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Factors Influencing the Transport of Actinides
in the Groundwater Environment

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by

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Abstract

This report summarizes our investigations of factors that significantly influence the transport of actinide cations in the groundwater environment. Briefly, measurements of diffusion coefficients for Am(III), Cm(III), and Np(V) in moist U.S. soils indicated that diffusion is negligible compared to mass transport in flowing groundwater. Diffusion coefficients do, however, indicate that, in the absence of flowing water, actinide elements will migrate only a few centimeters in a thousand years.

The remaining investigations were devoted to the determination of distribution ratios (K_d s) for representative U.S. soils, factors influencing them, and chemical and physical processes related to transport of actinides in groundwaters. Specifically, alpha track measurements on aqueous phases in contact with soils gave clear evidence for the existence of actinide-bearing soil particles. Filtration and centrifugation of the aqueous phase gave additional evidence for actinide-bearing colloids or radiocolloids. Further centrifugation experiments demonstrated that distribution ratios or K_d s can be resolved into two components, one due to ions and a second to actinide-bearing soil particles.

Gelfiltration experiments with the aqueous phases containing radionuclide-bearing soil particles revealed three groups: One included low molecular weight species (e.g. AmCl_2^+ , $\text{Am}(\text{OH})_2^+$, Am-fulvic acid complexes). A second contained large ($>10\text{nm}$) actinide-bearing particles, presumably actinides bound to colloidal clay fragments. The intermediate group contained the majority of the actinides bound to particles with molecular weights between 8000 and 50,000, which strongly suggested complexing with humic acid polymers or polyelectrolytes. TTA distribution measurements yielded an Eu(III)-humic acid formation constant of $(6.2 \pm 0.8) \cdot 10^6$, which agreed with other Am(III) and Eu(III) data.

The computer code GARD was modified to include complex formation to test the importance of humic acid complexing on the rate of transport of actinides in groundwaters. Use of the formation constant above and a range of humic acid, even at rather low concentrations of 10^{-5} to 10^{-6} molar, significantly increases the actinide transport rate in a flowing aquifer. These computer calculations show that any strong complexing agent will have a similar effect on actinide transport in the groundwater environment.

I. INTRODUCTION

When additional nuclear power plants go into operation, larger amounts of actinide elements will be generated and the number of accidental releases to the environment may also increase. Release of these actinide elements to the environment has potential long-term public health implications. Prevention of these releases (management of actinide element wastes) also has long-term societal consequences. Rowe and Holcomb(1) describe the management of radioactive wastes as a "Hidden Commitment"--the commitment to safely contain these materials for times approaching geological epochs. The fact that investigations continue on the chemical isolation and separation and the long-term storage of actinide elements and other radioactive wastes emphasizes the "Hidden Commitment." Consequently, from the point of view of siting nuclear power plants or fuel-processing facilities, etc., it is desirable to investigate the chemical behavior of the actinide elements in the natural environment. In particular, it is important to know the chemistry of americium, curium, neptunium and plutonium in the soil-aquatic environment. Knowledge of migration rates and distribution ratios of Am(III), Cm(III) and Np(V) in representative soil-aquatic environments enables engineers and scientists to predict more accurately the mobility of these elements and the associated potential environmental hazards after accidental, or possibly routine, releases (2).

Research on the chemistry of the actinide elements has been extensive and the results of this research have been the subject of several books (3). Other than radiocolloid formation, disproportionation equilibria and the information on oxidation

potentials, the data are not relevant to the chemical behavior of the actinide elements in the soil-aquatic environment. For example, these investigations were done at high ionic strength using perchloric acid.

Limited research has been directed toward the chemical behavior of the actinide elements in the soil environment (4,5,6). Most of this research has been done on arid desert soils low in organic matter (7,8). Except for the Andelman and Rozzell experiments (9), little is known about the carbonate complexing of the actinide elements under conditions approaching natural waters. Further, data related to carbonate complexing of PuO_2^{2+} (10) and related information about the behavior of neptunium, americium and curium are rather sparse. Except for the data of Bertha and Choppin (11) and that reported here little is known about the complexing of the actinide elements by the common but ill-defined soil components, fulvic and humic acids. Because fulvic acid is known to complex many cations (12), it is important to know how strongly fulvic and humic acids complex actinide elements. Formation constants for carbonate, fulvic and humic acids would be helpful when assessing the mobility of the actinide elements in various soil environments. Complexing of the actinide elements by fulvic, humic acids, and carbonates must be considered along with adsorption on clay and manganese dioxide hydrolytic polymerization, and disproportionation all are important factors in the transport of these elements in the soil-aquatic environment.

Similarly, little, except that which will be reported here, is known about the role that manganese dioxide plays in the sorption of actinide elements in a soil-aquatic environment. Hydrous iron and manganese oxides found in soils have high specific surface areas and are capable of interacting with many cations (13) including

radionuclides like $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ (14). Stumm and Morgan (14) claim that the roles of clays and biota in the transport of radionuclides are commonly recognized but the significance of the hydrous oxides of iron and manganese is not. Goldberg (15) observed that the amounts of trace elements in seawater sediments are proportional to the iron or manganese content of the sediments. Turekian and Scott (16) observed that fresh precipitates of hydrous manganese and iron oxides in streams or in soils act as metal ion scavengers. In fact, these hydrous oxides have been used in the laboratory as radiochemical scavengers for many years. Others (14) have noted that oxidized sediments have much greater adsorptive power than reduced sediments, supporting the idea that iron and manganese play a significant role in influencing the distribution and transport of cations. Finally, it should be noted that manganese nodules, composed primarily of ferric oxide (goethite), manganite and similar ferromanganese aggregations are ultimate sinks for trace metals. Since rare earth elements with their characteristic plus-three valence are found in manganese nodules and are chemical analogues of the actinide elements, it is very likely that Am^{3+} , Cm^{3+} , Np^{4+} , Pu^{4+} , etc., will be readily adsorbed by hydrous oxides of manganese and iron. Deposits of these materials may be the long-term environmental repositories of the long-lived actinide elements.

Complex formation of Am^{3+} , Cm^{3+} or Np(V) --designated "M"--by fulvic acids (H^+Fulv) or soil phenols (ϕOH) can be represented by

or

Aqueous complex formation by soil organic materials, which concentrates

actinide elements in the aqueous phase, has the potential to increase the mobility of Am, Cm and Np in a soil-aquatic environment.

Similarly, adsorption and cation exchange of Am^{3+} , Cm^{3+} or Np(V) on the soil components (humic acid (H^+Hum), manganese dioxide, hydrated ferric oxide and other materials) must be considered factors working in opposition to complex formation. These reactions can be visualized as

and

Hydrogen ion concentration obviously enters in these equations and obviously influences radiocolloid formation as well.

These equations should not be taken too literally because it is recognized that fulvic and humic acids are chemical compounds with rather indefinite composition (17,18) and there are many soil phenols (19). The equations are given to emphasize the importance of the distribution ratio or K_d and show that opposing factors may be operating, e.g., humic acid may act as a cation exchange resin and retain the actinide cations in the soil phase, while complexing by humic, fulvic acids and phenols favors the aqueous phase.

Formation of the ill-defined species, radiocolloids of Am^{3+} , Cm^{3+} and $^{237}\text{NpO}_2^+$ in the soil aquatic environment need to be clarified. Limited research on the formation of radiocolloids of Y^{3+} (20), La^{3+} (21) and Ce^{3+} (22) has been done. Experimental evidence reported above clearly demonstrates their existence. Thus, formation of actinide radiocolloid is a likely factor in the transport behavior of $^{241}\text{Am}^{3+}$, $^{244}\text{Cm}^{3+}$, $^{237}\text{NpO}_2^+$ and Pu^{4+} in the soil-aquatic phase.

Several factors mentioned above influence the transport of actinide elements in the soil-aquatic environment and they must be considered. The following sections report our investigations of these factors.

Radiocolloid Formation

Radiocolloids are particles of colloidal dimensions containing radioactive atoms. For the purposes of this investigation, they are composed mainly of a non-radioactive colloid occurring in the soil-aquatic environment and composed of fine soil particles, clays, and humic matter bearing adsorbed radioisotopes such as $^{241}\text{Am}(\text{III})$, $^{244}\text{Cm}(\text{III})$, $\text{Np}(\text{IV})$, $\text{Pu}(\text{IV})$, etc. Calculations based upon the solubility of $\text{Am}(\text{OH})_3$ and $\text{Cm}(\text{OH})_3$ indicate that the actinide concentrations required for precipitation are orders of magnitude higher than the Am or Cm concentrations employed (3.2×10^{-8} to $1.3 \times 10^{-9}\text{M}$). Radiocolloids can form at orders of magnitude lower solution concentrations than can be explained by normal solubilities. It has long been known that highly charged and readily hydrolyzable radionuclides such as Bi^{3+} , Ac^{3+} , and Th^{4+} are adsorbed to colloidal particles suspended in solution. In these experiments, the inert part of these radiocolloids, as defined by Wahl and Bonner (23), is assumed to be soil minerals, humic materials, or other soil constituents.

Several experiments of actinide radiocolloid have demonstrated their presence in the soil-aquatic environment. Experiments with $^{152}\text{Eu}^{3+}$, chemical analogue for $^{241}\text{Am}^{3+}$, suggested possible radiocolloid formation because 50 to 100 percent of the $^{152}\text{Eu}^{3+}$ was filtered from the aqueous phase. Cellulose nitrate track detectors recorded alpha particle tracks from soil particles equilibrated with $^{241}\text{Am}(\text{III})$ and $^{237}\text{Np}(\text{V})$. An aqueous phase from an equilibrated soil-aqueous sample

and filtered through number 50 Whatman paper. The residue was checked for nonuniform $^{241}\text{Am(III)}$ alpha track distribution. Another $^{241}\text{Am(III)}$ solution was allowed to stand for approximately two weeks before analysis of the aqueous phase. Three experiments with the cellulose nitrate track detectors clearly indicated the presence of actinide-bearing colloids. Figure 1 shows radioautographs of radiocolloids as viewed under a microscope at a magnification of 100 X. The cluster of tracks reveals the presence of an $^{241}\text{Am(III)}$ radiocolloid.

Radiocolloids appear to be partly responsible for the observed decline in the distribution ratios reported below. Chamie and Haissinsky (24) have shown that the amount of polonium centrifuged from solution depended on the solution's age. With time, the smaller particles formed aggregates more susceptible to centrifuging. Centrifugation experiments at 4500 rpm indicated constant production of the actinide-bearing radiocolloid with time. Further centrifugation of these actinide-bearing solutions results in a decreased apparent distribution ratio.

Another experiment was performed in which a soil (aqueous solution) was equilibrated with Am(III) for a period of ten days to form actinide-bearing colloids. The aqueous phase was centrifuged at speeds ranging from 1750 rpm to 7000 rpm. The concentration of $^{241}\text{Am(III)}$ in the aqueous phase was reduced by a factor of 10 going from 1750 to 7000 rpm. In related experiments, with Ritzville soil portions of the aqueous phase containing $^{241}\text{Am(III)}$, $^{244}\text{Cm(III)}$, $^{237}\text{Np(V)}$, and ^{152}Eu were filtered through a Whatman number 50 filter paper. In each case significant portions (50-100 percent) of these radiocolloids were removed from the aqueous phase.

Fig. 1. Radioautographs of soil-aqueous solution (magnification 100X) containing $^{241}\text{Am}(\text{III})$ radiocolloid clusters above uniform background distribution. Both radiographs are from a 10-day-old soil-aqueous suspension.

Incorporation of Actinides in Hydrous Manganese and Iron Oxides

Deep-sea ferromanganese deposits in the form of nodules containing relatively high concentrations of rare-earth elements have been known for some time (25,26,27). Because the plus three actinide and rare-earth elements are chemical analogues, experiments were performed to measure a fraction of these actinides removed from the soil-aquatic environment by the formation of hydrous Fe and Mn oxides.

A solution containing 10^{-4} M Fe(II) and Mn(II) (concentrations similar to seawater) was equilibrated with calcite crystals to make the solution slightly alkaline, and subsequently $^{241}\text{Am(III)}$, $^{237}\text{Np(V)}$ and $^{244}\text{Cm(III)}$ tracers were added. Small aliquots of the aqueous phase were taken daily for two weeks to determine aqueous actinide concentration. These experiments clearly demonstrated that the hydrated oxides of Fe and Mn rapidly removed $^{241}\text{Am(III)}$, $^{244}\text{Cm(III)}$, and Np (V) from solution. Am (III) and Cm (III) had identical removal half-times of 2.4 ± 0.3 days, compared to 8.8 ± 0.5 days for Np (V), as shown in Figure 2.

Hydrous oxides of Fe and Mn suspended in waters are frequently present in a microcrystalline form characterized by high specific surface areas. Sorption of actinide cations to these oxides can be interpreted as surface complex formation or as ion exchange. Under aerobic conditions, Fe^{2+} will undergo the reaction

Ferric oxide precipitates as a coating on the surface of soil particles, becoming an adsorbant for Mn^{2+} ions which then slowly oxidize to Mn oxides. Because of the large specific surface areas

involved, hydrous MnO_2 readily adsorbs highly charged cations like $^{241}\text{Am}(\text{III})$, $^{152}\text{Eu}(\text{III})$, etc. Some of the Mn oxides also react with Fe^{2+} or additional Mn^{2+} forming layers in which the sorbed actinides may become permanently fixed.

These experiments show that the actinides are very efficiently adsorbed onto the hydrous oxides of iron and manganese, along with the observation of high rare-earth concentrations in ferromanganese nodules (21), suggest that an unknown portion of the actinide elements released to the environment are adsorbed by these hydrous oxides.

The experiments described above clearly indicate that actinide elements can be bound to a wide variety of particulate, including clay and humic matter as well as hydrous oxides of Fe and Mn. As a first approximation it can be assumed that two classes of actinide species exist for aqueous phases in equilibrium with soils. The first can be defined as ionic and cannot be physically removed from the aqueous phase. That is they cannot be removed by centrifugation, filtration, etc. The second class, is the radiocolloids or actinide bearing particulate matter. Particulate matter, of course, can be separated by various physical processes ranging from centrifugation to gel filtration. The following sections describe research directed toward determining the relative concentrations of these species.

A. Distribution ratios as a function of centrifuging conditions (7,8).

For a well-defined condition where all parameters, other than centrifuge speed, are held constant an effective distribution ratio, R^* , can be defined by

$$R^* = \frac{\text{cpm of actinide per unit supernatant vol}}{\text{cpm of actinide per unit mass of soil before equilibration}} \quad (5)$$

where cpm is counts per minute of ^{241}Am , ^{244}Cm , or ^{237}Np . It should be noted that the denominator in Equation 1 differs from that usually employed in that the total actinide content of both phases, rather than the actinide content of the solid phase alone, is used.

The Components of R^* . From the definition of R^* , it is clear that the effective distribution ratio can be written as a sum:

$$R^* = R_p^* + R_I \quad (6)$$

where R_p^* is a particle component and R_I an ionic component. Use of R_I values require a demonstration that the aqueous phase containing a radionuclide is truly ionic. In general, it was found that R_I was small compared to R_p^* for these experimental conditions (10). (Additional experiments using Sephadex G-25M and Bio-Gel A-1.5M and centrifugation indicate the "ionic" contribution can be further subdivided into additional fractions. The Sephadex fraction includes actinide-bearing soil particles with radii less than 1nm (equivalent molecular weight of 5000). This fraction includes actinide cations and their hydrolysis products and, presumably, small humic and fulvic acid complexes and comprises less than 40% of R^* . Bio-Gel A-1.5M experiments with Fuquay, Ritzville, and Burbank soils indicated that most of the remaining actinide bearing particles were in the 1-10-nm range with peak molecular weights between 8000 and 50,000, respectively. Contributions of soil particles with radii greater than 10nm were negligible for these soils.

R_p^* is dependent on the details of the technique used to separate soil particles of various sizes. For any specific separation method, a function may be defined $S^*(a)$, which is the fraction of particles of

size A which is retained by the sample after separation. The method of calculating $S^*(a)$ is given by Sheppard, et. al. (7). Generally, $S^*(a) = 1$ for very small particles and falls to zero for particles above the cutoff size $a_{\max}$. Figure 2 shows a separation function for several centrifugation speeds, including a standard procedure used to measuring R^* (4500 rpm and 4-mm sampling depth). The cutoff size in this case is 26-mm equivalent spherical radius; no particles larger than this are sampled, but a proportion of the particles just below the cutoff size is lost.

Accepting this definition of $S^*(a)$, the following equation can be obtained:

$$R_p^* = \int_0^{a_{\max}} S^*(a) r(a) da, \quad (7)$$

where $r(a)$ is the particle size-dependent distribution ratio, defined for each soil as $r(a)da = (\text{fraction of actinide on particles with radii in the range } a \text{ to } (a + da) (M/V))$, where M is the total mass of the soil and V is the volume of the aqueous phase. The size-dependent distribution ratio will depend upon the product of the soil particle size distribution $n(a)$ {where $n(a) da$ is the number per unit soil mass of particles with radii between a and $(a + da)$ } and another function, $B(a)$, measure of the extent of actinide adsorption or chemical binding to the soil particles.

B. Variation of Distribution Ratios as a Function of Time.

Plots of distribution ratios as a function of equilibration time usually showed three distinct segments which were resolved into two quasi-exponential segments. Occasionally a final suggested that

Figure 3: The separation function for several centrifuge speeds. Note that fraction of radionuclide-bearing particles remaining in the supernatant decreases as the centrifuge speed (angular velocity) increases.

equilibrium had been actually attained. Because of the rapidity of the initial reaction, only the second reaction could be fitted to an equation of the form:

$$R^* = R_0^* e^{-t/\tau} \quad (8)$$

where R_0^* is the zero-time R^* , t = the equilibration time, and τ = mean time for R^* to be reduced by $1/e$. Table III contains a summary of the soils studied.

The decrease of R^* with time parallels those observed by Cleveland and Rees (5) for the extractability of Pu(IV) and Am (III) from Rocky Flat, Colo., soils. Rhodes (4) noted similar behavior for Pu(VI). In the case of the Np, Np(V), the principal Np species at zero time, may be slowly reduced by organic matter to more readily hydrolyzable Np(IV) and then adsorbed on soil colloids (28). However, regression analysis indicated no correlation between soil organic content and the observed R_s for Am, Cm, or Np. Similarly, no correlation (with a soil's cation exchange capacity) was found.

The slow decrease in R^* may represent growth of small particles, flocculation of particles, or redistribution of actinides from small to larger particles. Whatever the process, the rate varies. Values of R^* are generally larger for Np(V) than for Am(III) or Cm (III) for each soil, indicating that attachment of Np(V) to soil particles > 26 nm proceeds less rapidly than for the plus three actinides. Exceptions are BUR, HF-A, and HF-B, different samples of the same soil (see appendix II). These data can be used to estimate precision of the distribution determinations. Table I includes values of s_{yx} , the standard deviation of the points about the second line segment. Generally fits were good, but errors greatly exceeding the counting

Table I Zero Time Effective Distribution Ratios of Am(III), Cm(III), and Np(V) for the Second of "Slow" Exponentially Decreasing Line Segment^a

soil	²⁴¹ Am			²⁴⁴ Cm			²³⁷ Np		
	-log R	-log S _{yx}	τ _B , days	-log R	-log S _{yx}	τ _B , days	-log R	-log S _{yx}	τ _B , days
MUS	3.50 ± 0.44	0.29	127	3.00 ± 0.08	0.09	75	2.12	0.07	186
BUR ^b	2.61 ± 0.49	0.84		3.00 ± 0.10	0.08	1395	0.89 ± 0.19	0.05	49
HF-A	2.32 ± 0.13	0.09		1.97	0.14		1.07	0.05	79
HF-B	2.79	0.09	431	3.08	0.08		0.94	0.05	62
av	2.53 ± 0.32			2.66 ± 0.60			0.92 ± 0.16		
F-1	2.38 ± 0.34	0.04	30	2.85	0.05	35	1.24	0.01	51
F-2	2.48 ± 0.64	0.28	23	2.72	0.11	27	1.31	0.05	48
F-3	2.31 ± 0.71	0.22		3.02	0.07	91	1.33	0.06	94
ID-A	4.04 ± 1.00	0.18	52	4.29	0.14		1.71		
ID-B	3.22	0.33	14	4.14	0.01	43	2.15	0.01	202
ID-C	4.03 ± 1.05	0.10	13	3.58 ± 0.25	0.05	7	1.59	0.04	51
ID-D	3.75 ± 0.18	0.20	39	3.82 ± 0.25	0.17	7	1.60	0.09	361
AHN	4.01	0.20	101	4.01	0.19		2.01	0.02	173
RKS	4.23	0.17	59	3.63 ± 0.74			1.76	0.001	462
RITZ	3.14 ± 0.30			2.71 ± 0.13	0.06		1.15 ± 0.14	0.10	90
av	3.14 ± 0.66			3.32 ± 0.70			1.47 ± 0.45		

^a Centrifuge conditions: International 856 centrifuge head, 4500 rpm, $t = 30$ min, sampling depth 4 ± 1 mm. R^* is in g mL⁻¹. ^b Distribution ratios with standard errors represent duplicate and triplicate determinations. BUR, HF-A, and HF-B are "Burbank" soils obtained from different investigators; therefore, R^* values for these soils can also be compared, giving another indication of the precision of these experiments. The remaining R^* 's are the result of duplicate assays and counts. ^c The distribution ratios are fitted to the form $R^* = R_0 \exp(T/\tau_B)$, where R_0 is the "zero time" time value. ^d Average for all 14 soils.

error clearly exist. Causes of this scatter are unknown, but variations in sampling depth are suspected.

Further analysis of the distribution data suggested that the observed distribution Ratio, R^* , is related to a complex spectrum of actinide species which includes, ions, hydrolysis products, actinide-bearing particles (radiocolloids, as described above) and complexes of humic and fulvic acids. To analyze aqueous solutions previously equilibrated with the soil phase the following experiments were done.

1. Contributions of actinide-bearing particles with radii less than 1nm were obtained with Pharmacia PD-10 columns containing Sephadex G-25 (8). This fraction of the aqueous phase contained ions, hydrolysis products and contributions from small fulvic and/or humic acid complexes.

2. Contributions of actinide-bearing particles with radii between 1 and 10nm were obtained by Gel Filtration through a Bio-Gel A-1.5 column (8). These data were used to obtain estimates of contributions of larger actinide complexes of humic in the 10^4 to 10^5 molecular weight range.

3. Contributions of actinide-bearing soil particles greater than 10nm and less than 60nm were obtained by centrifugation (8).

To obtain contributions of actinide-bearing particles less than 10nm (mol wt = 2.5×10^6), the particle size dependent distribution ratio $r(a)$ was obtained from the gel filtration data. From molecular weight data for blue dextran and the gel manufacturer's calibration curve particle size limits of each fraction were obtained. By alpha or gamma counting the fraction and knowing the initial assay (i.e. the number of counts added), the fractional contribution of each sample of particles between A_{n+1} and A_n was obtained. With a measurement of the

total or observed distribution Ratio R^* and these fractional contributions $r(a)$ for the particle size range $a_{n+1} - a_n$ was obtained. Figures 3, 4, and 5 are representative of the data obtained.

~~For each of the soils investigated characteristic plots of $r(a)$~~ against particle size dependent distribution ratios $r(a)$ can be considered as unique spectra related to the physical properties and chemical composition of each soil. Thus the contribution of a particular particle size fraction is a function of the relative contributions of soil particles, humic acid complexes of differing molecular weights, particle size distributions, etc. For these soils, three broad classes of particles determine the observed distribution ratio, R^* : 1) ionic and small humic and fulvic acid complexes with radii less than 1 nm; 2) larger humic acid complexes and polymers with molecular weights in the 8000 to 50,000 range (2 to 3nm radii); 3) Humic acid complexes with MW's greater than 50,000 and soil particles greater than 3 nm.

These studies suggest that the ionic contribution to the distribution ratio is a small and not too significant. Furthermore, the contribution from larger actinide-bearing particles ($a > 10\text{nm}$) are even less important. Thus these data indicate that intermediate soil particles, most likely humic acid polymers, are the chief complexing agents of upper horizons soils. If this is characteristic of most soils, then it is important to obtain estimates of the magnitude of the humic acid formation constants of actinide cations.

Accepting the gel filtration experiments, that humic acid is a polyelectrolyte and a polymer of humic acid, and assuming that these polymers have the following composition (17) $[\text{C}_{20}\text{H}_{12}]$

Figure 4. Particle size distribution ratio as a function of particle radius.

Figure 5. Particle size distribution ratio as a function of particle radius.

Figure 6. Particle size distribution ratio as a function of particle radius.

$(\text{COOH})_6(\text{OH})_5(\text{CO})_2]_n$, where n is the number of humic acid monomer units per polymer [polyelectrolyte], humic acid polymers have the potential to complex many Am(III) cations. But many of the carboxyl and pheno groups must be involved in the hydrogen bonding that stabilizes the humic acid polymer. Assuming that half of the carboxyl and phenol groups are hydrogen bonded, the molecular weight ranges from 8000 to 50,000 (8) and only carboxyl groups complex metal metal cations, each humic acid polymer can complex 12 to 75 Am(III)s. However, in the soil aquatic environment many sites are occupied by Ca^{2+} and Fe^{3+} , and other cations, hence fewer Am(III) cations are complexed. Thus humic acid polymers have variable capacities for Am(III).

Distribution experiments were performed to test this hypothesis. Assume that the following reaction takes place between x cations (either Am^{3+} or Eu^{3+}) and the humic acid polymer, HA, and that the reaction is

where $M = \text{Eu}^{3+}$ or Am^{3+} .

$M_x\text{HA}$ = the humic acid polymer complex of M . The equilibrium quotient for this reaction is

$$\beta_x = \frac{[M_x\text{HA}]}{[M]^x [HA]} \quad (10)$$

and material balance equation for M in the aqueous phase is

$$[M]_{\text{tot}} = [M] + x[M_x\text{HA}]. \quad (11)$$

Substituting equation 1 into 2 the result is

$$[M]_{\text{tot}} = [M] + x\beta_x[M]^x [HA]. \quad (12)$$

The distribution ratio is defined as

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} = \frac{\text{metal ion concentration in organic phase, cation exchange resin, soil, etc.}}{\text{metal ion concentration in aqueous phase}} \quad (13)$$

$[M]_{\text{tot}}$ total metal ion concentration in aqueous phase

Substitution of equation 3 into 4

$$= \frac{[M]_{\text{org}}}{[M]} \cdot \frac{1}{1 + \beta_x [M]^{x-1} [HA]} \quad (14)$$

and where

$$D_o = \frac{[M]_{\text{org}}}{[M]} = \text{Distribution ratio in absence of humic acid.} \quad (15)$$

On rearrangement of equation 14 we obtain

$$\left(\frac{D_o}{D} - 1 \right) = Q_x = x \beta_x [M]^{x-1} [HA] \quad \text{and} \quad (16)$$

therefore a plot of Q_x against $[HA]$ should yield an apparent formation constant

$$\beta_{x,M} = x \beta_x [M]^{x-1}. \quad (17)$$

But the desired quantity is β_x not $x \beta_x [M]^{x-1}$. Consider two distribution measurements done at different metal ion concentrations, and let

$$R = \frac{\left(\frac{Q_{x,M1}}{Q_{x,M2}} \right) \frac{x[M]_1^{x-1} [HA]}{x[M]_2^{x-1} [HA]}}{\left(\frac{[M]_1}{[M]_2} \right)^{x-1}} \quad (18)$$

$$= \left(\frac{[M]_1}{[M]_2} \right)^{x-1} \quad (19)$$

Thus, distribution experiments done at two different metal ion concentrations may yield information about the number of metal cations bound to the humic acid polymer.

To simplify these experiments the distribution of Eu between an aqueous phase containing humic acid and a xylene phase containing the extractant TTA (thenoyltrifluoroacetone) was measured. The justification for this approach are 1) There are considerable data for the extraction of Am(III) by TTA; 2) Many investigators have used this

Figure 7. Distribution of $^{152}\text{Eu}(\text{III})$ between 0.1M TTA in xylene and aqueous phases of 0.01M NaAc - 0.09M NaClO_4 at 25°C.

that is only one Eu(III) is bound to the humic acid monomer/polymer, which greatly simplifies the modelling calculations.

TRANSPORT OF ACTINIDES IN AQUIFERS (29)

In the absence of humic acid complexing and any two phase distribution effects, actinide cations such as Am(III) are transported at the aquifer flow velocity. But the effect of the distribution between a porous soil phase is the reduction of the actinide transport velocity according to equation 20.

$$V(\text{act})/V(\text{H}_2\text{O}) = (1 + (p/\theta) K(d))^{-1} \quad (20)$$

where $V(\text{act})$ = actinide flow velocity,

$V(\text{H}_2\text{O})$ = aquifer flow velocity,

P = soil density, g/cm^3

θ = soil porosity,

$K(d)$ = the distribution between the soil and aqueous phases in the presence of a complexing agent (i.e. humic acid).

For any cation and soil combination $K(d)$ is less than that for a soil without significant amounts of humic matter (see, for example, Table I). The exact reduction is difficult to predict because the actual amount of soluble humic matter is generally variable and unknown. But if actinide complexing takes place, equation 21 is applicable

$$K(d) = K(d,0)/(1 + \beta [\text{HA}]) \quad (21)$$

where = the humic acid formation constant, and

$[\text{HA}]$ = the humic acid concentration.

Substitution of equation 21 into 20 yields

$$V(\text{act})/V(\text{H}_2\text{O}) = (1 + \beta [\text{HA}]) / (1 + \beta [\text{HA}] + (P/\theta) * K(d,0)). \quad (22)$$

When the humic acid concentration is zero, the actinide flow velocity

is determined by the actinide's $K(d)$ but in the presence of increasing humic acid concentrations, that is when $K(d,0) \rho/\theta \gg \beta[HA] \gg 1$, equation 22 simplifies to

$$V(\text{act})/V(\text{H}_2\text{O}) = \beta[HA]/(\rho/\theta) K(d,0). \quad (23)$$

Equation 23 suggests that:

- 1) The actinide flow velocity is proportional to the humic acid concentration,
- 2) Their transport rate are inversely proportional to their respective $K(d)$'s and,
- 3) The magnitude of the actinide flow velocity depends on the size of the formation complexing constant.

COMPUTER MODELLING OF ACTINIDE TRANSPORT IN AQUIFERS

In the following model calculations a hypothetical "spill" of an actinide-containing waste will be assumed without estimate of the probability of such an incident. Probabilities will be left for the more speculative and it will be assumed that a rather large quantity (megacuries) of a water-soluble actinide will be released and enter the groundwater. The differential equation describing the one-dimensional transport of a radionuclide is

$$K \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2} - \lambda C \quad (24)$$

where $K(1)$ is the retardation factor for a particular geologic environment (e.g. soil, sand, or fractured rock). The terms of equation 24 represent, respectively, the combined accumulation of the actinide in the sorbed (soil, sand, or rock) and the aqueous phases, the net convective and diffusive transport through a volume element,

and radioactive decay of the actinide in both phases. Respectively, the various parameters in equation are:

C = actinide concentration, g-atom/cm³,

Z = axial distance, cm,

t = time in years,

V = groundwater velocity, $V(H_2O)$. cm/yr,

D = axial diffusion coefficient, cm²/year, and

λ = radioactive decay constant, year⁻¹.

Two potential geologic environments must be considered: (1) the porous soils and sands and (2) fractured rocks. In the case of sands and soils K is simply equation 20. But the retardation factor (2,30) for conditions when water passes through fractured rock is

$$K = 1 + K_a R_f \quad (25)$$

where

$K(a)$ = the distribution coefficient for a particular type of rock, cm⁻¹; and

R_f = surface to volume ratio of the fracture system, cm⁻¹, and it must be emphasized that is descriptive of an unique, distinctive rock.

In these calculations only transport through a porous medium like sands and soils is considered. This is the initial, and possibly the last, medium that the actinide will be transported by water. Obviously, as the time scale is extended, fractured rock must be included in the analysis. However, such an analysis is beyond the scope of this research. Furthermore, diffusive transport of actinides will be considered negligible compared to groundwater transport. Calculations using measured Am(III) and Cm(III) diffusion coefficients (Appendix I) of about 3×10^{-7} cm²/sec and nominal groundwater velocity

of 3 cm/day indicate that it will require about one year for these radionuclides to diffuse this distance.

To further test the hypothesis that humic acid, and other complexing agents such as EDTA, accelerate the transport of actinide ions in groundwaters, the FORTRAN computer code GARD, developed by Rosinger and Tremaine (31) was changed to include complex formation. In particular, the K_d term of the retardation factor, K , was modified to be the equivalent of equation 22. Because the exact nature of the Am(III)-humic acid complexing is obscure, simple one to one complexes were assumed. Further, the Eu(III) humic acid formation constant, measured TTA extraction, was used to approximate the Am(III)-humic acid formation constant for the reasons specified previously. Use of the Am(III) or Eu(III) formation constants determined by Bertha and Choppin (11) does not significantly alter the results or conclusions of these computations because the two sets of formation constants differ slightly.

Several computer runs with the modified GARD were made for representative groundwater conditions. Groundwater flow rates of 0.3 and 3.0 meters/year were used as representative conditions. A wide range of humic acid concentrations were used because natural concentrations are largely unknown and probably unknown. However, actual humic acid concentrations are likely to be in this range. Also, these concentrations should indicate the magnitude of the influence of humic acid on rates of actinide ion transport in groundwater. Figures 8 and 9 graphically illustrate the profound influence of humic acid, and by implication any other strong complexing agent, has on the actinide transport rate in groundwaters. These figures also confirm the prediction of equation 23 that time for an actinide ion to reach a

discharge point is inversely proportional to the humic acid concentration. These computer calculations also confirmed the assumption that diffusive migration is a negligible contribution to the over-all transport process and minimally alters the shape of actinide pulse as it passes through the aquifer. Further, this pulse, as shown by figure 10 is altered by radioactive decay. Radioactive decay will only be an important factor when the transport time is greater than one half-life.

Figure 8

Figure 9

These calculations have emphasized the importance of humic acid complexing of the actinide elements and groundwater transport. But many man-made complexing agents such as EDTA and NTA have even larger formation constants and, therefore, greater capacities to accelerate the transport of actinide elements and other radionuclides. The investigations of Means, Crerar, and Duguld (32) have demonstrated that radionuclides such as Co-60 have increased mobility in the presence of complexing agents such as EDTA. This suggests that radioactive wastes containing such strong complexing agents should be chemically treated to destroy this mobilizing agent. However, it is important to note that the important quantity is $[HA]$. If $[HA]$ is small compared to one, the effect on actinide transport is negligible. But if $[HA]$ is much larger than unity, complex formation is significant relative to transport in aquifers and groundwater.

Summary

This research on the transport of actinide elements in the "soil-aquatic" environment started with two assumptions. One was that diffusive transport was significant with regard to migration of actinide cations ($Am(III)$, $Cm(III)$, and $Np(V)$) in the moist groundwater environment. The second was that the distribution ratio or K_d reduces the mobility of these ions in the groundwater-soil environment.

As demonstrated above the assumption that diffusion of the actinide cations in the groundwater is significant relative to mass transport was obviously incorrect. However, determination of diffusion coefficients did yield limiting distances that actinide cations could migrate in the absence of moving water. As expected, within the experimental error, $Am(III)$ and $Cm(III)$ have almost identical diffusion

coefficients because of almost identical ionic radii and the same charge. Neptunium (V) has a diffusion coefficient almost two orders of magnitude greater because of its plus one charge. Soil characteristics did not appear to be an important factor, and may not be significant influence in groundwater transport.

Because of the importance of distribution ratios to radionuclide transport, a large number of soils were investigated. Considerable variability of the distribution ratios was observed and could be attributed to a number of factors, including cation exchange capacity and organic matter content (possibly humic acid). High variability in the distribution ratios also suggested varying actinide complexing and some of the experiments mentioned below.

Much of this research has been directed toward "actinide-bearing" particulates, which at one time were called radiocolloids. Alpha track experiments, as shown in figure graphically demonstrated that such actinide-bearing matter was present in the aqueous phases in contact with soils. Filtration and centrifugation experiments yielded additional evidence for "actinide-bearing" particulates.

Subsequent centrifugation measurements showed that the distribution ratio or K_d is a function of the centrifugal angular velocity. Analysis of these data indicated that the K_d could be separated into two components, one being ionic, the other particulate. This suggested that the particle size distribution ratio be further investigated.

Particle size distribution ratio or K_d measurements using gelfiltration techniques revealed that a spectrum of complexes or particles were present in aqueous solutions in contact with the soil

phase. These measurements indicated that the molecular weight of these particles or complexes were in the 8000 to 50,000 range, with a minor contribution of higher molecular weight particles, presumably colloidal clay. Most important, the gelfiltration measurements strongly suggested that the dominant particles or complexes were humic acid polymers and that the formation constant of the Am(III)-humic acid complex be measured.

The final set of measurements used $^{152}\text{Eu(III)}$ as a stand-in for $^{241}\text{Am(III)}$ and TTA solvent extraction technique to determine a humic acid formation constant of about 6×10^6 , which agrees reasonably well with Eu(III) and Am(III) formation constants found by Bertha and Choppin who used the similar ion exchange technique.

The final portion of this research was to incorporate complex formation into the groundwater transport code GARD and demonstrate the affect of complexing of actinide element mobility. For humic acid concentrations as low as 10^{-6} moles/liter humic acid complexing significantly increases the groundwater transport rate of Am(III) and, presumably, other actinide cations.

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Diffusion Coefficients of $^{241}\text{Am}(\text{III})$, $^{247}\text{Cm}(\text{III})$,
and $^{237}\text{Np}(\text{V})$ in Moist U.S. Soils^a

Soil	Am cm^2/sec	Cm cm^2/sec	Np cm^2/sec
MUS	5.10×10^{-11}	1.4×10^{-11}	8.93×10^{-9}
BUR ^b	4.95×10^{-11}	1.2×10^{-11}	2.32×10^{-8}
HF-A	6.00×10^{-11}		2.98×10^{-8}
HF-A ^b	$1.50 \times 10^{-13}\text{c}$		
HF-B	8.45×10^{-11}		$2.70 \times 10^{-9}\text{c}$
Ave.	$(6.47 \pm 1.80) \times 10^{-11}$		$(2.65 \pm 0.47) \times 10^{-8}$
ID-A	1.14×10^{-11}		5.03×10^{-9}
RITZ	1.39×10^{-11}	1.91×10^{-11}	2.26×10^{-8}
F1	11.10×10^{-11}		8.03×10^{-8}
F2	2.00×10^{-11}		7.46×10^{-8}
F3	1.29×10^{-11}	0.6×10^{-11}	9.92×10^{-9}
ID-B	1.77×10^{-11}	6.2×10^{-11}	$8.10 \times 10^{-10}\text{c}$
ID-B ^b	5.06×10^{-11}		
ID-C	10.35×10^{-11}	1.2×10^{-11}	2.33×10^{-9}
ID-C ^b	1.77×10^{-11}		
ID-D	1.45×10^{-11}		1.49×10^{-9}
AHN	6.07×10^{-11}		3.17×10^{-9}
RKS	3.81×10^{-11}		3.75×10^{-9}
		$2.1 \pm 2.1 \times 10^{-11}$	
	$4.64 \pm 3.43 \times 10^{-11}$		$2.06 \pm 2.69 \times 10^{-8}$

^aWater content of these soils was at a moisture tension of 1.0 bar.

^bBUR, HF-A, and HF-B are different samples of Burbank loamy sand obtained from different sources.

^cThese "low" values suggest poor contact between half cells.

Appendix II

Physical and Chemical Properties of Soils Studied

soil code	sand, %	silt, %	clay, %	soil class	pH	C.E.C., mequiv/ 100 g	org material, %
MUS	12.6	65.8	21.6	silt loam	5.3	16.88	3.61
BUR	76.0	21.2	2.8	loamy sand	8.1	5.94	0.43
HF-A	65.2	29.0	5.8	sandy loam	8.1	6.14	0.45
HF-B	83.6	12.6	3.8	loamy sand	8.4	4.95	0.17
RITZ	32.0	56.0	12.0	silt loam	6.5	10.76	0.84
FQ-1	91.2	7.8	1.0	sand	4.0	2.01	1.19
FQ-2	91.6	5.4	3.0	sand	6.7	1.79	0.99
FQ-3	94.6	1.6	3.8	sand	5.2	0.69	0.21
ID-A	42.6	39.4	18.0	loam	8.3	15.04	0.60
ID-B	60.4	19.4	20.2	sandy clay loam	8.4	10.44	0.18
ID-C	83.4	8.8	7.8	loamy sand	8.4	6.38	0.16
ID-D	49.2	28.4	22.4	sandy clay loam	7.7	18.36	0.98

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