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The Migration of Plutonium and Americium in the Lithosphere

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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 paper will 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 which 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. 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 non-porous 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 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 that are discussed in this paper are Niagara limestone (chosen for its density and fine porosity), basalt from the National Reactor Test site, 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 employed 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 Pu 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.

It was also undertaken to identify the ionic species of Pu present. Because of the extreme dilution of the ions (tracer) it was not possible to use conventional methods of identification (absorption spectra etc.). On the other hand it was necessary to use this extremely diluted solution 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 employed.

It cannot be completely ruled 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 adsorption 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 National Reactor Test Site 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 which 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.

Experimental

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 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 employed to detect the attenuation of ^{238}Pu L x-rays as the Pu migrated into the body of a piece of rock. By measuring the changes in the L_{α}/L_{β} or L_{γ}/L_{β} ratios the penetration of Pu into the solid could be calculated after calibration with stone absorbers.

Tracer Solutions. 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 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

The ^{237}Pu and the ^{237}Np nitrate matrix was dissolved with 9 M 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 Pu 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 Np.

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

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. By setting each analyzer for the appropriate energy the two isotopes were 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 of .005" wide. The sample was placed on a movable table and advanced under the slit in a regular manner 0.010" 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.

The high pressure chromatographic apparatus used for forcing water through the relatively impervious Chicago dolomite is shown in Fig. 2 and its operation has been described elsewhere (2).

Migration of Plutonium in Los Alamos Tuff. These experiments were laboratory simulations of the movement of Pu and Am in Los Alamos tuff.

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

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 allowing the Pu tracer solution 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 inches" 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 Pu. Each core increment was 0.5 cm. The results are shown in Fig. 5. There are two zones of Pu activity distributed in the rock as a function of depth. The major quantity of Pu 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 one percent of the Pu and has migrated downward to a depth of about 10 cm.

These observations suggest that the Pu exists in two forms in aqueous solution. These "species" may be different oxidation states or differing degrees of polymerization of the Pu(IV) ion. It may also be possible that one of the zones may contain Pu 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 Pu in rocks. In addition there were also important effects due to flow velocity and in some cases as much as 35 percent of the Pu was observed in the fast moving zone.

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 gamma ray spectrometer. The 60 keV gamma ray of ^{241}Am and the 100 keV x-ray of ^{237}Pu are

readily resolved. This is important not only as a labor saving measure but it enables the direct comparison of the behavior of Am and Pu 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 per hour to each of the sites. The size of the aliquot varied from site to site; those sites to be cored last having the largest aliquot delivered to it. This was to compensate 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 naturally experienced more cycles of "rain" and "drought" and 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 Pu after successive rains and droughts. The curves in Fig. 7 show the comparative migration of Pu and Am in tuff.

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 ml, 30 ml, and 150 ml. In the first set the combined solution was deposited at each sample site in 15 minutes. The other set received its solution over a period of 15 hours per site.

Figures 8, 9 and 10 show the results obtained for the radial and vertical distribution of Pu as well as a comparison of Am and Pu.

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.

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 Pu deposit was measured, after which the entire apparatus was assembled. The cylinder of the apparatus was filled with water and pressure applied (approximately 1000 p.s.i.). 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 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 Pu. The results which are shown in Fig. 11 indicate a migration coefficient $m = 30 \pm 10$ micrometers/meter (μ/m) of waterflow for the limestone and $61 \pm 8 \mu/\text{m}$ for the basalt, where m is the average distance traveled by the actinide through the disk for every meter traveled by the water (2).

Movement of Actinides through Fissures. The movement of Pu 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 simulation of the fissure was accomplished by the apparatus shown in Fig. 12. Tablets of basalt were cut with smooth surfaces. Five of the six surfaces of the tablet 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 have otherwise related to more complex geometries.

The plutonium, in this case the α -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 adsorbed 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.

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 Pu will be absorbed as a single peak of Pu^{+4} (surface) calculable from equation 1.

As the rate of flow increases the two forms of Pu 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. Fig. 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.

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 hour intervals had become constant, this was regarded as evidence of the attainment of equilibrium. It was

found that the value of k for pure solutions of $\text{Pu}(\text{NO}_3)_4$ at $4 \times 10^{-5} \text{ M}$ was 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. In order 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, 16, and 17 illustrate the variation in k for americium and plutonium as a function of the concentration of these salts.

The concentrations of the ^{239}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 be in part caused by this effect. However, they may also be caused by hydrolysis or polymerization of the plutonium solutions.

It is clear that 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 Pu. 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 approximately 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 0.1 M. 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 which 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 0.5 M NaCl are given in Table 1 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).

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 , 2.5 cm^3 free column volume). The outer cylindrical surface was waxed to render it impervious and the cylinder then waxed into the end of a glass tube as shown in Fig. 19. Using the metering pump, a 0.30 ml solution containing $5 \times 10^5 \text{ c/m } ^{241}\text{Am}$ and $1.5 \times 10^5 \text{ c/m } ^{237}\text{Pu}$ was applied to the top of the column of rock over a twelve-hour period and allowed to dry.

At the conclusion of this period an attempt was made to elute the deposit of Am and Pu 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 meters a year for the rate of advance of the water through the stone.

At the end of this period a total of $1.5 \times 10^3 \text{ c/m } ^{237}\text{Pu}$ and $110 \text{ c/m } ^{241}\text{Am}$ 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) it was possible to determine the distribution of the activity. 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 $2 \times 10^4 \text{ ml}$ of water to remove it from the cylinder of tuff. It was therefore decided to reduce the column of tuff for this experiment to more manageable dimensions.

A small column packed with crushed washed tuff was constructed. The column volume was of the order of .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 Pu. About 0.75% of the total was contained in 1400 ml or 2×10^5 column volumes (Fig. 21). This implies that the boundary of the water progressed 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 to 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^{-5} to 1.6×10^{-5} km/year. It is obvious that 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 utilized here.

Electrochromatographic Behavior of Tracer Pu-Am in H_2O . It has generally been assumed that both Pu and Am in neutral aqueous solutions existed as positive ions with the Pu in the plus (IV) state and the Am in the plus (III) state. It was understood that the ions were not necessarily quadruply or triply charged and that hydroxylation or polymerization could effectively lower the net positive charge. However, experiments by Cohen (5) 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 H_2O was spotted on pre-wetted filter paper (7.5×25 cm) and a 400 volt dc potential applied for 110 minutes. Under these conditions a current of approximately 7 ma flowed. The data shown in Fig. 22 and listed in Table 2 indicate the activity of Am and Pu migrating to the negative and positive poles. As can be seen these results show that the Am is essentially neutral or slightly anionic (negatively charged) while the Pu is much more anionic. A small anionic Pu peak was observed at about 3.5 cm. This again indicates the existence of a second species of plutonium.

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 Pu and Am is very tenaciously held by the stony materials studied (tuff, basalt, limestone). This is evidenced by:
 - a. The slow rate of migration (10^{-5}) meters/meter 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 Pu 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 Pu (10^{-5} m/m of water flow) and

a water flow velocity of 0.16 km/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 Pu into an aquifer (in one of these media), the bulk of the Pu would not survive the migration to the external environment.

2. Some amount, less than 35% of the Pu in these experiments, appears to migrate at a rate of about ten times faster than the bulk of the Pu. 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 Pu, 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 Pu found during the fissure and modeling experiments.
 - b. The changing width of the Pu distribution in the fissure experiments.
3. Some small fraction of the Pu and Am 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. While rapid migration occurs upon addition of the original solution in the experiments, the activity distributions do not appear to change (or move) radically after adding amounts of rainfall much larger than the original solution volumes (see Fig. 6).
 - b. Varying the addition rate of Pu by an order of magnitude also changed the amount of rapidly moving Pu by an order of magnitude (from .1% to 1%) but did not change the maximum depth of penetration appreciably.

This rapid migration may be due to Pu 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, and thus the Pu 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, non-porous 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 reduce the unsaturated migration.

4. The chemical milieu can drastically increase the migration rate of Pu and Am. 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 Pu and Am. Concentrated solutions of lesser charged species, such as NaCl, cause much smaller but still appreciable desorption.

Therefore it is 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 which will maintain isolation from the environment even in the event of a major intrusion of water.

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- Figure 17. Variation of k for Americium Solutions in Basalts ANL Neg. #122-1600.

Figure 18. Absorption of Plutonium on Limestone as a Function of NaCl Concentration.

Figure 19. Schematic Diagram of Elution Column Made with Tuff Plug, ANL Neg. #122-75-103.

Figure 20. Comparison of Relative Migration Rates in Tuff.

Figure 21. Elution of Pu and Am in Column of Tuff.

Figure 22. Electromigration Behavior of Activity.

Figure 23. Migration of Plutonium for Hypothetical Depository.

Figure 24. Migration of Plutonium through an Aquifer.

TABLE I

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

ACTIVITY (counts per minute)						
Sample	Solution and Tube	NET/ml	Absorbed on Rock	NET/cm ²	k	Percent Absorbed
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

It was determined that a test tube containing 0.5 M NaCl would adsorb $4.04 \pm 0.68\%$ of the ^{237}Pu from the two ml of solution. The value given in the NET/ml column is less 4.04% due to this adsorption on the glass. The values for k fall within the range of the standard deviation.

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

TABLE II

Electromigration of Pu and Am ions.

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

BLOCK DIAGRAM FOR SODIUM IODIDE GAMMA
RAY SCINTILLATION SPECTROMETER

APPARATUS FOR FORCING WATER
THROUGH SAMPLES OF SOLID ROCK

VERTICAL DISTRIBUTION OF Pu AS A FUNCTION OF RATE OF DEPOSITION ON ROCK

RADIAL DISTRIBUTION OF Pu AS A FUNCTION OF
RATE OF DEPOSITION ON ROCK

COMPARATIVE VERTICAL DISTRIBUTION OF ACTINIDES ON TUFF

RELATIVE RATE OF MIGRATION OF Pu AND Am THROUGH LOS ALAMOS TUFF

Counts per minutes per 0.5 cm increment

MIGRATION OF Pu THROUGH AQUIFER

Pu^{239} $t_{1/2} = 2.4 \times 10^4$ yrs

Assumed Flow Rate of 100 m/yr
Relative Migration Rate: $m = 10^{-4}$

MIGRATION OF Pu THROUGH AQUIFER