ANL-78-8

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STUDIES OF NUCLEAR-WASTE MIGRATION
IN GEOLOGIC MEDIA

Annual Report
November 1976—October 1977

by

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Chemical Engineering Division

March 1978

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ABSTRACT

The confinement of nuclear wastes in geologic formations is
being considered as a method of permanently disposing of the waste.
Laboratory experiments (column infiltration, static absorption,
and batch partitioning experiments) were performed with nuclides
of cesium, plutonium, neptunium, and americium to examine the
migratory characteristics of long-lived radionuclides that could
be mobilized by groundwaters infiltrating a nuclear waste repository
and the surrounding geologic body. In column infiltration
experiments, the positions of peak concentrations of cesium in
chalk or shale columns; plutonium in limestone; americium in
limestone, sandstone, or tuff; and neptunium in a limestone column
did not move when the columns were infiltrated with water.
However, fractions of each of the nuclides were seen downstream
from the peaks, indicating that there was a large dispersion in
the relative migration rates of each of the trace elements in
the lithic materials studied.

The results of static absorption experiments indicate that
plutonium and americium are strongly absorbed from solution by the
common rocks studied and that their migration relative to
ground-water flow is thereby retarded, a conclusion that is
consistent with results of the column infiltration experiments.
In addition, the reaction rates of dissolved nuclides with rocks
were found to vary considerably in different rock-element systems.

Batch partitioning experiments were performed to test
whether absorption processes are reversible. After granulated
basalt and americium-bearing water were contacted in an absorption
step, part of the water was replaced with water free of americium
and the americium repartitioned between rock and solution.
The distribution of americium after desorption was comparable to
its distribution after absorption. In contrast, when tablets of
various rocks were allowed to dry between absorption and desorption
tests, plutonium and americium were not generally desorbed from
the tablets. This suggests that reversible reactions of nuclides
between waters and rocks may be upset by treatments such as drying.

In batch partitioning experiments with plutonium- and americium-bearing water and granulated basalt of several different particle sizes, the partitioning of americium and plutonium did not correlate with the calculated area of the fracture surfaces nor did the partitioning remain constant (as did the measured surface area). Partitioning is postulated to be a bulk phenomenon with complete penetration of the ~500-μm size and smaller particles.

I. INTRODUCTION

Fission products and some transuranic elements are wastes generateu in nuclear reactor fuel during power production. Because the waste is radioactive and represents a hazard to health, it must remain isolated from the biosphere. Some fission products and actinide elements are long-lived, requiring that the waste be isolated for long periods of time until they become radiologically innocuous. A method being considered for permanently disposing of the waste is to emplace it in geologic formations deep beneath the surface of the earth.

As part of the evaluation of the safety of geologic repositories, the duration of long-term isolation of the wastes must be accurately assessed. A geologic body may become unstable and a repository may be disrupted. Groundwater infiltrating the repository is considered the most credible mechanism for mobilizing nuclides from a disrupted repository in a well-chosen geologic site.

The current concept of migration by infiltration assumes that groundwater passes through a breached repository and leaches trace amounts of radionuclides from the solidified waste. The water then carries the radionuclides into the adjacent geologic formations, and constituents of the solution react with the rock. If it is assumed that the radionuclides are freely leached from the repository, it is their reaction with rock materials that determines their migratory behavior.

The experimental program has utilized three types of experiments (described in Table 1) designed to give information on the migration behavior of nuclides in aqueous solution-rock systems. The purposes of using different approaches are to establish nuclide behavior under a variety of experimental conditions and to identify the characteristics of nuclide absorption that are important to understanding nuclide migration in natural systems (recently fractured rock, weathered rock, porous rock, etc.).

Table 1. Experimental Methods Used to Investigate Migration Behavior of Nuclides[a]

Method	Material	Method Description	Parameters Measured	Potential Relationship to Nuclide Migration
Column infiltration	Solid rock columns	Aqueous solutions are forced through columns of permeable rock.	Dispersion in V_n	Migration behavior in solid rock
	Rock aggregate	Aqueous solutions percolate through crushed rock.	Dispersion in V_n	Migration behavior in fresh regolith
Static absorption and desorption	Rock tablets	Reaction of rock tablets with static solutions of minerals and nuclides.	Kinetics of the reaction, reversibility, and K_D	$V_n = \dfrac{V_w}{1 + K_D \rho/\varepsilon}$
Batch partitioning measurements	Rock aggregate	Granulated rock is reacted with stirred solutions of minerals and nuclides.	Surface saturation limits; dependence of K_D on particle size, and nuclide concentration	$K_D = K_D$ (grain size, C_n, f_{Cl^-})

[a]Symbols: V_n, velocity of nuclide in rock (cm/s).

V_w, velocity of aqueous solution in rock (cm/s).

K_D, partition coefficient (equal to nuclide concentration per gram of rock divided by nuclide concentration per milliliter of solution).

ρ, density of rock (g/cm^3).

ε, porosity of rock (fraction).

C_n, concentration of nuclide (ppm).

f_{Cl^-}, fugacity of chloride ion.

II. ROCKS, NUCLIDES, AND AQUEOUS SOLUTIONS

Rocks from geologic formations that may be suitable for siting nuclear waste repositories were selected for study. The rocks are from large, stable formations of low economic value and within the continental United States. The selected rocks are of a variety of chemical compositions and physical characteristics and included rocks of sedimentary, igneous, and metamorphic origin. Silicates such as granites, basalts, and metamorphic rocks common in geologically stable parts of the North American continent and carbonates such as limestone, chalk, and dolomite that are typical of rocks associated with salt formations were used in the study. Salt deposits are being seriously considered for waste repositories. However, salt was not included in this initial work because its study requires special experimental techniques not needed to study the other less-soluble rocks. X-ray diffraction analyses of the rocks used in the nuclide migration studies are given in Table 2.

The elements cesium, plutonium, neptunium, and americium in the waste produced during nuclear power generation contain long-lived isotopes and are of concern in the design of nuclear waste repositories. The nuclides cesium-134, plutonium-237, neptunium-239, and americium-241 were selected for study because they emit gamma rays during their decay and can be analyzed by counting of radioactivity without the need to make chemical separations or thin samples. Gamma ray spectra from liquids or rock solids were measured using NaI scintillation spectrometers. In the determination of nuclide concentration relative to its concentration in the starting solution, counting data was corrected for nuclide decay, background, Compton scattering, and interference from the decay of other nuclides.

Pre-equilibrated solutions were used in this work. Each such solution was prepared by reacting distilled water with particles of rock to be studied. Typically, mixtures consisting of 10 g of rock powder and 1 L of distilled water were stirred for two weeks; then the liquids with dissolved materials were decanted or filtered (through Whatman No. 1 paper) to remove suspended matter. This method of preparation was used to establish mineral contents that are similar to those existing in groundwaters that have reacted with the rock formations. Since the composition of a pre-equilibrated solution is established during extended periods in which the water is continuously mixed with granulated rock, subsequent contact of the water with rock in the experiments would be expected to lead to little change in the water chemistry. This procedure of pre-equilibrating water with rock contrasts to the use of solutions of arbitrary compositions; for the latter, there is, in general, no way to ensure that there will not be a major change in water chemistry upon contact with the rock.

Some of the pre-equilibrated solutions were filtered through 0.45-μm-pore Nuclepore filters, de-aired by bubbling nitrogen, and analyzed for total dissolved solids by evaporating aliquots of the solutions and weighing the residues after drying at 180°C. The results of these analyses are given in Table 3. Drying at 180°C is believed to have removed occluded water and most water of crystallization,[1] and possibly caused chemical changes of the organic and carbonate residues. The hydrogen ion concentrations of the pre-equilibrated solutions (expressed as pH values) were measured with an ion probe (Table 3). The oxidation potentials of the de-aired solutions (measured with an ion probe) are also reported in Table 3.

Table 2. X-Ray Diffraction Analyses of Rocks Used in Nuclide Migration Studies

Sample Description	Mineral Phases Identified		
	Major	Minor	Trace
Chalk, Selma	calcite ($CaCO_3$)	quartz ($\alpha-SiO_2$)	kaolinite, montmorillorite
Acid-Insoluble Residue of Selma Chalk (20% of chalk weight)	quartz	kaolinite, montmorillonite	
Shale, Pierre, Front Range	quartz, feldspar	meta-halloysite type pattern	
Limestone, Salem Formation	calcite		
Sandstone, Ohio Barrier	qurrtz	feldspar	
Tuff, Nevada Test Site	c linoptilolite, feldspar	black magnetic mineral	quartz
Granite, LI-6152 (white fraction)	quartz, microcline		
Granite, LI-6152 (dark fraction)	mica		
Columbia River Basalt	feldspar	augite	
Low-Temperature Metamorphic	chlorite, amphibole (ferropargasite)	feldspar	
Magenta	gypsum, anhydrite		
Georgia Marble	calcite		
Colitic Limestone	calcite		
Soapstone	talc	dolomite	antigorite or serpentine
Culebra, Sandia WIPP	dolomite		quartz

(Contd)

Table 2. (Contd)

Sample Description	Mineral Phases Identified		
	Major	Minor	Trace
Gneiss, FMS-LI-3896	feldspar, quartz		halloysite, mica or illite
Dolomite, Quantin Quarry	dolomite		
Chalcopyrite 26-12-03A	chalcopyrite		cordierite
Galena	galena		
Anhydrite (Gypsum), Sandia WIPP	gypsum, dolomite		quartz
Apatite	apatite		
Argillite, NTS Eleana Formation 784' 755.2'	quartz, meta-halloysite	siderite	
Witherite	barium carbonate		calcite
Bornite	bornite (Cu_5FeS_4)	molybdenite (MoS_2)	
Granite Monzonite, Nevada Test Site	feldspar, quartz		halloysite, mica or illite
Dolomite, Nevada Test Site	dolomite		calcite, quartz

Table 3. Total Solids, Hydrogen Ion Concentrations Expressed as pH Values
and Oxidation Potentials of Pre-Equilibrated Solutions

Rock used to Pre-equilibrate Solution	Total Solids, mg/L (dried at 180°C)[a]	Hydrogen Ion Concentration, pH	Oxidation Potential,[b] E_h, V
Chalk, Selma	173	7.8	0.269
Shale, Pierre, Front Range	111	8.0	0.269
Limestone, Salem Formation	46	7.6	0.277
Sandstone, Ohio Barrier	--	8.0	--
Tuff, Nevada Test Site	55	7.9	0.282
Granite, LI-6152	67	8.5	0.261
Columbia River Basalt	62	7.0	0.293
Low-Temperature Metamorphic	48	8.3	0.275
Magenta	2380	--	--
Georgia Marble	--	8.3	--
Barrier Sandstone	--	6.8	--
Soapstone	--	8.2	--
Culebra, Sandia WIPP	261	8.6	0.261
Gneiss, FMS LI-3896	173	7.9	0.273
Dolomite, Quantin Quarry	46	8.5	0.274
Chalcopyrite	--	5.4	--
Galena	50	5.5	0.328
Anhydrite, Sandia WIPP	2350	7.6	0.275
Argillite, NTS Eleana Formation	109	--	0.256
Witherite	115	7.6	0.270
Granite, Nevada Test Site	11	6.9	0.306

[a]Solutions for which analyses of total solids are given were filtered through 0.4-μm-pore filters.

[b]Oxidation potentials were measured in the de-aired solutions. A Zobell reference solution was measured to have an oxidation potential of 0.425 V.

Solutions of plutonium and americium for all three types of experiments were prepared under air with no reducing agents by evaporating nitrate solutions of the isotopes to dryness and dissolving the residue, or part of it, in distilled water. Plutonium and americium were believed to be in the +4 and +3 valence states, respectively in the final solutions. Small quantities of these solutions (10 μL) were added to water that had been pre-equilibrated with rock or were added directly to rock saturated with the water. The gamma activities were counted with the Na-I scintillation spectrometer. With an assumed efficiency of 50%, the activities and concentrations of the plutonium and americium used in static absorption experiments were 2.3 nCi/mL or $8 \times 10^{-13}\underline{M}$ plutonium-237 and 4.5 nCi/mL or $5.8 \times 10^{-9}\underline{M}$ americium-241.

Neptunium was extracted in a 0.1$\underline{N}$ HCl solution using tricaprylmethylammonium (TCMA·Cl)[2] from a solution where it was present as a daughter product of americium-243. The neptunium was believed to be in the +5 valence state and was used in the experiments without drying to prevent oxidation changes that would result during evaporation of the solution as a result of an increase in acidity.

In some column infiltration experiments, a solution of CsCl was added directly to rock material saturated with water. The quantity added was about 5.7 μCi/g of dry rock; alternatively, CsCl was added to a pre-equilibrated solution to produce a concentration of 0.01 μCi/mL.

The addition of small quantities of radionuclides to pre-equilibrated water was in analogy to the postulated leaching of radionuclides from solidified waste in the repository. In the experiments, the migratory behavior of the nuclides was studied by reacting the radionuclides with rock--either by contacting rock with nuclide-bearing solutions or by infiltrating rocks with pre-equilibrated water that contained radionuclides.

III. COLUMN INFILTRATION EXPERIMENTS

Column infiltration experiments were done to determine relative migration rates of nuclides in some geologic media and to examine the effects of different procedures on the experimental results. In these experiments performed at ambient temperature, pre-equilibrated solutions were employed; slightly pressurized (0-1400 Pa or 0-0.2 psi) to moderately pressurized (345 000 Pa or 50 psi) solutions were allowed to infiltrate columns of rock. The columns were either made with cut cylinders of rock or with rock aggregate. Prior to infiltration, the nuclides were added to the pre-equilibrated solutions or were placed directly on rock saturated with water. The former method is thought to be typical of conditions hypothesized for a repository from which solutions of low nuclide concentration would continually infiltrate an adjacent geologic body. On the other hand, the latter method was simpler to control and analyze because the total activity in the column and eluates was constant with time (once corrections were made for radioactive decay).

The water was collected after it passed through the column, then was analyzed to determine the amount of nuclide leaving the column. The infiltration experiments are analogous to elution procedures in column chromatography, with the pre-equilibrated water serving as the eluant. Several experimental designs were employed. In one method, a standing tube of water approximately 150 cm high was used as a source of pressurized water. The apparatus, incorporating a standing tube of water and designed to accommodate rock aggregate, is depicted in Fig. 1. In another method, a regulated pressurized air supply was used to provide pressures up to 2.8×10^5 Pa (40 psi). The air was isolated from the water solution by a movable rubber piston in a cylinder; this prevented dissolution of air in the water.

100 ml SOLUTION RESERVOIR

140 cm

GROUND GLASS FITTINGS

20 g ROCK AGGREGATE

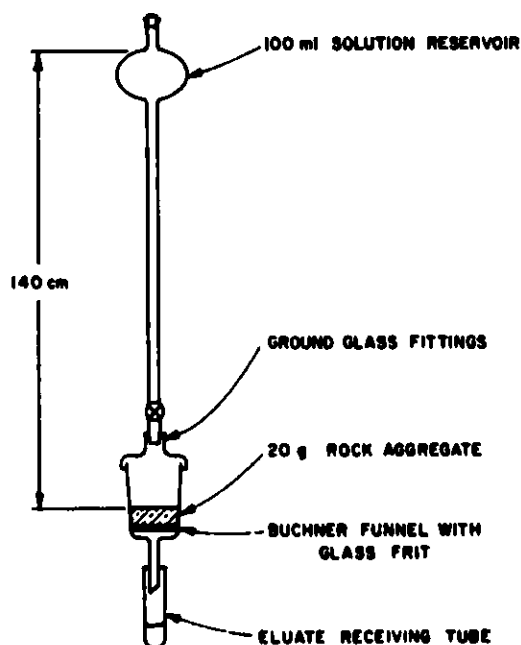BUCHNER FUNNEL WITH GLASS FRIT

ELUATE RECEIVING TUBE

Fig. 1. Infiltration Apparatus (Low Pressure) for
Use with Rock Aggregate

Analysis of the results of column-infiltration tests is simplified if certain conditions concerning the water-rock systems are maintained. One of these conditions is to utilize a rock column that is a continuous, homogeneous medium. Another condition is that dispersion effects mix successive volumes of solutions but do not destroy symmetrical distributions of nuclides.

To test whether these conditions have been met in these studies, criteria for judging the performance of columns have been used. For example, only columns free of visible cracks, voids, or other heterogeneities were considered to possibly be homogeneous. In columns of aggregated rock, the wetting fronts during the initial infiltration of water were observed. When wetting fronts, one of unsaturated flow and one of saturated flow, proceeded with uniform velocities through the columns, this was taken to be indicative of homogeneity in the columns. Solid rock columns for which there was an abrupt increase in flow rate (evidence of cracks) were abandoned. Other observations were used to diagnose conditions within the columns.

Thirteen experiments with cesium, plutonium, americium, and neptunium nuclides were performed in columns. The rocks and elements studied in these experiments are listed in Table 4.

Table 4. Rocks and Elements Studied in Infiltration Experiments

Rock Type	Elements and their Valence States	Rock Density, g/cm^3	Rock Porosity,[a] vol %
Shale, Pierre Front Range	Cs^+	1.2	27
Chalk, Selma	Cs^+	1.0	40
Limestone, Salem Formation	Am^{3+}, Np^{5+}, Pu^{4+}	2.3	13
Sandstone, Ohio Barrier	Am^{3+}, Np^{5+}	2.1	19
Tuff, Nevada Test Site	Am^{3+}	1.7	27

[a] Porosity measurements were performed by weighing a sample before and after its saturation with water. The difference in weight is indicative of the pore volume of the sample.

When solutions of very low concentrations of cesium are used, the absorption of cesium on glassware is of concern. To examine this, two glass tubes were filled with cesium-containing water, one with water pre-equilibrated with chalk and the other with water pre-equilibrated with shale. The solution activity was monitored for the duration of the infiltration experiments. No absorption of cesium onto the glass was detected; thus, the glass used in these experiments apparently performed satisfactorily. However, after 250 h, a precipitate did form in the shale-equilibrated water, accompanied by a decrease of 50% in the activity of the solution. The precipitate may be related to the organic content of the shale and may be of biological origin.

Five column experiments (1 through 5, Table 5) were performed with Selma chalk or Pierre shale. The chalk or shale was crushed and sieved to 18 mesh and then ground for 10 min in an automatic mortar and pestle; the material (rock aggregate) was then used to form the rock columns. This

Table 5. Relative Migration Rates of Cesium Measured in
Crushed Selma Chalk and Crushed Pierre Shale

Expt.	Material	Range of Column Elution Rates, mL/h	Elution Volume, mL	Final Quantity of Cesium on Column, $\mu Ci/g$	Relative Migration Rate[a]	
					Peak Activity,[b] V_{cs}/V_w	Maximum Detected, V_{Cs}/V_w
1[c]	Chalk	4.2–20	2 300	1.0	1×10^{-5}	0.16×10^{-2}
2[d]	Chalk	1.9–9	3 500	0.28	0.6×10^{-5}	0.24×10^{-2}
3[d]	Shale	0.7–0.9	560	0.028	9×10^{-5}	0.8×10^{-2}
4[c]	Shale	0.2–0.5	370	0.20	6×10^{-5}	0.2×10^{-2}
5[d]	Shale	0.4–1.1	530	0.28	70×10^{-5}	50×10^{-2}

[a]The relative migration rate is the velocity of the nuclide divided by the velocity of the infiltrating water. The calculation of relative migration rate uses the porosity values given in Table 4 and that fluid flows through all pores.

[b]These values represent maximum migration rates for the peak activities. However, no evidence of migration of the peak activity was detected; the peak migration rates were estimated by assuming that the activity had traveled the thickness of the sample that was taken from the top surface.

[c]Cesium added to pre-equilibrated solution.

[d]Cesium added to the top surface of the water-saturated column.

[e]In experiment 5, there was rapid migration of some cesium through large cracks in the crushed material.

treatment was chosen to separate the particles of shale or chalk while minimizing the fracturing of individual grains. In two experiments (Expt. 1 with chalk and Expt. 4 with shale), cesium was added to the mineral water. In the other three experiments, small volumes of solution containing cesium were added directly to water-saturated rock columns.

In each experiment, eluates were collected and analyzed for nuclide activity. Figure 2 gives the activity per mL in the eluate as the fraction of activity in the starting solutions versus the cumulative volume of eluate for Expt. 1 (Selma chalk). No activity was detected in the first 25 column volumes of eluate that passed through the column. There was measurable activity in eluates for the remainder of the experiment, but it was a small fraction of the activity of the infiltrating solution.
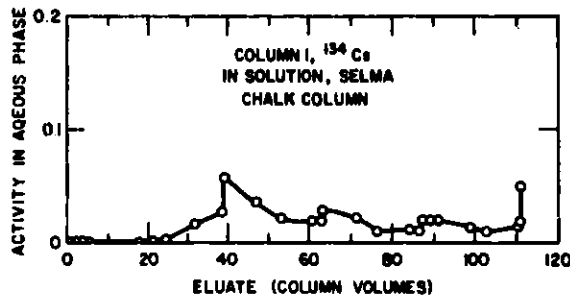
Fig. 2. Cesium-134 Activity in the Eluate Versus Cumulative Eluate Volume. Expt. 1 Selma chalk column.

In Expt. 5, activity was detected in the initial eluate obtained; this is believed to be a consequence of a wetting and drying sequence that preceded application of cesium solution and produced fissures in the shale material. The fissures closed after application of the radioactive eluant. The concentration of cesium in the eluate decreased gradually during the experiment.

Each experiment was terminated by stopping eluant addition. The column of rock aggregate was then sampled at various depths to determine how far the cesium had penetrated. The activity levels determined in the four columns in which no cracking occurred are plotted in Fig. 3. A small top sample was taken from each column which was the position of maximum concentration (*i.e.*, the peak activity) within the column. The peak activity did not move perceptibly within the columns during an experiment. However, all samples analyzed contained measurable concentrations of cesium. The final distribution of cesium in the columns is strongly skewed, with the maximum near the top surface of the column and a long tail of activity extending in the direction of water flow. The presence of cesium at the bottom of the columns implies a spread in the relative migration rates for the cesium. Data are given in Table 5 on the infiltration experiments and the migration rates based on (1) the position of the peak activity and (2) the detection of cesium in the eluate or in the bottom of the columns.
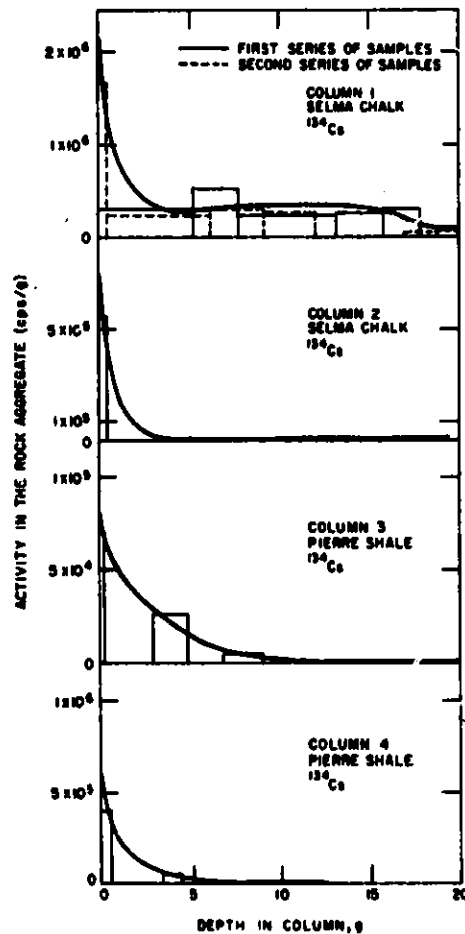
Fig. 3. Column Infiltration Experiments. Plot of the activity in
the rock at the end of an experiment versus depth in the
columns. All columns had measurable ^{134}Cs concentrations
at the bottom (20 g) level (not visible in all graphs).
Column numbers correspond to experiment numbers.

Eight experiments were done in columns to investigate the migration of
plutonium, americium, and neptunium through limestone, sandstone, and tuff.
Cylindrical rock columns were cut from rocks and were sealed with epoxy in
polyethylene tubes in a manner to prevent water bypassing. The rock columns
were wetted with mineral water, and nuclides were added to the top surfaces
of the columns in small volumes (1 mL) of water. After the radioactive water
soaked into a rock, the column was pressurized with mineral (equilibrated)
water. The eluates from each experiment were collected and were analyzed for
the amount of nuclide that had passed through the column. The relative migra-
tion rate was calculated as the distance the nuclide traveled, divided by the
distance the water front traveled (Table 6). For a nuclide detected in the
eluate, the distance traveled was the thickness of the entire rock column.
The results are expressed as the percentage of each nuclide that traveled at a
migration rate greater than the corresponding migration rate given in column
4. For the first experiment listed in Table 6, as an example, it can be seen
that 2.6% of the plutonium nuclide was eluted from the column at a migration
rate >0.001 times the travel rate of the water front. At this migration
rate, 2.6% of the nuclide passed from the top to the bottom of the column in
an eluate volume 1000 times the pore volume of the column.

Table 6. Cumulative Percentages of Nuclide (Column 5) with a Velocity
Greater than the Stated Migration Rate (Column 4) as
Determined in Column Infiltration Experiments

Sample	Expt.	Element and Valence State	Migration Rate[a] of Nuclide Relative to Water Front Travel Rate	Nuclide Passing Through the Core, Cumulative %
Limestone, Salem Formation	6	Pu^{4+}	1 0.5 0.006 0.001	0.007 0.1 0.11 2.6
Limestone, Salem Formation	7	Am^{3+}	0.3 0.05 0.01 0.007	0.002 0.005 0.024 0.031
Limestone, Salem Formation	8	Np^{5+}	1.0 0.5 0.02 0.009	0.030 0.053 0.092 0.69
Limestone Salem Formation	9	Am^{3+}	0.42 0.008 0.003 0.001	0.000 4 0.008 0.068 0.28
Limestone, Salem Formation	10	Np^{5+}	0.4 0.1 0.003 0.001	0.04 0.11 1.1 6.1
Sandstone, Ohio Barrier	11	Am^{3+}	0.3 0.05 0.04 0.011	0.000 2 0.002 0.024 0.033
Sandstone, Ohio Barrier	11	Np^{5+}	1 0.10 0.01 0.005	1.3 12.3 61.3 69.7

(Contd)

Table 6.   (Contd)

Sample	Expt.	Element and Valence State	Migration Rate[a] of Nuclide Relative to Water Front Travel Rate	Nuclide Passing Through the Core, Cumulative %
Sandstone, Ohio Barrier	12	Np^{5+}	0.4 0.09 0.03 0.005	0.45 12 28 45
Tuff, Nevada Test Site	13	Am^{3+}	0.03 0.15 0.09 0.06	0.000 3 0.001 0.004 0.009

[a]The relative migration rate, V_n/V_w, was calculated from the eluate volume, v_e, by the equation

$$V_n/V_w = T(\epsilon A)/v_e$$

where ϵ is the porosity of the rock (given in Table 4) and A and T are the cross-sectional area and the thickness of a column, respectively.

The effective migration rate for a fraction of the nuclides as measured experimentally (*e.g.*, as given in Table 6) is thought to be the result of dispersion in the migration rates of the nuclide population; a specific fraction of the nuclide is not thought to have a single migration rate that differs from that of the other fractions. That is, an atom is thought to have had different velocities within a spectrum of velocities common to all atoms as it moved through the column.

IV. STATIC ABSORPTION EXPERIMENTS

Static absorption experiments were done on a series of rock types (*i.e.*, rocks listed in Table 2 except for Selma Chalk and Pierre Shale which were excluded because they fell apart in water). In an experiment, a tablet of rock was suspended by a platinum wire inside a polyethylene tube and was immersed in a solution containing radionuclides of plutonium or americium or both. After various periods of immersion, the rock tablet was removed from the solution and the activity remaining in solution was monitored by gamma counting. After monitoring of the radioactivity, the rock tablet was reimmersed in the solution to continue the experiment. Generally, the activity absorbed by the rock increased very rapidly during the first few hours or days of contact of solution and rock. Correspondingly, the activity associated with the solution decreased rapidly at first and then changed slowly until it remained constant for the remainder of the experiment. Figure 4 is a typical plot of reaction time versus the amount of nuclide remaining with the solution. The amount of nuclide with the solution is expressed relative to the amount of nuclide in solution at the start of the experiment.
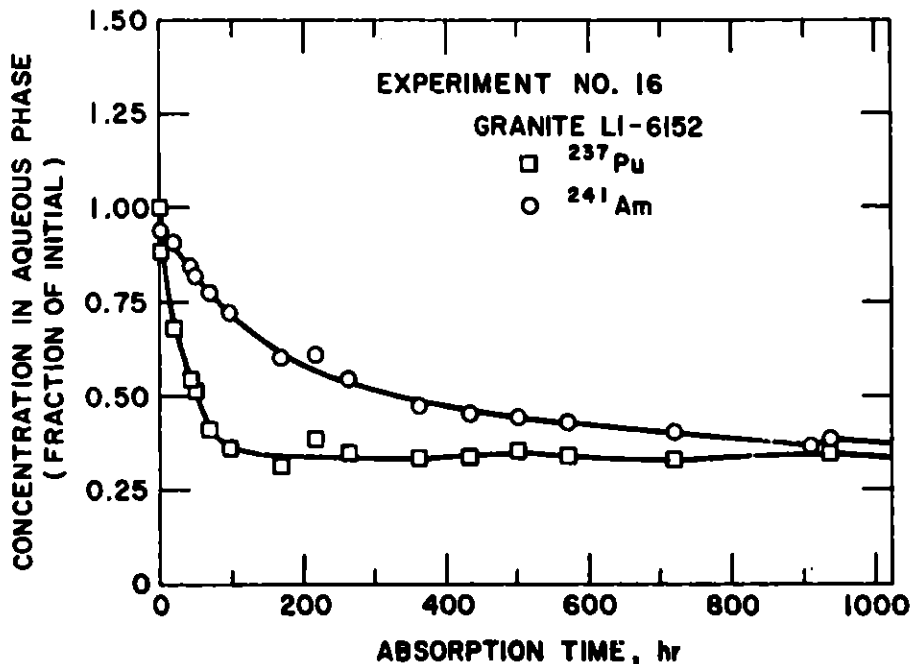
Fig. 4. Static Absorption Experiment 16. Activity of plutonium and americium in solution as a function of contact time with a rock tablet (granite LI-6152).

The amount of radionuclide, A_r, absorbed by the rock as a function of the time, t, that the solution and rock were in contact was approximated by the equation

$$A_r = A_f \left[1 - e^{-(t/t_r)} \right] \qquad (1)$$

where A_f is the final amount absorbed by the rock and t_r is the characteristic time of reaction. The exponential increase in the amount of nuclide absorbed by the rocks suggests that the reactions of both plutonium and americium with the rocks proceed with first order kinetics.

Some of the nuclides were absorbed on the polyethylene tubes used in the experiments. After the activities had attained constant values (at $t \gg t_r$), the tubes were emptied of rock and solution, lightly rinsed, and counted to determine the activity that adhered to them. The amounts of nuclides in the empty tubes were subtracted from the total amounts in the solution-containing tubes to obtain the amounts in the solutions, A_s. The latter amounts were used to determine K_D, the ratio of nuclide in the solid to nuclide in solution at the end of an experiment, by the equation

$$K_D(mL/g) = \frac{A_f/g \text{ of rock}}{A_s/mL \text{ of solution}}$$

In experiments with some rocks, the radionuclides were strongly absorbed by the rock tablets and the amount of nuclide absorbed on the polyethylene tubes was a large fraction (>50%) of the total activity remaining in the tubes. This effect resulted in large corrections to the nuclide concentrations of the solutions and in subsequent errors in the calculated ratios of nuclides in the rocks to nuclides in solution.

Results from the experiments with two isotopes added to each solution are listed in Table 7. Most experiments (20 out of 31) exhibited the behavior represented by Eq. 1, for which a characteristic time of reaction, t_r, and a partition coefficient, K_D, could be determined. The values of t_r were estimated from absorption curves, and the values of K_D were calculated from the counting data.

Table 7. Static Absorption Experiments with Plutonium and Americium Added Simultaneously to Each Solution at Ambient Temperature. The experiments were each run for 900 h or more.

Rock Type	Expt.	Characteristic Reaction Time, h		Partition Coefficient, K_D	
		Pu	Am	Pu	Am
Limestone, Salem Formation	13-A	40	10	>150[a]	~160[a]
Granite, LI-6152	16	25	160	30[a]	5
Columbia River Basalt	19	60	150	230[a]	320
Tuff, Nevada Test Site	22	180	5	39	370[a]
Low-Temperature Metamorphic	25	450	~20	130	2.6
Magenta	28	50	400	41[a]	47

(Contd)

Table 7. (Contd)

Rock Type	Expt.	Characteristic Reaction Time, h		Partition Coefficient, K_D	
		Pu	Am	Pu	Am
Georgia Marble	30	5	5	77[a]	162[a]
Georgia Marble	31	5	5	180[a]	160[a]
Georgia Marble	32	8	5	51[a]	220[a]
Colitic Limestone	33	5	<5	540[a]	415[a]
Colitic Limestone	34	5	<5	710[a]	520[a]
Colitic Limestone	35	5	<5	210[a]	690[a]
Barrier Sandstone	36	50	25	8.2	11
Barrier Sandstone	37	n.d.[b]	15	20	12
Barrier Sandstone	38	50	15	6.4	7.7
Soapstone	39	15	10	8.4[a]	23[a]
Soapstone	40	15	15	23[a]	67[a]
Soapstone	41	20	25	28[a]	105[a]
Culebra, Sandia WIPP	42	<5	<5	16[a]	58[a]
Culebra, Sandia WIPP	43	1	1	19[a]	84[a]
Culebra, Sandia WIPP	44	1	1	20[a]	59[a]
Gneiss, FMS LI-3896	45	75	≳600	10	18[c]
Gneiss, FMS LI-3896	46	150	≳600	17	8.3[c]
Gneiss, FMS LI-3896	47	150	≳600	16	4.4[c]
Dolomite	48	<5	<5	3.4[a]	10[a]
Dolomite	49	<5	<5	34[a]	150[a]
Dolomite	50	<5	<5	13[a]	26[a]
Chalcopyrite	51	100	75	25	0.6
Chalcopyrite	52	150	n.r.[d]	3	0.3
Chalcopyrite	53	200	n.r.	4.7	0.5
Galena	56	n.d.	n.r.	3.9[a]	0.1

[a] In these experiments, a considerable amount (>50%) of the radionuclide associated with the solution was retained on the walls of the polyethelene tube. The activity in the solution was determined by subtracting the activity on the walls from the activity of the tube plus solution. The corrections are large and may have led to errors in the calculated partition coefficients.

[b] "n.d." indicates that the activity curve did not fit the behavior indicated by Eq. 1.

[c] Partition coefficients were measured after a 1000-h experiment and do not represent equilibrium conditions.

[d] "n.r." indicates that reaction was insufficient to allow the characteristic reaction time to be measured.

The characteristic times of reaction for different nuclides and rocks show a considerable spread in these experiments, varying from about 1 h to in excess of 600 h. However, for a particular nuclide and rock, the time of reaction appears to be constant and well defined, as indicated by the consistency of results of triplicate experiments. With some rocks (*e.g.*, gneiss), the characteristic reaction times were long and steady-state behavior was not attained, even in the 1000-h experiments.

In most experiments, the plutonium and americium nuclides were absorbed by the rocks. Often, the isotopes were strongly fractionated to the rocks, leading to partition coefficients in excess of 100.

Some static-absorption experiments were performed with only one element, plutonium or americium, initially in solution. A solution was reacted with rock, and the activity of the solution was monitored as a function of time. After about 1000 h of contact of the solution and rock, a spike of the second element was added to the solution. The solution was again contacted with rock and the activities of both nuclides in the solution were monitored.

Twelve absorption experiments were run in a first series of experiments, six with plutonium and six with americium as the initial nuclide. Four additional experiments (1A, 2A, 4A, 5A) were run to investigate effects seen in the first series of experiments. The absorption experiments and results are listed in Table 8.

The parameters measured in the experiments were (1) the reaction time, defined as the time required to achieve 63% of the change between the initial and final nuclide concentrations, and (2) partition coefficient, defined as the activity of the rock per gram of rock divided by the activity of the solution per milliliter of solution.

For experiments in which plutonium was the initial nuclide in solution, the absorption behavior seen for the rocks is consistent with that seen previously--that is, there is an initial rapid decrease in the activity of the solution as the nuclide is absorbed by the rock. The change is less rapid with increased time until the activity attains a value that remains constant with time.

The addition of the americium spike to the solution had no measurable effect on the behavior of plutonium. This behavior is seen in Fig. 5. The measured reaction times and distribution coefficients of plutonium and americium are comparable to those measured when plutonium and americium are initially added simultaneously (see Table 7).

However, in the experiments in which americium was the initial nuclide, the addition of the plutonium spike often had a significant effect on the behavior of the americium. This can be seen in Fig. 6, which is a plot of the nuclide activities in a solution in which Columbia River basalt was immersed. In three experiments, absorption of americium on the rock was enhanced by the addition of plutonium (Expt. 14, 17, 20). In another experiment (Expt. 26), addition of the plutonium spike resulted in re-solution of americium from the rock. The net effects of the addition of plutonium in these four experiments were to decrease the reaction time (*i.e.*, to increase the reaction rate) and to change the absorption of americium. In two of six experiments in which americium was the initial nuclide, the addition of plutonium appeared to have no effect on the behavior of americium.

Table 8. Results of Static Absorption Experiments with
Plutonium and Americium Added Sequentially

Rock Type	Expt.	Reaction Time, h		Partition Coefficient	
		Pu	Am	Pu	Am
Experiments with Initial Plutonium Nuclide					
Limestone, Salem Formation	12	3	75	16	4.7
Granite, LI-6152	15	60	150	40	6
Columbia River Basalt	18	75	100	115	135
Tuff, Nevada Test Site	21	300	5	33	59
Low-Temperature Metamorphic	24	600	n.r.[a]	94	
Magenta, Sandia WIPP	27	7	50	9	6
Experiments with Initial Americium Nuclide					
Limestone, Salem Formation	14	200	150(40)[b]	20	12.7
Granite, LI-6152	17	50	300(75)[b]	40	18
Columbia River Basalt	20	100	500(75)[b]	99	280
Tuff, Nevada Test Site	23	n.r.[a]	500[d]	$\sim$0	2.8
Low-Temperature Metamorphic	26	>600[d]	5(5)[c]	19[d]	$\sim$0
Magenta	29	5	700	2	6
Limestone, Salem Formation	1-A[e]	75	200	60	120
Limestone, Salem Formation	2-A[e]	100	200	55	110

(Contd)

Table 8. (Contd)

Rock Type	Expt.	Reaction Time, h		Partition Coefficient	
		Pu	Am	Pu	Am
Limestone, Salem Formation	4-A[e]	100	250	9[f]	22[f]
Limestone, Salem Formation	5-A[e]	100	200	57	128

[a]n.r. = indicates that the reaction was insufficient to allow the characteristic reaction time to be measured.

[b]Significant absorption of americium was produced upon addition of the plutonium spike. The numbers in parentheses are the reaction times for americium after addition of the plutonium spike.

[c]Significant re-solution of americium was produced upon addition of plutonium spike.

[d]The length of time allowed for reaction (500 h) was insufficient to establish equilibrium.

[e]The plutonium solution was doubly purified in an exchange column prior to addition to the americium solution.

[f]Length of time allowed for reaction (350 h for Am and 150 h for Pu) was insufficient to establish equilibrium.
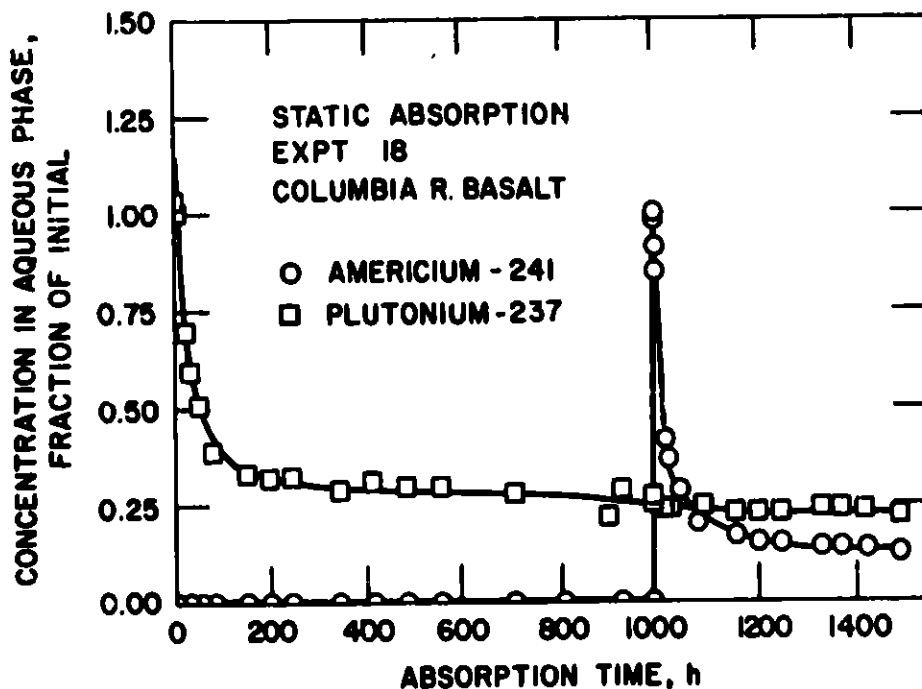
Fig. 5. Experiment 18. Absorption of Plutonium on a Tablet of Columbia River Basalt with the Addition of Americium Activity at 1000 h. No effects of americium addition on plutonium behavior are evident.
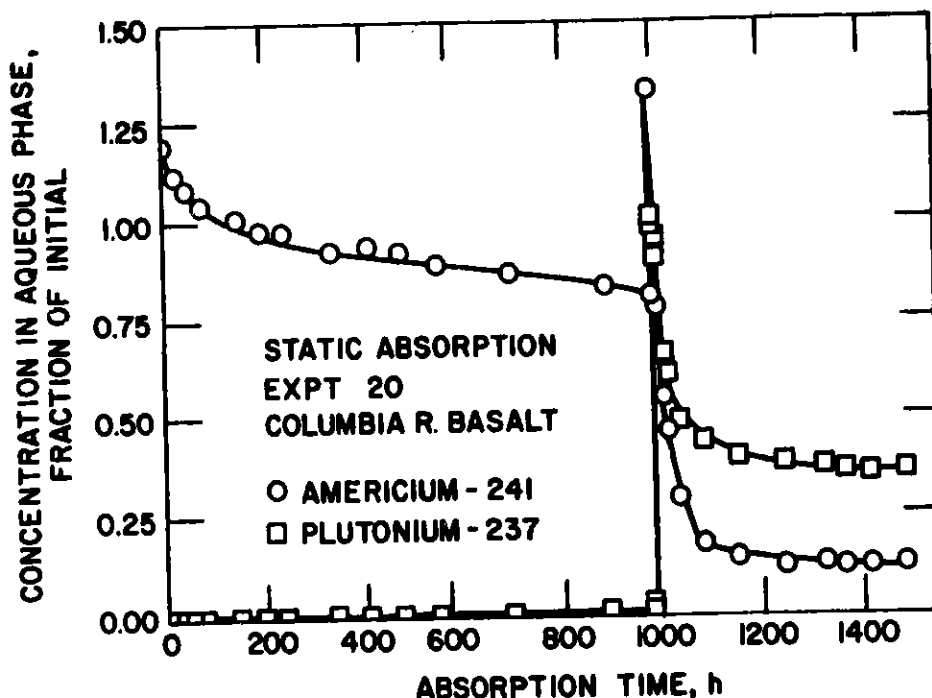
Fig. 6. Experiment 20. Absorption of Americium on Columbia River
Basalt with the Addition of Plutonium Activity at 990 h.
The plutonium spike is seen to markedly affect the
adsorption behavior of americium.

Four experiments (1A, 2A, 4A, 5A) were done to investigate the source
of synergistic behavior. In the experiments, absorption of americium on
limestone was followed by the addition of plutonium to the solution and
were performed in a manner similar to Expt. 14, in which synergistic behavior
was seen. However, in these experiments, the plutonium solution that was
added after the absorption of americium had been purified twice (rather than
once as previously done) to increase its purity. The plutonium solution
was otherwise treated similarly to that previously used (the solution was
dried, the plutonium was redissolved in distilled water, etc.). In these
four experiments in which plutonium was added to an americium solution which
had reacted with limestone (Table 8), no synergistic effect was observed.
This suggests that the purification procedure removed auxiliary chemicals that
affected the absorption of americium on limestone. In addition, the results
suggest that the plutonium itself does not produce the synergistic behavior.

Other possible reasons for the absence of an observed synergistic
effect are that the chemical form of the americium might differ or plutonium
or auxiliary chemicals in the initial americium solution might mask the
synergistic behavior in the experiments that were performed.

From the experimental results, interactive effects were present when a
plutonium spike was added to solutions containing americium. The interactive
behavior was eliminated by twice purifying the plutonium solution before it
was added to americium solution that had reacted with limestone.

V. BATCH PARTITIONING EXPERIMENTS

Three sets of batch partitioning experiments are described. The first set of experiments was performed to test the reversibility of the absorption process. The second set was performed to determine whether absorption increases with decreasing particle size of a rock. The third set of experiments was performed with various rocks under similar conditions, allowing the rocks to be ordered with respect to their ability to absorb nuclides of plutonium, americium, and neptunium.

Batch partitioning experiments were performed in stopper test tubes in which 0.1 to 0.5 g of granulated rock and 2 or 3 mL of solution were mixed by slowly turning the test tube end over end for periods up to 500 h. Temperature was either ambient (24°C) or maintained at slightly elevated temperatures in an oven. After the mixing, the tubes were centrifuged and the solution sampled and analyzed for radionuclide activity. Because the activities of the solutions were determined directly, corrections due to activity absorbed on the walls of the test tubes were not necessary. The activity on the granulated rock was determined from the difference in activities of the starting and final solution. Because much of the radionuclide was absorbed by the rock, corrections due to absorption on the test tube walls were small and were neglected.

A. Reversibility of Absorption Process

The migration behavior of nuclides depends sensitively on whether absorption processes are reversible. (Models used to predict nuclide migration generally assume that the chemical reactions involved are reversible.) To test whether the absorption of americium on a common rock is reversible, batch experiments were done with granulated Columbia River basalt of graded mesh size and americium-bearing solutions. After mixing of rock and solution for 500 h, one or two milliliters of solution was removed from the test tubes and analyzed for americium-241 activity. The partitioning of americium between solution and rock during absorption was determined from the initial and final activities of the solution.

The active solution that had been sampled from the test tubes was then replaced with rock-equilibrated water containing no activity, and the water-basalt system was agitated for an additional 500 h. The activity of the solution after this agitation period was determined and is indicative of the partitioning of americium during desorption. The experimental results are given in Table 9. The results indicate that americium desorbed from the basalt and that the reaction is reversible. However, the partition coefficients are higher after desorption, indicating that americium is preferentially retained by the rock. This effect is not large, considering that greater than 90% of the americium activity is retained by the rock after both absorption and desorption. The results may also include effects or rock-particle weathering that may have occurred during mixing of the particles with solutions and may alter the ratio of activity in solution and on rocks with time.

Table 9. Partition Coefficients for Values of Americium
in Granulated Columbia River Basalt After
Absorption and Desorption[a]

Expt.	Mesh Size	Partition Coefficeint, K_D, After Absorption	Partition Coefficient, K_D, After Desorption
1	16-20	83	156
4	16-20	70	124
7	16-20	95	121
2	30-40	138	247
5	30-40	148	336
8	30-40	121	164
3	50-70	147	316
6	50-70	164	322
9	50-70	115	215

[a]Equilibration times for absorption and desorption were
each 500 h. The experimental temperature was 24°C.

The existence of reversibility in these experiments contrasts with
results obtained when rock samples were allowed to dry after absorption. In
19 desorption experiments of that type, 11 showed no measurable desorption
of plutonium or americium, 6 experiments showed slight desorption of
americium, 1 experiment (with marble) showed slight desorption of plutonium,
and 1 experiment (with galena) showed complete reversibility of americium
during desorption. These results indicate that reversibility of the reactions
depends upon the history of the rock-nuclide system.

B.   Effect of Rock Particle Size on Absorptivity

Batch absorption experiments were done to determine whether decreasing
the particle size of material would increase its absorptivity since the
amount of absorption per gram of material may increase as the surface area
of the material increases if absorption is a surface phenomenon.

To test whether absorption is a surface phenomenon, a fine-grained basalt
(Columbia River basalt) was ground and was divided into three mesh sizes.
Basalt was chosen because of its moderate distribution coefficients for
plutonium(IV) and americium(III) and its presumed low permeability. The
surface areas of the three mesh-size samples were determined using the
B.E.T. (Brunauer-Emmett-Teller) method. These surface area measurements,
reported in Table 10, were similar for the three samples and indicated that
the basalt may have a fine pore structure yet still be of low permeability.
A porous structure may account for the large surface area compared to that
calculated assuming nonporous spheres (as presented in Table 10).

In each experiment, basalt was allowed to equilibrate under slight
agitation with water solutions to which plutonium(IV) and americium(III)
tracers had been added (Table 11). Six measurements were made for each
nuclide with each of the three mesh sizes used. The conditions used in these
batch partitioning experiments and the measured partition coefficients in

Table 10. Surface Areas of Three Mesh Sizes
of Columbia River Basalt

Mesh Size	Opening Width, μm	Surface Area Calculated for Nonporous Sphere, m^2/g	Surface Area from B.E.T. Measurem.,[b] m^2/g
16-20	850 to 1180	0.0020 to 0.0028	8.7
30-40	425 to 595	0.00398 to 0.0056	7.3
50-70	212 to 300	0.0079 to 0.0112	7.7

[a] Range of surface areas was calculated from the range of
particle sizes presumed to be in each size fraction.
Nonporous spheres were assumed.

[b] An indication of the sensitivity of the method was a
measurement giving a surface area of 0.1 m^2/g for a powdered
sample of $BaCO_3$.

the basalt materials of various particle sizes are given in Table 11. No
difference in partitioning was noted (using the Student T Test) for materials
of the two smallest mesh sizes (30-40 and 50-70 mesh) for either nuclide.
However, there was a significant increase in partition coefficient of
americium when the mesh size was changed from 16-20 to 30-40 (greater than
90% confidence that they represent different values). This grain-size
effect on americium is also evident from the data in Table 9. The
partitioning of plutonium was also seen to decrease with increasing particle
size for the two largest mesh sizes but less than for americium (plutonium
partitioning values increased from ~85 to ~115 when particle size was
decreased from 16-20 to 30-40 mesh).

C. Relative Absorptivity of Rocks

Batch partitioning experiments using a variety of rocks were performed
to compare their absorptivity. Conditions and results are listed in Table 12.
From these studies, it was seen that the nuclides of all the elements
(plutonium, americium, and neptunium) were absorbed strongly by the geologic
materials that were studied. In most experiments, greater than 85% of the
activity was absorbed from solution by the granulated rock. In many
experiments, greater than 98% of the activity was absorbed from solution.

Experiments performed with anhydrite (gypsum), witherite, and chalk
(with results listed in Table 12) were done with materials of several mesh
sizes. The greatest change in absorption related to changing particle size
was for plutonium absorption by the two smallest mesh sizes (30-40 and 50-70)
of anhydrite. However, even for the three mesh sizes of anhydrite, more
than 98% of the activity was absorbed by rock material of all mesh sizes. It
is concluded that the variations in absorption with varying grain size for
anhydrite, witherite, and chalk are small. Surface area measurements for
chalk, anhydrite (gypsum), and witherite of the three mesh sizes are given
in Table 13.

Table 11. Batch Partitioning Experiments—Conditions and Measured Partition Coefficients in Granulated Basalt of Various Particle Sizes (ambient temperature; absorption time of 500 h)

Mesh Size	Sample No.	Samplt Weight, g	Solution Volume, mL	Americium Absorbed, %	Americium Partition Coefficient	Plutonium Absorbed, %	Plutonium Partition Coefficient
16-20	147-1	0.262	2	91.6	83	n.p.[a]	n.p.
	147-4	0.561	3	92.9	70	n.p.	n.p.
	147-7	0.261	3	89.2	95	n.p.	n.p.
	157-1	0.207	2	89.4	81	91.6	106
	157-4	0.265	3	86.6	73	84.3	61
	157-7	0.408	3	93.0	98	91.7	81
	157-11	0.212	2	n.p.	n.p.	92.7	119
	157-14	0.211	3	n.p.	n.p.	78.6	52
	157-17	0.323	3	n.p.	n.p.	92.0	107
30-40	147-2	0.146	2	91.0	138	n.p.	n.p.
	147-5	0.120	3	85.6	148	n.p.	n.p.
	147-8	0.356	3	93.5	121	n.p.	n.p.
	157-2	0.145	2	92.3	165	91.3	144
	157-5	0.248	3	91.8	135	90.8	119
	157-8	0.330	3	91.4	97	89.4	77
	157-12	0.165	2	n.p.	n.p.	91.7	134
	157-15	0.179	3	n.p.	n.p.	79.7	66
	157-18	0.333	3	n.p.	n.p.	94.8	164
50-70	147-3	0.104	2	88.4	147	n.p.	n.p.
	147-6	0.151	3	92.5	164	n.p.	n.p.
	147-9	0.253	3	90.7	115	n.p.	n.p.
	157-3	0.120	2	94.4	280	91.8	187
	157-6	0.179	3	91.8	186	87.8	120
	157-9	0.286	3	94.0	165	92.1	122
	157-13	0.203	2	n.p.	n.p.	91.6	108
	157-16	0.133	3	n.p.	n.p.	83.5	114
	157-19	0.303	3	n.p.	n.p.	91.2	103

[a] "n.p." indicates that the element was not present in the batch partitioning experiment.

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Table 12. Conditions and Results of Batch-Partitioning Experiments with Various Geologic Materials

Sample	Experimental Series	Ion	Sample Weight, g	Mesh Size	Temp, °C	Time Allowed For Sorption, h	Activity in Solution, cpm	Volume of Solution, mL	Activity on Rock, cpm	Distribution Coefficient
Chalk, Selma[a]										
	111-2	Am^{3+}	0.286	60-100	50	24	<1	2	7 740	>54 100[b]
		Np^{5+}					16		1 720	752
	157-20	Am^{3+}	0.184	16-20	24	488	1	2	29 300	318 000
	157-21	Am^{3+}	0.152	16-20	24	488	15.3	3	28 100	36 400
	157-22	Am^{3+}	0.246	16-20	24	488	11.5	3	28 800	30 500
	157-23	Am^{3+}	0.101	30-40	24	488	1.4	2	29 700	419 000
	157-24	Am^{3+}	0.097	30-40	24	488	7.8	3	28 600	114 000
	157-25	Am^{3+}	0.161	30-40	24	488	1.1	3	29 200	497 000
	157-26	Am^{3+}	0.093	50-70	24	488	1	2	29 200	>497 000
	157-27	Am^{3+}	0.116	50-70	24	488	9.5	3	28 500	77 600
	158-28	Am^{3+}	0.116	50-70	24	488	2.9	3	25 900	230 000
	157-29	Am^{3+}	0.125	16-20	24	488	<1	2	27 700	>444 000
		Pu^{4+}					4.8		16 200	54 000
	157-30	Am^{3+}	0.208	16-20	24	488	6.4	3	26 800	60 600
		Pu^{4+}					<1		13 500	>194 000[b]
	157-31	Am^{3+}	0.260	16-20	24	488	2.6	3	24 200	108 000
		Pu^{4+}					<1		47 900	>554 000[b]
	157-32	Am^{3+}	0.108	30-40	24	488	1.3	2	28 600	408 000
		Pu^{4+}					4.2		11 500	50 900
	157-33	Am^{3+}	0.158	30-40	24	488	<1	3	27 600	>525 000[b]
		Pu^{4+}					<1		10 900	>207 000[b]
	157-34	Am^{3+}	0.199	30-40	24	488	5.22	3	24 100	69 400
		Pu^{4+}					5.34		54 400	153 000
	157-35	Am^{3+}	0.059	50-70	24	488	1.94	2	28 300	494 000
		Pu^{4+}					3.8		9 150	81 300
	156-36	Am^{3+}	0.078	50-70	24	488	10.6	3	27 000	98 200
		Pu^{4+}					<1		15 800	612 000
	157-37	Am^{3+}	0.156	50-70	24	488	<1	3	22 100	426 000
		Pu^{4+}					6.2		39 600	123 000
	157-38	Pu^{4+}	0.164	16-20	24	488	10.2	2	19 100	22 800
	157-39	Pu^{4+}	0.1566	16-20	24	488	2.55	3	17 800	134 000
	157-40	Pu^{4+}	0.210	16-20	24	488	<1	3	11 400	>163 000[b]
	157-41	Pu^{4+}	0.115	30-40	24	488	<1	2	18 800	>326 000
	157-42	Pu^{4+}	0.144	30-40	24	488	3.0	3	11 900	82 700
	157-43	Pu^{4+}	0.169	30-40	24	488	<1	3	14 500	>258 000[b]
	157-44	Pu^{4+}	0.087	50-70	24	488	9.4	2	16 400	40 200
	157-45	Pu^{4+}	0.073	50-70	24	488	2.55	3	8 060	130 000
	157-46	Pu^{4+}	0.119	50-70	24	488	5.7	3	12 100	53 300

(Contd)

Table 12. (Contd)

Sample	Experimental Series	Ion	Sample Weight, g	Mesh Size	Temp, °C	Time Allowed For Sorption, h	Activity in Solution, cpm	Volume of Solution, mL	Activity on Rock, cpm	Distribution Coefficient
Limestone, Salem Formation										
	109-12	Am^{3+}	0.397	60-100	50	24	20	2	8 850	2 230
		Np^{5+}					<1	2	1 500	>7 540[b]
	109-13	Pu^{4+}	0.416	60-100	50	24	40	2	2 440	293
Tuff, Nevada Test Site										
	109-16	Am^{3+}	0.319	60-100	50	24	1 790	2	6 520	23
		Np^{5+}					520		630	8
	109-17	Pu^{4+}	0.397	60-100	50	24	800	2	1 760	11
Columbia River Basalt[c]										
	111-1	Am^{3+}	0.115	60-100	50	24	1 190	2	6 890	101
	208-13	Pu^{4+}	0.265	16-20	24	819	650	3	3 560	62
	208-14	Pu^{4+}	0.362	16-20	24	819	550	3	4 400	67
	208-15	Pu^{4+}	0.323	30-40	24	819	700	3	4 060	54
	208-16	Pu^{4+}	0.226	30-40	24	819	640	3	4 160	86
	208-17	Pu^{4+}	0.215	50-70	24	819	1 040	3	3 660	49
	208-18	Pu^{4+}	0.369	50-70	24	819	720	3	4 660	53
Low-Temperature Metamorphic										
	111-3	Am^{3+}	0.185	60-100	50	24	36	2	8 570	2573
		Np^{5+}					360		1 340	40
Georgia Marble										
	109-14	Am^{3+}	0.295	60-100	50	24	20	2	9 050	3 080
		Np^{5+}					16		1 400	592
	109-15	Pu^{4+}	0.366	60-100	50	24	16	2	2 310	720

(Contd)

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Table 12. (Contd)

Sample	Experimental Series	Ion	Sample Weight, g	Mesh Size	Temp, °C	Time Allowed For Sorption, h	Activity in Solution, cpm	Volume of Solution, ml.	Activity on Rock, cpm	Distribution Coefficient
Soapstone										
	111-4	Am^{3+}	0.320	60-100	50	24	<1	2	7 650	>47 200[b]
Dolomite, Quantin Quarry										
	111	Am^{3+}	0.458	60-100	50	24	4	2	8 180	8 920
Chalcopyrite										
	109-4	Am^{3+}	0.310	60-100	50	24	2 420	2	5 290	14
		Np^{5+}					340		1 400	27
	109-5	Pu^{4+}	0.300	60-100	50	24	200	2	2 290	75
	109-8	Am^{3+}	0.751	60-100	50	24	870	2	7 640	23
		Np^{5+}					160		1 360	23
	109-9	Pu^{4+}	0.723	60-100	50	24	8	2	2 690	929
Anhydrite (Gypsum)[c]										
	208-1	Pu^{4+}	0.254	16-20	24	819	66	3	4 580	819
	208-2	Pu^{4+}	0.260	16-20	24	819	101	3	5 930	678
	208-3	Pu^{4+}	0.202	30-40	24	819	75	3	4 770	946
	208-4	Pu^{4+}	0.237	30-40	24	819	58	3	4 770	1 040
	208-5	Pu^{4+}	0.134	50-70	24	819	38	3	4 840	2 840
	208-6	Pu^{4+}	0.156	50-70	24	819	59	3	4 780	1 550
Apatite										
	109-1	Am^{3+}	0.444	60-100	50	24	4	2	8 310	9 350
		Np^{5+}					4		1 140	1 280
	109-2	Pu^{4+}	0.351	60-100	50	24	20	2	2 500	713

(Contd)

30

Table 12. (Contd)

Sample	Experimental Series	Ion	Sample Weight, g	Mesh Size	Temp, °C	Time Allowed For Sorption, h	Activity in Solution, cpm	Volume of Solution, mL	Activity on Rock, cpm	Distribution Coefficient
Argillite, NTS Eleana Formation										
	108-1	Am^{3+}	0.854	60-100	50	24	1 230	2	7 820	15
		Np^{5+}					340		4 000	27
	108-2	Pu^{4+}	0.591	60-100	50	24	670	2	1 710	9
Witherite[c]										
	208-7	Pu^{4+}	0.442	16-20	24	819	10	3	4 500	3 050
	208-8	Pu^{4+}	0.445	16-20	24	819	16	3	4 610	1 940
	208-9	Pu^{4+}	0.330	30-40	24	819	10	3	4 710	4 270
	208-10	Pu^{4+}	0.351	30-40	24	819	34	3	4 650	1 170
	208-11	Pu^{4+}	0.376	50-70	24	819	19	3	4 710	1 980
	208-12	Pu^{4+}	0.367	50-70	24	819	6	3	4 160	5 670
Bornite										
	109-19	Am^{3+}	0.365	60-100	50	24	8	2	8 280	5 810
	109-3	Pu^{4+}	0.434	60-100	50	24	4	2	2 130	2 450
Granite, Nevada Test Site										
	109-10	Am^{3+}	0.302	60-100	50	24	1 940	2	6 320	21
		Np^{5+}					320		1 030	21
	109-11	Pu^{4+}	0.272	60-100	50	24	8	2	2 230	2 050
Dolomite, Nevada Test Site										
	111	Am^{3+}	0.206	60-100	50	24	24	2	8 570	3 470
		Np^{5+}					40		1 620	395

(Contd)

31

Table 12. (Contd)

Sample	Experimental Series	Ion	Sample Weight, g	Mesh Size	Temp, °C	Time Allowed For Sorption, h	Activity in Solution, cpm	Volume of Solution, mL	Activity on Rock, cpm	Distribution Coefficient
Ferric Oxide (reagent)										
	109-6	Am^{3+}	0.212		50	24	<1	2	8 260	>78 000
		Np^{5+}					32		963	284
	109-7	Pu^{4+}	0.229		50	24	32	2	2 280	621

[a] The chalk disaggregated in solution. Therefore, the mesh sizes given are not indicative of particle sizes.

[b] The distribution coefficient was calculated assuming that the solution had an activity of 1 cpm.

[c] The rock-aggregate samples were washed prior to use to remove dust that adhered to the granulated material.

Table 13. Surface Areas of Three
Mesh Sizes of Rocks

Rock	Surface Areas from B.E.T. Measurements, m^2/g		
	16–20 Mesh Size	30–40 Mesh Size	50–70 Mesh Size
Chalk, Selma	13.8	13.9	12.7
Anhydrite (gypsum)	10.1	7.5	8.9
Witherite	>0.1	>0.1	>0.1

VI. DISCUSSION

In most static absorption experiments, the plutonium and americium were seen to be strongly absorbed into the rock. This strong affinity of nuclides for the rock phases would be expected to retard the migration of nuclides during infiltration. In infiltration experiments, nuclides of cesium, plutonium and americium were seen to migrate much more slowly than did the infiltrating fluid. Much of the cesium moved with low velocity, as evidenced by the peak concentration of cesium being near the top of the columns (Fig. 3). Similarly, the results in Table 6 show that most of the plutonium and americium was not eluted from the columns and therefore must have moved only a fraction of the distance of the water front. For example, for the first experiment listed in Table 6, it can be seen that only 2.6% of the activity was eluted from the column with a relative migration rate greater than 0.001 of the water front travel rate. This behavior is consistent with the high partitioning coefficients measured in the batch experiments and substantiates results reported previously.[1]

In order to model the transport phenomena of waste nuclides, simplifying assumptions concerning nuclide-rock reactions have been made in earlier work.[3-6] These assumptions generally include the following: (1) that exchange reactions of nuclides between rock and solution are reversible, (2) that the nuclide-rock reactions are instantaneous so that the equilibrium of the nuclide between solution and rock is locally maintained within the rock, (3) that a rock formation can be represented as a continuous homogeneous medium, and (4) that the concentration of each nuclide is sufficiently low that nuclides react independently of each other and do not affect macroscopic properties of the water.

Given these simplifying assumptions, a nuclide is expected to migrate down the column with a well-defined velocity. For a nuclide concentrated initially in a narrow band at the upper end of the column, continued elution of the column will move the band down the column. As the band moves down the column, it widens and assumes the shape of a Gaussian curve. The velocity of the peak of the nuclide band, V_n, relative to the velocity of the water front, V_w, is given by

$$V_n/V_w = \frac{1}{1 + (K_D \, \rho/\varepsilon)}$$

where ε is the porosity and ρ the density of the rock and K_D is the ratio of the nuclide between solid and solution as defined in Eq. 2.

Where diffusion is small in relation to the migration rate of the band, the band width due solely to the exchange reactions will be proportional to the square root of the distance the peak had traveled. Nuclide migration has been modeled to include dispersion of the type produced by diffusion of nuclides within the fluid.[7] Diffusion of nuclides within the fluid will increase the width of the peak but will not destroy the Gaussian shape of the band. This model of nuclide migration appears to accurately describe the movement of strontium in a column of glauconite aggregate.[4]

However, the simplified model of nuclide migration[3-6] does not, in general, accurately describe results of nuclide migration obtained in this experimental work. From results of the static absorption experiments, the reaction rates appear to be well defined for a particular nuclide-rock system but to be different for different nuclide-rock systems. The reaction times were seen to vary from about 1 h for some systems to in excess of 600 h for others. With some rocks (e.g., gneiss), the reaction times were long and steady state behavior was not attained, even in the 1000-h experiments (Table 7).

These results indicated that in different rock-nuclide systems, attainment of local equilibrium would require different reaction times and, consequently, different velocities of an infiltration fluid. Therefore, models of nuclide migration may need to consider conditions other than local equilibria during fluid flow. Specifically, the various reaction rates for different rock-nuclide systems may need to be included in the models.

Based on the distribution of nuclides in the rock columns or in the eluates during infiltration experiments, it is seen that the nuclides do not behave, in general, as predicted by models using simplifying hypotheses. For example, the skewed distributions of cesium seen in rock aggregate columns imply a large dispersion in the relative migration rates of cesium in both chalk and shale. Although a low migration rate of most of the cesium is evidenced by the high cesium concentrations at the top of the column, cesium is also present at the bottom of the columns, which is indicative of much higher migration rates for some of the cesium. The dispersion in migration rates is evident from the variation in migration rates seen in Tables 5 and 6. Similar dispersive characteristics were seen for plutonium, americium, and neptunium in rock columns; in all infiltration experiments with theses nuclides, activity was detected in the initial one or two column-volumes of eluate that passed through the columns and was also present in all subsequent eluates sampled. Similar skewed distributions were observed for plutonium migration in tuff; the plutonium concentrations were in the form of tails decreasing exponentially with depth in the direction of fluid flow.[8,9] The experimental results suggest that models assuming a simple gaussian distribution for these nuclides would not accurately represent their migration behavior in common rocks.

The skewed distribution in the observed relative migration rates implies that movement of nuclides, even in a uniform and homogenized material such as the rock aggregate used with cesium, has to be described by a model that accounts for this dispersion. Large field experiments which traced the advancing water front from one well to another[4,10] required a dispersive model of fluid flow to account for the observations. The dispersion was attributed to the channeling of water in the many cracks and the resulting many pathways in the permeated medium for the water. Similar dispersive effects may exist in the column infiltration experiments due to a void structure in the rocks. Fluids moving through a rock aggregate or within rock pores would be continuously divided into finer offshoots and would be recombined into larger streams at intersecting flow paths. Variations in path lengths a fluid velocities in the different paths from one point to another would result in additional spreading of a peak as it migrates through the column. This type of dispersion, as determined in simply characterized media, increases with the distance the peak has traveled but preserves the peak symmetry.[10] Therefore, it cannot account for the skewed nuclide distributions seen in the infiltration experiments.

Several conditions may have existed in the infiltration experiments that could have contributed to the nonidealized behavior seen. Possibly, for example, the dispersion in nuclide migration was caused by heterogeneities in the columns. Visible cracks in one column were found to result in greatly increased velocities of cesium. Channeled flow in similar but smaller cracks or in a few dominant pores within the solid rock columns may have contributed to the observed nuclide distribution by allowing solutions to pass through the columns with little reaction with the rock. Similar effects would be expected in a natural formation of the rock.

Alternatively, dispersion may have been due to the flow rates used in the experiments being high enough to prevent equilibration of the solution and rocks. Reaction rates measured in static absorption experiments could not be used to estimate the extent of equilibrium expected in the column infiltration experiments because the proportion of fluid to rock, and hence the reactants and reaction sites differ considerably in the two experimental techniques. In addition, in static absorption experiments, the nuclides in solution contact the rock by diffusion or advection processes, whereas in the column infiltration experiments, the nuclides in solution are forced through the rocks. Nonetheless, the solution residence time in column infiltration experiments (typically 0.4 to 2 h) is often only a small fraction of the characteristic reaction time in static absorption experiments (5-1000 h), suggesting that nonequilibrium behavior should be expected in the column infiltration experiments. This effect would allow some of the nuclide to be washed through the column without being retarded as a result of partitioning on the solid rock phase. The flow rates used in the column infiltration experiments reported here (calculated from the porosity in Table 4 and column elution rates in Table 5) are comparable to flow rates found for some groundwaters, and effects found in these experiments could be expected in natural systems.

Other factors that may have caused or contributed to the observed dispersive behavior are the formation of colloids of the nuclides that react only slowly with lithic materials, the migration of clay or other particulate material with radionuclide adherence, the effect of soluble organics, and the effect of bacterial activity. These conditions, except the last, may be present in geologic bodies considered for nuclear repositories.

The dispersive characteristics seen in the column infiltration experiments are likely to be important in assessing nuclide retention in geologic storage facilities. For example, plutonium is considered (on the basis of laboratory experiments) to have a strong affinity for lithic material and therefore a low migration rate relative to the advancing water front. From static partitioning measurements, plutonium in Salem limestone would be expected to have a relative migration rate of 4×10^{-4}. This calculated value is based on the simplifying assumptions[3-6] stated previously and is consistent with the observation (from column infiltration experiments) that most of the plutonium was retained by limestone, even after continued infiltration. However, it is seen in Table 6 that 2.6% of the plutonium travels at a relative migration rate greater than 0.001. This small but finite amount of activity may present a radiological hazard, and the greater velocity associated with this activity than with the bulk of the activity may be a limiting factor in nuclide retention. This assessment, that dispersion of relative velocities is important, differs from recent viewpoints which suggest that dispersion is not a governing factor in the confinement of waste.[6]

From the batch partitioning experiments, the absorption of nuclides was found to be reversible, in the absence of complicating steps such as drying of rock material prior to desorption. Drying of rocks after absorption was found to drastically reduce the desorption of nuclides from rocks. This effect may be important in assessing the evidence of nuclide migration at the fossil reactor site in Oklo, Gabon, where a sequence of cycles consisting of water infiltration, criticality, and then drying is suggested to have occurred.

The capacity of rock material to absorb nuclides was found to be not sensitive to the particle size of the material. This implies that the nuclides are able to penetrate rock particles to a depth comparable to that of the radius of the largest particle size material (16-20 mesh, radius ~500 μm) used in the batch partitioning experiments. The penetration may occur through pores within a rock (evident from B.E.T. surface area measurements). The measurements indicate that the surface area is much larger than the fracture surface of the granulated materials, suggesting that the surface areas of the materials are determined by rock porosity rather than particle size.

From batch partitioning experiments, a variety of rocks were found to be strong absorbers of nuclides of plutonium, americium, and neptunium. This suggests that many geologic formations may be suitable for siting of a nuclear waste repository. For example, the geologic materials generally found in conjunction with salt deposits (i.e., limestone, anhydrite (gypsum), chalk and witherite) absorb plutonium from solutions very strongly, indicating that the materials surrounding a salt bed form an effective barrier against plutonium migration. Similar behavior was observed for these nuclides with other rocks from the vicinity of a proposed nuclear waste repository.[11]

Rock surfaces from newly formed fractures that connect to a geologic repository are expected to change their chemical characteristics on contact with water. Reactive mineral surfaces will dissolve and the mineral may precipitate more stable crystalline forms. Residual material, left from incongruent dissolution of minerals, will hydrate, producing fine-grained alteration products at the water-rock boundary. These changes may progress sufficiently in days or weeks to affect nuclide partitioning and, therefore, the weathered rather than the fresh surfaces are the ones that govern nuclide migration for the long term.

The chemistry of weathered surfaces can be studied in the laboratory by reacting granulated rock with aqueous solution prior to the introduction of radionuclides. The weathering of fracture surfaces, in fact, is expected to proceed on freshly granulated rock used in partitioning experiments. In experiments that are run to examine the reversibility of nuclides in rock-water systems, the weathering of fracture surfaces could be responsible for what appear to be irreversible effects but which are, in fact, due to changes in the rock chemistry during experimentation. Experiments with crushed material, and specifically those experiments in which material is used in sequential tests, may best be performed with materials that had been reacted with water for extended periods prior to experimentation.

VII. CONCLUSIONS

In rocks of silicate and carbonate material studied in static absorption experiments, plutonium and americium were found to be strongly absorbed by rock tablets. Relative migration rates of plutonium and americium by fluid flow, based on results of the static absorption experiments, are considerably lower than the velocity of the infiltrating water. The experiments also indicate that the reaction rates of nuclides in solutions and rocks vary considerably for different rock-nuclide systems. Therefore, for a solution containing several nuclides and moving through rock, conditions of local equilibrium may exist for some nuclides and not for others. Thus, models of nuclide migration need to consider the reaction rates of the individual nuclides.

In column infiltration experiments with shale and chalk, the peak concentrations of cesium in the columns were seen to move with low velocity, which is consistent with a strong partitioning of the nuclide onto the rocks. However, cesium activity was also seen in a long tail extending through the column from the cesium peak in the direction of water flow; it resulted from relative migration rates up to three orders of magnitude greater than that for the peak concentration. Nuclide activity downstream from the peak activities was also seen for plutonium, americium, and neptunium in solid rock columns of limestone, sandstone, and tuff. Therefore, there is a large difference in the relative migration rates of these elements in the common rocks studied. This needs to be considered for accurate description of the behavior of these elements in geologic materials.

It was observed from batch partitioning experiments that nuclides of the elements plutonium, americium, and neptunium were strongly absorbed from solution by the various geologic samples studied. In many experiments, greater than 98% of the activity was absorbed from solution. The results of these experiments suggest that geologic materials can be effective barriers to the movement of radionuclides from a deep geologic repository.

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