculated from the ratio of the specific activities of solid and solution for each sample.

Several general conclusions can be made for the ^{237}Pu and ^{241}Am results: Very little americium or plutonium sorbs on the container walls when crushed argillite is present. Filtering a solution after contact helps remove any trace of remaining solid, which would otherwise have a large effect at these high R_d values since there is very little plutonium or americium activity in the final solution. On the other hand, filtering may well remove noncentrifugable, but filterable species that should in reality be considered as nonsorbed and therefore transportable in groundwater. The results from filtering some solutions twice are not conclusive but suggest that little or no sorption takes place on the polycarbonate filter membrane. Sorption ratios based on the specific activity of solutions which were centrifuged and then filtered are much higher than those for solutions which were only centrifuged. Sorption ratios in the first case tended to decrease with increasing temperature, but for filtered solutions the calculated ratios tended to increase with increasing temperature. This effect is probably related to the size of the particles which form at the different temperatures and which behave differently when centrifuged or filtered. Less activity is removed by centrifuging solutions contacted at 70°C but more activity is removed by the filter with these same solutions. There was no significant effect related to particle size or core sample within the range examined. Sorption ratios increased slowly with time up to eight weeks. Filtering the initial feed solutions appears to have had little effect except possibly with filtered effluent solutions which had been contacted at 70°C. At least for ^{237}Pu desorption, R_d values are approximately the same as sorption values within the rather large errors on the data.

Sorption ratios were determined by "sacrificing" a sample for each measurement; aliquots were not withdrawn from a given solution at different contact times. Considerable variation was observed among replicates, perhaps a factor of ≥ 10 in some cases. This cannot be entirely explained by the high sorption

TABLE IV
²³⁷Pu SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered ^a Feed ?	Sorp. Time (d)	Desorp. Time (d)	R _d (ml/g) ^b			pH	
						Unfilt.	Filt. 1	Filt. 2	Initial	Final
1	355-500	22	yes	13.7		c	37 000	63 000	8.47	8.49
					14.9	11 000	68 000	8.27	8.60	
			no	13.7			15 000		8.47	8.56
					14.9	3 800	41 000	8.27	8.64	
			yes	13.7			15 000		8.47	8.53
					14.9	1 400	25 000	8.27	8.65	
			no	13.7			19 000	19 000	8.47	8.57
					14.9	2 500	17 000	8.27	8.66	
			no	27.6			7 000		8.47	8.55
					14.9	3 300	41 000	8.27	8.58	
			yes	27.6			6 100		8.47	8.59
					14.9	2 300	27 000	8.27	8.61	
			yes	27.6			31 000	33 000	8.47	8.60
					14.9	3 200	4 800	8.27	8.64	
			no	55.7			69 000		8.47	8.64
					21.0	2 900	36 000	8.20	8.43	
			yes	55.7			2 100		8.47	8.64
					21.0	3 600	35 000	8.20	6.98	
			yes	56.7			41 000	46 000	8.47	8.56
					21.0	1 700	33 000	8.20	8.39	

TABLE IV (cont)
 ^{237}Pu SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (mm)	Temp. (°C)	Filtered ^a Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mL/g) ^b			pH	
						Unfilt.	Filt. 1	Filt. 2	Initial	Final
1	355-500	70	no	56.7		2 200	36 000		8.47	8.60
					21.0	2 700	30 000		8.20	8.54
			yes	56.7		33 000 ^c	27 000	47 000	8.47	8.56
					21.0	1 300	44 000		8.20	8.52
			no	13.7			100 000		8.26	8.50
					15.9	1 100	>100K		8.19	8.63
			yes	13.8			15 000		8.26	8.46
					15.9	3 000	40 000		8.19	8.64
			no	27.6		2 600	>100K		8.26	8.52
					15.9	1 700	>100K		8.19	8.42
			yes	27.6		2 500	6 000		8.26	8.55
					15.9	2 000	15 000		8.19	8.57
2	150-180	22	no	56.7		1 900	>100K		8.26	8.46
					21.1	1 300	67 000		8.25	8.42
			yes	56.7		1 800	18 000	>100K	8.26	
					21.1	2 200	>100K		8.25	8.39
			yes	13.7			11 000	38 000	8.47	8.54
					14.9	7 200	38 000		8.27	8.62
			yes	55.7		8 000	22 000		8.47	8.54
					21.0	19 000	>100K		8.20	8.52

TABLE IV (cont)
²³⁷Pu SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered ^a Feed ?	Sorp. Time (d)	Desorp. Time (d)	R _d (mL/g) ^b			pH	
						Unfil.	Filt. 1	Filt. 2	Initial	Final
2	355-500	22	yes	13.7			22 000		8.47	8.53
					15.9	8 100	28 000		8.27	8.43
			yes	55.7		11 000	>100K		8.47	8.65
					21.0	17 000	44 000		8.20	8.44
							3 600		8.26	8.40
3	355-500	70	yes	13.7					8.19	8.58
					15.9	1 700	33 000		8.26	8.33
			yes	56.7		1 500	23 000		8.25	8.32
					21.1	3 000	21 000			

^aThrough 0.4-μm polycarbonate membrane.

^bAll calculated R_d values >100 000 indicated as >100K.

^cCrushed rock was pre-equilibrated with groundwater for ≈ 276 d, as opposed to the usual 14 d.

TABLE V
 ^{241}Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. ($^{\circ}\text{C}$)	Filtered ^a Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mL/g)			pH	
						Unfilt.	Filt. 1	Filt. 2	Initial	Final
1	106-150	22	yes	6.8		b	57 000		8.65	8.57
					28.7				8.3	8.58
			yes	12.7		b	100 000		8.65	8.61
					28.7				8.3	8.60
			yes	27.6		91 000 ^b	320 000		8.65	8.66
					28.7				8.3	8.65
			yes	27.6		54 000 ^b	170 000		8.65	8.57
					28.7				8.3	8.59
			yes	54.7		99 000 ^b	420 000		8.65	8.21
					28.7				8.3	8.59
1	355-500	22	yes	12.7			62 000		8.65	8.69
					31.7				8.3	8.67
			yes	27.6		26 000 ^b	120 000		8.65	8.59
					28.7				8.3	8.59
			yes	27.6		54 000	180 000		8.65	8.63
					31.7				8.3	8.66
			yes	54.7		35 000 ^b	210 000		8.65	8.47
					28.7				8.3	8.53
			yes	54.7		28 000	250 000		8.65	8.66
					31.7				8.3	8.66

TABLE V (cont)
²⁴¹Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered ^a Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mL/g) ^b			pH	
						Unfil.	Filt. 1	Filt. 2	Initial	Final
1	355-500	70	yes	6.8			55 000		8.33	8.39
					32.9				8.3	8.69
			yes	12.7			67 000		8.33	8.44
					32.9				8.3	8.71
			yes	26.7		1 600	410 000		8.33	8.53
					32.9				8.3	8.64
			yes	55.7		7 300	810 000		8.33	8.02
					32.9				8.3	8.61
			yes	6.8		b	52 000		8.65	8.56
					28.7				8.3	8.56
2	355-500	22	yes	12.7		b	62 000		8.65	8.61
					31.7				8.3	8.65
			yes	12.7			85 000		8.65	8.68
					33.9				8.3	8.65
			no	13.0		12 000	83 000		8.65	8.78
					31.9				8.3	8.67
			yes	26.7		34 000	270 000		8.65	8.65
					33.9				8.3	8.63
			yes	27.6		12 000 ^b	77 000		8.65	8.63
					31.7				8.3	8.54

TABLE V (cont)
²⁴¹Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μ m)	Temp. (°C)	Filtered ^a Feed ?	Sorp. Time (d)	Desorp. Time (d)	R _d (mL/g)			pH	
						Unfil.	Filt. 1	Filt. 2	Initial	Final
2	355-500	70	yes	27.6		57 000 ^b	190 000		8.65	8.58
					31.7				8.3	8.67
			no	27.9		25 000	210 000		8.65	8.72
					33.9				8.3	8.63
			yes	29.7		70 000	280 000	330 000	8.65	8.72
					33.9				8.3	8.64
			yes	54.7		84 000 ^b	270 000		8.65	8.39
					31.7				8.3	8.67
			yes	54.7		140 000	560 000	790 000	8.85	8.36
					33.9				8.3	8.64
			no	54.9		150 000	620 000		8.65	8.68
					33.9				8.3	8.63
			yes	55.6		230 000	590 000		8.65	
					33.9				8.3	8.63
			no	12.7		3 300	130 000		8.33	8.50
					32.9				8.3	8.63
			yes	12.7			94 000		8.33	8.41
					32.9				8.3	8.66
			no	26.7		10 000	150 000		8.33	8.16
					32.9				8.3	8.45
			yes	26.7		1 700	160 000		8.33	8.48

TABLE V (cont)
²⁴¹Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered ^a Feed ?	Sorp. Time (d)	Desorp. Time (d)	R _d (mL/g)			pH	
						Unfil.	Filt. 1	Filt. 2	Initial	Final
					32.9				8.3	8.33
			no	55.7		15 000	370 000		8.33	7.88
					32.9				8.3	8.37
			yes	55.7		5 800	760 000		8.33	7.78
					32.9				8.3	8.39
			yes	55.7		3 700	300 000	380 000	8.33	7.73
					32.9				8.3	8.42

^aThrough 0.4-μm polycarbonate membrane.

^bCrushed rock was pre-equilibrated with groundwater for ≈ 276 d, as opposed to the usual 14 d.

TABLE VI
REPRESENTATIVE SORPTION RATIOS

		R_d (mL/g)	
		22°C	70°C
Pu sorption			
	unfiltered	4 200(1 100) ^a	2 100(220)
	filtered	37 000(12 000)	75 000(38 000)
Pu desorption			
	unfiltered	5 700(1 400)	2 000(250)
	filtered	34 000(3 700)	97 000(50 000)
Am sorption			
	unfiltered	75 000(15 000)	6 500(1 900)
	filtered	300 000(42 000)	450 000(120 000)

^aValues in parentheses are standard deviations of the means.

which results in very small amounts of activity remaining in the aqueous phase. Although count rates were frequently low with ²³⁷Pu samples, they were normally adequate with ²⁴¹Am. There may well be differences in the behavior of plutonium or americium even in supposedly identical solutions (same batch of traced feed) at pH $\approx$ 8 to 8.5, e.g., in the degree of polymerization and radiocolloid formation, and by hydrolysis resulting in variations in species (including charge) and particle size.

Grebenshchikova and Davydov⁸ reported that the charge on colloidal Pu(IV) species may be either positive (at low pH values) or negative (at high) and that the isoelectric pH, or point of zero charge, is in the pH region 8.0 to 8.5. Polzer and Miner⁹ presented a plot of effective charge (due to hydrolysis) on the americium species vs. pH of a 0.1 M LiClO₄ solution. Between pH 8.0 and 8.5 the average effective positive charge per atom of americium varies from $\approx$ 1.3 to essentially zero. Therefore, large variations in the behavior of both plutonium and americium could be expected in this pH range.

The method of handling the final samples, e.g., centrifuging or filtering, certainly influences the calculated R_d values, probably due to particle size effects. Species effects should not be as dependent on our method of handling but are probably truly variable.

Centrifuging the final solutions would appear to establish a lower limit to the sorption ratio since crushed rock particles and particulates remaining in solution would tend to lower the calculated R_d . Filtering the solutions would appear to provide a more accurate sorption ratio by removing rock particles and at least defining the particle size for a "solution." The 0.4- μm pore size may be a little large for particles which would be considered transportable in groundwater. The use of membranes with smaller pore sizes is being investigated; however, for large numbers of samples there is a practical limit to how fine a filter can be used. A useful definition of a "solution" may be one with no particles larger than 0.05- μm .

B. Sorption of Uranium(VI) on Argillite (B. P. Bayhurst)

1. Measurement Techniques. The measurement of the sorption behavior of uranium(VI) on argillite under atmospheric conditions involved geologic materials and groundwaters described in Ref. 3. The procedure used for these measurements at ambient temperature is described in Ref. 2 except that the amount of wash solution left with the solid was measured. The estimated uranium(VI) concentration was $\approx 4.3 \times 10^{-7}$ M. The pH measurements of the initial and final tagged solutions have not been completed.

2. Results and Conclusions. The results of the measurements of the uranium(VI) sorption ratios are presented in Tables VII and VIII. The fraction of ^{237}U in the control samples for the 1, 2, and 3 week contact times were 100%, 107%, and 98%, respectively.

As expected, uranium(VI) is poorly sorbed on argillite under the conditions used. This is presumably due to the rather high carbonate concentration in these waters, which would strongly complex the uranyl ion. For the smaller particle size ($<75 \mu\text{m}$) there is a decided increase in sorption ratio. This observation is not understood. However, one should note that the $<75\text{-}\mu\text{m}$ particle size material is not a sieve fraction. It was prepared by repeated grindings of the material until the entire sample passed through the sieve.

TABLE VII
U(VI) SORPTION RATIOS, ELEANA, CN1, AMBIENT TEMPERATURE

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mL/g) ^a
< 75	6.810		21.5(14)
		19.703	21.3(24)
	13.807		24.9(12)
		13.734	31.3(17)
	20.804		21.2(14)
106-150	6.810	7.905	34.1(18)
			2.1(72)
	13.807	19.703	- 2.0(509)
			1.7(87)
	20.804	13.734	- 4.6(213)
250-355	6.810		3.4(43)
		7.905	6.7(134)
	13.807	19.703	1.9(81)
			- 2.4(456)
	20.804	13.734	1.4(105)
355-500	6.810		- 5.9(180)
		7.905	3.1(48)
	13.807	19.703	7.4(140)
			1.9(82)
	20.804	13.734	- 2.5(444)
			1.2(121)
			- 6.6(183)
			3.1(51)
			7.7(150)

^aThe 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.

TABLE VIII
U(VI) SORPTION RATIOS, ELEANA, CN2-4 AMBIENT TEMPERATURE

Core and Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mL/g) ^a
CN2, <75	6.810		15.4(16)
		19.703	16.2(31)
	13.807		13.6(17)
		13.734	15.7(34)
	20.804		16.8(15)
CN2,355-500		7.905	22.8(25)
	6.810		5.5(31)
		19.703	7.0(100)
	13.807		5.1(31)
		13.734	5.0(123)
CN3, <75		20.804	7.1(25)
		7.905	14.5(50)
	6.810		95.5(8)
		19.703	84.2(11)
	13.807		94.9(8)
CN4, <75		13.734	86.9(11)
		20.804	107(8)
		7.905	108(10)
	6.810		83.2(9)
		19.703	72.6(11)
	13.807		74.4(9)
		13.734	69.0(11)
	20.804		77.2(9)
		7.905	89.6(11)

^aThe 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.

C. Variability of the Sorption Behavior of Tuff (E. N. Vine, S. J. DeVilliers, and K. Wolfsberg)

1. Measurement Techniques. Most of the measurements of the sorption behavior of various NTS tuff samples from hole UE25A#1 begun⁶ in the first quarter of FY-79 have been completed. After 20 and 40 d contact times, the aqueous and solid phases were separated by four centrifugings for 1 h at 16 000 rpm, each in a new polyethylene centrifuge tube. The pH of the solutions was recorded and an aliquot of the solid and solution phases was taken for counting. The remainder of the solid was then combined with fresh, untraced solution, and the desorption studies were begun.

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 our in-house gamma-ray analysis code RAYGUN. Each sample was counted at least two times and the results were simply averaged. The method of calculation of sorption ratios for cesium, strontium, and barium (from aqueous samples only) and for cerium and europium (from aqueous and solid samples, with cesium as internal monitor) has been previously described.^{2,3}

2. Results and Conclusions. The results of the measurements for 20 and 40 d sorption times at ambient temperature are given in Table IX for the 106-500 μm fractions and in Table X for the <106 μm fractions. Brief petrographic descriptions from LASL Group G-6 on the Yucca Mountain cores used are given in Table XI. Table XII gives the starting and final pH values of each solution. The desorption experiments and measurements with the "Barco Bond" and "Eco Bond" epoxys are still in progress.

It is evident from Table IX (YM-22 and 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 ratio and the particle sizes used in these studies. For example, the R_d values for YM-38, YM-48, and YM-49 for cesium, strontium, and barium decreased as the sieve fraction decreased, while the values for the remainder of the samples tended to increase with decreasing size. This may be the result of mineral fractionation in the sieving process. The cerium and europium do not seem to behave similarly. It is interesting that the YM-38, YM-48, and YM-49 samples have

TABLE IX
SORPTION RATIOS FOR YM TUFFS (106-500 μ m FRACTION)

Sample Number	Sorption Time (d) ^a	R_d (mL/g) ^b				
		Cs	Sr	Ba	Ce	Eu
YM-22	19.625	258(2.6)	47.5(2.3)	907(2.8)	1 390(3.9)	1 275(4.3)
		382(2.4)	47.5(2.8)	851(2.3)	1 250(5.3)	1 180(4.8)
	39.625	270(2.6)	55.2(2.2)	982(2.8)	1 670(4.8)	1 675(4.0)
		237(2.4)	48.5(2.8)	855(2.3)	1 127(4.8)	1 410(4.2)
YM-38	19.625	11 750(6.3)	18 150(4.3)	77 300(9.1)	896(8.9)	2 615(9.0)
	39.625	8 225(3.1)	10 195(2.5)	80 850(10)	642(4.4)	1 515(4.5)
YM-45	19.625	481(2.8)	167(2.3)	1 155(2.3)	1 008(5.3)	2 110(5.1)
	39.625	325(2.7)	175(2.4)	1 410(2.4)	711(5.2)	1 619(4.7)
YM-48	19.625	14 900(11)	1 800(2.5)	12 000(8.2)	871(16)	1 750(16)
	39.625	22 100(13)	2 495(3.2)	23 050(11)	1 855(19)	2 700(15)
YM-49	19.625	29 400(17)	2 685(2.8)	25 550(14)	557(25)	1 019(25)
		37 150(11)	2 575(2.5)	30 000(17)	491(17)	1 203(16)
	39.625	35 850(20)	3 790(3.7)	59 250(21)	814(25)	1 510(25)
		42 600(7.8)	3 825(2.4)	54 050(15)	351(12)	1 016(11)
YM-54	19.625	289(2.5)	87.5(2.5)	719(2.3)	178(4.7)	538(4.2)
	39.625	205(2.5)	80.5(2.6)	586(2.4)	106(4.4)	371(3.7)

^aThe two values given for a single sorption time represent results obtained by two different investigators.

^bThe 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.

TABLE X
SORPTION RATIOS FOR YM TUFFS (<106 μm FRACTION)

Sample Number	Sorption Time (d)	R_d (mL/g) ^a				
		Cs	Sr	Ba	Ce	Eu
YM-22	39.625	542(2.8)	66.2(2.2)	1 295(3.1)	1 555(5.2)	1 460(4.7)
YM-38	39.625	5 920(6.7)	7 375(5.0)	39 650(20)	954(9.6)	2 645(9.7)
YM-45	19.625	738(3.1)	217(2.3)	969(2.1)	539(5.0)	989(4.6)
	39.625	554(2.8)	218(2.3)	1 240(2.3)	669(5.0)	1 660(4.5)
YM-48	39.625	6 930(7.4)	1 200(2.5)	10 285(7.5)	2 945(11)	3 075(11)
YM-49	19.625	21 900(5.7)	1 520(2.1)	17 000(5.9)	568(8.8)	1 380(8.5)
	39.625	8 660(3.9)	1 680(2.2)	9 230(4.7)	529(6.5)	1 340(6.1)
YM-54	19.625	267(2.5)	95.0(2.5)	524(2.2)	113(4.7)	393(4.1)
	39.625	227(2.5)	97.1(2.5)	650(2.3)	174(4.6)	703(3.9)

^aThe 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.

TABLE XI
DESCRIPTION OF TUFF SAMPLES

<u>Sample</u>	<u>Member</u>	<u>Description</u>	<u>Comments</u>
YM-22	Topopah Springs	Densely welded, devitrified ash flow tuff; depth, 259 m.	Completely devitrified; mineralogically similar to microgranite.
YM-38	Tuffaceous beads of Calico Hills	Non-welded, devitrified bedded tuff; depth, 459 m.	Completely devitrified; some zeolite, clay(?)
YM-45	Prow Pass	Welded, devitrified ash flow tuff; depth, 588 m.	SiO ₂ and alkali feldspar
YM-48	Prow Pass	Slightly welded, vitric ash flow tuff; depth, 644 m.	Partly devitrified; zeolite (hevlantite?) in fractures.
YM-49	Prow Pass	Non-welded devitrified tuff; depth, 677 m.	Completely devitrified; zeolite in both vugs and matrix.
YM-54	Bullfrog	Welded, devitrified ash flow tuff; depth, 759 m.	No zeolite; SiO ₂ and alkali feldspar.

the highest sorption ratios observed in this study for cesium, strontium, and barium. Future detailed petrographic analyses hopefully will help explain these results.

Since the sorption ratios are high for some samples that are not highly zeolitized, alteration to zeolites or clays may not be a necessary condition for high sorption ratios of tuff. Devitrified tuffs also have high sorption ratios. YM-38 exhibits very good sorptive properties yet contains only a small amount of zeolites and no glass.

Previous work on sample JA-32 (Ref. 4) indicated that perhaps microgranite-like tuff samples would give generally low sorption ratios. This seems to be true for strontium, cesium, and barium which probably sorb by ion-exchange mechanisms. However, similar microgranite-like tuffs from Yucca Mountain exhibit considerably higher sorption ratios for cerium and europium than did JA-32. The relationship between mineralogy of tuff and sorption ratios will be examined in more detail when the detailed characterization of samples is completed.

TABLE XII
pH VALUES, AMBIENT TEMPERATURE

<u>Sample</u>	<u>Fraction (μm)</u>	<u>Sorption Time (d)</u>	<u>Final pH^a</u>	<u>Initial pH^a</u>
YM-22	106-500	19.625	8.36	8.28
			8.46	8.20
		39.625	8.37	8.28
			8.49	8.20
	<106	39.625	8.39	8.28
YM-38	106-500	19.625	8.45	8.17
	<106	39.625	8.44	8.17
		39.625	8.36	8.17
YM-45	106-500	19.625	8.15	8.13
		39.625	8.46	8.13
	<106	19.625	8.48	8.13
		39.625	8.46	8.13
YM-48	106-500	19.625	8.51	8.13
		39.625	8.34	8.13
	<106	39.625	8.37	8.13
YM-49	106-500	19.625	8.62	8.34
			8.46	8.14
		39.625	8.34	8.34
			8.46	8.14
	<106	19.625	8.49	8.14
		39.625	8.48	8.14
YM-54	106-500	19.625	8.47	8.12
		39.625	8.42	8.12
	<106	19.625	8.46	8.12
		39.625	8.48	8.12

^aThe two values given for a single sorption time represent results obtained by two different investigators.

D. Migration Rate Studies (W. R. Daniels, S. Maestas, and E. N. Vine)

1. Crushed Rock Columns. The migration of radionuclides through crushed rock columns (~35-106 μ m particle size) of NTS tuff and granite is being studied using the systems described in the last quarterly report.⁶ The columns are being eluted with the same rock-equilibrated waters previously described.^{2,4,5} Several 0.5 cm diameter by 2-4 cm long Bio-Rad Econo-Columns were run by gravity flow. In addition, a simple upflow column has been developed in order to maintain a known, steady flow rate. These columns are modifications of the Bio-Rad

columns, 0.5 cm diameter by ~2 cm long, which now have polyethylene bed supports and polypropylene luer fittings on each end. The flow rates are controlled by the Sage pumps previously described.⁶

The free column volumes (FCV) given in Table XIII were determined by use of both HTO and $^{131}\text{I}^-$. 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 by the three procedures and all measurements for a given column were averaged irrespective of the method used. For example, the FCV for YM-54 obtained with iodide (breakthrough) was 0.228 mL and with HTO was 0.223 mL. On YM-22, the iodide breakthrough method gave 0.262 mL and the iodide rinse gave 0.256 mL. Another YM-22 column (not yet used or included in Table XIV) gave 0.244 mL with HTO, 0.238 mL by the iodide breakthrough method, and 0.242 mL by the water rinse method. The values for the CS-5 and CS-7 granite samples were measured using ^{131}I only. The iodide breakthrough and rinse values for CS-5 were 0.266 mL and 0.254 mL, respectively, while the values for CS-7 were 0.242 mL and 0.248 mL, respectively.

A summary of the crushed rock column studies is given in Table XIII. The flow rates were determined by weighing the eluant 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 YM-54 columns began with flow rates of ≈ 0.08 and 0.07 mL/h and decreased to ≈ 0.04 and 0.03 mL/h, respectively. To eliminate such problems, we are now using the upward flow columns with syringe pumps. The activities were usually added to the column in a minimal volume (spike). YM-38 was chosen before batch R_d results on the Yucca Mountain cores were available. The sorption ratio for ^{85}Sr on YM-38 is now known (see above) to be $\approx 20\,000$. Therefore, it is not surprising that no ^{85}Sr has been eluted from the YM-38 column after 73 days. Another NTS core, JA-32 had previously been measured⁴ to have an $R_d \approx 50$ for ^{85}Sr . This material was therefore used for developing crushed column techniques. For comparison, three different JA-32 columns are being run: two gravity flow (one with a $15\ \mu\text{L}$ spike of activity, the other with continuous feed), and one upflow column.

When the data collection and processing is complete, information should be available for comparison with the batch studies performed earlier.

TABLE XIII
SUMMARY OF THE CRUSHED ROCK COLUMN STUDIES

Column Material	Type of flow ^a	Flow Rate (mL/d)	Free Column Volume (mL)	Activity Added	Spike Volume ^b (μL)	Duration of Measurement (d)	Activity in Eluent
Tuff							
YM-38	G	0.066	NA ^c	⁸⁵ Sr	15	73	0
JA-32	G	0.131	NA	⁸⁵ Sr	15	66	95% in 28 d
JA-32	G	0.131 ^d	0.291	⁸⁵ Sr	C	~ 0.5	50% in ≈ 1 h
JA-32	U	0.082	0.203	⁸⁵ Sr	10	17	84
YM-54	G	0.037	0.224	⁸⁵ Sr, ¹³⁷ Cs, ¹³³ Ba	10	27	NA
YM-54	G	0.033	0.338	⁸⁵ Sr, ¹³⁷ Cs, ¹³³ Ba	10	27	NA
YM-22	G	0.077	0.259	⁸⁵ Sr, ¹³⁷ Cs, ¹³³ Ba	10	27	NA
Granite							
CS-5	U	0.040	0.260	⁸⁵ Sr, ¹³⁷ Cs, ¹³³ Ba	10	17	NA
CS-7	U	0.044	0.242	⁸⁵ Sr, ¹³⁷ Cs, ¹³³ Ba	10	17	NA

^aG means gravity flow; U means an upflow column was used.

^bC means that the activity was fed continuously.

^cNA means that the results are not yet available.

^dDelivery rate.

2. Fracture Flow Studies. The apparatus described in the last quarterly report⁶ is being used for preliminary studies of cracked-granite-core columns. Flow rates of three 1.6 cm high by 2.54 cm diameter granite cores which were thought to have natural cracks were checked for periods of approximately one week. Confining pressures of 100 psi and driving pressures of 800 psi gave flow rates of approximately 0.05, 0.02, and zero mL/h. The elution behavior of one cracked core is being studied using ⁸⁵Sr tracer. The ⁸⁵Sr tracer was dried and then dissolved in pre-equilibrated synthetic water as for the batch R_d studies.² A total of 100 µL of the traced feed was placed in a clean, dry frit on top of the rock. Water from the same batch of synthetic groundwater, which had been filtered through a 0.4-µm polycarbonate membrane, is being passed through the rock at a flow rate of 0.0035 mL/h by using a confining pressure of 1000 psi and a driving pressure of 200 psi. Approximately 0.5% of the total activity was removed from the column gradually during the first 18 days of flow. The water now being removed from the column contains essentially no ⁸⁵Sr activity. The experiment will be continued to determine a elution behavior for comparison with batch results obtained earlier.

E. Measurements Under Controlled Atmosphere Conditions (B. R. Erdal)

All of the equipment needed to perform sorption measurements under reduced oxygen conditions or conditions having a specified atmosphere has been received and the installation of the various components is complete. 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 of LASL). The nitrogen gas is cleaned by a Vacuum/Atmospheres Co. gas purification system (model MO-40-2-H). The system works very reliably and the oxygen concentration is less than 0.5 ppm. Appreciable effort was expended in attaining this concentration. The preparation of rock materials and rock equilibrated waters is proceeding.

F. Microautoradiography (J. L. Thompson, E. N. Vine)

During our microautoradiographic studies it was observed⁵ that ²⁴¹Am is removed from solution more rapidly in droplets placed on rock thin-sections when these droplets are exposed to the atmosphere than when the droplets are protected from the atmosphere. Such observations suggest that the chemical properties of ²⁴¹Am at tracer concentrations may be strongly influenced by parameters other than those normally controlled (e.g., solution pH, ionic composition). The following

brief experiment was carried out in an attempt to discern whether the composition of the atmosphere surrounding the ^{241}Am solution would strongly affect the ^{241}Am solubility.

Americium-241 solution was available in a dilute HCl solution at concentrations of about 10^{-6} M and about 10^6 dpm/mL. Small quantities (100 μL) of this solution were taken to dryness in polypropylene tubes over a steam bath, and then redissolved in waters representative of various natural groundwaters: alluvial water from RNM-2, Jackass Flats water⁴ from well J-13, unfiltered Climax Stock water (hole U12S at the NTS), and synthetic Eleana groundwater³.

Portions of these four solutions were then placed in small polyethylene cups and stored in a glass container with an atmosphere highly enriched with carbon dioxide, oxygen, or nitrogen. Aliquots of these solutions were withdrawn periodically in order to monitor the activity level of the ^{241}Am . These aliquots were dried and alpha counted using a methane-flow proportional counter. Over the 2.5 h duration of the sampling period, the activity levels did not show changes which could be attributed to the composition of the atmosphere. This is in contrast to the previously mentioned observation that there appears to be an atmospheric effect when the solution is contacting a rock thin-section. Hence, the difference may be due to the different surfaces with which the solution is in contact. It is apparent that more experiments of this type should be performed, and activity levels monitored for periods of days or weeks, in order to better determine whether the composition of the atmosphere does indeed affect the ^{241}Am species chemistry.

G. Batch Sorption Measurements With Technetium (E. N. Vine)

The sorption behavior of three Yucca Mountain cores YM-22, YM-48, and YM-49 are being studied using technetium to look for the variability of the R_d values with concentration of technetium. Four concentrations of technetium are being 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 absorbed on the glass frit of a Millipore filter bed. Preparation of pre-equilibrated waters and samples was done as previously described⁶ 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 above). Samples from the

sorption experiments are now being counted and the desorption experiments are in progress.

H. Materials Characterization (R. D. Aguilar, B. P. Bayhurst, I. Binder, and S. J. DeVilliers).

1. Surface Area and Cation Exchange Capacity Measurements. The ethylene glycol surface area (SA) and cation exchange (CEC) capacities of the NTS Yucca Mountain tuff samples described in the last quarterly report⁶ were measured. The procedures described in Ref. 2 were used, and the results are given in Table XIV. The 106-500 μm particle size material was used.

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.⁶ The water samples currently being analysed are 1) the initial synthetic Climax Stock granite water², 2) the initial synthetic Eleana argillite water,³ 3) a sample of the seep water from the Climax Stock formation at the NTS, 4) the YM-49 rock equilibrated water, and 5) the YM-22 rock-equilibrated water. The results for the YM-49 rock equilibrated water are given in Table XV. The counting and data reduction for the remaining materials is in progress.

The instrumental neutron activation analysis method is also being utilized for analysis of several solid materials. Initially, four NTS Yucca Mountain tuffs (YM-22, YM-45, YM-48, and YM-49) are being used. The same counting procedures as used for the water samples are being utilized. Counting and data reduction are in progress.

3. X-ray Fluorescence Analyses. Our in-house capability for chemical analysis via tube excited X-ray fluorescence spectrometry has been used for samples utilized in previous studies^{2,3} This technique is relatively simple and gives results for most major and semi-major elements. In our analysis system, either a tungsten or molybdenum target can be chosen as the target for X-ray production by high-voltage electrons. The X-rays from the sample are detected with a Si(Li) detector which is sensitive down to the 1 keV line of sodium. The linear data from the detector is stored in a multichannel analyzer from where it is read into a small computer (PDP-11/04) at the termination of a run. Data reduction programs to perform the analytical calculations have been written locally (T. Bornhorst) for both qualitative and quantitative analysis. The

system is calibrated using samples having compositions similar to the unknowns. The results are given in Tables XVI-XVIII.

It is interesting that the total iron concentration in these materials does not change with the fraction used. One explanation for the observation^{2,3} that Tc(VII) sorbed on the finer particle size material was that iron was concentrated in these fractions. This could still be the case if the fine fractions were enriched in the non-Fe(III) materials. This could happen if a clay fraction had some preference for Fe(II), and this clay was concentrated in the finer sieve fraction.

TABLE XIV
SURFACE AREAS AND CATION EXCHANGE CAPACITIES
NTS YUCCA MOUNTAIN TUFF

<u>Core</u>	<u>Surface Area (m²/g)</u>	<u>Cation Exchange Capacity^a (meq/100g)</u>	
		<u>Cs</u>	<u>Sr</u>
YM-22	22	2	3
YM-38	103	109	54
YM-45	43	6	6
YM-48	19	51	21
YM-49		107	27
YM-54		4	4

^aThe cation exchange values are not final since the exact cesium and strontium concentrations have not been determined.

TABLE XV
NEUTRON ACTIVATION ANALYSIS, YM-49 TUFF WATER^a

<u>Induced Activity</u>	<u>mg element ℓ Water</u>	<u>Molarity</u>
²⁴ Na	40.3	1.8×10^{-3}
⁴⁷ Ca	19.0	4.7×10^{-4}
⁴⁶ Sc	0.000018	4.0×10^{-10}
⁵⁹ Fe	0.067	1.2×10^{-6}
⁶⁰ Co	0.000051	8.6×10^{-10}
⁶⁵ Zn	0.0067	1.0×10^{-7}
⁷⁶ As	0.0093	1.2×10^{-7}
⁷⁵ Se	0.00048	6.1×10^{-9}
⁸² Br	0.080	1.0×10^{-6}
⁸⁶ Rb	0.0085	1.0×10^{-7}
⁸⁵ Sr	0.056	6.4×10^{-7}
⁹⁹ Mo	0.023	2.4×10^{-7}
¹⁰³ Ru	0.00038	3.8×10^{-9}
¹²⁴ Sb	0.0011	9.0×10^{-9}
¹³⁴ Cs	0.00029	2.2×10^{-9}
¹³¹ Ba	0.011	8.0×10^{-8}
¹⁴⁰ La	0.00027	1.9×10^{-9}
¹⁴¹ Ce	0.0013	9.3×10^{-9}
¹⁴⁷ Nd	0.0012	8.3×10^{-9}
¹⁵³ Sm	0.00063	4.2×10^{-9}
¹⁵² Eu	0.000012	7.9×10^{-11}
¹⁶⁹ Yb	0.000025	1.4×10^{-10}
¹⁸¹ Hf	0.000038	2.1×10^{-10}
¹⁹² Ir	0.00000056	2.9×10^{-12}
²³⁹ Np	0.0085 ^b	3.5×10^{-8} b

^aRock equilibrated water.

^bConcentration of uranium.

TABLE XVI
CS-5 GRANITE X-RAY FLUORESCENCE ANALYSES ($\mu\text{g/g}$)^a

Element	Fraction (μm)			
	106-150	250-355	500-850 ^b	
K ₂ O ^c	4.63	4.23	4.67	4.63
CaO ^c	2.98	3.20	3.33	3.32
TiO ₂ ^c	0.50	0.40	0.44	0.43
V	58(9)	51(8)	46(7)	48(8)
Cr	19(11)	14(9)	11(7)	11(6)
Mn	495(7)	379(6)	403(6)	378(6)
Fe ₂ O ₃ ^c	3.72	2.96	2.56	2.56
Ni	16(5)	10(4)	10(4)	9(3)
Cu	31(6)	24(5)	30(6)	27(6)
Zn	78(9)	75(9)	74(9)	73(9)
Ga	< 25	< 25	< 25	< 25
Ge	1.29(0.06)	1.27(0.06)	1.28(0.06)	1.27(0.06)
As	< 100	< 100	< 100	< 100
Se	0.05(0.02)	0.04(0.02)	0.05(0.02)	0.04(0.02)
Pb	16(8)	16(8)	< 16	18(9)
Rb	193(6)	169(5)	179(6)	181(6)
Sr	564(8)	626(9)	660(9)	657(9)
Y	25(9)	22(8)	24(9)	24(8)
Zr	196(20)	186(19)	178(18)	177(18)
Ba	1 181(118)	1 083(108)	1 103(110)	1 112(111)

^aThe numbers in parentheses are the errors given in $\mu\text{g/g}$. If no error is quoted then the error is less than 0.1%.

^bDuplicate analyses are reported.

^cThe results are given in percent.

TABLE XVII
CS-7 GRANITE X-RAY FLUORESCENCE ANALYSES ($\mu\text{g/g}$)^a

Element	Fraction (μm)				
	106-150 ^b		250-355 ^b		500-850
K ₂ O ^c	3.46	3.42	3.25	3.25	3.93
CaO ^c	3.23	3.20	3.29	3.29	3.14
TiO ₂ ^c	0.35	0.35	0.29	0.29	0.43
V	46(7)	45(7)	42(7)	42(7)	45(7)
Cr	18(11)	19(11)	14(8)	13(8)	13(8)
Mn	358(5)	347(5)	401(6)	369(6)	659(10)
Fe ₂ O ₃ ^c	2.82	2.82	2.33	2.33	2.88
Ni	11(4)	12(4)	10(3)	9(3)	9(3)
Cu	18(4)	21(4)	19(4)	16(3)	18(4)
Zn	76(9)	76(9)	75(9)	75(9)	78(9)
Ga	< 25	< 25	< 25	< 25	< 25
Ge	1.29(0.06)	1.30(0.06)	1.29(0.06)	1.28(0.06)	1.28(0.06)
As	< 100	< 100	< 100	< 100	< 100
Se	0.04(0.02)	0.05(0.02)	0.04(0.02)	0.05(0.02)	0.04(0.02)
Pb	< 16	19(9)	< 16	< 16	< 16
Rb	126(4)	124(4)	124(4)	122(4)	167(5)
Sr	547(8)	543(8)	585(8)	587(8)	601(8)
Y	24(8)	24(8)	20(7)	20(7)	23(8)
Zr	184(18)	184(18)	179(18)	180(18)	188(19)
Ba	690(69)	664(66)	770(77)	735(74)	860(86)

^aThe numbers in parentheses are the errors given in $\mu\text{g/g}$. If no error is present then the error is less than 0.1%.

^bDuplicate analyses are reported.

^cThe results are given in percent.

TABLE XVIII
ARGILLITE X-RAY FLUORESCENCE ANALYSES ($\mu\text{g/g}$)

Element	CN1		CN2	
	Fraction (μm)		Fraction (μm)	
	150-180	355-500	150-180	355-500
K_2O^b	1.11	1.12	1.79	1.78
CaO^b	0.99	0.94	0.85	0.84
TiO_2^b	1.31	1.30	1.20	1.18
V	66(11)	58(9)	52(8)	51(8)
Cr	51(31)	47(28)	44(27)	44(27)
Mn	1 236(19)	1 153(17)	507(8)	504(8)
Fe_2O_3^b	7.09	6.76	5.94	5.90
Ni	29(10)	30(11)	29(10)	29(10)
Cu	45(9)	45(9)	47(9)	42(8)
Zn	94(11)	89(11)	96(12)	93(11)
Ga	< 25	< 25	< 25	< 25
Ge	1.33(0.06)	1.31(0.06)	1.26(0.06)	1.27(0.06)
As	< 100	< 100	< 100	< 100
Se	0.06(0.03)	0.05(0.03)	0.04(0.02)	0.04(0.02)
Pb	72(7)	60(6)	44(22)	51(5)
Rb	57(2)	59(2)	103(6)	124(4)
Sr	153(2)	154(2)	224(3)	222(3)
Y	36(12)	38(13)	35(12)	35(12)
Zr	272(27)	294(29)	176(18)	176(18)
Ba	< 25	32(3)	< 25	< 25

^aThe numbers in parentheses are the errors given in $\mu\text{g/g}$. If no error is quoted then the error is less than 0.1%.

^bThe results are given in percent.

IV. ACTIVITIES PLANNED FOR NEXT QUARTER

The following is a brief outline of some of the activities planned for the period April 1 - June 30, 1979.

A. Batch sorption measurements

1. Start some controlled atmosphere measurements for technetium, plutonium, and americium
2. Perform studies in salt systems as needed

B. Microautoradiography

1. Start neptunium sorption studies on petrographic thin-sections
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. Continue studies on granite
 - b. Continue studies on tuff
2. Whole cores
 - a. Continue fracture flow (granite) studies
 - b. Start porous flow (tuff) studies
 - c. Start modification of high-pressure equipment to use Teflon-lined components wherever possible

D. Materials characterization

1. Reactant solutions
 - a. Continue neutron activation analyses for the trace element concentration in the starting solutions
 - b. Start emission spectrographic analysis for beginning and ending concentrations of major cations
2. Solid phases
 - a. Continue analyses by X-ray fluorescence
 - b. Continue analyses for trace elements by neutron activation
 - c. Do the mineralogy/petrology on new materials as they are received (LASL Group G-6)

V. PROBLEMS

The major problem concerning the LASL portion of the WISAP, Task 4, program for FY-79 is the fact that the capital equipment funds have not been released. Due to the rather long lead-times for purchase of such equipment, there is some doubt that the necessary items can be obtained before serious impact on the milestones is observed.

MEETINGS

1. B. R. Erdal, NEA Ad Hoc Data Group meeting on "Feasibility of International Data Bank for Long-term Safety Assessments of Nuclear Waste Isolation in Geologic Formations," Battelle Pacific Northwest Laboratory, Richland, WA, February 14-15, 1979.
2. B. R. Erdal, Waste Management 1979 meeting on "The State of Waste Disposal Technology and the Social and Political Implications," University of Arizona, Tucson, AZ, February 26 - March 1, 1979.

VISITORS

1. Prof. Ivars Neretnieks, Royal Institute of Technology, Stockholm, Sweden (University of California, Berkeley); Feb. 6-7, 1979.
2. Prof. Jan Rydberg, Chalmers Institute of Technology, Göteborg, Sweden; March 30, 1979.

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APPENDIX A

CONTROLLED SAMPLE PROGRAM USING ^{85}Sr AND ^{137}Cs

B. R. Erdal, P. Q. Oliver, and R. D. Aguilar

I. INTRODUCTION

The main objectives of the WISAP Task 4 Controlled Sample Program are:

1) to ascertain whether different experimenters obtain the "same" results using common rocks, standard solutions and a dictated experimental design and 2) to ascertain the comparability of results obtained by individual laboratories using different experimental methodologies. In Objective Two Studies we will be investigating R_d or nuclide migration dependencies on experimental methodologies in hopes of formulating a standard " R_d " method or deriving calibration numbers

to convert R_d numbers derived from one method to R_d values applicable to another method. Peripheral objectives include generation of a R_d data bank on common rock-groundwater systems.

The rock materials to be used in this program were distributed by Battelle (PNL) and a standard procedure was dictated for the first phase of the work.

II. PREPARATION OF "SYNTHETIC" LIMESTONE AND BASALT WATERS

- 1) The appropriate quantities of the compounds (Table A-I) required for the specified composition of the water were weighed out using either analytical or electronic balances.
- 2) The weighed materials were transferred to a 2-ℓ beaker and sufficient deionized water was added in batches to dissolve the majority of the solids after stirring for ~0.5 h each time.
- 3) The solution (or suspension) was transferred to a pyrex bottle after measuring the volume with a graduated cylinder. Sufficient deionized water was added to give the required volume (Table A-I).
- 4) The solution was slowly sparged, while stirring with a Teflon-covered magnetic bar, with carbon dioxide through a medium-porosity gas dispersion tube for up to 4 d in order to assure complete dissolution (determined visually).
- 5) The solution was transferred to a polyethylene bottle, and was then sparged with nitrogen gas, using the same procedure as before, until a $\text{pH} \approx 8$ was reached (required a few hours).
- 6) The solutions were stirred for at least a week with daily observation of the pH; the pH seemed to stabilize at about 8.1.
- 7) The pH values were adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.
- 8) The concentrations of the major cations in these waters were measured (Table A-II) via atomic absorption spectrophotometry relative to diluted samples of standards supplied by Alfa Products (Ventron) (Table A-II). Lanthanum (1000 $\mu\text{g}/\text{mL}$) was used as a deionizer. In addition, aliquots of these solutions have been sent to the U. S. Geological Survey Central Laboratory (Denver) for analysis of Ca, Mg, K, Na, Sr, Ba, Fe, CO_3 , HCO_3 , Si, Cl, F, and SO_4 .

III. PREPARATION OF "SYNTHETIC" BRINE

- 1) Steps 1-4 of the procedure used for the limestone and basalt waters were followed (see Table A-I for the amounts).
- 2) The pH of the entire final solution was then adjusted, while stirring, with 0.1 M HCl or 0.1 M NaOH to a value of 6.5.
- 3) The pH of the stirred solution was monitored for a week, with adjustment to a pH of 6.5 with 0.1 M HCl or 0.1 M NaOH.

IV. PREPARATION OF THE "SPIKED" WATERS

- 1) The appropriate volumes (1 $\mu\text{L}/\text{mL}$ of final solution) of ^{85}Sr ($\sim 21 \mu\text{Ci}/\text{mL}$, 0.3 Ci/g Sr) and ^{137}Cs ($\sim 34 \mu\text{Ci}/\text{mL}$, carrier free) were placed in a rinsed and dried polyethylene bottle, and then heated on a steam bath overnight to dryness.
- 2) The appropriate volume of the specified water was added to the polyethylene bottle, and the solution was stirred with a Teflon covered magnetic bar.
- 3) The pH of the stirred solution was monitored daily for 4 d. The pH was adjusted daily, as needed, to the required value with 0.01 M HCl or 0.01 M NaOH (less than 0.5 mL total volume was used).
- 4) The solution was filtered through 0.45- μm Millipore HA filter paper with no prefilter.
- 5) 10.0 mL aliquot of the filtered solution was removed for counting and for measurement of the density of the solution (Table A-III).

V. MEASUREMENT OF THE SORPTION RATIO

- 1) Triplicate 1.0 g samples of the appropriate material as received were weighed out with an analytical balance, and placed into deionized-water-washed, dried, and tared Nalgene 40-mL polyethylene tubes.
- 2) A 15.0 mL aliquot of the appropriate water having the specified pH (Table A-III) were added to the samples, and the tubes were capped with size 13X Caplugs. The contents were thoroughly mixed and the tubes were placed in a Lab-Line Junior Orbit Shaker operating at 200 rpm, and shaken for about 48 h.
- 3) After removal of the Caplug, each sample was centrifuged at 16 000 rpm for 1 h in a Dupont SS-3 Superspeed Centrifuge. The supernatant solution was decanted and discarded.
- 4) Steps 2-3 were repeated one time.

TABLE A-I
COMPOSITION OF "SYNTHETIC" WATERS

	<u>GW#1 Limestone (g/8 ℓ)</u>	<u>GW#2 Basalt (g/8 ℓ)</u>	<u>GW#3 Brine (g/4 ℓ)</u>
Ca(OH) ₂	0.7400		
MgSO ₄	0.1440	0.0384	
NaCl	0.0464		1148.
KCl	0.0064	0.1183	0.2165
NaHCO ₃		0.6384	0.0568
Na ₂ SO ₄		0.1988	24.8
CaSO ₄ ·2H ₂ O		0.0482	
CaCl ₂ ·2H ₂ O		0.1520	13.2
KF		0.0186	
Na ₂ B ₄ O ₇ ·10H ₂ O			0.0638
NaBr			2.080
MgCl ₂ ·6H ₂ O			0.3421
SrCl ₂ ·6H ₂ O			0.0186
CsCl			0.0515

TABLE A-II
PRELIMINARY ANALYSIS OF WATERS
(mg/ml)

	<u>Limestone</u>	<u>Basalt</u>
Na	2.23	28.2
K	0.51	9.10
Mg	3.81	0.96
Ca	48.9	6.69

TABLE A-III
GENERAL EXPERIMENTAL PARAMETERS

	Experiment Number ^a			
	1	2	3	4
pH before first wash	8.22	6.52	7.96	6.52
Length of first wash (d)	1.97	~ 2.	2.08	~ 2.
pH before second wash	8.18	6.82	7.92	6.82
Length of second wash (d)	2.16	~ 2.	2.05	~ 2.
pH before measurement	8.33	6.55	7.96	6.55
Density of spiked water	0.993	1.179	0.993	1.179
Length of equilibration (d)	6.65	6.74	7.92	6.97
Activity (dpm) ⁸⁵ Sr in 10.0 mL	25 025	83 700	24 703	83 700
Activity (dpm) ¹³⁷ Cs in 10.0 mL	190 100	662 950	191 930	662 950

^aExperiment number 1 (oolitic limestone with GW#1); experiment number 2 (oolitic limestone with GW#3); experiment number 3 (basalt with GW#2); experiment number 4 (basalt with GW#3).

- 5) The tube and its contents were weighed, 15.0 mL of the appropriate spiked water of known pH (Table A-III) was added, the tube was capped, mixed, and shaken for about 7 d. Control samples containing spiked water only were also prepared in washed and dried Nalgene tubes.
- 6) After removal of the Caplug, each sample was centrifuged at 16 000 rpm for 1 h, and the supernatant solution was decanted into a washed and dried Nalgene 40-mL polyethylene tube.
- 7) Step 6 was repeated three times.
- 8) A 10.0 mL aliquot of the solution was removed for counting and the pH was measured on the residual solution. The results are given in Table A-IV.

VI. GAMMA-SPECTRAL ANALYSES

- 1) The aliquots removed for counting were placed in Packard 25 mL scintillation polyvials containing 2 mL of 6 M HCl.
- 2) The samples were counted on a Ge(Li) detector (11% relative to NaI). A minimum of two 4096 channel spectra were taken for each sample using a gain of ~0.5 keV/channel.

TABLE A-IV
EXPERIMENTAL PARAMETERS FOR EACH SAMPLE

Expt. No. ^a	Sample No. ^b	c/m ⁸⁵ Sr	c/m ¹³⁷ Cs	W (g)	g _r (g)	Final pH
1	1	20 925	26 965	1.01998	1.39	8.41
	2	20 920	25 740	1.00806	1.70	8.48
	3	20 570	28 510	1.01096	1.64	8.61
	C	25 470	189 000			8.88
2	1	79 465	631 800	1.02068	0.94	6.74
	2	76 740	612 600	1.02090	1.41	6.96
	3	77 475	621 400	1.03545	1.31	6.82
	C	82 720	658 400			6.75
3	1	3 793	10 090	1.00126	0.87	8.34
	2	3 847	10 414	0.99850	0.74	8.35
	3	3 874	10 246	0.99956	0.81	8.37
	C	25 360	191 100			8.38
4	1	81 030	621 300	1.02595	0.60	6.69
	2	78 700	605 900	1.02144	0.68	6.83
	3	79 730	613 200	1.02591	0.75	6.93
	C	83 995	664 750			6.84

^aSee the footnote on Table A-III.

^bC stands for the control sample.

- 3) The multichannel analyzer was connected to a PDP-9 minicomputer where the spectra were analyzed on-line at the end of each measurement. The RAYGUN computer code was used for the calculations. This code finds the peaks in the spectrum, determines their energies and areas, interprets the intensities, after correction for the detector efficiency, as to the radionuclide disintegration rate, and corrects the results to a given time.

VII. CALCULATIONS AND RESULTS

The following equation was used to calculate the sorption ratios (R_d) shown in Table A-V:

$$R_d = \frac{R \cdot A_f - A_t}{A_t} \cdot \frac{V}{W} \quad (A-1)$$

where

A_f = the activity per mL of a given radionuclide in the spiked water (feed added to the sample,

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

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

V = the total final volume of supernatant solution, and

R = the dilution factor to take the residual solution from the washed into account.

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 pre-washed, and the measured density (ρ_r) of the solutions used:

$$V_r = g_r / \rho_r .$$

Therefore, for these measurements (15.0 mL spike volume)

$$V = 15.0 + V_r$$

and

$$R = 15.0 / (15.0 + V_r) .$$

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

The standard deviation quoted for each measurement (Table A-V) 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.

TABLE A-V
SORPTION RATIOS

Expt. No. ^a	Sample No.	R_d (^{85}Sr)	R_d (^{137}Cs)
1	1	1.51 ± 0.40	88.0 ± 2.3
	2	1.22 ± 0.41	93.3 ± 2.5
	3	1.58 ± 0.41	82.2 ± 2.2
	Average ^b	1.44 ± 0.23	87.8 ± 1.3
2	1	0.00 ± 0.34	-0.057 ± 0.287
	2	0.10 ± 0.34	-0.194 ± 0.290
	3	0.09 ± 0.34	-0.104 ± 0.285
	Average ^b	0.08 ± 0.20	-0.118 ± 0.166
3	1	81.7 ± 2.4	269.1 ± 6.3
	2	80.7 ± 2.4	261.1 ± 5.9
	3	79.9 ± 2.5	265.3 ± 6.2
	Average ^b	80.8 ± 1.4	265.2 ± 3.5
4	1	-0.014 ± 0.325	0.484 ± 0.287
	2	0.368 ± 0.343	0.818 ± 0.296
	3	0.108 ± 0.337	0.566 ± 0.291
	Average ^b	0.154 ± 0.193	0.623 ± 0.168

^aSee the footnote on Table III.

^bThe uncertainty quoted for the simple average is that calculated assuming independence of each of the individual measurements.

TABLE A-VI
PERCENTAGE IN SUPERNATANT SOLUTION

Expt. No. ^a	Sample No. ^b	f (^{85}Sr)	f (^{137}Cs)
1	1	91.44	15.45
	2	93.16	15.09
	3	91.27	16.65
	C	101.8	99.42
2	1	104.5	100.4
	2	99.99	101.2
	3	98.99	100.7
	C	99.42	99.31
3	1	16.25	5.56
	2	16.35	5.70
	3	16.54	5.63
	C	102.7	99.57
4	1	100.1	96.90
	2	97.64	94.91
	3	99.30	96.42
	C	100.4	100.3

^aSee the footnote on Table III.

^bC stands for the control sample.

For completeness, the percentage of the activity (f) remaining in solution is given in Table A-VI where

$$f = 100(A_t)/A_f .$$

The data for the control samples is also included in Table A-VI.

APPENDIX B
CONTROLLED SAMPLE PROGRAM USING ^{237}Pu
F. O. Lawrence

I. PREPARATION OF MATERIALS

The crushed rock and "synthetic" waters prepared by the procedures described in Appendix A were used in these measurements.

Tracer preparation was governed by the problems encountered in controlling plutonium at neutral and higher pH values. One vial of the ^{237}Pu tracer produced at Argonne National Laboratory under contract with Battelle (PNL) was diluted with 0.5 ml 3 N HCl, and a number of aliquots were taken and standards made. Ten microliters of the tracer solution was pipetted into Oak Ridge (OR) type centrifuge tubes and allowed to air dry. When the tracers were dry, 17 ml of the ground water solution was added to the tracers (2×10^{-13} M), and the solutions were shaken for 3 d to equilibrate. The pH of each traced feed solution was checked, and adjusted if necessary on each of the three days and again just before filtering. The traced feed solutions were each filtered through a 0.5- μm Millipore filter before use.

The appropriate 1-g crushed rock samples were equilibrated two different times with untaged water for 48 h each. The preparation of the crushed rock samples and their equilibrating cold washes was accomplished by centrifugation for 1 h at 12 000 rpm (32 000 g), followed by decantation of the supernatant solution. The tube was then reweighed in order to obtain the weight of the residual wash solution left with sample.

II. MEASUREMENT OF THE SORPTION RATIO

The traced feed solutions and the crushed rock sample were contacted for 7 d, as were the four control samples. At the end of the seven day period, the effluent solutions were separated from the crushed rock by centrifugation for 1 h at 12 000 rpm, four times. Transfer of the supernatant solution was accomplished by decantation the first three times. The final supernatant solution removal was done with a plastic transfer pipette. A 5.0 ml aliquot was taken with an automatic pipettor. The sample was put into a one-ounce polyethylene screw-capped bottle and counted with several different NaI(Tl) detectors.

Other related samples were also counted on these detectors. Where it was impossible or was not feasible to transfer a sample (the crushed rock sample, or the empty tube) a NaI well counter was used. A large number of standards were made to be used as references for the samples. (See Table B-I)

The experimental parameters for the four types of measurements described in Appendix A are given in Tables B-II and B-III.

III. GAMMA-SPECTRAL ANALYSIS

An aliquot of the effluent solution, washes of the tracer preparation tube, filter flask washes, the filter which was used to filter the feed solution, and an aliquot of the feed solution, where available, were all counted in the screw-capped bottles on the several NaI scintillation counters. The filters were counted dry and in a 5-ml solution of 3 N HCl. The tubes which had seen

TABLE B-I
DESCRIPTION OF THE ^{237}Pu STANDARDS

Standard	Description	Use
5	10 μl of stock solution in 5 ml 3 M HCl in Packard 25 ml scintillation polyvial	Used for determining actual activity in the ^{237}Pu solution
6	10 μl of stock solution in 5 ml 3 M HCl in a 1-oz. bottle	For comparison with liquid samples
7	10 μl of stock solution on a 0.45 μm filter in a 1-oz bottle	For comparison with filter samples
8	10 μl of stock solution on 1-g crushed limestone in an OR tube	For comparison with limestone rock
9	10 μl of stock solution on 1-g crushed basalt in an OR tube	For comparison with basalt samples
10	10 μl of stock solution dried in an OR tube	For comparison with empty OR

TABLE B-II
GENERAL LIMESTONE EXPERIMENTAL PARAMETERS

	Experiment No. 1				Experiment No. 2			
	Sample 1	Sample 2	Sample 3	Control	Sample 1	Sample 2	Sample 3	Control
Final pH of influent	8.17	8.11	8.00	8.04	6.85	7.00	6.00	6.68
Volume of influent (mL)	15.0	15.0	15.0	15.0	15.0	15.0	13.9	14.0
Residual volume of water ^a	0.453	0.387	0.428		0.382	0.429	0.393	
Total volume of water	15.5	15.39	15.43	15.0	15.38	15.43	14.29	14.0
Weight of crushed rock (g)	1.0093	0.9924	0.9944		0.9981	0.9977	0.9829	
Activity/mL of original feed ^b (%)	5.89	5.89	5.89	5.89	5.89	5.89	5.89	5.89
Residual activity of influent (%)	15.2	12.9	23.8	9.4	9.0	10.6	20.5	9.7
Activity left in tracer tube (%)	58.7	49.5	55.2	48.1	80.1	83.8	66.4	79.0
Activity left in filter flask (%)	0.05	0.27	0.20	0.09		0.02	0.03	
Activity left on filter	26.0	37.4	20.9	42.4	10.9	5.6	13.1	11.3
Activity in 5 mL of effluent (%)	0.003	0.015	0.018	2.09	0.08	0.10	0.32	0.87
Activity on crushed rock ^c (%)	6.89	10.65	10.36		2.02	2.32	10.97	
Residual volume of water in crushed rock	1.34	0.47	0.47		0.52	0.49	0.44	
Activity left on control container (%)				0.3				0.0

^aResidual volume (wt water/ density water) of cold water wash left trapped in crushed rock.

^bAll activity measurements are given as percentages relative to 100% of the original aliquot.

^cThe number quoted has been corrected for residual influent.

^dResidual volume (wt water/density water) of influent left trapped in the crushed rock.

TABLE B-III
GENERAL BASALT EXPERIMENTAL PARAMETERS

	Experiment No. 3				Experiment No. 4			
	Sample 1	Sample 2	Sample 3	Control	Sample 1	Sample 2	Sample 3	Control
Final pH of influent	8.20	8.19	7.70	8.0	6.92	6.16	6.90	6.99
Volume of influent (mL)	15.0	14.0	15.0	15.0	15.0	15.0	15.0	15.0
Residual volume of water ^a	0.39	0.44	0.39		0.41	0.37	0.37	
Total volume of water	15.39	14.44	15.39	15.0	15.41	15.37	15.37	15.0
Weight of crushed rock (g)	0.996	0.976	0.983		1.00	0.993	1.01	
Activity/mL of original feed ^b (%)	5.89	5.89	5.89	5.89	5.89	5.89	5.89	5.89
Residual activity of influent (%)	22.6	22.5	28.3	19.1	20.0	15.3	12.5	6.9
Activity left in tracer tube (%)	72.8	74.0	66.8	75.7	47.7	74.2	76.8	88.8
Activity left in filter flask (%)	0.13	0.72	1.17					
Activity left on filter (%)	4.5	2.8	3.7	5.3	32.3	10.5	10.7	4.3
Activity in 5 mL of effluent (%)	0.04	0.02	0.08	2.5	0.03	0.05	0.04	0.79
Activity on crushed rock ^c (%)	4.08	6.26	6.53		1.61	2.43	2.28	
Residual volume of water ^d in crushed rock (2)	0.49	0.47	0.71		0.51	0.52	0.50	
Activity left on control (%)				0.0				0.3

^aResidual volume (wt water/density water) of cold water wash left trapped in crushed rock.

^bAll activity measurements are given as percentages relative to 100% of the original aliquot.

^cThe number quoted has been corrected for residual influent.

^dResidual volume (wt water/density water) of the influent left trapped in the crushed rock.

any portion of the experiment which contained activity, and the tubes which held the crushed rock samples were also counted. Several different NaI(Tl) detector systems were used: one 2-in x 2-in detector connected to a scalar; one 2-in x 3-in NaI detector; and one low background 3-in x 3-in NaI detector. The analyzers used with the two 2-in x 3-in NaI detectors were set for a gain of approximately 1.33 keV/channel. The windows of the NaI well and of the 2-in x 2-in NaI detector were set to include the 60 keV γ -ray and 100 keV X-rays. A minimum of two spectra or counts were taken for each sample. The data from the two 3-in x 3-in NaI detectors were summed over the 60 keV and 100 keV peaks. All data from the samples were compared to a ^{237}Pu standard which was counted in conjunction with the samples, and at least once a day. The use of the standards in this way eliminated decay corrections and possible variations due to electronic perturbations.

IV. CALCULATIONS AND RESULTS

The sorption ratios for the various experiments were calculated according to Eq. (A-1) using both the activity per milliliter of the initial solution and the activity per milliliter after filtration, and also by taking the ratio of the activity per gram of crushed rock versus the activity per milliliter of the final supernate. These results are shown in Table B-IV and summarized in Table B-V.

An activity balance can be obtained from the data in Tables II and III as follows: The Activity/ml of original feed (%) times the 17 ml original volume is equal to the sum of the Activity left in the tracer tube (%), the Activity left in the filter flask (%), the Activity left on the filter (%), and the Residual activity in the influent (%).

The row, Residual activity left on the filter (%), is the actual amount of activity available to the solid for the experiment. In the case of sample #1, experiment #1, this is only 15.2% of the activity that was in the original preparation. Eighty-four percent of the activity was left behind due to centrifugation and filtration.

TABLE B-IV
PARAMETERS^a FOR R_d CALCULATIONS

Expt.	Sample	R	A_f		A_t	V (mL)	W (g)	Activity ^b per g rock	Activity ^b per mL effluent
			Initial	post- filtrate					
1	1	0.971	5.89	0.964	0.002	15.45	1.0093	6.83	0.002
	2	0.975	5.89	0.838	0.003	15.39	0.9924	10.73	0.003
	3	0.972	5.89	1.563	0.004	15.43	0.9944	10.42	0.004
2	1	0.975	5.89	0.602	0.016	15.39	0.9981	2.02	0.016
	2	0.972	5.89	0.705	0.02	15.43	0.9977	2.33	0.020
	3	0.937	5.89	1.474	0.06	14.84	0.9829	11.16	0.064
3	1	0.975	5.89	1.51	0.008	15.39	0.9961	4.09	0.008
	2	0.970	5.89	1.61	0.004	14.44	0.9756	6.42	0.004
	3	0.975	5.89	1.89	0.016	15.39	0.9832	6.64	0.016
4	1	0.974	5.89	1.33	0.006	15.41	0.9998	1.61	0.006
	2	0.977	5.89	1.02	0.01	15.37	0.9928	2.45	0.010
	3	0.976	5.89	0.83	0.008	15.38	1.0087	2.26	0.008

^aSee Appendix A for the definitions.

^bAll activity measurements are given as percentages relative to 100% of the original aliquot.

TABLE B-V
SORPTION RATIOS (mL/g)
FROM Eq. (A-1)

Expt. ^a	R_d		R_d		R_d	
	Calculated using initial influent		Calculated using post-filtrate influent		$\frac{\text{Activity}^b/\text{g rock}}{\text{Activity/mL effluent}}$	
1	31 853	34% ^c	> 5 853	26%	3 198	16%
2	3 709	57%	458	28%	139	22%
3	12 594	62%	3 457	60%	843	78%
4	11 514	26%	2 124	49%	265	7%

^aSee Appendix A.

^bAll activity measurements are given as percentages relative to 100% of the original aliquot.

^cThe error given is the standard deviation for three replicate experiments.

APPENDIX C VARIABILITY OF SORPTION RATIOS B. R. Erdal and P. Q. Oliver

Several measurements of sorption ratios have been made on limestone and basalt using small variations of the procedure specified in the Appendix A. These measurements show a few of the possibilities for obtaining large variations in values of the sorption ratio even when using the same material and techniques. In all cases the solid material was used as received from Battelle (PNL). The limestone (GW#1), basalt (GW#2), and brine (GW#3) waters, as specified in Appendix A, were used, except as indicated. The measurement procedure specified in Appendix A was used throughout.

Four different sets of identical measurements were made using the limestone (see Table C-I) with GW#1. The only known differences between sets were that the ratio of the volume of solution to weight of solid (V/W) was varied, and in three sets, the length of time the solution was shaken with the solid was varied.

TABLE C-I
R_d (limestone + GW#1) REPRODUCIBILITY

Run	Contact Time (d)	V/W	R _D (Cs) (mL/g)	R _d (Sr) (mL/g)
1	6.96	20	158 ± 4	1.45 ± 0.41
	6.96	20	166 ± 4	1.60 ± 0.41
	6.96	20	156 ± 4	1.61 ± 0.44
	13.96	20	182 ± 4	2.06 ± 0.44
	28.03	20	228 ± 5	2.92 ± 0.47
	60.82	20	290 ± 7	3.50 ± 0.52
2	6.89	20	88.0 ± 2.2	1.42 ± 0.44
	6.89	20	88.6 ± 2.1	1.34 ± 0.42
	6.89	20	99.9 ± 2.4	1.30 ± 0.44
3	6.87	20	56.4 ± 1.4	1.83 ± 0.47
	6.87	20	55.6 ± 1.4	1.62 ± 0.48
	6.87	15	57.0 ± 1.4	1.38 ± 0.36
4	6.66	15	88.0 ± 2.3	1.51 ± 0.40
	6.65	15	93.3 ± 2.5	1.22 ± 0.41
	6.65	15	82.5 ± 2.2	1.58 ± 0.41
	12.55	15	112 ± 3	0.96 ± 0.36

TABLE C-II
R_d (basalt + GW#2) REPRODUCIBILITY

Run	Contact Time (d)	V/W	mg/L K	R _D (Cs) (mL/g)	R _d (Sr) (mL/g)
1	6.84	20	1.9	726 15	95.3 2.4
	6.79	20	1.9	714 14	93.6 2.2
	6.95	20	1.9	711 15	96.7 2.2
	13.90	20	1.9	888 19	101 3
2	6.89	20	1.9	677 15	88.0 2.1
	6.89	20	1.9	701 16	92.6 2.4
	6.95	20	1.9	687 16	93.3 2.4
	27.86	20	1.9	924 20	107 3
	56.84	20	1.9	1 165 30	110 3
3	6.80	15	9.1	257 6	79.1 2.0
	6.80	15	9.1	244 5	79.4 2.2
	7.02	15	9.1	226 5	78.0 2.3
4	6.92	15	9.1	269 6	81.7 2.4
	6.92	15	9.1	261 6	80.7 2.4
	6.92	15	9.1	265 6	79.9 2.5
	12.70	15	9.1	265 6	82.3 2.4

TABLE C-III
 R_d (limestone + brine) REPRODUCIBILITY

<u>Run</u>	<u>Contact Time (d)</u>	<u>V/W</u>	<u>R_d (Cs) (mℓ/g)</u>	<u>R_d (Sr) (mℓ/g)</u>
1	6.96	20	- 0.29 ± 0.36	- 0.19 ± 0.38
	6.96	20	- 0.40 ± 0.37	- 0.26 ± 0.40
	6.96	20	- 0.50 ± 0.38	- 0.41 ± 0.40
	13.90	20	0.48 ± 0.39	0.62 ± 0.40
	28.03	20	0.02 ± 0.34	0.23 ± 0.41
	60.82	20	- 0.02 ± 0.42	0.01 ± 0.64
2	6.89	20	- 0.46 ± 0.40	0.11 ± 0.41
3	6.75	15	- 0.06 ± 0.30	0.00 ± 0.34
	6.75	15	- 0.19 ± 0.28	0.16 ± 0.34
	6.75	15	- 0.10 ± 0.27	0.09 ± 0.33

TABLE C-IV
 R_d (basalt + brine) REPRODUCIBILITY

<u>Run</u>	<u>Contact Time (d)</u>	<u>V/W</u>	<u>R_d (Cs) (mℓ/g)</u>	<u>R_d (Sr) (mℓ/g)</u>
1	6.95	20	1.18 ± 0.40	0.21 ± 0.42
	6.95	20	0.99 ± 0.42	- 0.07 ± 0.42
	6.95	20	0.94 ± 0.41	- 0.09 ± 0.42
	13.90	20	1.30 ± 0.41	0.26 ± 0.40
	28.03	20	0.95 ± 0.40	- 0.21 ± 0.40
	60.77	20	1.15 ± 0.39	- 0.15 ± 0.47
2	6.83	20	0.82 ± 0.40	0.28 ± 0.42
	6.83	20	0.40 ± 0.38	- 0.22 ± 0.40
	6.83	20	0.75 ± 0.38	0.20 ± 0.40
3	6.97	15	0.48 ± 0.28	- 0.01 ± 0.34
	6.97	15	0.82 ± 0.30	0.37 ± 0.34
	6.97	15	0.57 ± 0.29	0.11 ± 0.34

Replicate measurements were made for all 7 d contact times. The limestone material was always shaken before the 1-g fractions were weighed out. However, it was observed that there was a pronounced tendency for the fines in the material to settle out between sampling for the different sets of measurements. Therefore, the reproducibility in the samples themselves is suspect.

Within a given set of measurements, the reproducibility of the sorption ratios is excellent and volume does not seem to be important. However, the measured value for cesium was extremely unreproducible. Perhaps the sample reproducibility itself is poor. There also is an increase in the cesium sorption ratio with the length of contact with water. The information content of the strontium sorption ratios is less due to the rather large uncertainties that must be assigned to the observed values when the error analysis is done.

The measurements using the basalt and GW#2 were made in a similar manner. However, in addition, the concentration of potassium (added as potassium chloride) was varied (see Table C-II). The higher potassium concentration is that specified in Appendix A. There does not seem to be any problem with the reproducibility between sets of measurements, although again the sorption ratios increase with time of contact with water. However, the effect of the change in potassium concentration on the sorption ratios is marked, particularly for cesium. While this is not particularly surprising, it does indicate the importance of the water composition on the value of the sorption ratio.

The results for use of the brine (GW#3) with limestone and basalt are given in Tables C-III and C-IV, respectively. The results are all consistent within the rather large errors that must be assigned to such low values. There does not seem to be any change with time or V/W.

APPENDIX D
ADDITIONAL MEASUREMENTS ON CONTROLLED SAMPLES USING ^{237}Pu
F. O. Lawrence

I. INTRODUCTION

The objective of this work was to attempt desorption measurements of ^{237}Pu from the crushed-rock samples prepared as described in Appendix B. A second sorption experiment using the crushed basalt was also done.

II. MEASUREMENT PROCEDURE

The desorption experiments were done using the crushed rock samples prepared as described in Appendix B and from a duplicate sorption experiment. The crushed basalt used in the duplicate sorption experiment was treated in the same manner as those previously described in Appendix B. The waters used for desorption experiments were prepared by contacting them with 1-2 g of the proper crushed rock for about three weeks. The pH values of the resulting prepared solutions were measured to be: basalt plus GW#3, 6.18; limestone plus GW#3, 6.62; GW#1, 8.12; GW#2, 8.58. Fifteen milliliter portions of these appropriate preequilibrated waters were pipetted onto the crushed rock samples.

The preparation of the tracers for the second sorption experiment was somewhat different from that used in Appendix B. As before, aliquots of the 3 M HCL solution of ^{237}Pu were dried in the bottoms of the Oak Ridge type centrifuge tubes and then "taken up" in the appropriate ground water or brine. In the preparation for the second sorption experiment, the particulate problem was handled by centrifugation. Each traced feed was centrifuged and transferred two times, the first time was by decantation, and the last time by use of a plastic transfer pipet. Each centrifugation was at 14 000 rpm (24 000 g) for 1 h.

The desorption contact times were 1, 2, and 4 weeks. The contact times for the second sorption experiment were also 1, 2, and 4 weeks; however, the desorption time for this experiment was two weeks.

The samples were prepared for counting in the same manner as described in Appendix B, except that the 5-ml samples were taken with a graduated seriological disposable plastic pipet instead of with a plastic automatic pipetor. The pipets were made by Falcon, a division of Becton, Dickinson and Co. The centrifugation and decantation was performed in the same manner as was previously used for the sorption experiments described in Appendix B. The crushed rock portion of the sample was not transferred from the original tube.

Wherever possible both the effluent solution and the crushed rock sample were counted in the NaI well counter. As an OR type tube will not fit directly into the well, some of the final effluents had to be counted both in the well counter and with the 3-in x 3-in NaI detector described in Appendix B. Whenever that was necessary, a correction was applied for the difference in counting efficiency. The ratio of the count rates on the 3-in x 3-in NaI detector to that in the well for aqueous samples was determined to be $0.55 \pm .01$. The analyzer

used with the 3-in x 3-in NaI detector was set for a gain of approximately 1.33 keV/channel, and the data were summed over the 60-keV and 100-keV regions. The window of the well counter was set to include the 60-keV γ -ray and the 100-keV X-rays.

The sorption ratios were calculated in the following manner:

$$R_d = \frac{\text{activity as measured in the well counter/gram of crushed rock}}{\text{activity as measured in the well counter/mL of effluent}}$$

III. RESULTS AND CONCLUSIONS

The results from these additional measurements are given in Tables D-I and D-II. The R_d values for the desorption experiments using the samples described in Appendix B were averaged as there seemed to be no difference due to different contact times which could be observed above the scatter in the data. The R_d values for the new sorption experiments were averaged also. These averages are given in Table D-III.

The variation in sorption ratios between replicate experiments clearly indicates the very real problems involved in the preparation of plutonium solution at pH $\approx$ 8 values.

When compared to the results given in Appendix B (summarized in Table D-III) the new sorption measurements indicate the strong effect of filtration on the results. Whether the removal from the solution after contact with the rock is due to filtration of a radiocolloid or polymer, or is due to adsorption on the filter, cannot be determined.

Definite conclusions cannot be unequivocally drawn concerning the desorption measurements. However, the trend seems to indicate, within the rather large uncertainties due to unreproducibility, that the desorption ratio is similar to the sorption ratio. This would indicate that plutonium sorption on limestone and basalt is only on the surface and does not involve diffusion, mineral alteration, etc., mechanisms.

TABLE D-I
DESORPTION RATIO (mL/g) MEASUREMENTS

Experiment	Contact Time (d)				Average ^a
	7	14	17	28	
Limestone + GW#1 ^b	804		762	1 275	947 ± 30%
Limestone + GW#3 ^b	687		84	611	461 ± 71%
Basalt + GW#2 ^b			1 500	387	944 ± 83%
Basalt + GW#3 ^b	532		166	104	267 ± 87%
Basalt + GW#2 ^c	2 179				3 230 ± 46%
	4 279				
Basalt + GW#3 ^c	3 162				2 580 ± 35%
	1 529				
	3 049				

^aThe error given is the standard deviation of the mean of all the R_d values.

^bThe traced feed was prepared using filtration as the method for particle removal.

^cThe traced feed was prepared using centrifugation as the method for particle removal.

TABLE D-II
SORPTION RATIO (mL/g) MEASUREMENTS

Experiment ^a	Contact Time (d)			Average ^b
	7	14	28	
Basalt + GW#2		6 160	1 340	2 590 ± 108%
Basalt + GW#3	814	974	707	785 ± 16%

^aThe traced feed was prepared using centrifugation as the method of particle removal.

^bThe error given is the standard deviation of the mean of all the measured values.

TABLE D-III
SUMMARY OF ^{237}Pu SORPTION RATIOS

Rock	Effluent	R_d (mL/g)		R_d (desorption)
		Sorption	Desorption	R_d (sorption)
Limestone	GW#1 ^a	3 198 $\pm$ 16% ^b	947 $\pm$ 30%	0.30 $\pm$ 0.10
	GW#3 ^a	139 $\pm$ 22% ^b	461 $\pm$ 71%	3.1 $\pm$ 2.5
Basalt	GW#2 ^a	843 $\pm$ 78% ^b	944 $\pm$ 83%	1.1 $\pm$ 1.3
	GW#3 ^a	265 $\pm$ 7% ^b	267 $\pm$ 87%	1.0 $\pm$ 0.9
Basalt	GW#2 ^c	2 590 $\pm$ 108%	3 230 $\pm$ 46%	1.2 $\pm$ 1.5
	GW#3 ^c	785 $\pm$ 16%	2 580 $\pm$ 35%	3.3 $\pm$ 1.3

^aTracers were prepared using filtration as the method for particle removal.

^bFrom Appendix B.

^cTracers were prepared using centrifugation as the method for particle removal.