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TITLE: CURRENT STATUS OF LABORATORY SORPTION STUDIES

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CURRENT STATUS OF LABORATORY SORPTION STUDIES

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ABSTRACT

LASL batch sorption methodology was used to obtain data on granite, argillite, and tuff samples. Effects of solution-to-solid ratio, isotope concentration, atmosphere, and mineralogy were investigated for the elements strontium, cesium, barium, cerium, europium, technetium, uranium, plutonium, and americium. A circulating system was used in making sorption measurements for comparison with conventional batch techniques. The mineralogy of several tuff, granite, and argillite samples was studied and compared with sorption ratios. A significant correlation between sorption of strontium, cesium, and barium and major rock phases was observed.

INTRODUCTION

The LASL batch sorption methodology (Erdal, et al. 1979-1, 1979-2, Wolfsberg, et al. 1979) was used to obtain data on several variables that influence sorption-desorption behavior. The sorption studies were limited to granite, argillite, and tuff. Although many of the results on tuff were 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, they are included because together with data obtained on granite and argillite they provide a more comprehensive basis for relating sorption and mineralogy.

DISCUSSION

Batch measurements have the advantage of being simple and relatively fast, enabling us to study the influence of many parameters. Although batch sorption ratios (R_d) alone may have questionable value for extrapolating to flow conditions in intact rock, either in the laboratory or in the field, a comparison of sorption ratios obtained by batch measurements where experimental parameters have been varied to observe the effect of those parameters certainly can be of value. A few of the parameters which could influence sorption are discussed here.

Solution-to-Solid Ratios

A series of batch measurements on granite at ambient temperature for 3 weeks in air were completed for solution-to-solid ratios of 5:1, 10:1, and 30:1. The same solution, in varying amounts, was used for all measurements. Five isotopes, ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu, were studied simultaneously. The ^{85}Sr was at a concentration of $\sim 10^{-9}$ M, and the other isotopes were at concentrations of $\sim 10^{-7}$ M. As shown in Table 1, little or no difference in sorption ratios was observed for ^{133}Ba, ^{141}Ce, or ^{152}Eu. The R_d's for ^{85}Sr and ^{137}Cs, however, increased as the solution-to-solid ratio increased, perhaps indicating a larger number of sorption

TABLE 1. Variation of R_d With Solution-to-Solid Ratio on Granite

Solution:Solid Ratio (mℓ/g)	R_d (mℓ/g)				
	Cs	Sr	Ba	Ce	Eu
5:1	738	47.8	1170	133	474
10:1	1130	32.3	1000	105	362
30:1	2190	141	998	158	570

sites available to those two isotopes. Measurements at additional times and on other crushed rocks are in progress. It should be noted that the solution-to-solid ratio in porous rocks is less than one.

Sorption vs. Concentration

Carrier stock solutions were prepared by adding europium, strontium, or barium nitrate, or cesium chloride to synthetic groundwater which had been pretreated with argillite or granite. Five solutions ranging in concentration from $\sim 10^{-3}$ to $\sim 10^{-9}$ M were prepared for each water by mixing appropriate volumes of carrier and tracer stock solutions with the appropriate rock-pretreated water. Later, it was found with a plasma-source emission spectrometer that $\sim 10^{-7}$ M of both Sr(II) and Ba(II) were present initially in the groundwater, thus limiting the range of concentrations studied for those elements to $\sim 10^{-3}$ to 10^{-7} M. Five "control" samples were prepared for europium in order to check on possible precipitation. An aliquot of each different concentration was placed in an empty tube and shaken with the regular samples.

The sorption ratios obtained are given in Tables 2 and 3, along with the corresponding total element concentration. Except for the most concentrated strontium (granite) solution ($\sim 10^{-3}$ M), strontium sorption ratios were not affected by concentration. The solubility product of a strontium compound might have been exceeded for the concentrated solution; however, the same effect was not observed with argillite, and argillite pretreated waters have ~ 5 times the total dissolved cations and anions of the granite-pretreated waters. With cesium, a strong correlation between concentration and sorption ratio was observed. The R_d values increased

TABLE 2 Influence of Element Concentration on Sorption
Ratios (ml/g) for Granite

Sr		Cs		Ba		Eu	
Moles/l	R_c	Moles/l	R_d	Moles/l	R_c	Moles/l	R_c
10^{-3}	90.1	10^{-3}	5.70	10^{-3}	7.75	10^{-4}	14??
10^{-5}	31.1	10^{-5}	37.6	10^{-5}	334	10^{-6}	1420
10^{-7}	43.1	10^{-7}	680	10^{-7}	805	10^{-7}	206?
		10^{-9}	1360			10^{-8}	153?
		10^{-10}	1070			10^{-9}	155?

TABLE 3 Influence of Element Concentration on Sorption
Ratios (ml/g) for Argillite

Sr Moles/l	Sr R_d		Cs Moles/l	Cs R_d		Ba Moles/l	Ba R_d		Eu Moles/l	Eu R_d	
	CN-1	CN-3		CN-1	CN-2		CN-1	CN-2		CN-1	CN-2
10^{-3}	13.2	19.5	10^{-3}	19.8	30.7	10^{-4}	107	505	10^{-4}	6160	10500
10^{-5}	17.2	38.7	10^{-5}	127	238	10^{-5}	174	532	10^{-6}	7980	14400
10^{-6}	17.3	33.9	10^{-7}	742	924	10^{-6}	111	473	10^{-7}	15300	29600
			10^{-9}	759	1170				10^{-8}	27900	77800
			10^{-10}	985	889				10^{-9}	15400	---

with decreasing cesium concentration, indicating an ion exchange mechanism
for cesium sorption on granite and argillite. Sorption ratios for barium
on granite increased greatly with decreasing barium concentration but
remained about the same on argillite. The opposite effect was observed
for europium on granite and argillite, with granite sorption ratios re-
maining approximately constant (except for the most concentrated solution)
and argillite values increasing with decreasing concentration. The control
solutions all showed the same amount of activity throughout the experiment,
indicating that, in the absence of rock, precipitation did not occur.

Atmospheric vs. Controlled-Atmosphere Conditions

A series of measurements were made in a nitrogen atmosphere having
≤ 0.2 ppm oxygen and ≤ 20 ppm carbon dioxide for comparison with similar
measurements made under natural atmospheric conditions. Sorption of the
radionuclides, ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, ^{152}Eu, ^{95m}Tc, ^{237}U, ^{237}Pu, and
^{241}Am, was measured on <75-μm and 75-500-μm samples from Climax Stock
granite core CS-7 (Erdal, et al. 1979-1), Eleana argillite core CN-3
(Erdal, et al. 1979-2) and Yucca Mountain tuff cores YM-22, YM-38, and

YM-54 (Vine, et al. 1980). The controlled-atmosphere conditions were not
truly representative of conditions to be found in deep geologic systems,
since essentially no carbon dioxide was intentionally present in the
atmosphere, and bicarbonate may have been lost from solution. This could
be particularly important for uranium(VI), which is strongly complexed by
carbonate ions. However, since the pH values of the rock-pretreated
waters were only ~0.4 pH units higher than those observed under atmospheric
conditions, the rocks themselves may have provided some bicarbonate-ion
buffering.

The effects of atmosphere on the R_d values for the three geologic
media and nine elements studied are summarized in Table 4. Of the geo-
logic media studied, it seems that the sorption behavior of argillite is
most affected by the atmospheric conditions, except for plutonium and
americium where the difference was greater for granite. All radionuclides
studied have different R_d values for argillite when measured under the
controlled-atmosphere than when measured in air, except possibly for
americium where any effect was smaller than the errors on the R_d values.
The R_d values for technetium on all three media and for plutonium and
americium on granite are most strongly dependent on the presence or ab-
sence of oxygen and carbon dioxide. The technetium sorption ratios are
greater for all media when measured under controlled-atmosphere conditions.
Interestingly, sorption of plutonium and americium on granite is much
lower under controlled-atmosphere conditions, while the sorption of
plutonium on tuffs is actually higher under the controlled-atmosphere.
We have been able to observe apparently negative E_h values only on some
tuff-water systems; none on argillite or granite systems. As expected,
strontium, cesium, and barium are least affected by the presence or
absence of oxygen and carbon dioxide.

Sorption Measurements Using a Circulating System

It has frequently been observed (Erdal, et al. 1979-1 and 1979-2,
Wolfsberg, et al. 1979) that sorption ratios determined by use of the
batch technique increase slowly with contact time. There are several

TABLE 4. Comparison of Sorption Ratios (R_d) Measured under Atmospheric and Controlled-Atomsphere Conditions[a]

Element	Granite	Argillite	Tuff
Cs	No effect	Lower in CA (factor of 2)	No effect
Sr	No effect	Lower in CA (factor of 5)	No effect
Ba	No effect	Lower in CA (factor of 10 or more)	No effect
Ce	Higher in CA (factor of 10 or more)	Higher in CA (factor of 10)	No effect
Eu	Higher in CA (factor of 10 or more)	Higher in CA (factor of 10)	No effect
Tc	Higher in CA (factor of 5-10)	Higher in CA (factor of 10)	Higher in CA (factor ≥10)
U	Lower in CA (factor of 10)	Lower in CA (factor of 10)	Higher in CA[b] (factor of 2-3)
Pu	Lower in CA (factor of 50)	Lower in CA	Higher in CA (factor of 2)
Am	Lower in CA (factor of 15)	Lower in CA	No effect[c]

[a]Nitrogen, ≤0.2 ppm oxygen and ≤20 ppm carbon dioxide; abbreviated by CA.
[b]YM-38 zeolitized tuff only; otherwise no effect.
[c]May depend on mineralogy.

explanations for this observation, including the possibility that there is self-grinding in the shaking operation inherent in the batch technique, which increases the rate of "weathering".

A series of experiments were initiated to determine if this is a possible mechanism. The 355-500-μm fraction of crushed rock was placed in the circulating system in a 1.0 (diameter) x 5.0 cm polycarbonate column, and the appropriate traced groundwater (at a solution-to-solid ratio of 20 mℓ/g) was continuously circulated through the column in a closed loop. The columns have polyethylene bed supports and polypropylene Luer fittings on each end. A peristaltic pump (Pharmacia model P-3) was used for circulation with either Teflon or silicon tubing. Flow rates were 0.6 mℓ/min.

Five different crushed rock columns of ~4.5 g were started, each using the groundwater characteristic of that sample: CS-5 granite, CN-2 argillite, and JA-37, YM-22, YM-54 tuffs. The circulation of the ground-water was done for two months to check out the system and to pretreat the rock samples. The rock-pretreated groundwaters were tagged with ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu by the usual evaporation-dissolution pro-cedure. Since the sorptive capacity of some of the components in the system was unknown, circulation of the tagged groundwaters through similar systems without the rock was checked. Sorption was observed in the control only with ^{141}Ce and ^{152}Eu; however, no data were obtained for those iso-topes since no activity remained in solution even at the first sampling time of 26 days.

The results obtained with the circulating system, averaged over sampling times of 26 to 49 days are given in Table 5, along with corres-ponding batch R_d values for comparison. With the exception of data on tuff JA-37 and cesium data on granite and argillite, R_d values obtained from the circulating system are lower than those from batch measurements and are in fairly good agreement with the values we have obtained on crushed rock columns.

Sorption vs. Mineralogy

Although minor components in a crushed rock sample can certainly play a .jor role in sorption, there is a fairly good correlation between major phases, as determined by X-ray diffraction, and sorption by the tuff, granite, and argillite samples studied to date. The approximate percentages of major phases in several of the tuffs studied, as well as in two granite and argillite samples, are shown in Table 6. Granite sample Cs-5, for example, is predominantly quartz and feldspar, as is devitrified YM-54 tuff. Their sorption ratios for strontium, cesium, barium, cerium, and europium (shown in Table 7) are quite similar. Tuff YM-42 also contains quartz and feldspar but has ~20% of the zeolite clinoptilolite as well, and sorption ratios on YM-42 are one or two orders of magnitude larger. The same is true of YM-49 (~60% zeolite) and

TABLE 5. Sorption Ratios (mℓ/g) for Crushed Rock

Sample	Batch			Circulating System		
	Sr	Cs	Ba	Sr	Cs	Ba
YM-22	51	264	945	19	252	81
YM-54	84	274	653	46	131	137
JA-37	283	627	747	395	1830	884
CS-5	12	251	84	7.9	384	55
CN-2	116	1950	1170	47	3760	650

JA-18 (~25% zeolite, 60% glass). The R_d values for cerium and europium, however, do not appear to be dependent on zeolite content, as are strontium, cesium, and barium. In addition to clinoptilolite, JA-18 also has glass as a major phase. YM-5 is glassy as well but contains no zeolite and has lower sorption ratios for strontium, cesium, and barium than does JA-18.

Experiments are now in progress on tuff cores which are primarily clay and quartz for comparison with argillite CN-1. Although these relationships are approximate, a more detailed correlation of sorption ratios vs. mineralogy may be possible, as more samples are studied and the data base increased.

CONCLUSIONS

The influence of several variables which could affect sorption ratios was studied. The sorption of barium, cerium, and europium on granite was found to remain approximately constant as the solution to solid ratio was varied from 5:1 to 30:1. Strontium and cesium sorption ratios, however, increased in the same experiment, perhaps indicating a larger number of sorption sites available to those two isotopes. The effect of concentration on sorption on granite and argillite was relatively small at concentrations $<10^{-4}$ M. Technetium sorption was most affected by atmosphere, increasing by at least one order of magnitude in ≤ 0.2 ppm oxygen and ≤ 20 ppm carbon dioxide.

Table 6. X-Ray Analyses: Approximate Percentage of Phases[a]

Sample	Quartz	Feldspar	Cristobalite	Glass	Clay	Clinoptilolite	Other[b]
Granite	30	50-60	--	--	--	--	biotite chlorite
Argillite CN-1	30	--	--	--	70	--	--
Tuff, YM-54	60	30	--	--	tr	--	--
YM-42	40	40	--	--	--	20	mica
YM-49	10	15	10	--	--	60	--
JA-18	tr	7	--	60	--	25	--
YM-5	tr	14	tr	70	10	--	--

[a]From J. R. Smyth, Los Alamos Scientific Laboratory, personal communication, 1980.

[b]$< 10\%$.

TABLE 7. Sorption Ratio vs. Mineralogy

Sample	Major Phases	Sr	Cs	Ba	Ce	Eu
Granite	Quartz, feldspar	16	320	164	240	550
YM-54	Quartz, feldspar	90	250	620	140	150
YM-42	Quartz, feldspar, zeolite	4000	19000	96000	40000	5000
YM-49	Zeolite	2700	29000	33000	550	1200
JA-18	Zeolite, glass	9000-18000	10000-18000	5000-130000	2600	1400
YM-5	Glass	480	6000	1100	200000	200000
Argillite, CN-1	Quartz, clay	135	1990	3950	42000	35000

Of all the parameters studied, minerology had the greatest influence on the sorption ratio. Samples which were predominatly quartz and feldspar (granite and devitrified tuffs) had the smallest sorption ratios for strontium, cesium, and barium, while zeolite (clinoptilolite)-containing tuff samples had the largest. Correlations between mineralogy and R_d values were not as good for cerium and europium.

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