

Actinides in the Environment

The colophon on the book cover is the “alchemical” symbol for plutonium devised by Charles A. Thomas in 1944 and used as the colophon of the book he and John C. Warner edited in 1944 entitled “The Chemistry, Purification and Metallurgy of Plutonium.”

Actinides in the Environment

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FOREWORD

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PREFACE

The probable growth of electrical generating capacity by the year 2000 has been projected to be about 1750×10^9 watts. Of this the total nuclear capacity is estimated to be 800×10^9 watts. We are well aware that major by-products of the nuclear power industry are the radioactive wastes involved. The U. S. Energy Research and Development Administration predicts a total of about 100,000 Megacuries of high level wastes produced by the year 2000.

The most hazardous radioactive wastes are the longer-lived actinides, especially ^{239}Pu and ^{241}Am . It is also predicted that by the year 2000 there will be 900 metric tons of actinide wastes stored in federal repositories. This would be about 12,000 Megacuries of alpha activity, the exact amount depending on the isotopic composition and age.

Because of this, it is highly important to understand the environmental behavior of Pu and Am. This symposium was organized in order to ascertain the current state of our knowledge about the behavior of these isotopes in rocks, soils, ground water, and biosystems.

Argonne, Ill.
August 1976

ARNOLD M. FRIEDMAN

The Role of Actinide Behavior in Waste Management

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One of the most important uses for information on the environmental behavior of the actinides is evaluation of safety for radioactive waste management. Commercial radioactive wastes are expected to be managed so that the actinides and other nuclides do not enter the environment. The process of selecting effective waste management methods requires, however, that release to the environment be considered and evaluated.

These safety assessments focus on nuclide migration in the environment and the consequences of migration. If the assessments are to be a viable basis for choosing from among alternatives or a basis for establishing the safety of a given concept, they must use predictive models and data that are well founded and appropriately coupled to each other.

The other papers in this symposium discuss details of available data and models. This is an overview discussion of the scope and types of models and data needed for safety assessment of radioactive waste management concepts.

Management of radioactive wastes involves four basic types of activities: waste treatment, interim storage, transportation, and final storage or disposal. Treatment, interim storage, and transportation might release actinides to the environment by accident. Under such circumstances the release would be a known, relatively instantaneous event; remedial action could be taken immediately. Existence, migration, and consequences of actinides in the environment could be highly constrained.

The primary concern for this symposium is the environmental behavior of actinides released to the environment after final action designed to keep the nuclides out of the environment. The action that could lead to such release is placement of the wastes in geologic formations. Such action is known, in waste management terminology, as geologic isolation since its objective is to isolate the wastes from the biosphere.

There are four candidate geologic isolation environments: the sea floor, ice sheets, deep continental geologic formations, and shallow continental geologic formations. In waste manage-

ment the latter are called burial grounds. Information on the sea floor and ice sheets is not yet well developed, so attention is focused on continental geologic formations.

There are two concepts for using geologic formations for waste isolation: storage and disposal. The storage concept involves placing the wastes in the geologic medium so that they are readily retrievable. Disposal involves emplacement without expectation of retrieval. Storage can be converted to disposal by changing the emplacement configuration or by withdrawing human control.

Geologic storage and disposal both rely on stability of the medium to keep the wastes in isolation; the geologic medium is expected to serve as a stable barrier between the wastes and the environment. In storage systems, the geologic barriers would be augmented by manmade barriers. The manmade barriers include the waste form (e.g. a monolithic, leach-resistant solid) and engineered structures. Long-term retention of radioactivity, which, as noted, is primarily expected to be attained as a result of geologic stability, can be aided if the geologic medium has ion exchange or other properties that restrict nuclide migration.

Repository Systems

Use of geologic media for waste isolation involves an action phase and a prediction phase. The action phase is concerned with site selection, waste repository design, waste form selection, etc.; i.e., all activities related to selecting a repository site and putting it into use.

The prediction phase is the part of waste management that is concerned with actinide behavior in the environment. It starts with the repository concept that emerges from the action phase and projects the capability of the repository and its surrounding geologic environment to keep the wastes isolated.

An essential feature of effective prediction is treatment of the repository as a system composed of the geologic medium and the contained waste. The basic objective is to predict the dynamic behavior of the system for long periods of time.

The dynamic behavior of the repository depends on the physical and chemical properties of the system, their change with time, the interactions between the waste and the geologic medium, and the processes involved in loss of barrier stability. Analysis of these phenomena requires models and data such as are discussed in this symposium.

Loss of repository stability and waste isolation can occur in two ways: as a result of sudden disruptive events and as a result of long-term degradation events. Analysis of the probability, characteristics and consequences of sudden disruptive events such as meteorite impacts and major earthquakes is the province of risk analysis. Such analyses produce estimates of the

probability and consequences of events that disrupt repository systems analogous to the analyses of reactor safety. They reflect one of the two essential methods for safety assessment of geologic repositories for waste. They may require information on actinide migration, particularly for phenomena such as aerosol suspension.

The other method of analysis of repository safety is concerned with degradation processes that can occur and persist over long time periods. One of the most familiar examples of such degradation is corrosion. On a geologic time scale, an ice age might produce events and processes that lead to long-term degradation.

Methods for analyses of degradation rate processes and their consequences are not yet fully developed. The approach used so far is to assume that degradation, i.e., long-term release, does occur and then to estimate the consequences of such phenomena.

Prediction of the consequences of degradation release conventionally involves data and models for three steps of analysis: geosphere transport, biosphere transport, and biosphere consequences. I will discuss these and add two others: analysis, rather than assumption, of repository degradation, and consideration of the geosphere/biosphere interface and its effect on biosphere consequences. These refinements to safety assessment procedures, when developed and implemented, can be expected to aid validation of results.

Repository Degradation

Aside from disruptive events such as meteorite impact, repository degradation can result from natural processes such as ice ages or from phenomena such as waste-geology interactions.

Placement of wastes in geologic media can initiate thermodynamic and kinetic effects, and their consequences, that would not occur in the undisturbed geologic medium. For example, radiation and heat emissions from the waste can affect the mechanical, thermal and chemical stability of the repository. In geologic storage systems adverse effects of such phenomena can be mitigated by repository design, e.g., by increasing the spacing between waste containers. The wastes can also be retrieved from storage if necessary. In geologic disposal systems, for which retrieval of wastes is impractical, projections of degradation phenomena and their effect on repository stability are essential for decisions on use of the disposal concepts.

Projections of nuclide migration involve, as one of the assessment parameters, consideration of elapsed time since waste emplacement in the repository and its effect on nuclide inventories. The effect of elapsed time on waste properties that could affect nuclide migration should also be assessed. The analyses of repository stability should, therefore, include estimates of changes in chemical and physical properties of waste radioactivity.

Geosphere Transport

Evaluation of nuclide migration in the geologic medium surrounding a waste repository is the first step in projecting the consequences of loss of repository integrity. The analyses require assumptions or data concerning many parameters:

- Radioactivity inventory in the repository at the time of release.
- Physical and chemical properties of the released radioactivity that can affect migration rates.
- Mechanisms and rates of release from the repository (e.g., leaching by water).
- Interactions between radioactivity and the transport medium.
- Length of the transport pathway.

Models to predict migration data have been developed. (1-4) The available models assume that water intrudes the repository, acts to release the radioactivity by leaching, and transports the radioactivity through the surrounding media to the biosphere. Potential changes in waste properties that result from thermodynamic and kinetic effects are not considered in present models.

The geosphere migration models account for effects of geologic structure on migration, effects on the radioactive decay chains on nuclide inventory, and the possibility of interactions between the geology and the radioactivity that would selectively retard nuclide migration. Numerous possible interaction mechanisms, including adsorption, ion exchange, colloid filtration, reversible precipitation, and irreversible mineralization, have been identified. Data on geosphere migration should be capable of pinpointing actual retardation mechanisms so that predictions using the models can be made with confidence.

Application of the geosphere transport models is highly site-specific; i.e., data for the proposed repository site should be used. This requirement imposes a need to assess the viability of, and methods for obtaining, laboratory and field data. Capability to produce representative information is needed. Data used to date can best be characterized as generic; for many nuclides, numerical values used to represent holdup phenomena are extrapolations of limited data for similar nuclides. The validity of such extrapolations should be evaluated.

The Geosphere-Biosphere Interface

Migration predictions usually assume that radioactivity would be transferred from the geosphere to the biosphere without change in physical or chemical properties. Such assumptions may be valid, but verification would help assure validation of the migration predictions. Evaluations should be made on a site-specific basis for the anticipated time and place of transfer of

radioactivity between regimes. The impact of any changes in nuclide properties on subsequent biosphere behavior should be evaluated.

Biosphere Transport

Radioactivity that enters the biosphere is subject to transport by a variety of pathways and mechanisms that need to be reflected in migration models for this regime. Factors to consider in biosphere transport models are similar in type to those considered for geosphere transport, but details will differ substantially. Pathways are more numerous in the biosphere, and phenomena such as weathering may change the physical and chemical properties of the nuclides. Such changes may alter the environmental behavior and biological consequences of the radioactivity.

Models of biosphere transport have been developed.^(5,6) As is the case for geosphere transport models, the data base for parameters in the biosphere models is limited. The scope of available data is being expanded, ⁽⁷⁻⁹⁾ but careful assessment is needed of the validity of the data, the validity of the models, and the need for the data and models to be site-specific. One site-specific factor to consider is the possibility that geosphere migration could extend for considerable distances from the repository; radioactivity might therefore enter the biosphere in an environment different from that of the repository site.

Biosphere Consequences

The last step in predicting nuclide behavior is to estimate consequences in the biosphere. The usual target for these predictions is consequences to humans, but the process of estimating such consequences necessarily involves consideration of ecological chains and man's interactions with his environment.

Prediction of biosphere consequences is coupled with modeling of biosphere transport.^(5,6) The key factors in the transition from biosphere transport to biosphere consequences are the assumptions made concerning man's interaction with his environment. The interactions depend, of course, on man's activities and the presence of nuclides with which he can interact.

A potentially important consideration concerning interactions between man and the environment is the long-term distribution and behavior of nuclides after they enter the biosphere. Work with the geosphere transport model has shown that geosphere holdup can chromatographically separate the radioactivity so that only specific nuclides would enter the biosphere at a given time. If the nuclides do not disperse significantly and remain biologically active, consequences could remain localized and be accumulated over decades or hundreds of years. Conversely, potential consequences would be limited to those nuclides that enter the biosphere during an individual's lifetime.

Summary

For purposes of assessing the safety of repositories of radioactive wastes placed in geologic isolation, actinide behavior in the environment has been interpreted in terms of five steps of prediction:

- analysis of repository stability
- geosphere transport
- the geosphere-biosphere interface
- biosphere transport
- biosphere consequences.

Each step in the analysis requires models of nuclide behavior and data on the physical and chemical properties of the radioactivity. The scope of information required in order to make reliable safety assessments has been outlined.

All steps in the assessment process are coupled; reliable models and data are therefore needed for each step.

The prediction phase of safety assessment is also coupled to activities concerned with waste treatment, selection of the final form of the waste, and selection of repository sites and designs. Results of the predictions can impact these activities.

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Moisture and Solute Transport in Porous Media

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Introduction

Natural earth materials, whether consolidated or unconsolidated, contain varying amounts of internal space not occupied by mineral material. This space is due to the presence of individual pores, and structural features such as joints and bedding planes. Generally, this internal space is interconnected, permitting the movement of water through the material and the associated transport of chemical species dissolved or suspended in the water. In some volcanic rocks, for example vesicular basalt, large portions of the pores are completely isolated from each other, with no opportunity for fluid movement between them; cementing agents, such as silicates or carbonates, may produce this same effect in granular materials. However, the bulk of the soil and rock material near the earth's surface contains interconnected pore spaces which allow the circulation of air or other gases and transport of water and associated materials. This paper discusses the interactions of porous geologic media with the water and solutes which effect the rate and direction of transport.

The Nature of Granular Materials

The individual particles composing granular materials vary in shape from irregular spheroids to flat plates. The shape and configuration of the intervening pores is dependent on the arrangement and relative size of the particles. Porosity is a measure of the total pore space contained in a given volume of material, and is dependent more on the arrangement and size distribution of the particles than on their absolute size. A wide range of particle sizes tends to reduce the porosity, by filling spaces between large particles with smaller particles. In addition to this interstitial porosity, secondary structures such as joints, fractures

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or soil aggregates will contribute to the total porosity of a material.

Figure 1 presents a plot of the grain size distribution for a soil with a high clay content, a silty soil, and a sandy soil.⁽¹⁾ Clayey material is composed of small particles, generally flat plates of relatively uniform size that do not nest well together, and has a porosity of 40-60%. Silty and sandy materials, on the other hand, contain grains of a more spherical shape, with a wider size range. These have porosities in the 20-40% range.

Occurrence of Water in Granular Materials

The pore spaces in granular material are irregularly shaped, with cusps or necks between adjacent pores as illustrated in Figure 2. Water placed in contact with granular materials will tend to displace the air or any other gases present in the pores. The term "saturation" is used to describe a condition where all of the pore spaces are filled with water. When some portion of the pore spaces are only partially water filled, the material is termed "unsaturated" or "partially saturated." In truth, it is exceedingly difficult to accomplish saturation for any granular material, in part due to the presence of pores that are not interconnected. In the remainder of this discussion, we will presume that "saturation" refers to the filling of all interconnected pore spaces.

Two forces tend to hold water in contact with granular material: adhesion between the water and the solid surface, and cohesion between the water molecules. This situation is identical to water rising in a thin capillary tube. If water is allowed to drain from an initially saturated material, it will be removed first from the center of the individual pores, leaving behind water in the cusps around the edges of the pores, and a relatively thin film of water on the surfaces of the grains. In Figure 2, the expanded view of the partially filled pores reveals various radii of curvature around the perimeter of the pores, dependent on the grain shape and the dimensions of the various cusps. As for capillary tubes, the smaller the radius of curvature, the more tenaciously the water is held. As greater amounts of water are removed from the material, the water surfaces retreat further into the cusps, and the films become thinner. Eventually these films become discontinuous, leaving only isolated pockets of water in the material. Note that some minerals (such as clays) can incorporate water into their crystal lattice or that chemical reactions may occur that will incorporate water into the mineral structure. This "bound" water does not participate in most inter-granular flow, and is not of significance to our discussion.

Soil Moisture Potential. Work must be performed to remove water from any saturated or partially saturated material. This work is, in effect, a negative potential energy, and provides a useful measure of the total force holding water in the material.

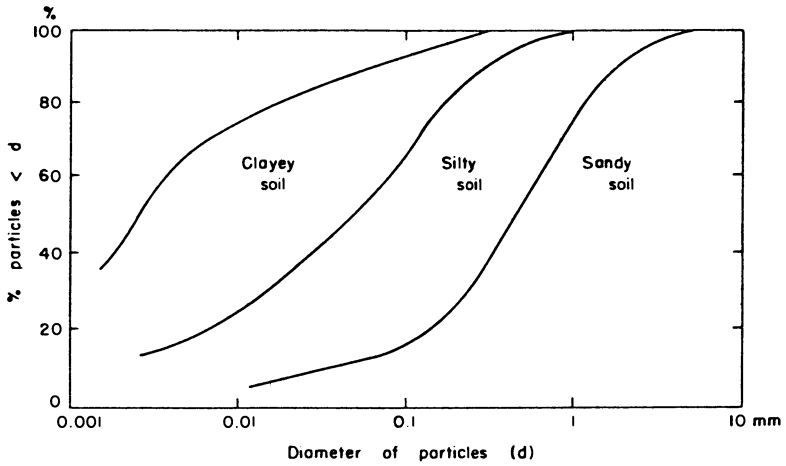


Figure 1. Grain size distributions for three soil types

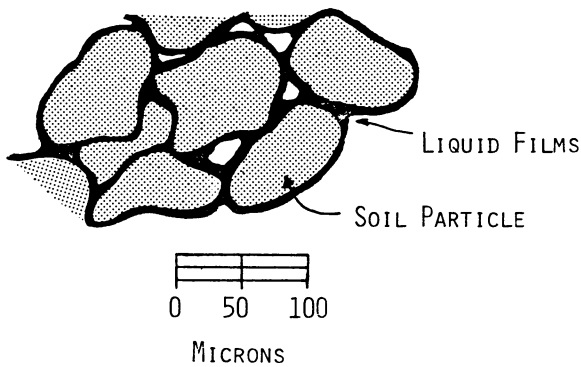


Figure 2. Soil water and internal pore structure

Briefly defined, the "total soil moisture potential" is equal to the work required to move a unit volume, mass or weight of the water in the soil at a defined elevation, temperature and pressure, to a container of pure water, a standard elevation, temperature and pressure. The soil moisture potential is commonly broken into five components: the matric component, resulting from the adhesive and cohesive forces of the water in the soil; the solute component resulting from the presence of dissolved chemical species; and the pressure, temperature and gravitational components, resulting from differences in these properties between the soil and the defined standard condition. Expressed in energy per unit mass, soil moisture potential is commonly measured in ergs/gram, or joules/kilogram. Expressed as energy per unit volume, the potential conveniently takes on units of pressure, and is commonly measured in atmospheres, or bars. Expressed as energy per weight of water, the potential is measured in length units, commonly centimeters of water.

Water content variations effect the pressure, solute, and matric components of the total potential in different ways. The pressure component will increase with depth in a saturated column, proportionate to the weight of the overlying water column. However, in partially saturated material the internal pore space is approximately in pressure equilibrium with the atmosphere, and the pressure component is nearly unaffected by water content variations. For most natural materials the solute component is in the range of zero to -1 bar, and is of principal concern as it effects plant water and nutrient uptake. The matric component, on the other hand, varies from a value of zero at saturation, to less than -100 bars for dry materials.

Soil Moisture Characteristic. The relationship between water content and the matric component is referred to as the "soil moisture characteristic." Although this relationship commonly displays hysteresis, the effect is not significant for most applications. The moisture characteristics for three granular materials is illustrated in Figure 3.(2) Note the steep slopes at high moisture contents for the sand and solid Los Alamos tuff. This results from a non-uniform pore size distribution; the sand contains a preponderance of large pores which drain at relatively high matric potentials; the solid tuff contains mostly smaller pores which drain at lower potential values. The relatively constant slope for the crushed tuff results from a fairly uniform pore size distribution. The moisture characteristics demonstrate the fact that materials at the same water content can display significantly different moisture potentials.

Moisture Flow

Water moves through granular materials in response to spatial variations in the total moisture potential; water always moving in

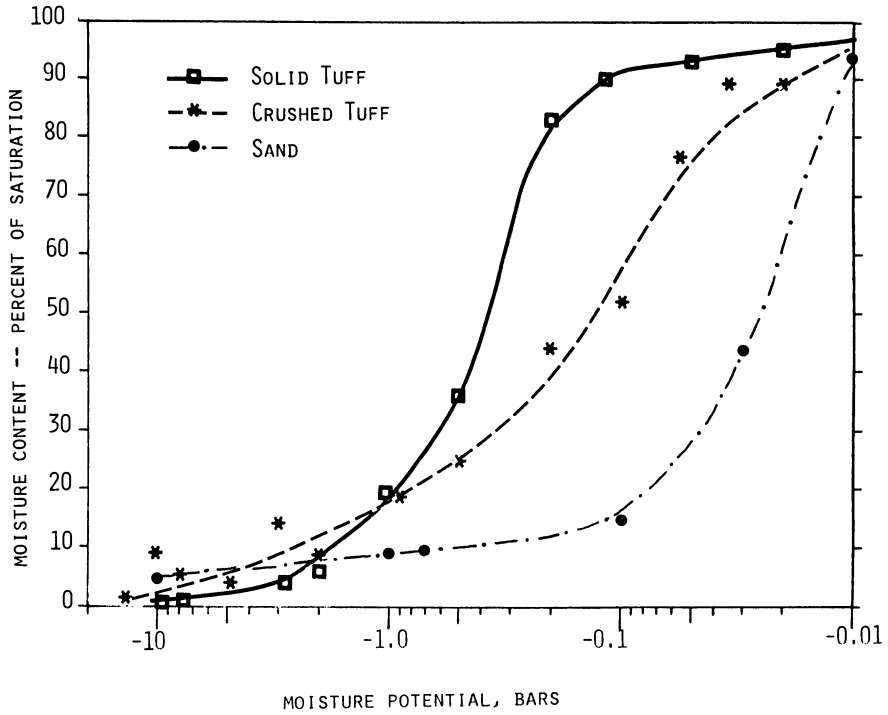


Figure 3. Moisture characteristics for three materials

the direction of decreasing potential. In both saturated and unsaturated systems, the rate at which water moves is dependent on the energy gradients as well as the hydraulic conductivity of the medium. This relationship is expressed in Equation 1.

$$q = K(\theta)\nabla H \quad (1)$$

where:

q = rate of water flow, as volumetric flux of water per unit cross-sectional area of the medium.

$K(\theta)$ = Water content-dependent hydraulic conductivity coefficient.

∇H = Gradient of moisture potential in direction of flow.

In saturated systems the conductivity coefficient is essentially constant, except for small stress-related changes in pore geometry. In unsaturated systems, the coefficient varies significantly with water content. This water content dependency results in part from the changing area available for flow as the moisture content changes. In addition, removal of water from the cusps or necks between pores increases the total flow path length. At water contents sufficiently low to produce discontinuous water films within the medium, water flow can only occur in the vapor phase; an important factor when considering moisture transport in very dry soils. However, with the exception of gaseous materials, very little if any solute transport occurs in the vapor state. The variation of hydraulic conductivity with moisture content for the sand and tuff previously described is illustrated in Figure 4.

Thus, water content variation is responsible for two significant changes in the factors controlling water flow; the hydraulic conductivity, and the relative magnitudes of the various components of the energy gradient. These variations produce marked distinctions in the character of flow under differing moisture conditions.

Saturated zones are common in porous material, and provide significant pathways for the subsurface transport of water and solutes. The term "ground water" commonly refers to continuously saturated zones of appreciable thickness. Saturated conditions also occur on a small scale or short term basis in association with the infiltration and drainage of precipitation or surface runoff. As indicated previously, the pressure and elevation components are the primary contributors to the total moisture potential in the saturated zone. These two are commonly combined into a "piezometric head", representing the addition of the water pressure head to the elevation at which the pressure head is measured. The hydraulic conductivity does not change significantly with

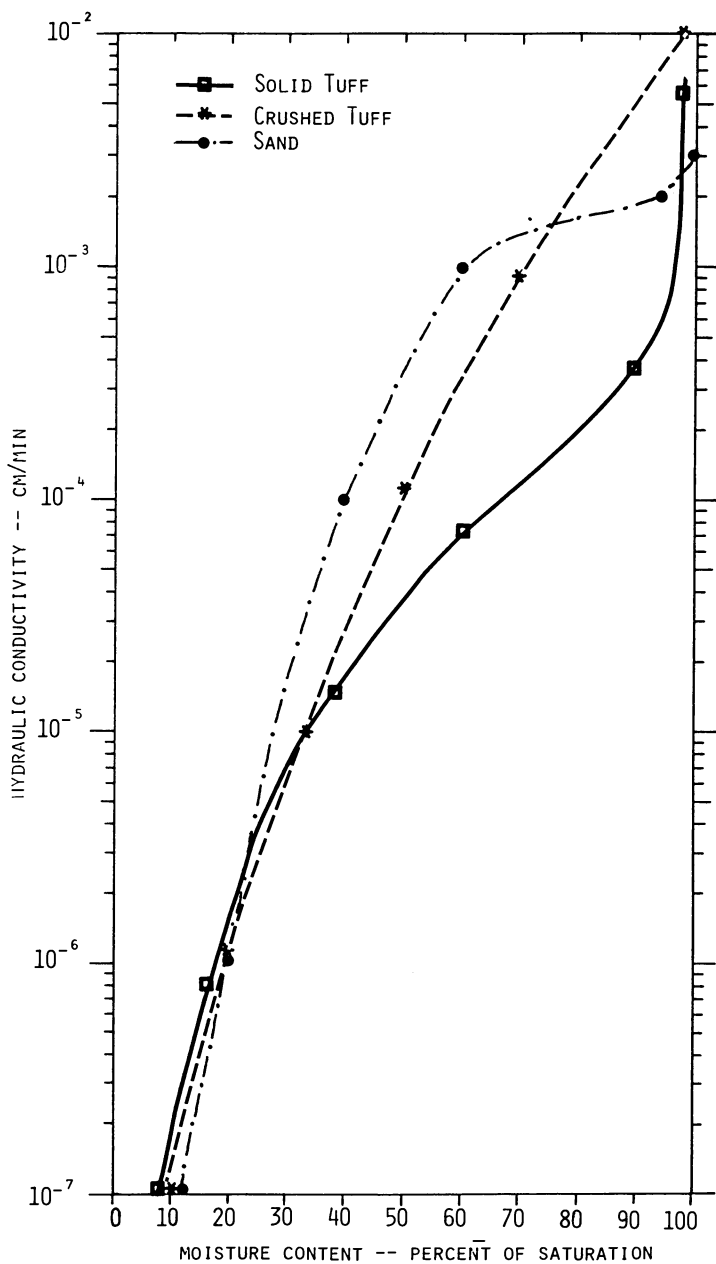


Figure 4. Hydraulic conductivity for three materials

changing piezometric head, and the variability in flow rate is a linear function of the piezometric head distribution.

When the water content of a material is below saturation, the internal pore pressure approximates atmospheric pressure throughout. Under these conditions, matric potential gradients arising from moisture gradients provide a significant fraction of the moisture driving force. Thus, water introduced into a trench in an initially dry soil will move laterally away from the trench at about the same rate as it moves vertically during the initial phases of infiltration. As the moisture content increases to saturation, the vertical gravitational component with a value of unity becomes more significant, increasing the downward flux over the lateral flux.

When water is applied to the surface of an initially dry soil column, a wetting front will move downward in the soil. The moisture and potential gradients at the front will be high, resulting in a rapid flux away from the surface. As the water content behind the wetting front increases, the average potential gradients will decrease, resulting in a continued decrease in the infiltration rate. If water is applied at a sufficient rate to develop a saturation zone at the surface of the column, the matric potential gradients will decrease to zero within this zone, leaving only the constant gravitational gradient with a magnitude of unity. Thus, flow through the saturated zone will approximate the saturated conductivity value for the material. If water is supplied at a rate just sufficient to maintain saturation at the surface, the downward flux will remain constant. Note that in this constant flux situation, the pore velocity of the water varies substantially with depth. As the moisture content decreases near the wetting front, the liquid area available for flow decreases and the path length increases, with a resultant increase in the pore velocity. In addition to the reduced water content, the presence of dead-end pores accounts for a further reduction in the flow area. The increased velocity is therefore not strictly proportional to the reduced water content. Further, as the flux is greatest during the initial stages of infiltration, the maximum pore velocities occur during that period.

Solute Transport

Chemical species dissolved or suspended in soil water move in response to two principal mechanisms: convection with moving water and diffusion within the flow field. Transfer rates due to these mechanisms are influenced by several factors. Diffusional movement results from concentration gradients within the solution and from micro-variations in the intra-pore velocity. The shape of the familiar break-through curve for nonreactive solutes results primarily from this diffusion. In general, diffusional velocities are small compared with convective velocities, but may be very important in computing the spatial distribution of a

contaminant introduced into a flow field.

Chemical species interact to varying degrees with the solid material. This interaction represents ion-exchange and chemical reaction phenomenon. If sufficient time is allowed, the concentrations of a particular species in the liquid and on the solid will equilibrate. One measure of the relative concentrations at equilibrium is the "distribution coefficient", defined in Equation 2.

$$K_d = \frac{\text{concentration on solid phase} \quad [\text{gm/gm}]}{\text{concentration in soil water} \quad [\text{gm/ml}]} \quad (2)$$

For relatively non-reactive species such as chlorides, K_d will approximate zero; for reactive materials, such as some actinides, the coefficient may exceed 10^5 . Note that this coefficient is kinetic in nature, with the time required to reach equilibrium dependent on many factors. For example, work by Rhodes(3) indicated that for a polymeric form of ^{239}Pu , over 85% of the adsorption occurred in the first 5 minutes, with continued adsorption over a period of several hundred hours. He observed that the approach to equilibrium was approximately proportional to the log of time.

The adsorption of chemical species on the solid material provides a retardation of the movement of that species relative to the liquid flow, as described by Equation 3.

$$\frac{V_i}{V_w} = \frac{1}{1 + \frac{\rho}{\theta} K_d} \quad (3)$$

where:

V_i = pore velocity of adsorbed species

V_w = pore velocity of migrating water

θ = volumetric water content

ρ = bulk density of medium

K_d = distribution coefficient

This relationship applies equally well to both saturated and partially saturated flow. Equation 3 presumes that flow velocities are sufficiently low to allow equilibrium to occur between the solid and liquid species, but this condition may not always pertain. A further complication on the application of this relationship is that the distribution coefficient is not constant with varying moisture content. The magnitude of K_d is strongly influenced by the macro-concentrations of other dissolved species in the soil solution, including calcium, sodium, and hydrogen (pH). Inclusion of these relationships in the solute transport process

requires applications of chemical thermodynamics as well as empirical measures of K_d at various species concentrations. (4)

It is worth examining the movement of a chemical species through porous material by combining a knowledge of water and solute transport. Consider an experiment where a solution containing a known micro-concentration of some chemical species is applied to an initially dry soil. The sorption of the species onto the soil is described by a time dependent distribution coefficient. At the wetting front, the moisture content may be sufficiently low to significantly reduce the magnitude of K_d , and the chemical may move at approximately the same rate as the infiltrating water.

In addition, water velocity through the pores is relatively high, so that water and the dissolved chemical may move rapidly into the soil. Behind the wetting front, water contents are substantially higher and liquid velocities slower, permitting more opportunity for equilibration between the chemical and the soil. If the foregoing assumptions hold, a separation would exist between material that moved with the wetting front, and the remainder, moving at a reduced rate behind the wetting front.

A precise theoretical description of the distribution of the dissolved species after significant movement has stopped requires a combined model of moisture flow and sorption process. However, in segments of the column where flow was sufficiently slow to allow sorption equilibrium, the quantity of tracer can be described by

$$C_s = K_d C_\ell \quad (4)$$

where:

$$C_s = \text{Amount of solid } [^{A}m_t/Gm]$$

$$C_\ell = \text{Amount in liquid } [^{A}m_t/ml]$$

If the concentration of the liquid entering that segment was C_0 , then the amount removed due to sorption is

$$C_s = (C_0 - C_\ell) \frac{\theta}{\rho} \quad (5)$$

then:

$$C_s = \frac{\theta C_0 K_d}{\frac{\theta}{\rho} + K_d} \quad (6)$$

Consider, for example, a soil with a K_d for ^{90}Sr of 10^3 , at a water content of 0.1 ml of water per cm^3 of soil and a bulk density of 1.0. For an influent concentration of 1 $\mu\text{Ci/ml}$, the resultant concentration on the soil is computed as

$$C_s = \frac{0.1 \times 10^{-6} \times 10^3}{0.1 + 10^3} \cong 0.1 \mu\text{Ci/g} \quad (7)$$

and the equilibrium concentration in the soil water is

$$C_\ell = \frac{C_s}{K_d} = \frac{10^{-7}}{10^3} = 10^{-3} \mu\text{Ci/g} \quad (8)$$

The total amount sorbed in any layer is seen to be dependent on both the distribution coefficient and the water content of the material in that layer. Inspection of Equation 6 reveals that for values of K_d substantially greater than the value of the gravimetric water content (θ/ρ), the concentration of the sorbed species on the solid phase is nearly equal to the product of the gravimetric water content and the influent concentration.

If the column is permitted to dry following initial penetration of the wetting front into the soil, redistribution of water in the column will accompany this drying. The redistribution will result in the transfer of any mobile material. Subsequent irrigations of the column will effectively duplicate the first, regarding distribution of both moisture and tracer. The extent of drying will obviously effect this distribution, as moisture penetrates a dry soil faster than an initially moist one.

Both moisture and solute transport in soils are dynamic processes, and difficult to describe analytically. Further, the processes strongly interact to affect the distribution of contaminants in the soil. Experiments regarding transfer of actinides, or any other material through porous media must therefore include an understanding and control of both processes.

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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

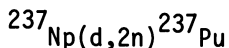
Most long-lived plutonium isotopes are alpha emitters and their use would require almost complete separation of extraneous solid materials for accurate determination by alpha counting.

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.

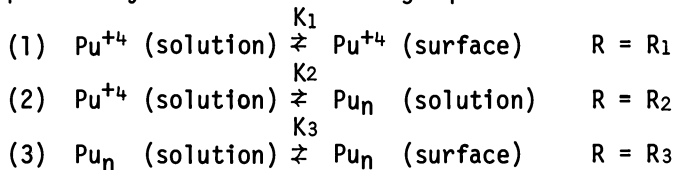
The plutonium, in this case the α -emitting ^{238}Pu , was introduced at the top of the fissure in a very small volume (about $50 \mu\text{l}$) by means of an infusion pump. The subsequent elution of the adsorbed plutonium from the surface of the basalt also made use of the infusion pump. Water was the 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 ^{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 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 cm³, 2.5 cm³ 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 5×10^5 c/m ²⁴¹Am and 1.5×10^5 c/m ²³⁷Pu 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 1.5×10^3 c/m ²³⁷Pu and 110 c/m ²⁴¹Am 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 2×10^4 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

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.

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. 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 H₂O. 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 H₂O was spotted on pre-wetted filter paper (7.5 x 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

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 |

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.

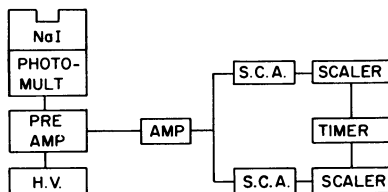
Therefore it is important to consider not only the geological quiescence of a storage site but also the chemical and migration-al behavior in case of an accidental influx of water.

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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5. Cohen, D., Argonne National Laboratory, private communication (1975).

Figure 1. Block diagram of scintillation spectrometer



APPARATUS FOR FORCING WATER
THROUGH SAMPLES OF SOLID ROCK

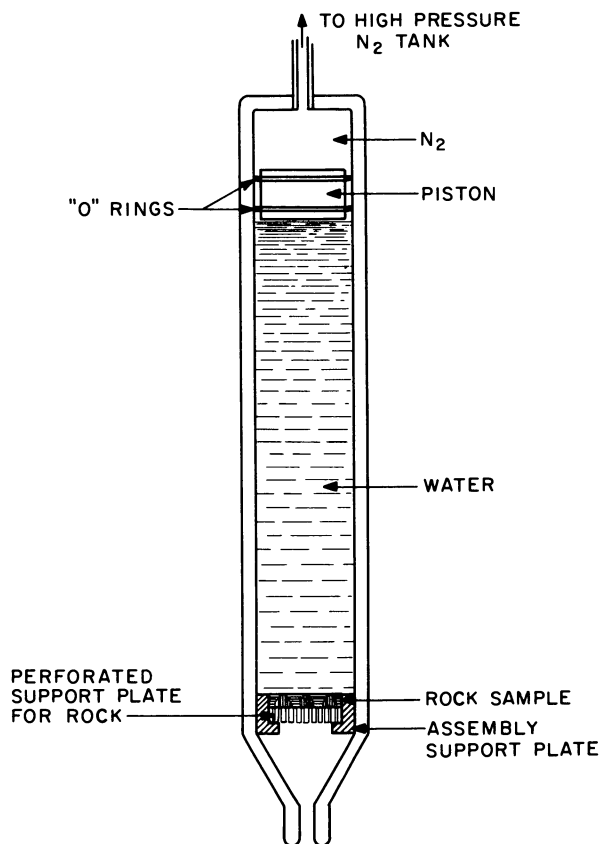


Figure 2. High-pressure chromatographic apparatus, ANL
Neg. # 122-903

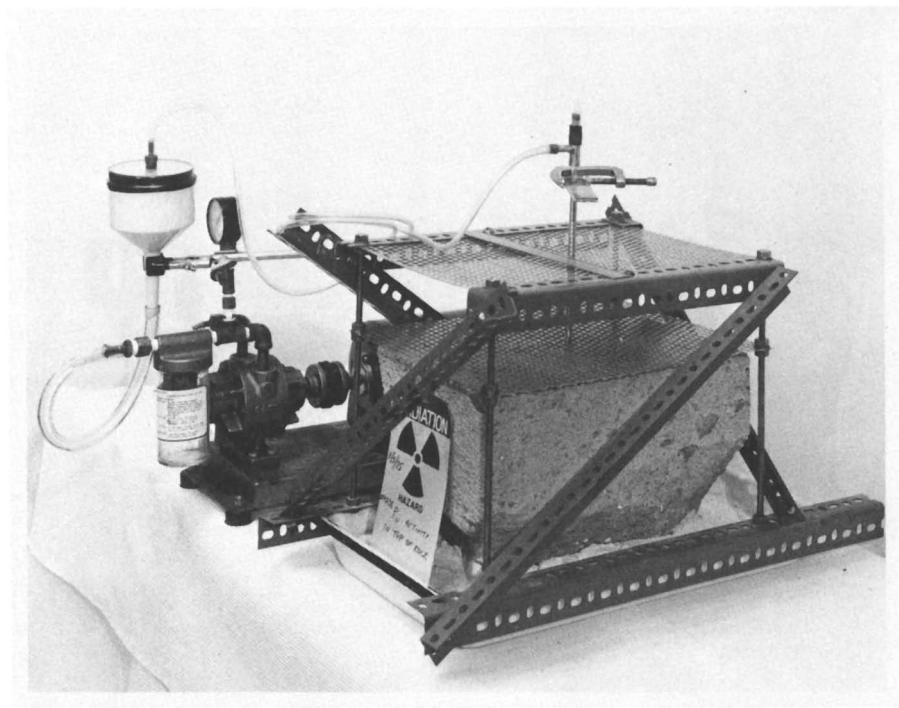


Figure 3. Experimental arrangement for coring experiment, ANL Neg. #122-2443

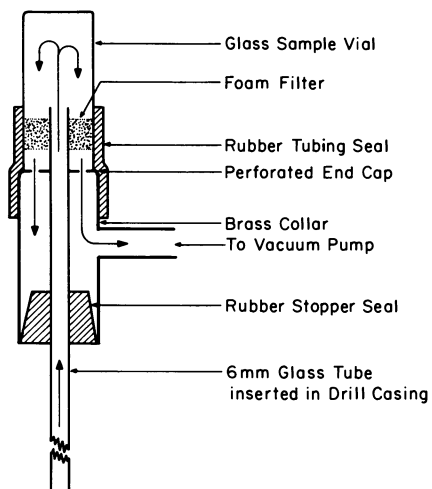


Figure 4. Schematic of coring apparatus, ANL Neg. #122-75-105

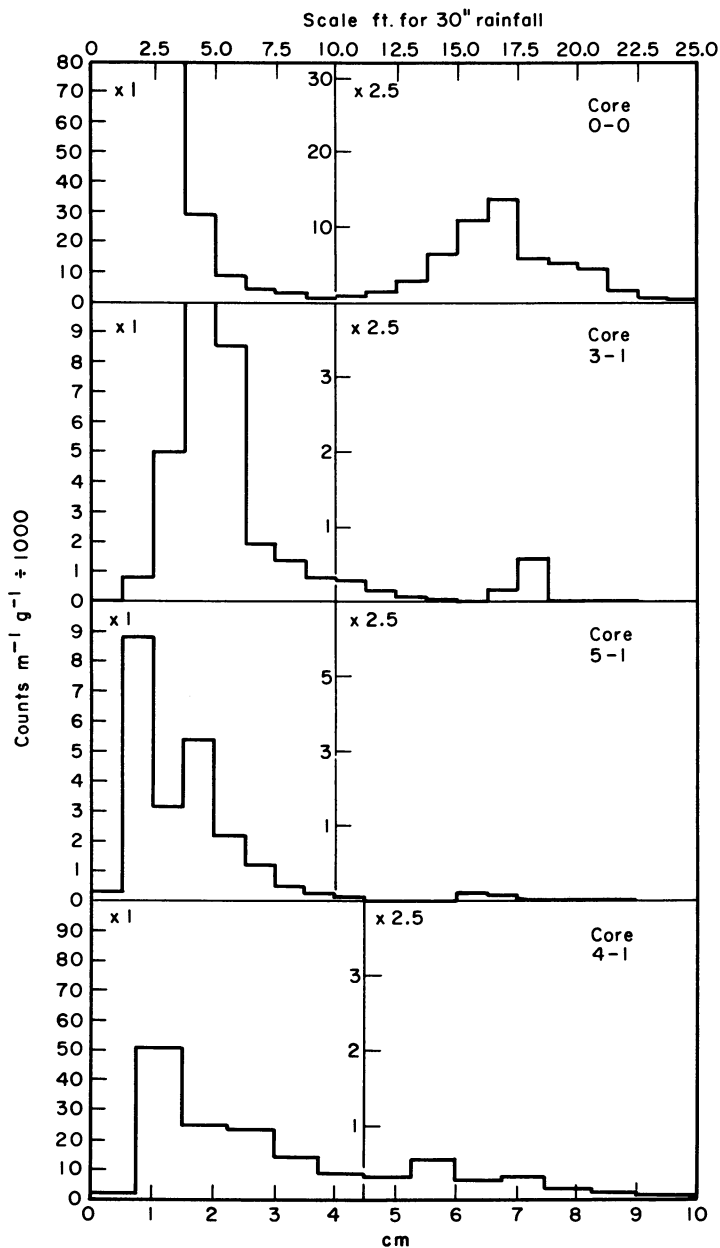


Figure 5. Results for cores taken at various radial distances from central core (0-0), ANL Neg. #122-75-104

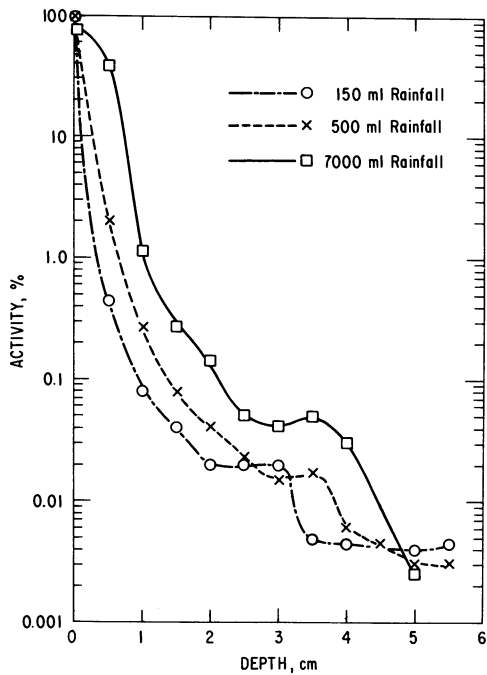


Figure 6. Vertical distribution of Pu in tuff as a function of rainfall

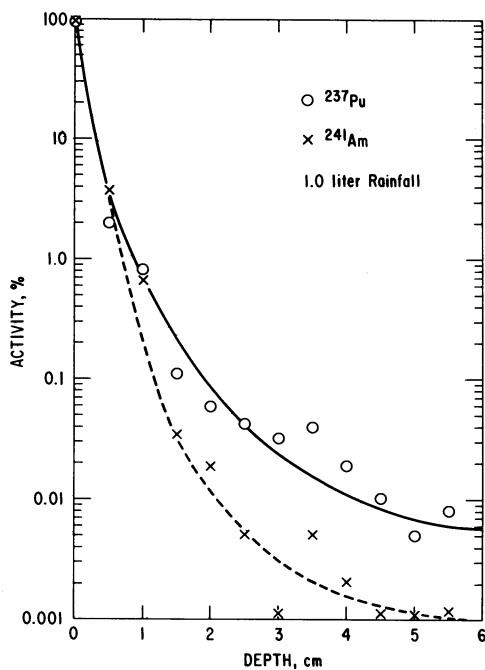


Figure 7. Comparative migration of Pu and Am in tuff

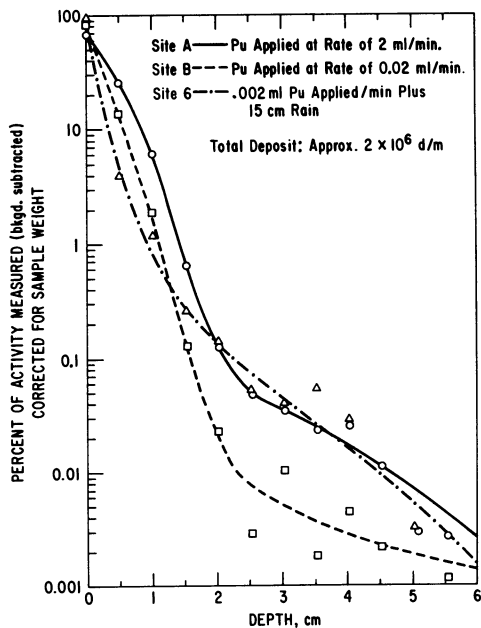


Figure 8. Vertical distribution of Pu as a function of deposition rate

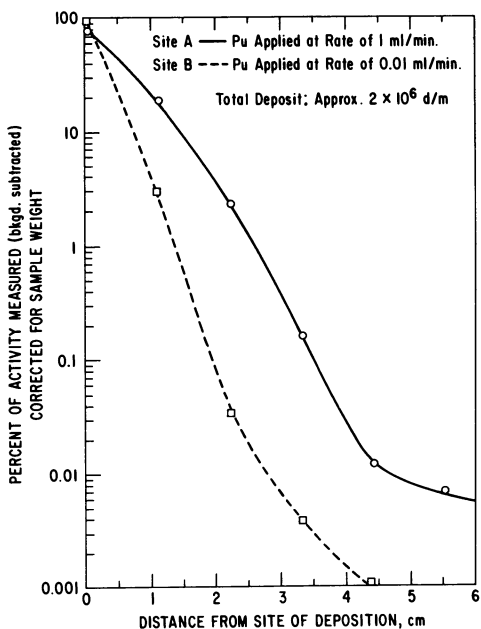


Figure 9. Radial distribution of Pu as a function of deposition rate

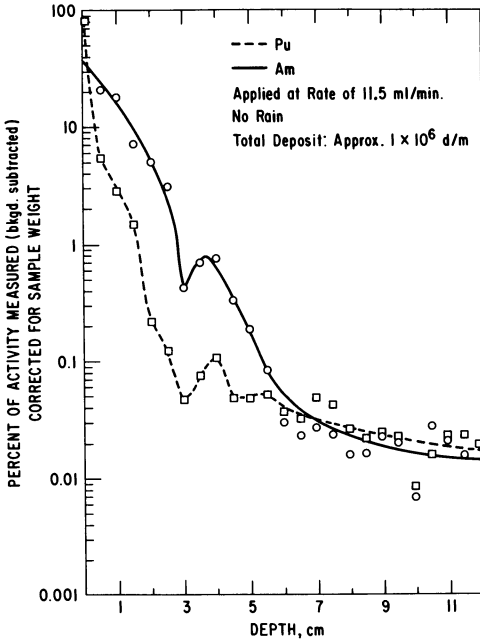


Figure 10. Comparative vertical distribution of actinides on tuff

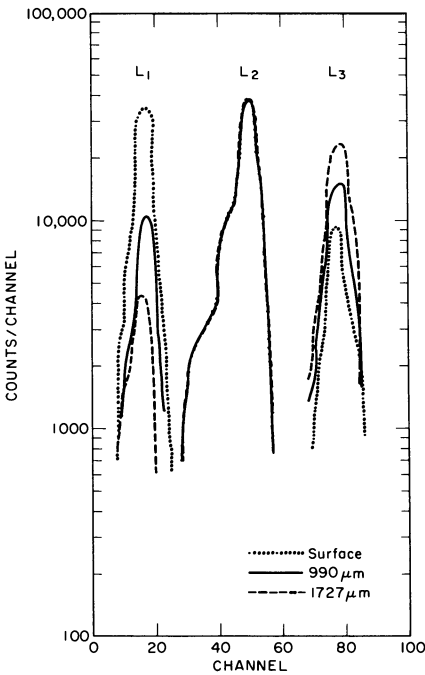


Figure 11. High-pressure chromatographic results on limestone, ANL Neg. #122-904

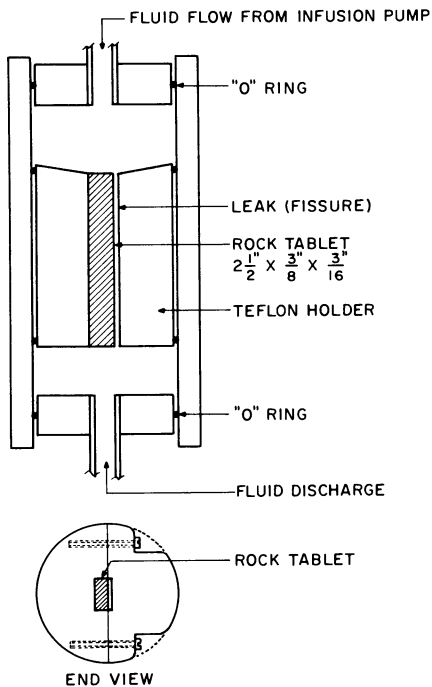


Figure 12. Fabricated fissure apparatus,
ANL Neg. #122-1309

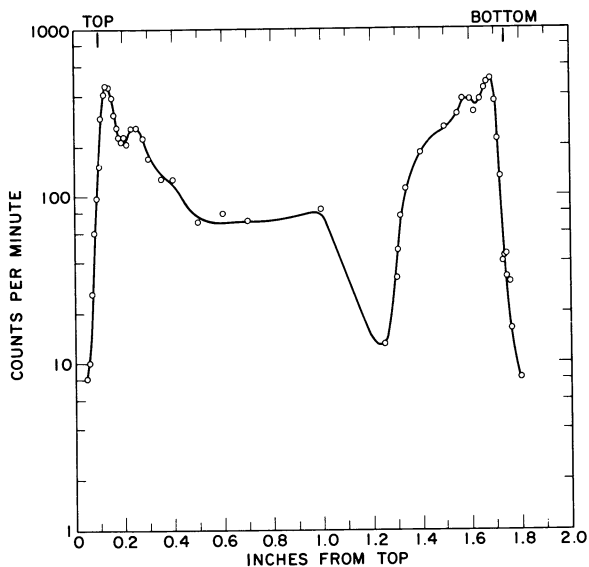


Figure 13. Distribution of
plutonium on basalt fissure,
ANL Neg. #122-910

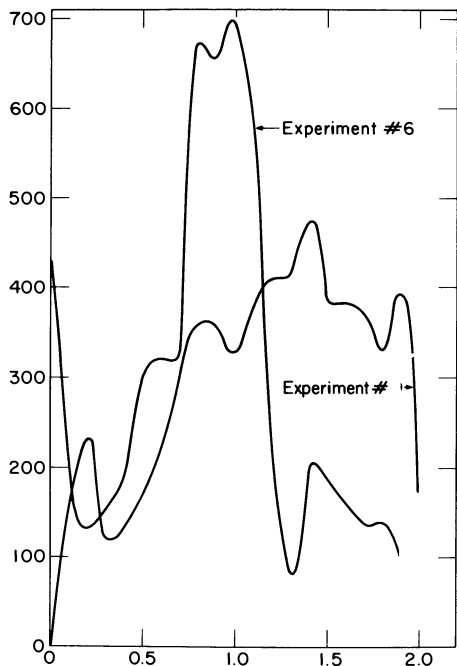


Figure 14. Effect of flow velocity on plutonium distribution on basalt, ANL Neg. #122-75-316

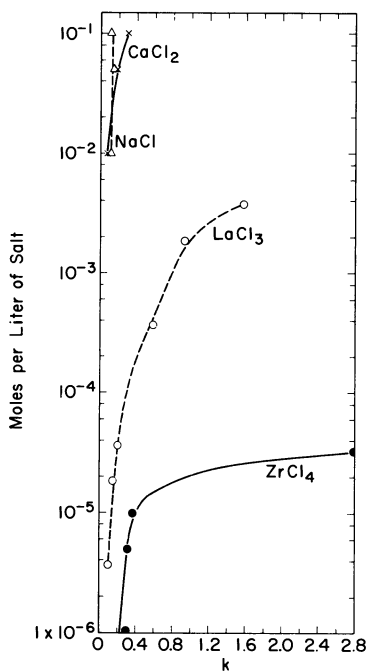


Figure 15. Variation in k for plutonium solutions in limestone as a function of other ionic concentrations, ANL Neg. #122-905

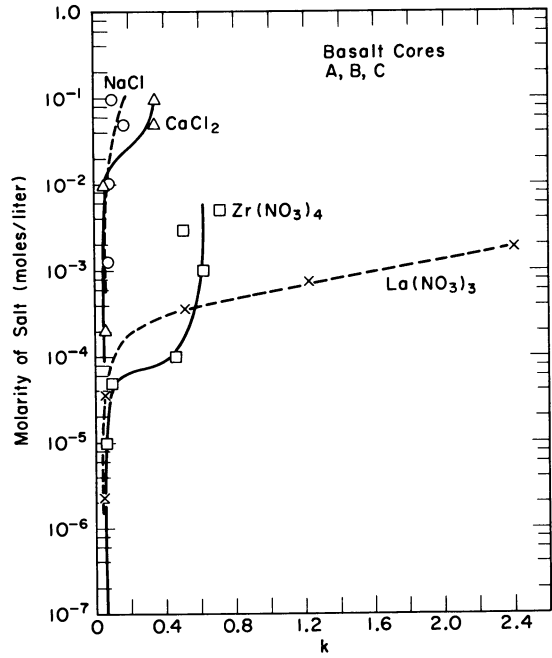


Figure 16. Variation of k for plutonium solutions in basalts, ANL Neg. #122-1014

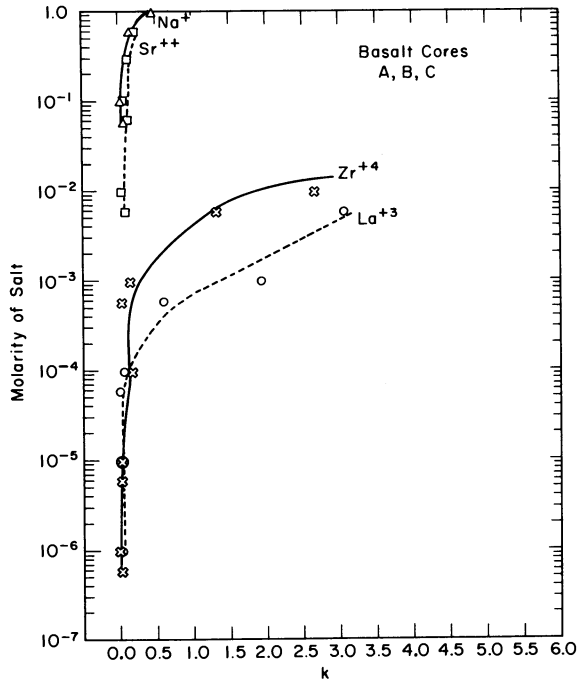


Figure 17. Variation of k for americium solutions in basalts, ANL Neg. #122-1600

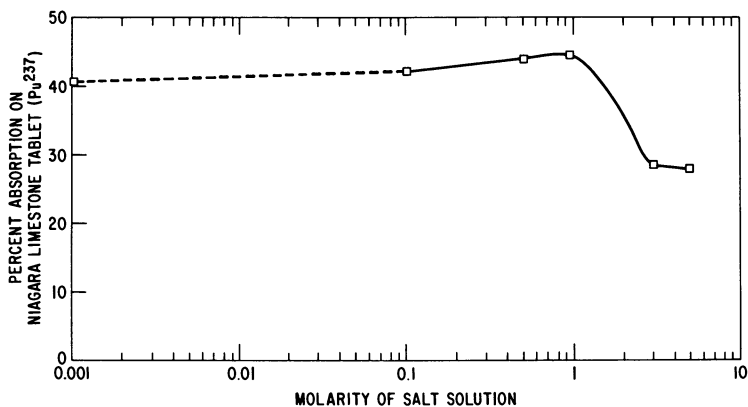


Figure 18. Absorption of plutonium on limestone as a function of NaCl concentration

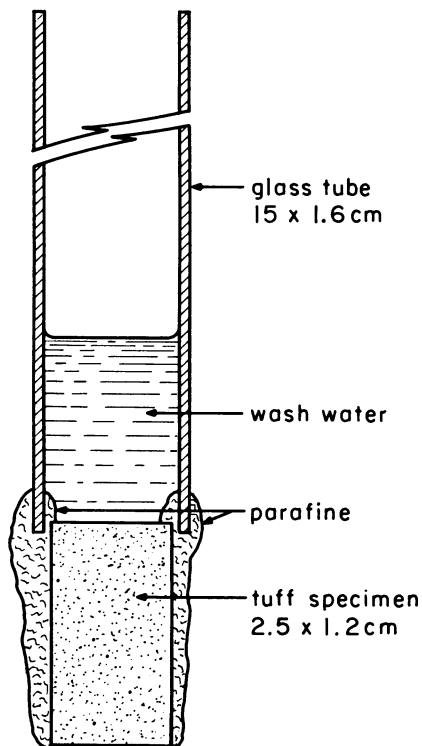


Figure 19. Schematic of elution column made with tuff plug, ANL Neg. #122-75-103

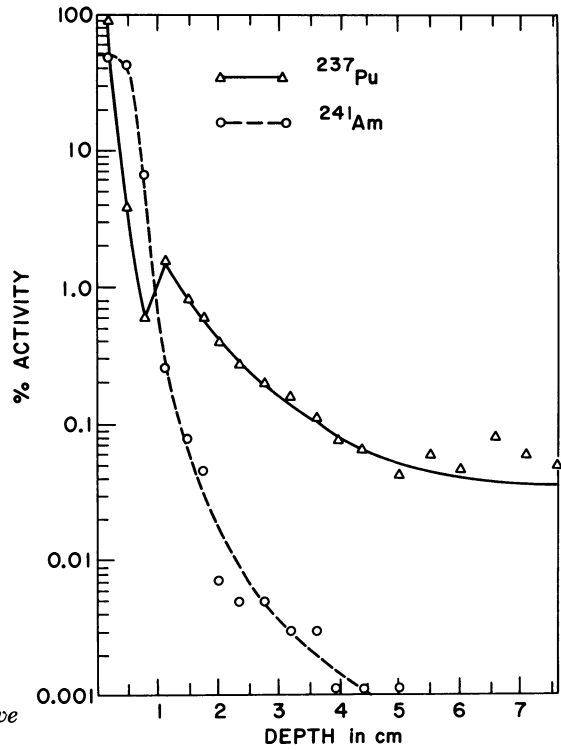


Figure 20. Comparison of relative migration rates in tuff

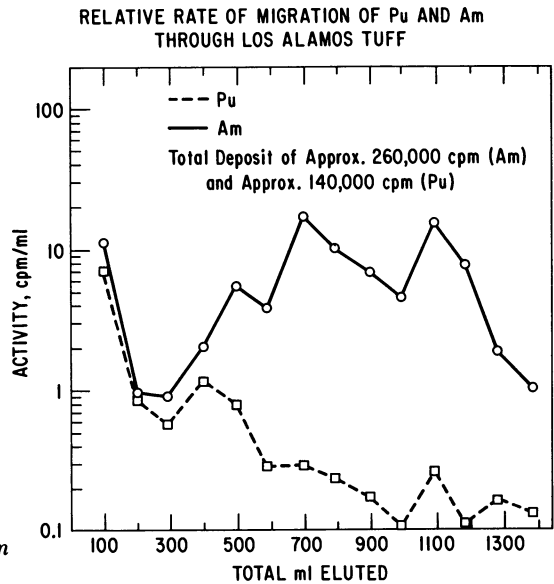


Figure 21. Elution of Pu and Am in column of tuff

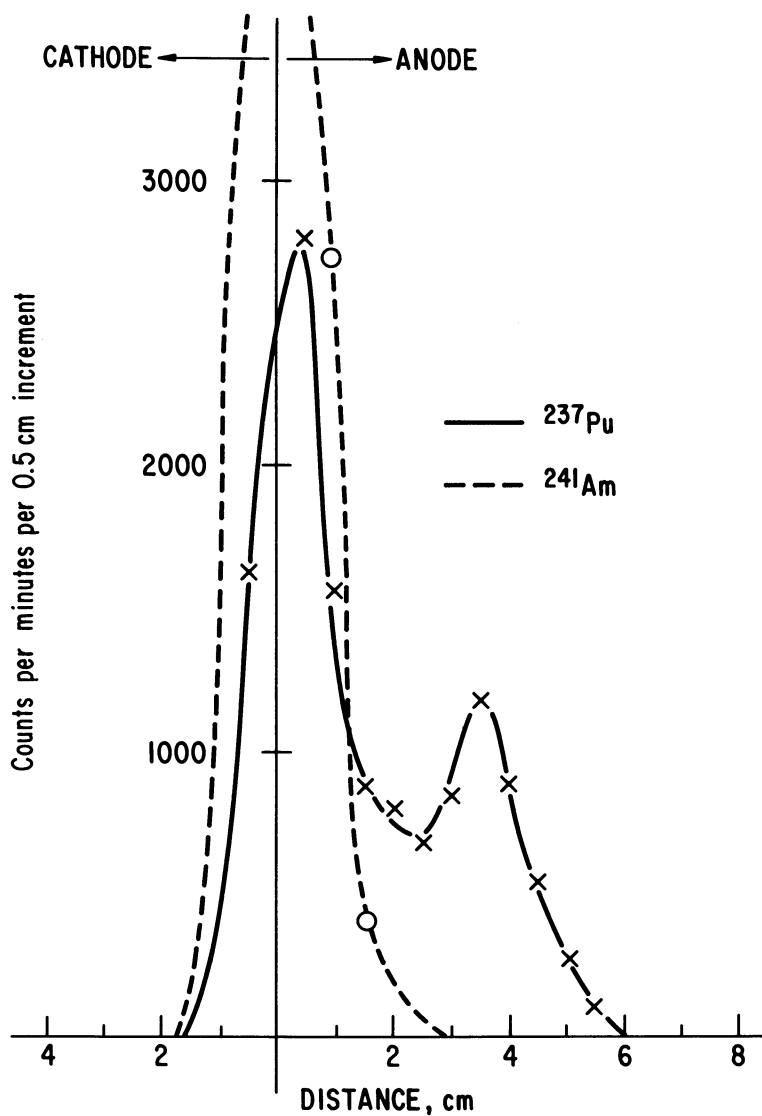


Figure 22. *Electromigration behavior of activity*

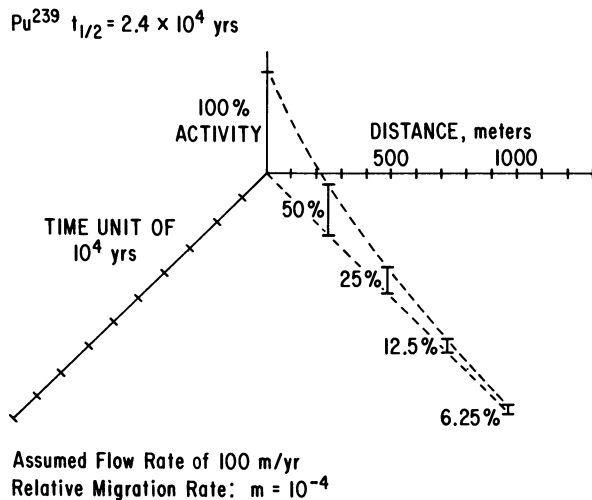


Figure 23. Migration of plutonium for hypothetical depository

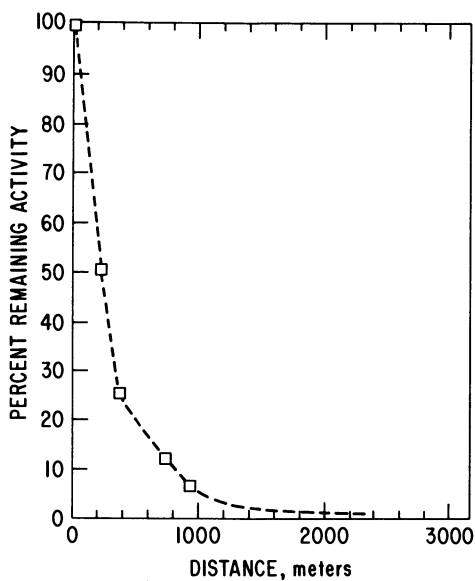


Figure 24. Migration of plutonium through an aquifer

Biological Pathways and Chemical Behavior of Plutonium and Other Actinides in the Environment

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1. Introduction

Plutonium will very likely play an important role in future power generation by nuclear reactors. Light-water reactors (LWR) already produce and burn Pu; future LWR recycle and breeder options will place greater emphasis on Pu fuel cycles in nuclear technologies (1). As a fuel, Pu is a valuable commodity; thus it will be meticulously recovered for reuse, and only a small quantity will likely be released to aquatic and terrestrial environments.

The principal long-lived actinide elements that may enter the environment from either U or Pu fuel cycles are Pu, Am, Cm, and Np. Approximately 25% of the alpha activity estimated to be released to the atmosphere from the Liquid Metal Fast Breeder Reactor (LMFBR) fuel cycle will be contributed by ^{241}Am , ^{242}Cm , and ^{244}Cm (2) (Table I). The balance of the alpha activity will come from Pu isotopes. With recovery of Pu from these fuel cycles, other transuranic elements will become dominant alpha emitters of wastes. Activities of ^{242}Cm , ^{244}Cm , ^{241}Am , ^{243}Am , and ^{237}Np in waste may exceed concentrations of Pu isotopes in waste after various

Table I. Principal Actinide Alpha Emitters of Nuclear Fuel Cycles

| U (Pu) fuel cycle | Waste | Th fuel cycle |
|----------------------|-------------------|-------------------|
| ^{238}Pu | ^{237}Np | ^{228}Th |
| ^{239}Pu | ^{243}Am | ^{229}Th |
| ^{240}Pu | | ^{232}U |
| ^{241}Am | | ^{233}U |
| ^{242}Cm | | |
| ^{244}Cm | | |

* Research sponsored by Union Carbide Corporation under Contract with the Energy Research and Development Administration. Publication No. 870, Environmental Sciences Division, ORNL.

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periods of decay (3). Thorium and uranium isotopes may also be released by operations of the thorium fuel cycle.

There is a very limited data base on the behavior of these elements in the environment. In relation to modes of element transport in the biosphere, a need exists for better information on the relationships between environmental chemistry and the pathways of movement to man for Pu and related actinide elements. A better understanding of food-chain mechanisms is needed in order to predict life-time exposures from ingestion of actinide elements consumed in food and water. Based on several decades of experience (a short time frame relative to the 24,000-year half-life of ^{239}Pu), there are very limited data on the long-term (period commencing with operation and extending into geological time) potential for remobilization of these elements by geochemical and ecological processes.

The purpose of this paper is to present data on the environmental behavior of selected actinide elements. Environmental chemistry factors that influence the mobility of these elements are discussed. Some of the variability of data on the uptake of actinide elements by plants is explained. The behavior of man-made actinides in a representative aquatic environment is also discussed. Except for general comparisons, exposure of man by the inhalation pathway is not considered in this paper, even though higher exposures are routinely calculated for this pathway relative to the ingestion pathway.

2. Sources of Man-Made Actinide Elements

At the present time, most of the Pu entering terrestrial and aquatic systems originates from nuclear weapons testing. Accidental releases of ^{238}Pu to the environment have also occurred from reentry burnup of the SNAP-9A satellite power source in 1964, and ^{239}Pu has been released from accidents related to weapons uses of Pu. Compared with present-day levels of Pu entering terrestrial, freshwater, and marine ecosystems from global fallout, only small additional quantities of actinide elements will be released from fuel cycles to the environment. Based on current fuel cycle concepts, operations involving fuel reprocessing and fabrication will be the principal contributors of actinide elements to the environment. In a recent comprehensive assessment of environmental impact of Pu related to the LMFBR program, it was estimated that 0.4 mCi of man-made actinides would be released routinely for each 1000-MW(e) year of operation (2). Negligible routine releases are expected from waste management operations. The intent of future management of radioactive waste is to contain hazardous material in geologic formations for infinite periods of time (4).

Actinides released from different operations of the nuclear fuel cycle will enter the atmosphere as aerosols or particulates (Fig. 1). Small particles (less than $1\mu\text{m}$ in diameter) will deposit on land or water (2). Particulates eroded from the landscape will also enter freshwater and marine environments. Direct input from

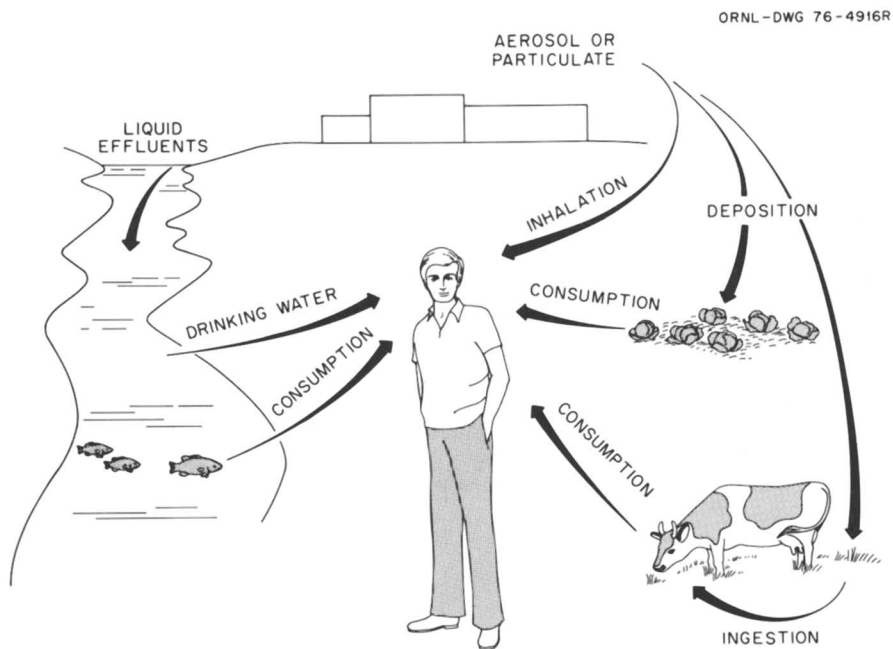


Figure 1. Major pathways through which man is exposed to actinide elements. Consumption of contaminated vegetables and inhalation are the most important terrestrial pathways. Consumption of aquatic plants is important likewise.

fuel cycle facilities to aquatic environments may also occur (5). The physical-chemical form of actinides entering terrestrial and freshwater environments from nuclear facilities may be different from refractory fallout of nuclear explosions. Source material possessing chemical characteristics different from refractory fallout can be expected to behave differently when released to the terrestrial and aquatic environments. Reaction of actinides with environmental media may also affect their availability to biota and long-term behavior in ecosystems.

3. Pathways of Exposure

Releases of actinides to the atmosphere during the finite period of fuel cycle operation will cause population exposure over the short term by inhalation. This mode of exposure has been extensively studied because it is considered responsible for the greatest initial radiological impact. A comparison of relative quantities of Pu inhaled or consumed shows that only a small fraction (10^{-6}) of the postulated releases is taken in directly by inhalation. A compendium of knowledge has been assembled on the effects related to the small fraction inhaled, but limited data are available on the fate and transport of the much larger fraction deposited on land and water. While only a small fraction of total ambient Pu is inhaled, assimilation by humans is stated to be much greater by the inhalation pathway than by the ingestion pathway [20% of lung burden (6) vs $3 \times 10^{-3}\%$ by gastrointestinal absorption (2)]. For detailed treatment of health hazards from inhalation, the reader is referred to ICRP Publication 19 (7), and to reports published by Richmond (8) and Bair and co-workers (9, 10, 11).

Actinide elements deposited on land and water can be incorporated into foods. Ingestion of food and water containing long-lived actinides will contribute to life-time exposures of man. Once these actinides are incorporated into foods, the most direct routes of consumption represent the highest levels of intake. Thus more actinide would be ingested from fresh vegetables, than from meat, than from milk. Results of a survey of Pu in the human diet confirms that vegetables contain higher levels of Pu than most other foods and drinking water. However, the tendency for some aquatic organisms to concentrate actinide elements requires that attention also be given to foods derived from freshwater and marine environments (12).

The low transport of Pu to humans by the food pathway is due to the failure of biological organisms to metabolize Pu at each stage of biological transfer. The USAEC provided data in the Environmental Statement for the LMFBR program illustrating that intake of actinide elements by ingestion would contribute 40% of total dose to bone and liver, the balance being contributed by inhalation (2). This estimate was based on assumptions believed to be conservative,* one of which was that "plants will incorporate

*Conservative means to provide a margin of protection because of possible uncertainties in assumptions or parameters.

actinide elements to a concentration that is 10% (on a weight basis) of the concentration in soil." The soil-to-plant transfer is one important parameter in the food pathway, because it serves as a prime mechanism for entry of actinide elements into foods. Much of man's life-time exposure will be dependent on the assimilation of actinides by plants and on the eventual ingestion of vegetable foods by humans.

Another biological transfer that influences ultimate deposition of actinide elements in critical organs of man involves absorption from the gastrointestinal (GI) tract. In the LMFBR Program Statement, an average value of 3×10^{-5} was used to estimate this fraction of Pu. This value generally describes absorption from the GI tract of oxide or hydrolyzed forms of Pu(IV) by mammals (7). Absorption was 500 times greater for Th(IV) than the Pu(IV) when nitrate solutions were administered to rats. Higher absorption from the GI tract also occurred when chelated Pu(IV) or Pu(VI) species were administered. Although limited comparative data are available on the absorption of other actinides by this pathway, particularly for Am, Cm, and Np, it appears that fractional uptake for these elements will exceed that observed for Pu.

Information is limited on the distribution of Pu and other actinides in aquatic environments, on their availability for uptake by resident fauna, and on the degree of bioaccumulation in aquatic foods that may be consumed by man. Most of the available information deals with marine environments in weapons testing areas and in areas associated with fuel reprocessing plants (13, 14, 15, 16). Reviews of the literature on plutonium in aquatic environments have been provided by Noshkin (16) and more recently by Schell and Watters (13). In general, results of research on Pu in aquatic environments indicate (a) most of the Pu in these environments is associated with sediment, with distribution coefficients* (Kd) ranging from 10^4 to 10^5 . Thus, contaminated sediments become the major source for intake by marine and freshwater biota; (b) Pu may be injected through the sediment-water interface to become hydrologically mobile after prolonged periods of residence in sediments; and (c) biomagnification in aquatic food chains (i.e., increasing concentrations with higher trophic levels) apparently does not occur.

4. Environmental Chemistry of Actinide Elements

The environmental chemistry of actinide elements at very low solution concentrations (nano-, pico-, or femto-molar), or in association with endemic environmental materials is poorly understood. There is evidence that chemical speciation and transformation of actinide elements in different environments will play a

* Distribution coefficient is defined as the ratio of the fraction sorbed to the fraction remaining in solution at equilibrium usually expressed in terms of ml g^{-1} .

major role in long-term immobilization, transport, and life-time exposure of humans. The environmental chemistry of the actinides, particularly Pu, is complex because of the tendency of the actinides to hydrolyze, polymerize, and exhibit variable valencies. Knowledge of the chemistry of actinide elements will be as important in studies of environmental behavior as it has been in understanding the biometabolism of Pu (7).

General Properties of the Actinides

The actinide elements display variable chemical characteristics depending on the valence state of the individual elements. Thus, elements in the same oxidation state exhibit similar properties while the same element in different oxidation states exhibits quite different properties. The problem of variable valencies is particularly important for Pu and Np because these two elements display multiple oxidation states in aqueous solutions.

The hydrolytic tendencies of metal ions are an important aspect of their aqueous chemistry. The order of decreasing tendency of these actinide species to complex with OH^- is $\text{Pu(IV)} > \text{Th(IV)} > \text{Am(III)} = \text{Cm(III)} > \text{U(VI)} > \text{Pu(VI)} > \text{Np(V)}$ (17). At environmental pH's, hydrolysis plays an important part in the behavior of all these elements except Np(V). The tendency of these elements to form complexes with organic and inorganic ligands follows the same order. Subsequently, hydrolysis (complexation by OH^-) competes with organic or inorganic complexation in neutral solutions containing dilute concentrations of these elements. An environmentally significant example of this relationship is the chemical fractionation that occurs between ^{238}U and its daughter ^{234}Th , or ^{234}U and its daughter ^{230}Th in nature. Uranyl $[\text{U(VI)}]$ ion, being less hydrolytic than Th(IV), tends to remain in solution as carbonate complexes while the more hydrolytic Th cation readily sorbs to abiotic and biotic surfaces and is removed from the water column of aquatic systems.

Sorption of Actinides

The differences in sorptive behavior of Th, Pu, U, and Np are evident by examining Table II. Plutonium and thorium isotopes at tracer concentrations (parts per billion, element mass/clay mass) were equilibrated for 24 hours with the $< 2\text{-}\mu\text{m}$ fraction (clay) of a silt loam soil. The pH of the equilibration solutions was 6.5 and the aqueous phase contained Ca at a concentration of 5 mM. Both tetravalent actinides failed to remain in solution. Whether this is a direct function of sorption mechanisms or simply related to the solubility of the ions in solution is not distinguished by the results. Uranyl ion was not removed to the same extent as the tetravalent species. Neptunium(V) sorbed very poorly. It should be noted that while Np(V) is a mono-charged cation, NpO_2^+ does not sorb like Na^+ .

Table II. Summary of Studies on Sorption of Pu, U, and Np to a Soil Clay

| Actinide | % sorbed ^a | K_d ^b |
|------------------------|-----------------------|--------------------|
| ²³⁷ Pu (IV) | 99.9 | 300,000 |
| ²³⁴ Th (IV) | 99.7 | 160,000 |
| ²³³ U (VI) | 95.6 | 4,400 |
| ²³⁷ Np (V) | 61.8 | 320 |

^aAt pH 6.5 and in 5 mm Ca(NO₃)₂ solutions

^b K_d is defined as the ratio of the amount adsorbed to the amount unadsorbed; the units are ml/g.

The low adsorption of Np(V) to soil colloids has also been reported by Routson et al. (18). Distribution coefficients for sandy subsoils were generally one or less than one, indicating a large fraction of the Np remained in solution. The K_d reported in Table II for Np(V) was 320 for the soil clay. Since the clay fraction of soils is generally the most reactive fraction, the conclusion from these results is that Np(V) should be the most mobile actinide element in the environment. Such mobility has important implications for long-term management of waste because of possible placement of wastes in geologic media that may not possess sorption characteristics as effective as surface soils. Furthermore, Pu(V), an analog species of Np(V), has been postulated to be the dominant soluble Pu species in natural waters (19).

Plutonium Oxidation State Studies

Plutonium can exist simultaneously in four oxidation states in acidic, aqueous solutions. All four oxidation state species [Pu(III), Pu(IV), Pu(V), and Pu(VI)] can be present in solution to give thermodynamically stable systems (17). At environmental acidities, Pu(III) is probably unstable to oxidation (20); thus, the three higher oxidation states are more likely to be encountered, with Pu(IV) being the most stable (17). Because of the relatively slow oxidation-reduction reaction (due to the Pu-O bond) occurring between Pu⁴⁺ and PuO₂²⁺, these two species should be the easiest to assay for by radiochemical methods. The presence of PuO₂⁺ [Pu(V)] is not easily detected at tracer concentrations. To date Pu(V) has not been found in our environmental-type experiments, and thus will not be discussed further, although it may be important (19).

While theoretical studies postulate different potential Pu oxidation state species in the environment (19, 21, 22), the actual presence of Pu(VI) in dilute, neutral solutions of Pu is an important aspect of environmental Pu research which has received inadequate experimental attention. In order to understand the mobilization mechanisms which might affect the short- and long-term distribution of Pu in the environment, the soluble species of Pu in experimental and natural systems must be understood. These soluble species might involve organic or inorganic complexes of Pu(IV) or inorganic complexes of Pu(VI). Organic complexes of Pu(VI) might occur, but given its fairly high oxidation potential, Pu(VI) is reduced by numerous organic groups, including substances found naturally (23). The fact that Pu(VI) is a cation species analogous to U(VI) would be important in terms of environmental mobility because of the tendency of U(VI) to form stable, soluble carbonate complexes.

Plutonium Dioxide. Plutonium dioxide is an important industrial form of Pu. Because of its highly insoluble nature, PuO₂ is expected to be fairly resistant to environmental weathering processes. Yet, the dioxide, because it is formed only at high temperatures, is not a stable phase once placed in contact with water (24). The measured dissolution rates of ²³⁹PuO₂ are extremely small, on the order of 10⁻¹⁰ g/cm² of oxide surface/day (24). This translates to about 10⁶ days for dissolution of a 0.3- μ m sphere of ²³⁹PuO₂. The higher specific activity ²³⁸PuO₂ undergoes dissolution at about 100 times this rate. The reason appears related to the higher specific activity affecting the integrity of the oxide lattice (24). Characterization of the Pu species dissolving from PuO₂ has to date been physical: ultrafiltration, ultracentrifugation, etc. Experiments are in progress at ORNL to evaluate the chemical characteristics of both dissolving and solid-phase Pu associated with PuO₂. This information has proved useful in understanding soluble Pu species present at dilute concentrations in a number of environmental systems.

Plutonium dioxide microspheres (149 to 177- μ m diam) were contacted with 10⁻³ M bicarbonate buffer (pH 7) for various periods of time. Some of the microspheres had been pre-incubated in pH 4 acetate buffer for two years prior to the bicarbonate experiments. Other microspheres were contacted with bicarbonate solution without any prior contact with water. The microspheres were primarily ²³⁹Pu (88.9% of Pu mass). The microspheres had been calcined at 1150°C and had a specific surface area of 0.012 m²/gram.

Table III shows that at least three forms of Pu were found in the bicarbonate solutions. For all samples, monomeric Pu(IV) and Pu(VI) species were found when aliquots were acidified to 1 M nitric acid. The identification of Pu⁴⁺ and PuO₂²⁺ was accomplished by several methods (25). Monomeric Pu(IV) was selectively determined by liquid-liquid extraction from 1 M HNO₃

Table III. Plutonium Species Identified in pH 7.0 Sodium Bicarbonate Solutions Contacting High-Fired PuO₂ Microspheres

| Microsphere sample ^a | Hours of HCO ₃ ⁻ contact | Soluble Pu (10 ⁻¹⁰ M) ^b | | |
|---|--|---|--------|------------|
| | | Pu(IV) | Pu(VI) | Refractory |
| 1. Dry PuO ₂ | 36 | 1.7 | 5.1 | 7.3 |
| | 1500 | 0.2 | 13.0 | < 0.01 |
| 2. Pre-incubated in acetate buffer | 190 | 0.15 | 0.38 | 10.0 |
| | 360 | 0.34 | 0.74 | 13.0 |
| | 528 | 0.48 | 0.92 | 11.0 |
| | 672 | 0.66 | 1.2 | 5.0 |
| 3. Same as (2), then washed with HCO ₃ ⁻ solution | 800 | 0.17 | 3.7 | < 0.01 |

^a2.2 - 2.7 mg of PuO₂

^bPu(IV) and Pu(VI) represent aqueous Pu species which revert to Pu⁴⁺ and PuO₂²⁺ in less than 1 hour in 1 M nitric acid. Refractory Pu includes Pu which did not revert.

with thenoyltrifluoroacetone (TTA) in xylene (26). The raffinate from this extraction was salted with calcium nitrate and extracted with hexone to determine monomeric Pu(VI) (27). Confirmation of these valence species was accomplished by selectively coprecipitating Pu(IV) on zirconium iodate and/or praseodymium fluoride (28). Plutonium(VI) was confirmed by precipitating sodium uranyl acetate (28). In addition to monomers, a species of Pu refractory to solvent extraction was found. This species displays the characteristics of Pu "polymer"; that is, it fails to extract into TTA-xylene prior to a rare earth fluoride precipitation step (Reference 27, Procedure 2), and it sediments in the ultracentrifuge. This polymeric material may be either classical Pu polymer or colloidal PuO₂ fragments originating from the microspheres.

Results in Table III suggest that the dynamics of the Pu species in solution is very complex. In general, there appeared to be an increase in the concentration of Pu(VI) with time. For example, for sample 2 which is representative of samples being studied over an extended time (months), the Pu(VI) concentration increased from 0.38 x 10⁻¹⁰ M at 190 hours of contact to 1.2 x 10⁻¹⁰ M after 672 hours of contact. The quantity of Pu(IV) was

always less than Pu(VI). Polymer-like species appeared to decrease with time. It was not clear whether the polymeric material was a precursor of the monomeric species; more precise data are required to reach this conclusion. The presence of Pu(III) and Pu(V) has not been demonstrated in any of the PuO₂ work. Small amounts of monomeric Pu(IV) and Pu(VI) species have been determined on the surface of distilled water-washed microspheres previously incubated in acetate buffer for two years.

Since the Pu of PuO₂ is tetravalent, the formation of Pu(VI) in this solution phase was totally unexpected. Extensive confirmatory experiments have been conducted by applying the various radiochemical methods previously mentioned as well as by using ²⁴²Pu (which is not present in the PuO₂ at any significant concentration) as an internal tracer in both the tetravalent and hexavalent states and by following its separation with the indigenous Pu in the analytical schemes.

Plutonium Oxide Dissolution Model. Based on the species observed dissolving from the oxide, a conceptualization of the fate of PuO₂ in the environment might be represented by Fig. 2. For this case, only monomeric Pu species are considered. For PuO₂ released to terrestrial or aquatic systems, a small fraction of Pu⁴⁺ and PuO₂²⁺, controlled by the hydrolysis constants for these species, is in "equilibrium" with soluble hydrolyzed and complexed forms of each species. The relative proportions of each oxidation state will be a function of pH, Eh, etc. (19). The various solution species are in "equilibrium" with the solid phase soil or sediment colloids. Undefined species are sorbed to the solid phase. While "equilibrium" is implied by the arrows, the net reaction represents very slow dissolution of PuO₂.

Reduction of Pu(VI). While Pu(VI) was observed as a soluble Pu species in the oxide work as well as in other studies where soluble Pu(IV) was initially added in clay sorption studies, the actual environmental importance of Pu(VI) is still unresolved. Both Pu(VI) and Pu(V) are relatively strong oxidants and are reduced by organic compounds (17). Reduction of Pu(VI) was observed when Pu(VI) was equilibrated with citric acid, humic substances extracted from soil, and acidic polysaccharides (23). This reduction of Pu(VI) by humic substances is illustrated in Table IV. After 13 days, 43% of the Pu(IV) and 84% of the Pu(VI) remained in solution. Of the Pu remaining in solution in the Pu(IV) experiment, only 32% would extract into TTA-xylene [i.e., ionic Pu(IV)] upon acidification of an aliquot of the Pu(IV)-bicarbonate solution. The remainder of the unextractable, soluble Pu was found to be mostly Pu polymer as well as a small amount of Pu(VI) formed through disproportionation of Pu(IV). When Pu(VI) was the initial

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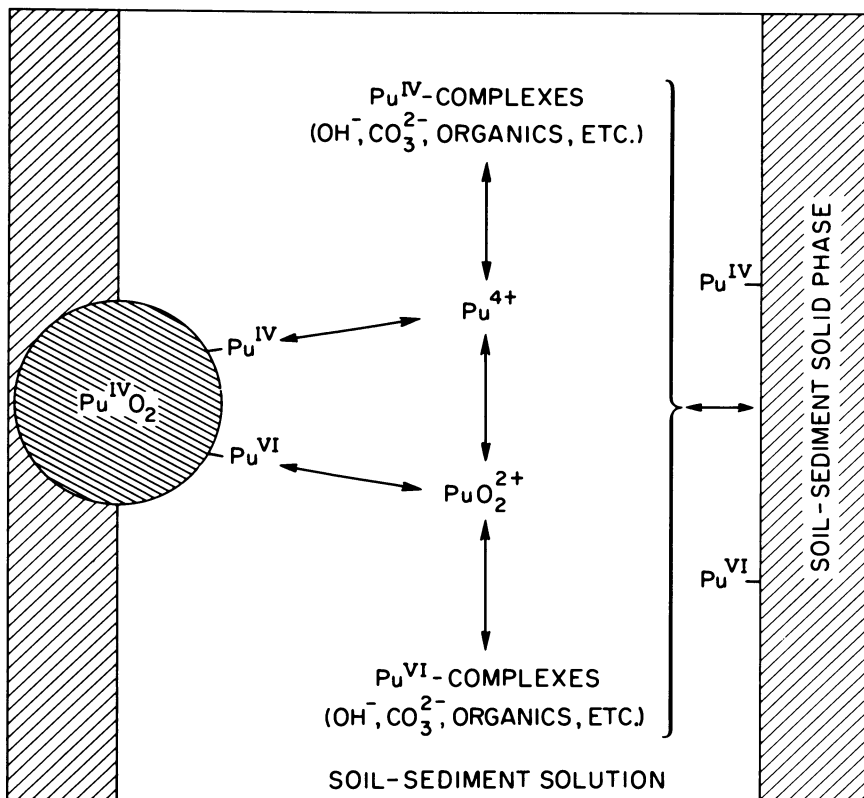


Figure 2. Possible fate of soluble plutonium species released during the dissolution of PuO_2 in aerobic environmental media. Both $\text{Pu}(\text{IV})$ and $\text{Pu}(\text{VI})$ species will complex with endemic ions or sequestering agents and eventually will be sorbed to the solid phase of soil or sediment.

Table IV. The Stability of $^{239}\text{Pu}(\text{IV})$ and $^{239}\text{Pu}(\text{VI})$ in 10^{-3} M NaHCO_3 at pH 8

| Plutonium distribution in aqueous phase | | | | |
|---|----------------------------------|--------------------------------------|--------------------------------------|--|
| Time (days) | Initial Pu form | Total remaining (% of initial added) | TTA extractable (Pu^{4+}) | |
| | | | Total (10^{-8} M) | Fraction of remaining ^a (%) |
| 13 | IV | 43 | 5.71 | 32 |
| | VI | 84 | 4.24 | 11 |
| 27 | IV | 17 | 2.18 | 30 |
| | VI | 59 | 1.78 | 6 |
| 36 | (added fulvic acid) ^b | | | |
| 44 | IV | 16 | 2.27 | 37 |
| | VI | 52 | 19.5 | 82 |

^aFraction of Pu in the aqueous phase extracting as Pu^{4+} .

^bFulvic acid, 10^{-3} M, as carboxyl groups.

valence state, 11% of the soluble Pu behaved as Pu(IV). Similar extraction results were obtained for 27 days of equilibration, showing further total Pu loss. After 36 days, fulvic acid, an acid-soluble humic substance obtained from soil, was added to the Pu-bicarbonate solutions. Eight days later it was observed that the fulvate had slowed the loss of Pu from solution and had apparently reduced the Pu(VI) present. This can be concluded from the fact that the amount of TTA extractable Pu(IV) in the Pu(VI) experiment increased from 1.78 to 19.5×10^{-8} M, indicating conversion from the non-TTA extractable Pu(VI) to the extractable Pu(IV) monomeric form. However only 82% of the Pu in the Pu(VI) experiment would extract into TTA-xylene. This does not necessarily mean incomplete reduction, because if monomeric Pu(IV) is added, the same extraction percentage results. The reason for the less than 100% extraction is competitive chelation of Pu(IV) by the fulvic acid, inhibiting complete extraction.

5. Uptake of Actinide Elements by Plants

The previous results show that the potential for entry of Pu and other actinides into food chains will be highly dependent on the environmental chemistry of actinides in the environment. An important question is whether chemical transformations in the environment will increase or decrease the uptake of these elements by plants and other organisms that are consumed by man. Long-term projections on changes in availability to biological systems are uncertain. There is no historical geochemical data base to substantiate hypotheses of either increased or decreased uptake and consequent hazards from man-made actinide elements resulting from long-term environmental interactions.

Plant Uptake of Plutonium from Soil 30 Years After Initial Contamination

One important source of time-dependent information that is presently available on the plant uptake of man-made actinide elements is described from environmental contamination caused by the Manhattan Project 30 years ago. Research on the cycling of actinide elements at such contaminated sites provides insight on how biogeochemical processes might affect the long-term behavior of Pu, Am, and Cm. Results are available from a site at Oak Ridge where waste effluents released from laboratory operations have contaminated terrestrial and aquatic environments with small quantities of fission and actinide elements. Following precipitation with soda ash, waste treatment effluents were released to White Oak Creek. Trace levels of Pu, Am, and Cm were deposited along the water course, in an intermediate retention pond, and finally in White Oak Lake(WOL). Deposition of these elements in the retention pond occurred over a 6-month period in 1944. From the time the pond drained in late 1944, a typical floodplain

forest has developed at this site (29). The concentration of $^{239+240}\text{Pu}$ in the top 12-cm layer of soil ranged from 25 to 150 pCi/g.

Laboratory studies which characterized the behavior of Pu in the soil showed that most of the Pu is tightly bound to the soil because extractants (citrate and diethylenediaminepentacetic acid (DTPA) that complex Pu removed less than 30% of the Pu from soil (23),(30). Part of the soil-bound Pu is associated with humic substances. The general mobility of the soil-bound Pu was evaluated by equilibrating the soil with cation exchange and chelating resin over a 14-week period. No transfer of Pu to the cation exchange resin occurred, and a maximum of 12% transferred to the chelating resin (23). These low transfer values indicate that the Pu is not very mobile in terms of diffusion and probably is not leaching from the soil. This is expected in view of the strong sorption observed for Pu (Table II). The predominant oxidation state appears to be Pu(IV). By using 10% sodium bicarbonate, an extractant which should preserve any Pu(VI) present, 58% of the soil Pu extracted. But at least 90% of this extractable Pu behaves as Pu(IV) rather than Pu(VI).

Research since 1974 has provided information on the uptake of Pu by native and crop plants 30 years after initial contamination of the floodplain soil. The distribution of Pu in native plants and soil has been determined for the 2 hectare (ha) floodplain, and assimilation of Pu has been determined for forage and vegetable crops planted in a field plot established on the floodplain. A measurable fraction of the Pu was assimilated by plants growing in the contaminated soil (Table V). Plutonium was determined in the foliage of 65% of the tree samples. When detectable*, the concentration ratios (CR) (see footnote a, Table V, for definition of CR) for Pu in native vegetation ranged from 2×10^{-3} to 6×10^{-5} . Higher CR values were determined for understory shrub and herbaceous species.

Forage and vegetable crops from the floodplain field plot also assimilated Pu (Table V). The average Pu concentration in foliage of both bushbean and soybean was 0.1 pCi g^{-1} dry wt of biomass. Millet foliage contained 0.03 pCi g^{-1} . Concentrations of Pu in fruits were generally 10 to 50% of the amount in foliage except immature soybean fruits, which contained levels of Pu equivalent to that of leaves. Concentrations of Pu in the vegetable species were twice that of native herbaceous species. The average concentration ratio for vegetable and soybean foliage was 2×10^{-3} . Tomato fruit exhibited the lowest CR value of all the vegetable tissues examined.

*Detectable limit $> 0.001 \text{ dpm g}^{-1}$ based on analysis of 10 g.d.w. samples of vegetation.

Table V. Content of $^{239,240}\text{Pu}$ and Concentration Ratios for Native and Crop Vegetation of a Floodplain Contaminated in 1944

| Plant | $^{239,240}\text{Pu}$ content | | Concentration ratio ^a | |
|---------------------------|-------------------------------|----------------------|----------------------------------|----------------------|
| | Average (pCi/g) | S.E. ^b | Average CR | S.E. |
| Tree species ^c | 2×10^{-3} | 0.5×10^{-3} | 6×10^{-5} | 1.5×10^{-5} |
| Understory species | | | | |
| Herbaceous | 5×10^{-2} | 1.2×10^{-2} | 2×10^{-3} | 0.2×10^{-3} |
| Shrub | 1×10^{-2} | 0.5×10^{-2} | 2×10^{-4} | 1.0×10^{-4} |
| Field crops | | | | |
| Millet | 3×10^{-2} | 1.7×10^{-2} | 2×10^{-4} | 0.7×10^{-4} |
| Bushbean | 1×10^{-1} | 0.2×10^{-1} | 2×10^{-3} | 0.2×10^{-3} |
| Soybean | 1×10^{-1} | 0.2×10^{-1} | 2×10^{-3} | 0.4×10^{-3} |
| Tomato fruit | 5×10^{-3} | 1.8×10^{-3} | 1×10^{-4} | 0.3×10^{-4} |

^aConcentration ratio (CR) is defined as $[\text{Pu}] \text{ vegetation} / [\text{Pu}] \text{ soil}$ on a per gram dry weight basis. Soil concentrations of $^{239,240}\text{Pu}$ used in the calculation of CR values ranged from 25 to 150 pCi/g dry weight for entire floodplain. Field crops were grown on soil (pH 7.6) containing 63 ± 0.4 pCi Pu/g of soil.

^bStandard error of mean estimate.

^cComposite data for ten hardwood species.

One important feature of these results is that the CR values represent uptake of Pu by plants in an environment where resuspension or surface contamination of foliage is not considered to be a serious problem. Furthermore, leaf surfaces were washed and wiped clean before samples were processed for Pu analysis. Thus, uptake of Pu by vegetation from the contaminated floodplain essentially represents assimilation by the root pathway.

Another feature of these results is their high variability. Measured assimilation of Pu by a given species or vegetation type may range over an order of magnitude; standard errors are typically 25 to 50% of the mean; coefficients of variation (CV) frequently exceed 100%. This level of precision is not unusual for research results obtained from natural systems.

The results of Table V illustrate that only a small fraction of Pu from the floodplain site is assimilated by native and cultured plants. The large majority (>99%) still remains associated with soil. Concentration ratios of 10^{-3} indicate that plants are not able to extract Pu effectively from soil of this contaminated environment.

Variability in the Estimates of Actinide Uptake by Plants

Great differences have been reported on the fraction of Pu, Am, and Cm assimilated by plants from soil. When results are expressed in terms of CR's, the values vary by as much as eight orders of magnitude according to different data sets reported for Pu and Am (Fig. 3). The large range of variability for Pu is probably dependent on chemical characteristics of the source material, on experimental conditions, and on unique characteristics of environments where field observations have been made. For example, the lowest CR values for Pu (10^{-6} to 10^{-5}) are observed for plants grown in soil contaminated with Pu solutions (31, 32, 33). With such amendments, the Pu possibly becomes a polymerized form on addition to the soil, because neutralization of acid solutions containing dissolved Pu may yield aggregate-type polymers. Conceivably these types of amendments produce micro-aggregates of Pu, a polymeric form rather than mono-dispersed Pu. In the micro-environment of the plant root system, the nonuniform Pu distribution resulting from aggregation would lead to lower assimilation of the element.

In nearly all pot culture experiments, the presence of a chelator increased the uptake of Pu and Am by plants (33, 34, 35, 36). The chelator likely favors mono-dispersed Pu forms and affects sorption of the elements to the solid soil phase. Because the chelator tends to promote mobility, it enables a greater fraction of the actinide to be assimilated by roots. The chelator is also able to complex soil Am directly and increase its uptake by plants (36).

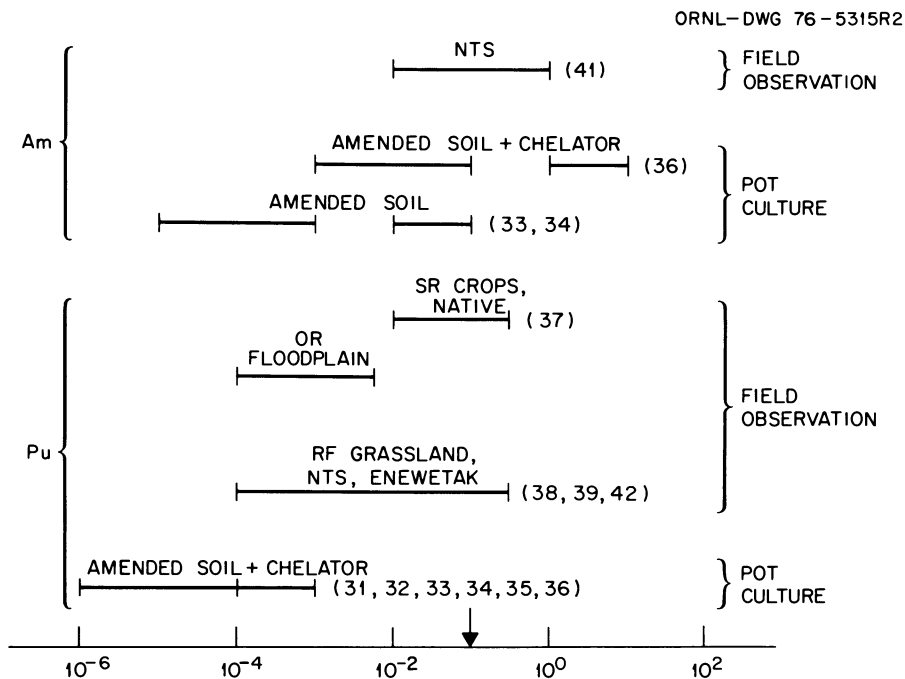


Figure 3. Concentration ratios (CR) for Pu and Am. CR is defined as the simple ratio of actinide concentration for plants vs. soil on a dry weight basis. Sites where data sets have been collected are NTS (Nevada Test Site, Nev.), SR (Savannah River, S. C.), OR (Oak Ridge, Tenn.), RF (Rocky Flats, Col.), Enewetak Atoll, South Pacific. Arrow denotes approximate value used in the LMFBR Program Impact Assessment (2).

The main feature of the collective data of Fig. 3 is that higher burdens of actinide elements occur under field conditions. The higher CR's determined under field conditions represent both uptake by roots and contamination of foliar surfaces. The array of values given in Fig. 3 make one point certain; a constant coefficient of uptake should not be used for all actinide elements nor should a single coefficient be applied to diverse environments. Parameters for simulation models should be a function of the respective actinide, should depend on the environmental chemistry of the actinide, and should be related to specific conditions prevailing in the environment being evaluated.

In addition to root uptake being responsible for maximum Pu CR's of 10^{-3} (Table V), contamination of foliar surfaces is responsible for the higher CR values exceeding 10^{-1} (37, 38, 39). Higher levels of Pu in plant foliage from direct foliar contamination is not surprising because this pathway was considered to be the principal mode of assimilation of fallout radiocesium by plants (40). Over 90% of ^{137}Cs in plants occurs from direct deposition, and it is reasonable to assume that airborne actinide elements associated with particulate vectors would behave similarly. Thus, where actinides are released to the atmosphere, as in postulated releases from nuclear fuel cycles, the maximum actinide burdens of vegetation would be associated with direct deposition on foliage. This has indeed been observed in the vicinity of chronic anthropogenic sources such as stack effluents at Savannah River. Measurements of isotopic ratios of Pu released from the stack and the Pu of foliage indicated that most of the Pu of plants came from fresh deposits of airborne Pu (37).

Foliage can also be contaminated by actinides associated with resuspended soil particles deposited on foliar surfaces (38, 39). In arid, windy environments, dust and soil particles become airborne, deposit on foliar surfaces, and may be retained by hirsute structures or crevices of leaves (41). Concentration ratios for both Pu and Am that approach 10^0 (Fig. 3) are observed for these types of environments (e.g., the Nevada Test Site). Concentration ratios approaching 10^{-2} for Rocky Flats grassland species are also related to deposition of windblown Pu on foliar surfaces (38).

An important observation concerning the CR's for vegetation of the Oak Ridge floodplain is that only a small fraction of Pu has been assimilated by plants following exposure to soil, geochemical, and ecological processes for a period of 30 years. We believe that the Pu in the floodplain soil is mono-dispersed (monomeric) because most of the Pu is extractable with cold 8 N HNO_3 , an extractant that does not readily depolymerize Pu polymer. Other mild extractants also removed Pu from the floodplain soil (see previous discussion). The mono-dispersed Pu of the floodplain soil has led to CR values that exceed those determined from pot culture tests by an order of magnitude. Yet the CR values are factors of 10 to 100 less than those for environments where

deposition on leaf surfaces is the main factor contributing to observed levels of Pu in vegetation. A fraction of the Pu in the soil of the Oak Ridge floodplain appears mobile as measured by resin transfer tests and may be available for uptake by plants via the root pathway. Whatever soluble fraction exists, however, is not readily assimilated by native or cultured species of the floodplain. While a small fraction of Pu indeed cycles in biotic components of this ecosystem, the very large majority remains associated with soil.

6. Distribution of Pu and Other Actinides in Components of White Oak Lake

Research on the behavior of Pu and other actinides in aquatic ecosystems of Oak Ridge National Laboratory involves field studies at White Oak Lake, a 10.5-ha impoundment formed by Mahattan Project operations. This final settling basin has received releases from the Laboratory and associated facilities since 1944. Some of the key questions addressed are: (a) the partitioning of Pu between the suspended particulate and soluble fractions in the water column, (b) the partitioning of Pu between the bed sediments and overlying water column, (c) the uptake of Pu by biota from these fractions, and (d) food chain transfers and trophic effect on Pu concentrations in biota of the system. A conceptual model of the internal kinetics and routes to man is illustrated in Fig. 4.

Solution Behavior of Actinides in White Oak Lake Water

Differences in behavior of actinides in the aquatic environment are shown by the data in Table VI. In WOL, we have noted that about 12% of the total Pu in the water column passes a 0.45- μ m filter and also passes a 10,000 mol wt membrane filter. Essentially all of this soluble Pu is retained when passed through an anion exchange column. Curium-244 behaves somewhat differently in that about 50% of the activity in WOL water is soluble, but it also behaves anionically. The reasons for a negative charge on Pu and Cm are complex and are not understood, but one possible explanation is the presence of Pu(VI) carbonate complexes, analogous to the soluble uranyl carbonate complexes found in natural waters. Experiments are in progress to determine the valence state of this soluble form of Pu. Another explanation for the observed soluble Pu would be organic complexes.

Behavior of Actinides in Biotic Components of White Oak Lake

Results from analyses of samples of various components of the lake system showed a general trend of decreased concentration of Pu at higher trophic levels (shad vs larger-mouth bass)

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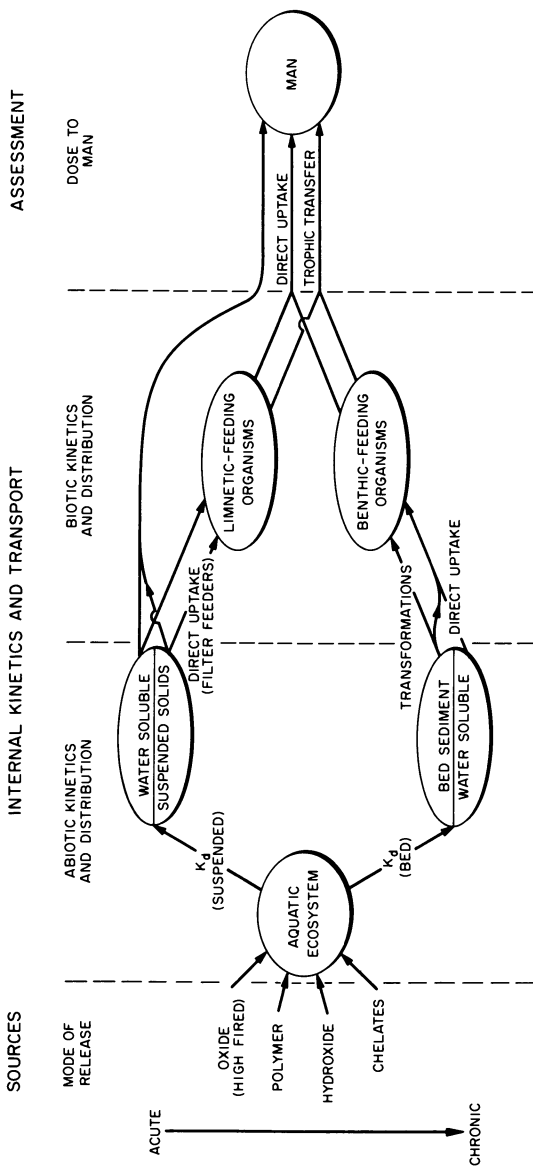


Figure 4. Potential pathways to man for actinides entering aquatic ecosystems, and internal kinetics in the environment which may affect availability for transfer to man

Table VI. Solution Behavior of Pu and Cm in White Oak Lake Water

| Transuranic | Characteristic fraction | Percent of total |
|---------------------------|---------------------------------|------------------|
| $^{238+239+240}\text{Pu}$ | Soluble (< 0.45 μm) | 12 |
| | anionic | 12 |
| | cationic | 2 |
| | < 10,000 mol wt | 12 |
| ^{244}Cm | Soluble (< 0.45 μm) | 50 |
| | anionic | 45 |
| | cationic | 3 |
| | < 10,000 mol wt | 40 |

(Table VII). Organisms living in or on the bottom of sediments of the lake have Pu concentrations that are two or three orders of magnitude higher than for predatory fish, large-mouth bass, and bluegill. Filamentous algae associated with sediments in shallow areas of White Oak Lake had the greatest concentration of Pu of any biotic component measured. Levels of Pu observed in various fish species were related to their feeding habits. Gastrointestinal contents of goldfish, gizzard shad, and bluegill had Pu concentrations higher than any biotic form in the system (Table VII), indicating the source of intake was probably sediment. Further evidence of sediment ingestion by these fish was the fact that the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio of gut contents was similar to that measured in sediments.

The major Pu pool in WOL is associated with sediments. The speciation and chemical form of Pu in this sediment system has not been determined, but a fraction of the sediment-plutonium inventory may be in a chemical form (i.e., chelated, associated with organic matter, complexed with inorganic substances, or soluble) that is more mobile in the system than the balance of the inventory. While ingestion of sediment appears responsible for the highest levels of Pu (body burden) in fish, this mechanism apparently has not enhanced availability of Pu to biota because concentration factors for biota in WOL were relatively low compared to those observed at other study sites. Concentration factors for biota of WOL were low even though 12% of the plutonium in the water column was a soluble form (Table VI).

Long-term chemically and/or biologically mediated transformations of plutonium compounds may be expected to occur in aquatic systems. These transformations may result in plutonium being complexed by naturally occurring chelating agents such as carboxylic acids (citrate), fulvic acid, or proteins. Several experiments were carried out in our laboratory to determine effects of pH, chelated, and non-chelated chemical forms on absorption of Pu from the GI tract by channel catfish (*Ictalurus punctatus*), an important benthic-feeding food fish in the United States. Results showed that mean absorption ranges from 1.3 to 3.1% when polymeric forms are administered. Essentially no effect on uptake was seen for administrations at $\text{pH} \sim 2$. The presence of 10^{-3} M complexing agents had little effect on uptake. Retention in different fish tissues after 30 days was 0.6% of the original dosage. The fraction retained is comparable to the values reported for immature mammals (0.25%) (43).

Experiments in which monomeric Pu was ingested in the presence of excess complexing agent showed significant differences in uptake as a function of the complexing agent used (1.5% Pu-fulvate vs 10.5% Pu-citrate). Uptake of the monomeric fulvate complex, a chemical form of Pu that may be associated with organic fractions of soils and sediments, was comparable to that of the polymeric form.

Table VII. Concentrations of $^{239,240}\text{Pu}$ and Concentration Factors for Fishes from White Oak Lake

| Species | $^{239,240}\text{Pu}$ Content | | | | Concentration Factor ^{c,d} | |
|-----------------|-------------------------------|--------------------|---------------------|--------------------|-------------------------------------|------|
| | Carcass ^a pCi/g | S.E. ^b | G.I. Tract pCi/g | S.E. | C.F. | S.E. |
| Largemouth bass | 2×10^{-4} | 6×10^{-5} | 6×10^{-3} | 4×10^{-4} | 0.4 | 0.2 |
| Bluegill | 1×10^{-3} | 8×10^{-4} | 4×10^{-2} | 5×10^{-5} | 3 | 2 |
| Goldfish | 1×10^{-3} | 1×10^{-3} | 8×10^{-2} | 3×10^{-2} | 3 | 3 |
| Shad | 2×10^{-3} | 3×10^{-5} | 4×10^{-1} | 7×10^{-2} | 4 | 0.1 |

^aTotal fish minus G.I. Tract

^bStandard Error

^cConcentration Factor (CF) is defined $[\text{Pu}]$ in organisms (wet weight)/ $[\text{Pu}]$ in water. Water concentration of Pu used in calculation of CF values = 4×10^{-4} pCi/g.

^dC. F. values for carcass.

Midge larvae (*Chironomus*), one important link in aquatic food chains, were reared in aquatic microcosms (organic sediment-water) equilibrated with ^{239}Pu . Distribution coefficients for sediment exceeded 10^4 in all microcosms indicating that the great majority of the Pu was associated with sediment. Sediment and gut contents of *Chironomus* larvae were radiologically indistinguishable, indicating that ingestion of contaminated sediment was an important mode of Pu intake. Mean ratios of total Pu burden of different tissues to that of gut contents were 4.4×10^{-3} and 6.5×10^{-3} for tissues (GI tract removed) and tissues plus GI tract (gut contents removed), respectively. These studies indicated that there is no significant biomagnification of Pu in the *Chironomus*-sediment component of a trophic system involving benthic-feeding biota.

7. Discussion

Chemical Behavior of Actinide Elements in Environmental Media

Results from research on the environmental chemistry and food-chain transport of actinides are beginning to provide an understanding of the long-term consequences of U, Pu, Am, Cm, and Np released from nuclear fuel cycles to the environment. Our results have illustrated that the ultimate environmental behavior of actinides will be determined by their environmental chemistry. Therefore, we have placed considerable emphasis on discussing the oxidation states of the actinides and on how the variable states may influence their behavior in the environment. It is important that attention is given to this subject because in large measure, the oxidation state of Pu, for example, governs the environmental behavior of that element. While Am(III), Cm(III), and Th(IV) are relatively stable oxidation states, Np and particularly Pu warrant close attention because of the potential presence of multiple oxidation states. In Table II the order of sorption of actinide oxidation states was IV>VI>V. Routson, et al. (18) showed that Am(III) was adsorbed to soil stronger than Np(V). Table VI demonstrates that Pu is more strongly associated with particulate phases in White Oak Lake water than is Cm. The reviews of Francis (46) and Price (47) concluded that Am and Cm are generally less strongly sorbed to soil than Pu. Plutonium(III) is sorbed more strongly than Pu(VI) (48, 49). The order of actinide valence state adsorption to environmental colloids thus appears to be IV>III>VI>V. This order follows the same trend of the hydrolytic behavior of oxidation states for these elements.

To interpret the behavior of Pu in experimental studies, it is important to define the chemical species present. The addition of Pu(IV) as nitrate or chloride salts to soil used in laboratory or greenhouse experiments does not guarantee that Pu polymer, Pu(VI), and possible other oxidation states are absent. The results

obtained from such studies are interesting, but may lead to conclusions that are not necessarily valid. For example, in adsorption experiments using Pu(III), Pu(IV) and Pu(VI), the order of sorption was Pu(III)>Pu(IV)>Pu(VI) (48, 49). Because concentrations of Pu(IV) in these experiments approached 10^{-6} M, the possibility of disproportionation of Pu(IV) into Pu(III), Pu(VI), and Pu(V) must be considered. If Pu(VI) was present in the Pu(IV) sorption studies, then the measured sorption results may not be valid. In similar studies conducted at ORNL at 10^{-8} M Pu(IV), formation of Pu(VI) has been observed. If laboratory experiments using Pu and other actinides are to aid in interpreting the behavior of these radionuclides in ecosystems, artifacts associated with experimental methodology must be recognized or eliminated. Mechanisms affecting Pu uptake by organisms likewise cannot be delineated until chemical forms and species in environmental media are defined and understood.

Entry of Actinides into Terrestrial Food Chains

The enlarged data base on the uptake of transuranic elements by food plants is improving the confidence that can be placed in estimates of life-time hazard to man by the ingestion pathway. Because of uncertainties about the long-term environmental behavior of actinide elements, including the magnitude to which these elements will be assimilated by plants and be consumed by man, the USAEC employed a conservative plant uptake value (approximately equivalent to a CR of 10^{-1}) in their environmental assessment of the LMFBR program (2). Accordingly, ingestion of vegetable food would contribute approximately 40% of the dose to liver and bone at this magnitude of actinide entry into vegetables. The contribution to dose from actinides in meats was ignored in the LMFBR assessment, because results of a dietary survey (12) showed that meat possesses one-fifth the radioactivity of vegetables. As more information becomes available on the plant uptake parameter, one may ask, "Is a CR of 10^{-1} , representing entry of actinides into the terrestrial food chain, overly conservative, realistic, or too low for estimates of life-time dose to man by the food pathway?"

From new data and from evaluation of published information, it appears that the magnitudes of uptake of actinide elements by plants from contaminated soil generally are less than the value used in the assessment of radiological impact for the LMFBR environmental assessment. The CR value of approximately 10^{-1} used in the impact assessment exceeds most observed values for Pu (Fig. 3), and appears conservative for incorporation into foods by the root pathway. Even after 30 years of residence time in the biologically active environment of the Oak Ridge floodplain, greater than 99% of the Pu in this ecosystem remains associated with the soil. The observed CR value is 10^{-3} . For this time frame, there is no evidence that ecological or soil processes will cause the soil-to-plant transfer of Pu to approach the 10^{-1} value used in the LMFBR

assessment. The recent data on assimilation of Pu by plants from soil tend to reinforce a conclusion reached more than a decade ago that Pu is strongly excluded from plants (50). Consequently, it would appear that the 10^{-1} value for Pu is adequate or perhaps too conservative for estimating life-time radiological impact from consumption of chronically contaminated foods.

In cases of suspected surface contamination of foilage, the CR for Pu approaches or exceeds 10^{-1} . For modes of direct contamination of vegetative surfaces, the value of 10^{-1} used for dose estimation would then appear realistic. When chronic airborne sources of Pu exist (global fallout, resuspension of contaminated soil, stack releases from reprocessing plants), incorporation of Pu directly into foods (bypassing the soil) is by far the most important mechanism of transport involving the food-chain pathway (40, 51), although the relative "availability" of surface-deposited vs biologically-assimilated Pu remains to be studied. It is difficult to distinguish between the fraction of contaminant retained on the surface of leaves and the fraction assimilated metabolically into internal tissues of foliage. Such distinction may not be important if only concentration of the element in the food consumed by man or livestock is the important factor. In any case, chronic anthropogenic release of Pu to the atmosphere followed by direct contamination of foliage would lead to the highest levels of Pu in plants. Thus, incorporation of actinides into foods by this pathway followed by ingestion and deposition of Pu in bone and liver of human populations may result in levels of Pu in these organs that approach those derived from inhalation.

The limited information on the plant uptake of other actinide elements (U, Np, Am, Cm) indicates that higher CR values can be expected relative to those observed for Pu. Values for Am based on uptake by roots and from deposition on foliage approach or exceed the 10^{-1} value used in the LMFBR assessment; thus, the value used in dose assessments is probably realistic but not conservative. Price (32) reported CR values of 10^{-1} to 10^{-2} for ^{237}Np assimilated by the root pathway. Based on these data and on the low K_d for Np (Table II), it appears that this element exhibits a higher mobility than the other actinides. A potential CR $> 10^{-1}$ due to uptake from soil and from direct contamination of foliage is hypothesized for Np. Curium-244 uptake by the root pathway yielded CR values of 10^{-3} to 10^{-4} , according to pot culture experiments (32, 52).

Relationships Between Chemical Behavior and the Uptake of Actinides by Biological Organisms

The array of information available on the uptake of actinide elements by plants permits qualified statements on the probable order of soil-to-plant transport. Plutonium exhibits the lowest level of uptake. Neptunium appears to be assimilated to the greatest extent, and U, Am, and Cm have intermediate values of

assimilation. A likely order of uptake by plants would be $\text{Np} > \text{Am} = \text{Cm} \sim \text{U} > \text{Pu}$ based on summarized results from several sources (32, 53). Because CR values for all five elements are very limited, and because data are not available for all five elements for the same experimental conditions, the relationship should be considered provisional. More data are needed for assimilation of Np, Am, U, and Cm by plants.

It appears that both the order of sorption of actinides to colloids and their order of uptake by plants is affected by oxidation state. The postulated order of uptake by plants ($\text{Np} > \text{Am} = \text{Cm} \sim \text{U} > \text{Pu}$) is approximately the inverse of their order of hydrolysis and their order of adsorption of oxidation states to colloids [$\text{Pu(IV)} > \text{U(VI)} \sim \text{Cm(III)} = \text{Am(III)} > \text{Np(V)}$]. Based on reported adsorption results for Pu(VI) (48, 49), and on preliminary results from our sorption studies dealing with oxygenated-"yl" species, the position of Pu(VI) would be between U(VI) and Np(V). Results from one study (48) showed that Pu(VI) is assimilated by barley plants more readily than Pu(IV) or Pu(III). The relative contribution of either Pu(IV) or Pu(VI) to the total quantity of Pu assimilated by plants from contaminated environments is not known, because the concentration of either oxidation species would be dependent on the redox environment near the plant root. It should be clearly understood that these ordered schemes are provisional, because of limited data on the uptake of Am, Cm, and U by plants.

The importance of oxidation state in evaluating the long-term biogeochemical behavior of Pu cannot be overemphasized. Results from laboratory and field research indicate that a small fraction of Pu in different environments appears soluble. This fraction may exist as complexes formed from either organic or inorganic substances, or it may be related to the presence of the Pu(VI) oxidation state. The potential existence of Pu(VI) in environmental or biological systems has profound implications for two reasons. First, the Pu(VI) form would most likely be the chemical species responsible for observed mobilities of Pu in the environment, while the majority of the Pu would remain immobile as Pu(IV). Redox conditions that determine oxidation species, thus the amount of Pu(VI) in ecosystems, will influence the long-term mobility of Pu. Second, if the Pu(VI) species can exist in bioenvironmental media, its greater characteristic mobility would influence its metabolism and membrane transport by biological organisms. According to summary data on absorption of Pu from the GI tract (7), absorption of the Pu(VI) species appears several orders of magnitude greater than that of other oxidation states and chemical forms. If the small fraction of mobile Pu in the environment is indeed the Pu(VI) species, then it may be necessary to consider a transfer coefficient greater than the 3×10^{-5} that conventionally is used in models of uptake of Pu from the GI tract when calculating dose to humans. In reference to long-term behavior of Pu in man's environment, it is important

to know the extent to which chemical transformations (i.e., chelation, oxidation or reduction) will increase or decrease the availability to biological organisms of Pu and other actinides.

The hypothesis that the Pu(VI) species is responsible for the limited mobile fraction of Pu needs further study. There is strong evidence that a small fraction of Pu is mobile and the Pu(VI) species is stable in simple simulated environmental systems. Yet Pu(VI) is also reduced to Pu(IV) by endemic organic substances. The environmental chemistry of Pu in natural and agricultural ecosystems is complex, and the various complexities undoubtedly are responsible for some of the variability reported for Pu mobility in different environmental systems.

Behavior of Plutonium in Freshwater Food Chains

Sediment serves as the primary repository in the aquatic environment for Pu and other actinides entering freshwater ecosystems. A significant portion of Pu is thought to arrive at the sediment surface as a result of incorporation (adsorption and/or absorption) by phytoplankton (algae) and subsequent sedimentation of dead cells to the bottom (54, 55). In a highly enriched waste-settling pond, Emery et al. (56) found that a filamentous algal floc associated with sediment actually had concentrations of Pu that exceeded sediment levels. There was a general decrease in Pu concentrations at higher trophic levels in that study. Concentration factors (see footnote c, Table VII, for definition) were reported to range from 10^5 in goldfish muscle to 10^8 in algal floc. Since the pond received decontamination wastes, including chelating agents, these extremely high CF values may be related to increased availability of Pu for uptake when associated with chelating agents. The primary source of Pu to biota of this system appears to be sediment.

Trophic level studies indicated a decrease in Pu concentration with increase in trophic level (57). The CF values for benthic organisms and bottom feeding fishes were significantly higher than for piscivorous fish or for planktivorous fish (~ 1000 and 270 vs 4 and 20, respectively). Concentration factors derived from studies in a wide variety of freshwater and marine ecosystems are shown in Fig. 5. Invertebrates and algae exhibit higher CF values ($10^0 - 10^4$) than fishes (0.0 - 50). The differences in CF values probably reflect differences in the source and chemical form of Pu at the various study sites.

Behavior of Plutonium in Marine Food Chains

Plutonium levels in marine invertebrates generally exceed the levels observed in marine vertebrates. Marine benthic invertebrates and those invertebrate predators feeding on benthic organisms have the highest levels of Pu. Noshkin et al. (57) found the moon shell, a carnivorous snail that feeds on other

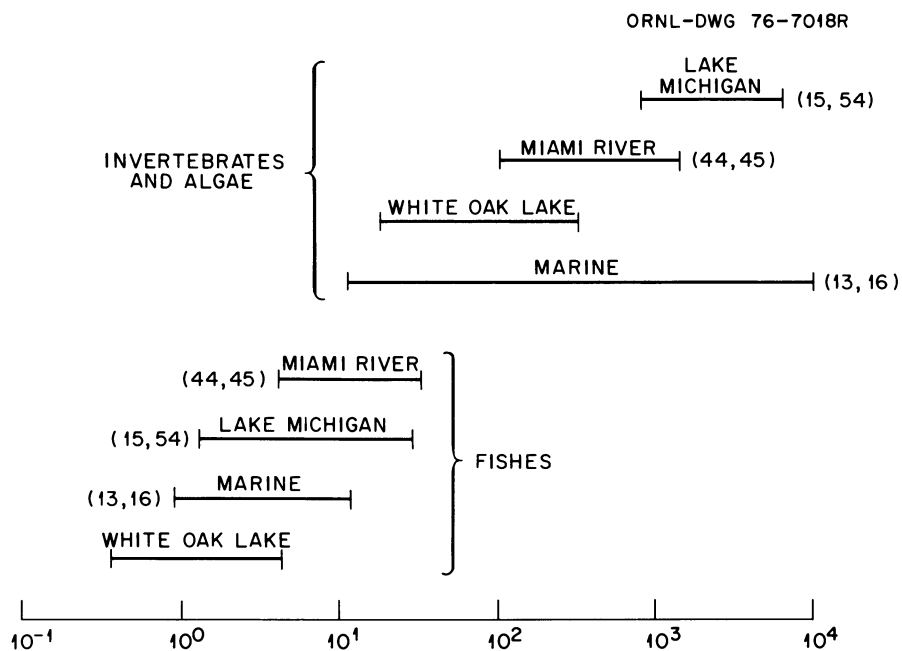


Figure 5. Ranges of concentration factors (CF) for Pu in various freshwater and marine environments. CF is defined as [Pu] in organisms(wet weight) divided by [Pu] in water.

molluscs, to have the highest whole body ^{239}Pu levels of predators collected in their studies. The $^{238}\text{Pu}/^{239}\text{Pu}$ ratio in this snail was similar to the ratio in sediments. They concluded that the Pu source originated in the sediment and moves up the food chain to the snail. The fractional body burden of Pu found in the muscle of oysters and scallops, which is the part consumed by man, was found to be lower than the rest of the body. The primary reservoir for Pu was found to be the shell (58) so that the consumable portion does not represent a significant source of Pu to man. Bottom feeding marine fishes such as flounder tend to concentrate more Pu than fishes such as bluefin, tuna, or bonito (16).

Two potential pathways of actinide transfer from marine environments to human populations may cause increased intake and concomitant radiological impact. These are the consumption by humans of seaweed and fish protein concentrate. For restricted human populations, seaweed in the form of laverbread (49, 60), for example, can serve as a basic component of the diet. Seaweed has been shown to concentrate Pu by a factor of 21,000 times its surrounding medium (57). Thus, where it may be a significant dietary item, seaweed is a potentially important vector for transfer of environmental Pu to human populations. The second potential source of Pu and other actinides to humans is from consumption of fish protein concentrate prepared by processing whole fish. Since concentrations of Pu in liver and GI tract may be 20 and 1000 times greater respectively than muscle, this food source may serve as a significant vector for Pu to human populations (16).

8. Summary

A summary of the recent information on biological pathways and the chemical behavior of actinides in the environment includes the following items:

1. Speciation and chemical transformation of actinide elements in aquatic and terrestrial environment will play a major role in their long-term immobilization of transport. The oxidation state of Pu appears to be very important. Plutonium(IV) strongly sorbs to soils and sediments. Stable soluble species may be dominated by Pu(VI). Anionic forms of Pu have been observed, but the significance of their behavior in environmental media is unknown.

2. Low rates of ^{239}Pu -oxide dissolution yield Pu(VI) as the most soluble monomeric species. About 10^6 days would be required for dissolution of a reference 0.3- μm spherical particle.

3. Mobility of Pu in the environment may be related to the more soluble Pu(VI) species. However this species may also be easily reduced to less mobile species.

4. Plant uptake of actinide elements varies greatly. Concentration ratios appear to be related to source characteristics, to chemical characteristics of the actinide in environmental

media, and to mode of contamination. Uptake of Pu by the root pathway yields maximum CR's of 10^{-3} ; contamination of foliar surfaces appears responsible for CR's as high as 10^{-1} . Concentration ratios greater than 10^{-1} are postulated for Np(V).

5. Exposure to soil, geochemical, and ecological processes for 30 years resulted in CR values of 10^{-3} for native and vegetable species; over 99% of the Pu remains associated with the soil.

6. Uptake of Am, Cm, and Np by plants exceeds that observed for Pu; differential uptake is postulated to be related to hydrolysis and sorption characteristics of the actinides. The order of uptake for these actinides (Np>Am<Cm<U>Pu) appears to be related to the order of oxidation state species, V>III<VI>IV.

7. In aquatic systems, most of the Pu is associated with sediment. Distribution coefficients are approximately 100,000. Americium, curium, and neptunium are probably more soluble than plutonium in aquatic environments. Sediment is the major source of actinide elements ingested by aquatic biota.

8. Plutonium is not very available to biota under most circumstances. There is no evidence for biomagnification by plants or organisms of terrestrial and aquatic food chains. More information is needed on magnitudes of uptake of non-plutonium actinides by biological organisms.

9. Availability of actinide elements to biota may be related to certain chemical species of the elements, and the environmental behavior of these species is not understood. Based on studies of chemical species of Pu in typical environmental media, and considering the magnitude of Pu uptake by vegetation growing in a floodplain contaminated 30 years ago, one would not expect to see great increases in availability to biota after extended residence times in the environment.

A balanced perspective of the potential hazards related to the long-term behavior of Pu and other actinides also encompasses both real and psychological phenomena. While pristine Pluto has remained stable in the 4.6 billion years since its formation, its namesake, plutonium, does change form and move in ecosystems. Magnitudes of redistribution of Pu in the environment appear to be slight however. A more comprehensive understanding of the mechanisms, species, and rates is necessary to evaluate the long-term consequences of Pu releases. At present, no potential hazard appears on the horizon.

The psychological phenomenon, aptly described by Thompson (61), is related to "the fear (associated with Pu) as a result of the measures taken to ensure there is no cause for fear." This "unreasoned fear," he continues, "is stimulated in part by our own best intentioned efforts to provide the ultimate in protection (and understanding) and may well prove to be the most damaging effect of this paradoxical element."

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Application of the Box Model Theory to the Geophysical Transport of PuO₂

Geochemistry of Pu(NO₃)₄

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1. Introduction

For predictions on the environmental impact of underground storage or disposal of α -emitting nuclides a precise knowledge of plutonium pathways in terrestrial ecosystems is required. In this respect it is of vital interest to know the rate of transfer from the lithosphere to the biosphere. Both these major parts of a terrestrial ecosystem are physically overlapping in the top soil. Therefore it is advisable to look at the soil as on an interface which acts between the compartments like a sieve in both directions.

Due to the above mentioned interface character of the soil, the kind of effects which influence the transfer of plutonium through the soil is of multiple character:

- a · Bio-redistribution caused by worms feeding on organic soil material can vertically translocate contamination to a depth of 100 cm; also their contaminated excrements may be brought to that depth. Burrowing of small animals also causes a redistribution. Furthermore, the uptake by plant roots, followed by death and decomposition of the plants causes changes in the distribution in the soil profile.
- b · For plutonium associated with the clay fraction of the soil the removal of clay minerals - a quite common process - may also become important. In the pH range 4.5 - 6.5 movement in the colloidal state is possible. The presence of Al and Ca ions facilitates this movement.
- c · Oscillation of physical soil properties like annual and diurnal variation of temperature, change of water content (wetting and drying) and shrinking and swelling certainly affect the retention or release of solid plutonium particles.

All the above mentioned mechanisms have a gross mixing effect. Thus we may look at the soil - if the portions considered well are chosen - as on a "reasonably well mixed box". In addition to the mixing function of the forces just described

there is also a one-dimensional effect due to the percolation of the soil water. The resulting effective movement is here referred to as geophysical transport.

2. Geophysical Transport

Some quantitative insight into the transfer through the soil may be obtained from the behavior of the fallout plutonium. This represents an analogy to an industrial contamination by high fired PuO_2 particles of a grain size about 0.04μ .

In a previous work (1) the frequency distribution of transit times was obtained by following the concentration of Pu-239,240 outflowing from a layer of loamy soil. Although the resulting function was not a perfectly monotonically decreasing one* an approximation of the transit time density distribution by the form $\exp(-kt)$, with $k = 0.17 \text{ a}^{-1}$ as turnover rate and $t = \text{time}$ in years, seemed to be reasonable enough.

Using the relationship:

$$\frac{dc}{dt} = 1 - j_n(t) \quad [1]$$

c = concentration of plutonium expressed as a fraction of the capacity of a soil layer

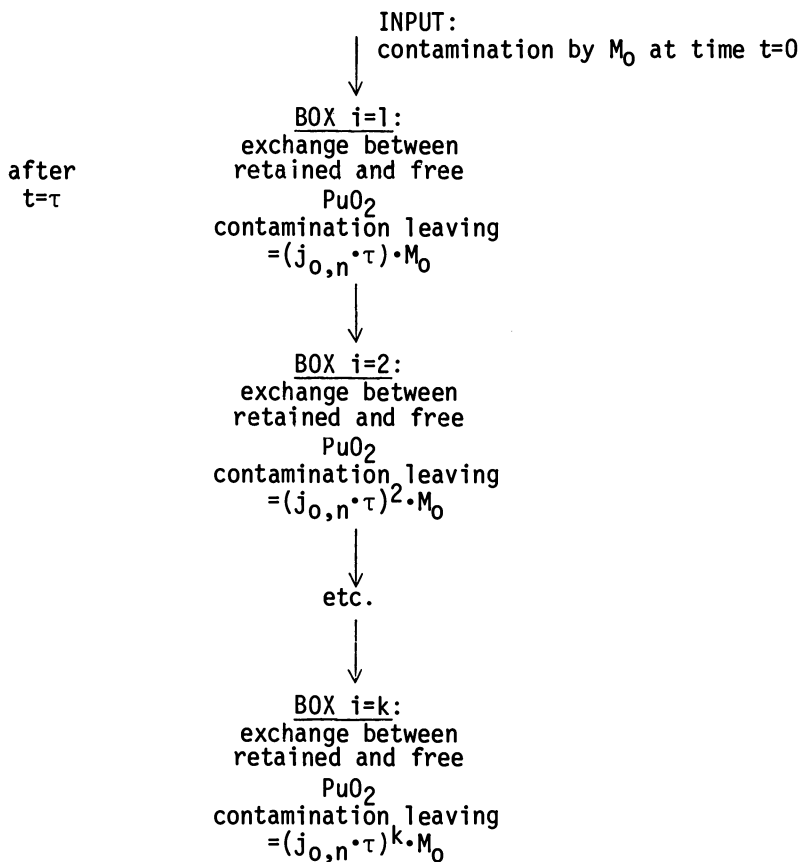
$$j_n = \left(\frac{j}{j_0}\right)_t ,$$

j is the flow in amount of contamination per unit time; j_0 is the steady state value of the flow; j_n is the normalized flow. The frequency distribution of residence times was calculated from [1].

The calculated transit time - which was under the conditions described taken as identical to the mean residence time - had a value of $\tau = 5-6$ years for a 5 cm thick layer of partially saturated natural loamy soil.

One approach to treat an instantaneous contamination moving through the soil is to use a box model consisting of a sequence of boxes to represent the soil layers (2):

*The irregularities were considered to be purely random. They were most probably contributed by a steady accumulation of errors with time.



The contamination in box i exchanges its excess plutonium with box $i+1$ over a certain period of time, e.g. $t=\tau$. When the soil is homogeneous enough - it means they can be represented by boxes of the same size - the same capacity C_0 for each of the boxes may be expected:

$$C_{0,1} = C_{0,2} = \dots C_{0,i} \quad [2]$$

If, in addition, a steady flow rate through the boxes and a negligible radioactive decay during the period of interest are assumed, a simple mass balance for the i^{th} box yields:

$$C_0 \dot{M} = j(M_{i-1} - M_i) \quad [3]$$

where M_i is the plutonium amount in the i^{th} box.

If the first box is initially contaminated by an amount M_0 , the analytical solution of the differential equation [3] leads to a Poisson-type equation [4] which describes the nuclide

distribution in the boxes by:

$$\frac{M_i}{M_0} = \frac{1}{(i-1)!} \left(\frac{j}{C_0} \cdot t\right)^{i-1} \exp\left(-\frac{j}{C_0} \cdot t\right) \quad [4]$$

As the equation is based on the assumption of a steady-state contamination flow rate in a homogeneous soil ($C_{0,i} = \text{const.}$, according to equation [2]), the same turnover time follows for each box:

$$\tau_1 = \tau_2 = \dots = \tau_n \quad [5]$$

From the definition of the turnover rate k in any hydrologic system, the turnover time τ can be identified as

$$k = \frac{j_{0,n}}{C_0} = \frac{1}{\tau} \quad [6]$$

Thus, equation [6] may be substituted into equation [4]:

$$\frac{M(i,t)}{M(i_0,t_0)} = \frac{1}{(i-1)!} \left(\frac{t}{\tau}\right)^{i-1} \exp\left(-\frac{t}{\tau}\right) \quad [7]$$

Using equation [7] and $\tau = 5-6$ years, the frequency distribution of an instantaneous plutonium contamination for different boxes and different times was computed. When i is used as a variable, t as a fixed parameter, the penetration of 50% of transported contamination can be estimated after summing up the distribution frequencies. From this and from the corresponding times, the transportation velocity of PuO_2 is obtained very easily (Table I).

Table I. Probable penetration and transportation velocity of an instantaneous PuO_2 contamination in the soil when the position of 50% contamination is followed.

| Time (a) | Number of Soil layers | Penetration range (cm) | Transportation velocity range (cm/a) |
|----------|-----------------------|------------------------|--------------------------------------|
| 1 | 0-1 | 0-5 | 0-5 |
| 10 | 1-2 | 5-10 | 0.5-1.0 |
| 50 | 8-10 | 40-50 | 0.8-1.0 |
| 75 | 12-15 | 60-75 | 0.8-1.0 |
| 100 | 16-20 | 80-100 | 0.8-1.0 |

The form of presentation of the penetration and of transportation velocity as a range instead of discrete values follows from the uncertainty of the turnover time and from the fact that equation [7] is not a smooth function. Anyway, on the whole, we can see from Table I that the mean velocity of PuO_2 lies most probably around 0.8-1 cm/a.

This transportation velocity applies to a loamy soil and weather conditions involving about 1000 mm annual precipitation. Under conditions like this a percolation velocity of infiltrated precipitation $v_w = 100$ cm/a was estimated by tracer experiments in the vicinity of Heidelberg (3).

3. Geochemistry of $\text{Pu}(\text{NO}_3)_4$

Finally it is useful to compare the transportation velocities of PuO_2 with those of $\text{Pu}(\text{NO}_3)_4$.

When plutonium in a nitrate form enters soil it precipitates very soon due to hydrolytic reactions. It becomes attached wherever a pH-gradient occurs: on the surface of the wetted mineral particles and at the top of the advancing acid front. After such an irreversible type of adsorption it is improbable that the amount of plutonium in the soil water depends on ion exchange. Therefore one would suspect a relatively higher contribution coming from the dissolution of precipitated $\text{Pu}(\text{OH})_4$. The evaluation of this amount can be done by means of the following equilibrium equations (4).

$$K_1 = \frac{[\text{Pu}^{3+}][\text{PuO}_2^+][\text{H}^+]^4}{[\text{Pu}^{4+}]} = 6.56 \cdot 10^{-4} \text{ or } 6.97 \cdot 10^{-4} \quad [8]$$

$$K_2 = \frac{[\text{Pu}^{3+}][\text{PuO}_2^{2+}]}{[\text{Pu}^{4+}][\text{PuO}_2^+]} = 12.8 \text{ or } 13.2 \quad [9]$$

$$K_3 = \frac{[\text{PuOH}^{3+}][\text{H}^+]}{[\text{Pu}^{4+}]} = 0.03 \quad [10]$$

$$K_4 = \frac{[\text{H}^+]}{[\text{Pu}^{4+}]} = 1.66 \quad [11]$$

and by using the known standard potentials E° (Table II).

Table II. Standard potentials E° between different oxidation states of plutonium (after data from (4)).

| $\frac{E^\circ}{V}$ | Pu(III) | Pu(IV) | Pu(V) | Pu(VI) |
|---------------------|---------|--------|--------|--------|
| Pu(III) | --- | | | |
| Pu(IV) | 0.9827 | --- | | |
| Pu(V) | 1.0761 | 1.1694 | --- | |
| Pu(VI) | 1.0228 | 1.0429 | 0.9164 | --- |

Between two oxidation states n and $n+1$ the relationship $R_{n+1,n}$ holds:

$$R_{n+1,n} = \frac{[Pu(n+1)]}{[Pu(n)]} = \exp(2.3026 \cdot \frac{Eh - E_{n+1,n}^\circ}{0.05916}) \quad [12]$$

The total amount of dissolved plutonium in a unit volume m_{Pu} then will be given by the sum of the equilibrium concentration of all oxidation states:

$$m_{Pu} = \sum_{n=3}^6 C_{Pu}(n) \quad [13]$$

Using equations [8] to [13] and the extreme - but observed - combinations of pH and Eh values for ground water the potentially soluble plutonium amounts are given in Table III.

Table III. Potentially soluble plutonium amounts in a unit volume of ground water.

| $\frac{C_{Pu}}{M/\ell}$ | pH: | 9 | 5 |
|-------------------------|-----|-----------------------|-----------------------|
| $\frac{Eh}{mV}$ | | | |
| 500 | | $2.82 \cdot 10^{-12}$ | $3.66 \cdot 10^{-12}$ |
| 300 | | $1.17 \cdot 10^{-15}$ | $2.02 \cdot 10^{-9}$ |

or

Table III. (Continued)

| $\frac{C_{Pu}}{M/\ell}$ | pH: | 7 | 6 |
|-------------------------|-----|-----------------------|-----------------------|
| $\frac{Eh.}{mV.}$ | | | |
| 600 | | $1.38 \cdot 10^{-10}$ | $1.38 \cdot 10^{-10}$ |
| -100 | | $1.17 \cdot 10^{-10}$ | $1.17 \cdot 10^{-6}$ |

Under conditions usually met in ground water only two plutonium forms are realistic:

- When oxidizing conditions prevail, it means $Eh < 0.51 - 0.0059$ pH, hexavalent $PuO_2(OH)_2$ may result.
- Normally most probable would be the tetravalent form, $Pu(OH)_4$.

The relative migration velocity of plutonium contamination when applied to soil in the form of a $Pu(NO_3)_4$ solution r_N , may be given by

$$r_N = 1 / (1 + K_d \rho \frac{1-p}{p}) \quad [14]$$

In accordance with the soil properties considered in the case of PuO_2 migration a bulk density $\rho = 1.59$ g/cm³ and a porosity $p = 0.40$ can be assumed. Some difficulty arises when choosing a value for the distribution coefficient K_d . As there is no real plutonium exchange going on in soil/water system, the definition of K_d doesn't suit the description of plutonium distribution between soil and water. Assuming, however, that plutonium is tetravalent a distribution coefficient of $K_d = 5 \cdot 10^3$ seems to be a reasonable one (5). Such conditions involve a relative migration velocity of $r_N = 8.4 \cdot 10^{-5}$

Obviously, the relative migration velocities of soil water $v(H_2O)$, plutonium oxide $v(PuO_2)$ and plutonium initially in nitrate form $v(Pu(NO_3)_4)$ appear to be related as:

$$\begin{aligned} v(H_2O) : v(PuO_2) : v(Pu(NO_3)_4) \\ 10^5 : 10^3 : 10 \end{aligned}$$

In other words, it means that if the soil water percolates 1 km, PuO_2 will migrate 10 m and Pu applied initially in nitrate form will move only 10 cm.

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Oklo, an Experiment in Long-Term Geologic Storage

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One of the more difficult problems relating to fission-reactor waste disposal is the evaluation of the suitability of a particular site for the long-term storage of actinide by-products from fuel reprocessing. Current U. S. plans call for underground storage in containers placed in a stable geologic environment. It is anticipated that the effectiveness of such storage would be required to last for several hundred thousand years. While the containers are intact, there is no possibility of dispersion of the radioactive contents. However, the question inevitably arises as to the likely consequences if the containers are breached. The subsequent rate of dispersal could well be so slow as to be unmeasurable in a man's lifetime, but could still be significant in relation to the decay time of the radioactive waste materials. There is a possibility that short term experiments could fail to identify processes which might be important in the long-term storage and dispersal.

Viewed in this perspective the 1.8-billion year old natural fission reactor discovered by scientists in the French CEA at the Oklo uranium mine in Gabon, Africa represents the end-product of a unique kind of experiment in long-term storage of reactor waste. As such, the phenomenon is being exploited as a source of pertinent information for waste storage planning and evaluation. In this paper we review information which has been obtained from analyses of samples of ore from the reactor site. At Los Alamos and at Idaho Falls we have carried out analyses of a limited number of samples; however a wealth of information on the subject has been published (1-5) and the Oklo phenomenon was the subject of an IAEA symposium in Gabon in the summer of 1975, sponsored by the French and Gabonese.

The Oklo anomaly, which was discovered as a result of isotopic assays of uranium from the Mounana mill, was first recognized as being the result of a natural fission reactor in 1972 (1,2). The Oklo uranium deposit, located in the southeast part of Gabon, occurs in one of the Francevillian series of sedimentary deposits. In the deposit the uranium concentration is

generally less than one percent by weight, however in the reactor zones themselves the uranium is very concentrated, being more than fifty percent of the dry weight in the richest portions. At least four and possibly six separate reactor zones have been located. These rich deposits coincide with argillaceous lenses interspersed in the more generally encountered conglomerate or coarse sandstone (6,7,8).

The reactor zones vary in size, as indicated in Fig. 1, but are generally of the order of one meter in thickness and the larger ones cover an area of a few hundred square meters. Borders are usually well defined with the uranium concentration dropping from more than ten percent to less than one percent in a distance of ten to twenty cm. The zones tend to be somewhat irregular in outline and thickness, and concentration profiles along vertical bore-holes through the beds also tend to be irregular, often exhibiting two or more distinct concentration peaks (6,7,8).

The total amount of uranium in the identified reactor zones is estimated to be of the order of 800 tons. Burn-up of the ^{235}U was really astonishing, amounting to about 15,000 megawatt-years of energy released in fission. Isotopic composition of the most depleted ore samples is 0.3% ^{235}U , compared to 0.7% for normal uranium (3,6). Bear in mind that 1.8 billion years ago when the reaction went critical normal uranium contained over 3% ^{235}U , comparable to the enrichment used in modern day reactors.

To a first approximation, and with a few obvious exceptions, the fossil remains now present in the reactor zones contain the residual fission products and actinides, or their decay products. This has been demonstrated by detailed analyses, isotopic and elemental, of a substantial number of samples from Zone 2, as well as some from Zone 1. These findings are summarized in Table I. Before considering Table I further it is appropriate to review the details of reactor operation, as well as the related uncertainties, which form the basis for the conclusions in Table I.

The fossil remains of the Oklo reactors were found to contain isotopic and elemental evidence from which one may deduce many of the operating parameters (4,5) as is illustrated by the neodymium data in Table II. The number of fission events is recorded by the number of residual fission products atoms, the neutron fluence and spectrum by the effect of neutron capture on the ratio of adjacent-mass fission products, the contribution of ^{238}U and ^{239}Pu to total fission by the relative yield of fission products over a range of masses, the conversion ratio (capture in ^{238}U per destruction of ^{235}U) by depletion of ^{235}U in relation to the neutron fluence, the age of the reactor by the inter-relation of fission products, uranium, and neutron fluence, and reactor life or duration by evidence for the fraction of fissions in ^{239}Pu or by competition between decay and neutron capture in ^{99}Tc . To the extent that all these observations can be tied

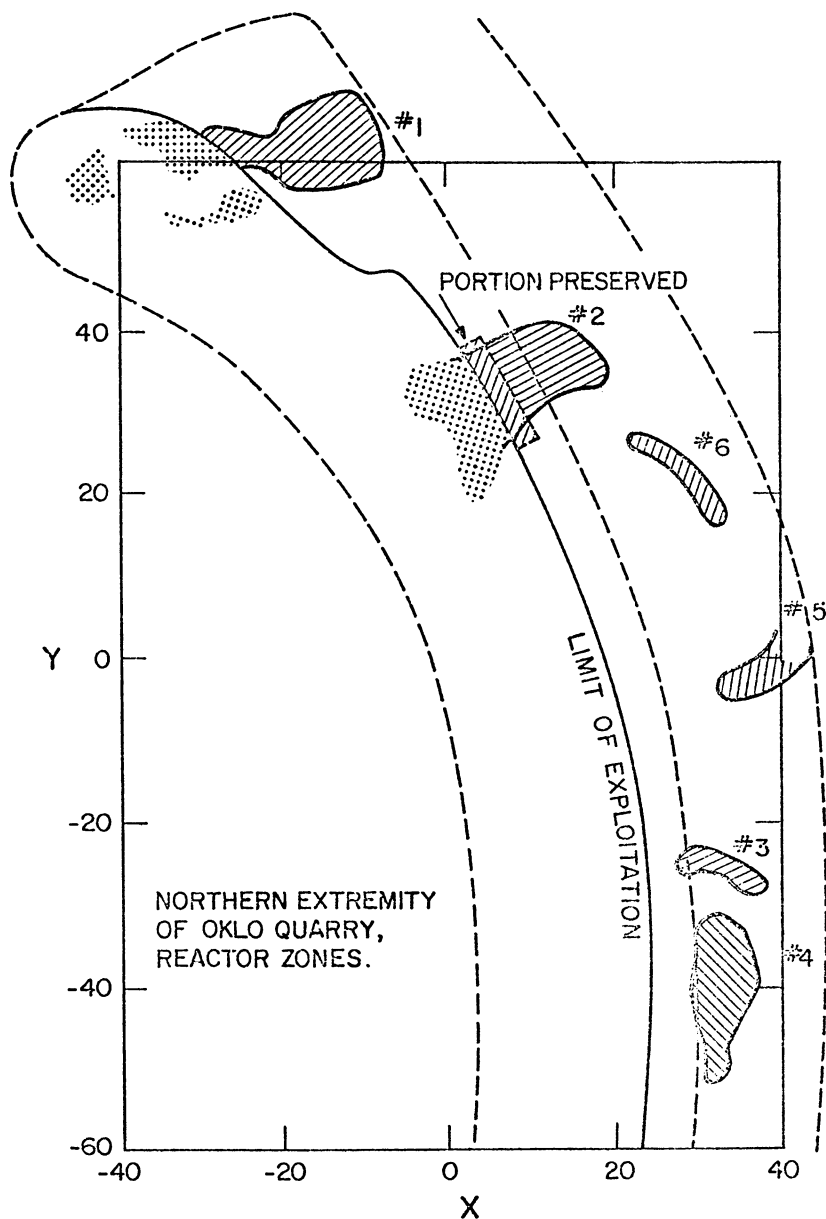


Figure 1. Plan view of reactor distribution at the Oklo mine (6). The bed containing the uranium deposits dips steeply to the east and north. The dotted areas were mined before the reactors were recognized. The surface originally lay about 80 meters above the deposits, and the grid spacing is given in meters.

Table 1. Migration of fission products and actinides in the "Zone 2" reactor at the Oklo mine.

| Element | Migration Behavior | References |
|---|--|-----------------|
| Kr | Measurable traces, 0.01 to 1% remaining. | 2,4,9 |
| Rb | Measurable traces, less than 1% remaining | 4,10,11,12 |
| Sr | Measurable traces, less than 10% remaining. | 4,11,12 |
| ^{90}Sr (Now ^{90}Zr) | Small migration, most decayed in place. | 9,11 |
| Zr | Redistributed, mostly in place | 9,11,18 |
| Nb | Mostly retained | 4,9 |
| Mo | ~ 90% missing | 4,9,11 |
| ^{99}Tc (Now ^{99}Ru) | Redistributed, migrated as Tc | 9,11 |
| Ru | Large fraction retained, redistributed | 4,9,11,15 |
| Pd,Ag | Mostly retained | 4,9 |
| Cd | ~ 90% missing | 4,13 |
| Te | Mostly retained | 4,9 |
| I | Mostly gone | 4,9 |
| Xe | Measurable traces, 0.01 to 1% remaining | 4,9,11 |
| Cs | Measurable traces (as Ba), mostly missing | 4,9,12 |
| Ba | Obscured by natural but mostly gone | 4,9,11 |
| Ce,Nd,Sm,Gd | Very little migration | 4,9,11,14,15,19 |
| Pb | Redistributed, ~ 2/3 missing from core | 4,16,17,18 |
| ^{232}Th (^{236}U , ^{240}Pu) | Mostly retained | 9,14 |
| ^{209}Bi (^{237}Np , ^{241}Pu) | Mostly retained | 9,14 |
| ^{235}U (^{239}Pu) | No ^{239}Pu separation from ^{238}U | 4,18 |
| U | Probably no major migration, some redistribution, (see text) | 4,9,14,19 |

Table 2. Neodymium from the Oklo reactor (Zone 2) compared with natural and fission-product neodymium.

| Mass Number of Nd Isotope | Atom ratios in: | | |
|---------------------------|-----------------|-----------|-----------------------------------|
| | Natural Nd | Oklo 1182 | ²³⁵ U Fission Products |
| 142 | 4.73 (0.13)* | 0.13 | 0.00 |
| 143 | 2.12 (0.06) | 2.63 | 3.51 |
| 144 | 4.16 (0.11) | 4.12 | 3.21 |
| 145 | 1.45 (0.04) | 2.18 | 2.32 |
| 146 | 3.01 (0.08) | 1.94 | 1.76 |
| 148 | 1.00 (0.03) | 1.00 | 1.00 |
| 150 | 0.98 (0.03) | 0.41 | 0.38 |

* Values in parentheses are the "natural" contribution to Oklo 1182, uncorrected for neutron capture.

Table 3. Calculated neutronic properties for various Oklo-like ores⁽²²⁾.

| | <u>1</u> | <u>2</u> | <u>3</u> |
|--|----------|----------|--------------|
| Uranium Concentration (Dry) | 35% | 60% | Pure Uranium |
| ²³⁵ U Enrichment | 3% | 3% | 1.2% |
| H/U Ratio | 10 | 5 | 2 |
| ²³⁸ U/ ²³⁵ U Fission Ratio | 0.026 | 0.049 | 0.059 |
| C (Conversion Ratio) | 0.40 | 0.49 | 1.1 |
| K _∞ | 1.13 | 1.28 | 1.002 |

together to form an integrated model which is consistent with neutronic calculations, one can assert with some confidence that this or that product did or did not migrate away from the reactor.

We are limited in this modeling process by the accuracy with which measurements can be made and by the accuracy of the fission yields and neutron reaction cross sections which are used to interpret the results. As an example consider the ^{143}Nd - ^{144}Nd fission product pair, which has been used as an indicator of thermal neutron fluence because the capture cross section for the former is large and for the latter is small. The thermal cross section for ^{143}Nd has recently been listed as 325 (± 10) barns (20), and more recently as 266 barns (11). Using the 325-barn value we deduce an age of about 2 to 2.1 billion years from neodymium to uranium ratios in the Oklo reactors, while an age of about 1.8 billion years is obtained using the 266-barn figure. The lead-uranium method for determining geologic age indicates an age of about 1.75 billion years, in substantial agreement with the "Nd/U" age deduced with the 266-barn cross section (4). The observed neodymium to uranium ratios can also be reconciled with an age of 1.8 billion years and a 325-barn cross section by adopting the unlikely proposition that a uniform twenty percent of the uranium has dissolved and been transported away from the reactor since it shut down (19).

The Oklo reactors were water-moderated thermal reactors with significant epithermal and fast components in the neutron spectra. Calculations of the neutron spectra for compositions typical of the rich Oklo deposits indicate that parameters deduced from measurements of residual fission products are reasonable (21). Results of some calculations carried out at Los Alamos are shown in Table III. For a composition typical of Oklo, with 35% uranium by weight (dry) and a hydrogen to uranium atom ratio of ten to one, Hansen and Smith (22) calculate a ratio of capture in ^{238}U to destruction of ^{235}U , "C", of 0.4 with 2.6% of the fissions occurring in ^{238}U . At a higher concentration the ^{238}U fission contribution increases as does the conversion ratio, C. In the last column they show it to be conceivable that nature could have created a breeder reactor, at just the right moment in history, when the ^{235}U made up about 1.2% of the uranium, i.e., 0.6 billion years ago.

One of the more interesting questions about the Oklo reactors is how long they remained critical. The answer is intimately related to the fraction of fissions in ^{238}U , for reasons discussed below, which is in turn related to the concentrations of uranium in the ore and to the amount of water present. If we assume that 1/2 of the radiogenic lead is now missing then a present day uranium concentration of 58% extrapolates to a 70% concentration 1.8 billion years ago. At such a concentration the optimum hydrogen to uranium ratio for criticality is in the range of two to ten as is shown in Fig. 2, while at lower concentration the optimum moves up to values of 5 to 20. Since it seems likely

that water played the role of a control rod (23) we assume that the hydrogen to uranium ratio was generally on the low side of the optimum, i.e., about ten or less. This in turn implies that the fraction of fissions in ^{238}U should be about 3% or more in regions with high uranium concentration.

In principle the duration of the Oklo reactors can be deduced from the competition between neutron capture or fission reactions and radioactive decay, e.g. fission vs. decay for ^{239}Pu or capture vs. decay for ^{99}Tc (24). From the isotopic distribution of various fission products it is relatively easy to distinguish between ^{235}U products and the sum of ^{238}U and ^{239}Pu products, but only a few opportunities exist for distinguishing between the latter. Based on data for ruthenium, palladium, neodymium, samarium, and gadolinium Ruffenach et al. (15) conclude that about 3% of the fissions were in ^{238}U and 4% in ^{239}Pu . From the 4% ^{239}Pu contribution Hagemann et al. (23) deduce a duration of approximately 600,000 years. Because of the uncertainties in fission yields and the difficult nature of the measurements these conclusions are subject to relatively large errors. Duration values from 400,000 to 1,000,000 years can be accommodated without doing great violence to the data. From a $^{99}\text{Ru}/^{100}\text{Ru}$ ratio measured on only one sample, selected because it seemed not to have suffered from migration of either Ru or Tc, the same authors derive a duration of 1.4 million years. It is noted that this figure is strongly dependent on the resonance integrals for neutron capture in ^{99}Tc and ^{99}Ru , which are not well known. At this time the best value for duration appears to be that based on ^{239}Pu fission, i.e. 600,000 years.

Analytical results for typical samples from the Zone 2 reactor are compared with some calculated values in Table IV. The last two sets of data represent results published by Ruffenach et al. (15) and Frejaques et al. (9); the first three sets of data as well as all the calculated values are the product of work at Los Alamos and Idaho Falls (11,14). Based on the reasonably good fit to bismuth and thorium data we conclude that their precursors, ^{237}U , ^{237}Np and ^{236}U , were largely retained in the reactor core. We are assuming that the low background level for bismuth and thorium, observed outside the core, is applicable to the interior region as well. It would be a remarkable coincidence if the natural bismuth and thorium were to have accumulated so precisely as to match the reactor-produced quantities so well. The overall agreement, between measurement and calculation which is illustrated by these data, has led to the conclusion that the reactor zone now contains essentially all the material present at the end of the reaction.

However, another sample (1421-5) from the lower periphery of the reactor with only 9% uranium content, shows a clear 20% excess of fission-product neodymium relative to uranium. Either the uranium has migrated away or fission-product neodymium has migrated in; the former seems more reasonable. Even for this

Table 4. Comparison of measured isotopic composition of several Oklo samples with calculated values. The age and duration were taken to be 1.8 billion years and 0.6 million years; parameters were adjusted to fit $^{144}\text{Nd}/^{143}\text{Nd}$, $^{146}\text{Nd}/^{145}\text{Nd}$, and $^{235}\text{U}/^{238}\text{U}$ ratios within 1%.

| SAMPLE ID | 1178 | 1182 | 1187 | 1413-3 | 1418 |
|--|---|-----------------------|-----------------------|-----------------------|-----------------------|
| U CONTENT, % | 53 | 22 | 48 | 37 | 58 |
| ISOTOPE | MEASURED ATOM RATIOS (DEVIATION FROM CALC. RATIO) | | | | |
| $^{235}\text{U}/^{238}\text{U}$ | 0.00484 | 0.00326 | 0.00422 | 0.00410 | 0.00574 |
| $^{144}\text{Nd}/^{143}\text{Nd}$ | 1.385 | 1.566 | 1.480 | 1.454 | 1.236 |
| $^{146}\text{Nd}/^{145}\text{Nd}$ | 0.873 | 0.994 | 0.904 | 0.877 | 0.856 |
| $^{150}\text{Nd}/^{143+144}\text{Nd}$ | 0.062(-3%) | 0.061(-3%) | 0.064(-3%) | 0.062(-1%) | 0.061(-2%) |
| $^{104}\text{Ru}/^{101+102}\text{Ru}$ | 0.227(+3%) | 0.227(+3%) | 0.231(+3%) | 0.223(+1%) | 0.226(+2%) |
| $\text{Nd}/^{238}\text{U}$ (x 100) | 0.651(-4%) | 0.742(+2%) | 0.763(+1%) | 0.699(0%) | 0.496(-6%) |
| $^{232}\text{Th}/^{238}\text{U}$ (x 100) | 0.45 (-17%) | 0.80 (+38%) | 0.67 (+16%) | 0.60 (+7%) | 0.45 (+2%) |
| $^{209}\text{Bi}/^{238}\text{U}$ (x 1000) | 0.24 (+14%) | 0.34 (+13%) | 0.29 (+3%) | 0.21 (0%) | 0.15 (-6%) |
| REACTOR PARAMETERS | | | | | |
| τ (n_{eff}/m^2) | 1.43×10^{25} | 1.89×10^{25} | 1.65×10^{25} | 1.66×10^{25} | 1.04×10^{25} |
| "R", Resonance Index | 0.10 | 0.10 | 0.10 | 0.08 | 0.12 |
| "C", Conversion Ratio | 0.61 | 0.40 | 0.55 | 0.52 | 0.69 |
| Natural Nd, % | 4.8 | 2.5 | 5.5 | 2.7 | 2.5 |
| ^{238}U Fissions, % | 3.2 | 3.9 | 4.9 | 3.1 | 4.1 |

sample the thorium, at 170 ppm, and the bismuth, at 1.2 ppm appear to be entirely related to the reactor production of ^{236}U and ^{237}U . The small deficiency in uranium seems to be typical of the upper and lower edges of the core (14,19) and may simply reflect one of the mechanisms by which the reactor was controlled. Water, being converted to steam at the center of the core, may have flowed out through fissures, condensed in the cooler surroundings and then flowed back toward the center of the core through finer pores, in the process moving the uranium toward the center of the core and leaving the less soluble fission products behind. Alternatively solubilization of a small fraction of the fission product neodymium from the core and redeposition at the periphery could account for the observation.

The possibility of accretion of fresh uranium into the deposit during the period of criticality can neither be excluded, nor proved (14,23,25), as a mechanism for reactor control, on the basis of available data. Reasonable fits to observations can be achieved with or without accretion.

The pattern of migration for heavy elements and fission products, presented above in Table I, is about what one would expect based on the known chemical behavior of the elements, and the availability of water to the core during and after the reaction. It is no surprise that the majority of the noble gases, krypton and xenon, have been lost, nor that there are still traces trapped in some of the core minerals. The relatively soluble alkali and alkaline earth elements have also been lost to a large extent, as have molybdenum, cadmium and iodine. The elements zirconium, technetium, lead, and to some extent ruthenium have at least been redistributed in the core. The rare earth elements, cerium, neodymium, samarium, and gadolinium as well as the actinides, thorium, uranium, neptunium, and plutonium show little evidence of migration, except possibly near the periphery of the core. By analogy to the rare earth elements it is probable that the transplutonium actinides, americium, curium, etc. would not migrate in this same environment.

We don't know a great deal about the environment affecting the Oklo reactor during the two billion years since it ceased functioning. There is mineralogic evidence such as the lack of fossil fission tracks and apparent recrystallization (4,25), that indicates the presence of water for a considerable period of time. In fact it seems likely that water acted as a control rod for the reactor, being present in sub-optimal concentration during the life of the reactor, approaching the optimal concentration at the end of the reactor life, and shutting off the reactor by exceeding the optimal concentration at the end. There is evidence that a significant redistribution of lead has occurred in the last billion years, possibly associated with a magmatic intrusion about 850 million years ago. All these observations tend to indicate that the core has been subject to the action of water for a significant portion of the period since it shut down. The

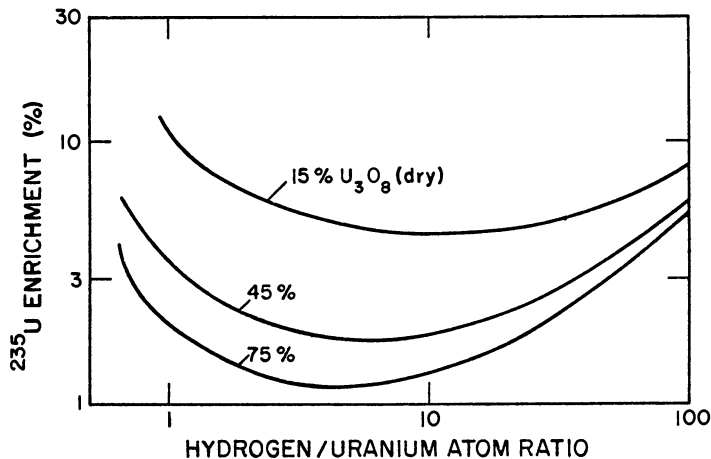


Figure 2. Minimum enrichment required for a critical configuration composed of U_3O_8 , water, and "Oklo" gangue, as a function of the hydrogen to uranium atom ratio (22)

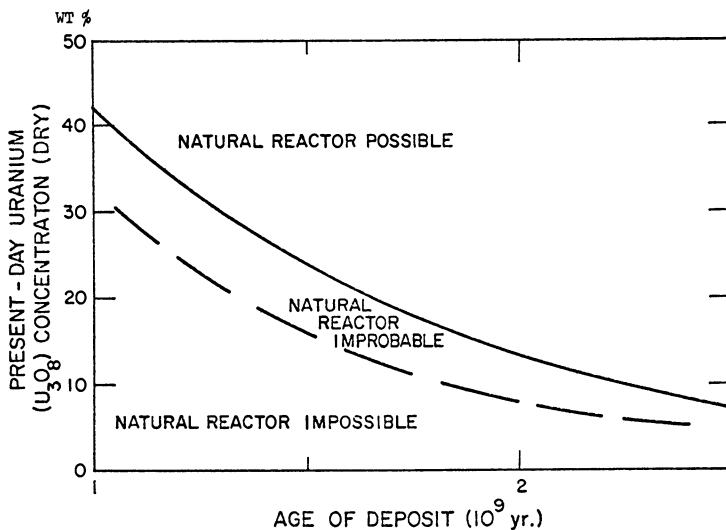


Figure 3. Minimum uranium concentration requirements for criticality in an Oklo-like environment expressed as a function of the age of the deposit

minerals in the surrounding strata do not show evidence of exposure to exceptionally high temperatures; it is estimated that temperatures of one to two hundred degrees and burial at a depth of about 4000 meters can account for the observed state of diagenesis. There is clear evidence of an ongoing alteration which began at about the Eocene and is related to the inflow of superficial waters through the fractures which cut across the reactor zones (26,27).

A SEARCH FOR OTHER NATURAL REACTOR SITES

The prevailing sentiment expressed at the IAEA conference in Gabon was that it is very unlikely that Oklo was a unique creation of nature and that a cooperative international search should be conducted to locate other fossil reactor sites. The requirements for the existence of a natural reactor have been investigated by Hansen and Smith at Los Alamos (22). They report that for a deposit of sufficient size (about a meter in minimum dimension), in a medium with minimal amounts of neutron poison, like the Oklo gangue, and an optimum amount of water, the minimum richness of ore for criticality at any given moment in history falls on the solid curve shown in Fig. 3. In an even more optimistic case, with the iron removed from the gangue, criticality can be achieved at even lower concentrations as shown by the dashed line. The sensitivity to water has already been presented in Fig. 2 above which graphs the ^{235}U enrichment required for criticality at constant total uranium concentration as a function of the hydrogen to uranium ratio. It is assumed that the hydrogen is present as water.

We have looked at existing mass spectrometry data on ^{235}U to ^{238}U isotopic ratios for signs of chain reactions. The isotopic ratios of natural ores, lunar samples, and meteorite samples are constant to within 0.1% (relative) which is the approximate standard deviation of most available data. However, a body of data exists within the U. S. production plants which, for the most part, has not been widely published and which is an order of magnitude more precise. When we examine a set of eighty-eight precise analyses performed by gas mass spectrometry on UF_6 at Oak Ridge, Paducah, Portsmouth, the National Bureau of Standards and in England (28-32) we find that natural ores do vary and fall into the following patterns: the Belgian Congo samples are consistently on the high side in ^{235}U content, most high-temperature vein and pegmatitic ores fall 0.03% lower in ^{235}U , and ores from New Mexico and immediately surrounding areas consistently measure 0.06 to 0.1% lower. The variability is illustrated in Fig. 4.

We can not immediately conclude that we are seeing evidence for nuclear reactions. This variability was recognized years ago within the A.E.C. and it has been hypothesized that the New Mexico effect is due to chemical exchange in the oxidation-reduction cycles which are largely responsible for the formation of the large sandstone deposits of uranium in the Colorado Plateau. Now

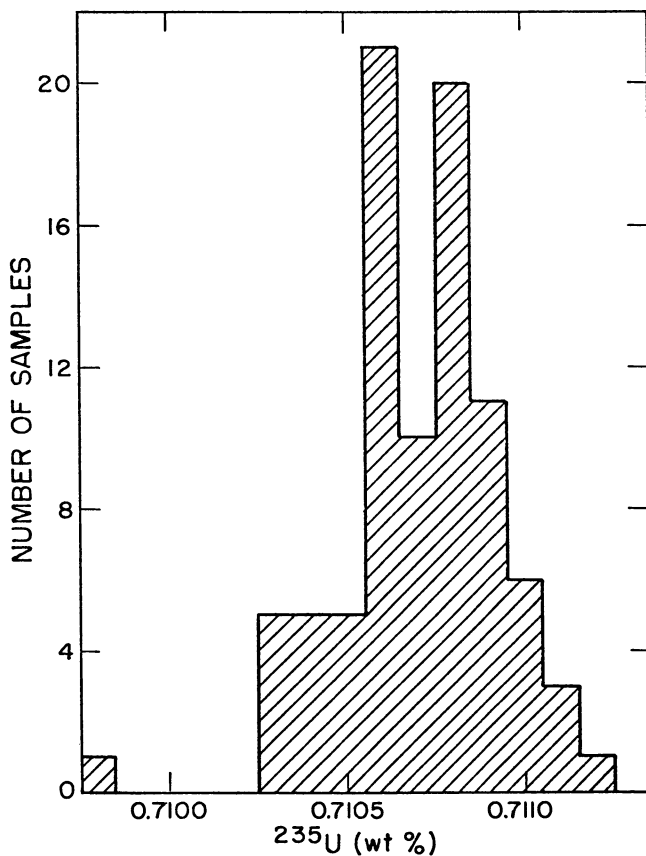


Figure 4. Variability of ^{235}U in natural uranium. Uncertainties in the ^{235}U data are approximately ± 0.0001 wt % (absolute).

that we are aware of Oklo we may also hypothesize that the effect could be due to the dissemination of older, more deeply buried uranium deposits which went critical in Precambrian times and were strongly depleted in ^{235}U .

Another more sensitive way to detect a natural reactor is to look for fission products such as ruthenium, palladium, or tellurium which are rare elements in the earth's crust. As a result of preliminary experiments conducted at the Idaho National Engineering Laboratory ruthenium from spontaneous fission of ^{238}U has been detected in a natural uranium ore, thus illustrating the sensitivity of the method and also the possibility of using ruthenium to uranium ratios to date uranium ores. The burn-up of 0.02% of the ^{235}U in a rich Precambrian deposit is barely detectable by uranium mass spectrometry but would produce 0.4 ppm of ruthenium, compared with 0.03 ppm from spontaneous fission and a crustal abundance of natural ruthenium of perhaps 0.001 ppm.

In the future we plan to make use of mass spectrometry of both uranium and ruthenium in a continuing investigation of natural reactors, the formation of rich, economic ore deposits, their rates of survival or destruction, and the relationship of ore deposit stability to long term storage of reactor products. The dialogue which was initiated in this investigation between specialists in the nuclear sciences and the geosciences will continue and will certainly make useful contributions to the solution of our common energy problems.

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