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STUDIES OF NUCLEAR-WASTE MIGRATION IN GEOLOGIC MEDIA Annual Report October 1977—September 1978

by

M. G. Seitz, P. G. Rickert, S. M. Fried, A. M. Friedman, and M. J. Steindler





ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Chemical Engineering Division

July 1979

Previous report in this series

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*Chemistry Division

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ABSTRACT

Experimental results obtained this year confirm the results obtained in the previous year--that nuclides migrating by fluid flow in rock often exhibit complex behavior (bleeding, dispersion of nuclide velocities, etc.) not predicted by simple chromatographictype models. The work reported here focused on two phenomena and quantitatively treated their effects on nuclide migration.

The first phenomenon is incomplete water-nuclide-rock reaction because of slow reaction kinetics. A kinetic factor derived from the experimental results for strontium migration through glauconite (a hydrous silicate) was expressed in terms of the linear flow rate of solution and can be used to predict migration due to solution flow t rates of 0 to about 12 cm/min (60 km/y).

Continuous-flow infiltration experiments with americium in fissures gave results that are predicted by a migration model that includes kinetic factors measured in experiments with static fluids. The results suggest that kinetic factors are as important as equilibrium adsorption parameters in predicting nuclide migration.

The second phenomenon studied was the amount of adsorbed nuclide not being proportional to the nuclide concentration in solution (nonlinear adsorption isotherm).

For cesium adsorption on limestone, a nonlinear isotherm was found to occur in the range of initial cesium concentrations from about 10^{-3} to 10^{-9} M. This adsorption property was confirmed by results of column-infiltration experiments in which cesiur migration through colitic limestone was found to be sensitive to the amount of cesium in solution. The existence of a nonlinear isotherm precludes the use of a single partition value (K_D) to describe cesium migration in limestone at cesium concentrations above about 10^{-9} M. Therefore, the effects of nonlinear isotherms are germane to nuclide migration. Nonlinear isotherms can be studied experimentally and their effects predicted quantitatively. The successful treatment of kinetic effects and the ability to treat effects of nonlinear isotherms suggests that considerably more rigor than has been employed previously is possible in the modeling of nuclide migration in geologic bodies.

SUMMARY

As a continuation of our work in the Waste Isolation Safety Assessment Program (WISAP) to assess the concept of geologic disposal of nuclear waste, we have performed laboratory experiments with nuclides of strontium, tin, cesium, plutonium, and americium to determine their migratory characteristics in rocks from formations that may be suitable as geologic repositories. Analytical procedures and data that characterize the solutions and rocks used in the program are described in this report.

To study nuclide migration, this work has used, principally, infiltration experiments in which solutions are forced through rock pores or rock fissures. In order to generalize the results of these experiments, data from the experiments have been related to a model (ARDISC-1) of nuclide migration developed by other Argonne workers.

Infiltration experiments have been performed at high pressures and at various solution flows, using columns of massive porous rock, porous beds of granulated minerals, or columns of impermeable rock having fissures. Radionuclidecontaining solutions for migration studies (1) have been formulated from soluble compounds of the radionuclides or (2) have been obtained by leaching at elevated pressures and temperatures solid waste forms with groundwater solutions (that have low oxygen levels).

For use in migration experiments, solutions were generated having low carbon dioxide partial pressure (calculated partial pressures of about 10^{-18} pa, based on the carbon dioxide reaction with calcium oxide) and low oxygen partial pressures (calculated partial pressures of about 10^{-78} pa, based on water in equilibrium with hydrogen gas at 10^5 Pa).

In parametric studies, strontium migration was found to be retarded in glauconite (a hydrous silicate) relative to the moving water front. Peak shapes for strontium broaden when solution flow rate is increased. These experimental results are accurately predicted by the ARDISC-1 migration model and occur because of kinetic effects (which control the extent of reaction between rock and solution).

Kinetic and partitioning data for americium in fissures of rock impermeable to water were used with the ARDISC model to predict the migration of americium through such fissures. The migration behavior predicted by the ARDISC model in which kinetics play a major role are comparable to the results of the infiltration experiments with americium. This agreement emphasizes the importance of reaction kinetics in migration. The results show that nuclide migration in rock fissures is predictable using both kinetic and partitioning data obtained from experiments with static fluids.

Radioactive strontium was found by column infiltration experiments to move through columns of solid porous oolitic limestone as rapidly as does a fluid stream containing 0.01M calcium, but moved through the limestone at one-tenth that rate when dissolved in a stream of water that had been reacted with the limestone (rock-reacted water or RRW). Results with RRW solutions were similar to results using a recipe solution (formulated from chemicals)

It simulated groundwater in limestone. The retardation of the strontium in .imestone indicates that there was a small mass loading for strontium (7 x 10^{-5} meq strontium per gram of limestone) under the conditions of the experiments. The migration of strontium in collic limestone is can times faster than that predicted from results of the controlled-sample program (discussed in Section IV. E. of this report). Contributing to the discrepancy may have been differences in strontium adsorption on solid and crushed limestone.

Experimental results obtained in this report period confirm results obtained in the previous report period--that nuclides migrating by fluid flow in rock often exhibit complex behavior (bleeding, dispersion of nuclide velocities, etc.) not predicted by simple chromatographic theory.

This year, two effects, that due to limited reaction of a nuclide between rock and fluid and that due to the amount of adsorbed nuclide not being proportional to the nuclide concentration in solution, were demonstrated to cause significant differences between observed behavior and behavior predicted by simple chromatographic theory. Consideration of these effects, experimentally, and treatment of kinetic and nonlinear adsorption phenomena, analytically, can lead to more rigor in predicting nuclide migration than previously existed.

I. INTRODUCTION

A method being considered for permanently disposing of radioactive waste generated during nuclear power production is to place the waste in a repository deep beneath the surface of the earth. Groundwater infiltrating the repository may leach radionuclides from solidified waste and transport them into the fissures or pores of the surrounding geologic formation.



A schematic of a breached repository is illustrated in Fig.1.

Fig.1 Schematic of a Breached Repository.

Reactions between groundwater and rocks retard the radionuclides relative to the flowing water and form a barrier to radionuclide dispersal. The effectiveness of this barrier depends on (1) which reactions occur and (2) the parameters of these reactions.

Underlying the work performed this year has been an attempt to generalize observed nuclide behavior by mathematical formulations which can be used for more rigorous analytical treatments to predict nuclide migration. This work is part of our effort to supply technical support to the National Waste Terminal Storage Program administered by the Office of Nuclear Waste Isolation for the U.S. Department of Energy.

A. Control of Oxidation Potential and Hydrogen Ion Concentration of Simulated Groundwater

The mobilities of trace elements also depend on the oxidation potential* (E_h) and hydrogen-ion concentration (expressed as pH) of flowing groundwater. For example, uranium in waters of high oxidation potential is mobilized as the hexavalent ion, while in waters of low oxidation potential, uranium is immobilized as the quadrivalent ion (forming insoluble silicates or oxides). Tin, an element of concern in nuclear waste disposal, dissolves in high-pH solutions and precipitates as hydrolysis products in neutral solutions.

Dissolved gases in groundwater, notably carbon dioxide, oxygen, and hydrogen sulfide, affect the E_h and pH of the water and hence can influence the migration of trace elements. Specifically, carbonate ions may complex with trace elements, and oxygen in solution may oxidize multivalent trace elements. Described in this report are techniques and apparatus that we have used to control the quantities of CO₂ and O₂ dissolved in the solutions used in experiments.

. Objectives and General Procedures

The experimental program discussed in this report was formulated to develop quantitative data describing those reactions of nuclides between solutions and rocks which control the transport of radionuclides in geologic media.

Nuclide behavior is determined by the properties of the solutions and rocks used in experiments. Information about rocks has been obtained, whenever possible, from characterization work reported in the literature or supplied by other laboratories. This report describes the analytical approaches we have taken to further characterize the solutions and the rocks. Spectrochemical techniques were used to give an overall view of the major-element constituents and of trace-element concentrations in the solutions and rocks. Ion electrode, physical, and wet chemical techniques were used for additional characterization of the solutions and rocks.

Of particular interest in determining nuclide migration by fluid flow are the hydrodynamic characteristics of the rocks. By infiltrating columns of rocks and minerals with tritiated water, we determined the porosity that is subject to fluid flow and the hydrodynamic dispersion of the fluid stream in the columns. Knowledge of thes properties is fundamental in relating the results of column infiltration speriments to the results obtained by other experimental techniques.

*The oxidation potential, E_h, of a redox reaction is the potential of a half cell of the reaction referred to the standard hydrogen half cell.

From results^{1,2} of earlier static adsorption experiments,^{*} we concluded that kinetic factors produce complex behavior of nuclides during migration. Additional factors (such as a lack of reversibility of reactions involving the nuclides, formation of colloids that contain nuclides, transport of mineral particles on which nuclides are adsorbed, and so on/ were suspected of causing the nonideal behavior seen in the earlier column-infiltration experiments and expected in natural systems of rocks and solutions. Because we cannot <u>a priori</u> anticipate all important factors that control the migration of a nuclide in a rock and then study such factors individually to predict migration, we have chosen to do dynamic experiments in which solutions containing nuclides are rorced into columns of solid rock or rock fissures and in which the collective effects of all factors that influence nuclide migration are represented in the resulting nuclide distribution. We can then attempt to separate individual effects by parametric studies.

We have developed a variety of experimental approaches (described in this report) to study migration during infiltration of geologic materials. Highpressure column infiltration apparatus with regulated solution flow has been used for parametric studies of nuclide migration in permeable rock and mineral columns. Leach-migration experiments conducted at high pressures and at elevated temperatures were designed to study the migration of radionuclides leached from a solid waste form heated by radioactive decay.

Infiltration experiments with fissured rock have been developed and used to study migration in geologic formations composed of impermeable rocks. This approach allows the control of rock-surface area, fissure width, and solution flow at extremely low flow rates.

Migration through impermeable rock was studied since geologic formations composed of impermeable rock have been considered as waste disposal sites. Difficulties in predicting migration in such formations from the results of batch tests arise because of the great dissimilarity of rock geometry in batch tests and natural cracks or fissures. To eliminate complex transformations in geometry, rock fissures that simulate natural crack geometry were used in our experiments. Data on kinetics and partitioning obtained have been used to predict migration, using the Argenne kinetic model of migration (ARDISC-1,³ hereafter referred to in this report as ARDISC). The predictions, in turn, were compared with results of flow experiments.

C. Advantages and Disadvantages of Several Experimental Approaches

Different experimental approaches to the study of nuclide migration have different advantages. Batch tests with granulated rocks and nuclides in solutions, for example, can be performed quickly with any nuclide on any rock,

The static adsorption experiments were performed by immersing tablets of rock in plutonium- and americium-bearing fluids and observing the residual activity not adsorbed onto the tablet at different time intervals.

independently of the porosity, brittleness, or other properties of the rock. Under specific conditions, the partitioning value so measured may be related to the migration of the nuclide caused by fluid flow in rock. Generally, however, complex geometric transformations of kinetic data are required that preclude the use of batch tests for predicting migration.

Column-infiltration experiments have the advantage that nuclide migration by fluid flow in rocks is measured directly. The disadvantage is that porous or fractured rock f distinct geometry is required for fluid flow. By comparing results obtained by different experimental techniques, we can determine under what conditions a simple experimental approach may be used in predicting migration without loss of understanding and accuracy. In this report, migration of strontium in oolitic limestone determined by column infiltration experiments is described. The results are compared with migration characteristics predicted from batch partitioning data.

Infiltration experiments with rock fissures also were performed to give results applicable to nuclide migration through cracks in fractured rock. The experiments require meticulous setup arrangements but have the advantage of eliminating the need for complex and unknown transformation of kinetic and exchange-population data from more simple batch tests.

In leach-migration experiments, radionuclide species generated upon leaching irradiated material are used in migration studies. This approach avoids the problem of formulating (for migration studies) the various radiochemical solutions of differing valence and chemical states that could be postulated to occur upon leaching.

II. NUCLIDES AND ROCKS STUDIED; SOLUTION PREPARATION

A. Nuclides Studied

The elements produced during nuclear power production that have longlived isotopes (i.e., half lives greater than 100 y) are of concern in geologic disposal schemes. Of these elements, we studied tin, cesium, plutonium, and americium in laboratory experiments to determine their migration behavior in rocks. Strontium was also studied because strontium-90, an isotope with a half life of 29 y, is abundant in nuclear waste. Furthermore, strontium exhibits chromatographic-type behavior⁴, and therefore exemplifies element migration controlled by adsorption-desorption reactions.

The nuclides, strontium-85, tin-113, cesium-134, plutonium-237, and americium-241, were used in these studies because they can be analyzed by the gamma rays they emit during decay without the necessity of separation of the nuclides from the liquids or rocks.

B. Rocks Studied

The rocks selected for this study are from large, stable geologic formations that are of low economic value, that are within the continental United States, and that may be suitable for containing nuclear-waste repositories. About 32 rocks were obtained from areas being investigated as potential repository sites, from museum collections, or directly from the field.

A chalk sample was kindly supplied to us by Mr. K. Reed of the United Cement Co., Artesia, MS. Dr. W. A. Cobban of the U.S. Geological Survey, Denver, CO, supplied a Pierre shale from Front Range, CO, together with sampling information. Detailed modal analyses and sampling information for the grey hornblende schist used in the fissure experiments were supplied by I.W. Marine.⁵ Four rocks (oolitic limestone, argillaceous shale, Sentinal Gap basalt and Westerly granite) rocks used in this study were distributed to WISAP contractors for the controlled-sample program.* These rocks are characterized by Ames.⁶

The rocks used in this study are of a variety of chemical compositions and physical characteristics and include rocks of sedimentary, igneous, and metamorphic origin. The rocks studied include silicates such as basalts, granites, and shales, sulfates such as anhydrite, and carbonates such as limestone, chalk, and dolomite. The anhydrite and limestone are typical of (1) rocks associated with bedded salt or (2) the cap rocks of salt domes.

In the controlled-sample program (described in Section IV.E of this report), nuclide adsorption data were obtained on samples of four rocks by WISAP subcontracting laboratories for laboratory intercomparisons.

C. Solution Preparation

Three types of solutions were prepared that simulated groundwaters. These solutions were subsequently used to force radionuclides into porous rock, mineral sand, or rock fissures.

Groundwater solutions (previously termed REW,² referred to here as rock-reacted water or RRW) were typically prepared by stirring 10 g of a powdered rock in 1 L of distilled water for two weeks and then filtering the solution through a 0.45-µm Millipore filter. A RRW solution was made for each rock used in a migration experiment. RRW solutions have the chemical compositions expected of groundwaters found in rock formations. Since compositions of RRW solutions are established during extended periods of continuous mixing of water with granulated rock, the compositions of the solutions and the rocks are expected to change little during subsequent contact of the solutions with rocks.

Three solutions termed recipe solutions, simulating groundwaters in specific rocks, were prepared by dissolving chemicals in distilled water and/or by sparging the water with CO_2 and/or adjusting the pH of the water. These solutions, initially used in the controlled-sample program (Section IV.E), were subsequently used in infiltration experiments.

A third type of solution, used to study migration in solutions of elevated ionic concentration, consisted of acetate or cabonate solutions containing 0.01M calcium.

Solutions containing either plutonium or americium were prepared under air by evaporating Pu(IV) and Am(III) nitrate solutions to dryness and dissolving the residue or part of it in distilled water. Small quantities of this solution were added to the RRW solutions or to recipe solutions. The gamma activities were counted with a NaI scintillation spectrometer. The activities and concentrations of the plutonium and americium were typically about 14 nCi/mL or 6 x 10^{-12} M plutonium-237 and 28 nCi/mL or 4 x 10^{-8} M americium-241 (calculated based on a measured counting efficiency of 7%).

Solutions of strontium or cesium were prepared under air or nitrogen by adding small quantities of neutral chloride solutions to RRW, recipe, or 0.01 Ca solutions. Solutions containing about 3 x 10^{-12} M 85Sr were used in batch tests (tests in the controlled-sample program, Section IV.E, and tests with rock test tubes, Section IV.D); solutions containing about 5 x 10^{-9} M 85Sr were used in column-infiltration experiments. These low strontium concentrations were often greatly exceeded by the quantities of strontium leached from rocks in making the RRW solutions or by the strontium present in the calcium used to make solutions from chemicals. Thus, the concentration of radiogenic strontium was not the concentration of strontium in the solutions. Solutions containing about 1 x 10^{-10} M 134Cs were used in batch tests, and solutions containing about $1 \times 10^{-7} \underline{M} \ ^{134}$ Cs were used in column-infiltration tests. The specific activity of the cesium was 134 Ci/g in February, 1978 so that stable 133 Cs was about 8.9 times more abundant than 134 Cs. Most of the cesium in solutions used in the infiltration tests was from cesium in the radiochemical solutions since the cesium concentration in oolitic limestone RRW was 4 x $10^{-8}\underline{M}$ (by neutron-activation analyses not described in this report).

A solution of tin was prepared by adding a ¹¹³Sn chloride solution to a 0.01M calcium, 0.0001M stannous solution. The latter solution had been prepared with deoxygenated water and had been stored under nitrogen; after the tin dissolved, it slowly formed hydrolysis products (as identified by X-ray diffraction) that precipitated over a period of several days. The solution was filtered each day until it was stable. The concentration of the tin carrier remaining in solution was found to be less than 1 x 10⁻⁷M. The concentration of ¹¹³Sn in the same solution was about 7 x 10⁻⁹M.

D. Treatment of Solutions to Lower CO2 and O2 Levels

Solutions used in some column-infiltration experiments were treated to obtain low levels of CO_2 and O_2 . The low- CO_2 , low- O_2 solutions were obtained either by sparging nitrogen gas having low CO_2 and O_2 concentrations through the solutions or by reacting the solutions with iron to remove O_2 . Solutions of intermediate CO_2 or O_2 levels could then be produced by mixing the purified nitrogen stream with nitrogen containing known CO_2 and O_2 levels and sparging the solutions with the gas mixture.

Apparatus shown in Fig. 2 was used to purify the nitrogen gas stream, which was then bubbled through solutions to be used for column-infiltration experiments to obtain low CO2 and O2 levels in them. In this apparatus, nitrogen gas derived from liquid nitrogen containing about 2 ppm oxygen was dried and reacted with CaO in Ascarite to remove CO2. The nitrogen gas was then stripped of oxygen by chemical absorbents. As an oxygen absorbent, we used dry flow-through traps ("Oxy-trap," supplied by Alltech Associates, Arlington Heights, Illinois) that do not require high temperatures to remove oxygen from the N2 gas. Alternatively, we used an oxygen-absorbing solution of chromous chloride ("Oxsorbent," manufactured by Burrell Corporation, Pittsburgh, Pennsylvania), which is highly reactive with gaseous oxygen. After oxygen removal, the gas was washed in water, both to remove any entrained particulate or liquid and to restore water vapor to the gas. The purified nitrogen was then bubbled through solutions in order to maintain low concentrations of dissolved carbon dioxide and oxygen in these aqueous solutions. The latter solutions had been prepared by deaerating distilled water by boiling.

The concentrations of CO₂ and O₂ in nitrogen-treated solutions are expected to be low. A solution in equilibrium with nitrogen gas that had equilibrated with CaO in Ascarite (and, thus, having a CO₂-gas fugacity calculated to be 10^{-18} Pa) would have a total dissolved-carbonate content



Fig. 2. Nitrogen Stream Line for CO₂ and O₂ Removal. ANL Neg. No. 308-78-427

of $10^{-23.6}$ M. A solution in equilibrium with nitrogen gas that had equilibrated with chromous chloride would have an oxygen partial pressure of about 2 x 10^{-78} Pa or <1 x 10^{-20} M. Since these concentrations are significantly lower than the concentrations of trace elements used in the experiments, complex formation by CO₂ or oxidation by O₂ is unlikely to affect the solutes. While the actual concentrations of CO₂ and O₂ are not measured, the treatment and equipment integrity makes it likely that the levels are below significance.

To promote solution-gas equilibrium, gases are passed as fine bubbles through tall columns (gas wash bottles about 20-cm long, Fig. 2) containing solution. Solutions of chromous chloride react rapidly with oxygen in gas. Nevertheless, it is not certain how extensively the liquids and gases react. Analyses by mass spectrometry of the purified nitrogen showed the absence of oxygen (<2 ppm oxygen). To establish an upper limit to the oxygen content of the nitrogen gas, a dry, flow-through oxygen trap with an indicator capable of detecting the presence of less than 0.1 ppm oxygen is used on line. This limit for oxygen corresponds to about 10^{-10} M oxygen in solution and is 'ower than the concentration of trace elements used in some of our experiments.

We know of no routine way to measure oxygen levels of 10^{-10} M in a solution. To establish and confirm an oxygen concentration below this level, we have used the apparatus depicted in Fig. 3. RRW solution is passed through iron filings which react with dissolved oxygen. The iron also reacts with the water itself to form hydrogen gas. The iron filings are heated to promote





their reaction with water. In the presence of a palladium catalyst, the hydrogen gas reacts with residual oxygen in solution. Thus, with excess hydrogen, this device produces solutions having oxygen partial pressures at the stability limit of water (calculated $P_{0_2} = 10^{-78}$ Pa).

Excess hydrogen is periodically bled from the vessel. Analyses of the gas in the vessel indicate that the gas is predominantly hydrogen along with a little nitrogen (presumably from air trapped in the iron filings) and with a minor amount of oxygen (that may have been introduced during sampling).

Iron(II) hydroxide, formed by oxidizing iron, dissolves in water but does not drastically affect the composition of the groundwater solution because of its low solubility. Nevertheless, the solution is repeatedly recycled through the apparatus depicted in Fig. 3 and then into air where an iron (III) precipitate is formed--presumably by oxidation of the iron (II) in solution to the more insoluble iron (III). The presence of even the small amount of iron in solution could be eliminated if aluminum were used in place of iron in the reaction vessel. Aluminum hydroxide is more insoluble than is ferrous hydroxide. The aluminum could be amaigamated with mercury to expose a reactive surface to the solution. Hydrogen dissolved in the solution is not removed in the apparatus depicted in P_{-6}^{-1} . 3 and can potentially reduce solutes and modify their migration characteristics--a point to consider when employing this approach to reduce oxygen levels.

The lowering of dissolved gas levels to those expected in deep groundwaters permits experimentation in which the migration characteristics of nuclides in natural geologic formations can be reproduced. However, control of dissolved gas concentrations in solutions does not, in itself, determine the E_h or pH of a solution reacted with a particular rock. These properties of the solution are determined rather by all constituents in the solution-rock system. By reducing carbon dioxide and oxygen levels in a solution, we allow the rock to control the constituents in solution and therefore the E_h and pH of the solution, as would occur in deep geologic formations in the absence of air. An additional method of ensuring controlled E_h and pH values would be passage of the deaerated solution through a rock column upstream from the sample-injection valve or the solid waste form in the infiltration apparatus (see Figs. 7 and 15).

III. CHARACTERIZATION OF SOLUTIONS AND ROCKS

Physical and chemical characteristics of the rocks and solutions can affect trace-element migration produced by solution flow through the rocks. Therefore, to make this description of trace-element migration complete, the solutions and rocks were characterized by a variety of analyses.

A. Types of Chemical Analysis

Groundwater (KRW) solutions and recipe solutions (formulated from chemicals) were analyzed for total dissolved solids; for oxidation potential; for hydrogen-ion concentration; for major, minor, and trace-element content by spectrochemical means; for bicarbonate concentration; and for titratable cations. To detect possible changes with time, the solutions were often analyzed as they aged or before and after an experiment. Particulate in solutions was analyzed by filtration, ultrafiltration, and dialysis techniques if particulate was suspected to have affected results of the experiments.

B. Types of Analysis of Rocks

Rocks were analyzed for major and minor minerals by X-ray diffraction, for major-element composition by wet chemical analyses, for minor and trace elements by arc and electrode-emission spectra, for surface area by gas adsorption, and for hydrodynamic flow characteristics by tritiated-water elucion. In addition to analyses in our laboratory, analyses of rocks from other laboratories and the literature were sought as part of our characterization effort. Not all of the solutions and rocks were subjected to each analysis. The following account gives examples of the analyses and general trends, as well as conclusions from the analyses. Not all analyses performed in the past year are listed here.

C. Compositions of Solutions

Total dissolved solids, pH, and oxidation potentials were measured in 25 groundwater solutions (RRW) and were reported in the last annual report.² The dissolved solids in the groundwater solutions indicate the extent of reaction of the rocks and water. The values found for the solutions (ranging from 11 mg/L for granite from the Nevada Test Site to 2380 mg/L for Magenta, a rock composed of gypsum and anhydrite) are comparable to or exceed the total dissolved-solids contents (reported as salinity) of some natural waters.⁷ However, the values are considerably below the dissolved-solids contents of waters in deep formations; the latter may have obtained their dissolved solids by reacting with embedded sediments⁷ and therefore may be more extensively reacted or matured than are the groundwater solutions used in this work.

The spectrochemical analyses of solutions gave the concentrations of 24 elements, including the concentrations of the major rock-forming metals. As examples, Table 1 lists analyses for three solutions, one each from the reactions with powdered Pierre shale, Selma chalk, and Columbia River basalt. Each of

	Concentrations (Made Us	mg/L) of Elements in ing the Specified Ro	the Solution
Element	Selma Chalk	Pierre Shale	Columbia River Basalt
A1	<0.03ª	0.2	0.1
В	N/D ^b	0.1	N/D
Ba	0.2	2	0.04
Be	<0.002	<0.0005	<0.0005
Bi	<0.1	<0.05	<0.05
Ca	50	30	2.5
Co	<0.1	<0.05	<0.05
Cr	<0.05	0.03	<0.02
Cu	<0.3	0.05	<0.05
Fe	<0.15	0.03	<0.05
ĸ	1.8	15	0.8
Li	0.01	0.02	0.001
Mg	6	3	0.5
Mn	<0.02	<0.005	<0.005
Mo	0.03	0.003	<0.005
Na	3.5	35	0.4
Ni	<0.2	<0.05	<0.05
Pb	<0.1	<0.05	<0.05
Rb	<0.1	0.05	0.05
Si	0.8	3	3
Sr	0.8	1	0.012
Ti	<0.05	<0.02	<0.02
V	<0.05	<0.02	<0.02
Zr	<0.05	<0.2	<0.2

Table 1. Spectrochemical Analyses of Solutions (RRW) Formed by Reacting Distilled Water with the Powdered Rocks Listed

^aA"less than" symbol, <, indicates that the element was not detected and the detection limit is the value listed.

bN/D indicates that the concentration was not determined.

about 25 solutions was found to have a distinct composition that was determined by the rock used in preparing the solution. The elements aluminum, calcium, iron, potassium, magnesium, sodium, and silicon, which are the major constitutents of the rocks used to make the solutions, are also generally major constituents of the solutions. Strontium is also a major constituent of many of the solutions, although it is generally a minor constituent of the rocks used to make the solutions. Other elements, notably barium and manganese, are abundant in the solutions formed from some rocks. None of the elements examined could be determined to be lower in concentration than the concentrations of radionuclides used in experiments or lower than the concentrations of nuclides expected from leaching of solidified waste. Thus, elements may exist in solution at concentrations exceeding that of the radionuclide under study, thereby affecting the migration of the radionuclide. In Table 2, the composition of the RRW solution prepared with oolitic limestone after sparging with nitrogen gas is listed, along with the nominal composition of the recipe solution that simulates groundwater in oolitic limestone (recipe specified in instructions of controlled-sample program).⁸

Constituent	RRW Oolitic Limestone, mg/L	Recipe Solution for Groundwater In Oolitic Limestone, mg/L
Ca	10	50
Sr	1	n.a. ^a
Mg	0.6	3.6
K	n.d.b	0.4
Na	0.6	2.3
A1	0.1	n.a.
В	0.4	n.a.
Cr	0.008	n.a.
Pr	0.15	n.a.
Li	0.0008	n.a.
Si	2	n.a.
HCO3	35	153
so42-	n.m.c	14.4
C1-	n.m.	3.5

Table 2. Chemical Composition of the RRW Solution Made With Oolitic Limestone and the Nominal Chemical Composition of the Recipe Solution Simulating Groundwater in Limestone.

^an.a. indicates that the element was not specifically added to the recipe solution, although it may have been introduced as an impurity with other elements.

bn.d. indicates that the element was not detected.

^cn.m. indicates that anion concentrations were not measured.

The RRW solution contains detectable quantities of aluminum, boron, chromium, praseodymium, lithium, and silicon; these elements were not specifically added to the recipe solution. The RRW solution is more dilute than the recipe solution, having lower concentrations of the major constituents, calcium and bicarbonate. (An RRW solution made with limestone in the presence of air had a higher concentration of calcium, 75 mg/L, than the RRW composition listed in Table 2--presumably because of reaction with CO₂ from the air.)

The bicarbonate alkalinities of solutions were measured by adding a known excess of standard NaOH to a solution to convert the HCO_3 to CO_3^{2-} by the reaction

Ca(HCO3)2 + 2NaOH + CaCO3 + Na2CO3 + 2H2O

Barium chloride was then added to precipitate carbonate from the solution. The excess sodium hydroxide was then titrated with standard HCl to a phenoiphthalein end point to determine the excess sodium hydroxide that had been added. The number of sodium hydroxide equivalents consumed before carbonate precipitation occurred is equal to the number of HCO3 equivalents in the original solution. Reagent grade NaHCO3 was used as a standard for the titration. Analyses of the simulated groundwater in limestone, oolitic RRW solution, and the standard solution are given in Table 3.

Solution	Titration	HC03
Recipe Solution No. 1ª	1	124 mg/L
	2	124 mg/L
Recipe Solution No. 2ª	1	174 mg/1
	2	178 mg/L
Oolitic RRW with added		
SrC03	1	36 mg/L
	2	35 mg/L
NaHCO3 Standard		
Solution	1	98.9% Recovery
	2	98.8% Recovery
	3	99.6% Recovery

Table 3. Bicarbonate in Solutions (Determined by Titration)

^aRecipe solutions No. 1 and No. 2 simulating groundwater in limestone were made using the same recipe but by different procedures (sparging with CO₂, adjusting pH, filtering precipitates, etc.), which is allowed by the directions.

As seen in the table, different batches of recipe solution had different concentrations of bicarbonate--caused, presumably, by differences in gas sparging procedures and amounts removed as precipitates.

Calcium in two solutions (Table 4) used in strontium-elution experiments was determined by a direct pH 10 buffered titration; the disodium salt of ethylenediaminetetracetic acid (2Na·EDTA) was the titrant, and Calmagite* was the indicator. Primary grade CaCO₃, converted to CaCl₂, was used to

^{*1-(1-}hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid., Eastman Co. Chemical.

standardize the 2Na EDTA (the 2Na EDTA was determined to be 94.8% pure). No other primary grade calcium salt was readily available for use as a standard. The results for the two solutions analyzed are shown in Table 4. The calcium concentrations in the colitic RRW solution determined by titration (Table 4) and by spectrochemical means (Table 2) are the same.

Solution	Titration		Calcium, ^a mg/L
0.01M CaSO ₄ with Strontium ^b	1	408	(0.0102 <u>M</u>)
	2	408	(0.0102 <u>M</u>)
Oolitic RRW with SrCO3 ^C	1	12	(3 x 10 ⁻⁴ <u>M</u>)
	2	8	(2 x 10 ⁻⁴ M)

Table 4. Calcium in Solutions, as Determined by 2Na EDTA Titration

^aThe titration is indicative of calcium, magnesium, strontium, and other titratable cations in the solution.

^bThe 0.01<u>M</u> CaSO₄ solution was determined by spectrochemical analyses to contain 18 mg/L (2 x 10^{-4} M)Sr, 0.4 mg/L (1 x 10^{-5} M) Al, and 0.1 mg/L (4 x 10^{-6} M) Mg.

^cSee Table 2 for a detailed analysis of the RRW solution made with oolitic limestone.

The compositions of RRW solutions formulated from crystalline rocks are plotted as phase diagrams in Figs. 4 and 5, together with the compositions of natural waters from regions of crystalline rock (Oklahoma water from a region of Tishomingo granite; Georgia water from a region of Elberton granodiorite). As is indicated by the two variables plotted in each figure, the compositions of the RRW solutions are similar to the compositions of groundwaters from the two regions. The RRW solutions, like the groundwaters, are not generally in equilibrium with minerals in the rocks from which they were derived. For example, the Los Alamos tuff contains sanidine, a potassium feldspar, whereas the RRW solution is in the region of stability of kaolinite (Fig. 4) rather than in the region of stability of the potassium feldspar. The kaolinite likely results from the reaction of feldspar with water and, therefore, exists on pore surfaces in contact with water.

There are two essential conclusions from these water analyses: (1) an RRW solution is, as expected, more complex than solutions formulated to simulate groundwater and (2) RRW solutions are similar, in compositions, to groundwaters and, like groundwater, are not necessarily in equilibrium with the major minerals in the rock or in the formation from which they were derived. These conclusions exemplify the advantages of using RRW solution in studies of nuclide migration.

D. Compositions and Physical Characteristics of Rocks and Columns

Mineral constituents of the rocks were determined by X-ray diffraction. Diffraction analyses of rocks added to the program this year are given in Table 5. Also, the weight fractions of the major-element oxides of aluminum, calcium, iron, magnesium, potassium, sodium, and silicon in thirteen rocks were determined. Analyses of three rocks, Pierre shale oolitic limestone, and granite, are given as examples in Table 6.



Fig. 4. Compositions of Natural Waters from Regions of Crystalline Rock and Compositions of RRW Solutions Formulated from Crystalline Rocks. Plotted on a phase diagram of the system, K₂O-Al₂O₃-SiO₂-H₂O, 25°C and 10⁵ Pa pressure (diagrams after Feth;⁹ data on compositions of natural waters from Harriss¹⁰)



Fig. 5. Compositions of Natural Waters from Region of Crystalline Rock and Compositions of RRW Solutions Formulated from Crystalline Rocks. Plotted on a phase diagram of the system, Na₂O-Al₂O₃-SiO₂-H₂O, at 25°C and 10⁵ Pa total pressure (diagrams after Feth;⁹ data on compositions of natural waters from Harriss¹⁰)

Analyses for barium, copper, sulfur, and sulfate were performed on an additional eight rocks (anhydrite, calcopyrite, etc.).

Spectrochemical analysis of the rocks gave concentrations or upper limits of the concentrations of 55 rock-forming elements. The analyses were used to characterize the minor and trace element compositions of the rocks. None of these analyses are given in this report.

Sample	Mineral P	hases Identifie	d
Description	Major	Minor	Trace
Green Sand	glauconite		
Gray Hornblende Schist	chlorite, amphibole (hornblende)	feldspar	
Oolitic Limestone Bulk	calcite		
Acid-Insoluble Fraction of Oolitic Limestone White Fraction Dark Fraction Grey Fraction	quartz quartz quartz	pyrite pyrite	calcite calcite
Argillaceous shale (Green)	quartz	muscovite 2M-type	
Sentinal Gap Basalt	feldspar	pyroxene	
Westerly granite White Fraction	feldspar, possible albite		quartz
Black Platelets in the Granite	mica	magnetic material	

Table 5. X-Ray Diffraction Analyses of Rocks Used in Nuclide Migration Studies

Table 6. Analyses (weight percent) by Wet-Chemical Techniques of Seven Constituents of Three Rocks Used in the Experimental Program

Oxide	Pierre Shale	Oolitic Limestone	Granite
A1203	21.8	<0.01	11.5
CaO	1.28	53.5	0.98
Fe203	6.21	0.04	2.37
MgO	1.76	0.49	0.15
K20	2.74	0.04	4.22
Na ₂ O	2.32	0.04	4.41
SiO2	56.4	0.50	68.8



of Oolitic Limestone. ANL Neg. No. 308-78-429.

		Poro	sity, %
	Length, cm	By Water Capacity	By Tritium Elution
Column 1	3.95	49	19
Column 2	3.56		19
Column 3	4.09		16

Table 7. Porosities of Solid Limestone Columns as Measured by Weight Loss on Drying a Water-Saturated Column and by Elution of Tritiated Water

Solid rock and mineral sand, formed into columns for infiltration experiments, were characterized by means of density and porosity measurements. Of considerable importance to interpreting the results of infiltration experiments are the flow characteristics of columns (i.e., the hydrodynamic dispersion and the porosity subject to fluid flow). These properties were measured

by injecting tritiated water into the fluid stream that flowed through all columns used in the work and measuring (1) the flow required to transmit the tritium from top to bottom of the column and (2) the peak shape of the tritiated water. A tritium elution curve for a column of porous limestone is given in Fig. 6. The tritium was transmitted with 0.60 mL of solution in a sharp peak (full width at half maximum = 0.4 mL). Porosities determined from the tritium peaks for limestone columns are presented in Table 7, along with a total porosity measured by weighing the column dry and saturated with water. The porosity of a limestone column that is subject to fluid flow is considerably less than its total porosity. This is also true for other rocks studied (e.g., shale, chalk) and is probably due to dead-ended pores that do not link to form part of the water flow path. (For glauconite, the porosity subject to flow and the total porosity are essentially the same.) The observed dispersion of a radionuclide passing through a limestone or a glauconite column often greatly exceeded that expected from hydrodynamic dispersion alone (see Sections IV. A.1 and IV. A.2, this report) because of kinetic effects, nonlinear sorption isotherm effects, etc.

As part of the characterization of solutions, the valence and chemical form should be determined for the nuclides whose migration characteristics are being determined. To determine the distribution of plutonium in its various oxidation states, we used a scheme described by Foti and Freiling.11 In the scheme, Pu(IV) is extracted from one sample of solution (acidified to a pH of 0.4 with hydrochloric acid) into a solution of 0.4M 2-thenoyltrifluoroacetone (TTA) in benzene. The pH of the aqueous solution after extraction of Pu(IV) is increased to 4.3 with ammonium acetate, and PU(III) is extracted with TTA. On a second sample of aqueous solution, Pu(III), and PU(IV) accompany lanthanum fluoride precipitation, and Pu(VI) is left in aqueous solution. Pu(V) is determined by difference. The quantities of plutonium in the different TTA solutions were determined radiochemically.

IV. EXPERIMENTAL PROCEDURE, RESULTS, AND DISCUSSION

The migration characteristics of a nuclide moving by solution flow in a rock depend on many variables, such as the rate of flow and the chemical composition of the water. Parametric studies were conducted with rocks and nuclides showing simple behavior in order to determine how these two variables affect migration. Experiments were also done to examine nuclide migration in fissures of nonporous rock. In addition, experiments were performed with a single nuclide and rock using different approaches so that the results of the different approaches could be compared. Finally, experiments were performed for the controlled-sample program. This section gives examples of the types of experimental results obtained in the program.

A. Column Infiltration Experiments

For initial experiments in this program, 12 we used standing tubes of water to infiltrate rock columns. Limitations to this approach include the inability to control the flow of solution in columns throughout the experiment and undesirable mixing of nuclide-free solutions with nuclide-containing solutions in the reservoir immediately above the columns.

We overcame these limitations by using the apparatus depicted in Fig. 7. The apparatus consists of a rock column in a stainless steel tube and a sample-



Fig. 7.

Apparatus for Column-Infiltration Experiments with Controlled Flow Rates

injection valve; the latter is connected by high-pressure tubing to a liquidmetering pump. The rock column is confined in the stainless steel tube by metal frits at the ends of the column; the ends of the stainless steel tube are sealed to the high-pressure tubing. The sample-injection valve, upstream from the column, is used to introduce trace-element solutions into the column. The liquid-metering pump can deliver solution to the column at a preset rate in the range 0.1 to 10 mL/min and at pressures up to 3.4 x 10⁷ Pa (340 bar). Syringe pumps and peristaltic pumps are used for extremely low flow rates at low pressures. Whether a liquid-metering or peristaltic pump is used, the solution is pumped from a low-pressure reservoir which can be replenished during an experiment, allowing uninterrupted infiltration of the column. The reservoir has a controlled-atmosphere blanket which is used to maintain the desired concentrations of dissolved gases in the solution.

The apparatus depicted in Fig. 7 is fabricated of stainless steel and is suitable for work with most geochemical solutions, but is not useful for solutions of high chloride content. Now available in the laboratory is alternative equipment, such as glass-lined, Teflon-lined, gold-plated, and nickel high-pressure tubing and nickel fittings in which chloride solutions can be contained and the chemical compatibility of the rock systems and apparatus maintained.

We prepared solid rock columns for use at high pressure by epoxy-mounting cores of porous rock (limestone and sandstone) in stainlesss steel tubing. The ends of the tubing and rock core were cut off to expose plane surfaces of rock that were free of epoxy. The epoxy sealed the sides of the core and prevented water from channeling between the core and the tubing. However, epoxy is not the ideal sealant since it has the potential disadvantage of dissolving in water, and this may affect the migration of some trace elements. We now have holders which seal the sides of cores with gold foil or Teflon sheet and eliminate the need for epoxy. Columns of mineral sand (glauconite) were made by filling the tubing with a slurry of the sand and holding it in place with stainless steel frits.

A solution that has flowed through a rock column is analyzed using the on-line automatic gamma counting system depicted in Fig. 7. The solution flows through tubing in a well in the NaI crystal; the number of gamma rays of specified energies counted and the duration of solution counting (time) are recorded on paper tape. The data are corrected for background, Compton scattering, and radioactive-decay loss to generate trace-element elution curves.

1. Effects of Solution Flow Rate (Strontium in Glauconite)

Glauconite [a hydrous silicate, nominally

 $(K,Na)(A1,Fe^{+3}, Mg)_2(A1,Si)_4O_{10}(OH)_2]$, was formed into two mineral columns. Glauconite sand was prepared by sifting it to obtain a fraction of uniform size (-40 +70 mesh). The sand was washed repeatedly in distilled water to remove dust adhering to the particles and was packed in stainless steel tubing to form columns, each 15-cm long by 1.0-cm diameter and 53% porous.

We prepared each column by eluting it with a solution of 0.01M CaSO4 and 0.0001M SrCO3 (nonradioactive). This solution was made with deaerated water and had been kept under an atmosphere of nitrogen to maintain its low oxygen level. To perform an experiment, we injected a small quarity (20 µL) of 0.01M CaSO4 solution with strontium-85 into the solution stream going to the glauconite column and then eluted the radioactivity from the column with 0.01M CaSO4 solution (analysis in Table 4). The eluate was collected in fractions, and each fraction was analyzed to determine the migration characteristics of the strontium in the column. Six infiltration experiments, each at a different flow rate, were performed in this manner. An additional three experiments (Experiments 85-98, 85-103, and 85-108) were performed in which strontium was eluted through limestone with a 0.01M Ca H302)2 solution at flow rates of 0.1 and 0.2 mL/min and the results were . e same as for the sulfate solution.

The radioactive strontium in various elucte fractions from the six experiments in which the sulfate solution was used is plotted in Fig. 8. The flow rates given in Fig. 8 were measured by collecting eluate fractions for specific periods of time. In each experiment, all radioactive strontium was eluted in the single peak seen. The strontium peak moved through the column with a well-defined velocity equal to 0.04 times the velocity of the water stream. This behavior of strontium arises, in all likelihood, from continuous and reversible partitioning of the strontium between liquid and solid phases.

The strontium peaks were delayed relative to the advancing water front (which traversed the column in the first 6.3 mL of eluer"). Moreover, each strontium peak seen in Fig. 8 (except possibly the one produced with the slowest flow) is wider than that predicted from the peak shape of tritiated water eluted through the column. (The predicted peak width for strontium from hydrodynamic dispersion is equal to the peak width for tritium divided by the retardation factor for strontium with respect to the water front. Therefore, for a tritium per with a width at half maximum of 2 mL and a retardation factor of 0.04, a peak width of about 50 mL for strontium is predicted and is comparable to the peak width seen at a flow rate of 0.1 mL/min in Fig. 8.) It is concluded that the strontium interacted with the glauconite column; as indicated by the different peak shapes, the strontium interacted differently at each flow rate. The sharpest peak was produced at the lowest flow rate; the widest peak was produced at the highest flow rate. There was a broadening of curve shape with increased flow (and a slight increase in velocity of the strontium) as a result of less reaction of the liquid with the solid at the higher flow rates. This effect (i.e., slow kinetics modifying trace-element migration at flows of 0.1 mL/min or greater) is expected from the results of static-adsorption experiments.²

It is unlikely that the water flow can be made slow enough for complete reaction (equilibrium) of the strontium between the water and glauconite to exist locally everywhere throughout the column. Although the reaction of strontium in the groundwater with solid particles of glauconite is rapid



Fig. 8.

Elution of Strontium from a column of Glauconite. Peak width increases with increasing flow rate (top to bottom), indicating nonequilibrium behavior. Flow at 0.1 mL/min corresponds to a linear flow rate of 1.2 km/y.

at the wetted surface adjacent to the fluid stream, a continued but slower reaction of the strontium with deeper layers of glauconite (accessible by capillaries, interlayer water, crystalline defects or solid-state diffusion) also proceeds. Complete equilibrium may require the adjustment of the major and minor constituents of the mineral and solution and, possibly, recrystallization of the solid phase to different mineral constituents. These processes may take thousands of years; can grossly change adsorption capacities, reaction rates, and adsorption constant; and are not simulated in the laboratory experiments. The potential for slow but extensive reactions can be argued for most rock-water systems and is not unique to the system discussed here.

Peak broadening may result not only from nonequilibration, but also from differences in stream paths within the column (hydrodynamic dispersion), from heterogeneity of solid media within a column, and from the exchange process itself (finite size of the theoretical plate). At flows slow enough that these effects dominate and determine the width of the elution peak, (as, for example, at 0.1 mL/min with strontium in glauconite), the migrating nuclide may be considered, without loss of accuracy, to be in "local equilibrium." Models, of course, need to include dispersive terms for hydrodynamic dispersion, etc. where these terms dominate elution-curve shape. For the elution of strontium through the glauconite used in these experiments, "local ecuilibrium" occurs at flows of 0.1 mL/min (equivalent to 1.2 km/y in a rock formation) or lower.

The glauconite column with strontium migration was modeled, using the Argonne Dispersion Code (ARDISC),³ which takes account of reaction kinetics. The elution curves in Fig. 9 predicted from the model were obtained to represent the strontium elution curves given in Fig. 8 and agreed very well. This was done by first estimating the number of theoretical units, N, in the glauconite column by the formula¹³

$$N = 16\sqrt{2}/8^2$$

where \bar{v} is the average elution volume of the peak (position of the peak for symmetric curves) and B is the base of the triangle drawn inside the elution curve obtained at the flow rate of 0.1 mL/min. The fraction, α , of strontium on the glauconite at equilibrium was determined from the peak position, v, of the strontium elution curve at 0.1 mL/min and the solution volume in the column, v, by the formula

$\alpha = 1 - \overline{\nu}/\nu_{\bullet}$

The solution volume, v., was determined from tritium elution curves to be 6.33 mL. Finally, a factor, F, representing the extent (from 0 to 1.0) of equilibrium attained by strontium in each theoretical unit was estimated for each flow rate. These constants were then used in the dispersion code to derive the modeled elution curves in Fig. 9. The curves represent the actual experimental data very well, suggesting that the behavior observed with different flow rates is attributable to kinetics as incorporated in the factor, F. A different but comparable analysis of the data in Fig. 8 is given by Rickert.¹⁴





Modeled Elution Curves vs Flow Rate for a Nuclide which is 96.2% Absorbed by the Geologic Material at Equilibrium. The material was taken to consist of 123 theoretical units, each with a volume of 51.5 µL of sc tion. The parameter, F, equals the fractional extent of reaction.

The factor, F, is simply related to the residence time of the solution in each theoretical unit of the column, as seen in Fig. 10. This relationship





can be expressed in terms of the linear flow rate, L (in cm/s), of the solution by the formula

F = - 10.7L

The linear flow rate is related to the bulk flow rate by the cross-sectional area (0.785 cm^2) and porosity (0.53) of the glauconite column.

The reaction kinetics appear to be first order (i.e., the reaction rate is proportional to the concentration of strontium-85 in solution). We conclude because it was demonstrated for strontium in glauconite, that nuclide migration often can be accurately predicted by models that consider the reaction kinetics of radionuclides between solution and rock.

This work with strontium in glauconite is an extension of work by Inoue and Kaufman.⁴ In their work, they modeled strontium migration in glauconite, using conditions of local equilibrium for flows up to 6.3 km/y. Although their model predicted the results of their experiments reasonably well, the difference between the model predictions and the experimental results may be due to the existence of nonequilibrium behavior, as seen in the results reported here.

2. Effects of Solution Composition (Strontium in Oolitic Limestone)

We prepared columns of solid oolitic limestone by epoxy-mounting cores (each approximately 5-cm long by 1-cm diameter) of limestone in stainless steel tubing in the manner described above. Two of the columns were used for strontium-elution experiments. In eight different experiments, three solutions (RRW solution made with oolitic limestone, the recipe solution to simulate groundwater in limestone, and a 0.01M CaSO4 solution) were used to elute strontium through the rock columns. Conditions for the experiments are listed in Table 8.

Expt. No.	Solution	Limestone Column	Solution Analyses ^a	Flow Rate, mL/min ^b
85-131	RRW	2	Fraction	0.1
128-33	RRWC	2	Fraction	0.1
128-39	RRWC	2	Fraction	0.1
128-43	Recipe	2	On-line	0.042
128-57	Recipe	2	On-line	0.045
128-62	Recipe	2	On-line	0.043
85-123B	0.01M CaSO4	1	Fraction	0.1
128-45	0.01M Cas04	2	On-line	0.1

Table 8. Experimental Conditions for Strontium Migration through Oolitic Limestone Columns

^aThe strontium-85 activity of the eluate either was measured by counting fractions of the eluates in test tubes ("fraction") or was counted "online" using a flow-through cell.

^bThe flow rate of 0.1 mL/min was the nominal setting on the pump. At this setting, the delivery rate of the pump was measured to be 0.096 mL/min. In the limestone column, flow rates of 0.096 and 0.043 mL/min correspond to linear flow rates of 3.4 and 1.5 km/y.

^cStrontium carrier was added to the solution in these experiments as SrCO₃. Undissolved SrCO₃ was removed by filtration leaving 0.15 mg/L strontium in solution.

Elution curves for the experiments using the three different solutions and typical of curves obtained in the other experiments with the three solutions are given in Figs. 11, 12, and 13.



Fig. 11. Elution Curve for ⁸⁵Sr Forced through an Oolitic Limestone Column with RRW Solution. Solution flow rate was 0.1 mL/min (3.4 km/y).



Fig. 12. Elution Curve for ⁸⁵Sr Forced Through an Oolitic Limestone Column with Recipe Solution. Solution flow rate was 0.043 mL/min (1.5 km/y).

With both the oolitic RRW solution and the recipe solution, strontium is eluted in a peak and is retarded relative to the water front. The peak occurs at 6 to 9 mL for RRW solution and at about 5 mL for the recipe solution; velocities of the strontium relative to the water front are 0.06 to 0.09 for RRW water and 0.11 for simulated groundwater. The peaks are broad and skewed, indicating that the elution of strontium is complicated by the (1) adsorbed



Fig. 13.

Elution of Strontium-85 Through a Column of Oolitic Limestone in a 0.01M CaSO4 Solution. Solution flow rate was 0.1 mL/min (3.4 km/y).

strontium population not being proportional to strontium concentration in solution (nonlinear isotherm), (2) kinetics (low reaction rates), (3) irreversibility, or (4) other properties of the strontium reaction with limestone.

Retardation of strontium by limestone was not seen when the 0.01M CaSO4 solution was used, as indicated by the elution curve in Fig. 13. When the 0.01M CaSO4 solution was used, only the strontium activity in the skewed tail of the peak was retarded, and that only slightly.

As seen from the three figures, the elution of strontium through limestone depends upon the composition of the water. However, although the two dilute solutions (the RRW solution and the recipe solution) have different compositions (see Table 2), only small differences in the migration of strontium are apparent. The presence of trace elements such as silica, praseodymium, and boron in the RRW solution and the fivefold difference in calcium and bicarbonate contents of the two solutions do not have a significant effect on strontium migration in limestone. These two solutions differ also in the composition of their suspended matter. The RRW solution, made by agitating rock particles in water, would be expected to contain tiny clay particles not filtered by the 0.4-µm-pore membrane. The recipe solution, made of purified chemicals, while possibly not free of tiny particles, would have very different amounts and types of suspended particles. That these two solutions produced very similar behavior for strontium suggests that suspended particles in RRW solutions do not affect trace-element migration.

The positions of the elution peaks (Figs. 11 and 12) indicate a loading of about 7 x 10^{-5} meq strontium per gram of limestone under the conditions of the experiments (the mass loading for strontium represents only a

part of the cation-exchange capacity of the limestone). Measurements of these small loadings are important in assessing geologic bodies as barriers to nuclide migration. Although rocks with these loadings can retard the movement of trace elements in solution, the rocks can be quickly overwhelmed by stable or radioactive elements present at concentrations higher than those used in these experimental solutions (<u>i.e.</u>, see Fig. 13). Thus, even if radionuclides are present in trace concentrations, the small mass loadings of rocks may limit the amount of radionuclides retained.

Because strontium moves through oolitic limestone in peaks having measurable velocities, we can compare the results of the column infiltration experiments with behavior predicted from batch-absorption experiments. In batch tests,¹⁵ the coefficients, K_D, for strontium partitioning between recipe solution and oolitic limestone were reported by us to be 5.09, 5.33, and 5.77 (avg. of 5.4 listed in contractors' report).¹⁶ The coefficient, K_D, is related to the velocity of the bulk of strontium relative to the velocity of water, v_{Sr}/v_w , by the equation:

$$v_{Sr}/v_w = \frac{1}{1 + \frac{K_{D\delta}}{\epsilon}}$$

where δ , the density of the limestone, is 2.35 g/cm³ and ε , the porosity of the limestone, is 0.19. In deriving this formula, we assume that local equilibration, reversible reactions, and linear adsorption isotherms (which would mean that the concept of a single K_D value is valid) exist during nuclide transport.

Relative migration rates calculated for the three measurements of K_D are 0.016, 0.015, and 0.014, respectively. These predicted values are nearly one order of magnitude lower than the value, 0.11, measured in the column infiltration experiment (reported above) with simulated groundwater. This difference suggests either (1) that differences in experimental technique (the use of crushed limestone in batch tests versus solid limestone in infiltration experiments. for example) preclude results from the two experimental techniques being compared or (2) that the assumptions (the assumed absence of local equilibrium, assumed linear absorption isotherms, etc) that were made in comparing the results of batch and infiltration experiments are not correct.

3. Tin Migration in Glauconite

One glauconite column was prepared by eluting it with a 0.01M CaSO₄ solution to which 0.0001M SnCl₂ had been added (of which less than $1 \ge 10^{-7}M$ remained in solution). We injected 20 µL of a sulfate solution containing $7 \ge 10^{-9}M$ ¹¹³Sn into the solution stream, which carried the radioactive tin to the glauconite column. Solution was pumped through the column at a

rate of 0.2 mL/min for about 3 days but did not wash a detectable quantity of tin out of the column. The location of the radioactive tin in the column (determined by disassembling and sampling the column) is plotted in Fig. 14.





Distribution of 113Sn in a Glauconite Column After Elution with 0.01M CaSO₄ Solution at 0.2 mL/min (2.4 km/y) for 38 days.

The tin was strongly retained on the glauconite; the peak activity was in the top sample of the glauconite. However, we detected radioactive tin in all samples of the glauconite, indicating that some of it had migrated the length of the column. The migration of the very small amount of tin through the column may be due to (1) movement of colloids of tin or particles with adsorbed tin, (2) complexes or oxidation changes of the tin, or (3) nonlinear adsorption isotherms for tin on glauconite.

B. Leach-Migration Experiments

As described above, we have formulated solutions that are representative of groundwaters in the rocks we are studying by allowing water to react with rocks.¹⁶ In column infiltration experiments, we have attempted to maintain the levels of dissolved gases in the solutions at the levels that may exist in deep underground waters. A remaining uncertainty in the infiltration experiments has been how a trace element added to an experimental solution is chemically related to the same trace element leached from solid waste. Presumably, any element leached into a solution from solid waste could hydrate, change valence state, or form complex alumino-silicate species that could affect its retention by geologic materials. These leached species would be difficult to characterize and to synthesize in free-standing solutions. We have chosen to generate these leached species experimentally and to determine their migration characteristics, rather than to try to formulate each species. Apparatus (Fig. 15) used for this type of experiment is similar to the apparatus illustrated in Fig. 7, except that the sample injection valve has been replaced by a solidified waste form, from which radioactive elements are leached at elevated temperature. (Elevated temperatures are used to promote leaching and to simulate the temperatures that will exist initially around a waste form if cesium and strontium have not been removed from the waste.) A different sample of simulated high-level waste glass containing uranium was used as source of radionuclides in each experiment. The glass was composed of Pw-8a-3 calcine and 76-68 glass¹⁷ and had been previously characterized by the Battelle group. A slice of this glass was irradiated in the ANL CP-5 research reactor to activate some nuclides.¹⁸ Elements of interest for geologic storage and having short-lived isotopes in the glass were zirconium, iodine, cesium, uranium, and neptunium. Other elements such as a light alkali (sodium) and rare earths were also present as short-lived radionuclides in the glass.



Fig. 15.

Apparatus for Leach/Migration Experiments in Which Nuclides Leached from a Solidified Waste Form at Elevated Temperature Migrate in Rock Columns

In ongoing experiments, trace elements leached from the waste form are carried in the fluid stream to an oolitic limestone column where their migration characteristics are monitored. Coincidentally, this apparatus indicates the leachability of waste forms in groundwater solutions at temperatures and under oxygen and carbon dioxide partial pressures that may exist in geologic repositories. Two experiments were performed. In the first (Expt. 128-89), 4.87 mg of irradiated glass was the source of radionuclides. The water that leached the glass at 80°C did not contain a measurable concentration of nuclides, and the experiment was terminated.

In a second experiment (Expt. 128-95), 0.35 g of irradiated glass (7.9 cm² surface) was the waste form. The glass was again heated to 80°C and was leached with a stream of RRW solution flowing at about 0.08 mL/min. The solution stream, after leaving the column of glass, was forced through a limestone column. The solution leaving the limestone column was collected in five fractions, and each fraction was analyzed for radionuclide concentrations. After 1560 mL of solution was collected, the experiment was terminated and the limestone column was cut into four pieces for analysis.

The solution fractions were dried and the residues were analyzed for activity with a NaI-well gamma spectrometer. Radioactivities of the four sections of the column were also determined with the NaI spectrometer. The preliminary results discussed here are from these analyses. The solution residues were subsequently dissolved in small quantities of acid solution. The sections of the limestone core were removed from the stainless steel tubing and epoxy by dissolving them in acid. These samples of solution and rock will be counted again, using a GeLi detection system to resolve more of the gamma peaks and to eliminate possible interferences.

Information on the eluate fractions and net count rates is given in Table 9. The activity in the eluate was predominantly from 134Cs with lesser amounts of activity from 7Be, 46Sc, 54Mn, 56Co, 60Co, 65Zn, 85Sr, 86Rb, 89Zr, 103Ru, 109Cd, 125I, 129Xe, 137Cs, and 170Tm. The eluate showed no systematic increase or decrease in cesium activity with continued elution. The first sample shows cesium activity comparable to that in the other samples so that, assuming activity was delivered continuously to the column, there appears to have been no significant retardation of the cesium activity by the column.

The radioactivity in the column was also found to be predominantly from cesium-134. Gamma ray peaks from other nuclides were not discernable in the NaI spectrum. The concentration of cesium along the length of the column is plotted in Fig. 16. The highest concentration of radioactive cesium is at the top (inlet end) of the column.

The leach-migration experiments were initiated because of the possibility that radionuclides leached from solidified waste may migrate differently from radionuclides formulated in solutions from soluble compounds. In a previous experiment (Expt. 128-56, not described in this report), the migration in

Solution Fraction	Fraction Size, mL	Measured Average Flow Rate, mL/min (km/y)	Solution Activity, cps/mL ^a
1	250	0.087 (3.1)	0.60
2	216	0.075 (2.6)	0.69
3	296	0.068 (2.4)	0.87
4	200	0.069 (2.4)	0.61
5	600	0.083 (2.9)	0.58

Table 9. Sizes, Flow Rates, and Activities of Eluate Fractions from Experiment 128-95

^aActivities counted were the 563.1-, 569.2-, and 604.6-keV gamma rays from the decay of cesium-134.



Fig. 16.

Cesium-134 in the Oclitic Limestone Column Used in Experiment 128-95

limestone of cesium formulated as a solution was studied. In the previous experiment no cesium activity was detected in any of the eluate fractions. This suggests, qualitatively, that cesium leached from the waste form did behave differently from cesium in solutions formulated by dissolving soluble compounds. The difference in cesium behavior is also illustrated by the partition coefficients (measured as the amount of cesium on the rock per gram of rock divided by the amount of cesium in solution per milliliter of solution) in Table 10, which lists results of (1) the infiltration experiment with a formulated solution, (2) batch experiments with cesium and limestone, and (3) the leach-migration experiment.

	Infiltration Expt 128-56	Batch Experiment	Leach/Migration Expt 128-95
K _D , cesium peak	120ª	80 ± 70 ^b	120 a
K _D , column exit end	>15c		2.4c

Table 10. Partition Coefficients, mL/g, Measured for Cesium Migration in Oolitic Limestone

^aThe partition coefficient, K_D, was determined from the movement of the cesium peak (relative to the flowing solution stream) by the equation

$$K_{\rm D} = \frac{v_{\rm w}}{v_{\rm Cs}} - 1 \frac{\varepsilon}{\delta}$$

where v_w is the velocity of the water stream, v_{CS} is the velocity of the cesium peak, ε which is equal to 0.19 is that porosity of the limestone (that is subject to fluid flow), and δ which is equal to 2.35 g/cm³ is the density of limestone. K_D is measured directly in batch experiments.

^bThe partition coefficient, K_D, was determined by dividing the activity on rock aggregate per gram of rock by the activity in solution per milliliter of solution that resulted by agitating the rock and solution for seven days in the batch test.

^cThe partition coefficient, K_D, was determined by dividing the activity in the column at the exit end by the activity of the eluate.

The partition coefficient measured for the cesium peak in the migration experiment agrees with the coefficient measured in the batch experiment. The partition coefficient, measured at the exit end of the column, differs considerably for the infiltration and the leach/migration experiments and suggests that characterization of cesium migration by a single partition coefficient is not valid. The observed dependence of the partitior coefficient on cesium concentration, which is described in Section E below, is likely the source of the apparent disagreement of results of conventional infiltration experiments (in which cesium concentration in groundwater solution is about 4×10^{-8} M) and leach migration experiments (in which cesium concentration in groundwater solution is 5×10^{-7} M, due principally to cesium leached from the glass waste form).

C. Adsorption-Desorption Kinetic Experiments and Infiltration Experiments with Fissures in Gray Hornblende Schist.

Many geologic formations under consideration for waste disposal are composed of rocks that are impermeable to water. Water flow in such formations would be through cracks or fissures in the rock. To investigate nuclide migration in these formations, we have performed experiments in which fissures consisted of uniform gaps between slabs of rocks cut to provide a rectangular geometry. The polished sides (approximately 2.5-cm wide by 5-cm long), of two slabs were held 0.027 cm apart by wax gaskets along their long edges. Each fissure was attached by tubing to a microliter pipette (as shown in Fig. 17) for injection and ejection of specific volumes of solutions (for static sorption experiments). Alternatively, for continuous-flow (or infiltration) experiments, a syringe pump was substituted for the pipette to suck solution from a reservoir on top of the fissure.



Fig. 17.

Rock Fissure Connected to a Microliter Pipette for Adsorption-Desorption-Kinetic Studies. ANL Neg. No. 122-78-838. The purpose of experiments with fissures of schist was to determine whether migration behavior could be predicted from kinetic and partitioning values measured in static sorption experiments. If at a particular ratio of surface area to liquid volume, the rate of adsorption, rate of desorption, and equilibrium concentrations of a nuclide partitioned between rock and solution are known, the rate of migration of a nuclide through that particular media can be predicted from our Argonne dispersion code (ARDISC).³ These predictions are, in turn, compared with actual migration behavior observed from infiltration experiments with the fissures.

1. Adsorption Experiments

In an adsorption experiment, RRW solution made with gray hornblende schist was injected into a fissure in schist from the top down. First, the RRW solution and fissure surface were kept in contact for approximately two days to allow the freshly polished surfaces to react with water. RRW was then ejected from the fissure, RRW solution which contained about 4×10^{-8} M americium-241 was injected into the fissure, and the solution was ejected after a predecided time. The activity of the solution before injection and after ejection was assayed.

Ten adsorption experiments were performed in this manner. The results, presented in Table 11, indicate a rapid exponential-like decrease of activity in the solution with time, similar to the behavior seen in staticabsorption experiments.²

Adsorptio	n Duration, s	Fissure No.	Activity Applied, nCi	Percent Remaining in Solution
	15	1	65	84.6 + 0.1
	54	5	0.98	71 ± 1
	150	8	0.97	63.1 ± 0.9
	300	2	1.1	50.7 ± 0.8
	600	7	1.7	36.3 + 0.5
3	600	4	56	32.3 ± 0.1
60	120	2a	173	25.0 ± 0.1
60	120	8a	184	17.4 ± 0.1
86	400	5a	111	$2 20 \pm 0.02$
250	200	6	0.84	0.05 ± 0.25

Table 11. Adsorption of ²⁴¹Am by Fissures of Gray Hornblende Schist. Static Sorption Experiments.

^aFissures 2, 5 and 8 were each used for two adsorption experiments. For those three fissures, the activity applied for the first experiment was insignificant in comparison to the activity applied in the second experiment. The partitioning of the nuclide between sample and solution at 250 200 s (69.5 h) is used as the equilibrium partitioning value. On the basis of surface area absorpt: n coefficients found for the sorption of 241 Am from RRW in "rock test tube experiments" described in Section D below and in batch experiments with cubes of rock, ¹⁹ it was predicted that for the surface area to liquid volume ratio in the fissure experiments, 99.55 to 99.81% would be adsorbed at equilibrium; this is in agreement with the value of 99.95 ± 0.25% found in the fissure absorption experiments.

2. Desorption Experiments

Desorption experiments performed with fissures 2 and 8 included five to seven desorption experiments for each of six time spans between 10 and 3600 s (60 min). Quickly after the conclusion of an adsorption experiment, the fissure was used in a desorption experiment by rinsing it and then filling it with RRW solution that contained no americium. Thereafter, the fissures were allowed to hold RRW for various periods of time to allow americium to transfer from the rock to the solution.

Table 12 presents the results of the desorption experiments with fissures 2 and 8. The results vary so much that no quantitative conclusion can be drawn about rates of desorption. It was assumed that desorption occurs at a rate equal to the adsorption rate.

	No. of	Percent of Equilibrium ^a						
Desorption Time Interval, s	, Desorption Runs	Fissure	No.	2	Fissure	No	. 8	
10	5	8 ±	5		4 ±	2		
20	7	13 ±	10		13 ±	4		
60	7	31 ±	47		19 ±	4		
360	6	8 ±	6		13 ±	5		
1 200	5	13 ±	8		6 ±	2		
3 600	7	14 ±	19					
3 600	6				22 ±	16		

Table 12. Desorption of Am³⁺ from Fissures of Gray Hornblende Schist. Static Desorption Experiments

^aIt was anticipated that 0.32% of the activity is desorbed by the rock at equilibrium. The percent of equilibrium is the percent of 0.32% found in the groundwater solution. Values given are arithmetic means and standard deviations for the experiments performed at the given time intervals

3. Column Infiltration Experiments

Column infiltration (continuous-flow) experiments were performed with four fissures (7, 8, 5, 6) at three solution flow rates $(1.13, 2.29, and 4.22 \text{ cm } \text{b}^{-1} \text{ or } 0.10, 0.20, and 0.37 \text{ km } \text{y}^{-1})$. Before an experiment was

started, the fissures were filled with americium-free RRW solution. To start an experiment, americium-bearing solution was sucked through the fissure from a reservoir at the top of the fissure, using a syringe pump. In experiments with fissures 7 and 8, after 66% of the fissure was filled with americiumbearing solution, the experiment was terminated by stopping the flow. For experiments with the other two fissures, the americium-bearing solution in the reservoir was replaced with americium-free RRW solution and the flow was continued until 20 column volumes of RRW solution had flowed through the two fissures. The experiments were then terminated by stopping the flow.

Following the experiments, the fissures were dismantled and dried to determine the distribution of americium in the fissures. Two methods of detecting americium were used. First, to allow the americium distribution to be visualized, autoradiographs of the fissure surfaces were made with Polaroid Land Black and White 3000 ASA film. Secondly, the distribution was quantified by counting horizontal strips or zones on the fissures' surfaces through a 0.32-cm wide slit of lead in front of a sodium iodide scintillation counter. The final fractions of the activity (in percent) counted in each zone of each fissure are illustrated in Figs. 18-23.

Also plotted in Figs. 18-23 is the percent of the total activity predicted to be in each zone by the dispersion code $(ARDISC)^3$ from the adsorption data given in Table 11 and the rate of desorption, which is assumed to equal the rate of absorption (which assumption is consistent with the data in Table 12). The adsorption data was used as follows: From the experimental flow rate, a residence time of solution in each zone was calculated which, in turn, was used to estimate the extent to which americium reacted in each zone. For example, at a flow of 1.1 cm/h (0.10 km y⁻¹), the solution will traverse one zone in 1047 s. In this time period, the activity in solution will have changed (increased or decreased) by 64.6% of the change required to attain equilibrium (from Table 11). The predicted values in Figs. 18-23 were calculated using the Dispersion Model (ARDISC) with this extent of reaction and with continued iterations for each zone to account for either the 0.67 or 20 fissure volumes of solution eluted in each experiment.

Also presented in Figs. 18-23 are autoradiographs of the fissure walls. Some complications in americium migration that were not treated in the experimental analyses or by the dispersion model (ARDISC)³ are visible from features on the radiographs. The fissure surfaces do not absorb uniformly, as evidenced by structures in the radiographs that highlight some features (mineral-filled veins, grain edge boundaries, etc.) in the fissure walls. In addition, as evidenced by the radiographs, flow through the fissure may not have been uniform across the fissure opening, being faster in the centers of the fissures than along the edges. Another complication not treated by the ARDISC model is that the kinetics of americium reaction with schist are not first order (from the data in Table 11), as assumed by the model.





A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.



B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.



- C. AUTORADIOGRAPH OF FISSURE SURFACE SHOWING AMERICIUM DISTRIBUTION.
- Fig. 18. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 0.67 Fissure Volume of Solution at a Flow Rate of 1.13 cm h⁻¹. Fissure No. 7. ANL Neg. No. 122-78-832



A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.



B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.



- C. AUTORADIOGRAPH OF FISSURE SURFACE SHOWING AMERICIUM DISTRIBUTION.
- Fig. 19. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 20 Fissure Volumes of Solution at a Flow Rate of 1.12 cm h⁻¹. Fissure No. 5. ANL Neg. No. 122-78-834



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A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.



B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.





- C. AUTORADIOGRAPH OF FISSURE SURFACE SHOWING AMERICIUM DISTRIBUTION.
- Fig. 20. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 0.67 Fissure Volume of Solution at a Flow Rate of 2.29 cm h⁻¹. Fissure No. 5. ANL Neg. No. 122-78-831

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A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.



B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.



- C. AUTORADIOGRAPH OF FISSURE SURFACE SHOWING AMERICIUM DISTRIBUTION.
- Fig. 21. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 20 Fissure Volumes of Solution at a Flow Rate of 2.29 cm h⁻¹. Fissure No. 6. ANL Neg. No. 122-78-833





A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.



B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.



- C. AUTORADIOGRAPH OF FISSURE SURFACE SHOWING AMERICIUM DISTRIBUTION.
- Fig. 22. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 0.67 Fissure Volume of Solution at a Flow Rate of 4.77 cm h⁻¹. ANL Neg. No. 122-78-836



A. AMERICIUM DISTRIBUTION ON SURFACE OF FISSURE.



B. MODEL PREDICTION OF AMERICIUM ON SURFACE OF FISSURE.



- C. AUTORADIOGRAPH OF FISSURE SURFACE SHOWING AMERICIUM DISTRIBUTION.
- Fig. 23. Experimental and Predicted Distributions of Americium on the Fissure Surfaces after Elution with 20 Fissure Volumes of Solution at a Flow Rate of 4.77 cm h⁻¹. ANL Neg. No. 122-78-835

4. Discussion

In spite of these complications, the migration behavior predicted using absorption parameters (partitioning and kinetic data) measured in static experiments do approximate the migration obtained experimentally. These results indicate that aigration of nuclides in rock fissures may be predictable and can be approximated by data from static experiments. The ability to successfully predict nuclide migration arose from the use of kinetic and partitioning data obtained with fixed geometries of rock surfaces and solutions. Therefore, it was not necessary to transform the kinetics obtained from a batch test (having one geometry) to the kinetics appropriate to a fissure (having another geometry). A similar predictive capability was obtained from kinetic data measured for strontium in glauconite (Section IV.A.1). This success should encourage the measurement of migration characteristics using geometries such as rock or mineral columns or rock fissures that are most similar to the geometries where the data will by .pplied.

It is emphasized that these results show that measurements of the kinetic parameters are as important to an understanding of migration behavior as are measurements of the equilibrium adsorption values.

D. Experiments with "Test Tubes" Fabricated of Rock

In previous batch and static adsorption experiments in which solutions reacted with rock that was contained in glass or plastic vessels, adsorption of nuclides from solution onto container surfaces was always observed. Rather than consisting of the desired two components, (a nuclide partitioned between rock and solution), the experimental system consisted of three components--the nuclide was partitioned among the solution, rock, and container surface. Table 13 presents the results of two experiments which illustrate a threecomponent system.

To produce a two-component system, rock "test tubes" were fabricated by drilling holes into slabs of rock. The holes were drilled with diamondimpregnated coring drills and carbide-tipped masonry drills. During drilling, distilled water was used for cooling. A step under consideration for removing any cutting material introduced during drilling was cleaning of the test tube walls by blasting with sand of the same rock used to form the "test tubes." This step was not employed since after the cut walls were washed with water, they appeared to be clean and free of any foreign contaminant.

These experiments with rock "test tubes" were performed in temperaturecontrolled baths under air. The adsorption of plutonium from solution by granite (from the Nevada Test Site) and the adsorption of plutonium and americium from solution by test tubes fabricated of du Pont core 7-3 1 M 213 (from the Savannah River project site) were studied.

		and the second
	Expt 332-2b	Expt 332-30
Americium Sorbed by		
the Rock, %	26.5	19.4
Americium Remaining in		
Solution, %	14.5	7.4
Americium Adsorbed by		
the Test Tube, %	59.0	73.2
the second division of		

Table 13. Results that Illustrate the Significance of Adsorption by Test-Tube Walls in Static Adsorption Experiments^a

^aExperiments were with tablets of du Pont core 7-3 1 M 213 (gray hornblende schist; chemical analyses show 55.8% SiO₂, 2.10% Ca, 2.74% Mg, 6.22% Fe, 5.20% A1, 1.93% Ma, and 1.22% K); adsorption proceeded for 404 h at a controlled temperature of 28.7°C. Solution volume was 3 mL in each experiment.

^bThe experiment was performed with a rock tablet having the dimensions, 0.928 cm, 0.970 cm, and 0.089 cm and weighing 0.216 g.

^cThe experiment was performed with a rock tablet having the dimensions, 0.915 cm, 0.970 cm, and 0.100 cm and weighing 0.242 g.

In an experiment, slabs of rock containing test tube holes were placed in a constant-temperature water bath at 28.7°C. No cracks were visible in either slab (schist or granite) that would allow infiltration of bath water into the tube sections. RRW solution containing plutonium or americium was placed in each rock "test tube" to a depth of 2 or 3 mL. The solution was removed from the holes, and the quantities of nuclides remaining in solution were compared utilizing a counting standard. The quantity of nuclide remaining in solution was used to calculate the surface area adsorption coefficients, K_s, where

> $K_s = \frac{Activity adsorbed}{cm^2 \text{ of surface}}$ Final activity in solution mL of solution

There was strong adsorption of plutonium from solution by test tubes fabricated of granite and a strong adsorption of americium from solution by test tubes fabricated of grey hornblende schist; there was moderate absorption of plutonium from solution by test tubes fabricated of the grey schist.²⁰ Surface area adsorption coefficients for static-adsorption experiments can be compared with those for rock-test-tube experiments to examine the amount of error that may be incurred by ignoring adsorption by test-tube walls. For the adsorption of Am (III) from solution in test tubes by tablets of the hornblende schist (data of Table 13), the surface area adsorption coefficients were 2.56 and 3.65 mL/cm². For the adsorption of Am (III) from solution by test tubes fabricated from the hornblende schist, the surface area adsorption coefficient was 5.71 mL/cm². This difference is significant and some applications may require the rigorous measurement of adsorption coefficients using rock test tubes.

By use of the method of Foti and Freiling,¹¹ we determined (as described at the end of Section III, Characterization of Rock and Solution) the oxidation states of plutonium in RRW solutions in rock-test-tube experiments. The residence time of plutonium-bearing solution in rock test tubes was varied. The plutonium in the RRW solutions was found to be in the III, IV, V, and VI valence states, initially. With increased contact time with the rock, the proportion of plutonium (III) and (V) increased and the proportion of plutonium (IV) decreased. This trend suggests that the valences change while the solution is in the rock hole rather than during analysis. However, the analytical method was not evaluated by us to determine whether the method affects the distribution of plutonium valence states.

E. Cont: olled-Sample Program

The controlled-sample program was initiated to compare nuclide absorption data obtained by different WISAP subcontracting laboratories. Relyea¹⁵ described the goals of the program and procedures to be used in the program to study the adsorption of plutonium, cesium, and strontium from solutions simulating groundwaters onto the four rocks listed at the bottom of Table 5. Results of the controlled-sample program obtained at Argonne National Laboratory were reported by Relyea.¹⁵

1. The Dependence of Cesium Adsorption by Limestone on Cesium Concentration

As an adjunct to the controlled-sample tests, we ran batch-partitioning experiments with limestone, using recipe solutions containing seven different concentrations of cesium to establish the dependence of cesium adsorption on cesium concentration. The batch-partitioning experiments were done using materials and procedures described for the Controlled Sample Program.¹⁵

Triplicate batch-adsorption experiments were run with each of seven solutions having different cesium concentrations and containing radioactive 137Cs. The cesium concentrations in the solutions are shown in Table 14. Before the addition of cesium, the cesium concentration of the simulated groundwater solution was found by atomic absorption analysis to be below about 1.5 x 10^{-7} M. Control tests to evaluate cesium adsorption on centrifuge

Solution	Added Cesium,b <u>M</u>	Activity ^c from 137 _{Cs} , cps/mL
S-7	1.62 x 10 ⁻⁹	131.9
S-6	1.20×10^{-8}	129.2
S-5	1.05×10^{-7}	131.1
3-4	1.05 x 10 ⁻⁶	130.6
S-3	1.04×10^{-5}	131.5
S-2	1.05×10^{-4}	131.3
S-1	1.15 x 10 ⁻³	128.7

Table 14. Cesium Concentrations and Activities in Recipe Groundwater Solution^a Used in the Batch-Adsorption Experiments.

^aThe recipe solution was made by adding nominally 92.5 mg Ca(OH)₂, 18 mg MgSO₄, 5.8 mg NaCl, and 0.8 mg KCl per liter of distilled water to give the composition for recipe solution in Table 2. The solution was allowed to set for several months, then was passed throug¹ a 0.45-µm-pore membrane filter prior to use in experiments.

^bStable cesium as dissolved CsNO₃ was added to the solutions except Solution S-7. The cesium added to solution S-7 was carrier-free 137Cs. Before cesium addition, the synthetic groundwater solution was found by atomic absorption analysis to contain less than 1.5×10^{-7} M cesium.

^cThe efficiency for the counting geometry employed (5 mL of solution in a test tube placed in a NaI well crystal) was determined to be 0.18 for the 0.662-MeV gamma ray from 137Cs decay.

tubes were performed by placing the solutions in centrifuge tubes not containing limestone. After a solution was contacted with rock aggregate, the limestone was centrifuged from the solutions and the solution was filtered through 0.4-um-pore membrane filters.

The results of one series of tests are shown in Fig. 24. The results of the three replicate series of experiments are similar and show that cesium adsorption by limestone depends very strongly on the cesium concentration of the solution. The partition coefficients were calculated by dividing the amount of cesium adsorbed on the rock per gram of rock by the amount of cesium in the solution per mililiter of solution. Cesium is extensively adsorbed from solution of low cesium concentration (about 10^{-8} M concentration or lower), as indicated by the high values of the partition coefficients at low concentrations. Little cesium is adsorbed from solution containing about 10^{-5} M cesium or more as evidenced by low values of the partition coefficients at these concentrations. Nowhere in the range of cesium concentrations investigated does the partition coefficient appear to be independent of the cesium concentration.



Fig. 24

Partition Coefficients for Cesium Adsorption by Oolitic Limestone Measured in a Series of Batch Experiments with Solutions Having Different Cesium Concentrations. ANL Neg. No. 308-78-172.

As seen in Fig. 24, pertition coefficients for solutions having 1.6 x 10^{-9} and 1.2 x 10^{-8} M added cesium differ greatly. This suggests that before the addition of cesium, the cesium concentration in the recipe groundwater solution must have been considerably below about 1 x 10^{-8} M. The results demonstrate that it would not be valid to use a single K_D value to describe cesium migration in limestone in solutions having cesium concentrations greater than about 1 x 10^{-9} M. The results also suggest that, unless the cesium concentration of a solution used in laboratory tests to measure a partitioning value is known, the measurement cannot be used correctly to evaluate the behavior of cesium in rock. This poses a significant task since normal sensitive methods of cesium analyses such as atomic absorption spectroscopy using the furnace techniques have sensitivities of only about 1 x 10^{-7} M Cs.

The effect illustrated in Fig. 24 may be a major source of the discrepancies in partition coefficients (ranging from 1 to 800 mL/g) for cesium on limestone measured in different laboratories for the controlled-sample program.15

2. Desorption Partition Coefficients

Desorption experiments were run with basalt and limestone samples that had adsorbed their radionuclides (experiments for the controlled-sample program). The experiments were performed by rinsing the aggregated material, then contacting the material for seven days with the appropriate recipe solutions of basalt, limestone, and brine. The results of both adsorption and desorption experiments are given in Table 15. The partition coefficients found for desorption were slightly higher than the partition coefficients found for adsorption.

		Adsorption ^a Distribution Coefficient, mL/g							L/g	
Sample	Recipe Solution	\$	Sr			Cs			Pu	
basalt	basalt	70	±	20	400	±	20	60	±	10
basalt	brine	0.047	±	0.005	1.48	±	0.05	1200	±	100
limestone	limestone	5.4	±	0.3	65	±	2	2080	±	50
limestone	brine	0.177	±	0.006	0.14	±	0.01	1430	±	60

Table 15. Partition Coefficients Found for Adsorption and Desorption with Controlled-Program Samples and Recipe Solutions.

Desorption	Distribution	Coefficients,	mL/g
Srb	Csc	P	u

basalt	basalt	75 ± 2	440 ± 60	d
basalt	brine	е	2.1 ± 0.2	d
limestone	limestone	19 ± 1	125 ± 15	d
limestone	brine	3.7 ± .4	2.0 ± 0.3	d

^aSeven days contact for adsorption.

^bSixteen days contact for desorption.

^cTen days contact for desorption.

^dUnable to establish desorption K_D; too little activity desorbed into solution; erratic results.

^eUnable to establish desorption K_D, too little activity remaining on sample.

3. Adsorption-Desorption Partition Coefficients with Groundwater Solutions

Adsorption-desorption experiments with cesium and strontium were performed with Sentinel Gap basalt and colitic limestone and the three groundwater solutions (RRW solutions made with basalt or limestone or with salt from the Waste Isolation Pilot Plant Site or WIPP, Sandia). The experimental methods were those used in the controlled-sample program work. The pH of each groundwater solution was adjusted to be comparable to the pH of the corresponding recipe solution. The pH and "measured" E_h (Ref. 2) of the solutions were: basalt RRW, pH 8.0, E_h 0.444 V; limestone RRW pH 8.1, E_h 0.389 V; and WIPP salt RRW, pH 6.8, E_h 0.319 V. Results of the adsorption-desorption experiments with cesium and strontium using RRW solutions are listed in Table 16.

Table 16. Partition Coefficients Found for Adsorption and Desorption with Controlled Sample Materials and RRW Groundwater Solutions^a

		Adsorption ^b Distribution Coefficients, mL/g					
Sample	RRW		Sr	Cs			
basalt	basalt	470	± 80	3300 ± 180			
basalt	WIPP salt ^c	0.13	± 0.01	4.7 ± 0.2			
limestone	limestone	6.7	± 0.3	80 ± 70			
limestone	WIPP salt	0.15	± 0.02	1.4 ± 0.1			

Desorption^d Distribution Coefficients, mL/g

Sample	RRW	Sr	Cs
basalt	basalt	170 ± 20	1060 ± 40
basalt	WIPP salt	3.0 ± 0.3	6.4 ± 0.1
limestone	limestone	20 ± 1	320 ± 290
limestone	WIPP salt	4 ± 1	4.3 ± 0.1

^aUncertainties were calculated to be one standard deviation from counting statistics. Where the uncertainty is large compared to the measured value, the uncertainty is not symmetric as implied in the table.

^bSeven days contact for adsorption.

^CWIPP salt RRW was made by contacting WIPP salt with distilled water. WIPP salt was added in excess. Chemical analyses of the three rock-reacted waters are being performed.

dSixteen days contact for desorption.

As with the case for recipe solutions, the partition coefficients found for desorption using RRW solutions were slightly larger than the partition coefficients found for adsorption except in the experiments with basalt.

Comparisons of data using recipe and RRW solutions are not fruitful because of the likelihood that the solutions differ considerably in their total cesium and strontium concentrations. As demonstrated in Section E.1 of this report, partition coefficients can depend sensitively on the traceelement concentrations, even at the very low concentrations used in these experiments.

V. FUTURE DIRECTION

In the future, we will use infiltration experiments, both of porous rock and mineral columns and of fissures of impermeable rock, to study nuclide migration. The leach-migration experiments in which a solid waste form is the source of radionuclides will be continued. In the latter experiments, leaching temperature may be used as a controlled variable. To study surfaces more representative of naturally formed fissures, fissure experiments will be extended to the use of fracture surfaces (laboratory-produced and natural) in addition to the use of polished surfaces. "Atmosphere-exposed experiments" (batch tests and static-adsorption experiments) will be conducted in atmosphere-controlled boxes to reproduce the oxygen and carbon dioxide fugacities expected in deep geologic waters.

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