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PLUTONIUM BEHAVIOR IN THE SOIL/WATER ENVIRONMENT, ³
PART I. SORPTION OF PLUTONIUM BY SOILS ³

F. J. Miner

P. A. Evans

*W. L. Polzer**

PART II. SELECTED CHEMICAL AND PHYSICAL CHARACTERISTICS
OF AQUEOUS PLUTONIUM AND THEIR EFFECTS
ON THE SORPTION OF PLUTONIUM BY SOILS

*W. L. Polzer**

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U. S. DEPARTMENT OF ENERGY
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ROCKWELL INTERNATIONAL
ENERGY SYSTEMS GROUP
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PLUTONIUM BEHAVIOR IN THE SOIL/WATER ENVIRONMENT

PART I: SORPTION OF PLUTONIUM BY SOILS

F. J. Miner, P. A. Evans, and W. L. Polzer

ABSTRACT

The sorption behavior of plutonium was investigated using equilibrium sorption and column elution techniques. Plutonium nitrate solutions were used as the source of plutonium. Equilibrium sorption was measured for 13 soils at plutonium concentration levels of 10^{-6} , 10^{-7} , and 10^{-8} molar. Three characteristics of plutonium sorption were apparent from the sorption data. First, the initial concentration of plutonium has an effect, in some cases, on the amount of plutonium sorbed, although on the basis of the percent of plutonium sorbed, this effect is small. Second, the rate of plutonium sorption is rapid. Third, plutonium sorption is quite high. Sixty-two percent of the time the equilibrium sorption of plutonium is 99% or higher; 87% of the time it is 96% or higher. Only 5% of the time is the equilibrium sorption less than 90% and in no case is it less than 87%.

Three soils were used to investigate the column elution behavior of plutonium. In two of these there were prompt pulses of plutonium through the column in the initial 20 ml effluent fractions. Subsequent elution fractions contained continually decreasing amounts of plutonium. In the third soil, there was no pulse of plutonium throughout the entire elution. Instead, the plutonium concentration in the effluent fractions varied randomly throughout the entire elution. In none of the soils was more than 2% of the added plutonium eluted from the column.

Statistically significant relationships were found between plutonium sorption and cation exchange capacity (CEC), clay, and sand contents of the soils. Although this would tend to indicate that a conventional ion exchange process is responsible for the sorption of plutonium, the total data and knowledge about the chemistry of plutonium would indicate

that there are other variables and cause/effect relationships that have not been identified.

INTRODUCTION

Plutonium has chemical and radiation characteristics that make it harmful physiologically to man. Because of this it is imperative that as much information as possible be obtained about the behavior of this element in the environment.

There has been some work related to the behavior of plutonium in the soil over the past two decades. Using a soluble form of plutonium Rhodes found that the sorption of plutonium was pH dependent.^{1,2} Between a pH of 2 and 8.5 the plutonium was, essentially, completely sorbed. Between a pH of 8.5 and 12.5 there was a decrease in sorption with a minimum sorption of approximately 85% occurring at a pH of 12. Above pH 12.5 there again was essentially complete sorption. Column experiments verified the importance of the pH. When a plutonium-containing feed solution was maintained at a pH of 4, no plutonium came through the column. But when the pH was maintained at 10, there was an immediate breakthrough of plutonium.

The observed behavior of plutonium was explained by Rhodes as resulting from the formation of polymers beginning with a pH of about 2. Some alteration of these polymers takes place in the pH 8.5 to 12.5 range which inhibits its sorption. Rhodes found that the sorption of plutonium could be influenced by the presence of complexing ions. As the concentration of acetate was increased, for example, the sorption of plutonium decreased. Acetate is known to form a complex anion with plutonium.

Plutonium distribution coefficients were determined by Prout on Savannah River soil as a function of pH and oxidation state of the plutonium.³ The soluble form of plutonium used was not identified. Plutonium sorption was more than 95% complete, i.e., $K_d > 100$, beginning at a pH of 2.5 for Pu(III) and Pu(IV), and at a pH of 7 for Pu(VI). Sorption reached a maximum at a pH of 6 to 7 for Pu(III) and Pu(IV) (K_d of approximately 10,000) and at a pH of 8 for Pu(VI) (K_d of approximately 1,000). The sorption of plutonium in all three oxidation states decreased as the pH increased. However, by a pH of 12, which was the highest investigated, the K_d values were still significantly greater than 100.

Christenson, et al. investigated the movement of plutonium in Los Alamos soil.⁴ Water spiked with plutonium nitrate was passed through columns of soil in the laboratory for times varying from 2 to 6 months. In all cases, 96% of the plutonium, or more, was retained by the soil. Analysis of the soil columns indicated that the plutonium penetrated essentially only the top 2 inches of the soil. The authors assumed that the plutonium was polymerized and would not enter into any ion exchange reactions with the soil. However, local areas were noted throughout the soil columns that had high plutonium concentrations. These high plutonium concentrations were attributed to the presence of localized concentrations of high ion exchange material such as montmorillonite clays.

In a later article, Christenson and Thomas noted that under field conditions, plutonium has penetrated at least 28 feet down in the Los Alamos tuff.⁵ This penetration took place along fissures. But again it was noted that along these fissures where there was a high percentage of clays there were also localized areas of high alpha activity from sorbed plutonium. Christenson and Thomas suggest that as the plutonium species percolate through the soil, changes in valence states may occur with changes in the chemical environment. As a result sorption, or even solution of the plutonium, may result.

At one time plutonium-containing waste solutions were stored in soil cribs at Hanford. The plutonium was presumably in a soluble form and was sorbed by the soil as the waste solution seeped down from the

cribs. Hajek investigated the movement of plutonium in these soils.⁶ Movement by contact diffusion was measured and the apparent contact diffusion coefficient was found to be 4.8×10^{-12} cm²/sec. Based on this coefficient, Hajek calculated that it would require 2.4×10^5 years for the plutonium to diffuse 8.5 cm. Movement of plutonium by this mechanism, therefore, is rather insignificant.

Distribution coefficients were measured by Hajek using the plutonium-containing soil and ground water. The coefficients were found to be greater than 10,000 indicating that an extremely high percentage of the plutonium was sorbed by the soil. Interestingly, however, about 0.1% of the plutonium in the soil could be leached out by ground water from a column of the soil. This amount was removed by 19 column volumes of water; additional water did not remove any additional plutonium. Leaching with 1N sodium nitrate, 3.5% of the total plutonium in the soil could be removed. Hajek was reluctant to consider this "exchangeable" plutonium, however, for the leaching curve suggested a solubility instead of an exchange mechanism.

Additional work has been done on the movement of plutonium in Hanford soil by Knoll.⁷ However, the work involved organic solvents rather than water. Some of the solvents removed plutonium that already had been deposited on the soil, whereas other solvents did not. Likewise, soil removed plutonium from some solvents but did not remove the plutonium from others. Although no explanation is given for the differences in behavior of the various organic solvents, it would not seem unlikely that these differences were related to complex formation.

Tamura reported on the sorption of plutonium by water suspensions of several different clays and charcoals, a commercial anion and cation ion exchange resin, alumina, apatite, and quartz.⁸ The sorption varied from 0% for the quartz to 99+% for the charcoal and apatite. Tamura suggested that the controlling factor for the plutonium removal might be the pH of the suspensions which varied from 1.8 to 9.6. Plutonium hydroxide is formed even at relatively low pH values. Sorption of plutonium

from water systems might not then be normal ion exchange but rather by "scavenging" of the hydroxides by the charcoals and clays.

In the work discussed above, plutonium was present in the soil, or was added to the soil, as a "soluble" species (soluble in this context means as a polymer, hydroxide, or soluble complexed ion). Plutonium can also be present in the soil in an insoluble oxide form. The movement of plutonium in this form has been investigated, but less extensively than where it is present in the soluble form. The published reports are based primarily on work done at the Department of Energy's Nevada Test Site. Here, high explosives, which involved plutonium, were set off. Little or no fission of the plutonium occurred. Under these conditions the plutonium would be present in the soil in the oxide form.

Mork investigated the site two years after the tests and found little downward movement of plutonium.⁹ When movement did occur, it was only under highly contaminated surface conditions. He found that the major portion of the plutonium was associated with particles greater than 44 μm in diameter.

A decade later the test site was again investigated. Romney, et al. observed a downward movement to depths of at least 9 to 12 cm.¹⁰ Alternate freezing and thawing, and wetting and drying of the soil, was believed to account for a mechanical downward movement of the high density particles of plutonium. Movement of plutonium in a solution form was considered unlikely because of the high degree of sorption of a polymeric form of plutonium known to occur in soils and because of the slow rate of diffusion and leaching of plutonium by ground water.

The distribution of plutonium in the soil surrounding the Rocky Flats Plant was reported by Krey and Hardy.¹¹ They indicated that significant quantities of the plutonium were below a soil depth of 5 cm. The authors postulated that the base exchange capacity, and perhaps other characteristics of the soil, were important in determining how much of the plutonium penetrated below the surface. However, they reported no measurements to verify this postulate. It should be noted that the

major source of the plutonium contamination at Rocky Flats is from leaking barrels of plutonium-contaminated machine cutting oil. The form of the plutonium in this oil is not known, but it probably is not the type of oxide found at the Nevada Test Site.

A summary of the literature on the behavior of plutonium in soils has been included in reviews by Francis¹² and Price.¹³

The purpose of the following work was threefold. The first was to obtain experimental information, under controlled conditions, about the sorption of plutonium in soil/water systems under both equilibrium and dynamic conditions. Equilibrium sorption and column elution experiments were used to obtain a measure of this sorption. The second purpose was to determine if there are significant relationships between the chemical and physical (mechanical) characteristics of the soils and the plutonium sorption. The third purpose was to relate the physical and chemical characteristics of plutonium in aqueous solutions to the sorption of plutonium in the soil. The results of the sorption measurements and the relationships between sorption and soil characteristics are summarized in this section (Part I) of this report. The work relating the physical and chemical characteristics of aqueous plutonium to sorption of plutonium by the soil is discussed in Part II of this report.

MATERIAL AND METHODS

Thirteen soil samples were obtained from seven sites. These sites were selected to be near areas that currently have, or were expected to have, facilities for handling plutonium. One or more surface soil samples were obtained at all seven sites and subsurface samples were obtained at two of the sites. Texture, classification data if available, and the code to be used in identifying the soils in this report are given in Table 1. The code includes the abbreviation of the state from which the samples came.

The soil samples were received in plastic bags. They were air dried, sieved through an 8 mesh screen (2.4 mm), then aliquants were sent to the Colorado

TABLE 1. Soils Investigated

Soil Code*	Texture	Soil Series
CO-A	Clay loam	Soil not classified
CO-B	Sandy clay loam	Soil not classified
CO-C	Clay	Soil not classified
ID-A†	Silty clay loam	Polatis
ID-B†	Clay loam	Polatis
ID-C	Sandy clay loam	Polatis
ID-D	Clay loam	Polatis
WA-A	Sandy loam	Soil not classified
WA-B†	Sandy loam	Soil not classified
TN	Sandy loam	Not available
SC	Sandy loam-silty clay loam	Fuquay sand
NY	Clay loam	Fulton silty clay loam
NM	Loam	Los Alamos

*The first two letters identify the state from which the soil came. A third letter, if present, differentiates between samples from the same state.

†Subsurface sample taken at about a 40-cm depth. The remaining samples were taken from the surface to about a 20-cm depth.

State University Soil Testing Laboratory for determination of their chemical and physical (mechanical) properties. Table 2 summarizes these properties.

Plutonium nitrate solutions were used as the source of plutonium. This is a "soluble" form of plutonium as contrasted to an insoluble form such as PuO_2 . Standard plutonium nitrate solutions were prepared by dissolving ultrapure (electrorefined) plutonium metal. To prevent the plutonium from hydrolyzing prior to its addition to the soil/water system, the standard solutions were made 0.5M in HNO_3 . The plutonium concentrations of these solutions were adjusted so that only 10 μl were required for each equilibration run. This small volume prevented the HNO_3 from altering the natural pH of the soil.

Three plutonium standard solutions were prepared. They contained 5.9×10^{-3} , 6.4×10^{-2} , and 6.0×10^{-1} g/l plutonium, respectively. For the equilibration experiments, 10 μl of each of these gave plutonium concentrations, in the final solutions, equivalent to 10^{-8} , 10^{-7} , and 10^{-6} M, respectively.

Six grams of soil, 30 ml of distilled water, and 10 μl of the appropriate plutonium standard solution were used for making the plutonium sorption measurements. Soil aliquants were weighed into each of four 50 ml polycarbonate centrifuge tubes, water was added and then the plutonium standard solution. The tubes were immediately capped with fraction-fit closures (pipe caps) and taped as an additional precaution against leakage, then placed on a Tube Rotator modified to accept the 50 ml centrifuge tubes. The tubes were then rotated around a slightly canted, vertical axis at approximately 25 rpm for time intervals ranging from 10 minutes to 48 hours, depending on the experiment.

Centrifugation was used to separate the aqueous phase for plutonium analysis from the solid (soil) phase. At the pH levels encountered in the near-neutral soil/water systems, plutonium will hydrolyze. In addition, it likely forms complexes, both soluble and insoluble, with various components of the soil. The composition, size, and weight of the

TABLE 2. Chemical and Physical Analysis of Soils

Soil Code	CEC meq/100 g	Soluble Salts mmhos/cm	Soluble Carbonate meq/l	Inorganic Carbon % CaCO ₃	Organic Matter %	pH*	Sand %	Silt %	Sand %
CO-A	20.0	3.8	5.97	0.4	2.4	5.7	44	20	36
CO-B	17.5	0.4	0.97	0.3	3.4	5.6	64	14	22
CO-C	29.6	0.4	1.98	2.4	0.7	7.9	5	31	64
ID-A	15.5	0.5	2.72	17.2	0.8	7.8	16	50	34
ID-B	13.8	0.8	2.52	7.9	0.2	8.3	44	24	32
ID-C	8.2	1.0	2.52	5.2	0.3	8.0	66	11	23
ID-D	17.5	1.2	4.85	0.0	1.0	7.5	38	32	30
WA-A	6.4	0.9	2.62	0.6	0.3	8.0	74	12	14
WA-B	3.8	0.4	2.30	0.0	0.1	8.2	74	12	14
TN	20.5	0.4	0.29	0.0	1.0	4.8	32	32	36
SC	2.9	0.4	0.53	0.2	0.7	5.4	78	2	20
NY	16.0	1.2	1.36	0.0	2.7	5.4	32	38	30
NM	7.4	1.7	2.81	0.2	0.7	6.4	36	42	18

*pH measurements were made on a saturated soil paste.

plutonium-containing species present in the aqueous phase are not well known and likely will change in soils. For purposes of centrifugation, however, it is assumed that plutonium sorbed by a soil particle will not significantly alter the weight of that particle. In addition, the plutonium that remains in the aqueous phase will not agglomerate to give particles with densities greater than 2.5 or diameters greater than 0.1 μm .

When agitation of the soil/water/plutonium mixture was completed, the tubes were removed from the rotator and centrifuged at 4,000 rpm (1900 RCF) (Relative Centrifugal Force) for 19 minutes. This settled particles with a density of 2.5 and diameters greater than 0.1 μm as calculated using equations by Jackson.¹⁴

After centrifugation, 4 ml of the aqueous phase was removed for plutonium analysis. An Eppendorf automatic pipet was used for this, and great care was necessary to prevent resuspension of the soil particles. After the removal of the sample, the remainder of the aqueous phase was poured into a beaker and used for Eh (oxidation-reduction potential) and pH measurements.

For plutonium analysis, an aliquant of the aqueous phase was pipetted onto a planchet and evaporated under a heat lamp. The size of the aliquants varied from 0.5 to 2 ml depending on the amount of plutonium sorbed by the soil. Each of the planchets was counted for 10 minutes in a proportional counter. These counts were averaged from the four replicates from each run and reported in d/min/ml. From these data, and the total amount of plutonium added initially to the sample, the amount of plutonium sorbed by the soil was calculated.

It was demonstrated experimentally that the amount of plutonium sorbed by the centrifuge cones during the soil/water equilibration was insignificant. Likewise, it was also shown experimentally that americium, an impurity which can interfere in the radioassay of plutonium, was not present in quantities sufficient to introduce errors.

The distribution of plutonium between soil and water was expressed in two ways. The first was % Pu Sorbed. This was calculated as follows:

$$\% \text{ Pu Sorbed} = \frac{\text{Pu}_s}{\text{Pu}_i} \times 100$$

where Pu_s = d/min in the soil phase = $Pu_i - Pu_{aq}$

Pu_i = total d/min added initially to the soil/
water system

Pu_{aq} = total d/min in the aqueous phase after
equilibration

The % Pu Sorbed values have the virtue of being quickly and easily calculated. It should be noted, however, that the values of % Pu Sorbed will change for a given plutonium concentration as the soil/water ratio changes. In this work, however, the soil/water ratios were constant (6 g soil/30 ml water). It was possible, therefore, to compare directly the % Pu Sorbed of the various soils. These % Pu Sorbed data were used primarily as a measure of the rates at which sorption equilibrium was attained.

When % Pu Sorbed data indicated that sorption equilibrium had been attained, the equilibrium that existed was expressed, additionally, by conventional distribution coefficients calculated as follows:

$$K_{d(m)} = \frac{Pu_s}{Pu_{aq}} \times \frac{V}{M}$$

where Pu_s and Pu_{aq} have the same meaning as above and

V = ml of aqueous phase after equilibration
 M = g of soil

For determining the elution characteristics of the soils, a specially designed glass column was developed. It consisted of a body which has a 3-cm-diameter glass tube, 8 cm in length, and a detachable bottom. For supporting the soil, the bottom contained a stainless steel mesh plate covered with a glass fiber filter paper. When an elution run was complete, the bottom was removed from the tube and the soil was pushed out through the bottom and sectioned.

For the elution characteristic measurements, 24 g of a soil were placed in the column. One gram of the same soil was thoroughly mixed with 10 μ l of a standard HNO_3 solution of plutonium containing 6 μ g (0.4 μ Ci) of plutonium. This plutonium-containing soil was distributed evenly on top of the

soil in the column, then the soil was packed by dropping the column two inches to a hard surface 40 times. Glass beads were placed on top of the soil to prevent disturbance of the surface when water is added. The soil column was then eluted with one liter of distilled water. This is equivalent to 54 inches of rainfall. A constant hydraulic head of two was maintained through each run. Effluent from the column was collected in 20 ml aliquants with a fraction collector and these fractions were analyzed for plutonium.

To determine the extent of downward movement of plutonium in the soil, the soil column, after elution, was cut into three sections approximately 1.3-cm long. These were dried for 1.5 hours at 175 °C, weighed, then analyzed for plutonium.

RESULTS AND DISCUSSION

Equilibrium Plutonium Sorption

Preliminary work with SC and CO-C soils showed that there was a variation between soils in the rate, and therefore in the time, at which equilibrium sorption was attained. As a result, a single equilibration time could not be used for all the soils. Instead, each soil was equilibrated at each plutonium concentration until there was no difference, statistically, in the % Pu Sorbed for two consecutive equilibration times.

The data relating % Pu Sorbed to equilibration time is summarized in Table 3. These data indicate that the time required to attain equilibrium sorption varied from 5 to 48 hours.

Three observations can be made from inspection of the % Pu Sorbed data in Table 3. First, the initial concentration of plutonium does, in some cases, have an effect on the amount of plutonium sorbed, although on the basis of the percent of plutonium sorbed, this effect is small. The difference between the % Pu Sorbed at equilibrium sorption for any of the 13 soils at the three levels of plutonium concentration ranged from 0% (for CO-C) to 7.5% (for WA-A). The average difference for all 13 soils was 1.9% Pu Sorbed.

The second observation from the % Pu Sorbed data is that the rate of plutonium sorption is relatively rapid

TABLE 3. Percent (%) Pu Sorbed at Various Time Intervals

Equilibrium Time	CO-A	CO-B	CO-C	Soil Code			
				ID-A	ID-B	ID-C	ID-D
Initial Pu Concentration $10^{-8} M$							
10 min	81.3	89.9	97.7	98.3	91.9	97.7	95.5
1 hr	91.9	92.4	98.2	98.9	96.2	98.3	95.5
3 hr	97.4	--	99.2	--	95.0	--	--
5 hr	98.2	95.2	--	99.7	92.9	99.2	98.9
16 hr	--	93.0	99.7	99.7	--	99.2	97.6
24 hr	99.2	95.8	--	--	97.8	--	99.2
48 hr	99.8	97.4	--	--	98.4	--	99.7
Initial Pu Concentration $10^{-7} M$							
10 min	86.1	91.3	97.3	97.8	93.1	98.2	97.3
1 hr	96.1	93.2	98.5	99.3	93.8	99.2	95.8
3 hr	98.2	--	99.5	--	94.7	--	--
5 hr	--	94.5	99.5	99.8	--	99.6	99.3
7 hr	--	--	99.6	--	--	--	--
16 hr	99.7	--	99.7	99.8	95.9	99.7	--
24 hr	99.8	99.3	--	99.9	97.8	99.9	99.7
48 hr	--	96.1	--	--	98.5	--	--
Initial Pu Concentration $10^{-6} M$							
10 min	85.8	80.7	95.4	97.2	89.5	96.7	92.8
1 hr	93.2	85.6	97.2	97.9	92.6	99.8	93.4
3 hr	97.9	--	98.8	--	91.6	--	--
5 hr	98.0	83.7	99.0	99.1	91.6	99.3	97.2
7 hr	--	--	99.2	--	--	--	--
16 hr	99.2	--	99.3	99.5	94.3	99.6	97.8
24 hr	99.4	83.4	--	99.9	96.9	99.9	98.3
40 hr	99.5	89.4	--	--	96.6	--	--
48 hr	--	--	99.7	--	--	--	--

TABLE 3. Percent (%) Pu Sorbed at Various Time Intervals (Concluded)

Equilibrium Time	WA-A	WA-B	Soil Code TN	SC	NY	NM
Initial Pu Concentration $10^{-8} M$						
10 min	82.5	91.8	99.3	95.7	94.6	94.1
1 hr	88.0	93.4	99.6	94.9	96.8	92.4
3 hr	--	--	99.7	95.7	99.0	--
5 hr	88.0	--	99.8	--	99.3	93.8
16 hr	96.2	98.5	--	98.1	--	92.4
24 hr	93.3	98.8	--	98.2	--	94.2
48 hr	--	--	--	--	--	95.4
Initial Pu Concentration $10^{-7} M$						
10 min	87.8	91.1	99.6	95.6	96.9	92.7
1 hr	87.4	93.9	98.6	96.0	98.2	95.9
3 hr	--	--	99.9	96.7	99.1	--
5 hr	93.0	99.0	99.6	97.0	99.2	95.4
7 hr	--	--	--	97.2	--	--
16 hr	--	98.8	--	97.0	--	--
24 hr	95.1	99.2	--	--	99.5	97.0
48 hr	--	--	--	99.4	--	97.5
Initial Pu Concentration $10^{-6} M$						
10 min	80.1	87.7	92.7	92.1	93.9	92.5
1 hr	84.0	86.4	95.8	95.3	96.7	95.1
3 hr	--	--	97.4	97.3	99.1	--
5 hr	85.6	89.0	99.4	97.3	98.7	96.1
7 hr	--	--	--	97.8	--	--
16 hr	87.6	--	--	98.0	--	--
24 hr	--	99.0	99.9	99.4	99.4	97.4
40 hr	--	--	--	99.5	--	97.8
48 hr	--	99.3	100.0	--	--	--

although it does vary somewhat between soils. This range of rates is indicated by comparing the % Pu Sorbed data of TN with those of WA-A.

The third observation is that plutonium sorption is quite high. Sixty-two percent of the time the equilibrium sorption is 99.1% or higher. Eighty-seven percent of the time it is 96.1% or higher. Only 5% of the time is the equilibrium sorption below 90% and in no case is it lower than 87%.

Distribution coefficients are the customary way of expressing equilibrium sorption in soil/water systems. These coefficients are conventionally associated in the chemical literature with a mechanism that involves the exchange of a simple ion, M^{n+} , in solution, with a comparable ion, X^{m+} , in the solid

exchange medium. But, as noted above, at the acidities associated with soil/water/plutonium systems, plutonium does not exist, for the most part, as simple ions such as Pu^{n+} , but rather as a series of hydrolyzed species (see Grebenshchikova and Davydov,¹⁵ for example). These species have varying charges and sizes that are determined by parameters such as the concentration of plutonium, the pH and Eh of the soil/water systems, and the presence and concentration of complexing ions. Each of these plutonium species will have different sorption behavior with both the mineral and the organic components of the soil.

Because of this complex chemistry of plutonium, the mechanism for its sorption in a soil/water system is complicated. To differentiate, therefore, between

this complicated mechanism and a simple mechanism that could be implicit in the use of K_d , the conventional notation for a distribution coefficient, a different notation— $K_{d(m)}$ —is used in this paper. It implies an experimentally measured sorption coefficient that is not necessarily related to any specific sorption mechanism and, indeed, might be the summation of a number of different mechanisms.

$K_{d(m)}$ values for equilibrium sorption were determined for each of the 13 soils at the three levels of plutonium concentration. Their mean values and associated standard errors are tabulated in Table 4, along with the % Pu Sorbed values at equilibrium sorption.

In Table 4, note the wide range of $K_{d(m)}$ values obtained—from a high of 14,100 for TN to a low of 35 for WA-A. Expressed as % Pu Sorbed, it is equivalent to 99.96% sorbed for TN to 87.55% sorbed for WA-A. This indicates the great sensitivity of $K_{d(m)}$ values to changes in plutonium concentration at high levels of plutonium sorption, a sensitivity not shared by % Pu Sorbed values.

Note also that the effect of the initial concentration of plutonium on the extent of plutonium sorption is

much more apparent in the $K_{d(m)}$ values than in the % Pu Sorbed values.

Mathematical Relationships Between Equilibrium Sorption and Chemical and Physical Characteristics of the Soil

Regression analyses were used to determine if significant relationships existed between plutonium sorption and the physical and chemical characteristics of the soils. These analyses were carried out using the independent variables in two forms. In the first, stepwise regression was performed using the chemical and physical characteristics of the soils (CEC, pH, % clay, etc.) as the independent variables. The dependent variables were the plutonium content of the aqueous phases at sorption equilibrium, expressed as count data (disintegrations/minute/milliliter). The relationships that resulted from this regression analysis are given in Table 5. These relationships are all statistically significant at a 95% or greater confidence level. The R^2 values, or coefficients of determination, are also included in Table 5. They indicate the percent of the total variance explained by the relationship. The larger the R^2 value, the less likelihood that significant variables or cause/effect relationships have been overlooked.

TABLE 4. Sorption Equilibrium

Soil	$K_{d(m)} \pm \text{S.E.}$ Initial Pu Concentration, M			% Pu Sorbed $\pm$ S.E. Initial Pu Concentration, M		
	10^{-8}	10^{-7}	10^{-6}	10^{-8}	10^{-7}	10^{-6}
CO-A	2200 $\pm$ 460	2700 $\pm$ 170	1200 $\pm$ 190	99.75 $\pm$ 0.04	99.81 $\pm$ 0.01	99.54 $\pm$ 0.07
CO-B	190 $\pm$ 24	130 $\pm$ 6	43 $\pm$ 2	97.35 $\pm$ 0.33	96.13 $\pm$ 0.18	89.42 $\pm$ 0.44
CO-C	1900 $\pm$ 110	1800 $\pm$ 100	2000 $\pm$ 270	99.73 $\pm$ 0.01	99.72 $\pm$ 0.01	99.73 $\pm$ 0.04
ID-A	1700 $\pm$ 70	4300 $\pm$ 160	5000 $\pm$ 290	99.71 $\pm$ 0.01	99.88 $\pm$ 0.01	99.90 $\pm$ 0.01
ID-B	320 $\pm$ 26	330 $\pm$ 12	140 $\pm$ 11	98.43 $\pm$ 0.14	98.52 $\pm$ 0.05	96.59 $\pm$ 0.27
ID-C	690 $\pm$ 110	4100 $\pm$ 150	4000 $\pm$ 230	99.23 $\pm$ 0.10	99.88 $\pm$ 0.01	99.87 $\pm$ 0.01
ID-D	2100 $\pm$ 640	1500 $\pm$ 80	310 $\pm$ 42	99.72 $\pm$ 0.07	99.66 $\pm$ 0.02	98.32 $\pm$ 0.26
WA-A	100 $\pm$ 7	98 $\pm$ 3	35 $\pm$ 1	95.16 $\pm$ 0.31	95.12 $\pm$ 0.14	87.55 $\pm$ 0.36
WA-B	430 $\pm$ 27	600 $\pm$ 44	680 $\pm$ 16	98.84 $\pm$ 0.05	99.15 $\pm$ 0.07	99.27 $\pm$ 0.02
TN	2600 $\pm$ 640	1200 $\pm$ 110	14000 $\pm$ 2700	99.77 $\pm$ 0.05	99.59 $\pm$ 0.03	99.96 $\pm$ 0.01
SC	280 $\pm$ 5	870 $\pm$ 52	1000 $\pm$ 20	98.23 $\pm$ 0.03	99.53 $\pm$ 0.03	99.51 $\pm$ 0.01
NY	820 $\pm$ 130	1100 $\pm$ 45	870 $\pm$ 57	99.34 $\pm$ 0.10	99.53 $\pm$ 0.02	99.42 $\pm$ 0.04
NM	100 $\pm$ 5	200 $\pm$ 8	220 $\pm$ 12	95.36 $\pm$ 0.22	97.54 $\pm$ 0.10	97.77 $\pm$ 0.12

TABLE 5. Stepwise Regression Analysis

Independent Variables: CEC, pH, % clay, etc.
Dependent Variables: Count data¹(d/min/ml)

Initial Pu Concentration, <i>M</i>	Relationship*	R ²
10 ⁻⁸	d/min/ml = 14.880 - 0.3025 (% clay)	37.4%
10 ⁻⁷	d/min/ml = 125.154 - 5.904 (% clay) + 6.965 (CEC)	33.9%
10 ⁻⁶	d/min/ml = 249.68 + 34.85 (% sand) + 233.41 (CEC) - 122.38	41.7%

*d/min/ml = disintegrations/minute/milliliter.

In the second regression analysis, the initial independent variables were grouped to form new independent variables. This was done by a principal component analysis technique.¹⁶ The purpose of the principal component analysis and subsequent regression analysis was to explore possible relationships among the set of independent variables that might have been overlooked in the initial regression analysis. These relationships, if they do exist, could provide additional clues to the processes that are involved in the sorption and movement of plutonium in the soil.

The new independent variables that resulted from the principal component analysis consist of a linear combination of the original variables and have the form

$$Z_i = a_1 X_1 + a_2 X_2 + \dots + a_8 X_8.$$

In these new variables, $X_1, X_2, \dots, X_8$ represent the original independent variables in the same order as they occur in Table 2, i.e., X_1 = CEC, X_2 = soluble salts, etc., except the X_8 = clay, not silt. Silt was eliminated in the principal component analysis for mathematical reasons. The relative absolute magnitude of the coefficients (a_i) indicate the relative importance of the original variable (X_n) in the new variable Z_n . The coefficients with the largest absolute values in each of the three new independent variables identified by principal component analysis are summarized in Table 6.

Stepwise regression analyses were performed using the new independent variables defined by the

TABLE 6. Relative Importance of the Original Independent Variables in the New Independent Variables

New Independent Variable	Original Independent Variables and Their Associated Coefficients
Z_1	CEC (0.56), Sand (-0.53), Clay (0.54)
Z_2	Soluble Salts (-0.34), Inorganic Carbon (0.48), Organic Carbon (-0.53), pH (0.56)
Z_3	Soluble Salts (0.59), Soluble Carbonate (0.72)

principal component analysis. The dependent variables were the count data. The results of the regression analysis are summarized in Table 7. Note that at all three plutonium concentrations, Z_1 is the only significant variable. And even though the values of R^2 are small, the relationship between the count data (plutonium concentration) and Z_1 are statistically significant at the 95% confidence level.

Of the original independent variables, the ones most significant in Z_1 are CEC, clay, and sand (Table 6). These same variables were the ones that were also found most important from the initial regression analysis using the original independent variables (Table 5). The importance of these particular variables would indicate that a conventional ion exchange process is responsible for the sorption of plutonium. However, two points should be noted. First, R^2 values decrease, as indicated in Table 7, with an increase in plutonium concentration. This would indicate that the ion exchange process is becoming less important with an increase in plutonium concentration. Since the ion exchange capacity of the soil is orders of magnitude higher than the highest plutonium concentration investigated, sorption by simple ion exchange does not seem logical. Second, as noted above, the closer R^2 values are to 100%, the more assurance there is that significant variables or cause/effect relationships have not been overlooked. The R^2 values in Tables 5 and 7 vary from 12 to 42%, indicating that other variables and relationships are likely involved in the sorption. Some of these are discussed in Part II of this report.

TABLE 7. Stepwise Regression Analysis

Independent Variables: Z_1, Z_2, Z_3
 Dependent Variables: Count data (d/min/ml)

Initial Plutonium Concentration, M	Relationship*	R^2
10^{-8}	d/min/ml = 6.192 - 2.220 (Z_1)	32.2%
10^{-7}	d/min/ml = 52.257 - 15.356 (Z_1)	14.7%
10^{-6}	d/min/ml = 1097 - 361.05 (Z_1)	12.6%

*d/min/ml = disintegrations/minute/milliliter.

Elution Characteristics

The transport of plutonium through soil by water was studied using columns of ID-B, CO-A, and ID-A soils. The rate of flow of the water through the columns was governed by the soil. It varied from approximately 15 minutes per 20 ml for CO-A to 90 minutes for ID-B and 180 minutes for ID-A.

Duplicate column elution runs were made for each of the three soils. The effluents were collected in 20 ml fractions and subsequently analyzed for plutonium. After each elution was completed, the soil column was sectioned and the soil analyzed for plutonium. The average plutonium content in each soil section, as well the total amount of plutonium in the effluent, are summarized in Table 8 for each of the three soils. These data indicate that the soil with the lowest $K_d(m)$ (ID-B) retains the least amount of plutonium while the soil with the highest $K_d(m)$ (ID-A) retains the most. In no case, however, was more than 2% of the original plutonium eluted from the column.

The fractions of the column effluents were analyzed for plutonium to determine its pattern of elution. In two of the soils, ID-B and CO-A, there were prompt pulses of plutonium occurring in the initial 20 ml effluent fractions. These pulses contained 0.9% of the original plutonium placed on the column for ID-B and 0.1% for CO-A. The remaining effluent fractions for these two soils contained continually decreasing amounts of plutonium.

TABLE 8. Elution Characteristics

Pu Source: Pu Nitrate
 Initial Amount Pu on Column: 2.5×10^{-8} Mole

Soil	$K_d(m)$	Depth, cm	% Total Pu
ID-B	144	0.0 - 1.3	93.9
		1.3 - 2.6	2.8
		2.6 - 3.9	1.5
		Eluate	1.8
CO-A	1180	0.0 - 1.3	98.3
		1.3 - 2.6	0.8
		2.6 - 3.9	0.5
		Eluate	0.4
ID-A	5020	0.0 - 1.3	99.5
		1.3 - 2.6	0.3
		2.6 - 3.9	0.2
		Eluate	<0.1

The behavior of the ID-A soil was different. There was no pulse of plutonium throughout the entire elution. Instead, the plutonium concentration in the effluent fractions varied randomly between 0.001 and 0.004% of the original plutonium on the column throughout the entire elution.

The pH of the effluent fractions was measured. For all three soils, the pH of the effluent increased with an increase in the amount of water through the column. Generally, the increase in pH was greatest at the beginning of the elution. The total increase in pH varied with the soils from a minimum of 0.3 (8.3 to 8.6) for ID-A to a maximum of 1.4 (5.8 to 7.2) for CO-A.

REFERENCES

1. D. W. Rhodes, "Adsorption of Plutonium by Soil," in *Soil Sci.*, Vol 84, p 465, (1957).
2. D. W. Rhodes, "The Effect of pH on the Uptake of Radioactive Isotopes From Solution by Soil," in *Soil Sci. Soc. Amer. Proc.*, Vol 21, p 389, (1957).
3. W. E. Prout, "Adsorption of Radioactive Wastes by Savannah River Plant Soil," in *Soil Sci.*, Vol 86, p 13, (1958).

4. C. W. Christenson, E. B. Fowler, G. L. Johnson, E. H. Rex, and F. H. Virgil, "Soil Adsorption of Radioactive Wastes at Los Alamos," in *Sewage Ind. Wastes*, Vol 30, p 1478, (1958).
5. C. W. Christenson and R. G. Thomas, "Movement of Plutonium Through Los Alamos Tuff," in *Second Ground Disposal of Radioactive Wastes Conference*, USAEC Report TID-7628, Vol 1, p 281, (1962).
6. B. F. Hajek, *Plutonium and Americium Mobility in Soil*, USAEC Report BNWL-CC-925, Richland, Washington, 1966.
7. K. C. Knoll, *Reaction of Organic Wastes and Soils*, USAEC Report BNWL-860, Richland, Washington, 1969.
8. T. Tamura, "Sorption Phenomena Significant in Radioactive Waste Disposal," in *Underground Waste Management and Environmental Implications*, pp 318-330, Memoir 18, Amer. Assoc. Petro. Geol., Tulsa, Oklahoma.
9. H. M. Mork, *Redistribution of Plutonium in the Environs of the Nevada Test Site*, USAEC Report UCLA-12-590, Los Angeles, California, 1966.
10. E. M. Romney, H. M. Mork, and K. W. Larson, "Persistence of Plutonium in Soils, Plants, and Small Mammals," in *Health Phys.*, Vol 19, p 487, (1970).
11. P. W. Krey and E. P. Hardy, *Plutonium in Soil Around the Rocky Flats Plant*, USAEC Report HASL-235, New York, New York, 1970.
12. C. W. Francis, "Plutonium Mobility in Soil and Uptake in Plants: A Review," in *J. Environ. Quality*, Vol 2, p 67, (1973).
13. K. R. Price, "A Review of Transuranic Elements in Soils, Plants and Animals," in *J. Environ. Quality*, Vol 2, p 62, (1973).
14. M. L. Jackson, *Soil Chemical Analysis - Advanced Course*, 3rd Printing, pp 127-131, published by the author, Department of Soils, University of Wisconsin, 1966.
15. V. I. Grebenshchikova and Y. P. Davydov, "State of Pu(IV) in the Region of pH 1.0-12.0 at a Plutonium Concentration of $2 \times 10^{-5} M$, in *Soviet Radiochemistry*, Vol 7, p 190, (1965).
16. D. F. Morrison, *Multivariate Statistical Methods*, McGraw-Hill Book Company, New York, 1967.

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PLUTONIUM BEHAVIOR IN THE SOIL/WATER ENVIRONMENT
PART II. SELECTED CHEMICAL AND PHYSICAL CHARACTERISTICS
OF AQUEOUS PLUTONIUM AND THEIR EFFECTS
ON THE SORPTION OF PLUTONIUM BY SOILS

W. L. Polzer and F. J. Miner

ABSTRACT

Sorption of plutonium in 13 soils, as measured by distribution coefficients, was observed in most cases to be dependent on the initial plutonium concentration which ranged from 10^{-8} to 10^{-6} molar. Several trends were observed with respect to changes in sorption. A decrease in sorption occurred in the presence of polymers compared to the absence of polymers. Polymers are likely to have a lower positive charge density than the non-polymerized species. The presence of polymers was assumed when the ratio of measured plutonium to that calculated to be in equilibrium with plutonium hydroxide exceeded unity.

In acid solutions, and in the presence of polymers, a decrease in sorption occurred with an increase in pH. This decrease is attributed to a lower positive charge density on the polymers at the higher pH values. A decrease in sorption also occurred, in the absence of polymers, with an increase in pH at values of approximately eight or greater. This decrease is attributed to the reaction of plutonium with hydroxyl and carbonate ions to form negatively charged complexes. At pH values of eight or greater, the concentration of these complexes is likely to exceed the concentration of the predominant noncomplexed species, thus reducing the sorption of plutonium.

INTRODUCTION

The determination of plutonium sorption by 13 soils and the various trends in sorption data are discussed in Part I of this report. Sorption, as measured by distribution coefficients, varied by as much as 300 times between soils and by as much as 30 to 60 times for an individual soil at the three levels of plu-

tonium concentrations used, 10^{-8} , 10^{-7} , and $10^{-6}M$. The distribution coefficient [$K_{d(m)}$] of plutonium in soil is defined as the ratio of the amount of plutonium sorbed by 1 gram of soil to the amount of plutonium in 1 ml of solution under equilibrium conditions. Therefore, with an increase in the total quantity of plutonium in the system, the amount of plutonium sorbed should be proportional to the concentration in solution if the $K_{d(m)}$ is to remain constant. A decrease in the amount sorbed relative to that in solution results in a lower $K_{d(m)}$ and an increase results in a higher $K_{d(m)}$.

In order to explain changes in sorption relative to the concentration of plutonium in the system, observations are made with respect to selected chemical and physical characteristics of plutonium in solution and the sorption of plutonium by soils. More specifically, sorption is discussed in relation to (1) the relative concentration of the various aqueous plutonium species, (2) polymerization of aqueous plutonium, and (3) the formation of complexes with other ions.

Most experimental work on plutonium in aqueous solutions has been conducted under conditions unlike those in a soil/water environment. Therefore, evaluations involving the aqueous chemistry of plutonium necessarily include theoretical as well as experimental considerations.

THEORETICAL AND EXPERIMENTAL CONSIDERATIONS

Aqueous Plutonium Species

In the initial "soluble" form of plutonium used in the experiments, plutonium was present as Pu(IV).

According to Polzer, under the experimental conditions that existed, soluble plutonium should form a number of species having oxidation states of III, V, and VI as well as IV.¹ Plutonium in these various oxidation states reacts with hydroxyl ions to form aqueous hydroxide complexes such as PuOH^{2+} , PuOH^{3+} , $\text{Pu}(\text{OH})_2\text{OH}^+$, and $\text{PuO}_2(\text{OH})_3^-$. Complexes with other ions may be formed also, provided the plutonium and the other ions are present in sufficient quantities.

The relative concentrations of the various oxidation states and species of plutonium vary with the pH and Eh of the soil solutions. In the experimental work the pH values ranged from 4.9 to 8.9 and the Eh from -0.54 to -0.40 V. Using these Eh and pH values in conjunction with theoretical data by Polzer,¹ calculations showed that Pu(V) is the primary oxidation state in all the soil solutions. The plutonium is probably present as PuO_2^+ since this is the predominant species of Pu(V). The calculations also indicate that the Pu(V) concentration is approximately equal to the total plutonium concentration. Other oxidation states and associated species such as Pu^{4+} , Pu^{3+} , PuO_2^{2+} , and their hydrolyzed counterparts are also present, but at much lower concentrations.

The conversion of plutonium from one oxidation state to another that is stable in a given aqueous medium has been observed experimentally by others. Costanzo, et al., found that the oxidation states of Pu(III), (V), and (VI) are all formed when Pu(IV) is put in aqueous solutions at high acidities (pH values less than 2).² Lingren found with an electrochromatographic technique that the behavior of migrating plutonium ions in sea water was independent of the oxidation state of the plutonium originally added, indicating conversion of all species to one more stable in sea water.³

Calculations also show that with the exception of some hydrolyzed Pu(VI) species, the concentrations of all species decrease relative to PuO_2^+ as the soil solutions change from more acidic and oxidizing conditions to more basic and reducing conditions.

Although Pu(V) is the predominant plutonium oxidation state in the soil solutions, less information is available about its sorption than the sorption of

other oxidation states. According to Cleveland⁴ and Metz and Waterbury (1964),⁵ the relative order of sorption on organic cation exchange resins is $\text{Pu}^{4+} > \text{Pu}^{3+} > \text{PuO}_2^{2+} > \text{PuO}_2^+$. From this it could be inferred that at least sorption by ion exchange would be lower for PuO_2^+ than some other species. Because of this, other species, even though they are present in very low concentrations, could significantly affect the total sorption of plutonium.

Polymerization of Plutonium

The concentration of plutonium in the soil solutions at equilibrium was generally in excess of what would have been expected from the solubility of plutonium(IV) hydroxide based on the data of Polzer.¹ Polymerization could account for this. In an attempt to equilibrate, the plutonium polymers would tend to depolymerize. At equilibrium then, the soil solution could contain plutonium in the form of polymers, monomers or low molecular weight polymers, and ionic forms. The latter could either be complexed or noncomplexed, as will be discussed later.

Lloyd and Haire showed that plutonium, on polymerizing, behaves as very small, discrete particles of an amorphous nature, probably hydrous PuO_2 .⁶ Upon extensive aging or heating the polymers may form into small crystallites. With increased concentration they may combine with other similar particulates to increase the total size even though they still maintain their particulate behavior.

Polymers may have different characteristics depending on the pH region in which they are formed. For example, two values for the solubility product of plutonium hydroxide can be found in the literature. One value, 10^{-52} , was calculated from the estimated oxidation potentials for various plutonium reactions in basic solutions.⁷ The other value, 10^{-55} , was determined by noting the pH at which colloidal $\text{Pu}(\text{OH})_4$ forms in acid solutions.⁸ It is conceivable that plutonium polymorphs can form, one in acid solution and the other in basic solution, and that each can have its own particular solubility product. This would be analogous to the existence of polymorphs of aluminum hydroxide

(each with a different solubility product) which result from the mode of stacking of successive layers if aluminum hydroxide.⁹

In a review of the sorption and colloidal properties of radioactive elements in trace concentrations, Kepák discusses sorption by both ion exchange and physical means.¹⁰ Increased concentrations of electrolytes will depress sorption of trace cations by ion exchange. However, if the trace concentration of the element is in a colloidal form, increased concentrations of electrolytes either do not influence the sorption of the trace element or increases it. An increase in sorption of a trace element with an increase in the concentration of electrolytes is attributable to a physical sorption mechanism involving a colloid, not an ion exchange mechanism. This physical sorption is irreversible. An element in trace concentrations may be incorporated into a solid phase of a compound of another element. When this occurs, the trace element loses its properties. Physical sorption of ionic species of trace elements can occur, but unlike sorption of colloids, the process is likely to be reversible.¹¹

According to Rozzell low molecular weight plutonium polymers behave like ionic species, whereas high molecular weight polymers or colloids behave differently.¹² For example, in high ionic strength solutions, other ions compete for exchange sites, thus decreasing sorption of the low molecular weight polymers. In comparable solutions, repulsion between large polymers is decreased, thus allowing coagulation and the formation of larger sized polymers. Sheidina and Kovarskaya noted that the charge on plutonium polymers (colloids) is dependent upon the plutonium concentration and the pH.¹³ At high concentrations of plutonium ($10^{-6}M$), the colloidal particles exhibit a net positive charge at low pH values and a net negative charge at a pH value of 7 or higher. At low concentrations ($10^{-8}M$), the colloidal particles exhibit a negative charge at a pH as low as 3.

In the soil solutions studied in these experiments, the ionic strength is low, probably on the order of 0.005 to 0.05 moles/litre. These values were estimated using the relationship between ionic strength and specific conductance of water as discussed by Griffin and Jurinak.¹⁴ Based on this ionic strength,

and information from Rozzell, any plutonium remaining in solution that is not in an ionic form will either be a low molecular weight polymer or will be complexed.

Formation of Plutonium Complexes

Plutonium has the ability to form complexes with most anions normally found in soil solutions. According to Gel'man, et al., doubly charged anions generally form stronger complexes with plutonium in any of its oxidation states than do singly charged anions.¹⁵ The anions may be arranged in the following order with respect to their disposition to form complexes:

Singly charged anions: $F^- > NO_3^- > Cl^- > ClO_4^-$

Doubly charged anions: $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

Gel'man et al., also concluded that the tendency of plutonium ions to form complexes generally decreases with a decrease in ionic potential, i.e., $Pu^{4+} > Pu^{3+} > PuO_2^{2+} > PuO_2^+$.

Plutonium can form strong complexes with organic anions. In this study, however, organic anions were considered to be in a low enough concentration so that any complex formed would have an insignificant effect on plutonium sorption.

Plutonium can also form complexes with inorganic anions. Of the inorganic anions generally found in soil, carbonate is the one most likely to be present in concentrations high enough to complex plutonium. Carbonate complexes of PuO_2^+ have not been reported. A carbonate complex of Pu^{4+} , $PuCO_3^{2+}$, has been reported,^{16,4} but because of the low concentration of Pu^{4+} in the soil solutions, it is not believed that this complex is important.

Carbonate complexes can also be formed by Pu(VI) in solutions whose pH is 8 or higher. The Pu(VI) would probably be present as PuO_2^{2+} since this is the primary species of hexavalent plutonium. The carbonate complexes have been identified by Gel'man, et al., as $PuO_2(CO_3)_2^{2-}$, $PuO_2(OH)(CO_3)$ and $PuO_2(OH)_2CO_3^{2-}$. (Reference 17). Their stability constants are given as 1.1×10^{15} , 7.1×10^{23} ,

and 1.0×10^{23} , respectively. When these stability constants were calculated, a value for the solubility product of $\text{PuO}_2(\text{OH})_2$ was used that differed from the solubility used by Polzer.¹ Therefore, in order to be internally consistent in this work, the stability constants of these complexes were recalculated and gave values of 2.5×10^9 , 1.6×10^{18} , and 2.2×10^{17} , respectively. Of the three complexes, the concentration of $\text{PuO}_2(\text{OH})(\text{CO}_3)^-$ would be greatest for conditions found in the soil solutions. An estimate of this concentration can be calculated as follows: For a pH of 8, the CO_3^{2-} concentration would be in the order of $10^{-4.5}$ molar. The PuO_2^{2+} concentration would be some fraction of the Pu(V) concentration. Since the Pu(V) concentration would be in the range of $10^{-6} M$ to $10^{-8} M$, a concentration of $10^{-7} M$ was assumed for calculation purposes. Selecting the PuO_2^{2+} concentration as $10^{-7.7}$ times this Pu(V) concentration--a not unlikely value, based on theoretical calculations--and substituting this value, plus those of the CO_3^{2-} and OH^- concentrations, into the expression

$$[\text{PuO}_2(\text{OH})(\text{CO}_3)]^- = [\text{PuO}_2^{2+}][\text{OH}^-][\text{CO}_3^{2-}]10^{18.2}$$

results in a value of $10^{-7} M$ for the Pu(VI) carbonate complex. This concentration is equal to that of the normally predominant Pu(V) species. Therefore, the Pu(VI) carbonate complex, with its negative charge, could be expected to significantly decrease the sorption of plutonium when it is present; assuming that the primary mechanism for sorption is one that involves charged species.

Carbonate complexes, or behavior that could be attributed to the presence of carbonate complexes, have been observed by previous workers. Lingren obtained results which indicated the presence of negatively charged carbonate complexes of plutonium in sea water.³ The pH of the sea water was 8 and the plutonium concentration was 3×10^{-7} molar. Rhodes observed a decrease in sorption of plutonium by soil above a pH of 8. (References 18, 19). This was attributed to a change in the characteristics of the plutonium species present. Carbonate complexes would be expected in this pH range.

METHODS AND PROCEDURES

Certain premises are used to explain the differences in sorption of plutonium at different plutonium

concentrations. These premises are based primarily on the chemical and physical characteristics of plutonium in aqueous solutions as discussed above. The premises are summarized as follows:

1. The primary mechanism for plutonium sorption involves some type of exchange. Although physical sorption may occur, a preliminary examination indicates that the sorption data does not conform to the Langmuir adsorption equation as given by Syers, et al.²⁰
2. Plutonium polymers are assumed to be present if the plutonium concentration in the soil solution at equilibrium sorption exceeds that calculated to be present based on the solubility of plutonium hydroxide. The solubility product of $\text{Pu}(\text{OH})_4$ used for calculations was $10^{-55.2}$ in acidic solutions and $10^{-51.9}$ in basic solutions.
3. Except in the very low pH region, the presence of low molecular weight polymers in the soil solution should decrease sorption because of their small size and low effective charge density. However, in the low pH region, the net positive charge density of the polymer may exceed that of any plutonium ion in solution and enhance sorption.
4. In acidic soil solutions (pH less than 7) the net positive charge density of polymers should decrease with an increase in pH. The relative sorption of plutonium polymers for a given soil should therefore decrease with an increase in pH. In basic solutions, the net charge on the polymers is assumed to be negative.
5. In soil solutions in which the pH is 8 or higher, negatively charged carbonate complexes of plutonium are assumed to be present. Their concentration approaches or exceeds the concentration of the other, noncomplexed species, thus decreasing the overall sorption of plutonium.

RESULTS AND DISCUSSION

Data are summarized in Tables 1 and 2 (of Part II) for each of the 13 soils that have been studied.

TABLE 1. Equilibrium Sorption of Plutonium in Soils

 $K_{d(m)}$ for Soils in Basic Solutions

Soil	Initial Pu Concentration, M	$K_{d(m)}$ *	pH	-Eh, V	Ratio, Pu_m/Pu_c
WA-A	10^{-8}	100	7.9	0.41	0.4
	10^{-7}	98	7.9	0.42	3.2
	10^{-6}	35	7.9	0.44	40
ID-D	10^{-8}	2000†	7.8	0.44	0.008
	10^{-7}	1500	8.0	0.41	0.4
	10^{-6}	310†	7.9	0.41	5.0
ID-A	10^{-8}	1700	8.4	0.45	0.005
	10^{-7}	4300	8.0	0.44	0.03
	10^{-6}	5000	7.8	0.45	0.2
ID-C	10^{-8}	690††	8.4	0.44	0.03
	10^{-7}	4100	8.0	0.43	0.06
	10^{-6}	4000	8.0	0.44	0.3
ID-B	10^{-8}	320	8.8	0.44	0.05
	10^{-7}	330	8.9	0.41	1.6
	10^{-6}	140	8.6	0.40	63
WA-B	10^{-8}	430	7.8	0.50	0.004
	10^{-7}	600	7.8	0.46	0.2
	10^{-6}	680	7.8	0.43	1.5
CO-C	10^{-8}	1900	8.0	0.49	0.001
	10^{-7}	1800	7.8	--	--
	10^{-6}	2000††	8.2	0.44	1.0

*Standard error of the mean is 8% or less, except as follows:

† 31%

†† between 11 and 16%

TABLE 2. Equilibrium Sorption of Plutonium in Soils

$K_{d(m)}$ for Soils in Acid Solutions					
Soil	Initial Pu Concentration, M	$K_{d(m)}$ *	pH	-Eh, V	Ratio, Pu_m/Pu_c
SC	10^{-8}	280	5.5	0.48	20
	10^{-7}	870	5.2	0.53	14
	10^{-6}	1000	5.2	0.53	100
NM	10^{-8}	100	6.9	0.48	20
	10^{-7}	200	6.0	0.47	600
	10^{-6}	220	6.2	0.51	1000
TN	10^{-8}	2600†	4.9	--	--
	10^{-7}	1200	4.9	--	--
	10^{-6}	14000†	5.0	0.53	8
CO-A	10^{-8}	2200†	6.5	0.49	2
	10^{-7}	2700	6.2	--	--
	10^{-6}	1200††	6.8	0.43	16000
CO-B	10^{-8}	190††	5.8	0.53	6
	10^{-7}	130	5.8	0.54	60
	10^{-6}	43	5.8	0.53	3200
NY	10^{-8}	820††	6.0	--	--
	10^{-7}	1100	6.0	0.54	6
	10^{-6}	870	6.1	0.49	600

*Standard error of the mean is 8% or less, except as follows:

†between 20 and 25%

††between 11 and 16%

Information is given in the tables on pH and Eh values, distribution coefficients [$K_{d(m)}$] and the ratios (Pu_m/Pu_c) of the measured plutonium concentration in the aqueous phase (Pu_m) to the calculated (or theoretical) plutonium concentration (Pu_c) assuming the aqueous phases were in equilibrium with plutonium hydroxide.

The data in Table 1 summarize information for those soils in which the equilibrium pH is greater than 7.

A lower plutonium sorption is observed at an initial concentration of $10^{-6}M$ for soils WA-A and ID-D than at the other initial concentrations. This decrease is attributed to the presence of polymers as indicated by a Pu_m to Pu_c ratio of greater than one. The data for soils ID-A and ID-C show a lower distribution coefficient at the initial plutonium con-

centration of $10^{-8}M$ that at the higher initial concentrations. This lower sorption is attributed to the formation of a plutonium carbonate complex, having a negative charge which should be significantly greater at pH 8.4 compared to the lower pH values observed at the higher initial plutonium concentrations.

The decrease in $K_{d(m)}$ for the ID-B soil may possibly be attributed to both the presence of low molecular polymers and carbonate complexing. In the ID-B soil, the pH is relatively high for all three initial concentrations. This suggests that a carbonate complex could be formed with PuO_2^{2+} . As noted earlier, this complex would probably be negatively charged, thus causing a decrease in sorption.

The data for the WA-B and CO-C soils indicate essentially no difference in plutonium sorption for

the three initial concentrations. A difference (increase) in the relative sorption might be expected at a pH 7.8 (less carbonate complexing) for the CO-C soil. However, the Eh, not measured in this instance, could possibly have been high enough to offset the effect of a lower pH.

The data in Table 2 summarize information for these soils in which the equilibrium pH is less than 7.

The results for SC and NM soils indicate a lower distribution coefficient and a higher pH at the $10^{-8} M$ initial plutonium concentration compared to that for the higher initial concentrations. The ratio of Pu_m to Pu_c indicates the presence of polymers for all concentrations. The reduced sorption can be explained on the basis of a difference in charge density; the higher the pH, the lower the positive charge density. In the case of the TN soil, lower distribution coefficients are observed at the two lower initial concentrations compared to that at the highest initial concentration. Although the ratio of Pu_m to Pu_c could not be calculated (Eh not measured) for the lower initial concentrations, polymers are most likely absent. At a pH of 5.0 the positive charge density of the polymers probably exceeds that for the nonpolymerized plutonium, thus resulting in a higher sorption in the presence of polymers.

The differences in the distribution coefficients at different initial plutonium concentrations for the CO-A and CO-B soils are attributed to a disproportionate amount of polymers in the solutions. For example, a disproportionately higher concentration of polymers should give a lower distribution coefficient due to a lower positive charge density for polymers compared to nonpolymerized species.

No significant difference is observed in the distribution coefficients for the NY soils. A difference (decrease) might be expected at the $10^{-6} M$ initial concentration due to disproportionately higher concentrations of polymers as estimated by the ratio of Pu_m to Pu_c . Apparently the increase in polymers is not great enough to cause a significant decrease in the sorption of plutonium.

SUMMARY AND CONCLUSIONS

Observations are made with respect to the experimentally measured plutonium sorption by soils.

Sorption by most of the soils, as expressed by $K_d(m)$ values, is found to be dependent on the initial concentration of plutonium in the system. In many cases, the $K_d(m)$ is lowest at the highest initial plutonium concentration but in other cases the reverse is true. Several trends are observed with respect to the changes in sorption. A decrease in $K_d(m)$ generally occurs for a soil when the ratio of measured plutonium to that calculated to be in equilibrium with plutonium hydroxide exceeds unity. In acid solutions, where differences in pH occur for different initial plutonium concentrations, and where the ratios of plutonium measured to that calculated exceed unity, a lower $K_d(m)$ usually occurs at the higher pH. Also a decrease in relative sorption occurs with an increase in pH when the pH values are approximately 8 or greater.

The changes in sorption of plutonium, as observed above, are attributed to several factors. One is the presence of monomeric or low molecular weight polymeric plutonium. The presence of these polymers is postulated on the fact that in some soil/water systems, more plutonium is found in the water phase than can be explained by the solubility of plutonium hydroxide.

Polymeric forms of plutonium tend to have a lower charge density, except possibly for the lower and higher pH regions, compared to the predominant nonpolymerized plutonium. The charge will tend to be negative in basic solutions, and positive in acid solutions, although the charge may even be negative in slightly acid solutions. The positive charge density should be greater at a lower pH in acid solutions and the negative charge density should be greater at a higher pH in basic solutions. These polymers should reduce sorption, assuming that the primary mechanism of sorption is one of exchange. In acid solutions, the reduced sorption is dependent on the pH lower sorption occurring at a higher pH.

Another factor which could affect sorption is the formation of negatively charged complexes of plutonium. At pH values of 8 or higher, the concentration of these complexes could exceed the concentrations of the noncomplexed plutonium species, thus reducing the sorption of plutonium.

The difference in sorption of plutonium by soils as a function of the initial concentration of plutonium in solution were much less than the extreme differences observed between soils. However, the factors accounting for the difference in the distribution coefficient for an individual soil—primarily polymerization and complex formation—can and probably do account for a significant part of the differences in sorption observed between soils.

The selected chemical and physical characteristics of aqueous plutonium that have been discussed in this report provide a reasonable explanation for most of the changes in sorption that occur with change in the initial plutonium concentration. However, further experimental work is warranted because other factors, such as physical sorption, could also likely contribute to the observed changes in sorption.

REFERENCES

1. W. L. Polzer, "Solubility of Plutonium in Soil/Water Environments," in *Proceedings of the Rocky Flats Symposium on Safety in Plutonium Handling Facilities*, USAEC Report CONF-710401, pp 411-430, (1971).
2. D. A. Costanzo, R. F. Biggers, and J. T. Bell, "Plutonium Polymerization. I. A Spectrophotometric Study of the Polymerization of Plutonium(IV)," in *J. Inorg. Nucl. Chem.*, Vol 35, p 609, (1973).
3. W. E. Lingren, *The Electrochromatography of Sea Water Containing Dissolved Plutonium*, USAEC Report USNRDL-TRC-85, San Francisco, California, 1966.
4. J. M. Cleveland, *The Chemistry of Plutonium*, Gordon and Breach, New York, 1970.
5. C. F. Metz and G. R. Waterbury, "Plutonium," in *Analysis of Essential Nuclear Reactor Materials*, p 260, USAEC, Washington, D. C., 1964.
6. M. H. Lloyd and R. G. Haire, *Studies on the Chemical and Colloidal Nature of Pu(IV) Polymers*, USAEC Report CONF-730927, pp 1-9, (1973).
7. W. M. Latimer, *Oxidation Potentials*, 2nd ed., Prentice-Hall, New York, 1952.
8. M. Kaska, "Reactions Between Plutonium Ions in Perchloric Acid Solution: Rates, Mechanisms and Equilibrium," in *The Transuranium Elements, Research Papers, Part I*, pp 327-328, McGraw-Hill, New York, 1945.
9. R. Schoen and C. E. Roberson, "Structures of Aluminum Hydroxide and Geochemical Implications," in *Am. Mineral*, Vol 55, p 43, (1970).
10. F. Kepák, "Adsorption and Colloidal Properties of Radioactive Elements in Trace Concentrations," in *Chem. Rev.*, Vol 71, p 357, (1971).
11. F. T. Hingston, R. J. Atkinson, A. M. Posner, and J. P. Quirk, "Specific Adsorption of Anions on Geothite," in *Int. Cong. Soil Sci., Trans. 9th (Adelaide)*, Vol 3, pp 669-677, (1968).
12. T. C. Rozzell, *Sorption of Aqueous Plutonium on Silica Surfaces*, Sc. D. Thesis, University of Pittsburgh, 1969.
13. L. D. Sheidina and E. N. Kovarskaya, "Colloidal State of Pu(IV) in Aqueous Solutions," in *Sov. Radiochem. (Engl. Transl.)*, Vol 12, p. 229. (1970).
14. R. A. Griffin and T. T. Jurinak, "Estimation of Activity Coefficients From the Electrical Conductivity of Natural Aquatic Systems and Soil Extractants," in *Soil Sci.*, Vol 16, p 26, (1973).
15. A. D. Gel'man, A. I. Moskvina, L. M. Zaitzeva, and M. P. Medvedeva, *Complex Compounds of Transuranium Elements*, (Translated by C. N. Turton and T. I. Turton), pp 65-66, Consultants Bureau, New York, 1962.
16. A. I. Moskvina and A. D. Gel'man, "Determination of the Composition and Instability

- Constants of Oxalate and Carbonate Complexes of Plutonium(IV)," in *Russ. J. Inorg. Chem.*, (Engl. Transl.) Vol 3, No. 4, p 198, (1958).
17. A. D. Gel'man, A. I. Moskvina, and V. P. Zaitseva, "Carbonate Compounds of Plutonyl," in *Sov. Radiochem.*, (Engl. Transl.), Vol 4, p 138, (1962).
18. D. W. Rhodes, "Adsorption of Plutonium by Soil," in *Soil Sci.*, Vol 84, p 465, (1957).
19. D. W. Rhodes, "The Effect of pH on the Uptake of Radioactive Isotopes From Solution by Soil," in *Soil Sci. Soc. Amer. Proc.*, Vol 21, p 389, (1957).
20. J. K. Syers, M. G. Browman, G. W. Smillie, and R. B. Corey, "Phosphate Sorption by Soils Evaluated by the Langmuir Adsorption Equation," in *Soil Sci. Soc. Amer. Proc.*, Vol 37, p 358, (1973).

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