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**Sorption of ^{99}Tc , ^{237}Np and
 ^{241}Am on Two Subsoils from
Differing Weathering Intensity
Areas**

May 1975

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SORPTION OF ^{99}Tc , ^{237}Np AND ^{241}Am
ON TWO SUBSOILS FROM DIFFERING
WEATHERING INTENSITY AREAS

by R. C. Routson, G. Jansen,
and A. V. Robinson

May 1975

On January 19, 1975, research and development programs of the U.S. Atomic Energy Commission (AEC) became part of the newly formed Energy Research and Development Administration (ERDA). In this report, since it refers to work done in 1974, most references are to AEC programs.

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ABSTRACT

Distribution coefficients (Kd values) were determined on subsoils from Washington and South Carolina for ^{241}Am , ^{237}Np , and ^{99}Tc as a function of equilibrium solution concentration of calcium (Ca^{+2}) and of sodium (Na^{+}). Kd values decreased in all cases with increasing solution concentrations of Ca^{+2} and Na^{+} . For the South Carolina subsoil Kd values ranged from 1.0 to 67 for ^{241}Am as a function of Ca^{+2} , 1.6 to 280 for ^{241}Am as a function of Na^{+} , 0.43 to 0.66 for ^{237}Np as a function of Ca^{+2} , and 0.16 to 0.25 for ^{237}Np as a function of Na^{+} . For the Washington soil Kd values were >1200 for ^{241}Am and ranged from 0.36 to 2.37 as a function of Ca^{+2} and from 3.19 to 3.90 for ^{237}Np as a function of Na^{+} . Kd values for ^{99}Tc were essentially 0 at all NaHCO_3 concentrations on the South Carolina subsoil.

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INTRODUCTION

The general evaluation of high-level nuclear waste storage alternatives requires an estimate of the probable reaction of these wastes with the soils and sediments of the United States (Schneider and Platt, 1974). Geologic disposal is one of the waste management concepts under active consideration. Geologic disposal of high-level wastes is the emplacement (storage) of these wastes in a terrestrial geologic repository allowing time for radioactive decay to reduce the waste's activity to an innocuous level. Present regulations require that all high-level wastes from fuel reprocessing be converted to solid material within five years, and this is the material which may be stored in a geologic environment. If contacted with water, all of the proposed solidified high-level waste forms have finite solubilities. Furthermore, there is a finite probability that any geologic environment will eventually be invaded by water, initiating a release event and the transport of some waste component from its safe geologic repository to man's environs. The transport rate of a given component may be controlled to a great extent by sorption of the component upon the solid phase through which the solution is flowing. Thus evaluation of any potential dose to man requires a quantitative estimate of the sorption reaction (Denham et al., 1973).

Radioisotopes of concern in high-level wastes originate from nuclear reactors due to neutron reactions with the original U isotopes and their reactions products as well as nuclear fission of these actinide elements. Nuclear fission is the spontaneous fragmentation of certain actinide elements into two radioactive parts. Fuel discharged from a

nuclear reactor is reprocessed to recover uranium and plutonium by chemical dissolution and treatment and used to fuel future reactors. The high-level wastes contain the unwanted radioactive residue to this process in addition to small amounts of U and Pu not recovered during reprocessing.

High-level radioactivity requiring storage accumulated through the year 2000 has been estimated, and its varying radioactive nature due to decay was calculated for 10^2 , 10^3 , 10^4 , 10^5 , and 10^6 years storage (Denham et al., 1973). Using the above estimated radioactivity data, a mathematical model, and assumptions about the leaching rate, site characteristics, and sorption parameters for the site's soils, a transport analysis of radionuclides from a hypothetical arid storage site was made. The study showed that ^{99}Tc , ^3H , ^{129}I , ^{237}Np , and ^{79}Se were the 5 radionuclides contributing the greatest potential dose to man (Denham et al., 1973). Of these 5 nuclides, sorption parameters for ^3H and ^{129}I (from ^{131}I data) are relatively well known. In contrast, the sorption data for ^{99}Tc and ^{237}Np are poorly known, and values used in the above study were estimated from the chemistry of these elements. Actual measurements of their sorption were unavailable. Thus this study was made to experimentally determine the sorption ^{237}Np and ^{99}Tc in some reference subsoils. In addition, it was suspected that ^{241}Am sorption was possibly low in acid soil systems, and thus the measurement of the sorption of this nuclide was added to that of the above two.

The distribution coefficient (K_d) is the measured empirical sorption parameter used in the above transport model to calculate the sorption of radionuclides. It is defined as:

$$K_d = \frac{As/W}{A1/V} \quad (1)$$

where:

As = the equilibrium concentration or activity sorbed on the solid phase

W = the weight of the solid phase in grams

$A1$ = the equilibrium concentration or activity of the solution phase

V = the volume of solution in milliliters.

Thus K_d is the ratio of the equilibrium sorbed activity per gram (g) of soil to the equilibrium solution activity per milliliter (ml) of solution and has the units of ml/g. The K_d value is a function of the soil type used and of the equilibrium concentration of all macro-ions in solution (Routson and Serne, 1972). Natural soil solution systems are primarily Ca^{+2} and/or Na^{+} systems with lesser amounts of Mg^{+2} and K^{+} (Routson and Wildung, 1969), and thus the K_d values were measured as a function of the solution concentration Ca^{+2} and Na^{+} in pure systems. K_d values of mixed Ca^{+2} and Na^{+} systems can be estimated from pure system data (Mercer, 1967; Baetsle et al., 1963).

MATERIALS AND METHODS

Two soils were chosen for the study which represent a range of weathering intensity. Soils of the arid western United States are represented by a coarse-textured (sandy), low-exchange capacity subsoil from a low rainfall area of Eastern Washington. Soils of the humid Southeastern United States are represented by moderate-exchange capacity subsoil from South Carolina. These soils represent extremes of weathering intensity and weathering stage common in the United States (Jackson et al., 1948).

Sorption was measured in a batch equilibrium system at a 2.5:1 (25 ml to 10 g) solution to soil ratio. Sorption values were measured on solutions composed of calcium nitrate [$\text{Ca}(\text{NO}_3)_2$] in concentrations of 0.002M, 0.02M, 0.05M, 0.10M, 0.20M, and sodium nitrate (NaNO_3) in concentrations of 0.015M, 0.030M, 0.30M, 0.75M, and 3.0M.

Tare weights were determined on 250-ml polyethylene screw cap centrifuge bottles. Approximately 10.0 grams of quartered and well mixed soil were weighed into the tared centrifuge bottles. Twenty-five ml of the Na or Ca solution (without spike) was then placed in each bottle. Bottles were then placed on a shaker and moderately agitated for 20 to 30 min. The bottles were next centrifuged at 20 to 30°C for approximately 29 min at 4000 rpm and the supernatant carefully aspirated from the soil. Two additional prewashes of the matrix solution (solution without spike) were

performed. After the third aspiration, the bottle was reweighed and the residual solution calculated by difference.

Twenty-five ml of the Na and Ca solution were then pipetted into the bottles, and the soil was swirled to assist mixing. Twenty-five μ l spikes of ^{241}Am or ^{237}Np were added individually to each bottle following solution and soil mixing. Influent activities (initial solution) per bottle and solution pHs were approximately 3.7 μCi and 2.5 pH units, and 1.0 μCi and 3.1 pH units for the Burbank sand and South Carolina soils, respectively. The bottles were then agitated at moderate speed for 21 to 24 hr. Following agitation, the bottles were centrifuged as before and the supernatants placed in 50-ml polyethylene bottles for subsequent use.

Influent and effluent solution activities of ^{237}Np and ^{241}Am were measured on aliquots of 10 to 100 microliters (μl) of supernatant placed and dried upon 1-in. planchettes. Also added to the planchettes were 300 μl of distilled water. Planchettes had been previously baked at high temperatures for several hours to remove any adhering grease or oil. Planchettes were dried on a low heat setting of a hot plate and subsequently counted in 2π gas flow system with suitable background and standards. An α energy analysis was performed on the influent ^{237}Np and ^{241}Am . The analysis of the ^{237}Np stock solution indicated that 0.61% of the counted α particles were from ^{239}Pu , ^{240}Pu by the summation of channels method. An α energy analysis of the effluent solution revealed negligible Pu ($<0.1\%$), and since it is known that Pu is strongly sorbed to soil, the subtraction of the 0.61% of the influent counts (C_0) from the total influent counts were made as a correction. The α energy analyses for ^{241}Am indicated no measurable content of any other α emitter.

Because of the possibility that absorbed ^{237}Np might be on soil particles of colloidal size, selected samples were filtered through 0.01 or 0.45 μm filters and subsequently counted and compared with their unfiltered counterparts. No significant difference was found between centrifuged and filtered samples.

To count ^{99}Tc , liquid scintillation counting was employed. The fluor (scintillation counting fluid) used was TTWC,^(a) was weighed out so that each vial contained $15.0 \pm \text{g}$ fluor. The sample size counted was 500 μl in all cases.

Calculations of K_d values were based on the following equation:

$$K_d = \frac{(r C_o - C_e)}{(C_e)} \frac{A}{B} = \frac{\text{ml}}{\text{g}} \quad (2)$$

where A = total milliliters of solution in the last treatment ($25.0 \text{ ml} + x$ residual ml), B = total grams (g) of soil present, r = ratio of trace solution to total solution ($25/25 + x$ residual ml), C_o = concentration of trace constituent in influent solution in cpm/ml, C_e = concentration of trace constituent in effluent solution in cpm/ml. All K_d data was run as four replicates per point.

The pH solution of selected samples was monitored with a single electrode pH meter. For characterizing the soils, the soil pH was measured in 0.01M CaCl_2 with a single electrode pH meter. Cation exchange capacity was measured by the small column procedure of Routson, Wildung, and Serne (1973). Calcium carbonate content was measured by the volumetric calcimeter method of Allison and Moodie (1965).

RESULTS AND DISCUSSION

Properties of soils used in the study are given in Table 1.

TABLE 1. Properties of Soil Samples

Soil	CaCO_3 mg/g	Silt %	Clay %	CEC me/100 g	pH units
Washington	0.8	10.1	0.5	4.9	7.0
South Carolina	<0.2	3.6	37.2	2.5	5.1

a. TTWC: 8 g 2,5 diphenyloxazole (PPO), 0.2 g para-bis [2-(5 phenyloxazole)] benzene (POPOP), 1000 ml toluene, 500 ml Triton X-100, 680 ml H_2O , 22 g $\text{Ca}(\text{OH})_2$.

KdAm values for the South Carolina soil are tabulated in Tables 2 and 3 and plotted on Figure 1 for the Ca and Na solutions, respectively. In both cases, it can be seen that the KdAm decreased with increasing concentration of either Na or Ca. It can be seen from Table 1 and Table 2 that divalent Ca has a much greater effect on Am sorption than does monovalent Na. Distribution coefficient (KdAm) data was used to develop linear $\ln$ -KdAm $\ln$ -concentration regression equations for predicting KdAm at intermediate Na and Ca concentrations in pure systems. Linear regression

FIGURE 1. KdAm as a Function of the Na and Ca Solution Concentrations for a South Carolina Subsoil

TABLE 2. KdAm as a Function of Calcium Nitrate Concentration for a South Carolina Subsoil

Concentration of Ca(M)	KdAm (ml/g)
0.20	1.0 $\pm$ 0.04 ^(a)
0.10	2.2 $\pm$ 0.2
0.05	3.6 $\pm$ 0.6
0.02	8.4 $\pm$ 1.0
0.002	67 $\pm$ 5.0

a. $\pm$ standard deviation

TABLE 3. KdAm as a Function of Sodium Nitrate Concentration for a South Carolina Subsoil

Concentration of Na(M)	KdAm (ml/g)
3.00	1.6 $\pm$ 0.1
0.750	2.9 $\pm$ 0.2
0.300	6.3 $\pm$ 0.7
0.030	130 $\pm$ 2.0
0.015	280 $\pm$ 24

analysis of the data for the South Carolina soil and Ca system (Table 2) gave a correlation coefficient (r) of -0.999, standard error of the estimated of 0.08, and an equation of the line: $y = -1.34 - 0.89x$ where y is the $\ln$ of the KdAm and x is the $\ln$ of the concentration. For the South Carolina subsoil and the Na⁺ system (Table 3), $r = -0.984$, $s = 0.47$, and $y = 1.11 - 1.02x$. Inspection of Figure 1 and the r values shows a high degree of correlation in both cases; however, the variance of data about the Na line is much greater than the Ca variance.

The sorption of ^{241}Am by the Washington subsoil being greater than anticipated resulted in only greater than values being determined. Calculated values of the $K_d\text{Am}$ ranged from 1200 to 8700 ml/g, with the values being essentially independent of concentration of Na and Ca. At K_d values of this magnitude, small errors in experimental procedure or counting variability result in a large change in the K_d value. For example, the percentage of Am sorbed at $K_d\text{Am}$ of 1200 and 8700 ml/g are 99.8% and 99.9%, respectively, with background counts being of the same order of magnitude as equilibrium solution counts. Thus relatively small variations in count rate result in large $K_d\text{Am}$ changes at high K_d values, and the $K_d\text{Am}$ for the Washington sand subsoil is best reported as >1200 ml/g although the actual values may be somewhat higher.

$K_d\text{Np}$ and $K_d\text{Tc}$ values are tabulated in Tables 4 to 8, with Tables 4 to 6 being plotted in Figure 2. In all cases, the general trend is, as expected, decreased $K_d\text{Np}$ with increased concentration of either Na or Ca. $K_d\text{Np}$ values are lower than anticipated, particularly on the South Carolina subsoil, and thus may necessitate reevaluation of the movement of ^{237}Np .

TABLE 4. $K_d\text{Np}$ as a Function of Calcium Nitrate ($\text{Ca}(\text{NO}_3)_2$) Concentration for a Washington Sand

Concentration of $\text{Ca}(\text{M})$	Average $K_d\text{Np}$ (ml/g)
0.002	2.37 ± 0.04
0.02	0.93 ± 0.07
0.05	0.78 ± 0.16
0.10	0.62 ± 0.04
0.20	0.36 ± 0.07

TABLE 5. KdNp as a Function of Sodium Nitrate (NaNO_3)
Concentration for a Washington Sand

Concentration of Na(M)	Average KdNp (ml/g)
0.015	3.90 ± 0.12
0.030	3.51 ± 0.19
0.300	3.28 ± 0.13
0.750	3.28 ± 0.35
3.000	3.19 ± 0.22

TABLE 6. KdNp as a Function of Sodium Nitrate (NaNO_3)
Concentration for South Carolina Subsoil

Concentration of Na(M)	Average KdNp (ml/g)
0.015	0.66 ± 0.08
0.030	0.57 ± 0.03
0.300	0.51 ± 0.09
0.750	0.45 ± 0.09
3.000	0.43 ± 0.16

TABLE 7. KdNp as a Function of Calcium Nitrate ($\text{Ca}(\text{NO}_3)_2$)
Concentration for South Carolina Subsoil

Concentration of Ca(M)	Average KdNp (ml/g)
0.002	0.25 ± 0.04
0.200	0.16 ± 0.06

TABLE 8. KdTc as a Function of Sodium Bicarbonate (NaHCO_3) Concentration for South Carolina Subsoil

Concentration NaHCO_3 (M)	Average KdTc (ml/g)
0.002	+0.019 $\pm$ 0.06
0.008	-0.052 $\pm$ 0.01
0.020	-0.033 $\pm$ 0.01
0.200	+0.010 $\pm$ 0.04

Linear regression analysis of the Ca system data for the Washington soil gave (Table 4) a correlation coefficient of $r = -0.986$, s (standard error of the estimate) = 0.11, and an equation of the line $y = -0.380x - 1.485$ where x is the independent variable $\ln$ (concentration) and y is the dependent variable $\ln$ (Kd). For the Na system (Table 5), $r = -0.843$, $s = 0.16$, $y = -0.0291x + 1.19$. For the South Carolina subsoil in the Na system (Table 6), $r = -0.974$, $s = 0.080$, $y = -0.077x - 0.79$. Inspection of Figure 2 and the r values shows a high degree of correlation in all three cases.

The low values (Table 7) obtained for KdNp as a function of Ca concentration on the South Carolina subsoil made further work statistically invalid. Small variations in count rate would result in relatively large KdNp changes when the KdNp is so low.

Preliminary work had shown Kd for Tc to be 0.12 in 0.01M CaCl_2 for the Washington soil (Wildung et al., 1975). It was, therefore, of interest to measure the Kd for Tc as a function of anion concentration for the South Carolina subsoil. The KdTc values shown in Table 8 are also low, confirming the earlier estimates which assumed Tc to sorb poorly on soils. Within the error of measurement, no sorption of ^{99}Tc occurs in this soil.

FIGURE 2. Distribution Coefficients of Neptunium in Selected Soils

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