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THEORETICAL AND EXPERIMENTAL EVALUATION OF WASTE TRANS - PORT IN SELECTED ROCKS: 1977 ANNUAL REPORT OF LBL CONTRACT NO. 45901AK. Waste Isolation Safety Assessment Program-Collection and Generation of Transport Data.

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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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THEORETICAL AND EXPERIMENTAL EVALUATION

OF WASTE TRANSPORT IN SELECTED ROCKS:

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Waste Isolation Safety Assessment Programs Collection and

Generation of Transport Data

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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 Experi-
mental 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 heterogenous 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^{-9} to 10^{-12} mole/kg. Principally as ionic species.	Difficult to estimate, but could be very large for amphoteric species near the isoelectric point (~10^{6})
3. Flow rate	Metastable equilibrium Transport Mechanisms Changes in apparent surface area contacted	~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	~10^{5} sec	Up to 10^{13} sec	None considered at this time.
6. Surface area	Adsorption	Up to 10^{5} cm²/g; Dispersed clays, humus, fine particulates, loess, etc.	~10^{2} cm²/g Fractures, microfractures, intergranular pores	~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
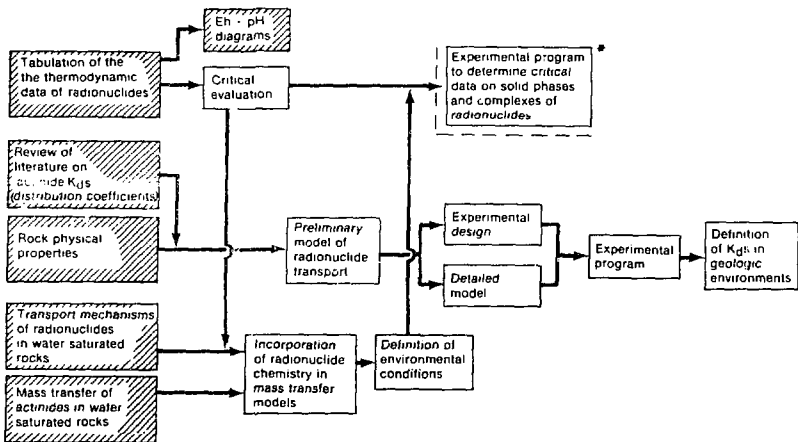
*Not included in current project.

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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 thermo-
dynamic 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 $25^{O}C$ 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	$\Delta G^o_{f,298^o}$ (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^+	-203.1 ± 1.8	Fuger and Oetting, 1976
PuO_2^{2+}	-180.9 ± 1.7	Fuger and Oetting, 1976
Solid Species		
Pu_2O_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 (^{o}K)	K	ΔG_R (kcal mole^{-1})	References
Pu III	$Pu^{3+} + H_2O \rightleftharpoons PuOH^{2+} + H^+$	titra.	0.069$\underline{M}$ $HClO_4$	298	7.5×10^{-8}	$+9.7$	Cleveland, 1970; Kraus and Dam, 1949 a,b,c
	$Pu(OH)_3(s) \rightleftharpoons Pu(OH)_3(aq)$				2×10^{-20}		Cleveland, 1970; Katz and Seaborg, 1957
	$Pu^{3+} + Cl^- \rightleftharpoons PuCl^{2+}$	ion ex.	1.0 $\underline{M}$ HCl	--	14.7[a]		Cleveland, 1970; Ward and Welch, 1956
		reduc.	1.0 $\underline{M}$ HCl	298	0.78	$+0.15$	Degischer and Choppin, 1975; Connick and McVey, 1953
		cal.	0.1 $\underline{M}$ HCl		3.72		Degischer and Choppin, 1975; Martin and White, 1958
		spec.	(conc. LiCl)	298	3.71×10^{-3}	$+3.3$	Degischer and Choppin, 1975; Shiloh and Marcus, 1966
	$Pu^{3+} + SO_4^{2-} \rightleftharpoons PuSO_4^+$	cat.ex.	$[H^+] = 1.0 \ \underline{M}$	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
	$Pu^{3+} + HSO_4^- \rightleftharpoons PuHSO_4^{2+}$	ion ex.	~1 $\underline{M}$ $NaClO_4$	301	9.94 ± 0.24	-1.37	Cleveland, 1970; Nair, 1968
Pu IV	$Pu^{4+} + H_2O \rightleftharpoons PuOH^{3+} + H^+$	poten.	I = 2$\underline{M}$ $HClO_4 - LiClO_4$	298	0.054 ± 0.001	$+1.73$	Cleveland, 1970; Rabideau, 1956; Perez-Bustamente, 1965
	$Pu(OH)_4(s) \rightleftharpoons Pu(OH)_4(aq)$				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	$Pu^{4+} + F^- \rightleftharpoons PuF^{3+}$	spec.	1$\underline{M}$ HNO$_3$	298	8.7×10^7[a]		Cleveland, 1970; Patil and Ramakrishna, 1976
		spec.	1$\underline{M}$ HNO$_3$	298	5.9×10^6	-1.1	Degischer and Choppin, 1975; McLane, 1949
	$Pu^{4+} + Cl^- \rightleftharpoons PuCl^{3+}$	cat. ox.	4$\underline{M}$ HClO$_4$	293	1.4 ± 0.2	-0.2	Cleveland, 1970; Grenthe and Noren, 1960
		spec.	2$\underline{M}$ HClO$_4$	298	0.38	+0.57	Degischer and Choppin, 1975; Hindman, 1949
		reduc.	1$\underline{M}$ 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.	1$\underline{M}$ HCl	298	0.8	+0.14	Degischer and Choppin, 1975; Kabanova and Palei, 1960
	$Pu^{4+} + HSO_4^- \rightleftharpoons PuSO_4^{2+} + H^+$	cat. ex.	0.5$\underline{M}$ acid	298	9.45	-1.3	Cleveland, 1970; Marov and Chmutova, 1961
	$Pu^{4+} + SO_4^{2-} \rightleftharpoons PuSO_4^{2+}$	reduc.	1.0$\underline{M}$ HClO$_4$	298	4.58×10^3	-5.0	Degischer and Choppin, 1975; Rabideau, 1955; Lemons, 1951
	$Pu^{4+} + 2HSO_4^- \rightleftharpoons Pu(SO_4)_2 + 2H^+$	cat. ex.	0.5 acid	298	20.0	-1.8	Cleveland, 1970; Marov and Chmutova, 1961
	$Pu^{4+} + 3HSO_4^- \rightleftharpoons Pu(SO_4)_3^{2-} + 3H^+$	cat. ex.	0.5 acid	298	125	-2.9	Cleveland, 1970; Marov and Chmutova, 1961
	$Pu^{4+} + HPO_4^{2-} \rightleftharpoons PuHPO_4^{2+}$	solub.	2.0$\underline{M}$ HNO$_3$ 0.012 - 2.0$\underline{M}$	298	8.3×10^{12}	-17.6	Cleveland, 1970; Denotkina, et al., 1960
	$PuHPO_4^{2+} + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_2$	solub.	H$_3$PO$_4$	298	6.7×10^{10}	-14.8	Cleveland, 1970; Denotkina, et al., 1960
	$Pu(HPO_4)_2 + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_3^{2-}$	solub.	H$_3$PO$_4$	298	4.8×10^9	-13.2	Cleveland, 1970; Denotkina, et al., 1960
	$Pu(HPO_4)_3^{2-} + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_4^{4-}$	solub.	H$_3$PO$_4$	298	6.3×10^9	-13.4	Cleveland, 1970; Denotkina, et al., 1960
	$Pu(HPO_4)_4^{4-} + HPO_4^{2-} \rightleftharpoons Pu(HPO_4)_5^{6-}$	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	$PuO_2^+ + Cl^- \rightleftharpoons PuO_2Cl$	poten.	--	--	0.67	--	Cleveland, 1970; Rabideau, 1958
Pu VI	$PuO_2^{2+} + H_2O \rightleftharpoons PuO_2OH^+ + H^+$	titra.	0.000186M HNO$_3$	--	4.7×10^{-4}	--	Cleveland, 1970; Krovinskaya, et al., 1960
	$PuO_2OH^+ + H_2O \rightleftharpoons PuO_2(OH)_2 + H^+$	titra.	0.000186M HNO$_3$	--	$9\pm1\times10^{-6}$	--	Cleveland, 1970; Krovinskaya, et al., 1960
	$PuO_2(OH)_2 + H_2O \rightleftharpoons PuO_2(OH)_3^- + H^+$	--	--	--	$2\ 10^{-10}$	--	Cleveland, 1970; Kraus and Dam, 1949 a,b,c
	$PuO_2^{2+} + Cl^- \rightleftharpoons PuO_2Cl^+$	spec.	$I = 1M$	296	$0.73\pm.07$	+0.19	Cleveland, 1970; Rabideau, 1956
		spec.	$2M$ HClO$_4$	293	0.56	+0.34	Degischer and Choppin, 1975; Rabideau and Lemons, 1951
	$PuO_2^{2+} + HF \rightleftharpoons PuO_2F^+ + H^+$	cat. ex.	$I = 2.0M$ [H^+]=2.0M	298	12.	-1.5	Patil and Ramakrishna, 1976
	$PuO_2^{2+} + H_2PO_4^- \rightleftharpoons PuO_2H_2PO_4^+$	electroph.	0.206-5.88M H$_3$PO$_4$	298	8.5×10^3	-5.36	Cleveland, 1970
	$PuO_2^{2+} + 2OH^- + CO_3^{2-} \rightleftharpoons PuO_2CO_3(OH)_2^{2-}$	solub.	0.17-0.44M NH$_4$CO$_3$	293	2.3×10^{22}	-30.0	Cleveland, 1970; Gel'man, et al., 1962
	$PuO_2OH^+ + CO_3^{2-} \rightleftharpoons PuO_2CO_3OH^-$	solub.	0.17-0.44M NH$_4$CO$_3$	293	4.5×10^{22}	-30.4	Cleveland, 1970; Gel'man, et al., 1962
	$PuO_2^{2+} + 2CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_2^{2-}$	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	$\Delta G^{\circ}_{f\ 298}, (kcal\ mole^{-1})$	Reference
Aqueous Species		
Np^{3+}	- 123.6 ± 0.8	*Fuger and Oetting, 1976*
Np^{4+}	- 120.2 ± 1.8	*Fuger and Oetting, 1976*
NpO_2^+	- 218.7 ± 1.3	*Fuger and Oetting, 1976*
NpO_2^{2+}	- 190.2 ± 1.3	*Fuger and Oetting, 1976*
Solid Species		
NpO_2	- 232.8	*Huber and Holley, 1968*

REACTION CONSTANT DATA (continued)

Species	Reaction	Method	Solution	T ($^{\circ}K$)	K	H_R (kcal mole^{-1})	References
Np III	$Np^{3+} + H_2O \rightleftharpoons NpOH^{2+} + H^+$	titra.	0.1 M NaClO$_4$	298	3.7×10^{-8}	+10.1	Mefodeva, et al., 1974
	$Np^{3+} + Cl^- \rightleftharpoons NpCl^{2+}$	spec.	conc. LiCl	298	3.8×10^{-1}	+3.3	Burney and Harbour, 1974; Shiloh and Marcus, 1966
Np IV	$Np^{4+} + H_2O \rightleftharpoons NpOH^{3+} + H^+$	--	--	--	9×10^{-3}	--	Burney and Harbour, 1974; Mikailov, 1973
	$Np(OH)_4(s) \rightleftharpoons Np(OH)_4(aq)$	--	--	--	6×10^{-16}	--	Burney and Harbour, 1974; Moskvin, 1971n
	$Np^{4+} + HF \rightleftharpoons NpF^{3+} + H^+$	ion ex.	4.0M HClO$_4$	293	1.6×10^4	+6.2	Burney and Harbour, 1974; Ahrland and Brandt, 1966
		extrac.	1.0M HClO$_4$	298	4.6×10^4	-6.4	Choppin and Unrein, 1976
		ion ex.	1.0M HClO$_4$	298	3.6×10^4	-6.2	Degischer and Choppin, 1975; Krylov, et al., 1968a
		ion ex.	1M HNO$_3$	293	1.7×10^4	-5.7	Degischer and Choppin, 1975; Krylov, et al., 1968a
	$Np^{4+} + Cl^- \rightleftharpoons NpCl^{3+}$	distri.	1.0M HClO$_4$	293	0.97	+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 Peekema, 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
	$Np^{4+} + SO_4^{2-} \rightleftharpoons NpSO_4^{2+}$	distri.	2.0M HClO$_4$	298	2.7×10^2	-3.3	Burney and Harbour, 1974; Sullivan and Hindman, 1954
		ion ex.	4.0M HClO$_4$	293	5.0×10^2	-3.6	Degischer and Choppin, 1975; Ahrland and Brandt, 1966

TABLE 2-2 (continued)

REACTION CONSTANT DATA (continued)

Species	Reaction	Method	Solution	T (°K)	K	ΔG_R (kcal mole^{-1})	References
Np V	$NpO_2^+ + H_2O \rightleftharpoons NpO_2OH(aq) + H^+$	poten.	$HClO_4$	--	1.25×10^{-9}	--	Burney and Harbour, 1974; Katz and Seaborg, 1957
	$NpO_2OH_{(s)} \rightleftharpoons NpO_2OH(aq)$	poten.	HNO_3	--	1.85×10^{-10}	--	Savostyanova and Khalturin, 1973
	$NpO_2^+ + Cl^- \rightleftharpoons NpO_2Cl$	ion ex.	2.0$\underline{M}$ $HClO_4$	298	0.51	+0.41	Burney and Harbour, 1974; Gainar and Sykes, 1964
	$NpO_2^+ + HPO_4^{2-} \rightleftharpoons NpO_2HPO_4^-$	ion ex.	0.2$\underline{M}$ NH_4ClO_4 $HClO_4$	293	7.1×10^2	-3.8	Degischer and Choppin, 1975; Zvagintsev and Sudarikov, 1958
	$NpO_2^+ + H_2PO_4^- \rightleftharpoons NpO_2H_2PO_4$	ion ex.	0.2$\underline{M}$ NH_4ClO_4 $HClO_4$	293	6.5	-1.1	Degischer and Choppin, 1975; Zvagintsev and Sudarikov, 1958
	$NpO_2^+ + HCO_3^- \rightleftharpoons NpO_2HCO_3$	ion ex.	μ=0	--	2.7×10^2	--	Burney and Harbour, 1974; Moskvin and Mefodeva, 1965
Np VI	$NpO_2^{2+} + Cl^- \rightleftharpoons NpO_2Cl^+$	distri.	4.0$\underline{M}$ $HClO_4$	298	0.69±0.05	+0.22	Burney and Harbour, 1974; Danesi, et al., 1971
		kin.	3.0$\underline{M}$ $HClO_4$	273	1.26	-0.13	Degischer and Choppin, 1975; Cohen, et al., 1955
	$NpO_2^{2+} + HF \rightleftharpoons NpO_2F^+ + H^+$	extrac.	1.0$\underline{M}$ $HClO_4$	294	8.6±2.1	-1.3	Burney and Harbour, 1974; Ahrland and Brandt, 1968a
		ion ex.	1.04$\underline{M}$ $HClO_4$	298	157±9	-3.0	Degischer and Choppin, 1975; Krylov, et al., 1968b
	$NpO_2^{2+} + SO_4^{2-} \rightleftharpoons NpO_2SO_4$	extrac.	1.0$\underline{M}$ $HClO_4$	293	79	-2.6	Burney and Harbour, 1975; Ahrland and Brandt, 1968b
		reduc.	1.0$\underline{M}$ ClO_4^-	298	13	-1.5	Degischer and Choppin, 1975; Stromatt and Peekema, 1958
		distr.	2.0$\underline{M}$ $NaClO$	298	43.7	-2.2	Degischer and Choppin, 1975; Sykes and Taylor, 1962
	$NpO_2^{2+} + H_2O \rightleftharpoons NpO_2OH^+ + H^+$	solub.	NH_4ClO_4	293	4.3×10^{-4}		Moskvin, 1971b
	$NpO_2OH^+ + H_2O \rightleftharpoons NpO_2(OH)_2 + H^+$	solub.	NH_4ClO_4	293	3.6×10^{-6}		Moskvin, 1971b
	$NpO_2(OH)_2 + H_2O \rightleftharpoons NpO_2(OH)_3^- + H^+$	solub.	NH_4ClO_4	293	2.0×10^{-10}		Moskvin, 1971b

TABLE 2-3. Thermodynamic data for americium.

FREE ENERGY DATA	$\Delta G^o_{f,298^o}$ (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	$Am^{3+} + H_2O \rightleftharpoons AmOH^{2+} + H^+$		$I = 0.1$ ClO_4^-	296	1.2×10^{-6}	$+8.0$	
	$Am(OH)_3(s) \rightleftharpoons Am(OH)_3(aq)$	--	--	--	3.9×10^6	--	Schulz, 1976; Weaver and Shoun, 1971
	$Am^{3+} + F^- \rightleftharpoons AmF^{2+}$	solv.ext.	$I = 1.0\underline{M}$ $NaClO_4$	298	3.09×10^3	-4.76	Schulz, 1976; Choppin and Unrein, 1976
	$Am^{3+} + Cl^- \rightleftharpoons AmCl^{2+}$	spec.	$13.7\underline{M}$ LiCl	298	6.2×10^{-3}	$+3.0$	Schulz, 1976; Marcus and Shiloh, 1969
		solv.ext.	$I = 1\underline{M}$ $NaClO_4 - NaCl$	303	1.04	-0.024	Schulz, 1976; Khopkar and Narayanankutty, 1971
		solv.ext.	$I = 1\underline{M}$ $NH_4ClO_4 - NH_4SCN$	303	1.33	-0.17	Schulz, 1976; Khopkar and Narayanankutty, 1971
		ion ex.	$I = 1\underline{M}$ $NaClO_4 - NaCl$	297	0.90	$+0.06$	Schulz, 1976; Bansal, et al., 1964
		solv.ext.	$1\underline{M}$ $HClO_4 - HCl$	295	0.90	$+0.062$	Schulz, 1976; Peppard et al., 1961
		solv.ext.	$4\underline{M}$ $NaClO_4$	298	1.41	-0.20	Schulz, 1976; Sekine, 1964; Sekine, 1965
		ion ex.	$0.5\underline{M}$ $HClO_4$		0.58		Schulz, 1976; Ward and Welch, 1956
		ion ex.	$I = 4.0\underline{M}$ $HClO_4 - HCl$	293	0.69	$+0.21$	Schulz, 1976; Grenthe, 1962
	$Am^{3+} + SO_4^{2-} \rightleftharpoons AmSO_4^+$	ion ex.	$I = 0.5 - 0.6\underline{M}$	298	72	-2.5	Schulz, 1976; Aziz, et al. 1968
		ion ex.	$0.75\underline{M}$ NH_4Cl	293– 298	60.0	--	Schulz, 1976; Lebedev, et al., 1960
		ion ex.	$1 - 1.3\underline{M} = I$ $NaClO_4$ 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	$Am^{3+} + SO_4^{2-} \rightleftharpoons AmSO_4^+$	ion ex.	1.5$\underline{M}$ NH$_4$ClO$_4$	293-298	57.6	--	Schulz, 1976; Lebedev, et al., 1960
(continued)		solv.ext.	1.0$\underline{M}$ NaClO$_4$	298	37.2	-2.1	Schulz, 1976; *Sekine*, 1964; Sekine, 1965
		solv.ext.	2.0$\underline{M}$ NaClO$_4$	298	26.9	-1.9	Schulz. 1976; DeCarvalho and Choppin, 1967
		ion ex.	0.5$\underline{M}$ NaClO$_4$	298	72.5	-2.5	Schulz, 1976; Aziz et al., 1968
		ion ex.	I = 1$\underline{M}$ HClO$_4$ - H$_2$SO$_4$	300	16.6	-1.7	Schulz, 1976; Naj:, 1968
	$Am^{3+} + H_2PO_4^- \rightleftharpoons AmH_2PO_4^{2+}$	ion ex.	I = 1$\underline{M}$ NH$_4$Cl	293	30.2	-2.0	Schulz, 1976; Moskvin, 1969

TABLE 2-4. Thermodynamic data for curium.

FREE ENERGY DATA	$\Delta G^o_{f,298^o}$ (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	$Cm^{3+} + H_2O \rightleftharpoons CmOH^{2+} + H^+$	extrac.	I = 0.1$\underline{M}$ HClO$_4$ - LiClO$_4$	300	1.20×10^{-6}	-8.0	Desire, et al., 1969
	$Cm^{3+} + F^- \rightleftharpoons CmF^{2+}$	extrac.	1.0$\underline{M}$ NaClO$_4$	298	4.10×10^2	-3.6	Choppin and Unrein, 1976
	$Cm^{3+} + Cl^- \rightleftharpoons CmCl^{24}$	ion ex.	0.5$\underline{M}$ HCl	--	1.51	--	Ward and Welch, 1956
	$Cm^{3+} + SO_4^{2-} \rightleftharpoons CmSO_4^+$	ion ex.	0.15$\underline{M}$ NH$_4$Cl NH$_4$ClO$_4$	293-298	56	, --	Ward and Welch, 1956; Lebedev, et al., 1960
		distri.	2.0$\underline{M}$ NaClO$_4$ Na$_2$SO$_4$	298	22	-1.8	DeCarvalho and Choppin, 1967
		ion ex.	0.5-0.6$\underline{M}$ NaClO$_4$	298	71.9	-2.5	Aziz. et al., 1968
		distri.	0.5$\underline{M}$ NaClO$_4$	297-298	73.3	-2.5	Aziz, et al., 1968
		distri.	0.5$\underline{M}$ NaClO$_4$	298	68	-2.5	Aziz, et al., 1968

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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 deter-mined by the reaction specified and by the free energies of participating species. The figures illustrating this chapter are all drawn for $25^{\circ}C$ 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:

$$PuO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons 4H^{4+} + 2H_2O \quad .$$
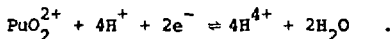
From this reaction, the number of electrons, hydrogen ions, and water molecules which participate in the reaction are noted. Next, the standard free energy of the reaction, ΔG_R^O is determined. In this case:

$$\Delta G_R^O = (-180.9) + (0) - (-115.1) - (-113.4)$$
$$= 47.6 \text{ kcal mole}^{-1} \quad .$$

Using the relationship between free energy and standard potential,

$$\Delta G_R^O = nFE_o$$

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

$$E_0 = 1.03 \text{ V} \quad .$$

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

$$Eh = E_0 + \frac{2.303 \text{ RT}}{nF} \log \frac{\left[Pu^{4+}\right]}{\left[PuO_2^{2+}\right]\left[H^+\right]^4}$$

where $n = 2$ and $T = 298K$. This equation is used to determine the boundary between the domains of two species where $\left[Pu^{4+}\right] = \left[PuO_2^{2+}\right]$. Hence the equation reduces to:

$$Eh = E_0 + 0.0295 \log \frac{1}{\left[H^+\right]^4}$$

or

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

Certain reactions have no pH dependence, such as:

$$PuO_2^{2+} + e^- \rightleftharpoons PuO_2^+$$
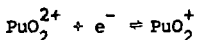
so that only the standard potential need be found. Hydrolysis reactions, which are only pH and not Eh dependent, such as

$$Pu^{3+} + H_2O \rightleftharpoons PuOH^{2+} + H^+$$
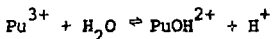
can be located using the hydrolysis constant alone.

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

$$PuO_2(s) + 4H^+ + e^- \rightleftharpoons Pu^{3+} + 2H_2 .$$
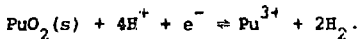
In this equation, the correlation of the aqueous species is assigned an arbitrary value, such as 10^{-6}, mole ℓ^{-1}. The activity of the pure solid is unity, by definition, and water is also assumed to have unit activity. The corresponding equation relating Eh and pH is

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

where $\left[Pu^{3+}\right]$ 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), $Pu(OH)^{2+}$(III), PuO_2^+(V), PuO_2^{2+}(VI), $PuO_2(OH)^+$(VI), $PuO_2(OH)_3^-$(VI) and the solid phase PuO_2(IV). Equations defining species boundaries are derived as follows.

Aqueous Species Boundaries

$$PuO_2^+ + 4H^+ + 2e^- \rightleftharpoons Pu^{3+} + 2H_2O$$
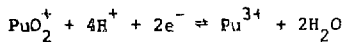
$$\Delta G_R^O = -48.6 \text{ kcal mole}^{-1}$$

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

$$Eh = 1.05 - \frac{0.059}{2} \log \left[H^+\right]^4$$

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

$$Pu^{4+} + e^- \rightleftharpoons Pu^{3+}$$

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

$$E_o = 1.00$$

$$Pu^{3+} + H_2O \rightleftharpoons PuOH^{2+} + H^+$$
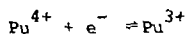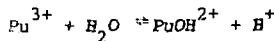
$$\Delta G_R^O = 7.6 \text{ kcal mole}^{-1}$$

$$2.303 \frac{-\Delta G_R^O}{RT} = \log K_H = -5.6$$

$$PuO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons Pu^{4+} + 2H_2O$$
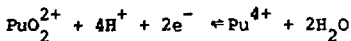
$$\Delta G_R^O = -47.6 \text{ kcal mole}^{-1}$$

$$E_o = 1.03$$

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

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

$$PuO_2^{2+} + e^- \rightleftharpoons PuO_2^+$$
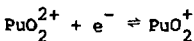
$$\Delta G_R^O = -22.2 \text{ kcal mole}^{-1}$$

$$E_o = 0.96$$

$$PuO_2^+ + 3H^+ + 2e^- \rightleftharpoons PuOH^{2+} + H_2O$$
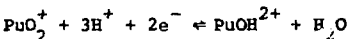
$$\Delta G_R^O = -41.0 \text{ kcal mole}^{-1}$$

$$E_o = 0.89$$

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

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

$$PuO_2^{2+} + H_2O \rightleftharpoons PuO_2OH^+ + H^+$$
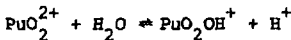
$$\Delta G_R^O = 4.6 \text{ kcal mole}^{-1}$$

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

$$PuO_2OH^+ + H^+ + e^- \rightleftharpoons PuO_2^+ + H_2O$$
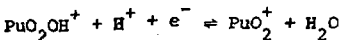
$$\Delta G_R^O = 26.8 \text{ kcal mole}^{-1}$$

$$E_o = 1.16$$

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

$$PuO_2OH^+ + 2H_2O \rightleftharpoons PuO_2(OH)_3^- + 2H^+$$
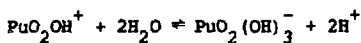
$$\Delta G_R^O = 21.0 \text{ kcal mole}^{-1}$$

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

$$e^- + PuO_2(OH)_3^- + 3H^+ \rightleftharpoons PuO_2^+ + 3H_2O +$$
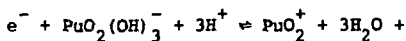
$$\Delta G_R^O = 47.8 \text{ kcal mole}^{-1}$$

$$E_o = 2.07$$

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

Solid-Aqueous Species Boundaries

$$PuO_2(s) + 4H^+ + e^- \rightleftharpoons Pu^{3+} + 2H_2O$$
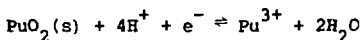
$$\Delta G_R^O = -11.3 \text{ kcal}$$

$$E_o = 0.49$$

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

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

$$PuO_2(s) + 3H^+ + e^- \rightleftharpoons PuOH^{2+} + H_2O$$
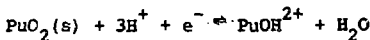
$$\Delta G_R^O = -3.7 \text{ kcal mole}^{-1}$$

$$E_o = 0.16$$

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

$$PuO_2^+ + e^- \rightleftharpoons PuO_2(s)$$

$$Eh = \frac{RT}{nF}\left(\frac{\Delta G_R}{RT} - \ln\left[PuO_2^+\right]\right)$$

$$PuO_2^{2+} + 2e^- \rightleftharpoons PuO_2(s)$$

$$Eh = \frac{RT}{nF}\left(\frac{\Delta G_R}{RT} - \ln\left[PuO_2^+\right]\right)$$

$$PuO_2OH^+ + H^+ + 2e^- \rightleftharpoons PuO_2(s) + H_2O$$
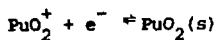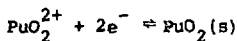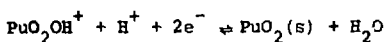
$$\Delta G_R^o = -64.1 \text{ kcal mole}^{-1}$$

$$E_o = 1.39$$

$$Eh = 1.39 - 0.059 \text{ pH} - 0.059 \log\left[(PuO_2OH^+)\right]$$
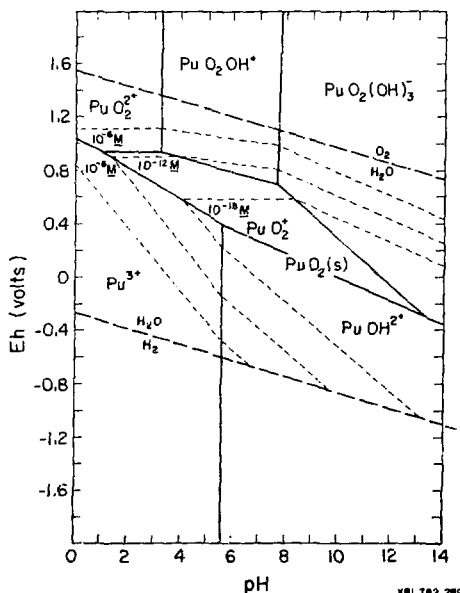
Figure 3-1. Eh-pH diagram for plutonium at 25°C and one atmosphere.

$$PuO_2(OH)_3^- + 3H^+ + 2e^- \rightleftharpoons PuO_2(s) + 3H_2O$$
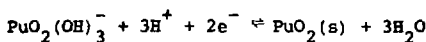
$$\Delta G_R^O = -85.1 \text{ kcal mole}^{-1}$$

$$E_o = 1.85$$

$$Eh = 1.85 - 0.177 \text{ pH} - 0.059 \log \left[PuO_2(OH)_3^-\right]$$

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 $Np^{3+}(III)$, $NpOH^{2+}(III)$, $Np^{4+}(IV)$, $NpO_2^+(V)$, $NpO_2OH(V)$, $NpO_2^{2+}(VI)$, $NpO_2OH^+(VI)$, $NpO_2(OH)_3^-(VI)$, and the solid phase $NpO_2(IV)$. Equations defining species boundaries are derived as follows.

Aqueous Species Boundaries

$$Np^{4+} + e^- \rightleftharpoons Np^{3+}$$
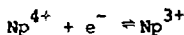
$$\Delta G_R^O = -3.4 \text{ kcal mole}^{-1}$$

$$E_o = 0.15$$

$$NpO_2^+ + 4H^+ + 2e^- \rightleftharpoons Np^{3+} + 2H_2O$$
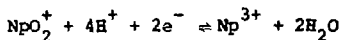
$$\Delta G_R^O = -18.3 \text{ kcal mole}^{-1}$$

$$E_o = 0.40$$

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

$$Np^{3+} + H_2O \rightleftharpoons NpOH^{2+} + H^+$$

$\log H_H = -7.4$ \hspace{1cm} (Mefodeva, et al., 1974)

$$NpO_2^+ + 4H^+ + e^- \rightleftharpoons Np^{4+} + 2H_2O$$
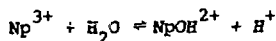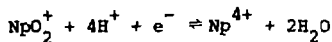
$\Delta G_R^O = -14.9$ kcal mole^{-1}

$E_o = 0.65$

$Eh = 0.65 - 0.236$ pH

$$NpO_2^{2+} + e^- \rightleftharpoons NpO_2^+$$

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

$E_o = 1.23$

$$NpO_2^+ + H_2O \rightleftharpoons NpO_2OH + H^+$$
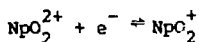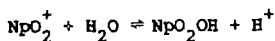
$\log K_H = -8.9$ \hspace{1cm} (Sevostyanova and Khalturin, 1973)

$$NpO_2OH^+ + 2H_2O \rightleftharpoons NpO_2(OH)_3^- + 2H^+$$
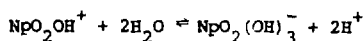
$K_{2-1} = \dfrac{[NpO_2(OH)_2][H^+]}{[NpO_2OH^+]} = 3.6 \times 10^{-6}$ \hspace{1cm} (from Moskvin, 1971)

$K_{3-2} = \dfrac{[NpO_2(OH)_3^-][H^+]}{[NpO_2(OH)_2]} = 2.0 \times 10^{-10}$

$K_{3-1} = \dfrac{[NpO_2(OH)_3^-][H^+]^2}{[NpO_2OH^+]} = 7.2 \times 10^{-16}$

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

pH = 7.6

Solid Aqueous Species Boundaries

$$Np^{4+} + 2H_2O \rightleftharpoons NpO_2(s) + 4H^+$$
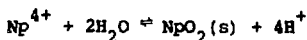
$$\Delta G_R^O = 0.80 \text{ kcal mole}^{-1}$$

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

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

$$E_O = 0.18$$

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

$$NpO_2^+ + e^- \rightleftharpoons NpO_2(s)$$
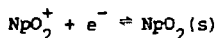
$$\Delta G_R^O = -14.10 \text{ kcal mole}^{-1}$$

$$Eh = \frac{RT}{nF} \left(\frac{\Delta G_R^O}{RT} - \ln \left[NpO_2^+\right] \right)$$

Solubility lines for $NpO_2(s)$ - NpO_2OH were drawn considering the hydrolysis reaction

$$NpO_2^+(s) + H_2O \rightleftharpoons NpO_2OH + H^+ + e$$
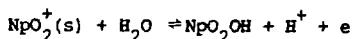
which means that the lines must have a slope of -0.059 and consistency requirements that they meet solubility lines for NpO_2^+.

The standard free energies of formation of NpO_2OH^+ and $NpO_2(OH)_3^-$ 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^+

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

$$NpO_2(OH)_3^- - NpO_2^+$$

$$NpO_2(OH)_3^- - NpO_2OH$$

$$NpO_2^+ - NpOH^{2+}$$

$$NpO_2OH - NpOH^{2+}$$
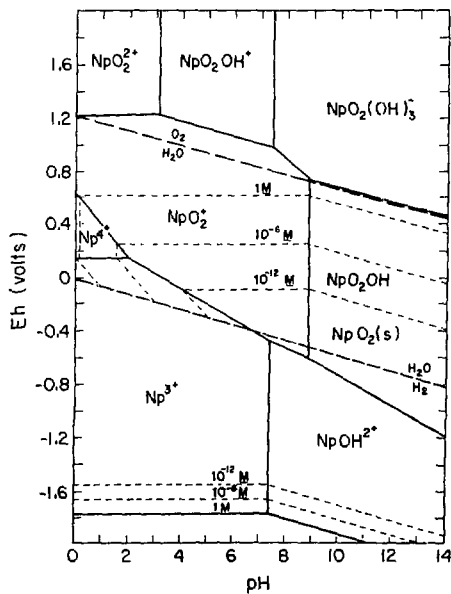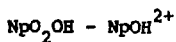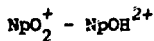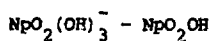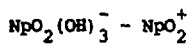
XBL 782-290

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.

$$AmO_2^+ + 4H^+ + 2e^- \rightleftharpoons Am^{3+} + 2H_2O$$
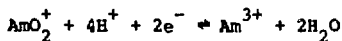
$$\Delta G_R^O = -79.5 \text{ kcal mole}^{-1}$$

$$E_o = 1.72$$

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

$$AmO_2^{2+} + e^- \rightleftharpoons AmO_2^+$$
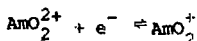
$$\Delta G_R^O = 37.0 \text{ kcal mole}^{-1}$$

$$E_o = 1.60$$
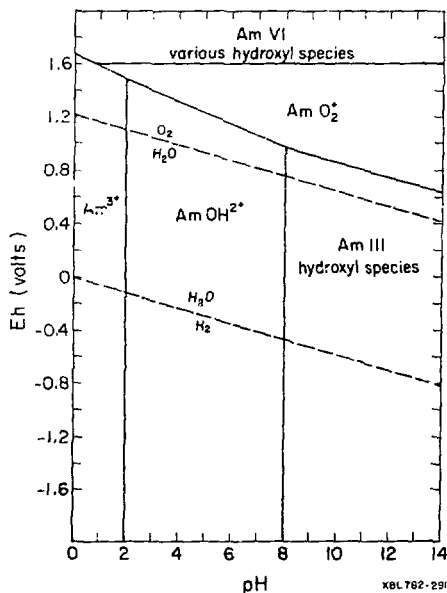
Figure 3-3. Eh-pH diagram for americium at 25°C and one atmosphere.

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.

$$Cm^O \rightleftharpoons Cm^{3+} + 3e^-$$
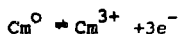
$$\Delta G^O_{f,298} = -142.4 \text{ kcal mole}^{-1} \quad \text{(Fuger and Oetting, 1976)}$$

$$E_O = -2.06$$
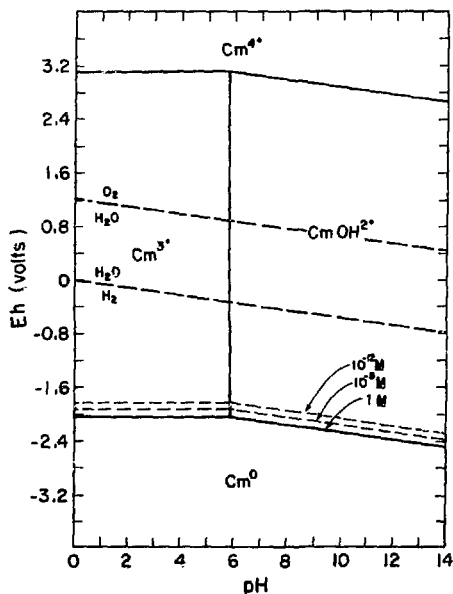
KBL 782-292

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

$$Cm^{3+} + H_2O \rightleftharpoons CmOH^{2+} + H \qquad \text{(Desire, Hussenois and}$$
$$\text{Guillaument, 1969)}$$

$$pK_H = -5.9$$

$$Cm^{3+} \rightleftharpoons Cm^{4+} \qquad \text{(Nugent, Baybarz and Burnett, 1971)}$$

$$E_o = +3.1$$
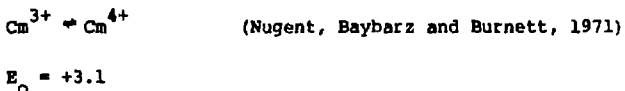
OXIDATION STATES OF PLUTONIUM, NEPTUNIUM, AMERICIUM, AND CURIUM IN THE NATURAL ENVIRONMENT

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.
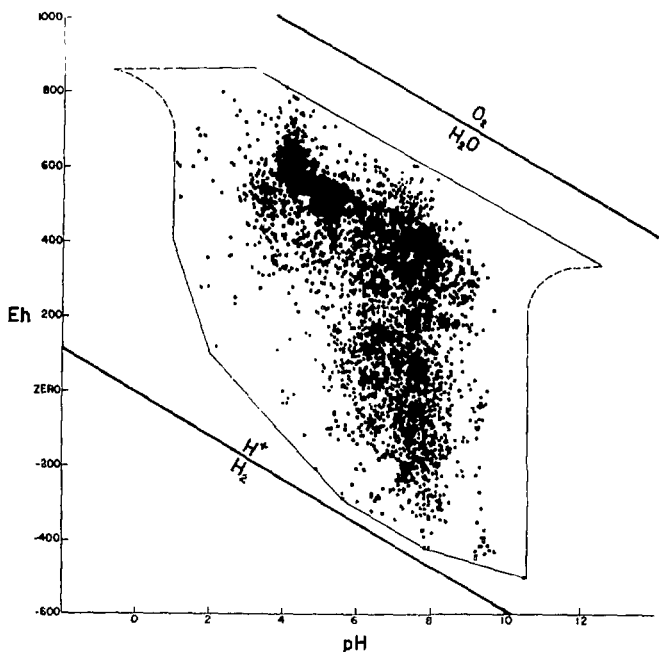
XBL 783-7642

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

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potential.   J. Geology, v. 68, no. 3, p. 243.

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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_ds, are a measure of the soil's ability to sorb actinides and other elements, our knowlege 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 de ermined 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 sorben , the chemical components in the solution, and the temperature. T' refore, wide discrepancies exist in the various K_d values assigne to different radionuclides.

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

THEORETICAL BASI 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 nuclid 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., 19 5) as:

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

or

$$K_d = \frac{As/W}{Al/V} \tag{1}$$

where

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

    W = weight of solid phase in grams,

    Al = 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_ds can be determined from laboratory tests or field tests. Generally, laboratory tests for K_ds 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 com-
peting 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 radio-
nuclide as a function of the throughput volume (Bensen, 1960). The
effluent radionuclide concentration (C) is then determined and com-
pared with the influent radionuclide concentration (Co). The ratio
C:Co 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):

$$V_{50} = \frac{K_d \times W}{2} \tag{2}$$

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_ds 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} $\underline{M}$ 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 $Pu(OH)^{n+}$. 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 $\underline{M}$ $NaNO_3$ and 2 $\underline{M}$ di-ammonium phosphate) had no effect on plutonium adsorption on soil (96.5% plutonium sorbed), whereas equal concentrations of organic salts (4 $\underline{M}$ ammonium acetate) drastically reduced soil adsorption
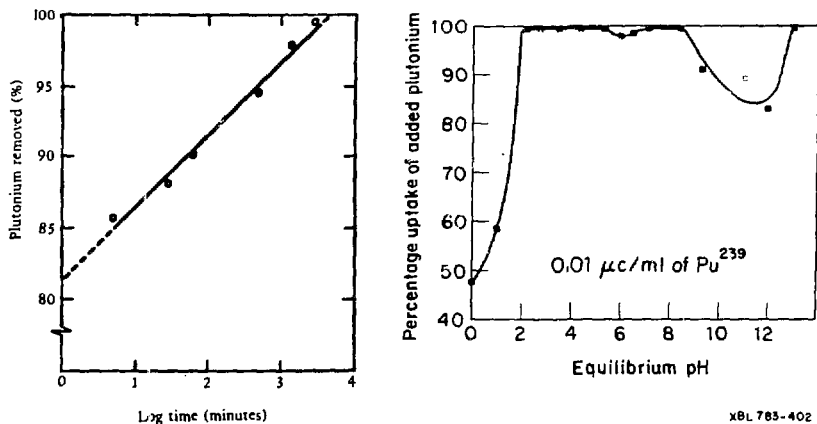
Figure 4-1. Left: plutonium adsorption by soil as a function of time of contact (Rhodes, 1952). Right: plutonium adsorption by soil as a function of pH (Rhodes, 1952, as cited by Bensen, 1960).

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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Society of America.

(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_ds 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 sub-
stantiated 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).

	Exchange capacity	
pH	meq/100 g soil[a]	meq/100 g clay[a]
4	0.012	0.06
5	0.10B	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

[a]Soil contained approximately 20% clay and 80% sand.
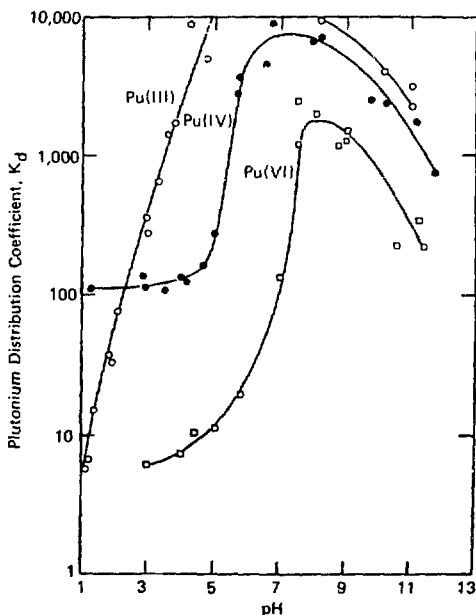
Figure 4-2. Effect of pH and plutonium oxidation state on the adsorption of plutonium by soil (Prout, 1959).

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 $\underline{M}$ 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

[a]Initial 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 $\underline{M}$ 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).

	K_d (ml/g)	
Organics	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 coefficient (ml/g)	Suspension pH
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 distri-
bution 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 R_ds. 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 per-
formed with various resins. In one test, 1 g of resin was shaken overnight
with 10 ml of synthetic waste supernate containing 1.75 x 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 dis-
tribution coefficients for various soil materials and clay samples taken

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

| | Oxic conditions pH = 7.8-8.0 | | | | | Anoxic conditions pH = 7.8-8.0 | | | | |
| | Sedimentation | | Thin Layer | | | Sedimentation | | Thin Layer | | |
Valence	K	R	K	R'	$T_{1/2}$	K	R	K	R'	$T_{1/2}$
III	1.6×10^4	10%	2.1×10^4	30%	3	1.9×10^4	2.5%	—	—	—
IV	1.8×10^4	9%	1.9×10^4 1.5×10^4	50% 31%	1 1	1.3×10^4	8.0%	$>9.4 \times 10^4$ $(>9.3 \times 10^3$	39% 35%	2.4 $1.3^{a)}$
VI	1.3×10^4	11%	5.7×10^4	9%	4	2.2×10^4	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.
[a]Paper filters rather than millipore filters used as blanks; paper filters strongly
   adsorbed Pu(IV) and reduced sediment uptake, therefore K is probably low.
[b]Precipitation 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-supernate 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

[a]Product of Union Carbide.

at various depths are given in Tables 4-9 and 4-10. Clay samples con-
sisting mainly of illite and kaolinite had plutonium distribution
coefficients of ~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} $\underline{M}$ $^{238}Pu(NO_3)_4$ and 10^{-7} $\underline{M}$ $Am(NO_3)_3$.
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

[a]Quaternary clay (mainly montmorillonite).

[b]Young tertiary clay (mixture of illite and kaolinite).

[c]Older tertiary clay (mixture of illite and kaolinite).

coefficient (K) for pure solution of $Pu(NO_3)_4$ at 4×10^{-5} $\underline{M}$ 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
$^{238}Pu(NO_3)_4$ tracer in neutral aqueous solution was placed on the surface
of the rock disk and was allowed to dry at room temperature. Water
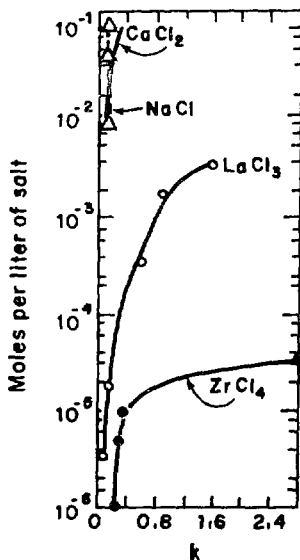
XBL 783-401

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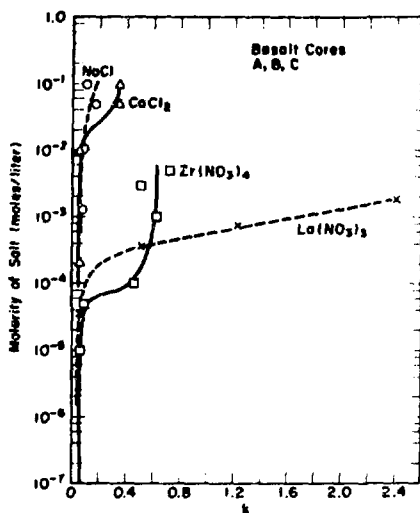
Figure 4-4. Surface adsorption coefficient of plutonium as a function of the concentration of other salts for dense basalt cores (Fried, et al., 1976a).

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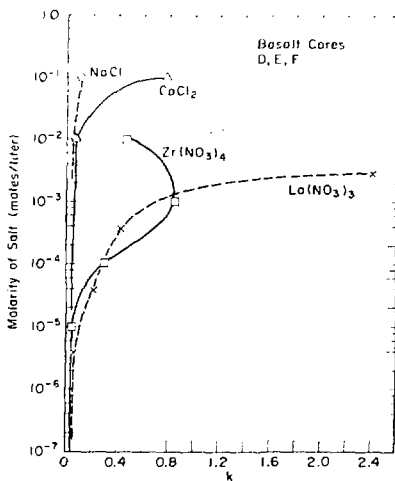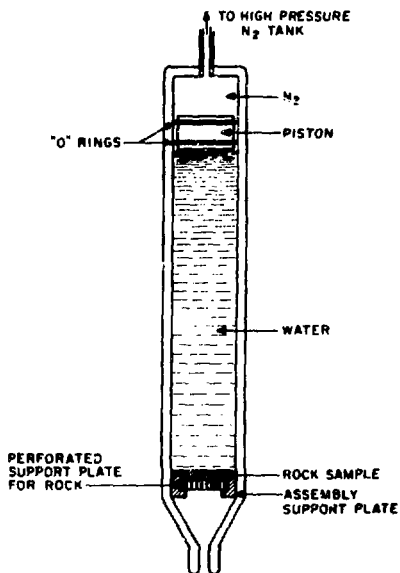
Figure 4-6.   Schematic diagram of the high-pressure stainless-steel
chromatographic column (Fried, et al., 1976a).

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 ± 10 μm/m of water
flow for the limestone and 61 ± 8 μm/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-μm 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} $\underline{M}$ calcium solutions $\left[\text{Ca-acetate and } Ca(NO_3)_2\right]$ 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} $\underline{M}$ $Ca(NO_3)_2$ 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

Island	Well	Depth (m)	Particulate (mg/1)	^{239,240}Pu (%σ)[f] (fCi/1)[a]	(fCi/mg)	ln K_d[d]	Fraction in particulates[e]	K_d
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			
		10.8	26.3	1.3 (50)	0.05			
	AEN3	Surface	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	1.76×10^5
		10	13.8	2.1 (25)	0.15	11.66	0.62	1.16×10^5
	AEN5	Surface	30.2	1.8 (90)	0.06			
		7	2.9	0.9 (70)	0.31			
	AEN9	Surface	0.8	2.4 (23)	3.0	13.12	0.29	4.99×10^5
	AEN2	10	12.8	25.0 (7)	1.95	12.87	0.83	3.88×10^5
Belle	ABM1	Surface	157	206 (2)	1.31	9.56	0.69	1.42×10^4
Elmer	APA1	Surface	4.4	0.2 (40)[b]				
				0.14(53)	0.08			
		10	19.6	0.4(100)[b]				
				0.2 (30)[c]	0.03			

Mean ln K_d = 12.42 ± 1.27
Mean K_d = 2.5 x 10^5

[a]0.4- and 1-μm filters were processed together except where indicated
[b]1.0-μm filter only
[c]0.4-μm filter only
[d]The 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:

$$\ln Kd = \ln\frac{(fCi/mg \ particulate) \ x \ 10^6}{fC/1 \ water}$$

[e]Fraction of ^{239,240}Pu in total particulates >0.4 m
[f](%σ) values in parentheses are 1σ 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	237Pu	IV	0.40	10.4×10^4
	238Pu	IV	0.25	16.8×10^4
	239Pu	VI[b]	0.62	7.5×10^4
Montmorillonite	239Pu	IV	2.0	2.1×10^4
	239Pu	VI	63.0	2.5×10^2

[a]Aqueous phase 5 m$\underline{M}$ in Ca^{2+}.

[b]Ca-acetate; remaining studies conducted in $Ca(NO_3)_2$.

Table 4-13. Sorption of 238Pu(IV) to treated clays: pH 4.0,
5×10^{-3} $\underline{M}$ $Ca(NO_3)_2$ (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	-	2.9×10^5
-O.M.[b]	50.0	-	4×10^2
-Fe + O.M.	99.8	-	2×10^5
Blank[c]	71	-	-
18 weeks			
Clay	99.8	No	-
-O.M.	61.5	Yes	3.5×10^2
-Fe + O.M.	99.9	No	-
Blank	71.7	Yes	-
52 weeks			
Clay	99.9	< 20% (VI)	1.9×10^5
-O.M.	99.8	50% (VI)	8.1×10^4
-Fe + O.M.	99.8	< 20% (VI)	8.1×10^4
Blank	78.6	25% (VI)	-

[a]By thenoyltrifluoroacetone extraction, PrF$_3$ precipitation (holding
oxidant method) and hexone extraction.

[b]O.M. = organic matter.

[c]No 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/1)	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	7.3	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	4.6	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 Clay loam
New York (West Valley)	NY	16.0	1.2	1.40							
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

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analyses of all but four soils were done. Three standard plutonium solutions containing initial plutonium concentrations of 10^{-8} $\underline{M}$, 10^{-7} $\underline{M}$, and 10^{-6} $\underline{M}$ (or 9,600 dis/min/10 μl, 103,000 dis/min/10 μl, and 972,000 dis/min/10 μl, respectively) were used for sorption measurements. A soil-to-solution ratio of 1 g to 5 ml was used and 10 μl 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 μl of 10^{-3} $\underline{M}$ 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] ± statistical error (ml/g) for plutonium at equilibrium sorption (Glover, et al., 1976).

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

[a]Glover, 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 conc. ($\underline{M}$)	$K_{d(m)}$ [b]	pH	$-Eh(V)$	Pu_m/Pu_c [a]
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

[a]Ratio 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 $Pu(OH)$ 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 conc. ($\underline{M}$)	$K_{d(m)}$ [b]	pH	Eh (V)	Pu_m/Pu_c [a]
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}	2,600[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}	260[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 ,0c3
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	0.6	26

Table 4-17. Continued.

Soil	Initial Pu conc. ($\underline{M}$)	$K_{d(m)}$ [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

[a]Ratio 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 $\underline{M}$ 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 $K_d(Am) < K_d(Pu)$. 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 ($\underline{M}$)	South Carolina K_d(Am) (ml/g)		South Carolina K_d(Np) (ml/g)		Washington 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

[a]Standard 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} $\underline{M}$ solutions of $Am(NO_3)_3$ 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.
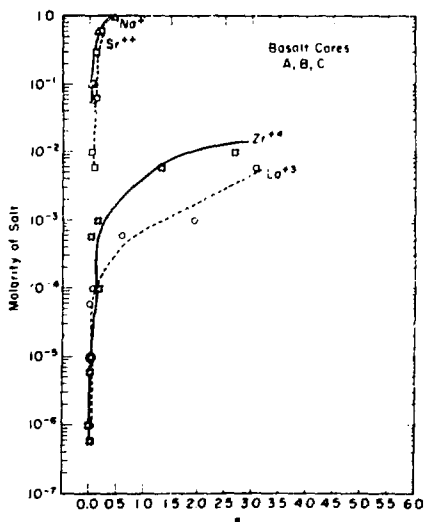
Figure 4-7. Surface absorption coefficient of americium as a function
of the concentration of other salts for basalt cores (Fried,
et al., 1976a).

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

REFERENCES CITED

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APPENDIX 4-1: SUMMARY TABULATION OF DISTRIBUTION COEFFICIENT

Table A Review of the literature on radionuclide K_ds. 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 μCi/ml	1:20	Three hours
Pu	III, IV, VI	From 6.0 to ≥ 10,000 (See Figure 4-2)	Solution prepared using distilled water, pH adjusted by adding NaOH or HNO₃	0.05 μCi/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 NO₃⁻) 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 × 10⁵ (see Table 4-6)	Solution prepared using distilled water, solution pH adjusted initially with NaOH to 7.0	Original spike of Pu⁴⁺ in 1 M HNO₃	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 nonsaline groundwater pH = 6.8-8.2 (See p. 3-55 of this reference for groundwater composition.)	not specified	not specified	not specified
^{237}Pu	III, IV, VI	For oxic conditions from 1.3 × 10³ to 5.7 × 10⁴. For anoxic conditions from 9.3 × 10³ to 9.3 × 10⁴ (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 AlO₂⁻, 6.75 M OH⁻, 2.2 M NO₃⁻, 1.1 M NO₂⁻, 0.3 M CO₃²⁻, 0.3 M SO₄²⁻, and 0.0002 M Cs⁺).	Supernate contained 1.75 × 10⁷ dis/(min·ml)²³⁸Pu	1:10	Resin shaken overnight with synthetic supernate
$^{239-240}Pu$ 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 Klem²/ml). For 4 × 10⁻⁵ M solution of Pu(NO₃)₄= 0.10 ± 0.02 for limestone, 0.07 ± 0.02 for basalts. For 10⁻⁷ M solution of Am(NO₃)₃= 0.041 ± 0.02 for basalts. (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 HNO₃. Am and Pu brought into 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 Pu(NO₃)₄ or 10⁻⁷ M Am(NO₃)₃	not specified	Alpha or gamma counting rate of aliquots counted at 12-hr. intervals until equilibrium.

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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 ≈ 2% free CaCO₃. 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	Adsorption was more than 90% complete from solutions of Pu(III) and Pu(IV) between pH 2.5 and 12 and from solutions of Pu(V) at pH > 6	Prout 1958, 1959
not specified	not specified	Soil 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	Adsorption from strongly acid or partially neutralized waste was minor. Adsorption from alkaline waste from precipitation was high. Introduction of a slug of organic reduced the K_d of both Pu and Am.	Hajek and Knoll, 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 CaCO₃ 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 oxic and anoxic conditions appear similar for all three valence states	Duursma and Parsi, 1974
ot 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. I. DuPont de Nemours & Co., 1975
not specified	not specified	Various soil materials (clay, sandstone, caprock and coarse river sand) from boreholes surrounding salt formations in NE Netherlands.	not specified	K_d values for caprock 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_ds. 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
$^{239,240}Pu$	not specified	Mean K_d for seven samples ~ 8 × 10⁴ Mean K_d for field particulates in the groundwater ~ 2.5 × 10⁵ (see Table 4-11)	Pu contaminated soil samples equilibrated in the laboratory with uncontaminated sea water	not specified	not specified	not specified
$^{237,238,239}Pu$	IV, VI	For soil clay fraction, K_d = 7.5 × 10⁴ to 16.8 × 10⁴, for reference montmorillonite K_d = 2.5 × 10² to 2.1 × 10⁴. (see Table 4-12)	Study conducted in Ca acetate and Ca nitrate solutions	not specified	Varied, not specified	not specified
^{238}Pu	IV	From 3.5 × 10² to 2.9 × 10⁵ (see Table 4-11)	Study conducted in 8 × 10⁻³ M Ca(NO₃)₂ solution	^{238}Pu added at about 0.6 ppm (Pu mass clay mass)	not specified	Equilibration time 3 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 prepare by dilut up in 0.5 HNO₃ standard solutions of plutonium and americium respectively. Solutions were kept acidic to prevent hydrolysis and poly merization 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
^{237}Np and ^{241}Am	not specified	K_d = 0.16 to 3.9 for Np, ≤ 1.0 to 280 for Am (see Table 4-20)	Study conducted in varying concentrations of Ca(NO₃)₂ and NaNO₃ solutions. Initial solution pH 2.5 for E. Washington, 3.4 for S. Carolina	Influent activity 3.7 μCi/25 ml for E. Washington, 1.0 μCi/25 ml for S. Carolina	1:2.5	20-30 minutes equilibration time ~ 21 to 24 hrs

data for plutonium, neptunium, americium, and curium (continued).

Initial soil pH	Soil cation exchange capacity (meq/100g)	Soil/material type and content	Particle size and distribution	Observation/comments	Reference
not specified	not specified	Pu - contaminated soil samples from the islands of Eniwetok Atoll	not specified	Kd values from field results (from particulates in the groundwater) and laboratory tests are very close	Noshkin, et al., 1976
6.5 (aqueous phase 5 mM in Ca²⁺)	not specified	Ca-saturated clay from Miami silt loam soil and montmorillonite as reference clay	not specified	Sorption of Pu (VI) to montmorillonite was substantially less (37%), whereas sorption of Pu to Miami silt loam clay was always above about 99.4%, regardless of initial valence	Bondietti, et al., 1976
4.0	not specified	Ca-saturated clay from Miami silt loam soil. The clay fraction was treated to remove organic matter and free iron oxides	not specified	After 18 weeks of equilibration, the presence of a significant fraction of the soluble Pu in the solution (soluble Pu species which do not sorb) suggested the formation of a different Pu oxidation state than that initially added (e., formation of a polymer (Pu VI or Pu V). Pu valence state identification in experimental systems is therefore necessary for adsorption studies	Bondietti and Reynolds, 1976
Ranged from 2.3 to 8.3 (see Table 4-14)	Ranged from 2.9 to 34.4 (see Table 4-14)	17 soil samples from various present and probable future Pu-handling areas in the U.S. (see Table 4-14)	See Table 4-14	Kd values are very sensitive to changes in Pu and Am concentration, especially at high levels of Pu and Am sorption (see Tables 4-15 and 4-21)	Glover, et al., 1976 Pelzer and Miner 1976
For E. Washington soil = 7.0, for S. Carolina < 5.1	For E. Washington soil = 4.9, for S. Carolina = 2.5	Subsoils from East Washington and South Carolina (see Table 4-19)	not specified	Distribution coefficients measured on subsoils as a function of equilibrium solution concentration of Ca²⁺ and Na⁺ decreased for both neptunium and americium. For South Carolina subsoil: $K_d(Np) = f(Ca^{2+}) = 0.43$ to 0.66, $= f(Na^+) = 0.16$ to 0.25 $K_d(Am) = f(Ca^{2+}) = 1.0$ to 67, $= f(Na^+) = 1.6$ to 280 For East Washington soil: $K_d(Np) = f(Ca^{2+}) = 0.36$ to 2.37, $= f(Na^+) = 3.19$ to 3.90 $K_d(Am) > 1200$	Routson, 1975, 1976

Table B Review of the literature on radionuclide K_ds. 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. 7 of this reference for breakthrough curves	Surface soil (< 20") from well at Z-1A tile field site, Richland, Wash., sieved to < 2 mm dia meter	not specified	Synthetic waste prepared by mixing ing high salt acidic aqueous phase (5.4 M SO_4) with organic com pounds (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 the excavation for 241-AX tank farm, Hanford, sieved to < 2 mm diameter	not specified	Various organic wastes from Han ford radionuclide- separations plant (TBP-CCl_4, DBBP-CCl_4, Fab Oil, 0.4 M D2EHPA-0.2 M TBP in NPH)
Pu	With dry soils K_d = 6000 for short column = 3000 for long column With moist soils K_d = 0.4 for solvent > 30 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 ≈14 to 20 (see Table 4-14)	Column elution study done using Pu nitrate solution

[a]TBP - tributylphosphate
DBBP - dibutylbutylphosphonate
D2EHPA - di-(2-ethylhexyl) phosphoric acid
Fab Oil - "fabrication oil," a commercial mixture of Lard oil and CCl_4 (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 and 0.01 for ^{241}Am	not specified	Uptake of Pu by the soil was very minor and of Am negligible	[reference] 1968
Organic wastes from Hanford separations plant spiked with ^{239}Pu and ^{241}Am	Length = 5.0 and 10.0 respectively, ID = 0.8	For TBP·CCl$_4$[a] 30 for Pu and 9 for Am For DBBP·CCl$_4$ 3.5 for Am and no adsorption of Pu by soil For Lab·Chl. erratic results For 0.4 M D2EHPA 0.2 M TBP in NPH No adsorption of Pu or Am by soil from this organic	See pp. 5–6 of this reference for permeabilities to organic wastes	Not removed ^{239}Pu and ^{241}Am of soil from some of the organic and most of the inorganics	[reference] 1962
Migration studies simulated postulated 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 columns are overly complexed for soil not migrate significantly the migration of large volumes in subsurface soil would be more realistic	[reference] 1975
Column packed with 24 g of soil, 1 g of which was mixed with 100 μl of 1 to 3 M Pu nitrate solution was distributed evenly on top of the soil in the column	4.0, 1.0	Column washed with 15 ml distilled water and effluent collected in 20 ml fractions and analyzed for Pu	Flow rates 15 mm, 90 mm and 180 mm per 20 ml respectively	Pu with the lowest K_d rates the least amount of Pu while the soil with the highest K_d rated the most	[reference] 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 ιadiation--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_O 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 μCi/ml
of mixed radioactivity (Beard and Godfrey, 1967).

intermediate-level

 liquid wastes Liquid wastes containing between 5×10^{-5} and
100 μCi/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:

$$K_d = \frac{A_{solid}}{A_{soln.}} \times \frac{cc_{soln.}}{g_{solid}}$$

where: A_{solid} is the amount of A that is associated with the adsorbent; $A_{soln.}$ is the amount of A that remains in the solution; $cc_{soln.}$ 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} µCi/ml of mixed radioactivity (Beard and Godfrey, 1967).

nuclide   A species of atom chracterized 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 radio-activity in a milliliter of solution to the radio-activity 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 concentra-
                tion 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 that the natural
                or regional water table (Schmalz, 1972).

SECTION 5: PRELIMINARY CONSIDERATIONS IN DETERMINING AN EXPERIMENTAL
METHOD TO MEASURE RADIONICLIDE 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	0.2-11.4	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, 197t 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., 19/6).

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 25Å^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:

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

where d = length of one side of a cube,

    a = radius of a mineral grain,

    N = Avogadro's number, and

    $\underline{m}$ = 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:

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

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

$$V_x = Q/A \quad . \tag{2}$$

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

$$kdP = (\mu Q/A) \ dx \quad . \tag{3}$$

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:

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

$$k(P_1 - P_2) = \frac{\mu QL}{A} \tag{5}$$

$$P_1 = \frac{\mu QL}{AK} + P_2 \tag{6}$$

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.

	1 day		5 days		10 days		20 days	
	Concentration		Concentration		Concentration		Concentration	
Rock type	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} $\underline{M}/1$. 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 b
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 $100^{O}C$. 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

$$\frac{R}{1 - R} = \frac{C_m V_m}{C_s V_s} \tag{1}$$

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

$$K_d = \frac{C_s}{C_m} \quad . \tag{2}$$

Therefore, equation (1) reduces to

$$\frac{R}{1 - R} = \frac{V_m}{V_s K_d} \quad . \tag{3}$$

Because the velocity of the solute is given by

$$v_i = vR \tag{4}$$

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

$$R = \frac{v_i}{v} = \frac{V_m}{V_m + K_d V_s} \tag{5}$$

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:

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

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.
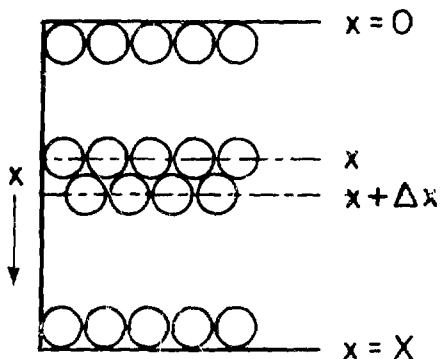
XBL783-400

Figure 6-1. Schematic representation of a packed bed. The material
balance is set up for the "plate" between x and x+Δx
(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 experi-
ments 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 ground-
water? 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 radio-
nuclide 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 Rysselberghe (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:

$$H_2SO_4 + Ca(OH)_2 = CaSO_4 \text{ aq} + 2H_2O \quad .$$

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

$$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O \quad .$$
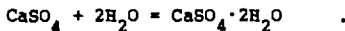
With continuing additions of slaked lime, nearly all of the sulfate ion will precipitate as gypsum and the slaked lime itself will become saturated. From then on, addition of more slaked lime will only result in its accumulation on the bottom of the beaker and no further chemical changes will occur in 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
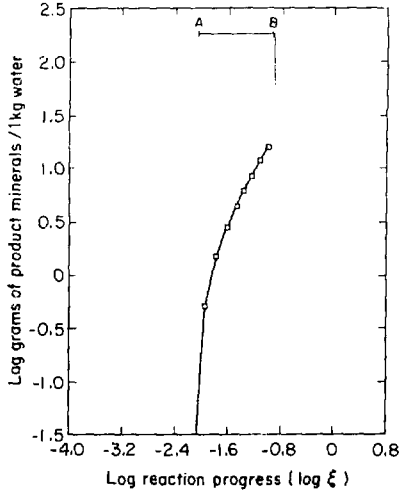

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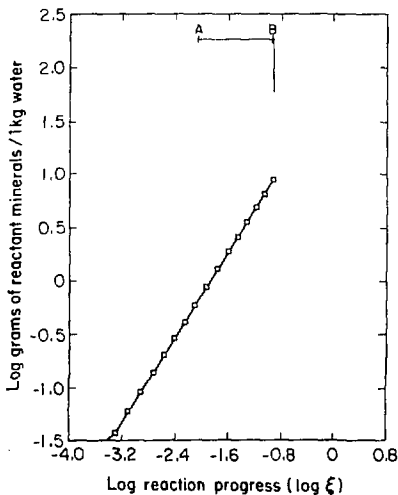
Figure 7-1. Correlation between reactant consumed and reaction progress. (A = gypsum, B = portlandite.)

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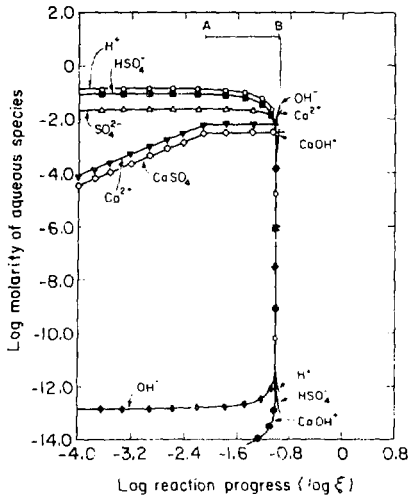
DEVELOPMENT OF A GENERAL CASE

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, orthoclose, 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.)

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 $25-50^\circ C$
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 solu-
bility and dissociation constants of well-characterized minerals and
aqueous species over a range of temperatures and pressures that encompases
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 ground-
water 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 tne effects on radionuclide K_ds
caused by the environmental conditions in waste-repository host rocks.
This information is vital in order to properly design experiments to
measure K_ds and will also serve to interpret the differences in K_ds
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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