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RADIONUCLIDE TRANSPORT AND RETARDATION IN TUFF

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INTRODUCTION

The suitability of tuff at the Nevada Test Site (NTS) for the isolation of radioactive waste is being investigated as part of the Nevada Nuclear Waste Storage Investigations. Tuff is a geological term applied to pyroclastic rocks composed of particles fragmented and ejected during volcanic eruptions. Such deposits are complex and may exhibit a wide range of properties, depending on their cooling and alteration history (see, for example, Ref. 1).

The migration of radionuclides from a deep geologic nuclear waste repository would likely be the result of transport by groundwater. Retardation due to interactions with the surrounding geologic media should be a significant factor in minimizing such transport. Many lithologic types of tuff contain highly sorptive minerals. In addition, long hydrologic flow paths are typical of the NTS. These are both important reasons for the consideration of tuff as a geologic medium for isolation of radioactive waste.

An understanding of the mechanisms of transport and sorption-desorption is essential for prediction of the behavior of radionuclides during the time required for decay to safe levels and, thus, for demonstration of the effectiveness of tuff, or any potential medium. Sorptive properties of tuff are being studied with both static (batch measurements) and dynamic methods (crushed and solid rock columns). Studies were made on tuff core samples from two drillholes at the NTS: J-13 (Jackass Flats)[2] and UE25a-1 (Yucca Mountain).[3] Water from well J-13 was pretreated at least two weeks with crushed tuff from the core being studied prior to use in the experiments.

The distribution coefficient, K_d, is commonly used to describe the partition of a radionuclide between solid and aqueous phases. K_d is defined as the concentration of a species per gram solid phase divided by its concentration per milliliter in the liquid phase at equilibrium. The term sorption ratio, R_d, which does not imply equilibrium but is otherwise identical to K_d is used here. In column experiments the relative velocity of a radionuclide with respect to the groundwater velocity is measured. This retardation factor, R_f, is related to the sorption ratio R_d, or K_d, by the simple expression $R_f = (\rho/\varepsilon)R_d + 1$, where ρ is the density of the rock column and ε is the porosity.

The sorption ratios calculated from flow measurements can be compared with data obtained by batch techniques. Because the batch experiments are simple and fast, it is feasible to measure the influence on R_d of a large number of parameters. It is hoped that such comparisons will lead to an understanding of the relationship between behavior in a dynamic laboratory experiment (and, ultimately, behavior in the field) and the many available batch R_d data.

SORPTION PROPERTIES: BATCH MEASUREMENTS

Several parameters were studied with batch experiments. Details of the batch technique and tracer preparation used have been reported.[4-7] Particle size had the least effect on R_d values; little or no variation was obtained among fractions of <106 μm, 106-150 μm, 355-500 μm and 106-500 μm. Measurements were also made at two temperatures and sorption ratios at 70°C were generally greater than at 22°C. Strontium, cesium, and barium sorption ratios increased by factors of approximately 1.5 to 4, 1 to 2.8, and 2.5 to 5.6, respectively. Americium values changed very little. Increases in R_d with sorption time were often observed, although the changes were generally small.

The effects of atmosphere on sorption behavior were investigated by comparing the results of studies performed in a pure nitrogen atmosphere having ≤0.2 ppm oxygen and ≤20 ppm carbon dioxide present with similar measurements made under natural atmospheric conditions on the same materials. The controlled-atmosphere studies are not truly representative of the conditions to be found in deep geologic systems since essentially no carbon dioxide was present and bicarbonate may have been lost from solution. However, the pH values when the rock was in solution were similar to those observed under atmospheric conditions, indicating that the rocks themselves may have supplied some bicarbonate ion buffering. The effects of atmosphere are summarized in Table 1. The sorption ratios for technetium were most affected and were higher when measured under controlled atmosphere conditions, as was the sorption of plutonium. For tuff samples YM-22 and YM-54 the sorption ratios of uranium were not affected by atmosphere; however, they were somewhat higher in a nitrogen atmosphere for YM-38 (zeolitized tuff). U(VI) was apparently not reduced to U(IV); only on zeolitized tuff YM-38 did the sorption ratio of uranium increase in the nitrogen atmosphere.

TABLE 1

Comparison of Sorption Ratios[a,b] (mℓ/g) Measured under Atmospheric and Controlled-Atmosphere Conditions

	YM-22		YM-38		YM-54	
	Air	Controlled	Air	Controlled	Air	Controlled
^{237}Pu	140(27)	220(21)	250(35)	800(11)	84(20)	120(24)
^{241}Am	4000(30)	1400(15)	5500(20)	5600(17)	590(34)	1000(22)
^{237}U	1.9(36)	0.48(140)	5.3(14)	14.7(7.1)	1.5(43)	1.48(43)
^{137}Cs	384(1.1)	243(1.8)	7870(2.6)	8515(4.2)	238(1.3)	246(1.8)
^{85}Sr	52.2(1.1)	56.5(1.9)	9880(2.0)	7900(3.7)	89(1.2)	84.9(1.7)
^{133}Ba	914(1.2)	210(1.6)	40500(3.9)	36300(11.9)	601(1.1)	426(1.2)
^{141}Ce	1348(2.1)	672(3.6)	675(3.7)	592(4.3)	141(1.8)	127(2.9)
^{152}Eu	1378(2.0)	751(2.8)	1670(3.8)	935(6.1)	443(2.0)	383(2.5)
^{95m}Tc	0.3[1.2]	2.1[18]	0.2[c]	2.8[120]		2.7[79]

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[a] Standard deviations expressed in percent are given in parentheses

[b] Desorption values are given in brackets.

[c] Value obtained using two similar, zeolitized tuffs

The U(VI) may remain strongly complexed, probably by carbonate, in all of these groundwaters. As expected, strontium, cesium, and barium were least affected by the presence or absence of oxygen and carbon dioxide. Although cerium and europium were also unaffected on tuffs, sorption of both those elements increased by a factor of 10 or more in a nitrogen atmosphere on granite and argillite.[7] We have been able to observe apparently negative E_h values only on some tuff-water systems; none on granite or argillite systems.

Groundwater composition may also influence the sorption ratio for many radionuclides. The compositions of the two solutions used were selected to represent extremes for media being studied. While the dependence of the sorption ratio on specific major ion concentrations could not be determined since the concentrations of several ions were simultaneously varied, overall effects were distinguished. The approximate initial compositions of the two solutions prepared and the amounts of the corresponding elements in water from well J-13 are given in Table 2. Results are also given for sorption times of ~60 days along with average sorption ratios (at ~40 days) of the same tuff samples and radionuclides in pretreated J-13 water for comparison. Water from well J-13 is intermediate in concentration compared to solutions I and II, and, in general, R_d values with J-13 water are also intermediate. The results indicate the importance of determining both the cation and anion compositions of the solutions used in making R_d measurements.

In addition to providing information on the influence of numerous variables, batch measurements are also providing relative sorption data on a wide variety of lithologic types of tuff. Although minor components in a rock sample can certainly play a major role in sorption, there is a fairly good correlation between sorption and major phases, as determined by x-ray diffraction, in the tuffs studied to date. Average sorption ratios are shown in Table 3,

TABLE 2

The Effect of Groundwater Composition on Sorption Ratios (mℓ/g)

Sample	Water[a]	Cs	Sr	Ba	Ce	Eu
JA-18	I	15200(7.6)	2700(7.5)	119000(12.9)	1470(11.3)	1700(10.7)
	II	8440(6.0)	4850(3.0)	82200(7.6)	≥34200	15400(10.6)
	J-13	13900	16200	86000	2900	570
JA-32	I	143(3.7)	85.0(2.0)	65.6(2.1)	≥54700	4200(7.6)
	II	73.0(3.3)	17.7(4.4)	182(1.8)	≥45900	≥61000
	J-13	130	63	479	---	---
JA-37	I	1390(3.6)	385(1.8)	882(1.9)	≥48400	≥25600
	II	757(7.8)	149(2.4)	339(1.8)	≥33000	50900(10.0)
	J-13	763	303	898	---	---

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[a] Water I, pH 8.17. Constituents (mg/ℓ): Na(10), K(5), Ca(10), Mg(2), SO_4(5), Cl(4.5)
Water II, pH 8.62. Constituents (mg/ℓ): Na(50), K(5), Ca(50), Mg(20), SO_4(70), Cl(15)
J-13 Water, pH 8.32. Constituents (mg/ℓ): Na(50), K(5), Ca(13), Mg(2), SO_4(20), Cl(7.6)

along with the approximate percentages of major phases (J. R. Smyth, Los Alamos Scientific Laboratory, personal communication, 1980). The devitrified tuff YM-54 has among the lowest sorption ratios of the samples studied. Cores YM-26 and YM-28 contain analcime in addition to quartz and feldspar, yet sorption ratios on those tuffs have R_d values very similar to those for YM-54. Analcime apparently does not behave as the zeolite clinoptilolite (and heulandite); sorption ratios for strontium, cesium, and barium on tuffs YM-42, YM-49, YM-38, and YM-48, all with clinoptilolite (or heulandite), are at least one to two orders of magnitude larger than analcime-containing cores. Cerium and europium sorption, however, does not seem to be dependent on zeolite content. Ranges of sorption values obtained on samples containing quartz and feldspar (with and without analcime), samples containing glass (with and without clay) and samples containing clinoptilolite (heulandite) are summarized in Table 4. Intermediate values for strontium, cesium, and barium were obtained on glassy cores. Additional samples now being studied include tuffs containing primarily cristobalite and feldspar, mordenite and clinoptilolite, glass, or montmorillonite. As more samples are studied, a more detailed correlation may be possible.

SORPTION PROPERTIES: COLUMN MEASUREMENTS

Crushed Rock Columns

The migration of radionuclides through crushed-rock-core columns (35-106 μm) was measured. Batch sorption ratios measured on the same cores provide a comparison with the column results. A description of the columns and apparatus used was published elsewhere.[7] Groundwater from well J-13 pretreated with crushed tuff was

TABLE 3

Sorption Ratio vs. Mineralogy

Tuff	Major Phases, ≥20%	R_d (mℓ/g) Sr	 Cs	 Ba	 Ce	 Eu
YM-54	quartz, feldspar	90	250	620	140	500
YM-22	quartz, feldspar	53	340	980	1400	1400
YM-26[a]	quartz, (feldspar)[b], analcime	35	487	209	305	118
YM-28[a]	quartz, (feldspar)[b], analcime	111	1230	720	1350	1170
YM-42	quartz, feldspar, clinoptilolite	2780	15300	42600	36400	49700
YM-49	clinoptilolite	2700	29000	33000	550	1200
JA-18	glass, clinoptilolite	~20000	16000	~70000	2600	1400
YM-38	feldspar, cristobalite, clinoptilolite	12000	86000	66000	830	2300
YM-5	glass	268	7640	1011	23700	19900
JA-8[a]	glass, clay	305	1963	358		1710
YM-48	glass, feldspar, (clinoptilolite)[b]	1800	17000	15000	1900	2300

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[a] Preliminary results, measurements still in progress.

[b] Abundance approximately 15%

TABLE 4

Ranges of Sorption Ratios (mℓ/g)

MAJOR PHASES	Sr	Cs	Ba	Ce	Eu
quartz, feldspar (+/- analcime)	35-100	250-1200	210-980	140-1400	500-1400
glass (+/- clay)	270-300	2000-7600	360-1000	24000	1700-20000
clinoptilolite (heulandite)	1800-28000	8600-17000	1500-130000	550-36400	1200-49700

used, and generally the columns were loaded with small (~10 μℓ) spikes of tracer. Flow rates generally ranged from 0.041-0.082 mℓ/h (30-60 m/y). The free column volumes (used to calculate the effective column porosity) were determined with both HTO and $^{131}I^-$, which gave identical results.

The calculated column sorption ratios for the isotopes ^{85}Sr, ^{137}Cs, and ^{133}Ba are given in Table 5 with data from batch sorption measurements for comparison. Several kinds of elution behavior were observed: symmetric peaks where fifty percent of the activity was eluted at the peak, asymmetric peaks, and "no peaks" - but instead a slow, usually uniform elution. With the exception of a J-18 column, the elution curves of ^{85}Sr were symmetric, and the column R_d values were one to three times lower than the corresponding batch R_d value. The JA-18 batch R_d value for ^{85}Sr was >10,000 mℓ/g. Strontium on a JA-18 column was eluted at a rate of ~0.07%/day for ~72 days, then a small, sharp peak was observed. Elution of JA-18 was continued, and the slow, uniform "leaking" resumed. JA-18 is a highly glassy tuff, and the slow elution may be due to a gradual dissolution of the glass. This, however, would

TABLE 5

A Comparison of Batch and Column R_d Values (mℓ/g)

Column	^{85}Sr		^{137}Cs		^{133}Ba	
	Batch	Column	Batch	Column	Batch	Column
YM-22 (core)	50	20				
YM-22 (crushed)	50	30	287	122	899	355
YM-38			8600	>"21900"		
YM-54	84	44	247	97	620	124
JA-18	16000	381(9%)[a]	6600- 15000	(b)	4800	(b)
JA-32	56	42				
JA-37	300	106	740	>560[b]		

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[a] Slow, "peakless" elution.

[b] In progress.

not explain the weak, sharp peak which seems to indicate that more than one "sorption" mechanism exists. Columns of JA-18 and YM-38 tuff were also loaded with ^{137}Cs, and the same slow "leaking", without a sharp peak, was observed. The slow elution of ^{85}Sr and ^{137}Cs might be the result of exchange of the sorbed radioactive species with stable isotopes in the waters used, which contain ~10^{-9} M cesium and ~6×10^{-7} M strontium.

Three JA-32 columns were loaded with ^{85}Sr and flow rates from 0.082 mℓ/h to 18 mℓ/h were used. The sorption ratio from a fast-flow column, run with ^{85}Sr added to the groundwater, was identical to that obtained from a slow-flow column loaded with a spike. However, an increase of 50% in R_d was obtained on another spike-loaded column run at a fast flow rate. When two granite columns were loaded with spikes of activity and run at 0.04 mℓ/h and 4.98 mℓ/h, a considerable increase in R_d was also observed at the faster flow rate.

Cesium column data are given in Table 5. The most straightforward results are from tuff columns of YM-54 (3 columns) and YM-22 (1 column), where the batch sorption ratios are fairly small and values from desorption and sorption experiments are approximately equal. Elution of the activity occurred in a peak. The three YM-54 columns were run at two ^{137}Cs concentrations, 10^{-6} M and 10^{-9} M; the R_d value calculated for cesium was not affected by the cesium ion concentration. On the JA-37 column there was a gradual elution of ^{137}Cs. In another column, ^{137}Cs was loaded onto YM-38 and run at 4-5 mℓ/h. Fifty percent of the total ^{137}Cs was eluted in 7680 mℓ, in slowly increasing amounts. A sharp peak was never observed. A "column R_d" value of 21900 mℓ/g could only be estimated from the volume required to elute 50% of the activity. This value is well above that obtained in batch measurements (8600 mℓ/g) and is probably due in part to the fast flow rate used. It is also indicative of the "complications" revealed by flow experiments.

Other isotopes studied were ^{237}U and ^{133}Ba. The columns completed with ^{133}Ba showed peaks, followed in some cases by a gradual elution of activity. The R_d values are ~2 to 5 times lower than the corresponding batch K_d values. An R_d value of 0.72 mℓ/g for uranium was obtained on tuff YM-54. The uranium peak was quite asymmetric, and the activity eluted per mℓ slowly decreased. Again, the marked asymmetry could be an effect of the complicated "sorption" illustrated by the large difference between batch sorption (1.5 mℓ/g) and desorption (11 mℓ/g) ratios.

Whole Core Columns

Because studies using crushed rock involve newly exposed mineral surfaces, experiments with intact rock cores were also undertaken. Such measurements should provide a better understanding of transport of radionuclides through rock, either by porous or fracture flow. In addition, they are an intermediate step in the extrapolation from batch and crushed-rock column studies to the field.

An "elution" curve was obtained on one tuff core YM-22, which was 15.9 mm high and 25.4 mm in diameter. The apparatus has been described elsewhere.[7] Approximately 40% of the ^{85}Sr loaded was eluted at a fairly constant, "peakless," rate in one year. The estimated sorption ratio of ~20 mℓ/g is less than the value obtained from batch measurements and similar to the value obtained on a column of YM-22. Other intact (and fractured) rock columns now being eluted should indicate whether this is a general trend.

SORPTION PROPERTIES: CIRCULATING SYSTEM MEASUREMENTS

Sorption ratios measured using a batch technique have frequently been observed[6,7] to increase slowly with contact time. A series of measurements were initiated to determine whether this effect is due to "weathering," and self-grinding which occur during the shaking operation used in the batch technique. A circulating system was developed in which a 355-500 μm fraction of crushed tuff, placed in a 1.0 cm diameter x 5.0 cm long polycarbonate tube, was contacted with groundwater continuously circulated through the crushed tuff in a closed loop. The tuff was held in place with polyethylene bed supports and polyproplyene Luer fittings at each end. Three tuff samples of ~4.5 g each were used: JA-37, YM-22, and YM-54. Results from groundwater tagged with ^{85}Sr, ^{137}Cs, ^{133}Ba are given in Table 6. In general, results from the circulating system are comparable to those from crushed rock columns and lower than those from batch measurements.

CONCLUSIONS

Batch measurements provide an understanding of which experimental variables are important. For example, sorption ratios vary little with particle size (and surface area); however, groundwater composition and rock composition are quite important. A general correlation has been identified between mineralogy (major phases) and degree of sorption for strontium, cesium, and barium. Although these are approximate, a more detailed analysis may be possible as more samples are studied and the data base increased.

Data from crushed tuff columns indicate that, except in simple cases where sorption coefficients are relatively low, and ion-exchange equilibria not only exist but are the dominant mechanism for removal of radioisotopes from solution, the simple relation between the sorption ratio R_d (or K_d) and the relative velocity of radionuclides with respect to groundwater velocity may be insufficient to permit accurate modeling of the retardation of radionuclides. Additional work on whole core columns and larger blocks of intact material is required to better understand radionuclide sorption and transport through rock.

TABLE 6

Sorption Ratios on Crushed Tuffs in mℓ/g

	Batch			Circulating System			Columns		
Sample	Sr	Cs	Ba	Sr	Cs	Ba	Sr	Cs	Ba
YM-22	51	264	945	28	423	129	30	122	355
YM-54	84	247	653	47	131	137	44	97	124
JA-37	283	627	747	396	1820	886	106	---	---

References

1. C. S. Ross and R. L. Smith, "Ash-Flow Tuffs: Their Origen, Geologic Relations, and Identification," U. S. Geol. Soc. Prof. Paper 366 (1961).
2. G. H. Heiken and M. L. Bevier, "Petrology of Tuff Units from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos Scientific Laboratory report LA-7563-MS (1979).
3. M. L. Sykes, G. H. Heiken, and J. R. Smyth, "Mineralogy and Petrology of Tuff Units from the UE25A-1 Drill Site, Yucca Mountain, Nevada," Los Alamos Scientific Laboratory report LA-8139-MS (1979).
4. B. R. Erdal et al., "Sorption-Desorption Studies on Argillite," Los Alamos Scientific Laboratory report LA-7455-MS (1979).
5. B. R. Erdal et al., "Sorption-Desorption Studies on Granite," Los Alamos Scientific Laboratory report LA-7456-MS (1979).
6. K. Wolfsberg et al., "Sorption-Desorption Studies on Tuff. I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada," Los Alamos Scientific Laboratory report LA-7480-MS (1979).
7. E. N. Vine et al., "Sorption-Desorption Studies on Tuff. II. A Continuation of Studies with Samples from Jackass Flats, Nevada and Initial Studies with Samples from Yucca Mountain, Nevada," Los Alamos Scientific Laboratory report LA-8110-MS (1980).