INTRODUCTION

If geologic repositories are used for the isolation of nuclear waste, intruding groundwater could lead to dissolution of radionuclides and their subsequent transport to the biosphere. Interaction with the geologic media is one of the most important factors retarding such transport. It is therefore necessary to understand the many interrelated factors and processes that govern radionuclide transport in geologic media. The effects of some of the parameters that may influence sorption and transport properties are being systematically investigated at the Los Alamos Scientific Laboratory. All earlier studies were performed on three media specific to the Nevada Test Site (NTS). These are a quartz monzonite porphyry (Climax Stock), an argillite (Eleana Formation), and several lithologic varieties of rhyolitic tuff (Jackass Flats). These materials and their associated groundwaters were described in Refs. 1-4. Several additional tuff samples, which are described below, have now been investigated.

The equilibrium distribution coefficient, $K_d$, for the distribution of radioisotopes between aqueous and solid phases is conventionally defined as the concentration in the solid phase divided by the concentration in solution. Since it is not known whether equilibrium is achieved for the interactions of radionuclides with geologic media, in this report the value is called the sorption ratio which is otherwise identical to the distribution coefficient but does not imply equilibrium.

This work was supported by the U. S. Department of Energy.
ADDITIONAL TUFF SAMPLES

Three additional tuff samples with lithologies different than those used earlier were obtained from the Yucca Mountain area (exploratory drill hole UE25A-1) at the NTS. These were obtained from depths of 258 m (YM-22), 459 m (YM-38), and 759 m (YM-54). Water from well J-13 at the NTS was also used with these samples.

Sample YM-22, a devitrified, densely welded tuff, was obtained from the Topopah Springs Member of the Paintbrush Tuff. The rock consists of relict pumices in a matrix of small shards and vugs (5-20 µm) filled with fine crystalline, pale brown to colorless phases. Coarser shards and pumice pyroclasts are zoned, ranging from 10-µm diameter colorless phases along the rims to 300-µm diameter phases in the centers. Rare phenocrysts include equant, slightly rounded plagioclase (An14-16), amphibole and biotite, replaced by hematite, alkali feldspar, and magnetite. Lithic fragments consist of rounded vitric tuff clasts. The rock is crossed by an echelon, 20-150 µm wide cracks, which are filled with quartz and parallel the fabric.

Sample YM-38, an altered, non-welded vitric tuff, was obtained from the Bedded Tuff at Calico Hills. This tuff consists of slightly compacted, 0.5-8 mm long relict pumice pyroclasts. Glass has been replaced by a finely crystalline mixture of authigenic quartz and clinoptilolite. Vesicles and voids are partially to completely filled with tabular, 10-30 µm long crystals of clinoptilolite. Phenocrysts include plagioclase (An15-24), sanidine (Or66), quartz, and biotite; nearly all are fractured. Lithic fragments from 300 µm to 5 mm in length consist of vitric and crystal-vitric welded tuff clasts.

Sample YM-54, a devitrified, welded tuff, is from the Bull Frog Member of the Crater Flat Tuff. In hand specimen this appears to be a welded tuff; however, in thin-section no relict pyroclasts have been preserved. There is only a fabric of lenticular zones of coarsely crystalline phases that may have been welded pyroclasts. Most of the rock consists of colorless to tan, 2-20 µm diameter, alkali feldspar and quartz crystals. Scattered throughout this "matrix" are irregular patches of more coarsely crystalline (150-100 µm diameter) alkali feldspar and quartz grains; the larger of these are sometimes roughly rimmed by spherulites. Phenocrysts include sanidine (Or65) and quartz with quartz overgrowths, oxidized biotite, plagioclase, and magnetite. Xenocrysts of mafic phases altered to phlogopite and hematite also occur.
STATIC (BATCH) MEASUREMENTS

The experimental methodology used to perform laboratory studies of some of the variables that may influence radionuclide transport was given in Refs. 1-4. The initial results on parameters such as time, temperature, exchange capacity, available surface area, particle size, element concentration, sampling location, and mineralogy were also given for the quartz monzonite, argillite, and tuff from Jackass Flats.

Representative values for the sorption ratios for the additional tuff samples from Yucca Mountain are given in Table 1. Generally, the conclusions reached earlier1-4 for other geologic media are also valid for these samples. However, in contrast to the earlier studies, there was no consistent correlation between the sorption ratio and particle size for either the sorption or desorption measurements. For example, the sorption ratio values for strontium, cesium, and barium on YM-38 decreased as the sieve fraction size decreased, while the values for the other samples tended to increase or remain approximately constant with decreasing size. It was thought that fractionation of minerals in the sieving process might explain these results; however, X-ray diffraction analyses indicate no difference in X-ray patterns or intensities. Therefore, unless the difference in sorption behavior is due to a relatively minor component which is not resolved by X-ray diffraction, it is unlikely that mineral fractionation is responsible for these results. More likely explanation may come from the fact that the smaller fraction (<106 μm) had been ground to particles smaller than natural grain sizes, exposing different surfaces, and perhaps destroying others.

Since the composition of the groundwater may have a pronounced effect on the sorption of many radionuclides, several experiments to assess this dependence have been performed. The initial composition of the two waters were (in mg/L) Na(10), K(5), Ca(10), Mg(2), SO₄(5), and Cl(4.5) for the "dilute" water (called Water I) and Na(50), K(5), Ca(50), Hg(20), SO₄(70), and Cl(15) for the "concentrated" water (called Water II). The 250-355 μm sieve fractions from the various materials were used with the same pretreatment and experimental techniques described earlier. The sorption of strontium, cesium, barium, cerium, and europium was studied at about the same concentrations as used earlier. Contact times of 28 and 60 days were used.

Assuming that other uncontrolled variables are not important, the composition of the water seems to be a major factor governing sorption (Table 2). As expected the sorption ratios for strontium, cesium, and barium decreased when Water II was used. This was undoubtedly due to the increased amount of competition for sorption
Table 1. Representative Sorption Ratios (mL/g) for Tuff from Yucca Mountain

<table>
<thead>
<tr>
<th>Element</th>
<th>YM-22</th>
<th>YM-38</th>
<th>YM-54</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>53 b</td>
<td>12 000</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>63 b</td>
<td>20 000</td>
<td>97</td>
</tr>
<tr>
<td>Tc(VII)</td>
<td>0.3</td>
<td>0.2 c</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>2.0 c</td>
<td>2.0 c</td>
</tr>
<tr>
<td>Cs</td>
<td>340</td>
<td>8 600</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>13 000</td>
<td>310</td>
</tr>
<tr>
<td>Ba</td>
<td>980</td>
<td>66 000</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td>1 000</td>
<td>190 000</td>
<td>660</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>1 400</td>
<td>830</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>6 100</td>
<td>3 800</td>
<td>990</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>1 400</td>
<td>2 300</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>3 600</td>
<td>8 700</td>
<td>1 800</td>
</tr>
</tbody>
</table>

a Atmospheric conditions.

b The second value listed for each element is that obtained from the desorption measurements.

c Obtained using a sample (YM-49) from the 678 m depth which is mineralogically similar to YM-38.

sites. For cerium and europium, the sorption ratios tended to increase with increasing ionic strength. This may be due to the enhanced tendency to form radiocolloids as the sulfate concentration increases, which is further indication that the sorption behavior of cerium and europium is quite different than that for cesium, strontium, and barium.

One should note that Water I and Water II are somewhat similar to the waters used for the earlier granite and argillite studies, respectively. The sorption ratio values obtained using these new waters are very consistent (within 20%) with the previous values, which is strong indication that our experimental method gives consistent results.

Under generally reducing conditions expected for groundwater not in contact with the atmosphere, one can anticipate that the sorption behavior of some elements would be different from that under atmospheric conditions. One could also expect some difference in the sorptive capacity of a rock if its surface had been altered.
Table 2. Effect of Water Composition on the Sorption Ratio (mL/g)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water</th>
<th>Cs</th>
<th>Sr</th>
<th>Ba</th>
<th>Ce</th>
<th>Eu</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-5</td>
<td>I</td>
<td>180</td>
<td>8.2</td>
<td>63</td>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>230</td>
<td>5.0</td>
<td>28</td>
<td>&gt;1000</td>
<td>4800</td>
</tr>
<tr>
<td>CN-2</td>
<td>I</td>
<td>2400</td>
<td>700</td>
<td>2300</td>
<td>5810</td>
<td>8340</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1600</td>
<td>170</td>
<td>700</td>
<td>12400</td>
<td>10700</td>
</tr>
<tr>
<td>JA-18</td>
<td>I</td>
<td>10900</td>
<td>23600</td>
<td>17200</td>
<td>945</td>
<td>1130</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>740</td>
<td>5030</td>
<td>46400</td>
<td>5200</td>
<td>1700</td>
</tr>
<tr>
<td>JA-32</td>
<td>I</td>
<td>130</td>
<td>84</td>
<td>587</td>
<td>2870</td>
<td>1690</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>85</td>
<td>18</td>
<td>656</td>
<td>&gt;3000</td>
<td>23500</td>
</tr>
<tr>
<td>JA-37</td>
<td>I</td>
<td>1330</td>
<td>415</td>
<td>840</td>
<td>27100</td>
<td>12000</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>844</td>
<td>174</td>
<td>375</td>
<td>&gt;36000</td>
<td>12700</td>
</tr>
</tbody>
</table>

aOnly the data for the 28-d contact time is shown; see Refs. 5 and 6 for the 60-d results.

bCS means Climax Stock quartz monzonite (Ref. 2), CN means an Eleana argillite, (Ref. 3), and JA means a tuff from Jackass Flats (Ref. 4).

by exposure to air. These effects were investigated by performing studies in a pure nitrogen atmosphere having ≤0.2 ppm oxygen present. It should be emphasized that these studies are perhaps not truly representative of the conditions to be found in deep geologic systems since no carbon dioxide or soluble carbonate was intentionally present. This could be particularly important for uranium(VI), which is strongly complexed by carbonate ions. However, since the pH values observed when the rock was present were not appreciably different than those observed under atmospheric conditions, the rocks themselves may have supplied some carbonate ion. All of the operations (including the grinding and sieving) needed to make the batch measurements were performed under these controlled atmosphere conditions. The same granite, argillite, and tuff from Yucca Mountain as described earlier were used.

The sorption ratios for cesium, strontium, and barium were generally somewhat less than those observed under atmospheric conditions for the argillite and tuff samples, but they were reasonably consistent for the granite samples. In contrast, the sorption ratio values for cerium and europium were appreciably higher for granite and argillite under the controlled atmosphere conditions, while the values obtained using tuff were consistent with those observed
under atmospheric conditions. These results are probably related
to the absence of carbon dioxide, which emphasizes the need to
understand the fundamental chemistry of even the "simpler" elements
in the region of pH 7-9.

The sorption ratio values for technetium under the reduced
oxygen and carbon dioxide conditions were consistently higher (by
more than a factor of 40) than under atmospheric conditions for
all three geologic media, which supports the conclusion that
pertechnetate ion can be easily reduced chemically to a less soluble
form.

Similar measurements for uranium on the granite and argillite
indicated that the sorption ratios were higher (by about a factor
of 10) for the <75-μm sieve fractions under atmospheric conditions
than in the absence of oxygen and carbon dioxide, and essentially
equal for the remainder of the material (75-500 μm). Elemental
analyses of these fractions did not indicate any difference between
the samples, particularly in the total iron content. Perhaps mineral
fractionation occurred in the sieving process. However, the rather
striking difference in the measured sorption ratio values may be
due more to the absence of carbon dioxide than to the absence of
oxygen.

In our usual experimental procedure for plutonium and americium
batch sorption experiments, the groundwater mixtures were separated
after contact by centrifuging the aqueous phase three times for at
least 1 h at about 12 000 rpm (32 000 g) with careful transfer of
the water following each centrifuging run. This process produces
plutonium solutions which generally can be passed through a poly-
carbonate filter membrane with pores as small as 0.05 μm without
loss of radioactivity. Some americium is normally removed when
such solutions are centrifuged. A microautoradiographic technique
has been used to examine the filter membranes. For solutions from
sorption experiments, α-ray "stars" or large radioactive clusters
were observed, indicating the presence of large agglomerates
containing many americium atoms even after the rigorous centrifuging
process. For solutions from desorption experiments, the filter
membranes showed americium only as single α-tracks, indicating that
agglomerates of the type observed in the centrifuged solution from
the sorption experiments were not present in the desorption solutions.
Apparently, such clusters were neither removed from the solid phase
once they had been "sorbed" nor formed in the desorption water.

The presence of single α-tracks suggests that americium sorbs
on the membrane itself. In related work B. M. Allard (Chalmers
University, Gothenberg, Sweden, personal communication) observed
sorption ratios for Millipore filter paper comparable to those for
Considering the above results, we have decided to take the conservative approach in calculating americium sorption ratios and use the results from the solutions after they have been centrifuged but not filtered. This is reflected in the values given in Refs. 1, 5, and 6.

MICROAUTORADIOGRAPHY

Microautoradiography has been employed at LASL as another technique for studying the sorption properties of certain elements on selected types of rocks. Whereas column or batch sorption methodologies yield information on sorption properties of gross rock, microautoradiography can indicate the specific mineral phase responsible for the sorption. Furthermore, this technique can give insight into the state of aggregation of the sorbed material. Since many of the transuranic elements tend to form polymeric or colloidal species in solution at groundwater pH values, observation of the degree of aggregation in adhering species is very important. This technique has been used for studies of the behavior of $^{233}$U, $^{237}$Np, $^{239}$Pu, and $^{241}$Am.

The results indicate that the majority (>90%) of the $^{233}$U activity sorbed onto the quartz monzonite thin-sections was confined to the clay-rich alteration bands in the plagioclase. This result indicates that the sorptive properties of granites for uranium may be controlled by a phase which comprises less than one percent of the rock. Most of the $^{233}$U is sorbed on the clay matrix in the argillite while very little sorption occurred on the detrital quartz and secondary calcite. For the tuff, most of the $^{233}$U was localized in the secondary zeolite minerals (clinozoisite) as compared to the phenocrysts of quartz and feldspar. This was not surprising since the zeolites have large cation exchange capabilities.

In general, $^{237}$Np, $^{239}$Pu, and $^{241}$Am showed the same trends as the uranium when sorption was definitely observed; however, stellate patterns of α-tracks frequently appeared on all media and did not correlate in any obvious way to the specific minerals in the thin-sections. These patterns most likely are due to particles or colloids which have come out of solution and do not represent ionic sorption, consistent with the previously described behavior of americium on filtering.

A number of autoradiograms were prepared using $^{85}$Sr, $^{63}$Ni, $^{233}$Pa, and $^{90}$Sr. Strippable emulsion, liquid emulsions, and a film-backed emulsion were utilized. The beta tracks (generally spots) were readily visible at moderate densities against a clear
background, but were difficult or impossible to identify except at very high densities against the mottled backgrounds typical of rock thin-sections. Thus, it appears that beta autoradiography may be limited in geologic applications to situations in which high resolution is not required and in which a rather large track density can be tolerated.

**DYNAMIC (COLUMN) STUDIES**

The logical next step in extending our knowledge of the behavior of radionuclides in geologic systems was to perform studies of migration rates. For crushed rock columns, assuming equilibrium between water and rock, the ratio of the velocity of a radionuclide to the groundwater velocity, the retardation factor, is given by $K = (p/c) + 1$, where $p$ is the bulk density and $c$ is the porosity (free column volume/bed volume). In fact, non-equilibrium "sorption ratios" are more appropriate in this expression for short-term experiments than are the equilibrium $K_d$ values.

Initial studies have been performed using the same materials and pretreated waters as used in the batch measurements, in order to compare the results with those from the "batch" tests. A simple, upflow, 0.4-0.5 cm inside diameter by 2-3 cm high column, lined with Teflon, with polyethylene bed supports on each end, was developed. Water delivery rates, as controlled by syringe pumps, were usually below 0.05 ml/h (~30m/y). Actual delivery rates were determined by weighing the eluate collected during a known time period. The free-column-volumes were usually determined by use of both tritiated water and $^{131}$I; no difference was observed between the two methods. The tracers, $^{85}$Sr, $^{137}$Cs, and $^{133}$Ba (all about $10^{-9}$ M), used singly or as a mixture, were usually added in a minimal (5-15 μl) volume. Since the elution peaks were reasonably symmetrical, the volume where 50% of the activity had been eluted corresponded closely with the peak concentration in the elution curve. This volume was used to calculate the retardation factor.

The sorption ratios obtained (Table 3) from the column data were always less than those obtained using the batch technique. In most cases, the agreement was within a factor of two to three; the largest differences were about a factor of five for $^{133}$Ba. This may be due to the rate of sorption on the rock being slow compared to the water flow rate. In comparing these results with batch data, we note that diffusion into the solid may contribute in batch experiments that last weeks or months but could be negligible in a column having a comparatively short, one day, residence time.
### Table 3. Comparison of Column and Batch Sorption Ratios (mL/g)

<table>
<thead>
<tr>
<th>Column Material</th>
<th>Sr</th>
<th>Cs</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM-22</td>
<td>30 (50)</td>
<td>122 (287)</td>
<td>355 (652)</td>
</tr>
<tr>
<td>YM-54</td>
<td>44 (84)</td>
<td>92 (247)</td>
<td>126 (652)</td>
</tr>
<tr>
<td></td>
<td>44 (84)</td>
<td>80 (247)</td>
<td></td>
</tr>
<tr>
<td>JA-32</td>
<td>52 (56)</td>
<td>113 (247)</td>
<td>122 (652)</td>
</tr>
<tr>
<td></td>
<td>37 (56)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35 (56)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN-1</td>
<td>43 (138)</td>
<td>b (1830)</td>
<td></td>
</tr>
<tr>
<td>CN-2</td>
<td>52 (56)</td>
<td>b (1580)</td>
<td></td>
</tr>
<tr>
<td>CS-5</td>
<td>9 (14)</td>
<td>b (328)</td>
<td>32 (154)</td>
</tr>
<tr>
<td>CS-7</td>
<td>15 (18)</td>
<td>b (347)</td>
<td>44 (175)</td>
</tr>
</tbody>
</table>

*a The sorption ratios obtained on the same materials using the batch technique are in parentheses.

*b The elution is not yet complete.

### ACKNOWLEDGEMENTS

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### REFERENCES


