New Rules for AAAS–Newcomb Cleveland Prize

The AAAS–Newcomb Cleveland Prize, which previously honored research papers presented at AAAS annual meetings, will henceforth be awarded annually to the author of an outstanding paper published from September through August in the Reports section of *Science*. The first competition year under the new rules starts with the 3 September 1976 issue of *Science* and ends with that of 26 August 1977. The value of the prize has been raised from \$2000 to \$5000; the winner also receives a bronze medal.

To be eligible, a paper must be a first-time presentation (other than to a departmental seminar or colloquium) of previously unpublished results of the author's own research. Reference to pertinent earlier work by the author may be included to give perspective.

Throughout the year, readers are invited to nominate papers appearing in the Reports section. Nominations must be typed, and the following information provided: the title of the paper, issue in which it is published, author's name, and a brief statement of justification for nomination. Nominations should be submitted to the AAAS–Newcomb Cleveland Prize, AAAS, 1515 Massachusetts Avenue, NW, Washington, D.C. 20005. Final selection will rest with a panel of scientists appointed by the Board of Directors.

The award will be presented at a session of the annual meeting at which the winner will be invited to present a scientific paper reviewing the field related to the prize-winning research. The review paper will subsequently be published in *Science*. In cases of multiple authorship, the prize will be divided equally between or among the authors; the senior author will be invited to speak at the annual meeting.

Reports

Retention of Plutonium and Americium by Rock

Abstract. *The relative migration ratio of plutonium in various rocks is approximately 100 micrometers per meter of water flow; the corresponding migration ratio for americium is about 500 micrometers per meter of water flow. Under these conditions radioactive decay will have taken place to such an extent that little plutonium and americium can reach the external environment from a well-designed and isolated geological repository site.*

The problem of the final disposal of radioactive wastes is a cause for concern when the difficulties of predicting long-term ($\sim 5 \times 10^5$ years) containment of such wastes in deep depositories subjected to geological disturbances are considered. We have now acquired experimental data from which the migratory behavior of actinides away from properly chosen disposal sites can be inferred. These data permit extrapolations which allow for the catastrophic intrusion of water and for seismic activity resulting in fissures.

By carrying out experiments to determine the retention of radionuclides in geological strata, we have developed techniques which also may be used as a basis for evaluating proposed repository sites. As a result of these investigations, quantitative estimates of actinide transport behavior at a site can be made. Our work indicates that the issue of the long-term retention of the actinides at a prudently chosen disposal site may not be as serious as had been thought, and the danger of escape of these elements into the environment can be minimized if one takes advantage of the geochemical interactions.

Experiments and conclusions were based on certain considerations that we believe are likely to be included wholly or in part in a prudent system of permanent storage. They are as follows [see (*1*), vol. 5, appendix C; vol. 4]: (i) deep burial (500 to 1000 m); (ii) use of stable, quiescent geological strata; (iii) solidification of wastes in the form of glass, ceramic, or some other difficultly soluble matrix; (iv) packaging of individual batches of solidified wastes in suitable containers prior to emplacement in the repository; and (v) consideration only of those storage sites for which sufficient hydrological and geological data are known or are ascertainable. Flowing groundwater is assumed to be the mobilizing agent. Thus, this report is concerned particularly with the transport or migration of the actinides by water.

We chose the long-lived actinides for study because they are the most likely to occur in significant quantities (as ^{239}Pu and ^{241}Am) in the process wastes that will have to be stored. The half-lives of these nuclides (^{239}Pu = 2.4×10^4 years, ^{241}Am = 458 years) are such that each is biologically hazardous in a radiological sense (*2*) as well as persistent.

We chose particular rocks for study that may already have been used as the matrices for small-scale disposal. Thus, Los Alamos tuff and unweathered basalt from the Experimental Breeder Reactor II site near Idaho Falls, Idaho, were examined. Niagara limestone from northeastern Illinois was used because it is a very widely distributed, fine-grained rock but is also capable of conducting water.

In our work we are concerned mainly with two aspects of the translocation of Pu and Am: migration through fissures and percolation through the pores of the rocks. In all experiments, ^{241}Am was used as the Am tracer and either ^{237}Pu or ^{238}Pu was employed as the tracer for Pu (*3*).

Four different sets of experiments were carried out. The first set consisted of an effort to delineate the migration of actinides through a fissure, the second set to determine the migration through a relatively impervious stone (Niagara limestone), the third to use a small sample of rock as an ion-exchange column to examine the elution characteristics, and the fourth to use large blocks of stone to measure the actual migration in terms of a scale model of rain and drying cycles.

Each set of experiments will be described in terms of a typical example. In dealing with heterogeneous, roughly defined materials such as natural rocks, only general pictures can be presented; evaluations of specific sites can be made only if experiments are carried out on representative samples of the strata.

We used neutral or almost neutral aqueous solutions (pH $\sim$ 6.7) because we believe that solutes would be diluted and dispersed by groundwater regardless of the original concentrations of ions or the initial form of deposition. Ultimately, the actinides will be transported only by water whose composition is in equilibrium with the particular stratum through which it has passed.

In the first set of experiments we studied the migration of Pu through a fissure since this mode of transport will certainly be a path for solutions containing Pu. We constructed an artificial fissure in the following manner. In a typical arrangement a tablet of basalt (approximately 7 by 1 by 0.5 cm) was sealed with wax on five of its six sides. The tablet was placed in a recessed holder in such a way that the unwaxed side faced a Teflon surface of equal dimensions about 0.01 cm away. This void (1 by 7 by 0.01 cm) constituted the "fissure." The unwaxed surface is the only one available for interaction with the ions in a solution flowing past, and thus this surface mimics in a controlled fashion the behavior of a crack or fissure.

Approximately 50 μl of an aqueous solution of ^{238}Pu was slowly delivered to one end of the fissure by means of a metering pump. When the delivery was complete, water was allowed to pass through the fissure slowly at a rate of 100 cm/hour. Once the experiment had been started, the surfaces of the fissure were not allowed to dry until the experiment had been completed. After a predetermined amount of water had passed through the fissure, the flow was halted and the basalt tablet was removed from the holder and allowed to dry. We determined the distribution of Pu on the surface by means of a scanning α counter. By varying the flow rate and the volume of water passing through the "crack," we could determine the amount of Pu adsorbed by the basalt surface as a function of the distance from the point of introduction. Figure 1 shows a typical distribution of Pu on the surface of the basalt tablet. These results indicate that the relative migration ratio, m, for Pu in this experiment is ~ 150 μm per meter of water flow. There are two migrating zones of Pu, as shown by the two peaks of activity in Fig. 1. This effect was also observed in other experiments with Pu and is discussed below.

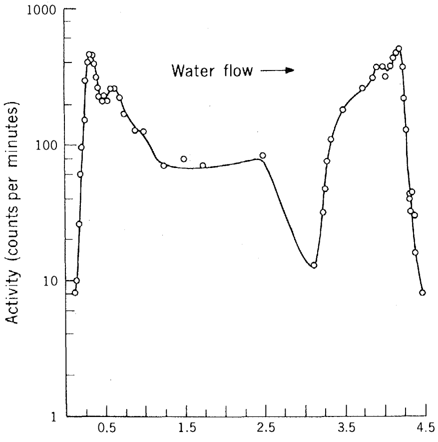

Fig. 1. Distribution of Pu α activity on the surface of a basalt tablet in an artificial fissure.

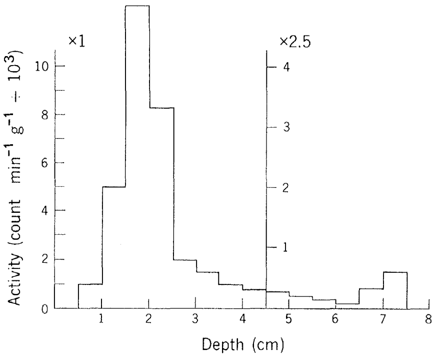

Fig. 2. Distribution of Pu activity in a central core as a function of depth.

In one experiment in which the Pu dried on the surface of the rock, the Pu apparently became fixed. When substantial quantities of water were allowed to flow through the reassembled apparatus, no further elution of Pu was observed.

In order to investigate the migration of Pu in fine-grained Niagara limestone, we found it necessary to use a pressurized system. A small amount of ^{238}Pu was placed on the surface of a wafer (approximately 2 cm in diameter and 0.2 cm thick), which was then placed in the pressure apparatus. Water was forced through the wafer at a pressure of about 70 atm. We determined the degree of penetration of Pu into the rock by observing the change in ratio of the intensities of the several Pu L x-rays. Since these x-rays have differing energies, they are attenuated in differing degrees by the absorption of the rock as the Pu migrates inward. We standardized and calibrated the system by fabricating very thin measured absorbers of Niagara limestone and using these to calibrate the attenuation of each x-ray. The results of these experiments yielded a relative migration ratio of m = 30 μm per meter of water flow through the pores.

In another set of experiments we constructed a quasi ion-exchange column using a small cylinder of Los Alamos tuff, a compacted volcanic ash. Wax was used to attach the cylinder, 2 cm in diameter and 7.8 cm long, to a glass tube, which constituted a reservoir. The outer cylindrical surface of the tuff was also waxed to prevent any lateral movement of water which flowed through the rock axially under its own head of pressure (generally less than 1 cm).

A mixture of ^{237}Pu and ^{241}Am was delivered to the top of the column in about 50 μl of water and allowed to dry. Water was then allowed to percolate through the column; the eluate was collected in batches and evaporated, and its activity was counted in a NaI γ-ray spectrometer. With this arrangement it was possible to determine each of the nuclides separately.

After 2500 ml (1000 free column volumes, in this case, the pore volume of the rock) of water had passed through, approximately 1 percent of the Pu and less than 0.1 percent of the Am had been eluted. We then abandoned any further attempt to elute the radionuclides and proceeded to section the cylinder of tuff. The individual sections were weighed and the radioactivity was counted to determine the distribution of the two actinides. These data yielded an upper limit for the relative migration ratio of m = 100 μm per meter of water flow for Am and 10 μm per meter of water flow for Pu.

In our final set of experiments, a block of Los Alamos tuff (25 by 25 by 20 cm) was used to model a former small-scale disposal site at the Los Alamos Scientific Laboratory. Most of the migration of the actinides at this site is related to the cycles of rain and drought, and an effort was made to simulate this condition in the laboratory.

An aqueous solution of ^{237}Pu (~ 300 μl) was deposited in an area (0.5 by 0.5 cm) on the surface of the block of tuff and allowed to dry. Alternate wetting and drying of the rock corresponded to cycles of "rainfall" and "drought"; such cycles were initiated until a total of 7 liters of water had been showered on the rock in 500-ml increments. The rock was then cored in several positions with respect to the site of the original deposition, and the sample was sucked out of the hole by means of a tube attached to a

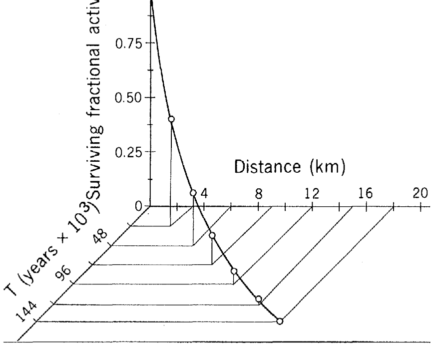

Fig. 3. Predicted migration and decay of ^{239}Pu through an aquifer. The migration ratio was taken as 125 μm per meter of water flow, and flow rates were assumed to be 0.6 km per year.

vacuum pump. Each successive sample was taken out from a depth 0.5 cm greater than the preceding one, and the radioactivity was counted in the NaI well detector. The data, normalized in terms of the weight of rock in each core sample, are shown in Fig. 2.

The curve (Fig. 2) indicates that Pu does move into the rock stratum. Since the rock has a porosity of about 10 percent, this motion corresponds to a limit of 600 μm per meter of water flow. We believe that in this case much of the migration is caused by the erosion of fine particles from the surface of our rock by "rain" and would not normally be present in a subsurface depository. Moreover, other observations (*4*) have shown that, once the initial penetration has taken place, further movement appears to be substantially reduced to amounts less than 100 μm/m.

In each set of experiments described the actinides have been subjected to conditions that would tend to maximize migration. Several important results have been observed consistently. First, most of the actinides (over 95 percent) are found very close to the point of deposition. All four groups of experiments indicate that the binding or absorption of the actinide on the rock is very strong. Relative migration ratios of 100 and 500 μm per meter of water flow seem to be the upper limits for Pu and Am, respectively. Second, once the deposits have dried on pore or fissure surfaces, they are virtually immobile. The application of large amounts of "rainfall" causes only slight additional migration at this stage. Third, in all our experiments two forms of Pu were observed. The more rapidly migrating form of Pu usually constituted 1 to 5 percent of the total activity. This form of Pu appeared to migrate three to five times faster than the "normal" Pu.

These results suggest that two distinct species of Pu are present in aqueous solution, either two different oxidation states or a combination of an ionic form and a polymer. Another possible explanation is based on differences in the nature of water flow in a porous medium. If the pores are filled, a saturated flow occurs, characterized by a comparatively slow rate. In places in the rock where water only partially fills the pores, the flow is unsaturated. This flow is faster and may possibly exceed the kinetic limits of the adsorption of the Pu on the rock. Thus the Pu migrates farther before it is bound to the rock. But even the more rapidly migrating form of Pu tends to become fixed if the solutions are allowed to dry on the rock and appears to convert to the slower form for low flow rates. This bonding seems to be so tenacious for Pu that we have thus far only been able to discern an upper limit for the migration rate of the Pu.

These results enable us to estimate the effect of flooding in a properly designed disposal site. If after a deep depository has flooded the water flows through the surrounding rock at a rate of 0.016 to 0.6 km per year (*5*) and if the migration ratio of Pu is taken as 125 μm per meter of water flow (*6*), then the Pu migrates no more than 12.5 cm per year. This rate amounts to a movement of 3 km per half-life. Examination of the migration and decay data of ^{239}Pu under such conditions (Fig. 3) shows that, with boundaries sufficiently distant from the site of deposition, the hazards due to migration will be mitigated by radioactive decay. If very conservative limits are used for water flow through an aquifer [flow rates three times faster than cited in (*5*)], at a distance of 30 km only 0.1 percent of the original ^{239}Pu remains whereas at 50 km only 0.001 percent remains. Similar considerations hold for ^{241}Am in spite of its higher migration rate; the amount of ^{241}Am reaching the 50-km boundary will be much less since its half-life is much shorter.

We can calculate the maximum ^{239}Pu activity at the 50-km boundary after this decay (*7*). The activity will be both dispersed along the line of flow and at right angles to it. The dispersion of the activity will vary with the uniformity and porosity of the medium but will always be at least as broad as a gaussian distribution (*8*) with

$$\sigma = (2\bar{d})^{1/2}$$

where σ is the full width at half maximum and d is the mean distance migrated. We therefore expect that, when $\bar{d} = 50$ km, the Pu activity will be dispersed along the flow path in a band 10 km long.

If the lateral dispersion at the boundary were only 100 m, the Pu would occupy a volume of 3×10^{14} cm^3. The amount of ^{239}Pu to be emplaced in a depository is estimated to be about 8×10^8 curies [see (*1*), vol. 1, pp. 3.12 and 3.21]. If all of this ^{239}Pu were to migrate as a single "injection," it would have decayed to 9600 curies at the boundary and would be dispersed to an average specific activity of 3×10^{-11} curies (66 disintegrations per minute) per cubic centimeter of rock.

The amount of activity to be found in 1 cm^3 of water in equilibrium with rock is several orders of magnitude smaller and may very conservatively be estimated as less than 1 disintegration per minute (1×10^{-6} μc). This amount is less than the "safe level" of 5×10^{-6} μc per cubic centimeter of water given in the tables of the U.S. Nuclear Regulatory Commission, Standards for Radiation Protection (*9*).

These estimates are calculated on the basis of two very conservative assumptions. (i) We have postulated instantaneous injection of soluble activity into an aquifer with very little lateral dispersion, about 0.1°. (ii) We have also assumed that the geochemical environment promotes migration rates comparable to those obtained in laboratory experiments. Rock strata from actual proposed sites must be tested for any realistic evaluation. The dimensions of the repository should, of course, be planned in accordance with the results of this evaluation. On the basis of our conservative estimates, the boundary for comparable "safe" Pu concentrations in a real site will be much less than 50 km.

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References and Notes

1. *Alternatives for Managing Wastes from Reactors and Post-Fission Operations in the LWR Fuel Cycle* (Publication 76-43, Energy Research and Development Administration, Washington, D.C., May 1976). Both volumes 4 and 5 of this work contain critical and exhaustive discussions of the various factors important in geological isolation.
2. This choice is not intended to ignore nuclides such as ^{90}Sr, ^{244}Cm, or others, but the shortness of their half-lives or their abundances in wastes excludes them from consideration for long-term immobilization within the context of this report. Nuclides such as ^{129}I or ^{99}Tc merit special concern, but these are not discussed here.
3. Because it decays by electron capture (~ 100-kev x-ray) with a 45.6-day half-life, ^{237}Pu is especially useful as a tracer in these experiments. This easily detectable radiation makes direct analysis of rock samples possible without the necessity of tedious Pu separations.
4. S. Fried, A. M. Friedman, J. Hines, L. H. Quarterman, in *Proceedings of Actinide-Sediment Reactions Working Meeting at Seattle, Washington*, L. L. Ames, Ed. (Publication BNWL-2117, Battelle Pacific Northwest Laboratories, Richland, Wash., in press), pp. 75–104.
5. O. E. Meinzer and L. L. Wenzel, *Hydrology*, O. E. Meinzer, Ed. (Dover, New York, 1942), p. 449.
6. This figure includes our upper limits for saturated flow and is based on the assumption that 10 percent of the stratum is fissured.
7. The choice of 50 km for the boundary is purely arbitrary. Since no permanent repositories have been built, we cannot know their dimensions. However, the Nevada Test Site may be considered as a model for a deep underground repository; in this case dimensions of about 50 by 85 km may be considered applicable.
8. S. Fried, A. M. Friedman, R. Weeber, *Adv. Chem. Ser. No. 153* (1976), paper 9; J. Bear, in *Flow Through Porous Media*, R. J. M. De Wiest, Ed. (Academic Press, New York, 1969), chap. 4.
9. U.S. Nuclear Regulatory Commission, Rules and Regulations, Title 10, Chapter 1, Code of Federal Regulations, Part 20, Standards for Radiation Protection (Government Printing Office, Washington, D.C., 14 November 1975), appendix B, p. 20-13.
10. This work was supported by the U.S. Energy Research and Development Administration, Division of Nuclear Fuel Cycle and Production.

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