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Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media

October 1—December 31, 1979

University of California

LOS ALAMOS SCIENTIFIC LABORATO
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Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media

October 1—December 31, 1979

Compiled by

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LABORATORY STUDIES OF RADIONUCLIDE DISTRIBUTIONS BETWEEN SELECTED GORUNDWATERS AND GEOLOGIC MEDIA

Quarterly Technical Progress Report for
October 1 through December 31, 1979

Compiled by

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ABSTRACT

This report presents the Los Alamos Scientific Laboratory contribution to the Waste/Rock Interactions Technology program, Tasks 3 and 4, for the first quarter of FY-1979. The majority of the effort involved extensive studies under reduced oxygen and carbon dioxide conditions, measurements of isotherms, microautoradiographic studies, and migration rate studies. Efforts to estimate uranium, plutonium, and neptunium solubilities were initiated.

I. INTRODUCTION

This report covers the technical activities on Waste-Rock Interactions and Technology (WRIT) contract 45855-AK to the Los Alamos Scientific Laboratory for the first quarter of FY-1980. Based on their applicability to the WRIT project, some results on tuff have been included from research supported by the Nevada Nuclear Waste Storage Investigations program and the Radionuclide Migration project, both managed by the Nevada Operations Office of the Department of Energy.

II. PROJECT OBJECTIVE

The Los Alamos Scientific Laboratory (LASL) contribution to the Waste Rock Interactions and Technology project (formerly Waste Isolation Safety Assessment Program) in FY-80 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. Second, the LASL batch sorption methodology[1-3] will be used to obtain data on several additional variables that influence sorption-desorption behavior and to perform studies on several new radionuclide-geomedia systems. Third, the microautoradiographic technique[4] currently utilized at LASL will be used for further studies of the sorption of radionuclides on polished or ground surfaces of mineral grains and for identification of the specific sorbing surfaces in natural (nonpulverized) systems. Finally, initial studies of the chemistry of several radionuclides in the pH $\cong$ 8 solutions that frequently occur in natural environments will be performed.

Most of the sorption 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 analyses of all materials will be made.

III. PROGRESS REPORTED PREVIOUSLY

The results obtained by the LASL program since its beginning in September, 1977, have been summarized in several reports.[1-8] Proper methods for performing batch sorption measurements were developed. These methods were 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, temperature, water composition, and sampling location were investigated for strontium, technetium(VII), cesium, barium, cerium(III), europium(III), uranium(VI), plutonium, and americium. Studies of the sorption of strontium, cesium, barium, cerium, europium, and uranium(VI) on granite and argillite were made under controlled-atmosphere (<0.2 ppm oxygen, <20 ppm carbon dioxide) conditions (nitrogen) and the results were compared to earlier measurements made under atmospheric conditions.

Extensive studies of the behavior of plutonium and americium in pH $\cong$ 8 groundwaters were made, particularly with respect to container sorption, filtering, and centrifugation. Significant improvements in the method used for measuring sorption ratios for these elements were developed, and their sorption-desorption ratios on argillite and tuff were measured.

Measurements of migration rates in crushed granite, argillite, and tuff were made and compared with batch results. Infiltration experiments involving the forced injection of activity into intact and fractured cores were also performed.

A microautoradiographic technique was used to identify the specific sorption sites for actinides on ground and polished surfaces of petrographic thin-sections. A modification of this technique was used to assess the amount of "aggregation" of actinides that occurred in some of the sorption studies.

Additional physical and chemical characterizations of the materials used in these studies were made, and new analytical techniques were developed.

IV. GEOLOGIC MEDIA - NUCLIDE INTERACTION STUDIES IN THE REPORTING PERIOD

Much of the activity during the first quarter of FY-80 involved those batch sorption studies needed to extend the current data base for tuff, to continue studies of the effect of controlled atmosphere conditions, to study iodine sorption on argillite, and to begin to measure the isotherms for some elements. Measurements of migration rates in crushed and fractured materials were continued, as were studies using the microautoradiographic technique. Development of additional chemical analysis and characterization techniques were also initiated. Finally, preparation of publications and reports, oral presentations and travel, have involved some effort.

A. Sorpton of Plutonium and Americium on Tuff Under Atmospheric Conditions - Continued (W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver)

Details of the batch experiments for the measurement of the sorption of plutonium and americium on tuff under atmospheric conditions were given in Ref. 8. Additional measurements have been made, primarily the analysis of ^{239}Pu in both solid and aqueous phases from Experiment 2 and the completion of six-month contact times for ^{241}Am in Experiment 4. The data have been added to those given in Ref. 8 and the updated tables are included here as Tables I-VI.

The general conclusions for these experiments were given in Ref. 8. The additional results for americium tend to confirm the observation that R_d values for the sorption of americium on tuff show very little increase with longer contact times, at least up to six months. The ^{239}Pu results did nothing to clarify the confusing situation in regard to plutonium sorption described before. Comparison of results for $\cong 4 \times 10^{-7}$ M ^{239}Pu and $\cong 1 \times 10^{-13}$ ^{237}Pu, at least for "pH adjusted" feed solutions, shows higher sorption R_d values for the more concentrated solutions but higher desorption R_d values subsequent to contacts with the less concentrated solutions. Also, for ^{239}Pu the sorption R_d values are greater than the desorption, but for ^{237}Pu the desorption R_d values are greater than the sorption. For the "dried" method of preparing the feed solutions, the desorption R_d values in all cases are greater than the sorption R_d values. These results are probably the effects of plutonium speciation and associated solubility differences in the two methods of feed solution preparation. Studies of the fundamental chemistry of plutonium and americium species in near-neutral solutions are essential to understanding the sorptive behavior of these elements.

B. Measurements under Controlled-atmosphere Conditions - Cesium, Strontium, Barium, Cerium, and Europium (S. J. DeVilliers)

The sorption of strontium, cesium, barium, cerium, and europium on argillite and granite under "anoxic" conditions was studied. The term "anoxic" means that the operations were performed in the controlled-atmosphere boxes which contain nitrogen having <0.2 ppm oxygen and <20 ppm carbon dioxide. This was done to see if there was any effect of reduced oxygen concentration on

TABLE I

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

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d (mℓ/g)		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
1	106-150	dried	7.0		200	170[a]		8.19
1			7.0		250			8.29
				14	270	160[a]	8.30	
2			7.6		96	70[a]	8.56	7.43
2			7.6		310			7.52
				59.8	810		8.51	8.58
3			13.8			110[b]	8.38	8.30
				13.7		710[b]	8.43	8.51
2			14.6		86		8.56	8.42
				34.7	440	260[a]	8.51	8.53
2			14.6		310			8.29
				59.8	710		8.51	8.57
2			28.6		120	81[a]	8.56	8.55
2			28.6		200		8.53	8.58
				34.7	1 200		8.51	8.15
2			28.6		360			8.60
				59.8	790		8.51	8.58
2			28.6		220		8.52	8.60
3			28.9			120[b]	8.38	8.41
				14.0		450[b]	8.44	8.56
3			55.7			220[b]	8.38	8.42
				17.8		97[b]	8.35	8.45
2			56.6		57	68[a]	8.56	8.36
2			56.6		100		8.52	8.57
				34.7	2 000		8.51	8.36
2			56.6		85			8.57
				59.8	2 300		8.51	8.52
2			56.6		85		8.53	8.49
4	106-150	pH adjust	32.9		450		8.55	8.42
				41.8	1 000		8.50	8.59
4			32.9		440		8.55	8.43
				41.8	930		8.50	8.64
4			60.9		420		8.55	8.27
				43.8	950		8.50	8.62
4			61.9		430		8.55	8.44
				44.8	970		8.50	8.65

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

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

TABLE II

Am AND Pu SORPTION RATIOS[a], TUFF SAMPLE JA-32, AMBIENT TEMPERATURE

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d (mℓ/g)		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
2	106-150	dried	7.6		110		8.50	7.60
				34.7	2 800	1 700	8.58	8.56
2			14.6		110	110	8.50	8.60
2			28.6		140	75	8.50	8.63
2			28.6		230		8.50	8.63
				34.7	1 500	420	8.58	8.34
2			56.6		79	140	8.50	8.64
1	106-150	pH adjust	7		1 600	1 200	7.92	8.26
1			14		1 000	1 800	7.92	8.19
1			28		1 100		7.92	8.32
				14	2 100	920	8.30	
1	355-500	pH adjust	7		890	1 000	7.92	8.19
4			13.0		1 300		8.59	8.49
				47.8	2 100		8.46	8.64
1			14		640		7.92	7.94
				14	920	580	8.30	
4			14.0		1 400		8.59	8.45
				47.8	3 900		8.46	8.69
1			28		490	820	7.92	8.23
4			61.9		1 200		8.59	8.50
				44.8	2 100		8.46	8.67
4			62.9		1 700		8.59	8.52
				47.8	2 600		8.46	8.69
4[b]			186.0		1 400		8.59	7.92
4[b]			186.0		1 700		8.59	8.06

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

[b]Desorption in progress.

TABLE III

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

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d (mℓ/g)		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
2	106-150	dried	7.6		430	390[a]	8.64	7.53
2			14.6		365		8.64	8.52
				34.7	14 000	6 500[a]	8.60	8.47
2			28.6		430	180[a]	8.64	8.67
2			28.6		1 500		8.64	8.62
				34.7	21 000	10 000[a]	8.60	8.28
2			56.6		640	930[a]	8.64	8.56
1	106-150	pH adjust	7		7 200	7 200[a]	7.92	8.53
1			14		5 200		7.92	8.23
				14	2 700	890[a]	8.30	
4			14.0		11 000		8.60	8.48
				47.8	12 000		8.58	8.64
4			14.7		10 000		8.59	8.44
				47.8	8 900		8.58	8.63
1			28		7 500	12 000[a]	7.92	7.94
				14	5 200	1 600[a]	8.30	
4			27.7			750[b]	8.35	8.33
				40.8		5 300[b]	8.58	8.60
4			27.7			720[b]	8.35	8.33
				40.8		8 600[b]	8.58	8.59
4			33.9		14 000		8.60	8.52
				42.8	11 000		8.58	8.56
4			34.7		14 000		8.59	8.57
				42.8	9 500		8.58	8.55
4			54.7			1 900[b]	8.35	8.30
				43.8		5 500[b]	8.58	8.56
4			60.9		12 000		8.60	8.31
				43.8	12 000		8.58	8.57
4			62.6		11 000		8.59	8.54
				44.8	10 000		8.58	8.59
4			63.6		13 000		8.59	8.56
				47.8	9 700		8.58	8.61
4			186.0		34 000		8.60	8.06
1	355-500	pH adjust	7		3 700	5 400[a]	7.92	8.38
1			14		2 800	7 200[a]	7.92	8.19
4			27.7			280[b]	8.38	8.40
				40.8		6 500[b]	8.58	8.61
4			27.7			320[b]	8.38	8.40
				40.8		3 600[b]	8.58	8.59
1			28		3 800		7.92	8.29
				14	5 800	670[a]	8.30	
4			32.9		12 000		8.60	8.50
				41.8	17 000		8.58	8.58
4			33.9		13 000		8.60	8.51

TABLE III (cont)

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

Experiment Number	Fraction (μm)	Tracer Prep	Time (d) Sorp	Time (d) Desorp	R_d (mℓ/g) Am	R_d (mℓ/g) Pu	pH Initial	pH Final
				42.8	17 000		8.58	8.55
4			54.7			450[b]	8.38	8.28
				43.8		1 000[b]	8.58	8.59
4			54.7			470[b]	8.38	8.46
				43.8		1 900[b]	8.58	8.56
4			60.9		14 000		8.60	8.37
				43.8	18 000		8.58	8.58
4			62.9		12 000		8.60	8.53
				47.8	33 000		8.58	8.60
4[c]			186.0		18 000		8.60	8.16
4[c]			186.8		8 100		8.60	8.18

[a]Approximately 10^{-6} M ^{239}Pu.
[b]Approximately 10^{-13} M ^{237}Pu.
[c]Desorption in progress.

the solid since one would not expect any major effect of oxygen on these elements. However, there was also a reduction in the amount of carbon dioxide in the solutions.

1. Preparation of Materials. The solids being used are the same as those previously described.[1-3,9] These are the Climax Stock quartz monzonite[1] and Eleana argillite[2] (core CN3), and three Yucca Mountain tuffs.[9] Solid samples of these materials were ground under "anoxic" conditions in a non-iron system using an agate mortar with a 50- or 70-mm agate ball (Tekmar Co., Pulverisette). Each material was graded by use of Tyler sieves (ASTM E-11 specfication) into two size fractions, <75 μm and 75-500 μm. The entire sample was ground until it passed into one of these fractions.

The same groundwaters as previously described[1-3] were used to prepare the rock-treated waters. These waters were prepared by contacting batches of the groundwater, which had been sparged with high purity nitrogen for at least 1 h, with pulverized material (20 to 40 g) that had not been sieved. The contact time was at least two weeks at ambient temperature with a solution volume to solid ratio of 50 mℓ/g. The phases were separated by centrifugation at 7 000 rpm (21 000 g's) for 1 h followed by filtration through a 0.4-μm Nuclepore filter membrane. All operations were performed in the controlled atmosphere boxes.

TABLE IV

Am AND Pu SORPTION RATIOS[a], TUFF SAMPLES JA-18, -32, AND -37, 70°C

Core Sample	Experiment Number	Fraction (μm)	Tracer Prep	Time (d) Sorp	Time (d) Desorp	R_d (mℓ/g) Am	R_d (mℓ/g) Pu	pH Initial	pH Final
JA-18	2	106-150	dried	7.6		220			7.19
	2				33.9	3 100		8.35	8.48
	2			7.6		190			7.32
				14.6		190			7.57
	2				33.9	3 600		8.35	8.42
	2			14.6		170	150		8.08
	2			28.6		290			8.61
	2			28.6		150	110		8.62
	2			28.6		340		8.60	
	2			28.6		370		8.57	8.50
	2			56.6		300			
				56.6		76	84		
JA-32	2	106-150	dried	7.6		120		8.46	7.33
	2			14.6		160	50	8.46	8.14
	2			28.6		130	72	8.46	8.57
	2			56.6		46	99	8.46	
JA-37	2	106-150	dried	7.6		520	240	8.58	7.33
	2			14.6		680	340	8.58	8.06
	2			14.6		2 100	1 500	8.58	8.18
	2			28.6		960	440	8.58	8.67
	2			56.6		800	990	8.58	
	2			56.6		730		8.58	8.52
JA-37	4	355-500	pH adjust	32.9		32 000		8.37	8.23
	4				41.7	3 800		8.41	8.59
				33.9		48 000		8.37	8.25
	4				42.7	7 200		8.41	8.46
				61.8		19 000		8.37	8.51
	4				44.7	5 500		8.41	8.58
				62.8		37 000		8.37	8.64
	4[b]				47.8	4 800		8.41	8.58
	4[b]			186.9		26 000		8.37	8.55
				186.9		68 000		8.37	8.52

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

[b]Desorption in progress.

TABLE V

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

Element	Core	Temp (°C)	Dried		PH Adjusted	
			Sorption	Desorption	Sorption	Desorption
Am	JA-18	22	180 (30)	1 100 (260)	435 (6)	960 (15)
		70	230 (30)	3 400 (300)		
	JA-32	22	130 (30)	2 200 (650)	1 200 (110)	2 300 (310)
		70	110 (30)			
	JA-37	22	670 (210)	17 000 (3 500)	11 000 (1 500)	12 000 (2 000)
		70	970 (240)		38 000 (7 200)	5 300 (720)
Pu	JA-18	22	120 (20)	340 (110)		
		70	110 (20)			
	JA-32	22	110 (20)	1 100 (640)	1 200 (210)	750 (170)
		70	74 (14)			
	JA-37	22	500 (220)	8 200 (1 800)	3 300 (1 200)	3 800 (950)
		70	700 (240)			

[a]Sorption ratios are given for both "dried" and "pH adjusted" methods of preparing the traced feed solutions. They are averaged over 1-, 2-, 4-, 8-, and 27-week contact times, 106-150 and 355-500 μm particle sizes, and $\cong 10^{-6}$ and $\cong 10^{-13}$ M plutonium concentrations. Values in parentheses are the standard deviations of the means (absolute values).

TABLE VI

AVERAGE SORPTION RATIOS FOR Am AND Pu ON TUFF, EXPERIMENT 4 DATA[a]

Element	Core	Temp (°C)	R_d (mℓ/g)	
			Sorption	Desorption
Am	JA-18	22	435 (6)	960 (15)
	JA-32	22	1 450 (85)	2 700 (420)
	JA-37	22	14 000 (1 700)	14 000 (2 100)
		70	38 000 (7 200)	5 300 (720)
Pu	JA-37	22	700 (210)	4 600 (1 000)

[a]Sorption ratios are given for the "pH adjusted" method of preparing the traced feed solutions. They are averaged over 1-, 2-, 4-, 8-, and 27-week contact times and 106-150 and 355-500 μm particle sizes. Values in parentheses are the standard deviations of the means (absolute values).

The solid samples were also pretreated with the appropriate oxygen-free groundwater by shaking weighed 1-g quantities of the crushed rock with 20 mℓ of the water for a period of two weeks at ambient temperature under anoxic conditions. The samples were contained in 40-mℓ polypropylene (Oak Ridge) screw-cap centrifuge tubes. All tubes were washed with deionized water prior to use. The phases were separated by centrifuging at 12 000 rpm (28 000g) for 1 h. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pretreatment.

2. Preparation of Tagged Solutions. The appropriate volumes of the tracer solutions for ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu needed for a set of measurements were evaporated to dryness in a washed polyethylene bottle overnight on a steam bath. Concentrated hydrochloric acid was added and the mixture was taken dry again. The appropriate volume of groundwater was added to the bottle inside the controlled atmosphere box and the mixture was mixed for about 2 d in an orbit shaker. The mixture was filtered through a 0.45-μm Millipore filter and the resulting tracer solution was used for the sorption measurements within about 0.2 d. An aliquot of the final solution was also removed for assay of the initial activity of each of the tracers. This aliquot was acidified with hydrochloric acid before assaying in order to stabilize the solution. The estimated molarities of the tracers were Sr(7.9×10^{-8} M), Cs(3.3×10^{-9} M), Ba(6.3×10^{-8} M), Ce(3.1×10^{-8} M), and Ba(6.3×10^{-8} M) for the argillite samples, and Sr(8.3×10^{-8} M), Cs(1.8×10^{-9} M), Ba(2.5×10^{-8} M), Ce(9.5×10^{-10} M), and Eu(1.3×10^{-9} M) for the granite samples.

3. Measurement Techniques. Batch sorption measurements were performed using the techniques described earlier[1-3] at ambient (32°C) temperature. The contact times were 3, 6, and 12 weeks. At the end of the shaking period the samples were centrifuged for 1 h at 12 000 rpm (28 000 g's). The solid phases were separated by transferring the liquid into a clean tube with a plastic pipet. After centrifuging for another hour at 12 000 rpm, the solutions were again transferred into a clean tube by pipet and centrifuged for 2 h. An aliquot was then taken for assay of radioactivity. The pH measurements were made on the remainder of the solution. A small amount of the solid was transferred to a counting vial for activity assay. All handling of the solid or solution samples was made inside the controlled atmosphere boxes. The assay and calculational methods described in Refs. 1 and 2 were used.

4. Results and Conclusions. The results of the measurements are given in Tables VII-XI. Tables XII and XIII gives the starting and final pH values of each of the solutions.

The sorption ratio values obtained for cesium, strontium, and barium on the CS-7 granite are consistent with the values obtained under atmospheric conditions. The R_d values were also found to be strongly dependent on the particle size (surface area) as observed before under atmospheric conditions. The sorption ratios for cerium and europium are higher than those obtained under atmospheric conditions. Perhaps this is due to the absence of carbon dioxide in the controlled atmosphere studies. Also, the R_d values for all elements increased with time.

The sorption values obtained on the argillite samples are somewhat different from those obtained under atmospheric conditions. The cesium, strontium, and barium values are smaller by factors of about 2, 10, and 50-100, respectively, while those for cerium and europium are larger by about a factor of 10. These results are not understood. However, it should be noted that the carbon dioxide concentration in the controlled-atmosphere boxes was <20 ppm which possibly results in a lower carbonate concentration on solution. Also, the R_d values for all elements increased with time. The sorption ratios obtained on all the tuff samples are consistent with the values obtained under atmospheric conditions. Only the R_d values for barium and in a few cases strontium seem to be lower (by a factor of 2) than those measured under atmospheric conditions.

C. Measurements under Controlled-atmosphere Conditions - Technetium

(E. N. Vine)

Measurements of the sorption ratios for ^{95m}Tc on samples of Climax Stock granite (CS-7), Eleana argillite (CN-3), and Yucca Mountain tuff (YM-22, YM-38, YM-54) under controlled atmosphere conditions (<0.2 ppm oxygen, <20 ppm carbon dioxide) have been completed. A batch technique[7] was used. The same particle-size fractions described in section IV. B were used. The sorption and desorption R_d values for contact times of 3 to 12 weeks are given in Tables XIV and XV, along with the final pH values in each solution. The initial pH values were 8.80, 8.10, 8.86, 8.82, and 8.62, for the granite, argillite, and YM-22, YM-38, and YM-54 tuff samples, respectively.

TABLE VII

SORPTION RATIOS, CS-7 GRANITE, CONTROLLED-ATMOSPHERE[a] CONDITIONS

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)[b]				
			Cs	Sr	Ba	Ce	Eu
<75	20.63		1 780 (2.7)	69.8 (2.5)	1 720 (1.7)	>2 640	1 140 (13.3)
		24.63	2 790 (7.8)	92.4 (8.7)	2 120 (8.7)		>9 070
	41.63		2 060 (3.5)	76.6 (2.5)	2 170 (2.0)	>2 970	>8 560
		41.63	2 540 (7.3)	86.6 (8.3)	2 320 (7.8)	>3 350	>8 620
	83.63		2 570 (3.7)	82.5 (2.5)	2 590 (2.1)		>6 350
75-500	20.63		752 (2.4)	19.4 (3.8)	245 (1.4)	>1 450	>5 320
	41.63		788 (2.5)	22.1 (3.8)	289 (1.4)		>1 240
		41.63	2 650 (7.2)	27.6 (8.3)	322 (7.6)		>5 890
	83.63		1 060 (2.8)	19.5 (4.0)	269 (1.5)		>6 810

[a]Ambient temperature (32°C), nitrogen atmosphere, <0.2 ppm oxygen, <20 ppm carbon dioxide.

[b]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 for change of variables in a moment matrix assuming independence of the variables.

TABLE VIII

SORPTION RATIOS, CN-3 ARGILLITE, CONTROLLED-ATMOSPHERE[a] CONDITIONS

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)[b]				
			Ce	Sr	Ba	Ce	Eu
<75	20.63		1 190 (2.2)	32.1 (3.1)	288 (1.4)	>110 000	>401 000
		20.63	1 690 (7.4)	32.8 (8.1)	524 (7.9)	>83 600	23 500 (11)
	41.63		1 250 (2.4)	39.1 (3.0)	372 (1.5)	>101 000	>354 000
		41.63	2 310 (7.5)	43.5 (8.3)	498 (8.1)	>73 500	>273 000
	91.63		1 670 (2.6)	29.3 (3.3)	397 (1.5)	>7 310	7 640 (5.7)
75-500	20.63		1 020 (2.6)	31.9 (3.2)	209 (1.6)	>128 000	>442 000
		20.63	2 370 (7.3)	30.2 (8.0)	306 (7.6)	>111 000	>486 000
	41.63		1 280 (2.5)	27.3 (3.4)	223 (1.3)	>98 700	35 000 (15)
		41.63	1 990 (7.5)	41.2 (8.1)	307 (8.1)	>118 000	46 400 (16)
	91.63		1 380 (2.5)	28.7 (3.4)	256 (1.5)	>107 000	6 980 (4.5)

[a]Ambient temperature (32°C), nitrogen atmosphere, <0.2 ppm oxygen, <20 ppm carbon dioxide.

[b]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 for change of variables in a moment matrix assuming independence of the variables.

TABLE IX

SORPTION RATIOS, YM-22 TUFF, CONTROLLED-ATMOSPHERE[a] CONDITIONS

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)[b]				
			Ce	Sr	Ba	Ce	Eu
<75	20.63		384 (2.5)	72.6 (2.5)	664 (1.8)	626 (4.7)	797 (3.8)
		24.63	489 (7.4)	104 (7.9)	1 260 (7.9)	2 150 (15)	1 900 (8.0)
	41.63		442 (2.2)	74.6 (2.5)	903 (1.5)	862 (4.9)	991 (3.5)
		41.63	533 (7.4)	124 (8.0)	1 120 (8.0)	2 360 (17)	2 160 (8.2)
	83.63		482 (2.4)	80.7 (2.5)	951 (1.7)	759 (8.5)	1 000 (3.5)
75-500	20.63		203 (2.5)	48.3 (2.8)	205 (1.6)	762 (5.4)	711 (3.9)
		24.63	276 (7.5)	70.3 (8.1)	456 (7.9)	2 120 (15)	3 130 (8.1)
	41.63		209 (2.3)	53.1 (2.7)	296 (1.5)	409 (18)	608 (5.8)
		41.63	345 (7.5)	118 (8.1)	473 (7.9)	2 720 (18)	2 550 (8.3)
	83.63		252 (2.4)	45.9 (2.8)	302 (1.5)	1 590 (17)	1 340 (3.7)

[a]Ambient temperature (32°C), nitrogen atmosphere, <0.2 ppm oxygen, <20 ppm carbon dioxide.

[b]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 for change of variables in a moment matrix assuming independence of the variables.

TABLE X

SORPTION RATIOS, YM-38 TUFF, CONTROLLED-ATMOSPHERE[a] CONDITIONS

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)[b] Cs	Sr	Ba	Ce	Eu
<75	20.63		9 490 (6.2)	9 090 (5.4)	57 000 (23)	647 (9.2)	1 130 (8.8)
		24.63	8 010 (8.4)	18 100 (14)	46 400 (17)	661 (10.2)	823 (9.6)
	41.63		14 100 (6.0)	23 400 (8.2)	>209 000	322 (8.9)	565 (8.5)
		41.63	12 400 (8.9)	23 000 (16)	63 300 (19)	2 150 (11)	2 140 (10.6)
	91.63		9 040 (5.0)	8 010 (1.5)	21 700 (6.6)	743 (8.0)	1 040 (7.2)
75-500	20.63		7 920 (5.8)	7 230 (5.1)	33 700 (14)	556 (8.7)	841 (8.3)
		24.63	14 700 (9.2)	14 200 (14)	89 100 (19)	3 220 (12)	4 300 (11)
	41.63		10 000 (5.2)	8 510 (5.5)	41 000 (12)	851 (7.8)	1 040 (7.3)
		41.63	14 900 (7.1)	12 900 (8.9)	58 100 (16)	1 300 (8.2)	1 260 (7.3)
	91.63		5 380 (4.1)	7 460 (7.2)	10 900 (5.8)	322 (6.5)	466 (5.8)

[a]Ambient temperature (32°C), nitrogen atmosphere, <0.2 ppm oxygen, <20 ppm carbon dioxide.

[b]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 for change of variables in a moment matrix assuming independence of the variables.

TABLE XI

SORPTION RATIOS, YM-54 TUFF, CONTROLLED-ATMOSPHERE[a] CONDITIONS

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)[b] Cs	Sr	Ba	Ce	Eu
<75	20.63		362 (2.5)	100 (2.4)	609 (1.7)	147 (4.1)	530 (3.5)
		24.63	416 (7.4)	124 (7.9)	661 (7.8)	2 420 (9.4)	2 650 (7.8)
	41.63		372 (2.3)	147 (2.3)	738 (1.6)	861 (3.9)	1 450 (3.2)
		41.63	457 (7.4)	147 (8.1)	628 (7.9)	842 (8.5)	1 740 (7.8)
	91.63		392 (2.3)	134 (2.4)	656 (1.6)	966 (4.9)	1 500 (3.2)
75-500	20.63		210 (2.4)	76.2 (2.4)	367 (1.6)	115 (4.1)	329 (3.4)
		24.63	307 (7.5)	119 (8.1)	641 (7.9)	2 080 (9.4)	2 100 (7.8)
	41.63		206 (2.3)	128 (2.3)	128 (2.3)	541 (3.8)	846 (3.1)
		41.63	258 (7.5)	115 (7.9)	469 (7.8)	678 (8.4)	1 550 (7.8)
	91.63		239 (2.3)	70.3 (2.6)	347 (1.5)	495 (1.1)	771 (3.1)

[a]Ambient temperature (32°C), nitrogen atmosphere, <0.2 ppm oxygen, <20 ppm carbon dioxide.

[b]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 for change of variables in a moment matrix assuming independence of the variables.

TABLE XII

pH VALUES, ANOXIC CONDITIONS

Sample	Fraction (μm)	Sorption Time (d)	Desorption Time (d)	pH Values Initial	pH Values Final
CS-7	<75	20.63		8.43	8.56
			24.63	8.43	9.06
		41.64		8.43	8.45
			41.63	8.43	8.45
		83.63		8.43	9.24
	75-500	20.63		8.43	8.52
			24.63	8.43	8.66
		41.63		8.43	8.36
			41.63	8.43	8.66
		83.63		8.43	9.12
CN-3	<75	20.63		8.43	8.40
			20.63	8.43	8.06
		41.63		8.43	8.71
			41.63	8.43	8.11
		91.63		8.43	8.37
	75-500	20.63		8.43	8.80
			20.63	8.43	8.01
		41.63		8.43	8.80
			41.63	8.43	8.22
		91.63		8.43	8.31

The sorption ratios tended to increase significantly with time. This may indicate that the rate at which Tc(VII) is reduced to Tc(IV) is slow or that the rate at which the reducing agent itself is released is also slow.

The ^{95m}Tc sorption ratios were highest on argillite; average values were 440 mℓ/g (<75 μm) and 240 mℓ/g (75-500 μm) for sorption and 760 mℓ/g (<75 μm) and 800 mℓ/g (75-500 μm) for desorption. A much larger difference in average sorption ratios between the two fraction sizes of granite was observed: ~80 mℓ/g (<75 μm) vs. 8 mℓ/g (75-500 μm) for sorption, and 160 mℓ/g (<75 μm) vs. 20 mℓ/g (75-500 μm) for desorption. In general, the R_d values obtained on tuffs on sorption were considerably lower (0.7 to 16 mℓ/g for both fraction sizes). However, a large difference between sorption and desorption ratios was found: desorption ratios were approximately 10 times larger (9 to 120 mℓ/g).

TABLE XIII

pH VALUES, CONTROLLED-ATMOSPHERE CONDITIONS

Sample	Fraction (μm)	Sorption Time (d)	Desorption Time (d)	pH Values Initial	pH Values Final
YM-22	<75	20.63		8.66	8.42
			24.63	8.66	9.03
		41.63		8.66	8.63
			41.63	8.66	8.81
		83.63		8.66	9.10
	75-500	20.63		8.66	8.50
			24.63	8.66	9.04
		41.63		8.66	9.19
			41.63	8.66	9.00
		83.63		8.66	9.08
YM-38	75-500	20.63		8.63	8.55
			24.63	8.63	9.50
		41.63		8.63	9.08
			41.63	8.63	8.83
		91.63		8.63	8.84
	75-500	20.63		8.63	8.68
			24.63	8.63	9.50
		41.63		8.63	9.16
			41.63	8.63	8.80
		91.63		8.63	8.79
YM-54	<75	20.63		8.65	8.68
			24.63	8.65	9.50
		41.63		8.65	8.85
			41.63	8.65	8.81
		91.63		8.65	8.62
	75-500	20.63		8.65	8.69
			24.63	8.65	9.60
		41.63		8.65	9.27
			41.63	8.65	8.89
		91.63		8.65	8.64

TABLE XIV

TECHNETIUM SORPTION RATIOS, GRANITE AND ARGILLITE, CONTROLLED-ATMOSPHERE[a] CONDITIONS

Sample	Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)	Final pH
CS-7	<75	20.67		40	8.58
			83.98	60	8.91
		41.67		80	8.79
			62.98	140	8.90
		83.67		120	8.88
			20.98	280	8.90
	75-500	20.67		15	8.95
			83.98	20	8.80
		41.67		4.0	8.75
			62.98	32	8.76
		83.67		4.2	8.65
			20.98	12	8.94
CN-3	<75	20.67		170	7.93
			83.98	480	8.10
		41.67		330	8.17
			62.98	1 100	8.14
		83.67		830	8.10
			20.98	730	8.07
	75-500	20.67		180	8.11
			83.98	300	8.06
		41.67		200	9.82
			62.98	170	8.32
		83.67		330	7.70
			20.98	220	8.21

[a]Ambient Temperature (32°C), nitrogen atmosphere, <0.2 ppm oxygen, <20 ppm carbon dioxide.

In previous measurements[7] with ^{95m}Tc on tuffs in air, average R_d values were 0.2 mℓ/g and 1.5 mℓ/g for sorption and desorption, respectively.

For all rock types, the sorption ratios tended to increase significantly with time.

TABLE XV

TECHNETIUM SORPTION RATIOS, TUFF, CONTROLLED-ATMOSPHERE[a] CONDITIONS

Sample	Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)	Final pH
YM-22	<75	20.67		3.8	8.81
			83.98	37	8.79
		41.67		6.5	8.84
			62.98	14	8.82
		83.67		3.2	8.73
			20.98	32	8.77
	75-500	20.67		0.4	8.64
			83.98	12	8.84
		41.67		0.3	8.94
			62.98	9.5	8.86
		83.67		1.5	8.47
			20.98	5.3	8.86
YM-38	<75	20.67		3.0	8.69
			83.98	160	8.64
		41.67		17	8.79
			62.98	160	8.70
		83.67		29	8.60
			20.98	46	8.84
	75-500	20.67		2.6	8.33
			83.98	180	8.75
		41.67		7.3	8.68
			62.98	87	8.71
		83.67		21	8.66
			20.98	73	8.75
YM-54	<75	20.67		0.7	8.72
			83.98	37	8.67
		41.67		0.8	8.78
			62.98	13	8.69
		83.67		3.4	8.60
			20.98	5.9	8.60
	75-500	20.67		4.7	8.69
			83.98	140	8.68
		41.67		3.8	8.75
			62.98	38	8.72
		83.67		33	8.53
			20.98	240	8.66

[a]Ambient Temperature (32°C), nitrogen atmosphere, <0.2 ppm oxygen, <20 ppm carbon dioxide.

D. Measurements under Controlled-atmosphere Conditions - Plutonium

(W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver)

1. Measurement Techniques. The equipment for use in controlled-atmosphere experiments and the general techniques for preparation of materials were described in Ref. 8 and in the previous section (IV.B). The Yucca Mountain tuffs and the groundwaters were described in Ref. 9. Traced feed solutions were prepared as for our americium and plutonium Experiment 4, as described in Ref. 8; the ^{237}Pu feed solutions were filtered through 0.4-μm Nuclepore membranes before use. After contact the phases were separated as in Experiment 4 (see above); after being centrifuged three times, the final solutions were passed through 0.05-μm Nuclepore membranes before being counted.

2. Results and Conclusions. The results for 3-, 7-, and 12-week contacts for ^{237}Pu traced groundwaters and three Yucca Mountain tuffs are given in Table XVI. Sorption ratios were calculated directly from solid and solution counts.

At the present time sorption ratios for the same rock types under atmospheric conditions are not yet available for comparison; however, the observed R_d values reported here appear to be comparable to those observed[8] for Jackass Flats tuffs under atmospheric conditions. In each case the altered tuff was found to have the highest R_d value. The data show a slight increase in sorption ratio with contact time, the 3-week values being the lowest in each set. Little particle size effect was observed. The desorption data suffer from the extremely low counting rates resulting from the ^{237}Pu decay during the 15-week period for sorption followed by desorption, especially for YM-38, which has the highest R_d values. As before, for "dried" feed preparations the desorption R_d values are significantly larger than the sorption values. The aqueous phases for YM-38 were too weak to count and limits were placed on the R_d values by setting an upper limit for the solution count. This value is probably conservative; actual desorption R_d values for YM-38 are probably greater than for the other two cores.

E. Sorption on Additional Tuff Samples (E. N. Vine)

Sorption measurements of strontium, cesium, barium, cerium, and europium on a group of six Yucca Mountain tuff samples from hole UE25a#1 at the NTS were reported previously.[9] Those measurements indicated, particularly for

TABLE XVI

MEASUREMENTS UNDER CONTROLLED-ATMOSPHERE[a] CONDITIONS, TUFF, PLUTONIUM

Core Sample	Fraction (μm)	Time (d) Sorp	Time (d) Desorp	R_d (mℓ/g)	Yield Through Tracer Prep(%)	≅M Pu[b]	pH Initial	pH Final
YM-22	<75	20.7		84	23	$8x10^{-14}$	9.25	9.01
			85.8	1 800			9.20	9.34
		48.7		250	23	$8x10^{-14}$	9.25	8.87
			54.7	2 200			9.13	9.32
		84.7		280	23	$8x10^{-14}$	9.25	9.22
			21.8	4 200			9.67	9.07
		Average Sorp.[c]		265(15)				
		Average Desorp.[d]		2 700(740)				
	75-500	20.7		130	23	$8x10^{-14}$	9.25	8.88
			86.6	2 800			9.20	9.69
		48.7		430	23	$8x10^{-14}$	9.25	8.72
			55.7	3 300			9.13	9.36
		84.7		280	23	$8x10^{-14}$	9.25	9.17
			24.8	3 900			9.67	9.01
		Average Sorp.		355(75)				
		Average Desorp.		3 300(320)				
YM-38	<75	20.7		510	9	$3x10^{-14}$	8.87	8.75
			85.8	>2 200			8.88	9.41
		47.7		1 200	9	$3x10^{-14}$	8.87	8.67
			54.7	>2 100			8.80	8.92
		83.7		1 000	9	$3x10^{-14}$	8.87	9.06
			21.8	>2 600			9.30	8.98
		Average Sorp.		1 100(100)				
			Desorp.	>2 100				
	75-500	20.7		640	9	$3x10^{-14}$	8.87	8.76
			86.8	>2 400			8.88	8.90
		48.7		760	9	$3x10^{-14}$	8.87	8.79
			55.7	>2 200			8.80	8.93
		83.7		1 000	9	$3x10^{-14}$	8.87	9.17
			24.8	>2 300			9.30	8.72
		Average Sorp.		880(120)				
			Desorp.	>2 200				
YM-54	<75	21.7		69	14	$5x10^{-14}$	9.29	8.88
			85.8	2 300			9.09	9.60
		48.7		100	14	$5x10^{-14}$	9.29	8.73
			54.7	4 100			9.13	9.22
		84.7		190	14	$5x10^{-14}$	9.29	9.25
			21.8	>500			9.50	9.08
		Average Sorp.		145(45)				
		Average Desorp.		4 600(1 500)				

TABLE XVI (cont)

MEASUREMENTS UNDER CONTROLLED-ATMOSPHERE[a] CONDITIONS, TUFF, PLUTONIUM

Core Sample	Fraction (μm)	Time (d) Sorp	Time (d) Desorp	R_d (mℓ/g)	Yield Through Tracer Prep(%)	≅M Pu[a]	pH Initial	pH Final
	75-500	21.7		96	14	$5x10^{-14}$	9.29	8.91
			86.8	3 000			9.09	9.33
		49.7		210	14	$5x10^{-14}$	9.29	8.82
			55.7	3 400			9.13	9.20
		84.7		260	14	$5x10^{-14}$	9.29	9.09
			24.8	3 200			9.50	9.02
		Average Sorp.		235(25)				
		Average Desorp.		3 200(120)				

[a]Ambient temperature (32°C), <0.2 ppm oxygen, <20 ppm carbon dioxide.

[b]Feed solutions prepared by drying and then redissolving the tracers. Resulting Pu concentrations at start of contacts are indicated.

[c]Averages of 7- and 12-week R_d values. Values in parentheses are the standard deviations of the means (absolute values).

[d]Averages of desorption R_d values, except for YM-38 where limits were set.

for strontium, cesium, and barium, that the presence of zeolites is important for high sorption ratios. In order to expand those studies and, hopefully, to better relate them to measurements made earlier[3] on tuffs from Jackass Flats, Nevada, four additional Yucca Mountain tuffs are being studied by the batch technique under atmosphere conditions. For comparison, measurements with JA-18 are being repeated.

The YM-30 sample is a densely welded devitrified tuff containing fractures with zeolites. The YM-5 sample is a fresh (glassy) non-welded tuff without zeolites. The YM-42 sample is an immature sandstone with a clay matrix, and the YM-46 sample, a devitrified densely welded vitric crystal tuff, has heavy iron staining but no zeolites.

Only measurements at a sorption time of 3 weeks have been completed to date. Preliminary results are given in Table XVII.

TABLE XVII

SORPTION RATIOS, YUCCA MOUNTAIN TUFF, 3-WEEK

CONTACT TIME, ATMOSPHERIC CONDITIONS

	R_d (mℓ/g)				
Sample	Sr	Cs	Ba	Ce	Eu
YM-42	2 600	15 000	64 000	280 000	37 000
YM-5	180	3 800	600	130 000	120 000
YM-30	94	760	1 800	110 000	7 700
YM-46	81	400	5 800	80 000	93 000
JA-18	14 000	14 000	86 000	1 200	1 400

F. Sorption of Iodine on Argillite (K. Wolfsberg)

1. Measurement Technique. The sorptive behavior of iodine on Eleana argillite (CN-2) was investigated in a procedure similar to that used for iodine sorption on alluvium[10] and tuff.[3] The initial solution for these batch experiments was made by leaching a sample from an underground nuclear test containing volatile fission products with synthetic Eleana argillite groundwater.[2] In addition to ^{131}I, the water also leached small but measureable quantities of ^{74}As, ^{99}Mo, ^{103}Ru, and ^{237}U. Sorption times were 13 and 26 d, and desorption times were 7 and 21 d, respectively. Separate 7-day sorption experiments were performed with the supernates from the earlier 13-day sorption experiments. The purpose of these later experiments was to investigate whether a single iodine species could be sorbed by the argillite from solution, assuming slow rates of change in solutions species. The pH values of all initial and final solutions were in the range of 8.55 to 8.65. Solutions are being retained for chemical analyses. The experiments were performed under atmospheric conditions.

2. Results and Conclusions. The experimental results for iodine show (Table XVIII) small but measureable sorption on the argillite with R_d values for sorption between 2 and 6 mℓ/g. This represents sorption of 10 to 20 percent of the iodine. Values for alluvium[10] and tuff[3] are 20 and 0 mℓ/g, respectively. Values for desorption are significantly higher, as they were for alluvium.[10]

TABLE XVIII

SORPTION RATIOS FOR I, As, Mo, Ru, AND U ON ARGILLITE, (CN-2), ATMOSPHERIC CONDITIONS, 22°C

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g) [a]				
			I	As	Mo	Ru	U
106-150	13.0		2.18 (13)	46 (30)	4 (48)	12 (60)	16 (25)
		7.1	59 (27)				
	25.6		3.72 (7)	48 (21)		14 (38)	
		20.9					
	7.1[b]		3.0 (26)				
355-500	13.0		4.8 (8)	44 (21)	3 (70)	13 (42)	7 (45)
		7.1	46. (28)				
	25.6		5.8 (8)	62 (22)		14 (38)	
		20.9	24. (39)				
	7.1[b]		4.1 (13)				

[a] 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 for change of variables in a moment matrix assuming independence of the variables.

[b] The measurements were made using the supernatant solution from the 13.0 d contact time experiment for the same fraction.

The experiments with the supernates from previous sorption gave approximately the same values. There does not seem to be favored sorption of a single species which does not reform rapidly.

Sorption ratios for molybdenum, ruthenium, and uranium are also low and arsenic values are somewhat higher. There was not enough activity present to allow desorption determinations to be performed.

Only the activity of the liquids was measured since container effects have not been observed for iodine, molybdenum, ruthenium, and uranium.

G. Dependence of the Sorption Ratio on Element Concentration (S. J. DeVilliers)

Experiments have been started to determine the effect of radionuclide concentration on the sorptive behavior of some rock types. This is commonly called the isotherm.

1. Preparation of Materials. The first radionuclide to be used for these investigations is ^{85}Sr. Climax Stock granite and Eleana argillite from the NTS are being used. The 250-355 μm sieve fraction was selected for the CN-1 and CN-2 argillite samples and two different particle sizes, <75 μm and 75-500 μm were selected for the CS-5 granite. All determinations are being conducted under atmospheric conditions and ambient temperature.

Groundwaters were the same synthetic granite[1] and synthetic argillite[2] waters utilized in previous experiments.

Each solid sample was equilibrated with the synthetic groundwater for at least 3 weeks before adding the tagged waters. The waters used to prepare the tracer solutions were rock-pretreated for at least 3 weeks prior to use.

2. Preparation of Tagged Solutions. A $Sr(NO_3)_2$ stock solution, 1.021×10^{-2} M, was prepared as a carrier solution by dissolving 0.2161 g $Sr(NO_3)_2$ in CS-5 rock-pretreated water to make 100 mℓ of solution. For the argillite samples a stock solution, 1.725×10^{-3} M was prepared by dissolving 0.0356 g $Sr(NO_3)_2$ in argillite rock-pretreated water to make 100 mℓ of solution.

Two ^{85}Sr stock solutions were prepared by drying the radionuclide in two plastic bottles and adding 50 mℓ of CS-5 rock-pretreated water to one of the bottles and 50 mℓ of CN-1 rock-pretreated water to the other. Both solutions were placed on a shaker for a few days before filtering through a 0.45 μm Millipore filter.

Five solutions of different Sr^{2+} concentrations were prepared for the granite and argillite samples by dilution and/or mixing of the two stock solutions already discribed for each set of solid samples. These are summarized in Table XIX. After the traced solutions were prepared, an aliquot was taken for assay of radioactivity.

3. Measurements. Pretreated granite and argillite samples are currently being shaken with the five solutions described above. Our standard batch measurement technique[1,2] is being used for contact times of 3 weeks.

H. Migration Rate Studies on Crushed Materials (E. N. Vine, B. P. Bayhurst)

1. Strontium, Cesium, Barium, Cerium, and Europium. Elutions of the columns described in Ref. 8 are continuing. Only ^{85}Sr on JA-37 tuff has been completely eluted since that report. On the same column, ^{137}Cs has not yet been removed, which would indicate an R_d of >270 mℓ/g. (The batch R_d value[3] was 680 ± 170 mℓ/g.) The R_d value for ^{85}Sr calculated from the column data was 106 mℓ/g, compared to a batch value[3] of 300 ± 30 mℓ/g. An R_d value approximately 2 to 3 times lower as obtained by use of the column method is in agreement with our previous results.[8] In each of those cases, the elution curves (for strontium, cesium, and barium on tuff, granite, and argillite) showed the reasonably symmetric peak shapes one generally finds with ion-exchange columns, and all of the activity was eluted in a relatively narrow volume range.

TABLE XIX

CONCENTRATIONS[a] AND pH VALUES FOR THE ISOTHERM MEASUREMENTS

	Granite		Argillite	
Solution	Sr(II) Molarity	pH	Sr(II) Molarity	pH
1	1.28×10^{-3}	7.59	1.44×10^{-3}	8.36
2	1.31×10^{-5}	7.72	1.72×10^{-5}	8.55
3	1.91×10^{-7}	7.70	1.98×10^{-7}	8.51
4	2.07×10^{-8}	7.71	1.97×10^{-8}	8.33
5	2.35×10^{-9}	7.77	2.16×10^{-9}	8.28

[a]Concentration of added tracer and salt; the natural concentration in the ground water is not included.

For several of the columns still being eluted, a more complex situation is evident. For example, after 49 d, at a flow rate ≅1 mℓ/d, ^{137}Cs began to be slowly eluted at a uniform rate from a Climax Stock column of CS-7. At present, 291 d later, approximately 18% of the ^{137}Cs has been removed from the column, indicating that the R_d value is greater than 460 mℓ/g; batch measurements gave about 350 and 530 mℓ/g for sorption and desorption, respectively. Similarly for column CS-5, a slow uniform elution of ^{137}Cs is observed. From the volume of solution eluted to date, a lower limit for the sorption ratio is 520 mℓ/g; batch R_d values are 330 and 730 mℓ/g for sorption and desorption, respectively. Of the crushed tuff columns studied to date only JA-18, which contains unaltered glass and a trace of zeolite, is showing the same kind of "peakless", slow, uniform elution: 7.6% ^{85}Sr and 7.3% ^{137}Cs have been eluted in the first 80 mℓ.

2. Uranium. Since the distribution coefficients measured for uranium(VI) have always been small, the retardation factor is expected to be small. With the use of the columns now used in this laboratory, the volume of eluate of interest will be small enough to require drop collection. A method to perform this has been devised using a syringe pump (Sage model 352) and a fraction collector (ISCO model 1200) used in the drop mode. Aluminum planchets have been made to fit the collection holders. The equipment is contained in a high-humidity enclosure to minimize evaporation of the drops as they form.

The columns are to be loaded with ^{131}I and ^{237}U simultaneously. This will eleminate any uncertainties caused by different conditions during determination of free column volume and radioisotope collection.

The ^{131}I and ^{237}U actvities on each planchet (1 drop) will be determined using a Ge(Li) detector in conjunction with an automatic sample changer. The 208-keV gamma-ray from ^{237}U and the 364-keV gamma-ray from ^{131}I are readily analyzed. Some difficulty has been encountered due to the tendency of iodide to be lost when dried in carrier free form. Experiments are in progress putting various "fixers" (Na_2SO_3 plus $AgNO_3$, and iodide salts) on the planchets before collection of the eluate.

I. Infiltration of Rock Cores (W. R. Daniels and S. Maestas)

The equipment and general technique used to force solutions of radionuclides into or through solid rock cores and the microautoradiographic technique subsequently used to examine those cores were described in Ref. 8, as

were several early experiments. Three additional experiments which are now in progress are discussed below.

1. Strontium in Tuff. About 2.5 x 10^5 cpm of ^{85}Sr in 50 μℓ of rock-pretreated groundwater was placed on the top face of a Yucca Mountain tuff core (YM-22) on June 18, 1979. The YM-22 is a devitrified, densely welded tuff. The system was allowed to stand under confining pressure but with no driving pressure, i.e., zero flow rate, for four days. Filtered, rock-pretreated groundwater has been pumped through the core since that time. The flow rate has been increased several times from an initial value of ≅0.8 mℓ/d for a total of 89 mℓ over 161 d. The residence time of the water on the rock column has probably been at least three days throughout the run. During the first 17 d of flow (2.57 mℓ) 0.6% of the activity was eluted from the rock; the activity per mℓ decreased with time. Very little activity, about 0.7%, was removed from the rock by the next 30 mℓ (60 d). Since that time the concentration of ^{85}Sr in the water has increased gradually in an essentially linear fashion; however, the total amount removed by the first 89 mℓ was only 9.8%.

Since the intent of this experiment was to elute the strontium, it will be continued.

2. Americium in Tuff. Approximately 2 x 10^6 dpm of ^{241}Am in 355 μℓ (≦50 μℓ portions) of synthetic groundwater was placed on the top face of a Yucca Mountain tuff core (YM-45) on November 16, 1979. The YM-45 is a devitrified, welded tuff. The liquid was allowed to dry or soak into the tuff, and then the core was allowed to stand for three days before the driving pressure was applied. The pressure was increased over a period of two days until flow started. Approximately 10 mℓ of water passed through the column during the first 16 d of flow, giving a residence time like five days on the rock. Essentially no ^{241}Am has been eluted. Water will be passed through the rock for several weeks, and then it will be sectioned for examination by microautoradiographic (MAR) and counting techniques in order to study the sorptive behavior.

3. Americium in Granite. A Climax Stock granite core showing signs of a sealed crack was placed in the usual Teflon sleeve and cracked along the pre-existing line by striking. The core was placed under confining pressure and synthetic groundwater was passed through it. The confining pressure was then released, and a clamp was placed around the sleeve. Groundwater traced

with ^{241}Am was placed on the top face of the rock in two 50 μℓ portions; however, addition of the second portion was followed by the appearance of liquid at the bottom of the crack. This excess liquid was removed. Over a period of about 24 h (November 29 and 30, 1979) an estimated 5×10^7 dpm of ^{241}Am in about 160 μℓ of groundwater was dried on the rock or retained in the crack. Confining pressure was applied, and the rock was allowed to stand several days. Considerable difficulty was encountered when trying to force flow using the driving pressure. Between the second and third days 0.85 mℓ was collected, but flow stopped and even with increased pressure did not really start again until day 14. About 12 mℓ passed through the column during the next four days, after which the flow rate was reduced to ≅0.2 mℓ/d, but this varied considerably. A barely detectable amount of ^{241}Am was eluted from the column by the first ≅13 mℓ. Flow will be continued for several weeks, and then the core will be sectioned to examine the sorption behavior using MAR and counting techniques.

J. Microautoradiography (E. N. Vine)

A microautoradiographic technique used to look at americium retained on filter membranes was described previously.[8] Studies of the "sorption" membranes had shown that not only was americium uniformly sorbed on the filter but also that americium species in a large range of particle sizes were retained. Most "desorption" membranes, however, showed only single alpha tracks, suggesting that large particulates were not removed from the solids (assuming they had been sorbed) nor were they formed in the aqueous phase during contact. Since it was not known if any of the complex species or polymers which were found to be present in the sorption solutions had been sorbed and were thus "available" to the desorption solutions, the microautoradiographic technique was used to look at the crushed rock itself, after completion of the desorption experiments. In five rock samples examined, all had "clusters" present indicating that large species were indeed sorbed. However, only in one case did the corresponding desorption solution indicate the (minor) presence of clusters.

K. Materials Characterization (B. P. Bayhurst)

1. Determination of Fe(II) in Silicate Rocks. The presence of Fe(II) and Fe(III) have important effects on the oxidation potential in geological systems. Total iron can easily be determined. However, a good method for

determination of Fe(II) in silicate rocks must involve careful techniques to keep the Fe(II) from oxidizing during preparation, dissolution, and determination. In most procedures, hydrofluoric acid is used. However, this restricts the container composition. The method[11] that has been selected for use is based on a procedure in which the silicate rock is dissolved with the simultaneous oxidation of Fe(II) with ICl to form I_2. This is immediately extracted into carbon tetrachloride which is present in the dissolving vessel. Iodine monochloride has a lower oxidation potential than either permanganate or dichromate. Therefore, Mn(II) and Cr(III) do not interfere. The pertinent half-cell reactions are:

$$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O \qquad E^\circ = +1.52\ V$$

$$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O \qquad E^\circ = +1.33\ V$$

$$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O \qquad E^\circ = +1.23\ V$$

$$2I^+(Cl^-) + 2e = I_2 + 2Cl^- \qquad E^\circ = +1.19\ V$$

$$Fe^{3+} + e = Fe^{2+} \qquad E^\circ = 0.77\ V\ .$$

The method described above has been modified and tested on several USGS "standard" rocks. The results (see Table XX) were usually within 2% of the stated Fe(II) concentration. The I_2 was determined by titration with a standardized KIO_3 solution under conditions where the carbon tetrachloride containing the iodine was kept from contact with the air.

The Fe(II) content of the rocks being studied in this laboratory will be determined for many of the systems already utilized: rock samples from studies performed under atmospheric and controlled-atmosphere conditions, rock samples and samples pretreated with groundwater, and rock samples ground with and without oxygen being present.

2. Determination of Fe(II) in Groundwater. Knowledge of the Fe(II)/Fe(III) concentration ratio in waters that have been pretreated with rocks under various conditions would help in the interpretation of sorption results for multivalent elements and help to substantiate laboratory Eh measurements. A method modified from that of Lee and Stumm[12] is being used. The limit of detection is about 0.2 μg/mℓ. The small interference of Fe(III) is corrected for. The

TABLE XX

Fe(II) ANALYSES ON USGS "STANDARD" ROCKS

	% FeO		%
	LASL	USGS	Deviation
DTS-1 (Dunite)	7.26	7.23	+0.4
PCC-1 (Peridotite)	5.11	5.24	-2.5
BCR-1 (Basalt)	8.81	8.80	+0.1
GSP-1 (Granodiorite)	2.23	2.31	-3.5
AGV-1 (Andesite)	2.02	2.05	-1.5

4,7-diphenyl-1,10-phenanthroline reagent used is more sensitive and the color developed is more stable than other phenanthrolines. Iron-free reagents have been prepared, and preliminary measurements are being attempted.

3. Determination of Redox Potentials in Groundwater. The method used by Grenthe[13] is being tested for use in measurement of redox potentials. Salt bridges have been constructed for use in determining Eh with a gold electrode in the half-cell used for the sample and a half-cell containing a silver electrode.

The measurements of the redox potentials of waters under controlled-atmosphere and atmospheric conditions and after equilibration with rocks under investigation will be studied.

V. CHEMISTRY STUDIES IN THE CURRENT QUARTER (T. W. Newton, and R. D. Aguilar)

The solubilities of the lighter actinide oxides and hydroxides (for example PuO_2 and $PuO_2 \cdot nH_2O$) depend not only on the pH of the solution, but also on the Eh. In order to illustrate this, we have calculated "contour maps" showing lines of constant solubility for the hydrous oxides of uranium, neptunium, and plutonium. The results are shown in Figs. 1-3. Many of the quantities required for the calculations are unknown, but various estimates have been published. For our purposes we have used the values recently selected by B. Allard et al.[17] (Tables XXI - XXIII). Although the accuracy of these data may be improved by future experiments, they are sufficient to show the complexity of the solubility

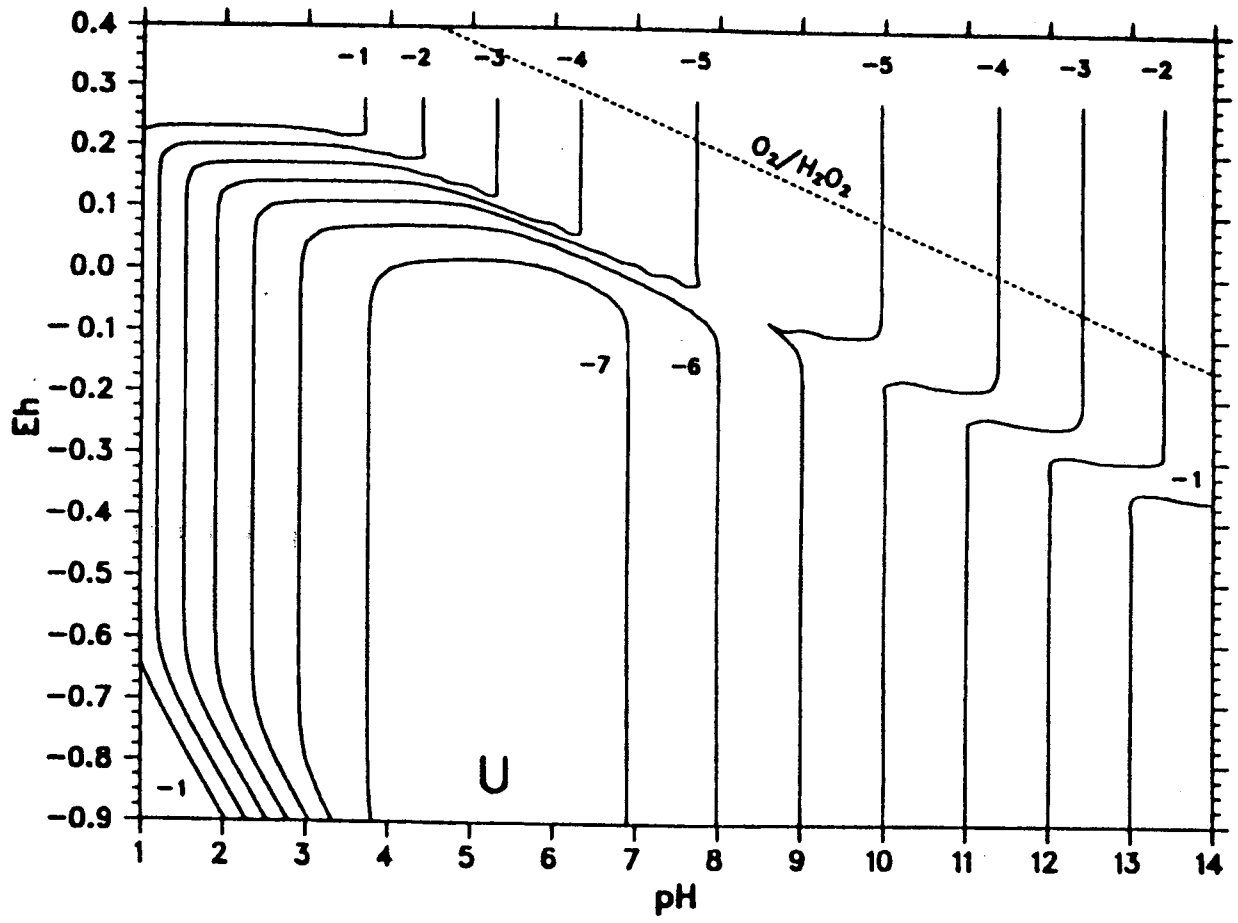

Fig. 1. Lines of Constant Uranium log(Solubility) vs. Eh and pH.

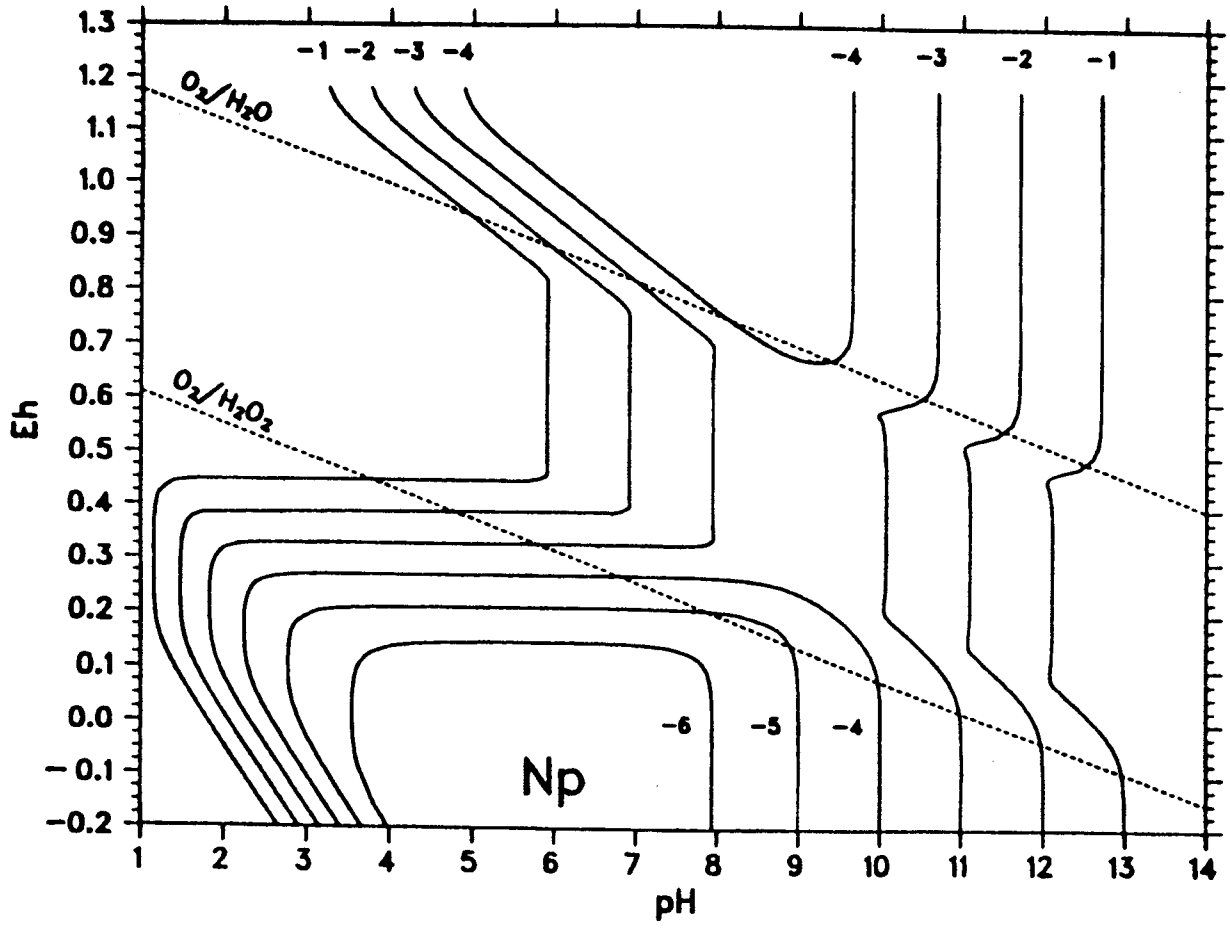

Fig. 2. Lines of Constant Neptunium log(Solubility) vs. Eh and pH.

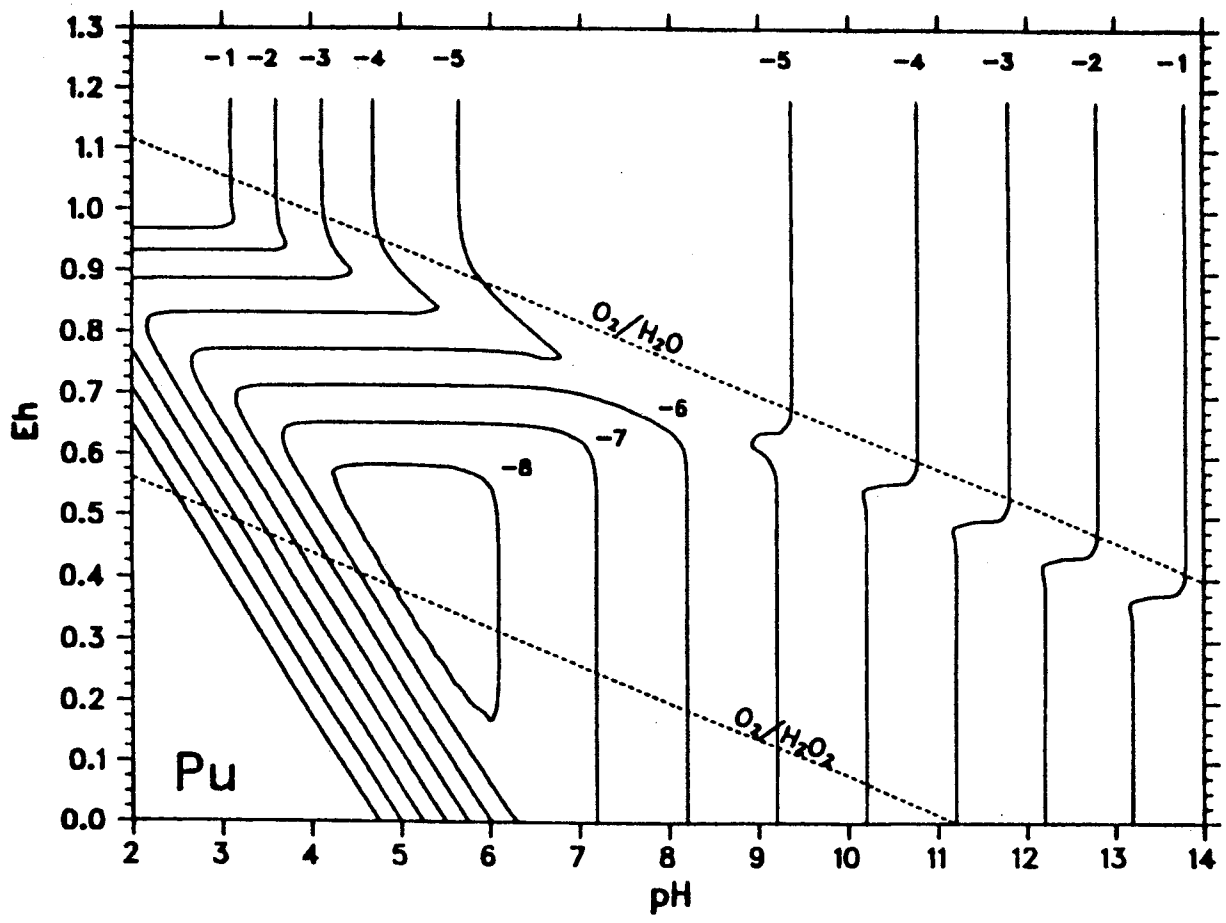

Fig. 3. Lines of Constant Plutonium log(Solubility) vs. Eh and pH.

TABLE XXI

EQUILIBRIUM CONSTANTS (LOG K) AT 25°C
AND ZERO IONIC STRENGTH FROM REF. 17

Reaction[a]	U	Np	Pu
Trivalent			
$ML/M.L$	7 ± 1	6.6 ± 0.5	7.2 ± 0.
$ML_2/M.L^2$	11 ± 2	11 ± 1	12.1 ± 1.
$ML_3/M.L^3$	15 ± 3	15 ± 2	16.7 ± 1.
$ML_4/M.L^4$	17 ± 4	18 ± 2	20.2 ± 2.
$M_2L_2/M^2.L^2$	15 ± 2	15 ± 2	16 ± 2.
Tetravalent			
$ML/M.L$	13.4 ± 0.4	13.2 ± 0.4	13.7 ± 0.3
$ML_2/M.L^2$	25.5 ± 0.8	25.2 ± 0.7	25.7 ± 0.6
$ML_3/M.L^3$	36.6 ± 1.2	36.4 ± 1.1	36.7 ± 0.9
$ML_4/M.L^4$	46.3 ± 1.6	46.1 ± 1.4	46.5 ± 1.2
$ML_5/M.L^5$	54.0 ± 2.0	53 ± 2	55 ± 2
$M_2L_2/M^2.L^2$	27 ± 3	26 ± 3	27 ± 3
$M_2L_3/M^2.L^3$	40 ± 4	39 ± 4	40 ± 4
$M_2L_4/M^2.L^4$	52 ± 5	51 ± 5	53 ± 5
$M_2L_5/M^2.L^5$	62 ± 6	61 ± 6	63 ± 6
Pentavalent			
$ML/M.L$	4 ± 1	5.0 ± 0.8	4.3 ± 0.8
$ML_2/M.L^2$	8 ± 2	10 ± 2	9 ± 2
Hexavalent			
$ML/M.L$	8.1 ± 0.2	9.1 ± 0.5	8.9 ± 0.3
$ML_2/M.L^2$	17.2 ± 0.8	17.8 ± 0.8	17.6 ± 0.5
$ML_3/M.L^3$	21 ± 2	23 ± 2	22 ± 2
$M_2L/M^2.L$	9.6 ± 0.5	10 ± 2	10 ± 2
$M_2L_2/M^2.L^2$	22.4 ± 0.2	21.6 ± 0.8	20.3 ± 0.3
$M_3L_4/M^3.L^4$	44.2 ± 0.5	43 ± 2	41 ± 2
$M_3L_5/M^3.L^5$	55 ± 1	53 ± 1	50.0 ± 0.5

[a]M stands for actinide and L stands for hydroxide.

TABLE XXII

log(SOLUBILITY PRODUCT) FROM REF. 17

Reaction[a]	U	Np	Pu
Trivalent			
$M.L^3/ML_3(s)$	-24 ± 3	-24 ± 2	-25 ± 2
Tetravalent			
$M.L^4/ML_4(s)$	-54 ± 2	-53 ± 2	-55.2 ± 1.2
$M.L^4/MO_2(s)$	-57.8 ± 2.0	-58.7 ± 2.0	-62.5 ± 1.2
Pentavalent			
M.L/ML(s)	-9 ± 2	-9.1 ± 1.0	-9.3 ± 1.0
Hexavalent			
$M.L^2/ML_2(s)$	-22.4 ± 0.2	-22.7 ± 1.2	-22.8 ± 1.0

TABLE XXIII

STANDARD POTENTIALS FOR U, Np, AND Pu FROM REF. 17

Valence Change	E° (V)		
	U	Np	Pu
IV-III	0.596	0.190	1.017
V-IV	0.558	0.684	1.115
VI-V	0.080	1.153	0.933

diagrams. The problem is complicated by the fact that hydroxides or oxides of the different oxidation states are stable at different Eh values, and further that amorphous hydrous oxides such as $PuO_2 \cdot nH_2O$ appear to be only metastable with respect to the crystalline oxides such as PuO_2. Our calculations are based on the assumption that the amorphous oxides can be oxidized or reduced depending on the Eh, but that conversion to the crystalline form is a much slower process. The data indicate that the hydroxides of U(III), Np(III), Pu(III), U(V), and Pu(V) are not stable in the Eh-pH range investigated.

The calculations are compilicated enough so that it was worthwhile to write a program so that they could be done by computer. The method of calculation is outlined in the Appendix. The availability of this program makes it a very simple matter to examine the effects of different assumed values for the approximately 25 parameters required for the calculation. For example, the solubility product for $PuO_2(c)$ rather than that for $PuO_2 \cdot nH_2O$ could be used to illustrate the solubility behavior if equilibrium with the crystalline oxide were attained.

VI. PROBLEM AREAS

No extrinsic problems are impeding this work.

VII. 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, controlled atmosphere conditions
   1. Continue the measurements for technetium, plutonium, americium, and uranium.
   2. Continue the measurements for strontium, cesium, barium, cerium, and europium.

B. Migration rate studies
   1. Crushed rock columns.
      a. Continue studies on granite.
      b. Continue studies on argillite.
      c. Begin uranium studies.
   2. Whole cores: continue fracture flow (granite) studies.
   3. Begin studies on kinetic parameters.

C. Batch sorption measurements, natural atmospheric conditions.
   1. Measurements of sorption isotherms for granite and argillite.
      a. Continue strontium measurements.
      b. Begin studies for cesium and barium.
   2. Continue plutonium and americium studies.

D. Microautoradiography.

1. Continue uranium, plutonium, neptunium, and americium sorption studies on petrographic thin-sections.
2. Continue development of procedure for determining the microstructural distribution of α-emitters on infiltrated rocks.

E. Redox potentials in groundwater

1. Continue development of analysis procedure for Fe(II).
   a. Silicate rocks.
   b. Groundwater.
2. Continue development of Eh electrode.

E. 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 the materials used for the controlled-atmosphere measurements (LASL Group G-6).

F. Chemistry studies.

1. Solubility calculations.
   a. Sensitivity analysis.
   b. Add PuO_2(s) phase.
2. Begin literature search related to Eh buffers.

VIII. RECENT PUBLICATIONS

None.

IX. ORAL PRESENTATIONS

B. R. Erdal, B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, G. M. Heiken, F. O. Lawrence, M. L. Lykes, J. R. Smyth, J. L. Thompson, E. N. Vine, and K. Wolfsberg, "Parameters Affecting Radionuclide Migration in Geologic Media,"

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APPENDIX

CALCULATION OF Pu, U, AND Np SOLUBILITIES AS A FUNCTION OF Eh AND pH

T. W. Newton

The input for the calculations included the following: 1) the set of Eh and pH values to be examined; 2) the solubility products for the possible solid species, e.g., $Pu(OH)_3$, $PuO_2 \cdot nH_2O$, PuO_2OH, and $PuO_2(OH)_2$; 3) the oxidation potentials, at unit activity, of hydrogen ion and the unhydrolyzed metal ions for the M^{3+}-M^{4+}, M^{4+}-MO_2^{+}, and MO_2^{+}-MO_2^{2+} couples; and 4) the hydroxide association constants for all the hydrolyzed species assumed to be present (Table XXII). These latter constants were defined by

$$\beta_{ij} = \frac{(M_iOH_j)}{(M^i)\ (OH^-)^j}$$

where M represents M^{3+}, M^{4+}, MO_2^{+} or MO_2^{2+}.

Reliable values for all the thermodynamic quantities listed above are not available. However, for the purpose of illustrating the general behavior of the solubility, it is sufficient to use the set of reasonable estimates provided by Allard, et al. (Tables XXI and XXII).

The calculations involved the following steps. First, for each pH value, the four solubility products were used to calculate the hypothetical concentration of the four unhydrolyzed ions (M^{3+}, M^{4+}, MO_2^{+}, and MO_2^{2+}). In general, only one of the four solid phases is stable with respect to the others.

Next, the stable phase at each Eh and pH value was determined by comparing the various ratios of the concentrations calculated in first step with the ratios required by the chosen Eh value and the Nernst equation. For example, if the $(PuO_2^{2+})/(Pu^{4+})$ ratio from the solubility products were greater than that from

$$Eh = E^\circ\ (IV\text{-}VI) + \frac{0.05915}{2} \log \frac{(PuO_2^{2+})\ (H^+)^4}{(Pu^{4+})}$$

then $PuO_2(OH)_2$ would be unstable with respect to $PuO_2 \cdot nH_2O$.

The concentration of the unhydrolyzed ion of the same oxidation state as the stable solid, calculated in the first step, was then used with each Eh value and the appropriate Nernst equation to calculate the concentrations of the other three unhydrolyzed ions. The sum of the concentrations of all species in each oxidation state was then calculated from the pH using the expression

$$\Sigma \text{ concentrations} = (M)(1 + \sum_{ij} i\beta_{ij}(M)^{i-1}(OH^-)^j).$$

The total solubility at each Eh and pH was then calculated from the sums for the individual oxidation states, and finally a simple linear interpolation scheme was use to find the values for Eh and pH that give solubility values that are integral powers of 10.

The calculations were run on the VAX-11/780 computer in LASL Group CNC-2.