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**THEORETICAL AND EXPERIMENTAL EVALUATION
OF WASTE TRANSPORT IN SELECTED ROCKS:
1977 ANNUAL REPORT OF LBL CONTRACT NO. 45901AK**

**Waste Isolation Safety Assessment Program—Collection and
Generation of Transport Data**

J. A. Apps, L. V. Benson, J. Lucas, A. K. Mathur, and L. Tsao

September 1977



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Work performed for the U.S. Department of Energy under Contract W-7405-ENG-48

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Printed in the United States of America

Available from

National Technical Information Service

U. S. Department of Commerce

5285 Port Royal Road

Springfield, VA 22161

Price: Printed Copy, \$ 7.25 Domestic; \$14.50 Foreign

Microfiche, \$ 3.00 Domestic; \$ 4.50 Foreign

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Waste Isolation Safety Assessment Program - Generation 1
Generation 1 Transport Data

J. A. Apps, L. V. Benson, J. Lucas, A. K. Mutter, and L. T. ...

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Work done under U. S. Department of Energy Contract W7405-ENG-4

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SECTION 1: INTRODUCTION

This report summarizes the progress and results obtained during fiscal year 1977 for LBL Contract No. 45901AK, "Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks." This project is part of the Waste Isolation Safety Assessment Program (WISAP), which is managed for the DOE Office of Waste Isolation by Battelle Pacific Northwest Laboratories. In particular, this project supports task 5 of WISAP, the collection and generation of transport data. Within task 5 is subtask 4, which addresses the problem of understanding the mechanisms of radionuclide transport and the impact of such mechanisms on radionuclide distribution coefficients. The goal of this project is to establish a basis on which radionuclide distribution coefficients can be reliably predicted for geological environments of the type anticipated for terminal radioactive waste storage facilities.

It is well known that the distribution coefficient (K_d), defined thus:

$$K_d = \frac{\text{mole of radionuclide sorbed/g}}{\text{moles of radionuclide in solution/ml}}$$

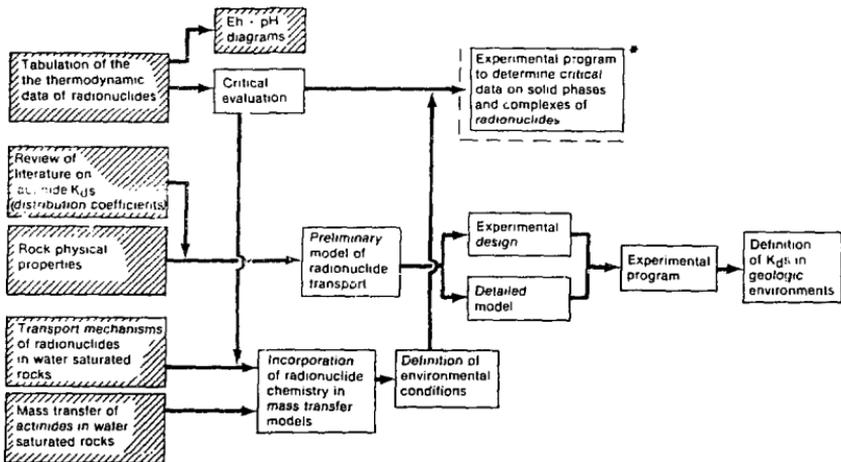
is a semiempirical parameter, subject to variation as a result of the chemical and physical conditions under which it is measured. These conditions vary greatly, depending on whether the environment is adjacent to a terminal storage facility or is similar to the environment normally encountered in a laboratory experiment. Laboratory measurements of K_d vary significantly from experiment to experiment. Therefore, the applicability of currently available measurements to the prediction of radionuclide behavior in rocks is questionable. Table 1-1 gives a tentative list of factors that might influence a typical K_d determination and the errors that might result from omitting these factors when extrapolating data from laboratory to subsurface conditions expected in a host rock adjacent to a terminal storage repository. It is obviously important to identify the critical factors influencing the magnitude of empirical distribution coefficients for given radionuclides, and to establish the variation in those factors under differing host rock conditions.

TABLE 1-1. Factors influencing K_d for a given radionuclide, based on a comparison between conditions in a typical soil column adsorption study and conditions expected in a terminal storage repository.

Parameters	Principal effect	Soil column test	Subsurface terminal storage facility	Potential effect on K_d
1. Solution chemistry				
a. Major components	Ionic strength Activity coefficients Complexing	Very variable. Composition determined by condition the test is designed to simulate.	Determined by host rock chemistry and by other factors including the leaching chemistry of the waste product.	Unpredictable - probably 10^{-3} to 10^{+3} .
b. Minor components	Complexing	Same as above.	Same as above.	Same as above.
c. pH	Complexing Chemical potential	2-11, depending on the nature of the test	5-8. Buffering of heterogeneous and homogeneous equilibria keep the pH range within narrow limits.	10^{-5} to 10^{+5}
d. Eh	Chemical potential	Variable, usually oxidizing, and dependent upon pH.	Variable, over a narrower range, usually reducing.	Up to 10^{10} or even more
2. Radionuclide concentration and speciation				
	Supersaturation Polymerization Metastable equilibrium	10^{-6} to 10^{-9} mole/kg. As ionic, polymeric, and particulate forms.	Uncertain, but probably very low, depending on leaching characteristics of waste product form (glass, possibly 10^{-3} to 10^{-11} mole/kg. principally as ionic species.	Difficult to estimate, but could be very large for amphoteric species near the isoelectric point ($\sim 10^6$)
3. Flow rate				
	Metastable equilibrium Transport Mechanisms Changes in apparent surface area contacted	$\sim 10^{-3}$ to 10^{-1} cm/sec	10^{-3} to 10^{-7} cm/sec	Sufficient flow rates could lead to different rate controlling transport mechanisms (e.g. ionic or molecular diffusion) also lead to different thermodynamic controls (0 to 10^6)
4. Permeability				
	Flow rate (see above)	10^{-2} to 10 Darcys	10^{-3} to 10^{-8} Darcys	Same as above.
5. Duration				
	Radionuclide decay Daughter formation Front reinforcement	$\sim 10^5$ sec	Up to 10^{13} sec	None considered at this time.
6. Surface area				
	Adsorption	Up to 10^5 cm ² /g; Dispersed clays, humus, fine particulates, loess, etc.	$\sim 10^2$ cm ² /g; Fractures, microfractures, intergranular pores	$\sim 10^3$
7. Path length				
	Dispersion	10^2 cm	2×10^7 cm	No anticipated effect on K_d .
8. Temperature				
	Complexing Solubility Adsorption	25°C	10 to 100°C	Up to 10^3

The radionuclides chosen for this study include thorium, uranium, plutonium, neptunium, americium, curium, iodine, and technetium. During fiscal year 1977, emphasis has been placed on the actinides plutonium, neptunium, americium, and curium. The host rock types being considered include acid igneous rocks (granite, rhyolite), basic igneous rocks (gabbro, dolerite and basalt), sedimentary rocks (argillites, sandstone, and limestone), and metamorphic rocks (if deemed appropriate). Although the study is generic and does not pertain to a specific site, greater emphasis is being placed on rocks from the Nevada Test Site and the Hanford Reservation near Richland, Washington.

The project includes both theoretical and experimental investigations organized into several interrelated subtasks, as illustrated in Fig. 1-1. These subtasks all support an attempt to define the environmental conditions expected in the water-saturated host rocks of a terminal storage



*Not included in current project.

KBL 782-512

Figure 1-1. Logic chart for LBL Waste Isolation Safety Assessment Program-5: Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks. Hatching indicates that task is complete.

facility and to determine the transport mechanisms of radionuclides in these rocks. This information can then be used to relate the thermodynamic and transport properties of radionuclides to the corresponding distribution coefficients, which then can be used with confidence in a computer simulation of radionuclide transport. Without such an effort, there is a danger that experimentally obtained distribution coefficients will be misinterpreted when calculations are made to determine transport through rock to the biosphere.

During fiscal year 1977, the following subtasks were performed.

1. Thermodynamic data were tabulated for those aqueous complexes and solid phases of plutonium, neptunium, americium, and curium likely to form in the natural environment.
2. Eh-pH diagrams were computed and drafted for plutonium, neptunium, americium and curium at 25°C and one atmosphere.
3. The literature on distribution coefficients of plutonium, neptunium, americium, and curium was reviewed.
4. Preliminary considerations were determined for an experimental method of measuring radionuclide transport in water-saturated rocks.
5. The transport mechanisms of radionuclides in water-saturated rocks were reviewed.
6. A computer simulation was attempted of mass transfer involving actinides in water-saturated rocks.

Progress in these tasks is reported in the following sections. Subtasks 1, 2, 3 and 4 are complete. The progress made in subtask 5 is represented by an initial theoretical survey to define the conditions needed to characterize the transport of radionuclides in rocks. This task will be refined and will continue in fiscal year 1978. Subtask 6 has begun but is not complete. Progress in this task will be reported more fully in 1978.

**SECTION 2: TABULATION OF THERMODYNAMIC DATA OF AQUEOUS COMPLEXES AND
SOLID PHASES OF PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM LIKELY
TO FORM IN THE NATURAL ENVIRONMENT**

INTRODUCTION

In subtask 1 of this study, information from the published literature was gathered on free energies of formation, solubility products, dissociation constants, and related topics as they pertain to plutonium, neptunium, americium, and curium. The information is summarized in Tables 2-1 through 2-4, below. No attempt was made to reinterpret or modify the published information. All sources are referenced and cross referenced where information has been published in review articles.

The table for each element is divided into two sections:

1. free energy data, including
 - a. aqueous species, and
 - b. solid species; and
2. reaction constant data.

The second section of each table gives additional information identifying the reaction studied, the technique used, the nature of the aqueous media, the temperature(s) at which the measurements were made, the value of the constant, the free energy of the reaction, and the source reference(s).

The compilation was made for three reasons.

1. To use "original source" information as the basis for computing refined free energy or reaction constant data that are internally consistent with and conform to standard state conditions. The processed data will be needed for use in computer simulations of ground water chemistry in the presence of the radionuclides under consideration.
2. To identify gaps or uncertainties in our knowledge regarding phase relations or speciation of the actinides, so that new experimental programs might be proposed in order to rectify these deficiencies.
3. To maintain a library of hard-to-find literature for use by other workers in the WISAP-5 program.

See References Cited for a complete list of references used in the tables.

TABLE 2-1. Thermodynamic data for plutonium.

FREE ENERGY DATA		ΔG_f° (kcal mole ⁻¹)	Reference				
Aqueous Species							
Pu ³⁺		-138.3 ± 0.8	Fuger and Oetting, 1976				
Pu ⁴⁺		-115.1 ± 0.8	Fuger and Oetting, 1976				
PuO ₂ ²⁺		-203.1 ± 1.8	Fuger and Oetting, 1976				
PuO ₂ ²⁺		-180.9 ± 1.7	Fuger and Oetting, 1976				
Solid Species							
Pu ₂ O ₃		-412.0	Polzer, 1971				
PuO ₂		-240.4	Polzer, 1971				
Pu(OH) ₃		-280.2	Polzer, 1971				
Pu(OH) ₄		-340.0	Polzer, 1971				
PuO ₂ (OH) ₂		-281.9	Polzer, 1971				
REACTION CONSTANT DATA							
Species	Reaction	Method	Solution	T (°K)	K	ΔG_R° (kcal mole ⁻¹)	References
Pu III	Pu ³⁺ + H ₂ O ⇌ PuOH ²⁺ + H ⁺	titra.	0.069M HClO ₄	298	7.5 × 10 ⁻⁸	+9.7	Cleveland, 1970; Kraus and Dam, 1949 a,b,c
	Pu(OH) ₃ (s) ⇌ Pu(OH) ₃ (aq)				2 × 10 ⁻²⁰		Cleveland, 1970; Katz and Seaborg, 1957
	Pu ³⁺ + Cl ⁻ ⇌ PuCl ²⁺	ion ex.	1.0 M HCl	--	14.7 ^a		Cleveland, 1970; Ward and Welch, 1956
		reduc.	1.0 M HCl	298	0.78	+0.15	Degischer and Choppin, 1975; Connick and McVey, 1953
		cal.	0.1 M HCl			3.72	Degischer and Choppin, 1975; Martin and White, 1958
Pu ³⁺		spec.	(conc. LiCl)	298	3.71 × 10 ⁻³	+3.3	Degischer and Choppin, 1975; Shiloh and Marcus, 1966
	Pu ³⁺ + SO ₄ ²⁻ ⇌ PuSO ₄ ⁺	cat. ex.	[H ⁺] = 1.0 M	301	18.13 ± 0.44	-1.73	Cleveland, 1970; Nair et al., 1967
		kin		298	10.0 est.		Degischer and Choppin, 1975; Newton and Baker, 1956
Pu ³⁺	Pu ³⁺ + HSO ₄ ⁻ ⇌ PuHSO ₄ ²⁺	ion ex.	~1 M NaClO ₄	301	9.94 ± 0.24	-1.37	Cleveland, 1970; Nair, 1968
Pu IV	Pu ⁴⁺ + H ₂ O ⇌ PuOH ³⁺ + H ⁺	poten.	I = 2M HClO ₄ - LiClO ₄	298	0.054 ± 0.001	+1.73	Cleveland, 1970; Pabideau, 1956; Perez-Bustamente, 1965
	Pu(OH) ₄ (s) ⇌ Pu(OH) ₄ (aq)				7 × 10 ⁻⁵⁶		Cleveland, 1970; Katz and Seaborg, 1957; Kraus, 1945; Latimer, 1952; Evans, 1949; Kasha, 1949; Kraus, 1949; Peppard et al., 1962

Table 2-1 (continued)

REACTION CONSTANT DATA (continued)								
Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole ⁻¹)	References	
Pu IV	$\text{Pu}^{4+} + \text{F}^- \rightleftharpoons \text{PuF}^{3+}$	spec.	1M HNO ₃	298	8.7×10 ⁷ (a)		Cleveland, 1970; Patil and Ramakrishna, 1976	
		spec.	1M HNO ₃	298	5.9×10 ⁶	-1.1	Degischer and Choppin, 1975; McLane, 1949	
	$\text{Pu}^{4+} + \text{Cl}^- \rightleftharpoons \text{PuCl}^{3+}$	cat. ex.	4M HClO ₄	293	1.4 ± 0.2		-0.2	Cleveland, 1970; Grenthe and Noren, 1960
		spec.	2M HClO ₄	298	0.38		+0.57	Degischer and Choppin, 1975; Hindman, 1949
		reduc.	1M HClO ₄	298	0.57		+0.33	Degischer and Choppin, 1975; Rabideau and Cowan, 1955
		reduc.	$\mu = 1.0$	298	1.38		-0.19	Degischer and Choppin, 1975; Rabideau, 1958
		reduc.	1M HCl	298	0.8		+0.14	Degischer and Choppin, 1975; Kabanova and Palei, 1960
$\text{Pu}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{PuSO}_4^{2+} + \text{H}^+$	cat. ex.	0.5M acid	298	9.45		-1.3	Cleveland, 1970; Marov and Chmutova, 1961	
$\text{Pu}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{PuSO}_4^{2+}$	reduc.	1.0M HClO ₄	298	4.58×10 ³		-5.0	Degischer and Choppin, 1975; Rabideau, 1955; Lemons, 1951	
$\text{Pu}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_2 + 2\text{H}^+$	cat. ex.	0.5 acid	298	20.0		-1.8	Cleveland, 1970; Marov and Chmutova, 1961	
$\text{Pu}^{4+} + 3\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_3^{2-} + 3\text{H}^+$	cat. ex.	0.5 acid	298	125		-2.9	Cleveland, 1970; Marov and Chmutova, 1961	
$\text{Pu}^{4+} + \text{HPO}_4^{2-} \rightleftharpoons \text{PuHPO}_4^{2+}$	solub.	2.0M HNO ₃ 0.012 - 2.0M	298	8.3×10 ¹²		-17.6	Cleveland, 1970; Denotkina, et al., 1960	
$\text{PuHPO}_4^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{Pu}(\text{HPO}_4)_2$	solub.	H ₃ PO ₄	298	6.7×10 ¹⁸		-14.8	Cleveland, 1970; Denotkina, et al., 1960	
$\text{Pu}(\text{HPO}_4)_2 + \text{HPO}_4^{2-} \rightleftharpoons \text{Pu}(\text{HPO}_4)_3^{2-}$	solub.	H ₃ PO ₄	298	4.8×10 ⁹		-13.2	Cleveland, 1970; Denotkina, et al., 1960	
$\text{Pu}(\text{HPO}_4)_3^{2-} + \text{HPO}_4^{2-} \rightleftharpoons \text{Pu}(\text{HPO}_4)_4^{4-}$	solub.	H ₃ PO ₄	298	6.3×10 ⁹		-13.4	Cleveland, 1970; Denotkina, et al., 1960	
$\text{Pu}(\text{HPO}_4)_4^{4-} + \text{HPO}_4^{2-} \rightleftharpoons \text{Pu}(\text{HPO}_4)_5^{6-}$	solub.	H ₃ PO ₄	298	6.3×10 ⁸		-12.0	Cleveland, 1970; Denotkina, et al., 1960	

Table 2-1 (continued)

REACTION CONSTANT DATA (continued)							
Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole ⁻¹)	References
Pu V	$\text{PuO}_2^+ + \text{Cl}^- \rightleftharpoons \text{PuO}_2\text{Cl}$	poten.	--	--	0.67	--	Cleveland, 1970; Rabideau, 1958
Pu VI	$\text{PuO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2\text{OH}^+ + \text{H}^+$	titra.	0.000186M HNO ₃	--	4.7×10^{-4}	--	Cleveland, 1970; Krovinskaya, et al., 1960
	$\text{PuO}_2\text{OH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2(\text{OH})_2 + \text{H}^+$	titra.	0.000186M HNO ₃	--	$9 \pm 1 \times 10^{-5}$	--	Cleveland, 1970; Krovinskaya, et al., 1960
	$\text{PuO}_2(\text{OH})_2 + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2(\text{OH})_3^- + \text{H}^+$	--	--	--	2×10^{-10}	--	Cleveland, 1970; Kreus and Dam, 1949 a,b,c
	$\text{PuO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{PuO}_2\text{Cl}^+$	spec.	1 = 1M	296	0.73 ± 0.07	+0.19	Cleveland, 1970; Rabideau, 1956
		spec.	~M HClO ₄	293	0.56	+0.34	Degischer and Choppin, 1975; Rabideau and Lemons, 1951
	$\text{PuO}_2^{2+} + \text{HF} \rightleftharpoons \text{PuO}_2\text{F}^+ + \text{H}^+$	cat. ex.	$I_3 = 2.0M$ $[H^+] = 2.0M$	298	12.	-1.5	Patil and Ramakrishna, 1976
	$\text{PuO}_2^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{PuO}_2\text{H}_2\text{PO}_4^+$	electroph.	0.206-5.88M H ₃ PO ₄	298	8.5×10^3	-5.36	Cleveland, 1970
	$\text{PuO}_2^{2+} + 2\text{OH}^- + \text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2\text{CO}_3(\text{OH})_2^{2-}$	solub.	0.17 - 0.44M NH ₄ CO ₃	293	2.3×10^{22}	-30.0	Cleveland, 1970; Gel'man, et al., 1962
	$\text{PuO}_2\text{OH}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2\text{CO}_3\text{OH}^-$	solub.	0.17 - 0.44M NH ₄ CO ₃	293	4.5×10^{22}	-30.4	Cleveland, 1970; Gel'man, et al., 1962
	$\text{Pu}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Pu}_2(\text{CO}_3)_2^{2-}$	solub.	0.17 - 0.44M NH ₄ CO ₃	293	6.7×10^{13}	-18.5	Cleveland, 1970; Gel'man, et al., 1962

^a corrected to the standard state, I = 0.

TABLE 2-2. Thermodynamic data for neptunium.

FREE ENERGY DATA		ΔG_f° (298), (kcal mole ⁻¹)		Reference			
Aqueous Species							
	Np^{3+}	-123.6 ± 0.8		Fuger and Dettling, 1976			
	Np^{4+}	-146.2 ± 1.8		Fuger and Dettling, 1976			
	NpO_2^+	-218.7 ± 1.3		Fuger and Dettling, 1976			
	NpO_2^{2+}	-190.2 ± 1.3		Fuger and Dettling, 1976			
Solid Species							
	NpO_2	-232.8		Raber and Kelley, 1966			
REACTION CONSTANT DATA (continued)							
Species	Reaction	Method	Solution	T (°K)	E (kcal mole ⁻¹)	References	
Np III	$\text{Np}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{NpOH}^{2+} + \text{H}^+$	titra.	0.1 M HClO_4	298	$4.7 \cdot 10^{-2}$	+1.3	Mefedova, et al., 1974
	$\text{Np}^{3+} + \text{Cl}^- \rightleftharpoons \text{NpCl}^{2+}$	spec.	conc. LiCl	298	$3.8 \cdot 10^{-3}$	+3.3	Burney and Harbour, 1974; Shiloh and Nazarov, 1966
Np IV	$\text{Np}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{NpOH}^{3+} + \text{H}^+$	--	--	--	$9 \cdot 10^{-3}$	--	Burney and Harbour, 1974; Mikhailov, 1973
	$\text{Np}(\text{OH})_4(\text{s}) \rightleftharpoons \text{Np}(\text{OH})_4(\text{aq})$	--	--	--	$6 \cdot 10^{-15}$	--	Burney and Harbour, 1974; Moskvina, 1973
Np^{4+}	$\text{Np}^{4+} + \text{HF} \rightleftharpoons \text{NpF}^{3+} + \text{H}^+$	ion ex.	4.0M HClO_4	293	$1.6 \cdot 10^{-4}$	+6.4	Burney and Harbour, 1974; Ahrlund and Brandt, 1966
		extrac.	1.0M HClO_4	298	$4.6 \cdot 10^{-4}$	+6.4	Choppin and Unrein, 1976
		ion ex.	1.0M HClO_4	298	$3.6 \cdot 10^{-4}$	+6.2	Deqischer and Choppin, 1975; Krylov, et al., 1968a
		ion ex.	1M HNO_3	293	$1.7 \cdot 10^{-4}$	+5.7	Deqischer and Choppin, 1975; Krylov, et al., 1968a
	$\text{Np}^{4+} + \text{Cl}^- \rightleftharpoons \text{NpCl}^{3+}$	distri.	1.0M HClO_4	293	0.91	+0.05	Burney and Harbour, 1974; Shilin and Nazarov, 1965
		emf	1.0M HClO_4	298	0.49	+0.42	Burney and Harbour, 1974; Stromatt and Peckema, 1958
		distri.	2.0M HClO_4	293	1.02	-0.12	Burney and Harbour, 1974; Shilin and Nazarov, 1966
		distri.	4.0M HClO_4	298	0.77 ± 0.06	+0.15	Burney and Harbour, 1974; Danesi, et al., 1971
Np^{4+}	$\text{SO}_4^{2-} \rightleftharpoons \text{NpSO}_4^{2+}$	distri.	2.0M HClO_4	298	$2.7 \cdot 10^2$	-3.3	Burney and Harbour, 1974; Sullivan and Hindman, 1954
		ion ex.	4.0M HClO_4	293	$5.0 \cdot 10^2$	-3.6	Deqischer and Choppin, 1975; Ahrlund and Brandt, 1966

TABLE 2-2 (continued)

Species	Reaction	Method	Solution	T (°K)	K	ΔC_R^{-1} (kcal mole ⁻¹)	References
Np V	$\text{NpO}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2\text{OH}(\text{aq}) + \text{H}^+$	poten.	HClO_4	--	1.25×10^{-5}	--	Burney and Harbour, 1974; Katz and Seaborg, 1957
	$\text{NpO}_2\text{OH}(\text{s}) \rightleftharpoons \text{NpO}_2\text{OH}(\text{aq})$	poten.	HNO_3	--	1.85×10^{-10}	--	Sovostyanova and Khalturin, 1973
	$\text{NpO}_2^+ + \text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}$	ion ex.	2.0M HClO_4	298	0.51	+0.41	Burney and Harbour, 1974; Gainar and Sykes, 1964
	$\text{NpO}_2^+ + \text{HPO}_4^{2-} \rightleftharpoons \text{NpO}_2\text{HPO}_4^-$	ion ex.	0.2M NH_4ClO_4 HClO_4	293	7.1×10^2	-3.8	Degischer and Choppin, 1975; Zvagintsev and Sudarikov, 1958
	$\text{NpO}_2^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{NpO}_2\text{H}_2\text{PO}_4$	ion ex.	0.2M NH_4ClO_4 HClO_4	293	6.5	-1.1	Degischer and Choppin, 1975; Zvagintsev and Sudarikov, 1958
	$\text{NpO}_2^+ + \text{HCO}_3^- \rightleftharpoons \text{NpO}_2\text{HCO}_3$	ion ex.	$\mu=0$	--	2.7×10^2	--	Burney and Harbour, 1974; Moskvin and Mafodeva, 1965
Np VI	$\text{NpO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}^+$	distri.	4.0M HClO_4	298	0.69 ± 0.05	+0.22	Burney and Harbour, 1974; Danesi, et al., 1971
		kin.	3.0M HClO_4	273	1.26	-0.13	Degischer and Choppin, 1975; Cohen, et al., 1955
	$\text{NpO}_2^{2+} + \text{HF} \rightleftharpoons \text{NpO}_2\text{F}^+ + \text{H}^+$	extrac.	1.0M HClO_4	294	8.6 ± 2.1	-1.3	Burney and Harbour, 1974; Ahrland and Brandt, 1968a
		ion ex.	1.04M HClO_4	298	157±9	-3.0	Degischer and Choppin, 1975; Krylov, et al., 1968b
	$\text{NpO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{NpO}_2\text{SO}_4$	extrac.	1.0M HClO_4	293	79	-2.6	Burney and Harbour, 1975; Ahrland and Brandt, 1960b
		reduc.	1.0M ClO_4^-	298	13	-1.5	Degischer and Choppin, 1975; Stromatt and Peekema, 1958
		distri.	2.0M NaClO_4	298	43.7	-2.2	Degischer and Choppin, 1975; Sykes and Taylor, 1962
	$\text{NpO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2\text{OH}^+ + \text{H}^+$	solub.	NH_4ClO_4	293	4.3×10^{-4}		Moskvin, 1971b
	$\text{NpO}_2\text{OH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2(\text{OH})_2 + \text{H}^+$	solub.	NH_4ClO_4	293	3.6×10^{-6}		Moskvin, 1971b
	$\text{NpO}_2(\text{OH})_2 + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2(\text{OH})_3^- + \text{H}^+$	solub.	NH_4ClO_4	293	2.0×10^{-10}		Moskvin, 1971b

TABLE 2-3. Thermodynamic data for americium.

FREE ENERGY DATA		$\Delta G_{f,298}^{\circ}$ (kcal mole ⁻¹)	Reference				
Aqueous Species							
Am^{3+}		-143.2 ± 0.3	Fuger and Oetting, 1976				
Am^{4+}		-89.2 ± 2.4	Fuger and Oetting, 1976				
AmO_2^+		-177.1 ± 1.3	Fuger and Oetting, 1976				
AmO_2^{2+}		-140.4 ± 0.8	Fuger and Oetting, 1976				
REACTION CONSTANT DATA							
Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole ⁻¹)	References
Am III	$\text{Am}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AmOH}^{2+} + \text{H}^+$		I = 0.1 ClO_4^-	296	1.2×10^{-6}	+8.0	
	$\text{Am}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Am}(\text{OH})_3(\text{aq})$	--	--	--	3.9×10^6	--	Schulz, 1976; Weaver and Shoun, 1971
	$\text{Am}^{3+} + \text{F}^- \rightleftharpoons \text{AmF}^{2+}$	solv. ext.	I = 1.0M NaClO_4	298	3.09×10^3	-4.76	Schulz, 1976; Choppin and Unrein, 1976
	$\text{Am}^{3+} + \text{Cl}^- \rightleftharpoons \text{AmCl}^{2+}$	spec.	13.7M LiCl	298	6.2×10^{-3}	+3.0	Schulz, 1976; Marcus and Shilo, 1969
		solv. ext.	I = 1M $\text{NaClO}_4 - \text{NaCl}$	303	1.04	-0.024	Schulz, 1976; Khopkar and Narayanankutty, 1971
		solv. ext.	I = 1M $\text{NH}_4\text{ClO}_4 - \text{NH}_4\text{SCN}$	303	1.33	-0.17	Schulz, 1976; Khopkar and Narayanankutty, 1971
		ion ex.	I = 1M $\text{NaClO}_4 - \text{NaCl}$	297	0.90	+0.06	Schulz, 1976; Bansal, et al., 1964
		solv. ext.	1M $\text{HClO}_4 - \text{HCl}$	295	0.90	+0.062	Schulz, 1976; Peppard et al., 1961
		solv. ext.	4M NaClO_4	298	1.41	-0.20	Schulz, 1976; Sekine, 1964; Sekine, 1965
		ion ex.	0.5M HClO_4		0.58		Schulz, 1976; Ward and Welch, 1956
		ion ex.	I = 4.0M $\text{HClO}_4 - \text{HCl}$	293	0.69	+0.21	Schulz, 1976; Grenthe, 1962
	$\text{Am}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{AmSO}_4^+$	ion ex.	I = 0.5-0.6M	298	72	-2.5	Schulz, 1976; Aziz, et al., 1968
		ion ex.	0.75M NH_4Cl	293-298	60.0	--	Schulz, 1976; Lebedev, et al., 1960
		ion ex.	1-1.3M I NaClO_4 , pH=3	299	30.9	-2.0	Schulz, 1976; Bansal, et al., 1964

TABLE 2-3 (continued)

REACTION CONSTANT DATA (continued)							
Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole ⁻¹)	References
Am III	$\text{Am}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{AmSO}_4^+$	ion ex.	1.5M NH_4ClO_4	293- 298	57.6	--	Schulz, 1976; Lebedev, et al., 1960
		(continued)					
		solv. ext.	1.0M NaClO_4	298	37.2	-2.1	Schulz, 1976; Sekine, 1964; Sekine, 1965
		solv. ext.	2.0M NaClO_4	298	26.9	-1.9	Schulz, 1976; DeCarvalho and Choppin, 1967
		ion ex.	0.5M NaClO_4	298	72.5	-2.5	Schulz, 1976; Aziz et al., 1968
		ion ex.	I = 1M $\text{HClO}_4 - \text{H}_2\text{SO}_4$	300	16.6	-1.7	Schulz, 1976; Najr., 1968
		ion ex.	I = 1M NH_4Cl	293	30.2	-2.0	Schulz, 1976; Moskvina, 1969
		$\text{Am}^{3+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{AmH}_2\text{PO}_4^{2+}$					

TABLE 2-4. Thermodynamic data for curium.

FREE ENERGY DATA		
	$\Delta G_f^\circ, 298^\circ$ (kcal mole ⁻¹)	Reference
Aqueous Species		
Cm^{3+}	-142.4 ± 1.5	Fuger and Oetting, 1976
Cm^{4+}	~ -214	Calculated from Nugent et al., 1971; Myasoedov, et al., 1974

REACTION CONSTANT DATA

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole ⁻¹)	References
Cm III	$\text{Cm}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{CmOH}^{2+} + \text{H}^+$	extrac.	I = 0.1M $\text{HClO}_4 - \text{LiClO}_4$	300	1.20×10^{-6}	-8.0	Desire, et al., 1969
	$\text{Cm}^{3+} + \text{F}^- \rightleftharpoons \text{CmF}^{2+}$	extrac.	1.0M NaClO_4	298	4.10×10^2	-3.6	Choppin and Unrein, 1976
	$\text{Cm}^{3+} + \text{Cl}^- \rightleftharpoons \text{CmCl}^{2+}$	ion ex.	0.5M HCl	--	1.51	--	Ward and Welch, 1956
	$\text{Cm}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{CmSO}_4^+$	ion ex.	0.15M NH_4Cl NH_4ClO_4	293- 298	56	--	Ward and Welch, 1956; Lebedev, et al., 1960
		distri.	2.0M NaClO_4 Na_2SO_4	298	22	-1.8	DeCarvalho and Choppin, 1967
		ion ex.	0.5-0.6M NaClO_4	298	71.9	-2.5	Aziz, et al., 1968
		distri.	0.5M NaClO_4	297- 298	73.3	-2.5	Aziz, et al., 1968
distri.	0.5M NaClO_4	298	68	-2.5	Aziz, et al., 1968		

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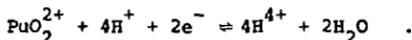
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**SECTION 3: Eh-pH CALCULATIONS AND ILLUSTRATIONS FOR PLUTONIUM,
NEPTUNIUM, AMERICIUM, AND CURIUM AT 25°C AND ONE ATMOSPHERE**

INTRODUCTION

Eh-pH diagrams are useful in identifying the stability fields of solid phases and aqueous species for a given element over a range of oxidation states, pH levels, and other predetermined conditions. The purpose of this chapter is to compute simple Eh-pH diagrams of the actinides plutonium, neptunium, americium, and curium and to predict their oxidation states and the stability of their hydroxyl species under conditions expected in the natural environment. Eh-pH diagrams are based on the assumption that Eh and pH are independent variables. The stability fields and phase or species boundaries delineated on the diagrams are defined by equations in which the coefficients are determined by the reaction specified and by the free energies of participating species. The figures illustrating this chapter are all drawn for 25°C and one atmosphere, and use free energy data compiled in Section 2 of this report.

The equations used to prepare the Eh-pH diagrams follow the procedure given in Krauskopf (1967). First a chemical equation for a reduction reaction is written. For example:



From this reaction, the number of electrons, hydrogen ions, and water molecules which participate in the reaction are noted. Next, the standard free energy of the reaction, ΔG_R° is determined. In this case:

$$\begin{aligned} \Delta G_R^\circ &= (-180.9) + (0) - (-115.1) - (-113.4) \\ &= 47.6 \text{ kcal mole}^{-1} \quad . \end{aligned}$$

Using the relationship between free energy and standard potential,

$$\Delta G_R^\circ = nFE_o$$

the standard potential of the reaction, E_o , is obtained. Here, n is the number of electrons participating in the reaction and F is Faraday's constant. In this example

$$E_o = 1.03 \text{ V}$$

To obtain the oxidation potential, the Nernst equation is used, thus:

$$E_h = E_o + \frac{2.303 RT}{nF} \log \frac{[\text{Pu}^{4+}]}{[\text{PuO}_2^{2+}][\text{H}^+]^4}$$

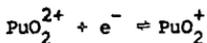
where $n = 2$ and $T = 298\text{K}$. This equation is used to determine the boundary between the domains of two species where $[\text{Pu}^{4+}] = [\text{PuO}_2^{2+}]$. Hence the equation reduces to:

$$E_h = E_o + 0.0295 \log \frac{1}{[\text{H}^+]^4}$$

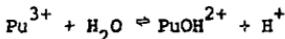
or

$$E_h = 1.03 = 0.118 \text{ pH}.$$

Certain reactions have no pH dependence, such as:

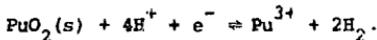


so that only the standard potential need be found. Hydrolysis reactions, which are only pH and not Eh dependent, such as



can be located using the hydrolysis constant alone.

Boundaries between aqueous species and solid phases can be determined in an analogous manner to those between aqueous species. For example,



In this equation, the correlation of the aqueous species is assigned an arbitrary value, such as 10^{-6} , mole l^{-1} . The activity of the pure solid is unity, by definition, and water is also assumed to have unit activity. The corresponding equation relating Eh and pH is

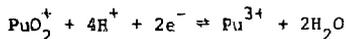
$$E_h = 0.49 - 0.236 \text{ pH} - 0.059 \log [\text{Pu}^{3+}]$$

where $[\text{Pu}^{3+}]$ is 10^{-6} , 10^{-17} , or 10^{-18} .

The actual equations used for each of the diagrams are listed under the respective headings for the actinides being considered.

PLUTONIUM

The Eh-pH diagram for plutonium given in Figure 3-1 shows the stability fields of the aqueous species Pu^{3+} (III), $\text{Pu}(\text{OH})^{2+}$ (III), PuO_2^+ (V), PuO_2^{2+} (VI), $\text{PuO}_2(\text{OH})^+$ (VI), $\text{PuO}_2(\text{OH})_3^-$ (VI) and the solid phase PuO_2 (IV). Equations defining species boundaries are derived as follows.

Aqueous Species Boundaries

$$\Delta G_R^\circ = -48.6 \text{ kcal mole}^{-1}$$

$$E_O = \frac{\Delta G_R^\circ}{nF} = 1.05$$

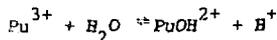
$$E_h = 1.05 - \frac{0.059}{2} \log [\text{H}^+]^4$$

$$E_h = 1.05 - 0.118 \text{ pH}$$



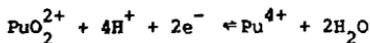
$$\Delta G_R^\circ = -23.2 \text{ kcal mole}^{-1}$$

$$E_O = 1.00$$



$$\Delta G_R^\circ = 7.6 \text{ kcal mole}^{-1}$$

$$2.303 \frac{-\Delta G_R^\circ}{R^2} = \log K_H = -5.6$$

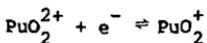


$$\Delta G_R^\circ = -47.6 \text{ kcal mole}^{-1}$$

$$E_o = 1.03$$

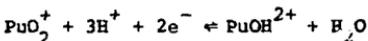
$$E_h = 1.03 - \frac{0.059}{2} \log [\text{H}^+]^4$$

$$E_h = 1.03 - 0.118 \text{ pH}$$



$$\Delta G_R^\circ = -22.2 \text{ kcal mole}^{-1}$$

$$E_o = 0.96$$

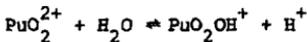


$$\Delta G_R^\circ = -41.0 \text{ kcal mole}^{-1}$$

$$E_o = 0.89$$

$$E_h = 0.89 - \frac{0.059}{2} \log \frac{1}{[\text{H}^+]^3}$$

$$E_h = 0.89 - 0.089 \text{ pH}$$



$$\Delta G_R^\circ = 4.6 \text{ kcal mole}^{-1}$$

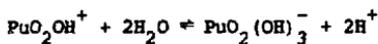
$$2.303 \frac{-\Delta G_R^\circ}{RT} = \log K_H = -3.4$$



$$\Delta G_R^\circ = 26.8 \text{ kcal mole}^{-1}$$

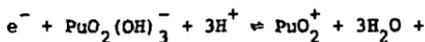
$$E_o = 1.16$$

$$E_h = 1.16 - 0.059 \text{ pH}$$



$$\Delta G_R^{\circ} = 21.0 \text{ kcal mole}^{-1}$$

$$2.303 \frac{-\Delta G_R^{\circ}}{RT} = \log K_H = -7.70$$

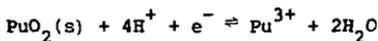


$$\Delta G_R^{\circ} = 47.8 \text{ kcal mole}^{-1}$$

$$E_o = 2.07$$

$$Eh = 2.07 - 0.177 \text{ pH}$$

Solid-Aqueous Species Boundaries

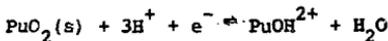


$$\Delta G_R^{\circ} = -11.3 \text{ kcal}$$

$$E_o = 0.49$$

$$Eh = -0.49 - 0.236 \text{ pH} - 0.059 \log [\text{Pu}^{3+}]$$

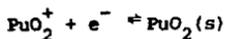
$[\text{Pu}^{3+}]$ is set at 10^{-6} , 10^{-12} , and $10^{-18} \text{ mol } \ell^{-1}$, and the equation is then plotted on the Eh-pH plane.



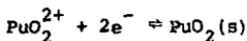
$$\Delta G_R^{\circ} = -3.7 \text{ kcal mole}^{-1}$$

$$E_o = 0.16$$

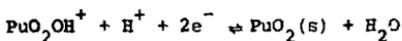
$$Eh = -0.16 - 0.177 \text{ pH} - 0.059 \log (\text{PuOH}^{2+})$$



$$E_h = \frac{RT}{nF} \left(\frac{\Delta G_R}{RT} - \ln [\text{PuO}_2^+] \right)$$



$$E_h = \frac{RT}{nF} \left(\frac{\Delta G_R}{RT} - \ln [\text{PuO}_2^{2+}] \right)$$



$$\Delta G_R^0 = -64.1 \text{ kcal mole}^{-1}$$

$$E_0 = 1.39$$

$$E_h = 1.39 - 0.059 \text{ pH} - 0.059 \log [(\text{PuO}_2\text{OH}^+)]$$

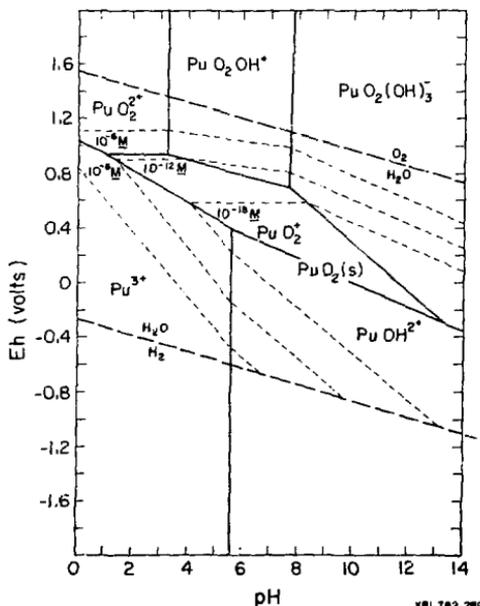
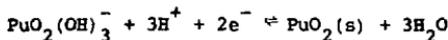


Figure 3-1. Eh-pH diagram for plutonium at 25°C and one atmosphere.



$$\Delta G_R^\circ = -85.1 \text{ kcal mole}^{-1}$$

$$E_o = 1.85$$

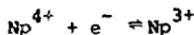
$$E_h = 1.85 - 0.177 \text{ pH} - 0.059 \log [\text{PuO}_2(\text{OH})_3^-]$$

The thermodynamic data for the plutonium Eh-pH diagram were taken from Fuger and Oetting, 1976 and Polzer, 1975. The diagram (Figure 3-1) is very similar to that produced by Polzer (1975). Discrepancies are negligible and are due to small differences in thermodynamic values used by Polzer for the reaction equations.

NEPTUNIUM

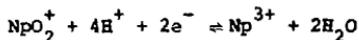
The Eh-pH diagram for neptunium given in Figure 3-2 is plotted to show the stability fields of the aqueous species Np^{3+} (III), NpOH^{2+} (III), Np^{4+} (IV), NpO_2^+ (V), NpO_2OH (V), NpO_2^{2+} (VI), NpO_2OH^+ (VI), $\text{NpO}_2(\text{OH})_3^-$ (VI), and the solid phase NpO_2 (IV). Equations defining species boundaries are derived as follows.

Aqueous Species Boundaries



$$\Delta G_R^\circ = -3.4 \text{ kcal mole}^{-1}$$

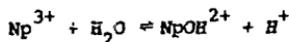
$$E_o = 0.15$$



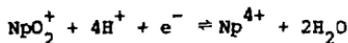
$$\Delta G_R^\circ = -18.3 \text{ kcal mole}^{-1}$$

$$E_o = 0.40$$

$$E_h = 0.40 - 0.118 \text{ pH}$$



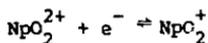
$$\log K_H = -7.4 \quad (\text{Mefodeva, et al., 1974})$$



$$\Delta G_R^\circ = -14.9 \text{ kcal mole}^{-1}$$

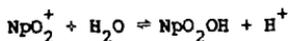
$$E_O = 0.65$$

$$E_h = 0.65 - 0.236 \text{ pH}$$

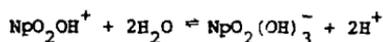


$$\Delta G_R^\circ = 28.5 \text{ kcal mole}^{-1}$$

$$E_O = 1.23$$



$$\log K_H = -8.9 \quad (\text{Sevostyanova and Khalturin, 1973})$$



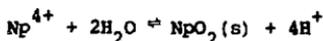
$$K_{2-1} = \frac{[\text{NpO}_2(\text{OH})_2][\text{H}^+]}{[\text{NpO}_2\text{OH}^+]} = 3.6 \times 10^{-6} \quad (\text{from Moskvina, 1971})$$

$$K_{3-2} = \frac{[\text{NpO}_2(\text{OH})_3^-][\text{H}^+]}{[\text{NpO}_2(\text{OH})_2]} = 2.0 \times 10^{-10}$$

$$K_{3-1} = \frac{[\text{NpO}_2(\text{OH})_3^-][\text{H}^+]^2}{[\text{NpO}_2\text{OH}^+]} = 7.2 \times 10^{-16}$$

$$[\text{H}^+] = 2.68 \times 10^{-8}$$

$$\text{pH} = 7.6$$

Solid Aqueous Species Boundaries

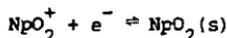
$$\Delta G_R^\circ = 0.80 \text{ kcal mole}^{-1}$$

$$2.303 \frac{-\Delta G_R^\circ}{RT} = \log K_H = -0.15 \quad \text{when} \quad [\text{Np}^{4+}] = 1\text{M}$$

$$\Delta G_R^\circ = -4.2 \text{ kcal mole}^{-1}$$

$$E_o = 0.18$$

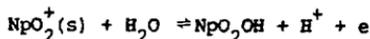
$$E_h = 0.18 = 0.059 \text{ pH}$$



$$\Delta G_R^\circ = -14.10 \text{ kcal mole}^{-1}$$

$$E_h = \frac{RT}{nF} \left(\frac{\Delta G_R^\circ}{RT} - \ln [\text{NpO}_2^+] \right)$$

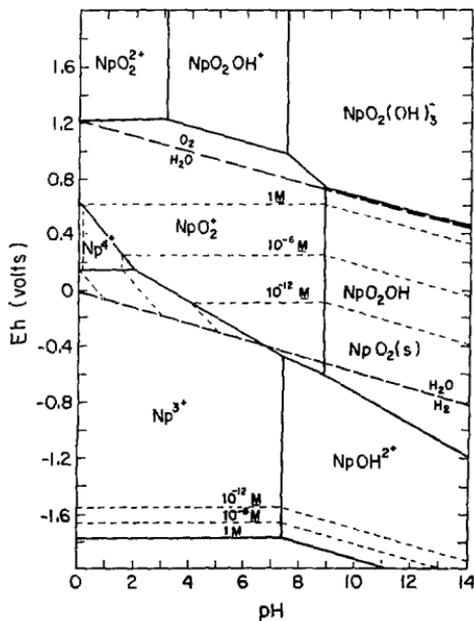
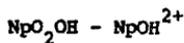
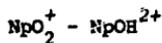
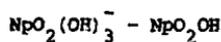
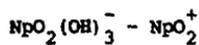
Solubility lines for $\text{NpO}_2(\text{s}) - \text{NpO}_2\text{OH}$ were drawn considering the hydrolysis reaction



which means that the lines must have a slope of -0.059 and consistency requirements that they meet solubility lines for NpO_2^+ .

The standard free energies of formation of NpO_2OH^+ and $\text{NpO}_2(\text{OH})_3^-$ have not been calculated. However, their domain boundaries may be determined from their hydrolysis constants and the hydrogen ion dependence of their reduction reactions to NpO_2^+ and NpO_2OH . For example, the domain boundary between NpO_2OH^+ and NpO_2^+ has a slope of -0.059 and must intersect with the domain boundaries between NpO_2^{2+} and NpO_2^+

and between NpO_2^{2+} and NpO_2OH^+ . Similar consideration of consistency requirements produced domain boundaries for

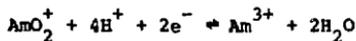


XBL 782-290

Figure 3-2. Eh-pH diagram for neptunium at 25°C and one atmosphere.

AMERICIUM

Very little data is available on aqueous species of americium, and no information on oxide phases has been found. The Eh-pH diagram for americium is illustrated in Figure 3-3. Equations used in its construction are given below.



$$\Delta G_R^{\circ} = -79.5 \text{ kcal mole}^{-1}$$

$$E_{\text{O}} = 1.72$$

$$\text{Eh} = 1.72 - 0.118 \text{ pH}$$



$$\Delta G_R^{\circ} = 37.0 \text{ kcal mole}^{-1}$$

$$E_{\text{O}} = 1.60$$

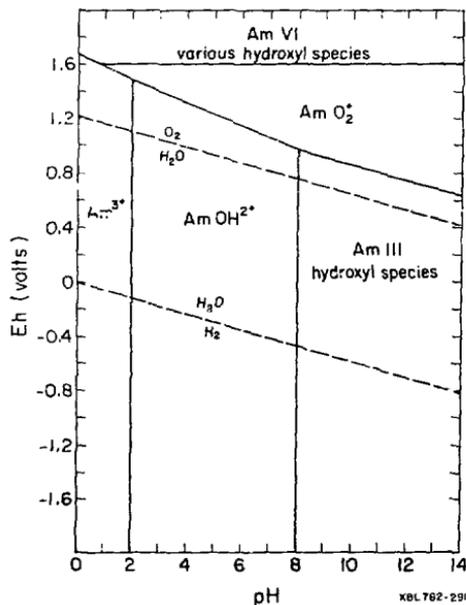
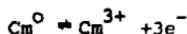


Figure 3-3. Eh-pH diagram for americium at 25°C and one atmosphere.

Data on hydrolysis of americium III is only qualitative. From work done by Korotkin (1975), the first pK_H can be expected to fall between -1 and -3. Schulz (1976) states that americium(IV) exists only in a few complexed states.

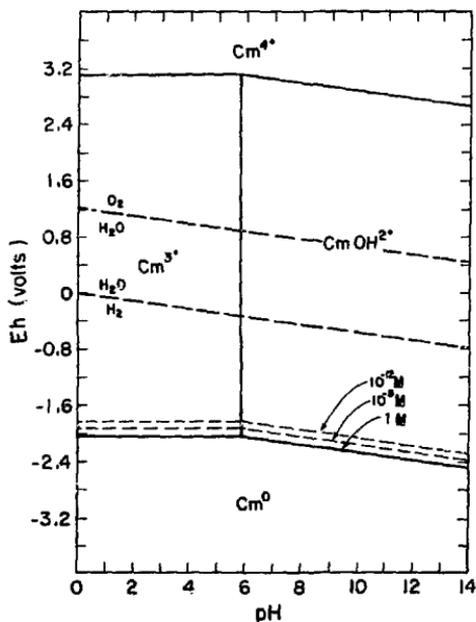
CURIUM

The Eh-pH diagram for curium is illustrated in Figure 3-4. The limited data available to construct this diagram are used below to compute the species boundaries given.



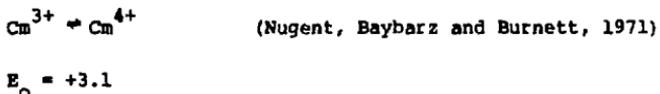
$$\Delta G_{f,298}^{\circ} = -142.4 \text{ kcal mole}^{-1} \quad (\text{Fuger and Oetting, 1976})$$

$$E_{\circ} = -2.06$$



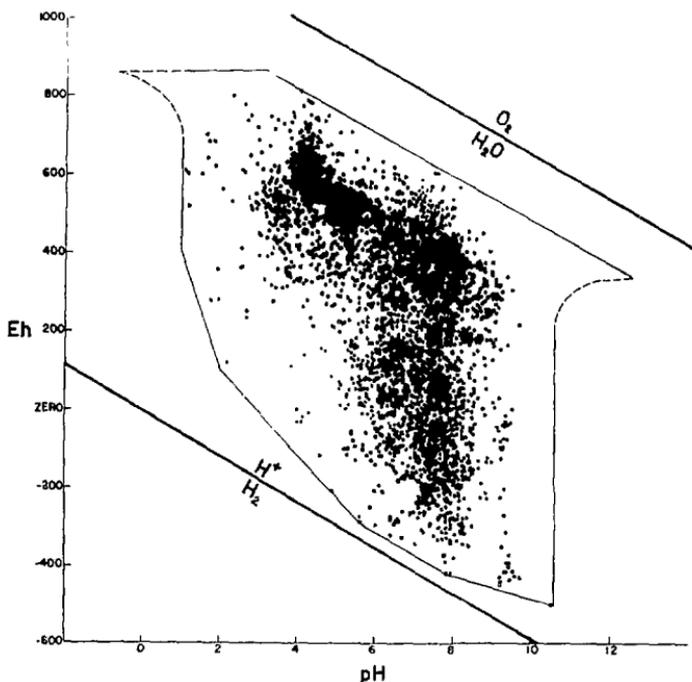
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Figure 3-4. Eh-pH diagram for curium at 25°C and one atmosphere.



OXIDATION STATES OF PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM IN THE NATURAL ENVIRONMENT

The oxidation state and pH range of natural groundwaters have been investigated by Baas Becking, et al. (1960) and are illustrated in Figure 3-5. Most subsurface groundwaters range in oxidation state from -400 to +400 mV and from pH 6 to pH 9. These ranges indicate that plutonium is most likely to be found in the III and V states, neptunium in the V state, and americium and curium in the III state. However, complexing and the effect of temperature may result in other oxidation states becoming significant. In addition, the data used for calculation of the diagrams have not all been corrected to standard state conditions. The effects of ionic strength may have altered some of the species boundaries. The data used in the calculations are also subject to error. Therefore, the Eh-pH diagrams presented should be considered provisional.



XBL 783-7642

Figure 3-5. Eh-pH range found in waters in the natural environment. (Source: Baas Becking, et al., 1960, *J. of Geology*, v. 68, no. 3, p. 276. Copyright 1960 by the University of Chicago.)

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SECTION 4: REVIEW OF THE LITERATURE ON THE DISTRIBUTION COEFFICIENTS
OF PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM

INTRODUCTION

Sorption is one of the mechanisms governing transport of radionuclides by water in porous media. Because distribution coefficients, or K_d s, are a measure of the soil's ability to sorb actinides and other elements, our knowledge of their values is important in assessing the safety of high-level radioactive-waste storage facilities in geological formations. The distribution coefficient is an experimentally determined quantity, and therefore varies with the conditions under which it is determined. There can be as many K_d values as there are combinations of parameters for a given radionuclide such as the kinds of sorbent, the chemical components in the solution, and the temperature. Therefore, wide discrepancies exist in the various K_d values assigned to different radionuclides.

This study reviews all the available literature containing data on K_d s for use in radionuclide transport models and is confined to four actinides--plutonium, neptunium, americium, and curium. The K_d values for these radionuclides are shown in Appendix 4-1, Tables A and B.

THEORETICAL BASIS FOR K_d DETERMINATION

The equilibrium distribution coefficient of sorption, or K_d , is a measure of the moles of nuclide in the sorbed state per unit mass of the geologic medium, divided by the moles of nuclide in the dissolved state per unit volume of groundwater, when the groundwater and the geologic medium are in equilibrium with one another (Routson, 1973).

The K_d in ml/g may be defined (Routson, et al., 1975) as:

$$K_d = \frac{\text{concentration of radionuclide sorbed on the soil } (\mu\text{Ci/g})}{\text{concentration of radionuclide in solution } (\mu\text{Ci/ml})}$$

or

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

where

A_s = equilibrium concentration or activity sorbed on the solid phase,

W = weight of solid phase in grams,

A_l = equilibrium concentration or activity of the solution phase, and

V = volume of solution in milliliters.

The distribution coefficient is an experimentally determined number and is a practical measure of the relative affinity of ions for the soil. The variables affecting the exchange of radionuclide on the soil are numerous and the process is very complex. Because of its empirical nature, the K_d varies with the conditions under which it is determined (pH of the groundwater, dissolved salts concentration, solution temperature, and kinds of sorbent). K_d is therefore applicable only to specified conditions.

EXPERIMENTAL METHODS

Radionuclide K_d 's can be determined from laboratory tests or field tests. Generally, laboratory tests for K_d 's are of two types: equilibrium batch tests and column tests.

Equilibrium Batch Tests

In equilibrium batch tests, a known volume of a real or simulated waste solution (that is, a known amount of radiotracer such as ^{239}Pu or ^{241}Am added to an aqueous solution) is mixed (shaken) with a known weight of sorbent (sediment or soil) until equilibrium is attained. The activity of the solution before and after contact is measured by radiometric counting procedure, and the amount of radionuclide adsorbed is calculated. The K_d is then calculated using equation (1).

In a typical batch experiment with simulated waste solution (Prout, 1959), a measured amount of distilled water is poured into a polyethylene bottle and the solution pH is adjusted by adding a measured amount of NaOH or HNO_3 . Next, radionuclide is transferred into the bottle by pipet and thoroughly mixed with the solution giving the final radionuclide

concentration required. The exact concentration of the radionuclide is determined by removing an aliquot of the solution. A weighed amount of soil is then added to the bottle and the sample shaken on a mechanical shaker until equilibrium is attained. The sample is then centrifuged and an aliquot of the supernatant liquid removed to determine the radioactive constituent concentration. The difference in the solution activity before and after contact with soil gives the amount of the radionuclide adsorbed by the soil. (See Schmalz, 1972, for details on experimental procedure.)

By varying the conditions of the test solution, the influence on K_d of geochemical parameters such as ionic strength, pH, and competing ions (such as Ca^{2+} and Na^+) present in the system can be obtained.

Column Tests

Column experiments are laboratory studies designed to simulate field conditions by packing soil in a glass or metal tube (ion exchange column). In contrast to batch experiments, column tests are open tests in which a liquid containing a radionuclide is pumped or percolated through the column at a flow rate simulating field conditions. The effluent is collected in quantities related to the volume of the column and sampled to determine the breakthrough of any given radionuclide as a function of the throughput volume (Bensen, 1960). The effluent radionuclide concentration (C) is then determined and compared with the influent radionuclide concentration (C_0). The ratio $C:C_0$ is plotted against the effluent column volumes (V) and an S-shaped breakthrough curve is obtained. The distribution coefficient can be calculated using the following expression (Schmalz, 1972):

$$V_{50} = \frac{K_d \times W}{2} \quad (2)$$

where

- V_{50} = the volume required to load a column to the 50% point
or the volume at 50% breakthrough, and
- W = weight in grams of the soil in the column.

The distribution of a radionuclide can also be represented by an error function plot, that is, by plotting the breakthrough curve on log probability paper, which usually results in a straight line (Reisenauer, 1959).

Small columns have also been used to calculate K_d values for radionuclides (Eliason, 1966, and Glover, et al., 1976). In this method a small volume of sediment is placed in tubes with fritted-disc bottoms and trace solutions are passed through the sediment until the system comes to equilibrium. Equilibrium is attained when the solution activity of the trace ion equals the influent solution activity. K_d values are calculated using equation (1).

Column experiments are subject to dispersion and are expected to yield K_d values representative of field conditions. However, column experiments are very time-consuming, particularly in situations where K_d values are large.

According to Bensen (1960), the results obtained by column experiments are not directly comparable with those of equilibrium experiments when the column influent is equilibrated with the same soil. In passage through a soil column, the influent solution carries away solubilized electrolytes liberated by the soil. In the equilibrium case, the solubilized soil electrolytes remain in the system to inhibit the adsorption of the radionuclides and the radionuclide concentration decreases during adsorption. Soil column data are more directly comparable with those of equilibrium experiments when the soil column influent is adjusted to the same composition as that found in the equilibrium supernatant liquid after equilibration.

Field Tests

Field experiments are the most direct means of obtaining accurate K_d data. Some field experiments have been conducted to measure migration characteristics and breakthrough data of radionuclides, such as ^{90}Sr , ^{137}Cs , ^{106}Ru , ^{99}Tc and others at Hanford (Knoll and Nelson, 1959; Knoll and Nelson, 1962; Brown, 1966). Field investigations at Test Reactor Area, Idaho, gave higher values of K_d for ^{137}Cs and ^{90}Sr than predicted by laboratory techniques (Schmalz, 1972). Field methods may also involve

injecting radionuclide-tagged water into the groundwater flow system at the point of interest and then monitoring the movement of the tracer by soil sampling or well or piezometer sampling (Cherry, 1977). However, because of the cost and time required to conduct the experiments, this approach has not been widely used.

A comparison of the experimentally determined K_d s for ^{137}Cs and ^{90}Sr obtained by different methods indicates a wide variation in their values (Table 4-1).

LITERATURE REVIEW

Because this study was confined to plutonium, neptunium, americium, and curium, the literature reviewed includes only publications containing K_d data on these actinides.

Plutonium

Some of the first studies on plutonium distribution coefficient determination in soils were done by Rhodes (1952, 1957a, and 1957b). In laboratory equilibrium studies, soil from the Hanford Project containing

Table 4-1. Comparison of distribution coefficients for ^{137}Cs and ^{90}Sr determined by different methods (Schmalz, 1972).

Determined by	K_d (ml/g)	
	^{137}Cs	^{90}Sr
Laboratory batch technique	285	7.2
Sorption equations	360	10.5
Exchange column experiment	1000	10.5
Field data		
(1968 investigations)	600	--
Field data		
(1970 investigations)	450-950	40

92% sand and 2% free CaCO_3 was contacted with a neutral solution containing approximately 4×10^{-7} M of plutonium. A soil-to-solution ratio of 1 g to 20 ml was used. The adsorption of plutonium was found to be dependent on contact time, pH, and the concentrations of nonradioactive salts (see Fig. 4-1 and Table 4-2).

In the pH range of 2 to 8.5, about 98% to 100% of the plutonium ($K_d > 1980$) was sorbed from the solution; the sorption was lowered between pH 8.5 and 12.5. Rhodes concluded that at pH > 2 plutonium polymers were formed and plutonium was adsorbed to soil as positively charged polymers $\text{Pu}(\text{OH})^{n+}$. The adsorption decrease in the pH range 8.5 to 12.5 was believed to be due to change in the characteristics of the polymer, which caused the charge to become negative (plutonium speciation). Rhodes further demonstrated that the high concentrations of inorganic salts (4 M NaNO_3 and 2 M di-ammonium phosphate) had no effect on plutonium adsorption on soil (96.5% plutonium sorbed), whereas equal concentrations of organic salts (4 M ammonium acetate) drastically reduced soil adsorption

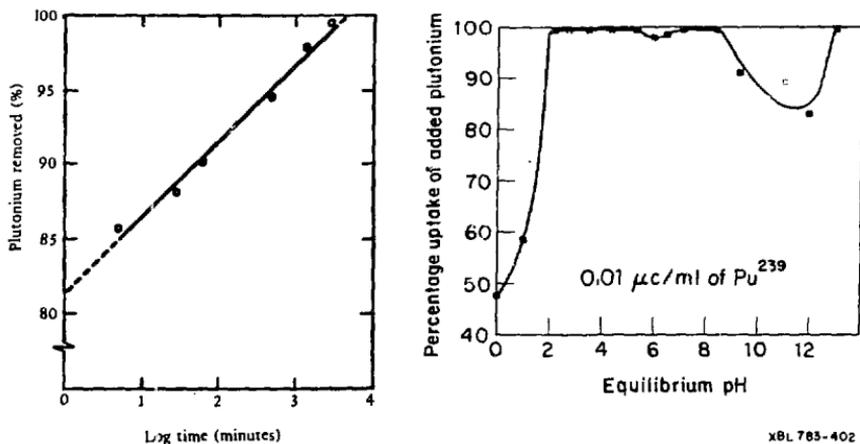


Figure 4-1. Left: plutonium adsorption by soil as a function of time of contact (Rhodes, 1952). Right: plutonium adsorption by soil as a function of pH (Rhodes, 1952, as cited by Bensen, 1960).

Table 4.2. Equilibrium distribution coefficient values for ^{239}Pu as a function of pH (Rhodes, 1957b).

pH	K_d (ml/g)	pH	K_d (ml/g)
0	18	6.5	1314
1.0	28	7.1	>1980
2.2	>1980	8.4	>1980
2.7	>1980	9.3	200
3.5	>1980	11.1	178
4.4	>1980	12.0	96
5.3	>1980	13.0	1980
6.0	888	14.0	1980

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(58.9% plutonium adsorbed). Rhodes attributed the above data on plutonium adsorption to ion exchange mechanisms. Later, Bensen (1960), reinterpreting Rhodes' data, concluded that precipitation reactions and not ion exchange probably control plutonium sorption on soils.

Prout (1958 and 1959) investigated plutonium adsorption by soil from the Savannah River Plant that contained 20% clay and 80% sand with kaolinite as the dominant clay mineral (Table 4-3). In the equilibrium experiments, K_d s were determined by contacting plutonium-spiked ($\approx 10^{-6}$ M) solution with soil and using a soil-to-solution ratio of 1 g to 10 ml. Plutonium adsorption was measured as a function of the oxidation state (valence) of plutonium and the pH of the solution. Prout's study substantiated Rhodes' results and showed that the sorption phenomenon is dependent on the plutonium oxidation state and the hydrogen ion activity (pH). Figure 4-2 shows K_d values for plutonium as a function of solution pH for various plutonium oxidation states.

Table 4-3. Exchange capacity and pH of soils (Prout, 1959).

pH	Exchange capacity	
	meq/100 g soil ^a	meq/100 g clay ^a
4	0.012	0.06
5	0.108	0.54
6	0.372	1.86
7	0.504	2.52
8	0.600	3.00
9	0.744	3.72
10	1.24	6.18

^aSoil contained approximately 20% clay and 80% sand.

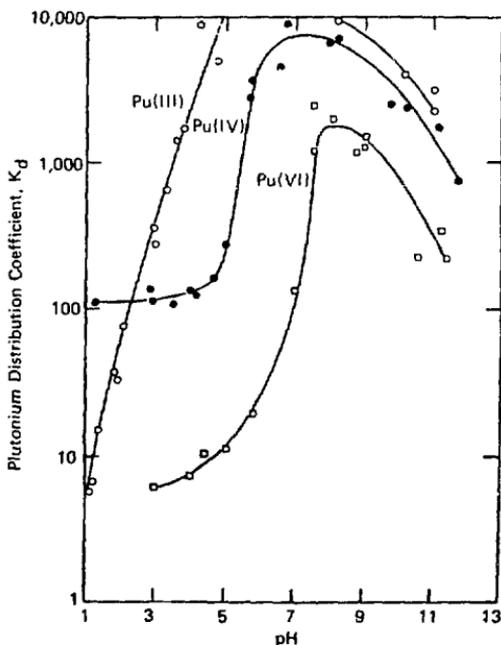


Figure 4-2. Effect of pH and plutonium oxidation state on the adsorption of plutonium by soil (Prout, 1959).

Plutonium adsorption was more than 90% complete from solutions of Pu(III) and Pu(IV) between pH values of 2.5 and 12, and from solutions of Pu(VI) at pH values greater than 6. Because plutonium ions undergo extensive hydrolysis in alkaline solutions, strong sorption between pH values of 2.5 and about 9 was probably due to a combination of cation exchange and precipitation of hydrolysis products. Above pH 9, formation of negatively charged plutonium complexes probably results in decreased adsorption.

Knoll (1965, 1969) and Hajek and Knoll (1966) did sorption studies using column and batch tests on high-salt wastes (5.4 M NO_3^-) spiked with organic contaminants typical of a radionuclide separations plant. The soil used for the study was selected from the samples obtained from two wells at the Z-1A tile field site (subsurface storage cribs) in Richland, Washington. K_d values obtained in batch tests on high-salt wastes from the reprocessing plant are given in Table 4-4.

As seen from Table 4-4, upon neutralization of the waste, plutonium K_d values increased from 2.4 ml/g to 2.9 ml/g. When organic contaminants

Table 4-4. Adsorption of plutonium and americium by soil
(Hajek and Knoll, 1966).

Solution	Equilibrium distribution coefficient (ml/g)	
	Pu	Am
Aqueous acid waste (AAW) untreated	2.4	<1
pH 2 (soil neutralized)	2.7	<1
pH 3 (NaOH neutralized)	2.9	<1
Alkaline waste from precipitation		
Supernate--		
aqueous	a	212
aqueous and organic	1.4	42
Sludge leachate	1540	500

^aInitial plutonium concentration and equilibrium concentration were too low for confident analysis.

(20% by volume) were added to this neutralized waste, the K_d value decreased to 1.4. The K_d value for plutonium increased to 1540 ml/g when water leachates of the sludge, produced on neutralization, were contacted with soil. In soil column experiments (Knoll, 1969) tap water spiked with plutonium was percolated through the columns of soil. Various organic solutions were then percolated through the columns and the quantity of plutonium leached was measured by sampling the effluent at intervals. When the plutonium and americium are added to the organics and then percolated through the soils, the K_d values given in Table 4-5 are observed (Ames, et al., 1976). A column bulk density of 1.5 g/ml is assumed.

Using the batch method, Tamura (1972) measured K_d values for plutonium for selected sorbents. In his study, 0.1 g of sorbent was mixed with 25 ml of water spiked with plutonium ions. The original spike was of Pu^{4+} in 1 M HNO_3 and the initial solution pH was adjusted to 7.0 using NaOH. For the anion and cation resins, an equivalent amount of wet resin was used to give 0.1 g of dry weight. The amount of plutonium added was not specified. The K_d values are given in Table 4-6.

According to Tamura, since plutonium can exist in different oxidation states and is subject to hydrolysis in the pH range normally encountered in natural-water systems, its adsorption from a water system is not by normal ion exchange but more likely by "scavenging" of the hydroxide or oxide precipitates. Table 4-6 shows that with the exception of anion resin, bone charcoal, and quartz, the amount of plutonium removed appears to depend on the pH of the suspension. This suggests that the higher pH favors formation of hydroxides that are scavenged by the clays, resulting in greater plutonium adsorption.

Schneider and Platt (1974) estimated distribution coefficients for movement of selected radionuclides through a typical western desert soil in contact with typical nonsaline ground water. The typical soil used was a sand of moderate cation exchange capacity (CEC; about 5 meq/100 g) to sandy loam containing about 1 mg of free CaCO_3 per gram of soil. The soil pH ranged between 7.0 and 8.2. The K_d value determined for plutonium for the above soil was 2000 ml/g. No details were given either about the experiment or about the method used.

Table 4-5. Distribution coefficients of americium and plutonium as a function of organic solution (Ames, et al., 1976).

Organics	K_d (ml/g)	
	Am	Pu
Tributylphosphate (20%): CCl_4 (80%)	1.6	5.4
Dibutylbutylphosphonate (30%): CCl_4 (70%)	0.6	0
di-(2-ethylhexyl) phosphoric acid in hydrocarbons	0	0

Table 4-6. Removal of plutonium from pH 7 water by selected sorbents (0.1 g sorbent/25 ml; Tamura, 1972).

Material	Removal (%)	Distribution	Suspension pH
		coefficient (ml/g)	
Attapulgite	94.6	4,370	9.60
Montmorillonite	71.6	630	9.20
Alumina (activated)	75.1	755	8.35
Kaolinite	58.5	352	6.25
Illite	34.0	129	5.90
Quartz	0.0	--	6.35
Dowex 50W-XI	4.2	11	1.82
Dowex I-XI	12.9	37	7.60
Bone charcoal	99.6	62,000	6.65
Coconut charcoal	99.0	25,000	6.80
Apatite	99.7	83,000	6.70

Duursma and Parsi (1974), using a ^{237}Pu tracer in valence states 3+, 4+, and 6+, conducted a series of experiments to determine distribution coefficients of plutonium onto marine sediments with oxic and anoxic sea waters at pH 7.8 to 8.0. Water-column and thin-layer methods were used to determine the K_d s. All three valence states showed K_d values of the order of 10^4 for both oxic and anoxic conditions (Table 4-7).

Experiments on radionuclide migration through soil and on distribution coefficient determination were conducted at Savannah River, South Carolina, with radionuclides containing synthetic, high-salt basic wastes (E. I. Du Pont de Nemours and Company, 1975). Batch equilibrium tests were performed with various resins. In one test, 1 g of resin was shaken overnight with 10 ml of synthetic waste supernate containing 1.75×10^7 dis/min·ml of ^{238}Pu . Distribution coefficient values for plutonium varied from 1 to 240 on various resins and are given in Table 4-8.

The migration of solvent-complexed plutonium from separations-process waste through dry and moist soils was determined. Laboratory column tests with dry soils using short columns (2.6 in.) and long columns (5.8 in.) yielded a plutonium K_d (ml/g) value of 6000 for the short column and 3000 for the long column. Column tests with moist soils yielded a plutonium K_d value of ≈ 0.4 for the solvent phase, and $K_d > 30$ for the aqueous phase.

The above test showed that dry (ground-surface) soil effectively sorbs and immobilizes small volumes of solvent-complexed plutonium, but moist (subsurface) soil allows extensive migration of large volumes of solvent-complexed plutonium.

Hamstra and Verkerk (1977) reported distribution coefficient measurements for plutonium and americium using different soil materials taken from boreholes surrounding salt formations in the northeast Netherlands. In batch equilibrium studies, they used stock solutions of the radionuclides in the form of 90% saturated NaCl solutions and a soil-to-solution ratio of 1 g to 150 ml. Equilibrium pH of the solutions was mostly between 7 and 8. The amount of radionuclide (plutonium or americium) added was not specified. The measured distribution coefficients for various soil materials and clay samples taken

Table 4.7. Plutonium-237 sorption by Mediterranean sediment (Daursma and Parsi, 1974).

Valence	Oxic conditions pH = 7.8-8.0					Anoxic conditions pH = 7.8-8.0				
	Sedimentation		Thin Layer			Sedimentation		Thin Layer		
	K	R	K	R'	T _{1/2}	K	R	K	R'	T _{1/2}
III	1.6x10 ⁴	10%	2.1x10 ⁴	30%	3	1.9x10 ⁴	2.5%	-	-	-
IV	1.8x10 ⁴	9%	1.9x10 ⁴	50%	1	1.3x10 ⁴	8.0%	>9.4x10 ⁴	39%	2.4
			1.5x10 ⁴	31%	1			(>9.3x10 ³	35%	1.3 ^a)
VI	1.3x10 ⁴	11%	5.7x10 ⁴	9%	4	2.2x10 ⁴	9.0%	-	-	b

K = distribution coefficient; R = % reduction in water/day without sediment;
R' = glasswall adsorption after three weeks; T_{1/2} = half uptake time to apparent
equilibrium in days.

^aPaper filters rather than millipore filters used as blanks; paper filters strongly
adsorbed Pu(IV) and reduced sediment uptake, therefore K is probably low.

^bPrecipitation of Pu on the blank millipore filters with the thin-layer experiments
decreased from 50% for Pu(III) to 12% for Pu(VI) and 3% for Pu(VI).

Table 4-8. Resin-supernatant distribution coefficients for plutonium.
(E. I. Du Pont de Nemours and Co., 1975).

Resin	K_d (ml/g)
"Duolite" ARC-359	240
Linde AW-500 ^a (Zeolite)	24
"Chelex" 100	7
"Dowex" 50W-X8	~ 1
HZO-1 (hydrated zirconium oxide gel)	100

^aProduct of Union Carbide.

at various depths are given in Tables 4-9 and 4-10. Clay samples consisting mainly of illite and kaolinite had plutonium distribution coefficients of $\sim 10^4$; river sand had a K_d of 200 ml/g.

Fried, et al. (1974, 1976a, 1976b), in their studies on the migration of actinides in the lithosphere, measured plutonium and americium surface-absorption and migration coefficients on the rock samples found in the vicinity of disposal sites.

In the experiments on the surface-absorption coefficient of plutonium and americium on limestones and basalts, disks of the rock were immersed in solutions of 4×10^{-5} M $^{238}\text{Pu}(\text{NO}_3)_4$ and 10^{-7} M $\text{Am}(\text{NO}_3)_3$. Small aliquots (0.05%) were removed at 12-hr intervals, dried, and measured for alpha counts (or gamma counts for americium) until the attainment of equilibrium. After equilibration the activity in the solutions was measured again. Initial pH of the solution used was 7.0 and the final pH ranged between 7 and 8.

Sorption on the rocks was measured in terms of surface-absorption coefficient, K , which was defined as:

$$K = \frac{\text{(activity of actinide/ml of solution)}}{\text{(activity of actinide/cm}^2 \text{ of rock)}}$$

The results of the experiment showed that on a surface-area basis, basalts sorbed more plutonium than limestone. The surface-absorption

Table 4-9. Distribution coefficients for plutonium and americium for different soil materials (Hamstra and Verkerk, 1977).

Soil material	Distribution coefficient (ml/g)	
	Pu	Am
Clay (mainly illite and kaolinite)	10^4	5×10^4
Sandstone (certain amount of clay)	1×10^3	1×10^4
Caprock (mainly gypsum, no clay)	5×10^2	3×10^3
River sand (mainly quartz, no clay)	2×10^2	4×10^2

Table 4-10. Distribution coefficients for plutonium and americium measured for clay samples taken at various depths (Hamstra and Verkerk, 1977).

Depth of sample (m)	Distribution coefficient (ml/g)	
	Pu	Am
20-30 ^a	10^4	8×10^4
55-60 ^b	5×10^3	6×10^4
100-125 ^b	6×10^3	5×10^4
120-130 ^b	5×10^3	6×10^4
120-160 ^c	7×10^3	2×10^4
200-225 ^c	6×10^3	9×10^4
245-275	8×10^3	4×10^4
300-325	9×10^3	4×10^4
328-348	8×10^3	5×10^4

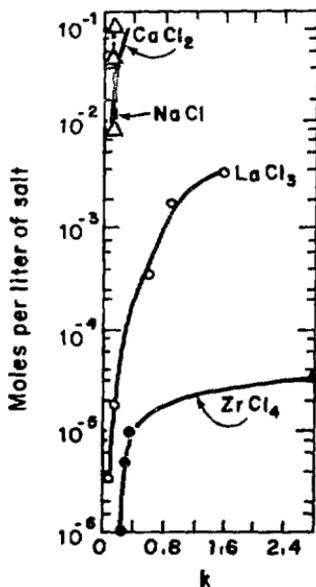
^aQuaternary clay (mainly montmorillonite).

^bYoung tertiary clay (mixture of illite and kaolinite).

^cOlder tertiary clay (mixture of illite and kaolinite).

coefficient (R) for pure solution of $\text{Pu}(\text{NO}_3)_4$ at $4 \times 10^{-5} \text{ M}$ was 0.10 ± 0.02 for limestone and 0.07 ± 0.02 for basalts. The effects of salt solutions of Na^+ , Ca^{2+} , La^{3+} , and Zr^{4+} at various concentrations on the surface absorption coefficient were also studied (see Figs. 4-3, 4-4, and 4-5). The salts displaced some of the plutonium from the rocks and the displacement became easier with increasing salt concentration and increasing valence.

In determining migration coefficients of plutonium for flow through porous limestone and basalt, Fried, et al. (1976a) used a high-pressure chromatographic absorption apparatus (Fig. 4-6). A small amount of $^{238}\text{Pu}(\text{NO}_3)_4$ tracer in neutral aqueous solution was placed on the surface of the rock disk and was allowed to dry at room temperature. Water



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Figure 4-3. Surface absorption coefficients of plutonium as a function of the concentration of other salts (i.e., ZrCl_4 , LaCl_3 , CaCl_2 , NaCl) for limestone (Fried, et al., 1976a).

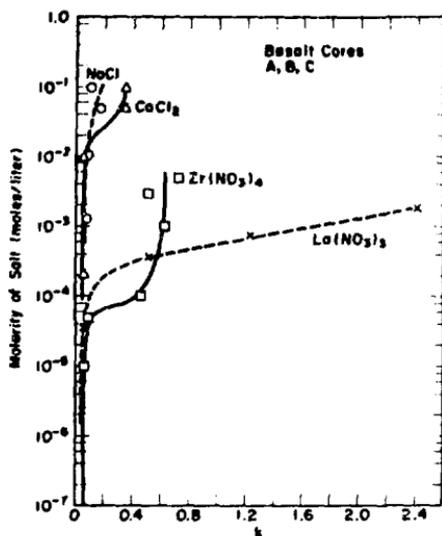
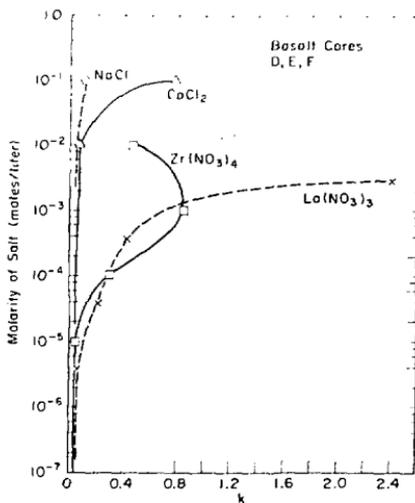


Figure 4-4. Surface adsorption coefficient of plutonium as a function of the concentration of other salts for dense basalt cores (Fried, et al., 1976a).

Figure 4-5. Surface adsorption coefficient of plutonium as a function of the concentration of other salts for porous basalt cores (Source: Fried, S., Friedman, A. M., and Weeber, R., 1976. The distribution of plutonium in a rock containment environment, in Campbell, M. H., ed., High-level radioactive waste management, Advances in Chemistry Series No. 153. Washington, D.C.: American Chemical Society.)



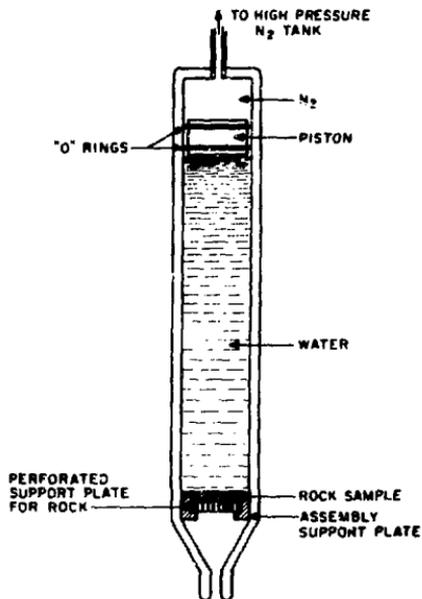


Figure 4-6. Schematic diagram of the high-pressure stainless-steel chromatographic column (Fried, et al., 1976a).

was then forced through the limestone disk in increments by means of a piston, which exerted pressure on the water isolating it from the pressurizing gas. The depth of penetration of the plutonium tracer was measured using an x-ray absorption technique. The results of these experiments yielded a migration coefficient M of $30 \pm 10 \mu\text{m}/\text{m}$ of water flow for the limestone and $61 \pm 8 \mu\text{m}/\text{m}$ of water flow for the basalts, where M = the average distance traveled by the plutonium atoms for every meter traveled by the water molecules.

Noshkin, et al. (1976) collected seven plutonium-contaminated soil samples from Eniwetok Atoll and equilibrated them separately with uncontaminated sea water. Water was filtered at intervals through

an 0.4- μ m filter and soil and water were analyzed for plutonium at equilibrium. The mean K_d value for these samples at equilibrium was 8×10^4 . Field results from particulates in the groundwater vs the groundwater itself gave an average K_d value of 2.5×10^5 (Table 4-11). The two laboratory and field values are quite close.

Bondietti, et al. (1976) determined plutonium distribution coefficients for Ca-saturated clays separated from Miami silt loam soil and for a reference montmorillonite. They used 5×10^{-3} M calcium solutions [Ca-acetate and $\text{Ca}(\text{NO}_3)_2$] at pH 6.5 and determined K_d values for two plutonium valence states. K_d values as a function of plutonium valence states are given by Table 4-12.

According to Bondietti, et al. (1976), the high sorption of Pu(VI) to the soil clay compared with montmorillonite indicates that plutonium reduction by clay components must have occurred, yielding sorption values similar to those for Pu(IV). Pu(VI) also appears to adsorb less than the tetravalent Pu.

Bondietti and Reynolds (1976) in later work studied the sorption of plutonium when Pu(IV) was added at about 0.6 ppm (Pu mass/clay mass) to treated clays separated from Miami silt loam soil using ^{238}Pu as the tracer. A solution of 5×10^{-3} M $\text{Ca}(\text{NO}_3)_2$ at pH 4.0 was used and K_d values were determined as a function of time and treatment of the clay fraction. The clay fraction was first equilibrated with organic matter present; then the clay was treated to remove organic matter and the resultant solution equilibrated again. Next, free iron oxide was also removed and the clay equilibrated. These procedures were repeated after equilibrating for 3 weeks, 18 weeks, and 52 weeks. The K_d values obtained for different treatments and equilibration times are given in Table 4-13. According to Bondietti and Reynolds (1976), the results shown in Table 4-13 suggest that sorption studies using Pu(IV) should be carefully examined because the soluble species that do not sorb may be in a different oxidation state than that initially added.

Glover, et al. (1976) using 17 selected soils of wide-ranging physical and chemical characteristics (Table 4-14), studied their equilibrium sorption and elution characteristics with plutonium and americium nitrates as the source of the actinides. Complete chemical and physical

Table 4-11. Concentrations of $^{239,240}\text{Pu}$: groundwater particulates in May 1974 (Noshkin, et al., 1976).

Island	Well	Depth (m)	Particulate (mg/l)	$^{239,240}\text{Pu}$ ($\% \sigma$) ^f		$\ln K_d$ (d)	Fraction in particulates ^e	K_d	
				(fCi/l) ^a	(fCi/mg)				
Janet	XEN2	Surface	10.4	21.0 (9) ^b					
				3.79 (14) ^c	2.38	13.85	0.92	1.04×10^6	
	XEN4	Surface	2.5	2.9 (30)	1.16	12.08	0.31	1.76×10^5	
	XEN1	Surface	15.0	47.0 (9) ^b					
				0.95 (13) ^c	3.20	13.19	0.87	5.35×10^5	
		7	7.8	6.0 (18) ^c					
				0.26 (33) ^b	0.80	13.33	0.82	6.15×10^5	
	AEN1	7	7.5	1.5 (16)	0.2				
				1.3 (50)	0.05				
	AEN3	Surface	10.8	5.1	1.3 (60)	0.25	11.23	0.28	7.54×10^4
				7	3.1	0.9 (40)	0.30	12.08	0.35
		10	13.8	2.1 (25)	0.15	11.66	0.62	1.16×10^5	
	AEN5	Surface	7	30.2	1.8 (90)	0.06			
				2.9	0.9 (70)	0.31			
AEN9	Surface	10.8	0.8	2.4 (23)	3.0	13.12	0.29	4.99×10^5	
AEN2	10	12.3	12.3	25.0 (7)	1.95	12.87	0.83	3.88×10^5	
Belle Elmer	ABM1	Surface	157	206 (2)	1.31	9.56	0.69	1.42×10^4	
				0.2 (40) ^b					
Elmer	APAL	Surface	4.4	0.14 (53)	0.08				
				10	19.6	0.4 (100) ^b			
				0.2 (30) ^c	0.03				

Mean $\ln K_d = 12.42 \pm 1.27$

Mean $K_d = 2.5 \times 10^5$

^a0.4- and 1- μm filters were processed together except where indicated

^b1.0- μm filter only

^c0.4- μm filter only

^dThe distribution coefficient is the dimensionless ratio of the quantity of Pu per gram of suspended material (dry weight) to that per gram of water: K_d is calculated by the equation:

$$\ln K_d = \ln \frac{(\text{fCi/mg particulate}) \times 10^6}{\text{fCi/l water}}$$

^eFraction of $^{239,240}\text{Pu}$ in total particulates > 0.4 m

^f($\% \sigma$) values in parentheses are 1 σ counting errors expressed as percentages of listed values.

Table 4-12. Effect of valence on plutonium distribution coefficient to Ca-saturated clays, pH 6.5^a (Bondietti, et al., 1976).

Material	Tracer	Initial actinide valence	% unabsorbed to clay	K _d (ml/g)
Clay separated from				
Miami silt loam soil	²³⁷ Pu	IV	0.40	10.4 x 10 ⁴
	²³⁸ Pu	IV	0.25	16.8 x 10 ⁴
	²³⁹ Pu	VI ^b	0.62	7.5 x 10 ⁴
Montmorillonite	²³⁹ Pu	IV	2.0	2.1 x 10 ⁴
	²³⁹ Pu	VI	63.0	2.5 x 10 ²

^aAqueous phase 5 mM in Ca²⁺.

^bCa-acetate; remaining studies conducted in Ca(NO₃)₂.

Table 4-13. Sorption of ²³⁸Pu(IV) to treated clays: pH 4.0, 5 x 10⁻³ M Ca(NO₃)₂ (after Bondietti and Reynolds, 1976).

Time and treatment	Percent sorbed	Evidence of Polymer or Pu(VI) ^a	K _d (ml/g)
3 weeks			
Clay	99.86	-	2.9 x 10 ⁵
-O.M. ^b	50.0	-	4 x 10 ²
-Fe + O.M.	99.8	-	2 x 10 ⁵
Blank ^c	71	-	-
18 weeks			
Clay	99.8	No	-
-O.M.	61.5	Yes	3.5 x 10 ²
-Fe + O.M.	99.9	No	-
Blank	71.7	Yes	-
52 weeks			
Clay	99.9	< 20% (VI)	1.9 x 10 ⁵
-O.M.	99.8	50% (VI)	6.1 x 10 ⁴
-Fe + O.M.	99.8	< 20% (VI)	8.1 x 10 ⁴
Blank	78.6	25% (VI)	-

^aBy thenoyltrifluoroacetone extraction, FeF₃ precipitation (holding oxidant method) and hexone extraction.

^bO.M. = organic matter.

^cNo clays present.

Table 4-14. Physical and chemical characteristics of soil (Glover, et al., 1976).

Source	Soil code	CEC (meq/100 g)	Soluble salts (mmhos/cm)	Soluble carbonate (meq/l)	Inorganic carbon (% CaCO ₃)	Organic matter (%)	pH	Sand (%)	Silt (%)	Clay (%)	Texture
Colorado A (Rocky Flats)	CO-A	20.0	3.6	5.97	0.4	2.4	5.7	44	20	36	Clay loam
Colorado B (Sugar Loaf)	CO-B	17.5	0.4	0.97	0.3	3.4	5.6	64	14	22	Sandy clay loam
Colorado C (Rocky Flats)	CO-C	29.6	0.4	1.98	2.4	0.7	7.9	5	31	64	Clay
Idaho A (ERDA)	ID-A	15.5	0.5	2.71	17.2	0.8	7.5	16	50	34	Silty clay loam
Idaho B	ID-B	13.8	0.8	2.51	7.9	0.2	8.3	44	24	32	Clay loam
Idaho C	ID-C	8.2	1.0	2.52	5.2	0.3	8.0	66	41	23	Sandy clay loam
Idaho D	ID-D	17.5	1.2	4.90	0.0	0.1	7.5	38	32	30	Clay loam
Washington A (Hanford)	WA-A	6.4	0.9	2.60	0.6	0.3	8.0	74	12	14	Sandy loam
Washington B	WA-B	5.8	0.4	2.30	0.0	0.1	8.2	74	12	14	Sandy loam
Tennessee (Oak Ridge)	TN	20.5	0.4	0.30	0.0	1.0	4.8	32	32	36	Sandy loam
South Carolina (Barnwell)	SC	2.9	0.4	0.50	0.2	0.7	5.4	78	2	20	Sandy loam-silty
New York (West Valley)	NY	16.0	1.2	1.40							Clay loam
New Mexico (Los Alamos)	NM	7.0	1.7	2.80	0.0	2.7	5.4	32	32	36	Clay loam
Arkansas A	AR-A	34.4	0.5	0.10	0.2	0.7	6.4	48	48	18	Loam
Arkansas B	AR-B	3.8	0.4	0.10	0.9	3.2	6.2	10	34	56	Silty clay
					0.7	0.6	4.8	82	9	9	Fine sand
Arkansas C	AR-C	16.2	0.3	0.10	0.6	2.3	2.3	9	54	37	Silty clay loam
Illinois	IL	17.4	0.5	0.10	0.7	3.6	3.6	31	53	16	Loam

analyses of all but four soils were done. Three standard plutonium solutions containing initial plutonium concentrations of 10^{-8} M, 10^{-7} M, and 10^{-6} M (or 9,600 dis/min/10 μ l, 103,000 dis/min/10 μ l, and 972,000 dis/min/10 μ l, respectively) were used for sorption measurements. A soil-to-solution ratio of 1 g to 5 ml was used and 10 μ l of the required concentration of the standard plutonium solution were added to this mixture. Depending on the experiment, from 5 to 48 hours were required for equilibrium sorption. The distribution coefficients for each of the 17 soils are given in Table 4-15. Tables 4-16 and 4-17 give the same K_d values obtained by Glover, et al. (1976) along with pH and Eh data of the system.

Results shown in Table 4-15 show a wide range of K_d (ml/g) values obtained from a low of 35 to a high of 14,000. This indicates the great sensitivity of K_d values to changes in plutonium concentration, especially at high levels of plutonium sorption.

In plutonium column elution studies by Glover, et al. (1976) with three different soils, 24 g of soil were added to a 1-cm-internal-diameter, 4-cm-long glass column. One gram of the same soil was mixed with 10 μ l of 10^{-3} M plutonium nitrate solution and then distributed evenly on top of the soil in the column. After packing, the column was washed with one liter of distilled water and the effluent collected and analyzed for plutonium. The K_d values for plutonium obtained by this elution study are given in Table 4-18.

Regression analyses are being performed to determine whether or not relationships exist between plutonium sorption and soil characteristics such as cation exchange capacity, particle size and distribution, and sand and clay content.

Neptunium

Very little work has been done on the distribution coefficient determination of neptunium in sediments and soils. Only two references indicate K_d value determinations for neptunium. A K_d value of 15 ml/g for neptunium between water and a typical western desert soil has been estimated by Schneider and Platt (1974). The soil characteristics

Table 4-15. Mean $K_d(m)$ values^a \pm statistical error (ml/g) for plutonium at equilibrium sorption (Glover, et al., 1976).

Soil code	Initial Pu concentration (M)		
	10 ⁻⁸	10 ⁻⁷	10 ⁻⁶
CO-A	2200 \pm 460	2700 \pm 170	1200 \pm 190
CO-B	200 \pm 24	130 \pm 6	40 \pm 3
CO-C	1900 \pm 110	1800 \pm 100	2000 \pm 3
ID-A	1700 \pm 70	4300 \pm 160	5000 \pm 290
ID-B	320 \pm 26	330 \pm 12	140 \pm 11
ID-C	690 \pm 110	4100 \pm 150	4000 \pm 23
ID-D	2100 \pm 640	1500 \pm 80	310 \pm 42
WA-A	100 \pm 7	100 \pm 3	35 \pm 1
WA-B	430 \pm 27	600 \pm 44	680 \pm 16
TN	2600 \pm 640	1200 \pm 100	14000 \pm 2700
SC	280 \pm 5	870 \pm 52	1000 \pm 20
NY	810 \pm 130	1100 \pm 45	870 \pm 57
NM	100 \pm 5	200 \pm 8	220 \pm 12
AR-A	710 \pm 36	660 \pm 33	760 \pm 45
AR-B	80 \pm 3	230 \pm 9	260 \pm 35
AR-C	430 \pm 23	570 \pm 44	870 \pm 30
IL	230 \pm 10	630 \pm 95	320 \pm 130

^aGlover, et al. (1976), use a different notation-- $K_d(m)$ rather than the conventional notation K_d --to imply that because of the complex chemistry of polyvalent radionuclides, the experimentally measured sorption coefficient may be related to a summation of a number of different mechanisms rather than any specific sorption mechanism.

Table 4-16. Sorption of plutonium in soils; distribution coefficients for soils in basic solutions (Polzer and Miner, 1976).

Soil	Initial Pu		pH	-Eh (V)	Pu _m /Pu _c (a)
	conc. (M)	K _d (m) (b)			
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
WA-B	10 ⁻⁸	430	7.8	0.46	0.0004
	10 ⁻⁷	590	7.8	0.46	0.2
	10 ⁻⁶	110	7.8	0.41	7.9
ID-D	10 ⁻⁸	2100 ^e	7.8	0.44	0.008
	10 ⁻⁷	1500	8.0	0.41	0.4
	10 ⁻⁶	310 ^c	7.9	0.41	5.0
ID-C	10 ⁻⁸	690 ^c	8.4	0.45	0.03
	10 ⁻⁷	4100	8.0	0.43	0.06
	10 ⁻⁶	4000	8.0	0.44	0.3
ID-A	10 ⁻⁸	1700	8.4	0.45	0.0005
	10 ⁻⁷	4300	8.0	0.44	0.03
	10 ⁻⁶	5000	7.8	0.45	0.2
ID-B	10 ⁻⁸	320	8.8	0.44	0.05
	10 ⁻⁷	300	8.9	0.41	1.6
	10 ⁻⁶	140	8.6	0.40	63
CO-C	10 ⁻⁸	1900	8.0	0.49	0.0001
	10 ⁻⁷	1800	7.8	-	-
	10 ⁻⁶	2000 ^c	8.2	0.44	1.0

^aRatio of Pu concentration measured in the water phase at sorption equilibrium (Pu_m) to the Pu concentration calculated to be present if the water were in equilibrium with Pu(OH)₄ (Pu_c). Pu_c is based on a solubility product for Pu(OH)₄ of 10^{-51.9} in basic solutions.

^{b-e}The standard error of the mean is: b, 8% or less; c, between 11% and 16%; d, between 20% and 25%; and e, 31%.

Table 4-17. Sorption of plutonium in soils; distribution coefficients for soils in acid solutions (Polzer and Miner, 1976).

Soil	Initial Pu		pH	Eh (V)	Pu _m /Pu _c (a)
	conc. (M)	K _d (m) (b)			
SC	10 ⁻⁸	280	5.5	0.48	20
	10 ⁻⁷	870	5.2	0.53	14
	10 ⁻⁶	1,000	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	1,000
TN	10 ⁻⁸	2,500 ^d	4.9	-	-
	10 ⁻⁷	1,200	4.0	-	-
	10 ⁻⁶	14,000 ^d	5.0	0.53	8
AR-B	10 ⁻⁸	80	5.6	0.58	1.0
	10 ⁻⁷	230	5.3	0.55	.0
	10 ⁻⁶	250 ^c	5.0	0.64	3.0
CO-A	10 ⁻⁸	2,220 ^d	6.5	0.49	2
	10 ⁻⁷	2,700	6.2	-	-
	10 ⁻⁶	1,200 ^c	6.8	0.43	1,000
CO-B	10 ⁻⁸	190 ^c	5.8	0.53	6
	10 ⁻⁷	130	5.8	0.53	60
	10 ⁻⁶	40	5.8	0.53	3,200
AR-C	10 ⁻⁸	430	5.9	0.40	100
	10 ⁻⁷	570	5.9	0.42	680
	10 ⁻⁶	870	6.0	0.57	13
IL	10 ⁻⁸	230	5.8	0.61	0.1
	10 ⁻⁷	630 ^c	5.4	0.65	0.06
	10 ⁻⁶	27	5.7	0.61	26

Table 4-17. Continued.

Soil	Initial Pu conc. (M)	K_d (m) (b)	pH	Eh (V)	Pu_m/Pu_c (a)
AR-A	10^{-8}	710	6.7	0.51	1.6
	10^{-7}	660	6.5	0.54	5.8
	10^{-6}	760	7.0	0.50	200
NY	10^{-8}	810 ^c	6.0	-	-
	10^{-7}	1100	6.0	0.54	6.0
	10^{-6}	870	6.1	0.49	600

^aRatio of Pu concentration measured in the water phase at sorption equilibrium (Pu_m) to the Pu concentration calculated to be present if the water phase were in equilibrium with $Pu(OH)_4$ (Pu_c). Pu_c is based on a solubility product for $Pu(OH)_4$ of $10^{-55.2}$ in acid solutions.

^{b-e}The standard error of the mean is: b, 8% or less; c, between 11% and 16%; d, between 20% and 25%; and e, 31%.

Table 4-18. Distribution coefficient values for plutonium as a function of soil as obtained by column elution method (Glover, et al., 1976).

Soil	K_d (m) (ml/g)
ID-B	144
CO-A	1180
ID-A	5020

are described in the earlier reference to Schneider and Platt in the section on plutonium, above. Routson, et al. (1975 and 1976), using batch tests, determined K_d values for neptunium and americium as a function of calcium (Ca^{2+}) and sodium (Na^+) ion concentration for eastern Washington and South Carolina subsoils. Batch tests were conducted with a soil-to-solution ratio of 1 g to 25 ml and influent solution pHs of 2.5 and 3.1. The system was equilibrated for 24 hours. The K_d values were found to decrease with increasing solution concentrations of Ca^{2+} and Na^+ . Properties of soil samples and the results of adsorption studies are given in Tables 4-19 and 4-20 respectively.

Americium

The distribution coefficients of americium have been measured by several investigators. Between water and a typical western desert soil a K_d value of 2000 ml/g for americium has been estimated by Schneider and Platt (1974).

In americium adsorption studies, Hajek and Knoll (1966) used acidic high-salt wastes (5.4 M NO_3^-) spiked with organics typical of a fuel reprocessing plant. K_d values obtained in batch tests are given in Table 4-4. When comparing K_d values for americium with K_d values for plutonium (Table 4-4), in most cases $K_d(\text{Am}) < K_d(\text{Pu})$. The K_d values for americium as a function of organic solution from a column study are given in Table 4-5.

Table 4-19. Soil sample properties (Routson, et al., 1975).

Soil	CaCO ₃ (mg/g)	Silt (%)	Clay (%)	CEC (meq/100g)	pH
Washington	0.8	10.1	0.5	4.9	7.0
South Carolina	<0.2	3.6	37.2	2.5	5.1

Table 4-20. Distribution coefficient values for neptunium and americium as a function of soil and solution Na and Ca ion concentration (Routson, et al., 1976).

Solution (M)	South Carolina		Washington
	K _d (Am) (ml/g)	K _d (Np) (ml/g)	K _d (Np) (ml/g)
Na			
3.00	1.0 ± 0.1 ^a	0.43 ± 0.16	3.19 ± 0.22
0.75	2.9 ± 0.2	0.45 ± 0.09	3.28 ± 0.33
0.30	6.3 ± 0.7	0.51 ± 0.09	3.28 ± 0.13
0.030	130 ± 2.0	0.57 ± 0.03	3.51 ± 0.19
0.015	280 ± 24.0	0.66 ± 0.08	3.90 ± 0.12
Ca			
0.20	1.0 ± 0.04	0.16 ± 0.06	0.36 ± 0.07
0.10	2.2 ± 0.2		0.62 ± 0.04
0.05	3.6 ± 0.6		0.78 ± 0.16
0.02	8.4 ± 1.0		0.93 ± 0.07
0.002	67 ± 5.0	0.25 ± 0.0	2.37 ± 0.04

^aStandard deviation.

Hamstra and Verkerk (1977) reported distribution coefficient measurements for Dutch subsoils using 90% saturated NaCl solution at pH 7 to 8. A soil-to-solution ratio of 1 g to 150 ml was used. Clay samples consisting of mainly illite and kaolinite had a K_d of 5×10^4 ml/g; river sand had a K_d of 400. Clay- and gypsum-bearing sandstones had intermediate K_d values (Tables 4-9 and 4-10).

Fried, et al. (1974, 1976a and 1976b) determined the sorption of americium onto a basalt. The value of the surface-absorption coefficient, K , for 10^{-7} M solutions of $\text{Am}(\text{NO}_3)_3$ was 0.041 ± 0.02 for basalts (see the earlier reference to Fried, et al. in the section on plutonium, above, for the definition of K and other details). The effect of other ions on the absorption constant was also studied. Addition of salts to the solution lowered americium adsorption. Higher valence cations (La^{3+} and Zr^{4+}) lowered the americium adsorption much more than lower valence cations (Na^+ and Sr^{2+}). See Figure 4-7.

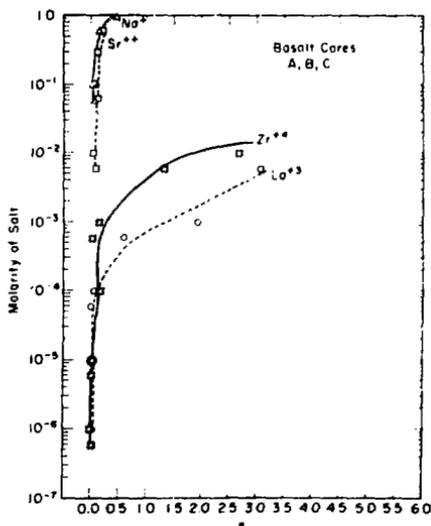


Figure 4-7. Surface absorption coefficient of americium as a function of the concentration of other salts for basalt cores (Fried, et al., 1976a).

Routson, et al. (1975, 1976) used batch sorption experiments to determine K_d values for South Carolina subsoil (sandy clay) as a function of calcium and sodium ion concentration. They used a soil-to-solution ratio of 1 g to 2.5 ml at an initial solution pH of 2.5 and 3.1 and equilibrated the system for 24 hours. The americium K_d values are given in Table 4-20. For Washington subsoil, americium K_d was found to be greater than 1200 ml/g for all concentrations of calcium.

Glover, et al. (1976) used basically the same procedure for americium sorption measurements as was used for plutonium experiments (see the earlier reference to Glover, et al. in the section on plutonium, above). Initial americium concentrations were 10^{-10} M and 10^{-8} M. From 24 to 48 hours were required for equilibrium sorption. The K_d values for americium are given in Tables 4-21, 4-22, and 4-23. Table 4-21 shows that K_d values for americium are very sensitive to changes in americium concentration, especially at high levels of americium sorption.

Curium

Only one reference in the literature indicated distribution coefficient values for curium. Schneider and Platt (1974) gave an estimated K_d value of 600 ml/g for curium between water and typical western desert soil. No details were given either about the experiment or about the method used.

Table 4-21. Mean distribution coefficient values \pm statistical error (ml/g) for americium at equilibrium sorption (Glover, et al., 1976).

Soil code	Initial Am concentration (M)	
	10^{-10}	10^{-8}
CO-A	2500 \pm 210	2600 \pm 110
CO-B	600 \pm 24	840 \pm 20
CO-C	5200 \pm 970	8100 \pm 400
ID-A	5900 \pm 230	510 \pm 8
ID-B	300 \pm 10	610 \pm 86
ID-C	820 \pm 43	1300 \pm 31
ID-D	10000 \pm 15000	8500 \pm 660
WA-A	120 \pm 7	200 \pm 14
WA-B	230 \pm 5	430 \pm 28
TN	2600 \pm 470	9700 \pm 1100
SC	82 \pm 1	190 \pm 9
NY	920 \pm 79	2300 \pm 330
NM	400 \pm 11	420 \pm 7
AR-A	2900 \pm 1800	3300 \pm 240
AR-B	390 \pm 20	760 \pm 72
AR-C	1800	2300 \pm 50
IL	1600 \pm 190	1900 \pm 22

Table 4-22. Sorption of americium in soils; distribution coefficients for soils in basic solutions (Polzer and Miner, 1976).

Soil	Initial Am concentration (\underline{M})	K_d (m)	pH	-Eh (V)
WA-A	$10^{-9.4}$	120	8.0	0.43
	$10^{-7.4}$	200	7.8	0.46
WA-B	$10^{-9.4}$	230	8.0	0.44
	$10^{-7.4}$	430	7.9	0.44
ID-D	$10^{-9.4}$	10,000 ^b	7.8	0.45
	$10^{-7.4}$	8500	7.9	0.44
ID-C	$10^{-9.4}$	820	8.4	0.47
	$10^{-7.4}$	1,300	8.2	0.47
ID-A	$10^{-9.4}$	6,200 ^d	8.1	0.44
	$10^{-7.4}$	514	8.4	0.42
ID-B	$10^{-9.4}$	300	8.7	0.43
	$10^{-7.4}$	610 ^b	8.5	0.42
CO-C	$10^{-9.4}$	5200	8.0	0.42
	$10^{-7.4}$	8100	8.0	0.44

^{a-d}The standard error of the mean is: a, 10% or less; b, between 12% and 20%; c, 32%; and d, 60%.

Table 4-23. Sorption of americium in soils; distribution coefficients for soils in acid solutions (Polzer and Miner, 1976).

Soil	Initial Am concentration (M)	K_d (m)	pH	-Eh (V)
SC	$10^{-9.4}$	82	6.1	0.54
	$10^{-7.4}$	190	5.9	0.55
NM	$10^{-9.4}$	400	6.9	0.49
	$10^{-7.4}$	420	7.3	0.48
TN	$10^{-9.4}$	2000 ^b	5.2	0.49
	$10^{-7.4}$	9700 ^b	5.1	0.49
AR-B	$10^{-9.4}$	390	6.6	0.57
	$10^{-7.4}$	760	6.5	0.56
CO-A	$10^{-9.4}$	2500	6.6	0.41
	$10^{-7.4}$	2600	6.4	0.43
CO-B	$10^{-9.4}$	600	6.4	0.52
	$10^{-7.4}$	840	6.4	0.43
AR-C	$10^{-9.4}$	1800	5.9	0.57
	$10^{-7.4}$	2300	6.0	0.60
IL	$10^{-9.4}$	1600 ^b	5.9	0.56
	$10^{-7.4}$	1900	5.8	0.56
AR-A	$10^{-9.4}$	820 ^c	6.6	0.57
	$10^{-7.4}$	3300	6.5	0.56
NY	$10^{-9.4}$	920	6.2	0.45
	$10^{-7.4}$	2300 ^b	6.0	0.50

a-d The standard error of the mean is: a, 10% or less; b, between 12% and 20%; c, 32%; and d, 60%.

SUMMARY AND RECOMMENDATIONS

Published literature concerning the sorption distribution coefficients of plutonium, neptunium, americium, and curium on soils and sediments was reviewed and the K_d data for the four radionuclides were compiled in tabular form. Very few studies for K_d determination have been conducted for neptunium and there is only one reference in the literature for curium K_d . The available sorption data show a wide variation in radionuclide K_d values.

The recommendations for future studies are as follows:

1. A detailed investigation should be done of the mechanisms (such as ion exchange, precipitation or formation of complex anions), involved in the uptake of the polyvalent radionuclides (such as plutonium and americium) by soil.
2. In future adsorption studies, multiple regression analysis techniques should be employed to determine the combination of soil properties (such as particle size distribution, soluble salt, silt, clay, organic carbon, CEC, or pH) that best account for the retention of radionuclides in soils.
3. Tests should be done under conditions that are close to those existing in the field, that is, with undisturbed samples. Most tests in the literature for K_d determination have been conducted either on artificially prepared soil samples or on field samples that were highly disturbed (exposed to the atmosphere and disaggregated).
4. Studies should be done to understand and identify the radionuclides species or element valence states [such as Pu(IV) or Pu(V)] that are adsorbed in the soil.
5. Studies are needed on the anion species that combine with polyvalent radionuclides to form complex anions and thus inhibit nuclide uptake by soil.

6. Because the ultimate secondary container in a repository for disposal of high-level radioactive waste will be some rock stratum, sorption data on rocks are required. Experiments should be conducted to determine the distribution coefficients on rocks.

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APPENDIX 4-1: SUMMARY TABULATION OF DISTRIBUTION COEFFICIENT

Table A. Review of the literature on radionuclide K_d s. Batch

Tracer element	Actinide valence	Equilibrium distribution coefficient K_d (mL/g)	Solution/waste composition and pH	Actinide concentration in solution before contacting with soil	Soil-to solution ratio (g/mL)	Shaking time
^{239}Pu	not specified	From 18 to ≥ 1980 (see Fig. 4-1 and Table 4-2)	Solution prepared using distilled water, pH adjusted by adding NaOH or HCl	0.01 $\mu\text{Ci/mL}$	1:20	Three hours
Pu	III, IV, VI	From 6.0 to $\geq 10,000$ (See Figure 4-2)	Solution prepared using distilled water, pH adjusted by adding NaOH or HNO_3	0.05 $\mu\text{Ci/mL}$	1:10	Two hours
^{239}Pu and ^{241}Am	not specified	For Pu, from 1.4 to 1540 for Am, from < 1.0 to 500 (see Table 4-3)	Synthetic waste prepared by mixing high salt, acidic aqueous phase (5.4 M NO_3^-) with organic compounds	Synthetic waste spiked with actual chemical processing waste containing Pu and Am.	not specified	not specified
Pu	IV	From 11 to 8.3×10^2 (see Table 4-6)	Solution prepared using distilled water, solution pH adjusted initially with NaOH to 7.0	Original spike of Pu^{4+} in 1 M HNO_3	1:250	not specified
Np, Pu, Am, Cm	not specified	K_d for Np = 15, K_d for Pu = 2000, K_d for Am = 2000, and K_d for Cm = 600	Typical non-alkaline groundwater pH = 6.8-8.2 (See p. 355 of this reference for groundwater composition.)	not specified	not specified	not specified
^{237}Pu	III, IV, VI	For oxic conditions, from 1.4×10^3 to 5×10^4 . For anoxic conditions, from 9.1×10^3 to 9.3×10^7 (see Table 4-7).	Sea water, pH = 7.8-8.0 for both oxic and anoxic conditions	Pu added to sea water in III, IV, and VI valence states	not specified	not specified
^{238}Pu	not specified	From 3.0 to 240 (see Table 4-8).	Simulated plant waste supernate (5.75 M Na^+ , 0.5 M AlO_2^- , 6.75 M OH^- , 2.2 M NO_3^- , 1.1 M NO_2^- , 0.3 M CO_3^{2-} , 0.3 M SO_4^{2-} , and 0.0002 M Cs^+).	Supernate contained 1.75×10^7 dis/(min)(mL) ^{238}Pu	1:10	Resin shaken overnight with synthetic supernate
$^{239-240}\text{Pu}$ and ^{241}Am	not specified	For Pu, from 200 to 10,000; for Am, from 400 to 50,000; (see Table 4-9 and 4-10).	90% saturated NaCl solution, pH = 7-8	not specified	1:150	not specified
^{238}Pu and ^{241}Am	IV for Pu, III for Am	Equilibrium surface absorption constant $K(\text{cm}^2/\text{mL})$. For 4×10^{-5} M solution of $\text{Pu}(\text{NO}_3)_4$ = 0.10 \pm 0.02 for limestone, 0.07 \pm 0.02 for basalt. For 10^{-7} M solution of $\text{Am}(\text{NO}_3)_3$ = 0.041 \pm 0.02 for basalt. (See Figures 4-3, 4-4, 4-5 for the effect on K of other ions.)	Tracer solutions prepared using aliquots of small solutions of the tracer and evaporating them to dryness with HNO_3 . Am and Pu isotopes: 200 solution with distilled water; original solution pH = 7.0, final pH ranged between 7 and 8.	Disks of limestone and basalt immersed in solutions of 4×10^{-5} M $\text{Pu}(\text{NO}_3)_4$ or 10^{-7} M $\text{Am}(\text{NO}_3)_3$	not specified	Alpha or gamma counting rate of aliquots counted at 12-hr. intervals until equilibrium.

DATA FOR PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM

equilibrium test data for plutonium, neptunium, americium, and curium.

Initial soil pH	Soil cation exchange capacity (meq/100g)	Soil/material type and content	Particle size and distribution	Observations/comments	Reference
8.6	5.0	Subsurface soil from Hanford Project. Unconsolidated, unweathered sediments having silt, clay, and $\approx 2\%$ free CaCO_3 . (Clay fraction contains montmorillonite and kaolinite in the ratio of 3:1.	As percent by weight > 2 mm diam, 6% 2 to 0.2 mm, 67% 0.2 to 0.02 mm, 19% 0.02 to 0.002 mm, 6% < 0.002 mm, 2%	K_d values in Table 4-2 suggest existence of a Pu polymer in solution at pH > 2 with the exception of pH range 8.5 to 12.5. Apparently the polymer formed carries a positive charge that enables it to be taken up rapidly by the soil.	Rhodes 1952, 1957a, 1957b
not specified	Ranged from 0.012 for soil pH 4 to 1.24 for soil pH 10 (see Table 4-3).	Soil samples from water table at Savannah River Plant contained 20% clay and 80% sand. Dominant clay mineral - kaolinite.	not specified	Absorption was more than 90% complete from solutions of Pu(III) and Pu(IV) between pH 2.5 and 12 and from solutions of Pu(VI) at pH > 6 .	Prout 1958, 1959
not specified	not specified	Sc^{3+} from various depths between the surface and groundwater from wells at 7.1A tile field site, Richland, Wash., air-dried and sieved to < 2 mm diameter.	not specified	Absorption from strongly acid or partially neutralized waste was minor. Adsorption from alkaline waste from precipitation was high. Introduction of a slug of organics reduced the K_d of both Pu and Am.	Hjck and Soil, 1966
not specified	not specified	Study conducted with different minerals (see Table 4-6).	not specified	The amount of radionuclide removed (adsorbed) from the solution appears to depend on the pH of the suspension; the higher pH favors greater removal by formation of nuclide hydroxides which are scavenged by the clays (see Table 4-6).	Tamura, 1972
7.0 to 8.2	5.0	Typical western desert soil - sand or sandy loam containing ≈ 1 mg of free CaCO_3 per gram of soil.	not specified		Schneider and Platt, 1974
not specified	not specified	Study conducted on marine sediments from Mediterranean Sea using sedimentation (water column) and thin layer methods.	not specified	K_d values for both oxoic and anoxic conditions appear similar for all three valence states.	Dourson and Paris, 1974
not specified	not specified	Synthetic ion exchange resins (see Table 4-8).	not specified	Out of the five resins tested, sorption of Pu was maximum by "DuoLite" ARC-359.	E. J. DuPont de Nemours & Co., 1975
not specified	not specified	Various soil materials (clay, sandstone, ciprock and coarse river sand) from boreholes surrounding salt formations in NE Netherlands.	not specified	K_d values for ciprock and river sand were lower than clay containing material due to the absence of clay material in them.	Hamstra and Verkerk, 1977
not specified	not specified	Thin wafers or disks (25 mm diam. and 1.5 mm thick) of dense Illinois Niagra limestone and basalt from EBR-II site (Idaho National Engineering Laboratory).	not specified	The surface absorption coefficients are affected by the types and concentrations of other salts. For example, all curves for both Pu and Am in Figures 4-3, 4-4 and 4-5 show the same trend, i.e., displacement of the actinide ions from the rock lattice by higher concentrations of other metallic ions.	Fried, et al., 1974, 1976a, 1976b

Table A. Review of the literature on radionuclide K_d s. Batch equilibrium test

Tracer element	Actinide valence	Equilibrium distribution coefficient K_d (mL/g)	Solution/waste composition and pH	Actinide concentration in solution before contacting with soil	Soil to solution ratio (g/ml)	Shaking time
$^{239,240}\text{Pu}$	not specified	Mean K_d for seven samples = 8×10^3 Mean K_d for field peat/soils in the groundwater = 2.5×10^5 (see Table 4-11)	Pu contaminated soil samples equilibrated in the laboratory with uncontaminated sea water	not specified	not specified	not specified
$^{237,238,239}\text{Pu}$	IV, VI	For soil clay fraction, $K_d = 7.5 \times 10^3$ to 16.8×10^3 , for reference montmorillonite $K_d = 2.5 \times 10^2$ to 2.1×10^3 (see Table 4-12)	Studies conducted in Ca acetate and Ca nitrate solutions	not specified	Varied, not specified	not specified
^{238}Pu	IV	From 3.5×10^2 to 2.9×10^5 (see Table 4-13)	Study conducted in 5×10^{-5} M $\text{Ca}(\text{NO}_3)_2$ solution	238Pu dissolved at about 0.6 ppm (Pu mass/clay mass)	not specified	Equilibration time 4 weeks to 52 weeks
Pu and Am	IV for Pu, III for Am	For Pu, from 35 to 14,000 (see Tables 4-15, 4-16 and 4-17) For Am, from 82 to 10,000 (see Tables 4-21, 4-22 and 4-23)	Solutions prepared by diluting up to 5 (1N) standard solutions of plutonium and americium, respectively. Solutions were kept acidic to prevent hydrolysis and polymerization of plutonium	Initial Pu concentrations of 10^{-8} M, 10^{-7} M and 10^{-6} M, respectively Initial Am concentrations of 10^{-10} M and 10^{-8} M	1-5	Equilibration time 5 to 48 hours for Pu, 24 to 48 hours for Am
^{241}Am and ^{241}Pu	not specified	$K_d = 0.16$ to 3.9 for Pu , 1.0 to 280 for Am (see Table 4-20)	Study conducted in varying concentrations of $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 solutions. Initial solution pH = 2-4 for F. Washington, 14 for S. Carolina	Influent activity 3.7 $\mu\text{Ci}/25\text{ ml}$ for F. Washington, 1.0 $\mu\text{Ci}/25\text{ ml}$ for S. Carolina	1-2.5	20-30 minutes equilibration time + 21 to 24 hrs

Table B. Review of the literature on radionuclide K_d s. Column test

Tracer element	Equilibrium distribution coefficient K_d (ml/g)	Soil material type and content	Soil cation exchange capacity (meq/100g)	Solution waste composition and pH
^{239}Pu and ^{241}Am	See p. 2 of this reference for breakthrough curves	Surface soil (≈ 20) from well at 7.1A tile field site, Richland, Wash., sieved to < 2 mm diameter	not specified	Synthetic waste prepared by mixing mg/ligh salt acidic aqueous phase (5.3 M NaCl) with organic compounds (See p. 2 of this reference for waste composition.)
^{239}Pu and ^{241}Am	For TBP/CCl ₄ ^a $K_d = 5.4$ for Pu and 1.6 for Am For DBBP/CCl ₄ $K_d = 0$ for Pu and 0.6 for Am For D2EHPA/TBP $K_d = 0$ for both Pu and Am (see Table 4.5)	Soil from the bottom of 2- excavation for 241 AX tank farm, Hanford, sieved to < 2 mm diameter	not specified	Various organic wastes from Hanford Radiochemical Separations plant (TBP/CCl ₄ , DBBP/CCl ₄ , Fab Oil, 0.4 M D2EHPA, 0.5 M TBP in NPH)
Pu	With dry soils $K_d = 0000$ for short column $= 3000$ for long column With moist soils $K_d = 0.4$ for solvent > 10 for aqueous phase instead of solvent	Dry (ground surface) and moist (subsurface) soils from Savannah River plant waste burial ground.	not specified	Separations process (radioactive) solvent from underground tanks (See p. 53 of this reference for chemical composition.)
Pu	From 144 to 5020 (See Table 4.18)	Three soil samples from various present and probable future Pu-handling areas in the U.S. (see Table 4-14)	Ranged from 8.14 to 20 (see Table 4-14)	Column elution study done using Pu nitrate solution

^aTBP = tributylphosphate

DBBP = dibutylbutylphosphonate

D2EHPA = di(2-ethylhexyl)phosphoric acid

Fab Oil = "fabrication oil," a commercial mixture of Lard oil and CCl₄ (25-75 vol. %).

NPH = "normal paraffin hydrocarbons," a commercial mixture of straight chain hydrocarbons including decane, undecane, dodecane, tridecane, and tetradecane.

data for plutonium, neptunium, americium, and curium

Actinide concentration in solution	Column length and inner diameter (cm)	Column volumes needed for 50% breakthrough	Permeability flow rate	Observations/comments	Reference
Synthetic waste spiked with actual chemical processing waste containing Pu and Am	10.0, 1.9	Between 1.5 and 4.0 for ^{239}Pu ; < 1.0 for ^{241}Am	not specified	Uptake of Pu by the soil was very minimal and is Am negligible	Kneil, 1963
Organic wastes from Hanford separation plant spiked with ^{239}Pu and ^{241}Am	Length = 3.0 and 10.0 respectively; ID = 0.8	For DBP CO_2 3.5 for Pu and 9.0 for Am For DBBP CO_2 3.5 for Am and no adsorption of Pu by soil For 0.4 M D21 HPA 0.2 M DBP or SDF No adsorption of Pu or Am by soil in this organic	See pp. 5.6 of this reference for permeability to organic wastes	Soil removed ^{239}Pu and ^{241}Am studied in terms of the organic and soil in this column	Kneil, 1963
Migration studies simulated potential leaks into the ground using solvent complexed Pu from tanks	Length = 6.6 and 14.7 respectively	not specified	not specified	Tests showed that small volumes of solvent complexed Pu did not migrate significantly through the soil. Large volumes in these subsurface soil would be more effective	U. S. Dept. of Energy, <i>Soil Zones</i> & Co., 1975
Column packed with 24 g of soil, 1 g of which was mixed with 10^{-2} g of 10^{-5} M Pu nitrate solution and distributed evenly throughout the column	4.0, 1.0	Column washed with 1.3 distilled water and effluent collected in 20 ml fractions and analyzed for Pu	Flow rates = 15 mm/90 min and 180 mm per 20 ml respectively	Soil with the lowest K_d retained the least amount of Pu while the soil with the highest K_d retained the most	Clover, et al. 1976

APPENDIX 4-2: GLOSSARY

adsorption	The observed decrease in the initial solution concentration of a nuclide in which the most probable mechanism is identified as a coulombic attraction of the nuclide to the surface of the adsorption solid (Bensen, 1960).
alpha	Used with respect to radiation--a positively charged particle consisting of two protons and two neutrons (ASME, 1957).
basalt	Dark grey to black, dense, fine-grained, igneous rock consisting of plagioclase, augite, and magnetite (G. & C. Merriam Co., 1965).
beta	Used with respect to radiation--a negatively charged particle emitted from the nucleus of an atom and having a mass and charge equal in magnitude to those of an electron (ASME, 1957).
breakthrough	The first detectable concentration of a nuclide in a column effluent (Bensen, 1960).
C/C ₀	The amount of a nuclide in the effluent of a soil column divided by the amount of that nuclide added in the influent (Bensen, 1960).
cation exchange capacity	The concentration of an exchangeable cation adsorbed by a soil at pH 7 determined by a standard method (Bensen, 1960).
count	A radiation measurement or indication of a device designed to enumerate disintegrations or events. It may refer to a single detected event or a total registered in a given period of time. It should not be confused with disintegration, as the two terms do not mean the same. The relationship between count and disintegration must be established by a calibration procedure (ASME, 1957).

curie	A measure of radioactivity meaning the quantity of a nuclide disintegrating at the rate of 3.7×10^{10} atoms per second; abbreviated as Ci; a microcurie (μCi) is one millionth of a curie (3.7×10^4 disintegrations per second); a picocurie (pCi) is one millionth of a microcurie (ASME, 1957).
gamma	Relates to radioactivity and means a ray of short wavelength which is emitted from a disintegrating nucleus (ASME, 1957).
half-life	Refers to the time that a substance is radioactive-- the time required for a radioactive element to lose 50% of its activity. Each nuclide has a unique half-life (ASME, 1957).
Hanford soil	Representative soil of the Hanford Works, Richland, Washington (Bensen, 1960).
high-level liquid wastes	Liquid wastes containing greater than 100 $\mu\text{Ci/ml}$ of mixed radioactivity (Beard and Godfrey, 1967).
intermediate-level liquid wastes	Liquid wastes containing between 5×10^{-5} and 100 $\mu\text{Ci/ml}$ of mixed radioactivity (Beard and Godfrey, 1967).
ion exchange	The equivalent replacement of an adsorbed ion on a solid adsorbent by another ion from the solution (Bensen, 1960).
isotope	One of several forms of one element having the same number of protons in the nucleus and thus the same atomic number, but having a different number of neutrons and thus a different mass number; e.g., strontium-89, strontium-90 and strontium-91 all with atomic number 38 (ASME, 1957).

- K_d A term representing the equilibrium distribution coefficient of a nuclide, A, between the solid adsorbent and the solution at equilibrium:
- $$K_d = \frac{A_{\text{solid}}}{A_{\text{soln.}}} \times \frac{CC_{\text{soln.}}}{g_{\text{solid}}}$$
- where: A_{solid} is the amount of A that is associated with the adsorbent; $A_{\text{soln.}}$ is the amount of A that remains in the solution; $CC_{\text{soln.}}$ is the total volume of solution in cc; and g_{solid} is the total weight of adsorbent in g (Bensen, 1960).
- leach To subject to the action of percolating water or other liquid in order to separate and remove soluble compounds (G. & C. Merriam Co., 1965).
- leachate The percolating solution (Schmalz, 1972).
- loam A soil consisting of a friable mixture of varying proportions of clay, silt, and sand (G. & C. Merriam Co., 1965).
- loessial A buff to yellowish brown loamy deposit (soil) believed to have been deposited by wind (G. & C. Merriam Co., 1965).
- low-level liquid wastes Liquid waste containing less than 5×10^{-5} μ Ci/ml of mixed radioactivity (Beard and Godfrey, 1967).
- nuclide A species of atom characterized both by number of protons and neutrons; e.g., strontium-90, atomic number 38 and cesium-137, atomic number 55 (ASME, 1957).
- percolate To pass through a permeable substance, to penetrate (G. & C. Merriam & Co., 1965).
- surface absorption coefficient Represented as K and defined as the ratio of radioactivity in a milliliter of solution to the radioactivity absorbed per square centimeter of rock:
- $$K = \frac{\text{(activity of actinide/ml of solution)}}{\text{(activity of actinide/cm}^2 \text{ of rock)}}$$
- (Freid, et al., 1976a).

- uptake** The observed decrease from the initial concentration of a solution contacting soil, regardless of the mechanism of removal such as adsorption, precipitation, etc. (Bensen, 1960).
- vadose** Of, or relating to, or being in the earth crust above the permanent ground water level (Schmalz, 1972).
- water table** The upper limit of the portion of the ground wholly saturated with water--a plain or surface (G. & C. Merriam Co., 1965). The natural water table is different from a perched water table, which is usually caused by the activity of man such as waste disposal or irrigation, etc. Perched water, whether caused by man or other natural causes, is localized in extent at a higher elevation than the natural or regional water table (Schmalz, 1972).

SECTION 5: PRELIMINARY CONSIDERATIONS IN DETERMINING AN EXPERIMENTAL
METHOD TO MEASURE RADIONUCLIDE TRANSPORT IN WATER-SATURATED ROCKS

INTRODUCTION

One of the most pressing problems in this task was choosing an experimental configuration to measure radionuclide transport in rocks. At first, it seemed reasonable to treat a rock rather like a chromatographic column in which the migration of radionuclides might be examined as a function of time. Water could be forced through a given thickness of rock, and the degree of retardation of the radionuclide measured. In order to test this approach, information on rock physical properties was gathered as a first step. The data obtained were then used to compute the differential pressures needed to force specified volumes of water through a cylindrical rock core of given diameter in an experimentally reasonable length of time.

The calculations showed that for practically all rock types, the pressures required were experimentally unreasonable. In fact, it became obvious that for most host rocks, flow along fractures could be the only means by which radionuclides might migrate significant distances. The experiment should therefore be designed to study radionuclide migration principally along fractures, with diffusion into the rock on either side.

The following subsections contain a brief description of the results obtained from a literature study of the physical properties of rocks and give the calculations used to determine the experimental feasibility of forcing water through solid rock cores.

ROCK PHYSICAL PROPERTIES

The rate of transport of a radionuclide through a porous medium depends on the physical and chemical properties of the medium in question. This section reviews the physical properties of selected rocks that may be candidates for radioactive waste storage repositories.

The ranges of values of these physical properties are presented in Table 5-1. The most abundant data were found on rocks that bear some economic interest, such as oil sands. On such rocks, ample data afford crude statistics of the reproducibility and credibility of the data range. For rocks of low economic association, such as rhyolites, no direct data were found on such physical properties as porosity and

Table 5-1. Rock physical properties.

Rock type	Dry density (g/cm ³)	Water saturated density (g/cm ³)	Water content (%)	Grain size (mm)	Porosity (%)	Permeability (cm ²)	References
Argillite	2.70-2.94			<0.0625	2.69-10	5.68×10^{-12}	Kemp, 1970; Jackson, 1970; Reich, 1973; Schoeller, 1962
Basalt	2.76-2.95	2.763-3.03 ^a	1-2.7	<0.1	0.1-11.4	3.35×10^{-20} ^b -1.33×10^{-13}	Kemp, 1970; Fried, et al., 1974; Hyndman and Drury, 1976; Schoeller, 1962; Duncan, 1969; Griffith, 1937; Davis, 1969
Gabbro	2.55-3.12	2.56-3.15 ^a	0.37-1.0	>0.5	0.29-3.0	$<9.87 \times 10^{-11}$	Jackson, 1970; Duncan, 1969; Vinayaka, 1965; Hyndman and Drury, 1976; Kemp, 1970; Griffith, 1937; Davis, 1969
Granite	2.52-2.81	2.52 ^a -2.81	0.0 ^a	0.7-1.3	7-1.3	4.6×10^{-14} -5×10^{-16}	Jackson, 1970; Kemp, 1970; Vinayaka, 1965; Duncan, 1969; Griffith, 1937; Brace, 1968
Limestone	2.21-2.76	2.39-2.77	0.36-7.5 ^a	0.0625	1.0-37.6	3.36×10^{-9} -9.86×10^{-12}	Jackson, 1970; Schoeller, 1962; Locke and Bliss, 1950; Murray, 1960; Davis, 1969
Rhyolite	2.32-2.62			<0.05	4-15.5		Jackson, 1970; Kemp, 1970; Schoeller, 1962
Sandstone	1.93-2.50	2.2-2.55	2.0-14 ^a	0.0625	5.4-27.1	5×10^{-12} 3×10^{-8}	Jackson, 1970; Vinayaka, 1965; Scheidegger, 1960; Davis, 1969

^a Calculated in this report from saturated densities.

^b Calculated in this report from hydraulic conductivity values (in Atlantic Richfield Hanford Co., 1976).

permeability. Permeability values for basalt were calculated from hydraulic conductivity formulas (Davis, 1969) employing statistically averaged literature values of density and viscosity. Hydraulic conductivity data were taken from Atlantic-Richfield Hanford Co. (1976).

DIFFERENTIAL PRESSURE REQUIREMENTS FOR FORCING WATER THROUGH ROCK CORES

Experiments on K_d values and migration rates of ions in geologic formations can be done by at least two methods: (a) forcing a given volume of solution through a column of rock; or (b) allowing solution to adsorb on the surfaces of rock specimens. An intercorrelation of the migration coefficients and surface-adsorption coefficients to the migration through porous rock has been demonstrated by Fried, et al. (1974). The purpose of this section is to determine the differential pressure needed to force a given volume of solution through a column of rock. These calculations should provide valuable insight on how to design experiments to measure migration rates and K_d values.

In order to make the necessary calculations, a conceptual model of a rock was specified. This model assumes that the rock grains are uniform packed spheres, that the radionuclide is adsorbed as a monolayer on the exposed surfaces of the rock mineral grains, and that one atom is adsorbed for each 25\AA^2 of surface area. Implicit in the last assumption is an infinitely large K_d . In other words, all of a radionuclide is quantitatively removed from solution, as long as there are available sites upon which the radionuclide might adhere. This represents a limiting case, which is useful in determining experimental constraints.

By using the data on grain size given in Table 5-1 and the assumptions given above, it is easy to calculate the volume of fluid needed to saturate the internal surface of a cubic volume of rock. Thus:

$$\text{volume of liquid needed to saturate} = \frac{\pi d^3 N m}{2a}$$

where d = length of one side of a cube,

a = radius of a mineral grain,

N = Avogadro's number, and

m = molality of the radionuclide.

The time needed to saturate a given internal volume of rock depends on the permeability, thickness, and exposed surface of the rock, the properties of the fluid, and the pressure applied to the fluid to force it through the rock. In order to calculate the pressure required to saturate the rock in an experimentally reasonable length of time, an expression relating these parameters must be derived.

If v_x is the velocity of the fluid (measured as fluid flux across a unit area of porous medium) in the direction x , and dP/dx is the pressure gradient at the point to which v_x refers, then Darcy's law may be expressed as:

$$v_x = (k/\mu) \frac{dP}{dx} \quad (1)$$

where k is the permeability of the medium and μ is the viscosity of the fluid. In addition, if A is the cross-sectional area of the column and Q is the volume of liquid passing through it per unit time, then

$$v_x = Q/A \quad (2)$$

Furthermore, by combining and rearranging equations (1) and (2), one gets:

$$k dP = (\mu Q/A) dx \quad (3)$$

Consider a slab of material of thickness, L , with liquid being forced through and with P_1 and P_2 as the terminal pressures. Equation (3) can be integrated over the slab thus:

$$k \int_{P_2}^{P_1} dP = \left(\frac{\mu Q}{A} \right) \int_0^L dx \quad (4)$$

$$k(P_1 - P_2) = \frac{\mu Q L}{A} \quad (5)$$

$$P_1 = \frac{\mu Q L}{A k} + P_2 \quad (6)$$

Using average values of permeability for six rock types (argillite, basalt, gabbro, granite, limestone, and sandstone), the pressure differential was calculated across 2.54-cm-diameter cores 1-cm long. It was assumed

Table 5-2. Pressure differentials required across rock cores to ensure experimentally reasonable aqueous solution flow rates.

Rock type	1 day		5 days		10 days		20 days	
	Concentration		Concentration		Concentration		Concentration	
	10^{-9} M	10^{-6} M	10^{-9} M	10^{-6} M	10^{-9} M	10^{-6} M	10^{-9} M	10^{-6} M
Argillite								
Volume to saturate (l)	3.34×10^2	3.34×10^{-1}						
Pressure (atm)	3.31×10^4	3.41	6.62×10^3	7.62	3.31×10^3	4.31	1.66×10^3	2.66
Basalt								
Volume to saturate (l)	2.09×10^2	2.09×10^{-1}						
Pressure (atm)	3.51×10^{12}	3.51×10^{-9}	7.02×10^{11}	7.02×10^8	3.51×10^{11}	3.51×10^8	1.76×10^{11}	1.76×10^8
	to	to	to	to	to	to	to	to
	8.84×10^5	8.84×10^2	1.78×10^5	1.78×10^2	8.84×10^4	8.84×10^1	4.42×10^4	4.42×10^1
Gabbro								
Volume to saturate (l)	4.17×10^1	4.17×10^{-2}						
Pressure (atm)	2.38×10^3	3.38	4.77×10^2	1.48	2.39×10^2	1.24	1.20×10^2	1.12
Granite								
Volume to saturate (l)	1.60×10^1	1.60×10^{-2}						
Pressure (atm)	1.81×10^7	1.81×10^4	3.62×10^6	3.62×10^3	1.81×10^6	1.81×10^3	9.04×10^5	9.04×10^2
	to	to	to	to	to	to	to	to
	1.96×10^5	1.96×10^2	3.90×10^1	1.96×10^1	1.96×10^{-4}	1.96×10^1	9.83×10^3	9.83
Limestone								
Volume to saturate (l)	1.04×10^1	1.04×10^{-2}						
Pressure (atm)	5.97×10^2	1.50	1.20×10^2	1.12	6.0×10^1	1.06	2.1×10^1	1.03
	to	to	to	to	to	to	to	to
	1.8	1.02	4.50	1.00	2.80	1.00	1.9	1.00
Sandstone								
Volume to saturate (l)	1.04×10^2	1.04×10^{-1}						
Pressure (atm)	1.18×10^3	2.18	2.36×10^2	1.24	1.19×10^2	1.12	6.0×10^1	1.06

that the water required to saturate the core could be forced through in 1, 5, 10, or 20 days. The initial concentration of the radionuclide was assumed to be 10^{-9} and 10^{-6} M/l. Table 5-2 shows the resulting pressure differentials for the different cases being considered.

Pressures were relatively high for rocks with low permeability, leading to the conclusion that any significant flow in those rocks must be along fissures. Measurement of K_d values would have to be made by a surface adsorption method because, if the rocks were homogeneous and free of incipient fractures, solid core studies would require relatively high pressures to force solutions through the rocks.

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**SECTION 6: REVIEW OF TRANSPORT MECHANISMS OF RADIONUCLIDES
IN WATER-SATURATED ROCKS**

INTRODUCTION

Transport of radionuclides in water-saturated rock involves both physical and chemical processes. The physical nature of the system determines the rate of fluid flow, while chemical processes lead to exchange of mass between the fluid and the solid phases. A variety of chemical processes can occur, including dissolution, precipitation, ion exchange, sorption, and ultrafiltration. Physical processes can be grouped into two principal categories of transport--advection and diffusion. Diffusion occurs in solids, along surfaces, and in the aqueous phase. Solid-state diffusion is an extremely slow process and may be ignored in all but exceptional situations in natural systems having temperatures less than 100°C. Diffusion in the aqueous phase (or longitudinal diffusion, which is taken to mean three-dimensional diffusional processes) is not a rapid process compared with the speed of certain chemical reactions, such as hydrolysis reactions. However, diffusion in the aqueous phase may proceed at a rate comparable with the rate of advection in many natural systems. The nature of the porous media also leads to a process known as dispersion or eddy-diffusion. As the mobile phase flows around obstacles in its path it encounters regions where flow is hindered and those where flow is relatively unimpeded. Because the fluid avoids obstacles along the path of least resistance, the velocity fluctuates over wide limits. Thus velocity varies from channel to channel because of the viscous constraint of the containing walls. The phenomenon of eddy-diffusion is caused by such point-to-point variations in flow velocity. A molecule in a fast streampath will take a step forward to the center of mass (zone), while a molecule in a slow streampath will take a step backwards relative to the center of mass. As a molecule follows its original streampath, it is carried into a part of the channel network that has a velocity differing from the velocity of the original streampath. Lateral diffusion will also cause a molecule to enter a new velocity regime. As a result of these processes, zone spreading occurs and the chemical front "flattens."

CHEMICAL RETARDATION AND THE DISTRIBUTION COEFFICIENT

In the absence of competitive processes, the center of mass of a solute zone would move at about the same rate as the mobile aqueous phase. However, various physico-chemical processes, such as sorption, tend to retard the passage of solute. Giddings (1965) has generalized the dynamics of zone migration. A zone migrates smoothly at some fraction R of the mobile phase velocity. Thus the zone velocity is Rv , where v is the average velocity of the mobile phase. If R is the fraction of solute in the mobile phase, then $1 - R$ is the fraction in the stationary phase or the amount adsorbed. The term $R/(1-R)$ is thus the ratio of the solute in the mobile phase to solute in the stationary phase, and

$$\frac{R}{1 - R} = \frac{C_m V_m}{C_s V_s} \quad (1)$$

where C_m is the concentration in the mobile phase, V_m is the volume of the mobile phase, C_s is the concentration of the stationary phase, and V_s is the volume of the stationary phase.

The distribution coefficient, K_d , is defined as

$$K_d = \frac{C_s}{C_m} \quad (2)$$

Therefore, equation (1) reduces to

$$\frac{R}{1 - R} = \frac{V_m}{V_s K_d} \quad (3)$$

Because the velocity of the solute is given by

$$v_i = vR \quad (4)$$

the relative velocity of the solute species i with respect to the mobile phase yields the classical expression of Martin and Synge,

$$R = \frac{v_i}{v} = \frac{V_m}{V_m + K_d V_s} \quad (5)$$

which reveals the relation between retardation and the distribution coefficient.

QUANTITATIVE TREATMENT

Measurements of distribution coefficients have been done principally by two methods, batch experiments and column experiments. The theoretical treatment of column processes can be roughly divided into two groups, rate theories and equilibrium theories (Helfferich, 1962).

In rate theories, calculations are based on continuous flow through the column and finite rates of ion exchange or adsorption. These theories are predictive but are also mathematically complex. Therefore, rate laws and assumptions about equilibrium are often simplified. Such theories (for example, Giddings, 1965, pages 119-193) fail to bring out the self-sharpening effects of favorable equilibrium.

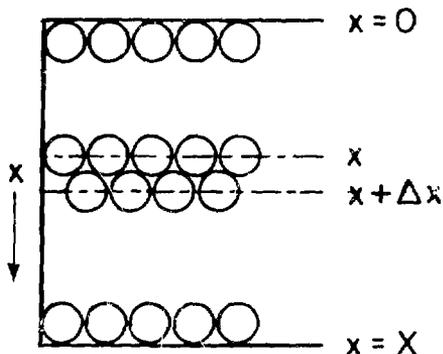
In equilibrium theories, local equilibrium between the liquid and bed is assumed. In practice this assumption is usually not valid and deviations from local equilibrium are accounted for by introducing the concept of "effective plates." In this concept, continuous column processes are approximated by fictitious discontinuous processes. Unfortunately, this formulation is semiempirical in nature and is not predictive.

Rate Theories

One of the most general approaches to column processes can be found in the material balance treatment of Glueckauf (1949). The natural balance for an infinitesimal layer for an arbitrary species i (see Fig. 6-1) is:

$$\left(q \frac{\partial X_i}{\partial V} \right)_z + \left(\frac{\partial C_i}{\partial z} \right)_v - \frac{\Delta z}{2} \left(\frac{\partial^2 C_i}{\partial z^2} \right)_v - \frac{D_B}{v\sqrt{2}} \left(\frac{\partial^2 C_i}{\partial z^2} \right)_v = 0 \quad (6)$$

where q is the column cross section; X_i is the amount of species i in sorbent and solution per unit volume of bed; C_i is the concentration of species i in the interstitial solution; V is the solution volume, which has passed the layer since the experiment was initiated; z is the space coordinate downstream; D is the effective diffusion coefficient; β is the fractional void volume; and v is the linear flow rate.



XBL783-400

Figure 6-1. Schematic representation of a packed bed. The material balance is set up for the "plate" between x and $x + \Delta x$ (from Helfferich, 1962).

The material balance is quite general since no assumptions about local equilibrium and ion exchange or sorption isotherms have been made. Local equilibrium is a limiting case in which X_i is a function of C_i only; this function is given by the isotherm. For nonequilibrium conditions, the functional relationship between X_i and C_i must be obtained by combining equation (5) with the rate equations of ion exchange or sorption (Helfferich, 1962). It should also be noted that source and sink terms are needed to describe dissolution and precipitation reactions.

Equilibrium Theories

Although local equilibrium is difficult to achieve in column experiments, it can be achieved in batch experiments. Therefore, X_i as a function of C_i can be obtained in batch experiments and substituted into equation (6). A rigorous formulation of the thermodynamics of ion exchange was first done by Gaines and Thomas (1953). Laudelout et al. (1967) and van Bladel and Laudelot (1967) have shown how the

theoretical formulation of Gaines and Thomas could be used experimentally to derive the thermodynamic equilibrium constant K for any ion exchange reaction. The beauty of the thermodynamic approach is that with a limited number of experiments, the distribution coefficient can be predicted as a function of solution concentration. The drawback to the thermodynamic approach is that it assumes a homogeneous substrate having only a single type of site.

TRANSPORT IN NATURAL SYSTEMS

In order to apply experimental data to natural systems, the experimental conditions must closely approximate those in natural environments.

Local Equilibrium

Fluid flow rates in basalt and granite environments are thought to be on the order of a few centimeters per year. Longitudinal diffusion may, in this case, dominate advection as a means of transport. Under these conditions local equilibrium probably exists between ions in exchange sites and ions in the aqueous phase. It follows that experiments should also be performed under equilibrium conditions. Certain types of batch tests, including the equilibrium dialysis method, fulfill the requirement. However, column experiments are often run at unnaturally high rates of fluid flow. In such experiments, nonequilibrium effects may dominate and the results may not be transferable to natural systems.

Geometry of the Medium

In certain natural systems, such as granite and basalt systems, fluid transport occurs primarily along fractures. These fractures are often coated with alteration products such as clays and zeolites. Other avenues of preferred flow occur along void systems that were formed subaerially when the rocks were exposed to weathering processes, which enabled clays to form. These observations suggest that clays and zeolites should be the subject of laboratory experiments.

Chemical Processes

Natural environments host not only ion exchange and sorption phenomena but also dissolution and precipitation reactions. Invariably geologic environments contain phases that were originally found under conditions of higher pressure and temperature. These metastable phases dissolve slowly over time, gradually enriching the aqueous phase in their component species. Continued dissolution leads to saturation with respect to product phases such as clays and zeolites. The precipitation of these phases provides additional substrate for ion exchange and sorption and additional solute species, which compete with radionuclides for surface sites. Laboratory experiments should reflect these interacting processes.

CONCLUSION

Transport of radionuclides in natural systems is accompanied by reactions at solid-liquid interfaces. Existing chromatographic theory cannot be used to adequately describe these processes. Extensions of chromatographic theory should include the effect of nonequilibrium and equilibrium interfacial processes. The rate of fluid transport in subsurface environments is slow. Thus, diffusional transport may be of the same order as advection transport; and fluid flow algorithms must be designed to minimize numerical dispersion. Transport occurs primarily along fracture systems in igneous terraines and the fractures are commonly coated with secondary phases such as zeolite and clays. Thus secondary, not primary, mineral phases should be the subject of sorption-desorption experiments.

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SECTION 7: COMPUTER SIMULATION OF MASS TRANSFER INVOLVING
ACTINIDES IN WATER-SATURATED ROCKS: PRELIMINARY CONSIDERATIONS

INTRODUCTION

To understand radionuclide transport it is important to know the chemical behavior of the radionuclide in the environmental conditions found in the saturated rocks surrounding the waste storage repository. In general, we can expect that ground water saturating rocks fractures and pores has reached partial or complete equilibrium with respect to the mineral phases composing the rock. Alteration of the rock is also expected to have taken place where the rock minerals were in contact with an aqueous fluid not in initial equilibrium with the rock minerals. The composition of the groundwater therefore reflects the host rock and its interaction with the groundwater. If a terminal storage repository is leached by this groundwater, the groundwater composition will be modified by reaction with the waste product. Subsequent transport of the waste by groundwater movement away from the storage site will lead to a renewed attempt by the modified groundwater to reestablish equilibrium with the host rocks.

Several questions must be answered before we can establish what happens to a given radionuclide under the conditions described above. First, is it true that the groundwater achieves final equilibrium with respect to the host rocks? To what extent do bicarbonates or chlorides influence the overall composition of the groundwater? Second, what are the reactions that take place between the waste product and the groundwater? Third, what degree of complexing of the radionuclide will occur and what solid phases, if any, will precipitate? Fourth, what kind of reactions take place that lead to the removal of the radionuclide from solution? Is it adsorption, ion exchange, or precipitation? How are these reactions described?

In the introduction to this report, we emphasized that these factors can all have a critical bearing on the magnitude of the K_d value to be assigned to a particular environment. Their significance must therefore be established before more extensive computer simulations of radionuclide transport in groundwater can be made. Not all the questions posed can be addressed by the present project. For example, the leaching behavior of the waste product form is the subject of separate study

under task 2 of the Waste Isolation Safety Assessment Program. However, the nature of the groundwater composition and the resulting interactions among the ground water, the radionuclide, and the host rock are relevant to this study.

COMPUTER SIMULATION OF MASS TRANSFER

During the last ten years, a powerful technique has been developed which allows for the computer simulation of complex chemical reactions between groundwater or hydrothermal fluids and rocks. This technique, originally developed by H. C. Helgeson and his coworkers at Northwestern University and described in several papers (Helgeson, 1968; Helgeson, et al., 1970), has subsequently been modified and refined by others such as the staff of the Kennecott Computing Center in Salt Lake City, C. Herrick of the Los Alamos Scientific Laboratory, T. Wolery of Northwestern University (Wolery, 1978), and T. Brown of the University of British Columbia.

The technique permits us to calculate the progressive mass transfer between solids and an aqueous phase as a function of reaction progress, ξ , which was conceived by De Donder and Van Rysseberghe (1936) to describe the changes in the mass of a species undergoing chemical reaction. They originally called this reaction progress the "degree of advancement" of a reaction. In order to understand what is meant by this term and how it is used we will give a simple, specific example followed by reference to a more general, complex case.

A SIMPLE CASE IN WHICH LIME REACTS WITH SULFURIC ACID

Consider a beaker containing one kilogram (~1 liter) of approximately 0.1 molal sulfuric acid (H_2SO_4) having a specified initial pH of 1.0. Into this beaker are added small increments of slaked lime $Ca(OH)_2$. The sulfuric acid will react with and dissolve the slaked lime as it is added according to the following reaction:



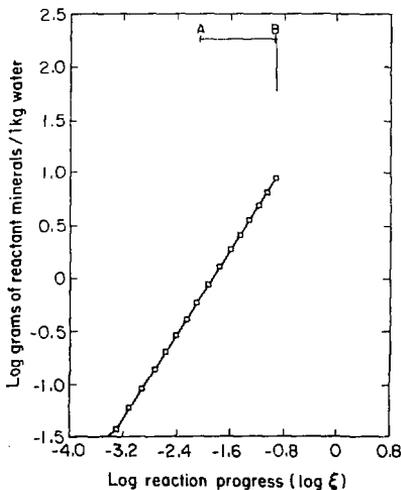
Eventually, so much slaked lime will be added that saturation will be reached with respect to the mineral gypsum which will then precipitate:



With continuing additions of slaked lime, nearly all of the sulfate ion will precipitate as gypsum and the slaked lime itself will become saturated. From then on, addition of more slaked lime will only result in its accumulation on the bottom of the beaker and no further chemical changes will occur in the solution.

The chemical changes taking place during this experiment can be studied in terms of the amount of slaked lime added to the beaker, where the addition of each mole (74 g) of slaked lime added represents the degree of advancement or one unit of reaction progress, ξ . This relationship can be represented as shown in Figure 7-1.

What happens in the beaker can also be studied as a function of reaction progress. Thus, we can plot how much gypsum or slaked lime precipitates, or what happens to the distribution of aqueous species



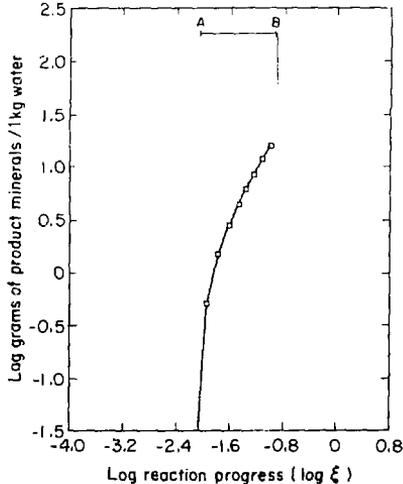
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Figure 7-1. Correlation between reactant consumed and reaction progress.
(A = gypsum, B = portlandite.)

in solution, as a function of ξ . Schematic diagrams illustrating precipitation and speciation are given in Figures 7-2 and 7-3, respectively.

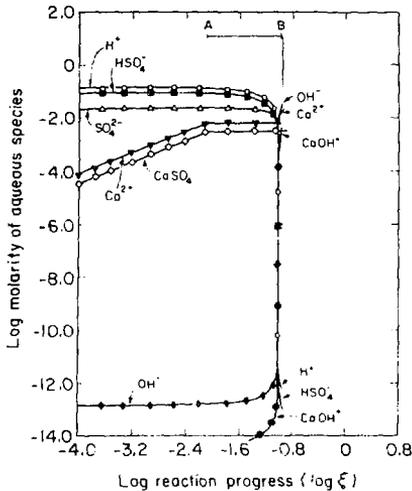
DEVELOPMENT OF A GENERAL CASE

Now consider a more complicated case in which one kilogram of surface water is allowed to react with the surrounding country rock. In this case, the water contains carbonates, sulfates, chlorides, and other dissolved constituents. The rock is also made up of several minerals. A granite, for example, may contain quartz, orthoclase, albite, muscovite, and biotite in varying proportions. In this case, we react the mineral constituents according to their molar ratios in the rock and identify one ξ unit of reaction progress as having taken place when an aggregate mole of minerals has reacted with the water. The chemical reactions that take place as a function of reaction progress are far more complex. There are many more potential product minerals



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Figure 7-2. Relationship between product phases and reaction progress, ξ . (A = gypsum, B = portlandite.)



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Figure 7-3. The variation in the concentration of aqueous species as a function of ξ . (A = gypsum, B = portlandite.)

to take into account and many more aqueous species to monitor in the solution. Furthermore, chemical changes may occur in solution, which lead to the dissolution of already precipitated phases, and equilibrium between the water and the country rock may never be achieved.

To examine the progressive chemical changes which would take place in such a complex system over space and time, we would normally require detailed knowledge of the thermodynamic properties of the precipitating phases, their alteration products, and the chemical species in the solution. We would also need to understand the rates and mechanisms of the heterogeneous chemical reactions that proceed during mineral dissolution and precipitation, and the influence that the rock structure (grain size, micropores, and connecting fractures) has on reaction rates. With our present knowledge, we are in no position to model the

kinetic behavior of such complex chemical reactions between rocks and groundwater. However, by making a few simplifying assumptions, we can model the behavior of a complex chemical system, such as that described above, which provides a fair representation of what is actually observed to happen.

The assumptions are as follows.

1. The reaction proceeds isothermally.
2. Reactions are studied as a function of ξ rather than time. This eliminates the need to know the reaction rate or mechanisms of the participating reactions.
3. Reactant minerals dissolve in the aqueous phase in proportion to their molar ratios.
4. Thermodynamic equilibrium is always maintained both within the aqueous phase and with respect to the product minerals.

For relatively long time periods (about 10^3 to 10^8 years), the above statements are assumed to be valid. Their validity is based on comparative observations with natural systems and has not been tested in any formal way. For periods of less than 10^3 years, deviations can occur and care must be taken in interpreting the results of a computer simulation.

The mathematical algorithms developed to permit study of a complex chemical system as a function of reaction progress have been fully documented elsewhere (see Helgeson et al., 1970). All computer codes subsequently developed employ the same basic principles, so that the choice of code depends on its availability and suitability for the solution of a particular problem.

All codes depend on an extensive thermodynamic data base, consisting of solubility products for solids and dissociation constants for aqueous species given at discrete temperatures (usually at 25-50°C intervals). Because of the magnitude of the task required to collect the needed thermodynamic data, the data are usually obtained from the literature without critical review. Therefore, the data are of variable quality and are rarely, if ever, internally consistent. Recent efforts by Helgeson and his students to develop an internally consistent set of

data of naturally occurring solids and aqueous complexes have culminated with the development of SUPCRT. This code permits calculation of solubility and dissociation constants of well-characterized minerals and aqueous species over a range of temperatures and pressures that encompasses most conditions expected in the earth's crust.

FUTURE PLANS

Given sufficient thermodynamic information, it should also be possible to predict the behavior of actinides in the presence of groundwater modified by the host rock composition. During fiscal year 1977, available thermodynamic data were collected on the actinides plutonium, neptunium, americium and curium as described in Section 2 of this report. This information will be incorporated in the existing data base of FASTPATH, the code developed by Kennecott Copper Corporation staff, and simulation of the chemistry of the actinides will be made in the presence of typical groundwaters in representative host rock environments. Results of such computer runs will provide tentative answers to the following uncertainties: (a) the relationship between groundwater composition and the environment; (b) the effect of bicarbonates and chlorides on overall groundwater composition; (c) the degree of complexing of actinides under subterranean conditions; (d) the effect of oxidation potential and pH on actinide solubility; (e) to what extent the K_d of a given radionuclide will be affected by complexing; and (f) the limits of solubility of actinides as determined by known phases.

Providing answers to these uncertainties will not solve all of the problems identified at the beginning of this section. Nevertheless, they do provide insight and quantify the effects on radionuclide K_d s caused by the environmental conditions in waste-repository host rocks. This information is vital in order to properly design experiments to measure K_d s and will also serve to interpret the differences in K_d s measured by different laboratory techniques.

In addition to the collection of actinide data, work has proceeded on updating the data base and debugging the code, which developed mysterious and obscure problems when modified to run on the CDC 7600 at LBL. The

problems have been partially resolved, although further work remains to be done.

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