
ANL-76-127

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

ANNUAL REPORT FOR FY 1976
ON PROJECT AN0115A:
THE MIGRATION OF PLUTONIUM AND
AMERICIUM IN THE LITHOSPHERE

by

S. Fried, A. M. Friedman, J. J. Hines,
R. W. Atcher, L. A. Quarterman,
and A. Volesky

Chemistry Division

December 1976

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

34

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	7
I. INTRODUCTION.	7
II. RADIOASSAY PROCEDURE AND TRACER PREPARATION	9
III. INSTRUMENTATION.	10
IV. EXPERIMENTAL PROCEDURES	11
A. Migration of Plutonium in Los Alamos Tuff	11
B. Study of the Effect of Rainfall	13
C. Effect of Deposition Rates and Volumes.	14
D. Migration of Plutonium into Dense Stone Samples	14
E. Movement of Actinides through Fissures	17
F. Surface Absorption Coefficients: Variation with Concentration of Dissolved Salts	21
G. Attempts to Determine Relative Migration Rates.	23
H. Electrochromatographic Behavior of Tracer Pu-Am in Water .	27
V. CONCLUSIONS.	28
REFERENCES	31

BLANK PAGE

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Block Diagram of Scintillation Spectrometer.	11
2.	High-pressure Chromatographic Apparatus	11
3.	Experimental Arrangement for Coring Experiment	12
4.	Schematic Diagram of Coring Apparatus	12
5.	Results for Cores Taken at Various Radial Distances from Central Core (0-0)	13
6.	Vertical Distribution of Plutonium in Tuff as a Function of Rainfall	15
7.	Comparative Migration of Plutonium and Americium in Tuff	15
8.	Vertical Distribution of Plutonium as a Function of Deposition Rate	16
9.	Radial Distribution of Plutonium as a Function of Deposition Rate	16
10.	Comparative Vertical Distribution of Actinides on Tuff.	17
11.	High-pressure Chromatographic Results on Limestone	18
12.	Fabricated Fissure Apparatus	18
13.	Distribution of Plutonium on Basalt Fissure.	19
14.	Effect of Flow Velocity on Plutonium Distribution on Surface of Basalt	20
15.	Variation in k for Plutonium Solutions in Limestone as a Function of Other Ionic Concentrations	21
16.	Variation of k for Plutonium Solutions in Basalts	22
17.	Variation of k for Americium Solutions in Basalts	22
18.	Absorption of Plutonium on Limestone as a Function of NaCl Concentration	24
19.	Schematic Diagram of Elution Column Made with Tuff Plug	25
20.	Comparison of Relative Migration Rates in Tuff	26
21.	Elution of Plutonium and Americium in Column of Tuff.	26
22.	Electromigration Behavior of Activity.	27
23.	Migration of Plutonium for Hypothetical Depository.	29
24.	Migration of Plutonium through an Aquifer	29

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Absorption of ^{237}Pu on Niagara Limestone (Chicago Dolomite); Data for Samples in a 0.5M Solution of NaCl at Equilibrium	24
II.	Electromigration of Plutonium and Americium Ions	28

ANNUAL REPORT FOR FY 1976
ON PROJECT AN0115A:
THE MIGRATION OF PLUTONIUM AND
AMERICIUM IN THE LITHOSPHERE

by

S. Fried, A. M. Friedman, J. J. Hines,
R. W. Atcher, L. A. Quarterman,
and A. Volesky

ABSTRACT

Studies have been carried out on the migration of plutonium and americium in solutions flowing through porous and crushed rock and through fissures. The migration process can be described in terms of the surface absorption of these elements. In addition, chemical effects on the absorption have been observed. One of these effects is possibly due to the presence of a plutonium polymer that migrates at a more rapid rate than normal plutonium.

I. INTRODUCTION

When radionuclides are stored as wastes, either in permanent repositories or in waste-storage areas, the possibility of escape into the environment must be considered. This escape may result in airborne contamination or in contamination of environmental surfaces. This report does not concern itself with airborne contamination, but rather with the surface contamination and the transport and migration of radionuclides into the lithosphere through the agency of water.

Regardless of the original manner of escape of radionuclides from their containers and the character of the material with which they come in contact, they must perforce ultimately be found in the rocks that form the conduits and aquifers. Water in the form of rain will inevitably wash contaminants into soils and thence into conducting rocks. The migration of radionuclides must follow widely varying paths. In the porous rocks, for example, water percolates easily under a slight pressure gradient, and rapid movement of large volumes of water can result--with possible concomitant transport of large amounts of contaminating materials.

In relatively nonporous rocks such as Niagara limestones the transport meets much more resistance and the volumes of water conducted are correspondingly reduced. In such situations, much of the migration of water and its

BLANK PAGE

solutes may be through cracks and fissures in the rock. Certain strata of rock or rock products may be almost impervious to flow of water and by this token may be considered to be an especially suitable "container" for long-term safe storage of nuclear wastes, particularly if these strata are quiescent. A series of investigations was undertaken to examine the properties of rocks in acting as a retarding agent in the migration of radionuclides.

The rocks discussed in this report are Niagara limestone (chosen for its density and fine porosity), basalt from the Idaho National Engineering Laboratory, and Los Alamos tuff. The latter two were chosen because certain amounts of radiochemical wastes have been introduced into them over the past few decades, and it becomes of practical interest to study migration behavior in rock from a real site.

Attempts have been made to study the interaction of various rocks with plutonium and americium in very dilute aqueous solution ($\sim 10^{-11}M$ to $10^{-7}M$). These extreme dilutions were used because it seems likely that the general dispersal of contaminants, even from a zone of high concentration, will ultimately lead to very dilute solutions in a real situation.

The binding of plutonium to rock as a function of the salt content of water in contact with the rock was also considered. It was deemed important to examine the consequences of coming in contact with aqueous salt solutions. Sodium chloride was chosen as the most probable candidate because of its ubiquity and also because of the possibility of using bedded salt as a repository. It is not meant to disregard other ions as potential solutes. Obviously, Ca^{++} , Mg^{++} , SO_4^- , and CO_3^- are also of importance and should also be examined in this context.

We also undertook to identify the ionic species of plutonium present. Because of the extreme dilution of the ions (tracer) conventional methods of identification (absorption spectra, etc.) could not be used. On the other hand, this extremely diluted solution had to be used because, as pointed out earlier, it most nearly simulates the natural situation. Extremely minute amounts of radionuclides may be leached from a source and somehow find their way through the pores of rocks. These amounts of radionuclides in any perceptible amount of water carrier would constitute a solution of dilution comparable with or less than the tracer solutions used.

We cannot completely rule out that the radionuclides or part of them are not in true solution but may be carried on colloidal particles or themselves are colloidal.¹

Experiments in electromigration show that the plutonium is charged, but in itself, this observation does not prove the ionic nature of plutonium in solution, since radiocolloids frequently are charged.

Experiments were also carried out to determine the effects of salts on the absorption of actinides on rock surfaces. The effects of the formal cationic charge of the added salts, as well as the concentration of the salts, were investigated.

Source Material

Los Alamos tuff, a naturally compacted volcanic ash, already has had actinide wastes deposited in selected locations, and it was naturally of interest to compare a controlled laboratory experiment with the actual situation at a disposal site. Los Alamos tuff is also a particularly desirable material to work with in the laboratory since its physical characteristics permit easy handling and coring. Consequently, experiments were carried out using Los Alamos tuff to measure the migration of plutonium into massive blocks under conditions simulating the "natural" ones occurring at the Los Alamos site.

Basalt was also tested because it has been used at the EBR-II site for disposal purposes and its properties were studied for the reasons listed previously. Basalts occurring in the regions around the Idaho National Engineering Laboratory tend to be more or less porous, but are much harder and more difficult to deal with than the Los Alamos tuff.

Finally, a dense limestone was selected (Chicago dolomite). This choice was made because the material is only slightly pervious to the flow of water, but at the same time is a well-known Illinois aquifer. It was thus of interest to measure the relative migration rates of actinides and water through this material.

Los Alamos tuff is so porous that water readily flows through it. Basalt, being much less porous, was used mainly in surface-absorption experiments in which fissures and cracks were simulated. Finally, the relatively impervious Chicago dolomite was used in conjunction with a high-pressure apparatus that was found necessary to effect movement of water through the material. The two latter rocks mentioned also were tested to observe the alteration of binding ability in the presence of salt solutions.

II. RADIOASSAY PROCEDURE AND TRACER PERPARATION

Most long-lived plutonium isotopes are alpha emitters, and their use would require almost complete separation of extraneous solid materials for accurate determination by alpha counting.

In the experiments in this laboratory, the 47-day half-life, K-capturing isotope ^{237}Pu was frequently employed because of its easy detectability. The 100-keV X ray is readily observed in a gamma-ray spectrometer, and the results may be made quantitative by controlling the geometry of the detecting

arrangement. Consequently, laborious plutonium separations from large quantities of rock were avoided, and the sample cores were counted directly. The ^{241}Am was likewise determined by observation of its gamma ray. The spectrometer used permitted the simultaneous determination of americium and plutonium in the sample and canceled out any corrections due to geometry. Similarly, an X-ray spectrometer was used to detect the attenuation of ^{238}Pu L X rays as the plutonium migrated into the body of a piece of rock. Measuring the changes in the L_{α}/L_{β} or L_{γ}/L_{β} ratios permitted the penetration of plutonium into the solid to be calculated after calibration with stone absorbers.

Tracer solutions were prepared by using aliquots of stock solutions of the tracer and evaporating them to dryness with HNO_3 in a small volumetric flask. The evaporation was carried out at a comparatively low temperature to avoid decomposing the solid nitrates obtained as a residue. The americium and plutonium were brought into "solution" with distilled water, and this aqueous solution was used in the rock-migration experiments.

The isotope ^{237}Pu was obtained by bombardment of ^{237}Np as the dried nitrate with 21-MeV deuterons in the Argonne cyclotron according to the reaction $^{237}\text{Np}(d,2n)^{237}\text{Pu}$. The ^{237}Pu and the ^{237}Np nitrate matrix was dissolved with 9M HCl. Five percent HNO_3 was added to the HCl solution to ensure that the actinides would be retained on an ion-exchange column (Dowex A-1) as Pu(IV) and Np(VI). Subsequently, however, addition of iodide ion (as HI or NH_4I) reduced the plutonium to the III state which was no longer bound by the anion resin and was collected in a receiver as the acid solution passed through the column.

Generally, more than one cycle was required to free the ^{237}Pu completely from the neptunium.

Americium was obtained by allowing plutonium containing ^{241}Pu to decay. This isotope beta decays to ^{241}Am . The americium was separated from the plutonium by ion-exchange or solvent-extraction procedures.

III. INSTRUMENTATION

The gamma-ray scintillation spectrometer (Fig. 1) consisted of two single-channel analyzers coupled to a common sodium iodide well detector, preamplifier, amplifier, and scalars. Setting each analyzer for the appropriate energy enabled the two isotopes to be determined.

The X-ray spectrometer was a SiLi detector made by KEVEX capable of resolving differences in X-ray energies of 180 eV.

The scanning alpha detector SADSAC was constructed at Argonne National Laboratory and consisted of a proportional counter whose aperture

was a slit 0.005 in. (0.127 mm) wide. The sample was placed on a movable table and advanced under the slit in a regular manner 0.010 in. (0.254 mm) at a time by a micrometer arrangement. A scaler and timing device completed the system. Counts were made at appropriate intervals and the total recorded as a function of position on the sample.

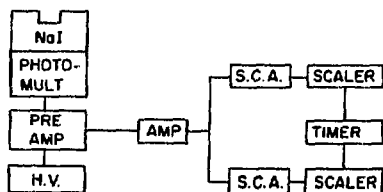


Fig. 1

Block Diagram of Scintillation Spectrometer. ANL Neg. No. 122-76-720.

The high-pressure chromatographic apparatus used for forcing water through the relatively impervious Chicago dolomite is shown in Fig. 2; its operation is described in Ref. 2.

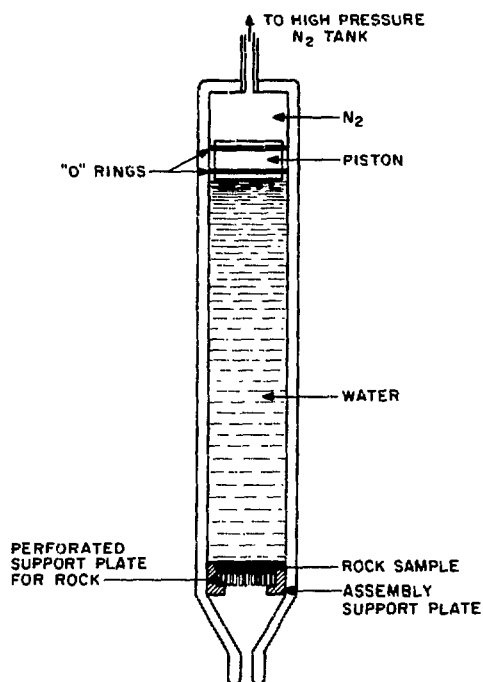


Fig. 2

High-pressure Chromatographic Apparatus. ANL Neg. No. 122-903.

IV. EXPERIMENTAL PROCEDURES

A. Migration of Plutonium in Los Alamos Tuff

These experiments were laboratory simulations of the movement of plutonium and americium in Los Alamos tuff.

In a typical experiment, a block of Los Alamos tuff about 30 cm on edge was used. The coring-location apparatus described in Ref. 3 was installed and used to determine the deposition site of the sample of plutonium. The apparatus is shown in Figs. 3 and 4.

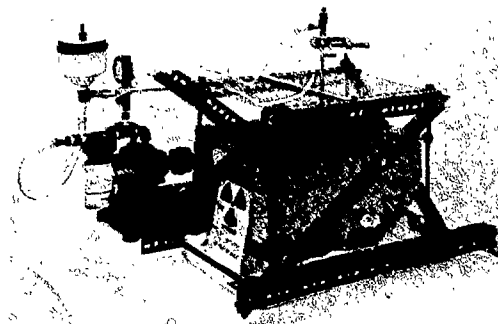
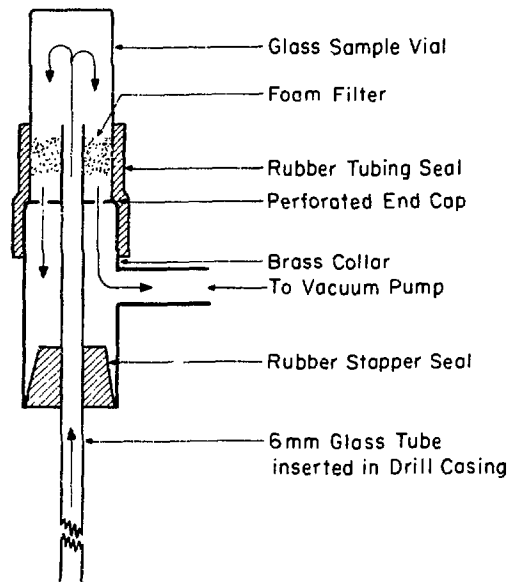


Fig. 3
Experimental Arrangement for Coring
Experiment. ANL Neg. No. 122-2443.

Fig. 4
Schematic Diagram of
Coring Apparatus. ANL
Neg. No. 122-75-103.



At a chosen deposition site, a small depression was drilled and an aqueous solution of ^{237}Pu very slowly deposited at that point by means of a metering pump.

After the plutonium tracer solution was allowed to dry, the surface was wet with a water shower of known volume and then allowed to dry. This cycle was repeated several times until the total amount of "rainfall" was the equivalent on a laboratory scale of "30 in." of rain. The block of tuff was never saturated with water during any particular application of "rain."

After a final sequence of "raining" and "drought," the tuff was cored at the site of introduction of the plutonium. Each core increment was 0.5 cm.

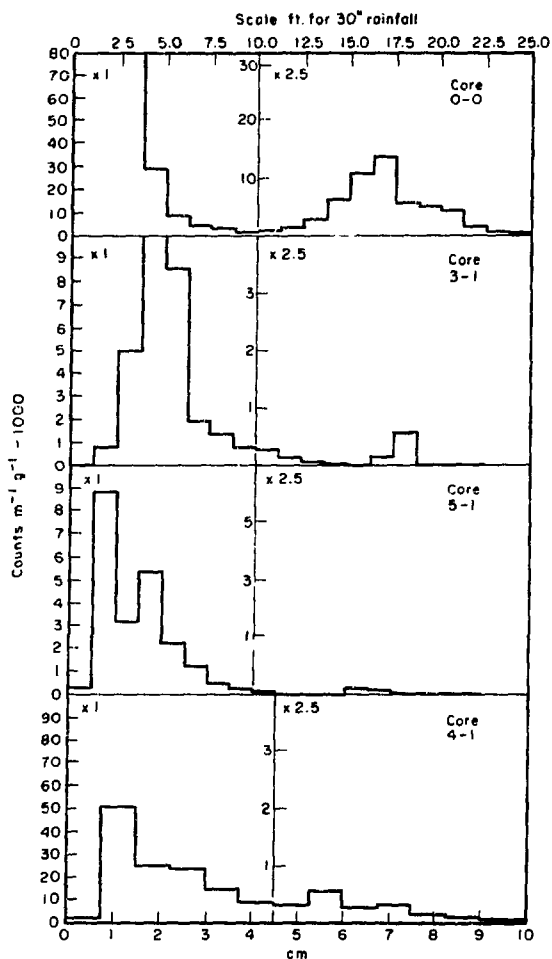


Fig. 5. Results for Cores Taken at Various Radial Distances from Central Core (0-0). ANL Neg. No. 122-75-104.

The results are shown in Fig. 5.

Two zones of plutonium activity are distributed in the rock as a function of depth. The major quantity of plutonium is found very close to the original site of deposition and has only migrated to a maximum depth of about 2 cm. The secondary zone contains about 1% of the plutonium and has migrated downward to a depth of about 10 cm.

These observations suggest that the plutonium exists in two forms in aqueous solution. These "species" may be different oxidation states or differing degrees of polymerization of the Pu(IV) ion. One of the zones may also contain plutonium on colloidal particles as opposed to the ionic condition of its more tightly bound counterpart. At the extreme dilution of these tracer solutions ($10^{-11}M$), it is difficult to come to definite provable conclusions as to which of the aforementioned possibilities is correct. This "double-zone" observation seems to be more or less general in regard to the migration of aqueous solutions of plutonium in rocks. In addition, there were also important effects due to flow velocity, and in some cases, as much as 35% of the plutonium was observed in the fast-moving zone.

B. Study of the Effect of Rainfall

To determine the migration as a function of the total "rainfall" experienced, the experiment described above was modified in that six separate sites for the application of tracer were located by the coring apparatus. Americium and plutonium tracers (^{241}Am and ^{237}Pu) were used simultaneously. This permitted migration rates of these nuclides to be simultaneously determined by detecting the characteristic radiation by means of the gamma-ray spectrometer. The 60-keV gamma ray of ^{241}Am and the 100-keV X ray of ^{237}Pu are

readily resolved. Not only is this important as a labor-saving measure, but it enables the direct comparison of the behavior of americium and plutonium under the same conditions. The ambiguities of sequential-type experiments due to possible inhomogeneity of the rock matrix are eliminated. Aliquots of the tracers were applied by means of a metering pump at a rate of 0.05 ml/hr to each site. The size of the aliquot varied from site to site, those sites to be cored last having the largest aliquots delivered to them. This compensated for the anticipated deeper penetration of the plutonium.

Simulated rainfall was intermittently applied between intervals of drying and covered the entire upper surface of the tuff. As before, the tuff was never saturated with water during any particular application of "rain."

Since the sites were cored successively, those cored later experienced more cycles of "rain" and "drought"; thus the migration of plutonium was measured as a function of the quantity of "rainfall." The cycles of artificial rainfall-drying were initiated, and after a predetermined number of these cycles, the first site was cored. When the coring of each site was complete, the hole resulting from this operation was filled with melted paraffin and the "rain"- "drought" cycle continued with occasional coring. Since the "rainfall" covered the entire upper surface of the rock, each succeeding site experienced more "rain" and more "drought."

The results of these experiments are shown in the following figures. Figure 6 shows the vertical distribution of plutonium after successive rains and droughts. The curves in Fig. 7 show the comparative migration of plutonium and americium in tuff.

C. Effect of Deposition Rates and Volumes

The logical extension of the previous experiment was to deposit the plutonium in successively increasing volumes and deposition rates. Three large blocks of tuff were used and two sites chosen on each such that mutual interference was avoided. Two sets of three samples of mixed ^{241}Am - ^{237}Pu were used. In each set, the volumes were 0.3, 30, and 150 ml. In the first set, the combined solution was deposited at each sample site in 15 min. The other set received its solution over a period of 15 hr per site.

Figures 8-10 show the results obtained for the radial and vertical distributions of plutonium as well as a comparison of americium and plutonium.

D. Migration of Plutonium into Dense Stone Samples

Thin wafers or disks of dense Illinois Niagara limestone and basalt from the EBR-II site were fabricated. The dimensions were approximately 25 mm in diameter and 1.5 mm in thickness. The wafers were waxed into the high pressure chromatographic apparatus as shown in Fig. 2.

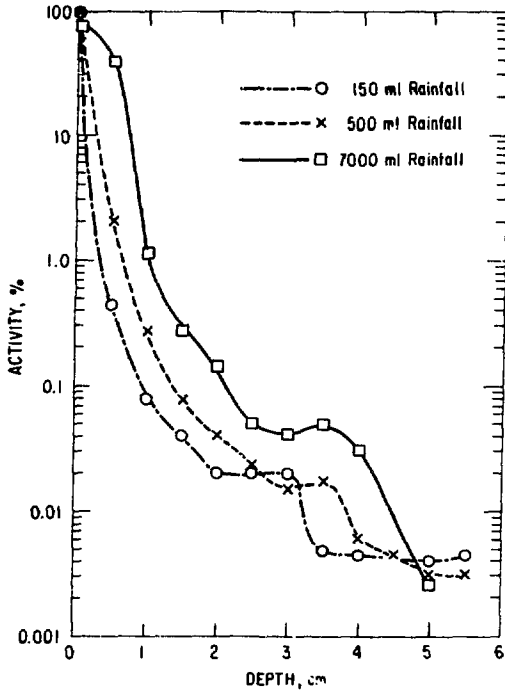
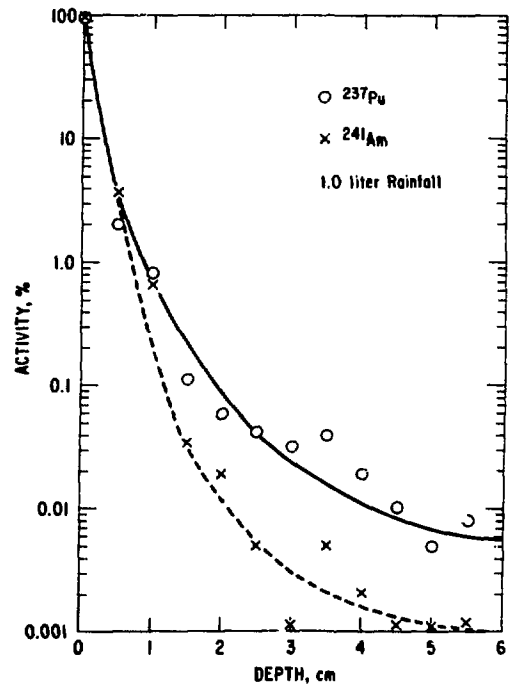


Fig. 6
Vertical Distribution of Plutonium in Tuff as a Function of Rainfall. ANL Neg. No. 122-76-724.

Fig. 7
Comparative Migration of Plutonium and Americium in Tuff. ANL Neg. No. 122-76-718.



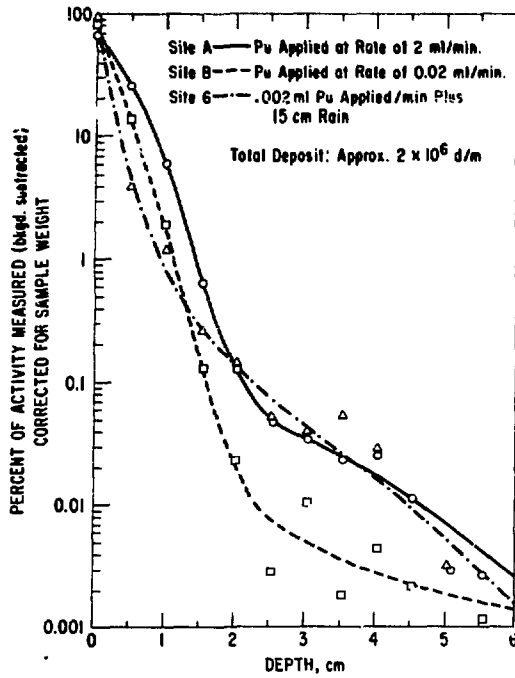
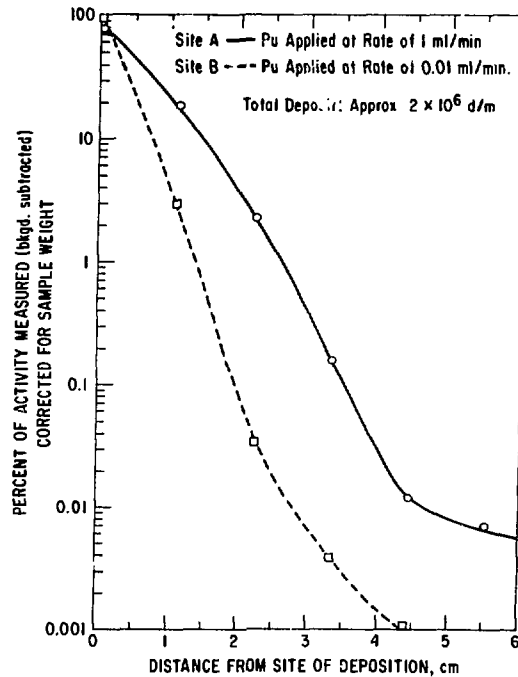


Fig. 8
 Vertical Distribution of Plutonium as a Function of Deposition Rate. ANL Neg. No. 122-76-728.

Fig. 9
 Radial Distribution of Plutonium as a Function of Deposition Rate. ANL Neg. No. 122-76-725.



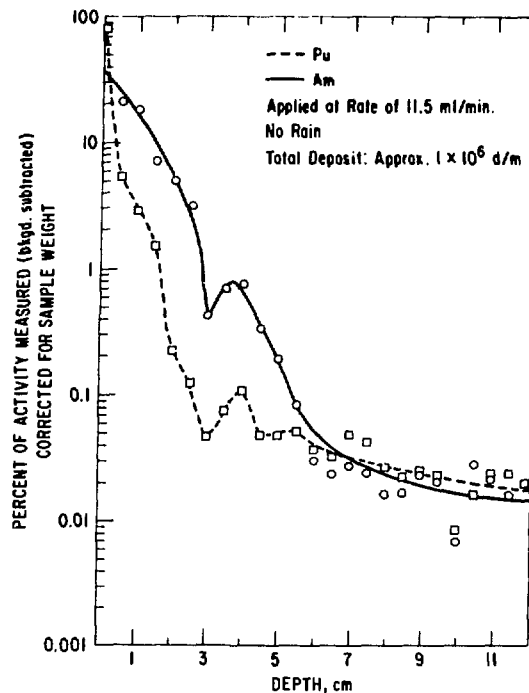


Fig. 10
Comparative Vertical Distribution
of Actinides on Tuff. ANL
Neg. No. 122-76-729.

A small amount of ^{238}Pu tracer was deposited in the center of the disk and allowed to dry. The ratio of the intensities of the various L X rays from the plutonium deposit was measured, after which the entire apparatus was assembled. The cylinder of the apparatus was filled with water and pressure applied (about 1000 psi). About one liter of water was forced through the stone wafer over a period of one week.

At the conclusion of this operation, the disk was removed from the apparatus and allowed to dry. The ratio of intensities of the various L X rays was remeasured and compared with the original determinations. The change in the ratio of the intensities is a measure of the depth of penetration of the plutonium. The results, which are shown in Fig. 11, indicate a migration coefficient $m = 30 \pm 10$ micrometers/meter ($\mu\text{m}/\text{m}$) of waterflow for the limestone and $61 \pm 8 \mu\text{m}/\text{m}$ for the basalt, where m is the average distance traveled by the actinide through the disk for every meter traveled by the water.²

E. Movement of Actinides through Fissures

The movement of plutonium in aqueous solution through fissures in basalt from the EBR-II site was modeled by construction of an artificial fissure designed to give controlled width of the fissure and rate of percolation of water through it.

The fissure was simulated by the apparatus shown in Fig. 12. Tablets of basalt were cut with smooth surfaces. Five of the six surfaces of the tablet

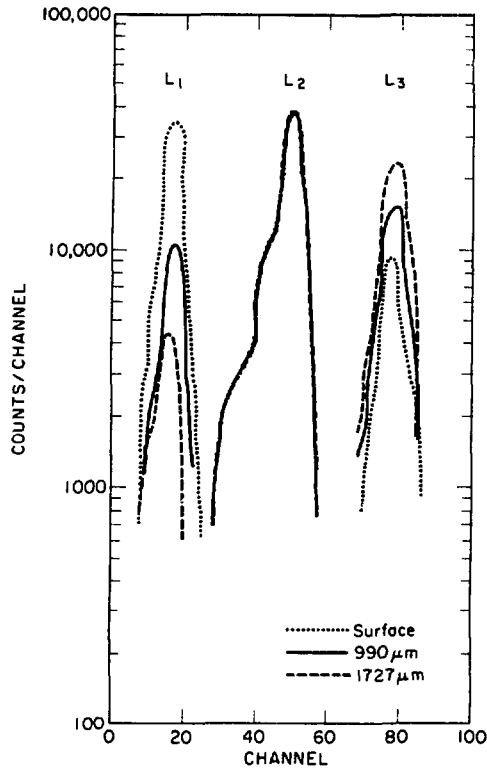
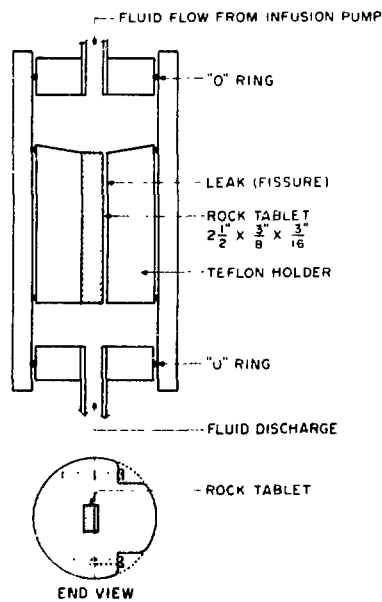


Fig. 11
High-pressure Chromatographic Results
on Limestone. ANL Neg. No. 122-904.

Fig. 12
Fabricated Fissure Apparatus.
ANL Neg. No. 122-1309.



were rendered impervious to water by coating them with wax. The sixth surface was left untreated and was held in the apparatus in such a manner as to be exposed to and wetted by a solution containing plutonium. This "active" surface was held in the apparatus in such a way that it faced an inert surface (Teflon) a short distance away (about 0.01 cm), as shown in Fig. 12. The space between the basalt and Teflon surfaces then constituted the fissure through which the aqueous medium could flow. Since all other surfaces of the basalt were waxed, they did not participate in the experiment. Consequently, all results on the distribution of plutonium on the surface of the basalt were unperturbed by effects that would otherwise have related to more complex geometries.

The plutonium, in this case the alpha-emitting ^{238}Pu , was introduced at the top of the fissure in a very small volume (about 50 μl) by means of an infusion pump. The subsequent elution of the absorbed plutonium from the surface of the basalt also made use of the infusion pump. Water was the elution medium, and, since the pump was constructed to deliver predetermined volumes at a slow, steady rate, it was well suited for this kind of experiment.

After the requisite amount of water had been allowed to flow over the surface of the basalt, the flow was stopped and the basalt tablet was removed from its holder and dried. Scanning the surface of the rock for alpha activity by means of the scanning alpha counter (SADSAC) delineated the distribution of the plutonium on the rock.

Here too, the distribution was found to occur in a double peak. This is clearly shown by the graph in Fig. 13, where there appears to be a more loosely bound, rapidly migrating component as well as a tightly bound component on the surface of the basalt "fissure." Thus the same effect is seen in two dimensions with basalt that was seen in three dimensions with Los Alamos tuff.

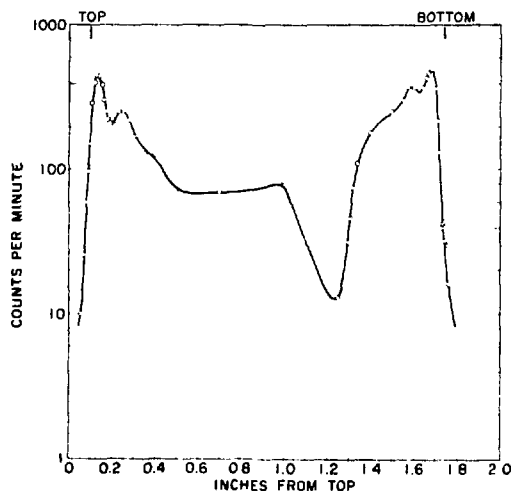
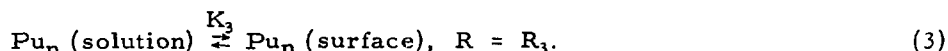
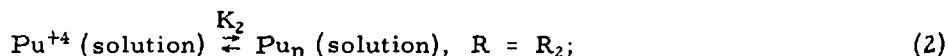
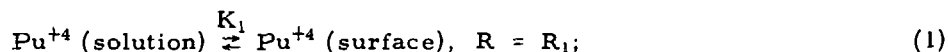


Fig. 13

Distribution of Plutonium on Basalt Fissure. ANL Neg. No. 122-910.

A further objective was to study the kinetics of the process. The absorption of the monomer and polymer, and their exchange, can be expressed by the three following equations:



If the rate R_2 is much slower than R_1 or R_3 and if the equilibrium constant K_1 is much larger than K_2 or K_3 , then, at sufficiently slow flow rates, the plutonium will be absorbed as a single peak of Pu^{+4} (surface) calculable from Eq. 1.

As the rate of flow increases, the two forms of plutonium will not have time to interchange and two peaks will be absorbed due to reactions 1 and 3. At moderate flow rates, the peaks will be overlapping and appear as a broad peak. At faster flow rates, they will be completely separated. Figure 14 shows this effect and is a composite plot of the results of experiments on similar slabs of basalt. The curve marked experiment 6 was taken using a flow velocity of 17.2 cm/hr; experiment 9 used 51.7 cm/hr. As can be seen, at the slower velocity the peak is much sharper.

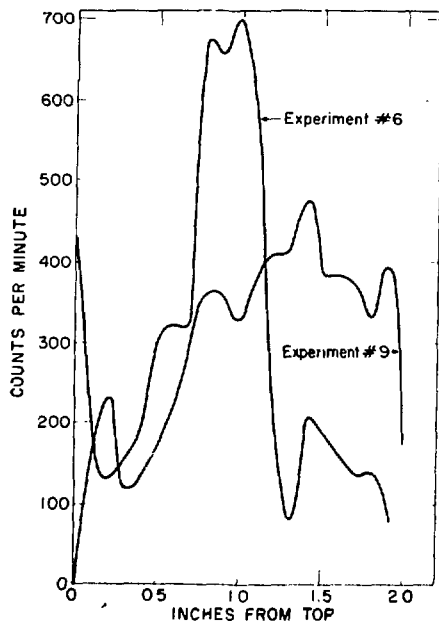


Fig. 14
Effect of Flow Velocity on Plutonium
Distribution on Surface of Basalt. ANL
Neg. No. 122-75-316 Rev. 1.

F. Surface Absorption Coefficients: Variation with Concentration of Dissolved Salts

This aspect of the investigation attempted to determine the effect of dissolved salts, which may be present in natural ground waters, on the surface absorption coefficient k , defined as

$$k = (\text{activity/ml solution})/(\text{activity/cm}^2 \text{ stone}).$$

There were three sets of experiments. The first set consisted of measurements of the surface absorption coefficient of americium and plutonium on basalts and limestones. In these experiments, disks of the stone were immersed in solutions of $4 \times 10^{-5} \text{M}$ $\text{Pu}(\text{NO}_3)_4$ or 10^{-7}M $\text{Am}(\text{NO}_3)_3$. Small aliquots (0.05%) of the solutions were removed, dried on tantalum planchets, and then placed in an internal alpha proportional counter. When the counting rate of samples taken at 12-hr intervals had become constant, this was regarded as evidence of the attainment of equilibrium. The value of k for pure solutions of $\text{Pu}(\text{NO}_3)_4$ at $4 \times 10^{-5} \text{M}$ was found to be 0.10 ± 0.02 for limestone and 0.07 ± 0.02 for basalts. The value of k for 10^{-7}M solutions of $\text{Am}(\text{NO}_3)_3$ was 0.041 ± 0.02 for basalts. To observe the effect on this absorption constant of other ions, the value of k was measured for solutions containing Na^+ , Ca^{++} , Sr^{++} , La^{+3} , and Zr^{+4} ions at various molarities. Figures 15-17 illustrate the variation in k for americium and plutonium as a function of the concentration of these salts.

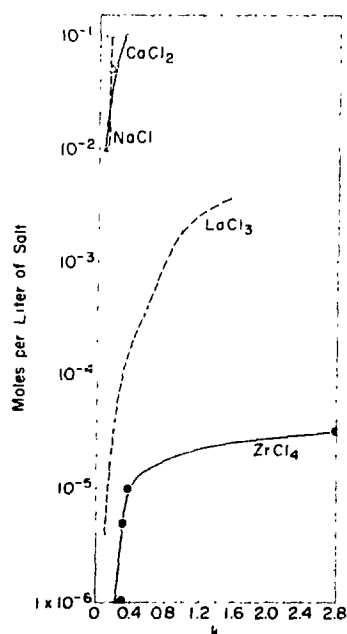


Fig. 15

Variation in k for Plutonium Solutions in Limestone as a Function of Other Ionic Concentrations. ANL Neg. No. 122-905.

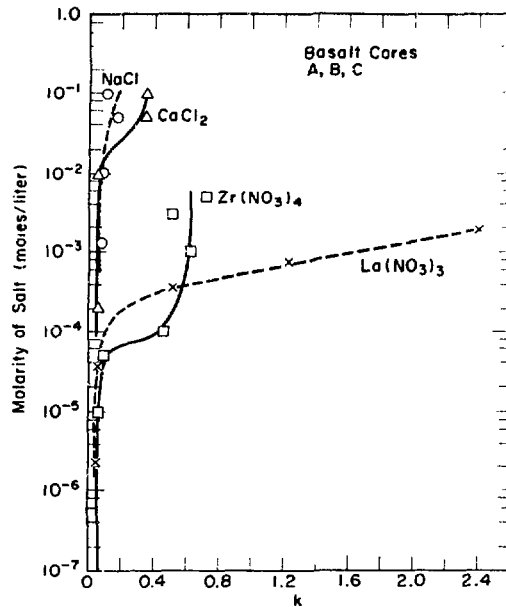


Fig. 16
Variation of k for Plutonium Solutions
in Basalts. ANL Neg. No. 122-1014.

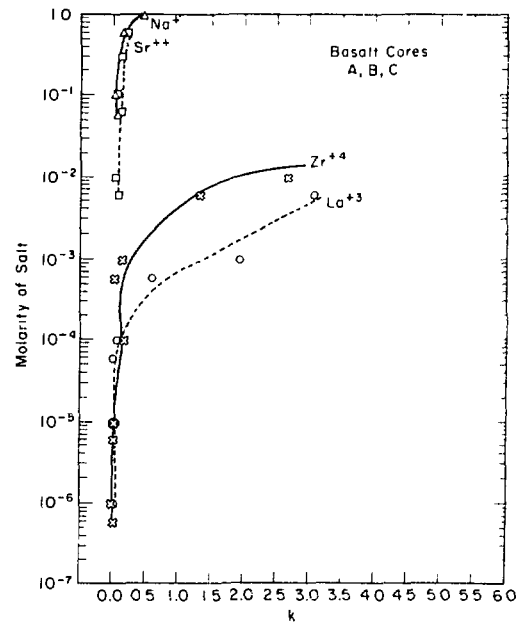


Fig. 17
Variation of k for Americium Solutions
in Basalts. ANL Neg. No. 122-1600.

The concentrations of the ^{238}Pu in the salt solutions shown in Figs. 15 and 16 were determined by alpha counting; the concentrations of americium in the salt solutions shown in Fig. 17 were determined by gamma counting. Since the alpha-counting techniques are much more susceptible to sample thickness,

the abrupt bends in the curves in Fig. 16 at high salt concentrations may in part be caused by this effect. However, they may also be caused by hydrolysis or polymerization of the plutonium solutions.

All curves for americium and plutonium show the same trend: displacement of the actinide ions from the binding sites on the rock matrix by higher concentrations of other metallic ions and increasingly easier displacement by more highly charged ions.

An effort was made to avoid the inaccuracies inherent in attempting to count alpha particles from concentrated salt solutions of plutonium. The use of ^{237}Pu was indicated, and accordingly aqueous solutions of ^{237}Pu in separate tubes were prepared into which tablets of carefully cleaned, accurately measured Chicago dolomite were immersed. After allowing contact for about five days, the tablets were removed from the plutonium solution and counted in the gamma-ray spectrometer and the amount of ^{237}Pu absorbed determined. Experience showed that equilibrium was attained at the end of this period.

At this point, solid NaCl was added to the aqueous plutonium solutions to make each solution 0.1M. Each tablet was reimmersed in its own tube and again allowed to come to equilibrium with the solution as before (five days). At the end of this time, the amount of activity remaining in the solution was separately determined. This was accomplished by withdrawing the tablets of rock by means of a fine platinum wire affixed to them and counting the solution alone. The increase of the activity in the solution was a measure of the amount of plutonium desorbed. When the activity in the solution reached a constant value, equilibrium was assumed.

The tablets were each immersed in successively more concentrated NaCl solutions, made by adding solid NaCl in the proper amounts, and the sequence of measurements repeated until equilibrium was again achieved for each molarity of NaCl and for each tablet and tube. By this means, a set of values was obtained that permitted the calculation of surface absorption coefficients as a function of the molarity of the salt solution in contact with the dolomite. The data for a typical set of experiments in 0.5M NaCl are given in Table I, and the curve in Fig. 18 represents the plot of the average values of the surface absorption coefficients k for each concentration of NaCl. The details of these experiments are given by Volesky.⁴

G. Attempts to Determine Relative Migration Rates

A cylinder of Los Alamos tuff was fabricated whose dimensions were 2.0 cm in diameter and 7.8 cm long (volume = 24.5 cm^3 ; free-column volume = 2.5 cm^3). The outer cylindrical surface was waxed to render it impervious, and the cylinder was then waxed into the end of a glass tube as shown in Fig. 19. With the metering pump, a 0.30-ml solution containing 5×10^5 counts/min (c/m) of ^{241}Am and 1.5×10^5 c/m of ^{237}Pu was applied to the top of the column of rock over a 12-hr period and allowed to dry.

TABLE I. Absorption of ^{237}Pu on Niagara Limestone (Chicago Dolomite);
Data for Samples in a 0.5M Solution of NaCl at Equilibrium^a

Sample	Solution and Tube	Activity (counts per minute)				Percent Absorbed ^d
		NET/ml ^b	Absorbed on Rock	NET/cm ²	k ^c	
18	7070	3393	7464	2466	1.37	42.09
19	8636	4144	6754	3213	1.28	43.67
20	8834	4239	6817	3200	1.32	43.02
21	8769	4208	5896	3148	1.33	42.79
22	7832	3758	7004	3201	1.17	46.00
23	7296	3501	7348	3244	1.07	48.09
24	6587	3161	8321	2885	1.09	41.72
25	9220	4424	7075	3270	1.34	42.50
27	8571	4113	7515	3917	1.04	48.78
28	8076	3875	7398	3195	1.20	45.19
29	8821	4233	7704	3327	1.26	44.01
Average					1.24	44.35

^aIt was determined that a test tube containing 0.5M NaCl would adsorb $4.04 \pm 0.68\%$ of the ^{237}Pu from the 2 ml of solution.

^bThe value given in the NET/ml column is less 4.04% due to this adsorption on the glass.

^cThe values for k fall within the range of the standard deviation.

^dThe value given in the Percent Absorbed column is the average for that sample of the plutonium absorbed from 1 ml of solution to 1 cm² of rock.

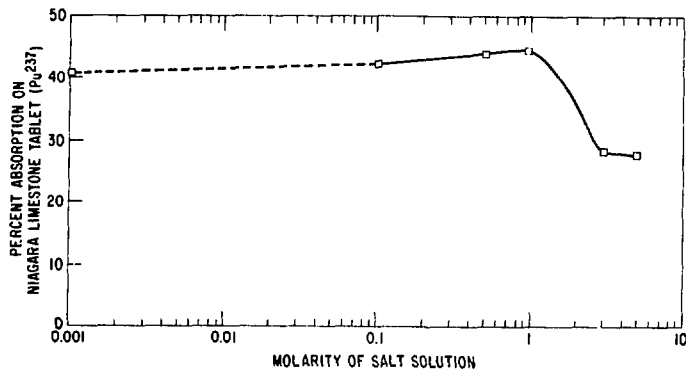


Fig. 18. Absorption of Plutonium on Limestone as a Function
of NaCl Concentration. ANL Neg. No. 122-76-726.

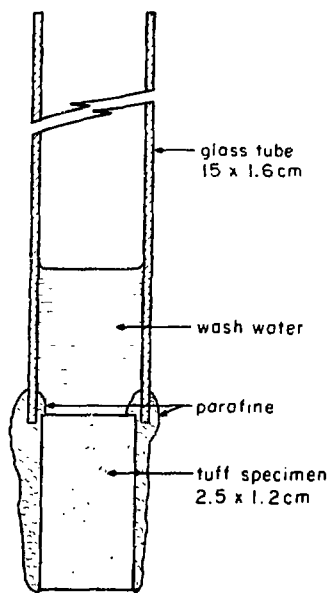


Fig. 19
Schematic Diagram of Elution Column Made
with Tuff Plug. ANL Neg. No. 122-75-103.

At the end of this period, an attempt was made to elute the deposit of americium and plutonium through the 7.8-cm length of rock by passing water through the system. This elution was carried out over an eight-week period using 2500 ml of water during the process (1000 free-column volumes). This corresponds to a rate of about 52 m a year for the rate of advance of the water through the stone.

At the end of this period, a total of 1.5×10^3 c/m of ^{237}Pu and 110 c/m of ^{241}Am had been collected, indicating that the bulk of the activity was still bound to the tuff.

The column was disassembled and an effort made to locate the activity in the body of the cylinder of tuff. By successive sectioning of the material, and measuring the activity in each section (normalized for the weight of tuff), the distribution of the activity could be determined. The results are shown in Fig. 20.

It can be seen that the activity had not advanced through the rock more than 1 or 2 cm. When this is compared with the movement of water, it is seen that the water advances about 25,000 times more rapidly through the pores in the tuff, assuming a 10% pore volume.

At this rate, if the apparent advance of the radionuclides represents an equilibrium condition, it would require about 2×10^4 ml of water to remove it from the cylinder of tuff. We therefore decided to reduce the column of tuff for this experiment to more manageable dimensions.

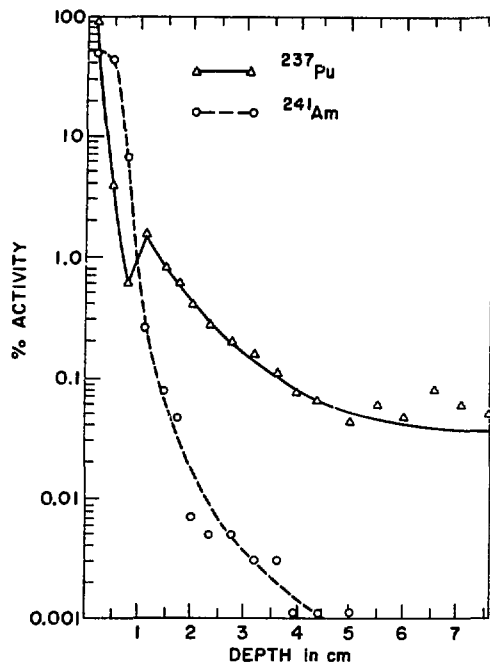


Fig. 20

Comparison of Relative Migration Rates
in Tuff. ANL Neg. No. 122-76-722.

A small column packed with crushed washed tuff was constructed. The column volume was of the order of 0.07 ml, and assuming about 10% void, the free-column volume was 0.007 ml.

Plutonium-237 was deposited on the top of the column. The first 100 ml, or 1.4×10^4 free-column volumes, contained about 0.5% of the plutonium. About 0.75% of the total was contained in 1400 ml or 2×10^5 column volumes (see Fig. 21). This implies that the boundary of the water progressed

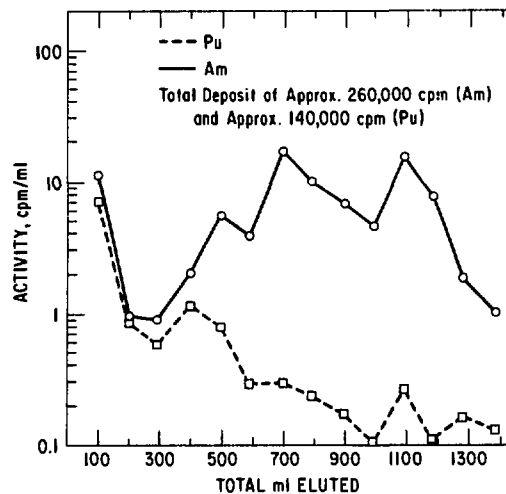


Fig. 21

Elution of Plutonium and Americium in Column
of Tuff. ANL Neg. No. 122-76-722.

2×10^5 times more rapidly than the bulk of the plutonium. A typical aquifer will have a rate of water flow between 0.16 and 1.6 km per year. The rate of plutonium advance from a site in such a stratum having the same binding properties as tuff would be from 1.6×10^{-6} to 1.6×10^{-5} km/year. Obviously, a tracer experiment such as this is only an approximation to real field conditions, but it may be argued that the tracer experiment is essentially conservative and that a real stratum would be a much more effective filter for colloidal particles than the short column used here.

H. Electrochromatographic Behavior of Tracer Pu-Am in Water

It has generally been assumed that both plutonium and americium in neutral aqueous solutions existed as positive ions with the plutonium in the plus (IV) state and the americium in the plus (III) state. It was understood that the ions were not necessarily quadruply or triply charged and that hydrolysis, or polymerization could effectively lower the net positive charge. However, experiments by Cohen⁵ cast some doubt on these assumptions, and an experiment was therefore carried out to determine the sign of the charge on these ions in water equilibrated with tuff.

A mixture of ^{237}Pu - ^{241}Am in water was spotted on prewetted filter paper (7.5×25 cm), and a 400-V dc potential was applied for 110 min. Under these conditions, a current of about 7 mA flowed. The data shown in Fig. 22 and

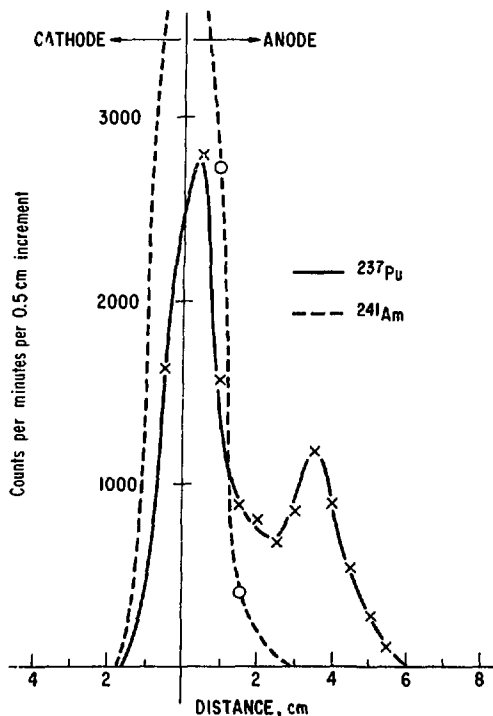


Fig. 22
Electromigration Behavior
of Activity. ANL Neg.
No. 122-76-719.

listed in Table II indicate the activity of americium and plutonium migrating to the negative and positive poles. As can be seen, these results show that the americium is essentially neutral or slightly anionic (negatively charged) while the plutonium is much more anionic. A small anionic plutonium peak was observed at about 3.5 cm. This again indicates the existence of a second species of plutonium.

TABLE II. Electromigration of Plutonium and Americium Ions

Cathode Zone		Anode Zone		Distance from Center, cm
²⁴¹ Am, c, m	²³⁷ Pu, c, m	²⁴¹ Am, c, m	²³⁷ Pu, c, m	
11909	1638	41563	2805	1
56	41	2729	1576	2
20	16	409	986	3
1	24	132	805	4
7		21	684	5
		29	857	6
		19	1160	7
		-	884	8
		-	543	9
		-	266	10
		-	119	11
		-	-	12
		-	-	13

V. CONCLUSIONS

The objective of these experiments is the determination of the important parameters concerned in the prediction of the migration of actinide wastes from geological storage sites. Several conclusions concerning this objective may be inferred from these data.

1. The bulk of the plutonium and americium is very tenaciously held by the stony materials studied (tuff, basalt, limestone). This is evidenced by:

a. The slow rate of migration (10^{-5} m/m of water flow) in the modeling experiments.

b. The fissure experiments and surface absorption measurements, which yield similar results when corrected for pore size.

c. The penetration of plutonium into limestone, as measured by X-ray absorption, yielding a relative migration rate of, at most, $30 \mu\text{m}/\text{m}$ of water flow. This is in substantial agreement with the other types of experiments using the average value of the relative migration coefficient for plutonium ($10^{-5} \text{ m}/\text{m}$ of water flow) and a water-flow velocity of $0.16 \text{ km}/\text{year}$. Figure 23 is a plot of the activity distribution of ^{239}Pu migrating from a hypothetical depository.

As can be seen in Fig. 24, the bulk of the ^{239}Pu would decay long before it could migrate 1 km. Thus, in the event of a catastrophic intrusion of plutonium into an aquifer (in one of these media), the bulk of the plutonium would not survive the migration to the external environment.

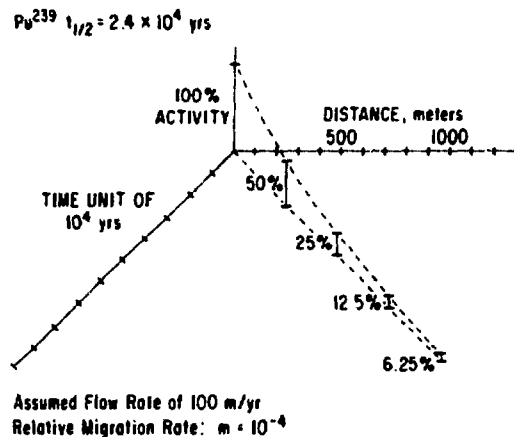


Fig. 23. Migration of Plutonium for Hypothetical Depository. ANL Neg. No. 122-76-721.

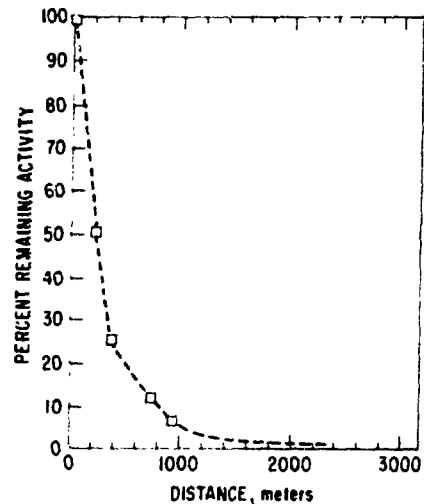


Fig. 24. Migration of Plutonium through an Aquifer. ANL Neg. No. 122-76-723.

2. Some amount, less than 35% of the plutonium in these experiments, appears to migrate about ten times as fast as the bulk of the plutonium. The amount of the more rapidly migrating species appears to vary widely and is undoubtedly affected by the chemical milieu and kinetics. The rapidly migrating species may be a polymeric form of plutonium, either by itself or absorbed on fine mineral particles. Evidence for these conclusions is shown by:

- a. The presence of two peaks in the distribution of plutonium found during the fissure and modeling experiments.
- b. The changing width of the plutonium distribution in the fissure experiments.

3. Some small fraction of the plutonium and americium migrates more rapidly (either vertically or radially) than the bulk of these species and

appears to give an "exponential leading edge" in a plot of concentration of these species against distance migrated. However, once fixed, even this fraction becomes much less mobile. This is evidenced by the observations that:

a. Although rapid migration occurs upon addition of the original solution in the experiments, the activity distributions do not appear to change (or move) radically after amounts of rainfall much larger than the original solution volumes (see Fig. 6) are added.

b. Varying the addition rate of plutonium by an order of magnitude also changed the amount of rapidly moving plutonium by an order of magnitude (from 0.1 to 1%) but did not change the maximum depth of penetration appreciably.

This rapid migration may be due to plutonium solute being carried through the pores by a high-velocity, unsaturated flow of solution, which may not have had sufficient time to absorb on the pore surfaces. In addition, the thin solvent film present under unsaturated flow conditions may contain very large concentrations of dissolved salts; thus the plutonium absorption may be considerably diminished. Therefore it would appear to be most important to minimize this type of unsaturated migration of the wastes in a storage site in the event of a calamitous incursion of water. This could be accomplished by placing the storage site in high-exchange-capacity, nonporous strata and by surrounding the wastes with a stable, ion-exchanging absorptive material. Both of these measures would have the effect of slowing the original outflow of dissolved wastes and thus reducing the unsaturated migration.

4. The chemical milieu can drastically increase the migration rate of plutonium and americium. This can be inferred from the facts that:

a. The surface absorption coefficients are affected by the types and concentrations of other salts. Even solutions as dilute as $10^{-4}M$ of highly charged ions can effect a substantial desorption of plutonium and americium.

b. Concentrated solutions of lesser charged species, such as NaCl, cause much smaller but still appreciable desorption.

It is therefore important to consider not only the geological quiescence of a storage site but also the chemical and migrational behavior in case of an accidental influx of water.

These conclusions indicate that if appropriate attention is given to the geological and chemical media, it is possible to construct an actinide waste depository, that will maintain isolation from the environment, even in the event of a major intrusion of water.

REFERENCES

1. D. R. Rogers, *Behavior of Plutonium-238 Solutions in the Soil and Hydrology at Mound Laboratory*, Monsanto Research Corp., Mound Laboratory, Miamisburg, Ohio, presented at the Actinide-Sediment Reactions Working Meeting, Feb. 10-11, 1976, Seattle, Wash.
2. S. M. Fried, A. M. Friedman, and L. A. Quarterman, *Annual Report on Project ANO115A: Fiscal Year 1974*, ANL-8115 (July 1974).
3. S. M. Fried, A. M. Friedman, J. J. Hines, and L. A. Quarterman, *Annual Report on DWMT Project ANO115A: Fiscal Year 1975*, ANL-75-64 (Sept 1975).
4. A. F. Volesky, Argonne National Laboratory, private communication (1976).
5. D. Cohen, Argonne National Laboratory, private communication (1975).