FINAL REPORT

Adsorption and Diffusion of Plutonium in Soil
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SUMMARY

Phase I. Adsorption & Diffusion

The behavior of Plutonium (Pu) was studied in three soils that varied in texture, CEC, pH, organic matter content and mineralogy (Fuquay, Muscatine, Burbank). Two isotopes, ^{238}Pu ^{239}Pu , were used in order to detect Pu over a range of several orders of magnitude. Unless added in a chelated form, Pu was added to the soil as a nitrate in $.01 \text{ N HNO}_3$ to simulate the release of acidic waste on the soil and to prevent rapid Pu hydrolysis or polymerization.

Equilibrium adsorption studies showed that the adsorption of Pu from solution in some soils was limited. The adsorption (Kd) of Pu in Fuquay sand was found to decrease with an increase in the Pu concentration in solution. The decrease was fit to an empirical equation given by:

$$S = C (348 - 50,050 C^{1/3})$$

Equilibrium adsorption by the Muscatine and Burbank soils tended to decrease with Pu concentration increases but not significantly. The adsorption in these two soils was adequately described by the linear adsorption model:

$$S = Kd C$$

Adsorption of Pu in the soil was found to be dependent on the pH, organic matter content, type of minerals in the soil,

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carbonates and the initial Pu form added to the soil.

In the Muscatine soil a pH 2.0, organic matter did not affect the adsorption of Pu. At higher pH levels (4 to 6) organic matter was apparently effective in adsorbing Pu from chelate solutions of EDTA. Increasing the EDTA concentration from 10^{-3} M to 10^{-2} M reduced the Kd by a factor of 10. DTPA was a stronger chelate and reduced Kd values in all soils to one or less at a concentration of 10^{-3} M DTPA.

The mineral fraction of the soil was found to adsorb Pu. In the sand and silt fraction ($> 2 \mu\text{m}$) adsorption was greatest by the most unweathered minerals. The feldspars orthoclase and plagioclase, volcanic tuff and granodinite that dominate in the Burbank sand and silt were most effective in Pu adsorption ($K_d = 7500 \text{ ml/g}$). The quartz sand found in the Fuquay soil had a Kd of about 20 ml/g. Clay adsorption varied widely with the soil type. The clay in the Fuquay soil had a Kd of $2 \times 10^4 \text{ ml/g}$ but kaolinite had a Kd of only 40 ml/g. The adsorption by the Fuquay clay was probably due to Al and Fe hydroxides. The organic matter removal treatment removed a portion of these hydroxides from the soil and reduced the Kd values.

Carbonates in the Burbank soil were found to be responsible for much of the adsorption of Pu in soil not treated for organic matter removal. After this treatment, carbonates were also eliminated and Kd values for the soil fractions changed. Carbonate removal freed exchange sites previously saturated by calcium in the Burbank clay which increased the Kd from 1.5×10^4 up to $4.2 \times 10^4 \text{ ml/g}$. The sand and silt fraction Kd decreased from 1.6×10^4

to 7.5×10^3 after the removal of carbonates, indicating the removal of Pu adsorbing carbonate coatings or particles from this fraction of the soil.

It can be concluded then that Pu is adsorbed in the soil by organic matter, weathered and unweathered minerals, carbonates and Al-Fe hydroxide coatings on soil particles.

The adsorption process was found to be rapid in the Muscatine and Burbank soils (more than 93% in Muscatine and 87% in Burbank soil within six minutes after the addition of Pu to the soil) and somewhat slower in the Fuquay sand (less than 80% in six minutes) when Pu was added as a nitrate. The addition of Pu as a chelate of EDTA slowed the adsorption process significantly by increases in temperature. The adsorption behavior of Pu was also influenced by the Pu concentration but the behavior depended on both the soil used and the initial form of Pu when added to the soil.

The adsorption rate of Pu by Fuquay sand from .01 N HNO_3 was only one low enough to be studied in detail. Adsorption was found to fit a third order equation given by:

$$\frac{\partial(C/C_0)}{\partial t} = -k' (C/C_0)^3$$

The adsorption rate constant k' was found to be higher for aged solutions than for freshly prepared Pu solutions in .01 N HNO_3 , however the k' from fresh solutions does not reflect the behavior of all of the Pu in solution. Adsorption was also found to fit the third order equation better for aged Pu solutions.

Adsorption kinetics showed that two different Pu species take part in the adsorption process. Small charged species predominated in fresh solution and were rapidly adsorbed. The rate constants obtained for fresh solutions reflected the behavior of a small

fraction of the Pu in those solutions. As the solution aged, larger aggregates of Pu were formed and were adsorbed more slowly due to the lower mobility and charge to mass ratio of colloidal Pu.

The transport of Pu by diffusion also showed that the equilibrium adsorption of Pu in Muscatine and Burbank could be described by a linear model. The linear model predicted that apparent diffusion coefficients in soil obey the equation:

$$D_A = D_0/R$$

where D_0 is the diffusion coefficient of the solute in the solution phase and R is the retardation factor:

$$R = 1 + \frac{\rho_b}{\theta_v} K_d$$

Predicted values for diffusion coefficients in the Muscatine and Burbank soils agreed well with the values found by direct measurement.

Diffusion of Pu in the soil occurred in the solution phase. Factors affecting the amount and mobility of Pu in solution also affected its diffusion rate. A reduction in the soil moisture content reduced the Pu migration rate. Continued adsorption and movement of Pu into previously uncontaminated soil reduced its diffusion rate in soils not described by a linear adsorption isotherm.

Apparent diffusion coefficients can be accurately predicted in soils that adsorbed Pu according to a linear isotherm. Adsorption K_d values measured over a period of two weeks, and aqueous diffusion coefficients measured in a few days, were used to predict values for D_A that require five months or more to measure directly. The Pu diffusion coefficients in Fuquay sand however, were lower

than predicted values. The non-linear behavior of Pu adsorption in Fuquay sand caused the K_d to be higher for Pu diffusing into uncontaminated soil than it was in the tagged soil. This caused Pu to accumulate near the interface on the uncontaminated side. Continued adsorption of Pu with time also reduced apparent diffusion coefficients so that measured values of D_A decreased with time as Pu became more immobile in the soil.

Apparent diffusion coefficients in this study were largest for Pu in Fuquay sand and lowest in the Muscatine soil. This coincided with the adsorption and mobility studies conducted. Adsorption was greatest in the Muscatine and Pu mobility was also lowest. In the Fuquay sand Pu adsorption was least of the three soils and Pu mobility was highest. Addition of Pu EDTA to the Muscatine increased D_A due to a decrease in adsorption and increased Pu mobility. The study showed that Pu diffusion is a solution process and that adsorbed Pu is immobile.

Transport of Pu with moving water was studied using steady-state saturated flow of Pu solutions through a column packed with Fuquay sand. The third order adsorption was used to describe Pu movement. Dispersion was assumed to be negligible compared to the removal of Pu from solution by adsorption. Effluent from the soil column studies showed that a constant mobile fraction passed through regardless of the solution age. The dominant Pu species Pu (IV) and Pu (III) were completely adsorbed within the 4 cm cores. Transport of Pu in aged solutions was found to fit the third order adsorption model better than fresh solution. The fresh solution contained more Pu particles than aged solutions

and accumulated near the soil-solution interface in the column. Aged solutions contained particles that were fewer in number but larger in size. The larger particles were adsorbed more slowly than the small ones in fresh solution. Because there were fewer particles in the aged solution the exchange sites were not saturated so quickly and the adsorbed Pu concentration was predicted as a function of distance in the core by:

$$(S)^{-2/3} = \left(\frac{\rho b}{C_0 k' \theta_{V_0} T} \right)^{2/3} \left(\frac{2\sqrt[3]{k'}}{V_0} \right) \left(\frac{\rho b}{C_0 \theta_{V_0} T} \right) (x)$$

The effluent Pu concentration was predicted by:

$$C/C_0 = (1 + 2k' x/V_0)^{-1/2}$$

Measured values of C/C_0 at 4 cm failed to obey the steady state equation $[C = C_0(1 + 2k' x/V_0)^{-1/2}]$ because the dominant forms; Pu(IV and Pu(III) were completely adsorbed. Measured values of C/C_0 were also independent of V_0 which indicated a constant mobile fraction passing unadsorbed through the 4 cm cores.

A greater fraction of Pu also passed through the cores when added as a Pu-EDTA complex. The adsorbed concentration of Pu measured in the core was linearly decreasing function of $\log(x)$. The effluent Pu concentration continued to increase linearly with the volume of solution passing through the soil. No differences were observed between the behavior of Pu added in 10^{-3} M or 10^{-5} M EDTA for EDTA solutions aged for one or twenty days.

Movement of Pu may be estimated with the equation $\bar{x} = \sqrt{D_A t}$. The time required for a root mean square Pu displacement of 1 cm in Fuquay sand is two years, 350 years in the Burbank soil and 1900 years in the Muscatine soil. Chelated Pu can be expected to move the same distance in about 140 years in the Muscatine soil.

The chelate would biodegrade long before this time and the Pu would move as an unchelated form.

Phase II. Soil - Plutonium Oxide Particle Interactions

A. Dissolution of Pu-239 in the soil solution

- (1) rate of release to soil solution. Pu-239 particles (~ 5.0 mg of particles; 75 uM diameter) were sealed in a permeable envelope and reacted with soil solution from Muscatine, Burbank, Fuquay, and Wrightsville soils. The reaction was measured in soil solution alone and the solution in the presence of the soil surface.

B. Adsorption and diffusion of Pu 239 from the soil solution.

The teflon dissolution - diffusion cell permitted the interaction of the soil solution with four diffusion soil cores. Adsorption and diffusion of Pu-239 from solution into the soil cores was measured over a 150-day time period.

C. The following key points are detailed here:

1. The rate of release of Pu-239 from particles was a function the pH and salt concentrations of the soil solution. Thus, the rate of release was related to the chemical properties of the soil in which plutonium reacts.
2. The presence of a soil interface to the soil solution represents an adsorption sink for plutonium in solution, which tends to increase the release of

Pu-239 to the solution phase. To obtain a realistic measure of the rate of release of Pu-239 from oxide particles to a soil solution the soil surface must be present.

3. The rate of release was very erratic due to mechanism of release - (a) solution, (b) release of colloidal particles, (c) change in chemical form and valence of plutonium. The release reached a maximum in 4 days and then declined to an insignificant release at 150 days.
4. The diffusion rates of Pu-239 into the soil in contact with soil in solution was of the order $1 \times 10^{-12} \text{ cm}^2/\text{sec}$.
5. The diffusion rate of Pu-239 in the soil with the plutonium particle in contact with soil was of the order of $1 \times 10^{-9} \text{ cm}^2/\text{sec}$.
6. The diffusion coefficient of Pu-239 in the soil solution phase was of the order of $1 \times 10^{-6} \text{ cm}^2/\text{sec}$.
7. The adsorption of Pu-239 from the soil solution was concentrated (97%) within the first 1 mm of the soil core.
8. Movement in the soil is extremely slow, varying from 1 cm/year in the Fuquay soil to 1 cm in 1900 years for the Muscatine soil.

Publications

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