Solid Phases and Solution Species of Different Elements in Geologic Environments

**Dhanpat Rai
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March 1978

Pacific Northwest Laboratory
Richland, Washington 99352
Operated for the
U.S. Department of Energy
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SOLID PHASES AND SOLUTION SPECIES OF DIFFERENT ELEMENTS IN GEOLOGIC ENVIRONMENTS

INTRODUCTION

Among factors that influence radionuclide behavior in the environment, the nature of the solid phases and solution species of the radionuclide is one of the most important. Through their precipitation and dissolution, solid phases would cause changes in solution concentration which, in turn, would affect adsorbed ions. The environmental occurrence of most radionuclides is expected to be low so that discrete solid phases of the element may not be present in the terrestrial environment. In this case the element may be distributed throughout the soil and rock matrix and adsorption reactions may control solution concentrations. However, if the concentration of the element in solution is such that a solid phase of the element can precipitate, the knowledge of this solid phase and solution ions would help in predicting the solution concentrations available for transport (Dutt, Shaffer, and Moore, 1972; Jurinak and Medrano, 1974; Rai and Franklin, 1973; Tanji and Doneen, 1966). Granted the importance of the total solution concentrations of the element, the nature of the predominant solution species are important since they affect 1) charge dependent ion exchange; 2) adsorption because of changes in the nature of the species due to alteration of solution properties such as pH, Eh, competing ions and complexing ions; 3) movement through the soil and rock matrix because of their physical size; and 4) plant uptake.

The objectives of this report are:

- 1) to predict from thermodynamic data the nature of the solid phases and solution species in various weathering environments of different elements (Am, Sb, Ce, Cs, Co, Cm, Eu, I, Np, Pu, Pm, Ra, Ru, Sr, Tc, T, U, Zr) that are present in radioactive wastes
- 2) to predict the degree of adsorption of different elements by the solid matrices and to compare these predictions with observed results

(a) This study was done for the Department of Energy under a WISAP program.

- 3) to determine the influence of different factors (such as pH, Eh, complexing ligands) on total pore-water concentration and the nature of solution species of selected elements

The diagrams used in this document were constructed on an EPA sponsored program to critically assess the available literature on radionuclide migration in geologic materials. The EPA program will result in the publication of a two volume report which will be published in the first half of 1978 (Ames, 1978; Ames and Rai, 1978). As the EPA program was underway when this related DOE task was formulated, a decision was made to utilize the EPA funded material rather than performing separate but duplicative work.

METHODS AND MATERIALS

Laboratory information on possible solid phase and solution species of elements of interest in radioactive waste is almost nonexistent (Ames and Rai, 1978). What little information is available is very site and solution specific with such poorly defined system variables that no few extrapolations can be made to other situations. In order to bridge this gap, thermodynamic data are generally used to construct Eh-pH diagrams to predict stable phases and solution species (Pourbaix, 1966; Garrels and Christ, 1965). This approach also has several limitations, but is the best method until extensive laboratory data become available.

DATA COLLECTION

The laboratory information regarding the solid phases and solution species and the adsorption of different elements by the geologic media was selected from a comprehensive literature review which is underway concurrently with this study (Ames, 1978; Ames and Rai, 1978).

In order to develop solid phase-solution species diagrams, accurate values of the equilibrium constants of all the reactants and products are required. Equilibrium constants were selected from several readily available sources, the most important of these sources being Sillen and Martell (1964); NBS publications (Rossini et al., 1952; Wagman et al., 1968, 1969, 1971; Parker et al., 1971; Schumm, 1973), Latimer (1952); Pourbaix (1966); Cleveland (1970); Keller (1971); Burney and Harbour (1974); and Baes and Mesmer (1976). The thermodynamic data were used to develop equilibrium constants for chemical equations that describe the behavior of various species. Generally these equations are used to develop Eh-pH diagrams (Pourbaix, 1966; Garrels and Christ, 1965) that provide the information regarding the stable compounds and solution species in the whole range of pH and Eh. However, Eh-pH diagrams can be used only for elements that exist in more than one oxidation state, and these diagrams do not indicate the total amount of the element and the relative amount of various species in solution under specified conditions. Therefore, activity-pH diagrams rather than Eh-pH diagrams were developed.

The solid phase-solution species diagrams of elements affected by oxidation-reduction were developed at an assumed partial pressure of oxygen (0.2 atmospheres in most cases). However, the changes in solution concentration or the stability of the solid phases that would occur due to the decrease in oxygen pressures are also discussed. This approach is similar to the one used by Lindsay (1972), Baes and Mesmer (1976), and Rai and Serne (1977).

LIMITATIONS OF THEORETICAL APPROACH

Using thermodynamic data to predict the stable solid phases and the concentration and nature of species in different environments is a powerful approach. The major limitation lies not in the approach but in the paucity and the accuracy of the available thermodynamic data. Some other limitations are 1) no consideration of the kinetics of reactions; and 2) the predictions apply only under equilibrium conditions.

Selected thermodynamic data were made internally consistent. These data were then used to estimate solid phases and solution species equilibria. It should be pointed out that in most cases there are large variations in the equilibrium constants reported by different authors (especially for actinides). It is very difficult to determine the accuracy of these constants without actually redoing the experiments. A rigorous selection process may help determine accurate values, but for this report the most recent data were selected.

The theoretical predictions outlined in this report regarding the relative 1) stability and dissolution of different solid phases; 2) abundance of different solution species; and 3) changes in total concentration and the nature of species of an element with changes in solution properties (such as pH, Eh, CO₂ pressure, concentration of various cations and anions) can be considered fairly reliable. However, the absolute concentration of an element in solution, in equilibrium with different solid phases and environmental conditions should be considered questionable, because of the uncertainties in the accuracy of the thermodynamic data. In order to further illustrate this statement an example of plutonium equilibria is given below.

Rai and Serne (1977) predicted 1) PuO_2 followed by $\text{Pu}(\text{OH})_4$ to be the most stable solid phases of the Pu compounds for which data are available; 2) the total concentration of Pu in acidic-oxidizing solutions in equilibrium with these compounds can be approximated by the concentrations of PuO_2^+ and PuO_2^{2+} ; and 3) the concentration of Pu in acidic-oxidizing solutions in equilibrium with PuO_2 or $\text{Pu}(\text{OH})_4$ would decrease with the increase in pH. Using the most reliable ΔG_f° values available in the literature for (Table 1), the concentration of PuO_2^+ and PuO_2^{2+} in equilibrium with PuO_2 is plotted in Figure 1 (dashed lines).

When $\log K_{s10}$ of PuO_2 estimated by Baes and Mesmer (1976) is combined with ΔG_f° of PuO_2^+ and PuO_2^{2+} in Table 1, the PuO_2^+ and PuO_2^{2+} lines are approximately 2.3 log units higher than the dashed lines (Figure 1). The cross hatched area in Figure 1 indicates the Pu concentration variation due to differences in thermodynamic data reported by various authors and due to the standard errors involved in the determination of various data. It can be seen from the Figure 1 that a variation in Pu concentration of approximately 5 log units or 100,000 times can be expected at any given pH. Clearly, accurate predictions of Pu concentrations in equilibrium with PuO_2 cannot be made from the above data. Rai, et al. (1977) have shown that the observed Pu concentrations in equilibrium with PuO_2 under environmental pH and Eh values are higher than the highest predicted values (Figure 2). Variation of approximately 5 orders of magnitude in predicted Pu concentration in equilibrium with $\text{Pu}(\text{OH})_4$ is also observed when the thermodynamic data are plotted in a similar fashion to PuO_2 . Although there is an uncertainty about the absolute Pu concentrations in equilibrium with PuO_2 and $\text{Pu}(\text{OH})_4$, the predicted relative solubility of PuO_2 and $\text{Pu}(\text{OH})_4$ is the same as the observed relative solubility of these compounds (Rai, et al., 1977).

CONSTRUCTION AND INTERPRETATION OF THE DIAGRAMS

The details of the method of constructing the diagrams presented in this report can be found in Rai and Lindsay (1975) and Rai and Serne (1977). In these diagrams the $\text{pCO}_2(\text{g})$, pK^+ , and pNa^+ , etc., refer to the negative

logarithm of the activity (in moles/l for solution species and atmospheres for gases). The oxidation-reduction conditions are denoted by partial pressures of oxygen.

In the solid phase diagrams, any compound that lies below another compound at a given pH is more stable. Thus, for any two solids at a specific pH, the solid that maintains lower ionic activity is more stable. In addition to stability, information regarding weathering and formation can also be obtained from these diagrams. If, in a given soil, the soil solution composition is below the solid line, the soil is under-saturated with respect to the solid represented by the line, and that mineral will dissolve or weather. On the other hand, if a soil solution concentration is above the solid stability line, the soil is supersaturated with respect to the mineral represented by the line, and the mineral should precipitate.

The solution species diagrams were developed assuming a given oxidation-reduction environment, equilibrium with a given compound, and set ionic activities of various cations (Ca^{2+} , Na^+ , NH_4^+) and anions (Cl^- , HCO_3^- , CO_3^{2-} , NO_3^- , F^- , SO_4^{2-} , and PO_4^{3-}) that may be present in the terrestrial environment. Organic ligands and colloids that may be present in the solutions were not considered. The solution species diagrams depict anionic, cationic, and several neutral or uncharged species for which data were available.

The equilibrium constants involving specific elements of interest are reported under appropriate headings. Some of the additional reactions required to construct the diagrams presented in this report are given in Table 2.

TABLE 1. Gibbs Free Energy of Formation
(ΔG_f°) for Some Pu Species

<u>Species</u>	<u>ΔG_f° (KCal/mole)</u>	<u>Reference</u>
PuO_2	-240.4 ± 0.8	Holley et al. (1958)
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)

FIGURE 1. Variation in Predicted PuO_2 Solubility

FIGURE 2. Comparison of Predicted vs. Observed PuO₂ Solubility

TABLE 2. Additional Equilibrium Constants (K°) at 25°C and One Atmosphere Pressure Required to Construct the Diagrams in the Report

Reaction		Log K°	Reference
Al(OH) ₃ (gibbsite)	$\rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	-33.80	Lindsay et al. (1959)
CO ₂ (gas) + H ₂ O	$\rightleftharpoons \text{H}_2\text{CO}_3$	- 1.46	Sillen and Martell (1964)
H ₂ CO ₃	$\rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	- 6.35	"
HCO ₃ ⁻	$\rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	-10.33	"
CaCO ₃ (calcite)	$\rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	- 8.35	"
H ⁺ + Cl ⁻	$\rightleftharpoons \text{HCl}$	4.05	"
HPO ₄ ²⁻	$\rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$	-12.33	"
H ₂ PO ₄ ⁻	$\rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+$	- 7.20	"
H ₃ PO ₄	$\rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+$	- 2.12	"
AlPO ₄ ·2H ₂ O(variscite)	$\rightleftharpoons \text{Al}^{3+} + \text{H}_2\text{PO}_4^- + 2\text{OH}^-$	-30.50	"
CaHPO ₄ ·2H ₂ O(dicalcium phosphate dihydrate)	$\rightleftharpoons \text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{H}_2\text{O}$	- 6.56	"
Ca ₄ H(PO ₄) ₃ ·3H ₂ O(octacalcium phosphate)	$\rightleftharpoons 4\text{Ca}^{2+} + \text{H}^+ + 3\text{PO}_4^{3-} + 3\text{H}_2\text{O}$	-46.90	"
HSO ₄ ⁻	$\rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	- 1.96	"
H ₂ O(water)	$\rightleftharpoons \text{H}^+ + \text{OH}^-$	-14.00	"
H ₂ O(water)	$\rightleftharpoons 2\text{H}^+ + 1/2\text{O}_2(\text{gas}) + 2\text{e}^-$	-41.55	"
SiO ₂ (soil) + 2H ₂ O	$\rightleftharpoons \text{H}_4\text{SiO}_4$	- 3.10	Elgawhary and Lindsay (1972); and Helgeson (1969)

DISCUSSION OF SOLID PHASES AND SOLUTION SPECIES

AMERICIUM

Information regarding the possible solid phases of americium in soil and rock environments is lacking. However, the relative solubilities of several americium solids based upon estimated thermodynamic data (Table 3) are given in Figure 3 as a function of pH. These are oxides and hydrous oxides of americium assumed to be present in an oxidizing environment ($pO_2 = 0.68$ atm). The solubility of the solids decreases rapidly in the direction of increasing pH. As the environment becomes less oxidizing, the activity of Am^{+3} associated with each of the solid phases [except $Am(OH)_3$] increases rapidly. At $pO_{2(g)} = 8.68$ atm, for example, the curve for Am^{3+} activity from $Am(OH)_4(s)$ increases by two log units.

The activity of various americium species in solution in equilibrium with $AmO_2(s)$ in an oxidizing environment ($pO_2 = 0.68$ atm) is given in Figure 4. The thermodynamic data used to construct Figure 4 are reported in Table 3. In the normal soil pH range, the complex species $Am(OH)^{2+}$ and $AmSO_4^+$ would control the total activity of americium, with Am^{3+} of somewhat lesser importance. In the environmental conditions chosen, chloride, nitrate and phosphorus species were relatively unimportant in terms of the total americium present in solution. However it should be kept in mind that in a relatively high chloride environment, the $AmCl^{2+}$, for example, could become the principal americium species in solution. With an increase in pO_2 (more reducing environment) and the concentration of anions, the curves given in Figure 4 would move upwards. However, the relative position of most of the isotherms would not change. The americium species are all cationic in the normal soil pH range of from 4 to 8. It is to be expected, therefore, that ion exchange could be an important americium removal mechanism.

TABLE 3. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Americium

Reaction	Medium ^(a)	Log K	Reference
<u>Solid Compounds</u>			
$\text{Am}(\text{OH})_3 \rightleftharpoons \text{Am}^{3+} + 3\text{OH}^-$	0	- 19.57	Latimer (1952)
$\text{Am}(\text{OH})_4 \rightleftharpoons \text{Am}^{4+} + 4\text{OH}^-$	1.0 OH^-	- 52.12	Keller (1971)
$\text{AmO}_2\text{OH} \rightleftharpoons \text{AmO}_2^+ + \text{OH}^-$	1.0 OH^-	- 33.29	"
$\text{AmO}_2(\text{OH})_2 \rightleftharpoons \text{AmO}_2^{2+} + 2\text{OH}^-$	1.0 OH^-	- 41.69	"
$\text{AmO}_2 + 4\text{H}^+ \rightleftharpoons \text{Am}^{4+} + 2\text{H}_2\text{O}$	0	- 6.23	Latimer (1952)
$\text{AmF}_3 \rightleftharpoons \text{Am}^{3+} + 3\text{F}^-$	Var. (0.1-0.5)	- 15.11	Keller (1971); Sillen and Martell (1964)
<u>Oxidation-Reduction Reactions</u>			
$\text{Am}^{2+} + 2\text{e}^- \rightleftharpoons \text{Am}(\text{s})$	1.0 HClO_4	- 91.29	Keller (1971)
$\text{Am}^{3+} + 3\text{e}^- \rightleftharpoons \text{Am}(\text{s})$	0	-121.0	Sillen and Martell (1964)
$\text{Am}^{4+} + \text{e}^- \rightleftharpoons \text{Am}^{3+}$	0	41.0	"
$\text{AmO}_2^+ + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{Am}^{4+} + 2\text{H}_2\text{O}$	0	21.0	"
$\text{AmO}_2^{2+} + \text{e}^- \rightleftharpoons \text{AmO}_2^+$	0	27.0	"
<u>Other Reactions</u>			
$\text{Am}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AmOH}^{2+} + \text{H}^+$	0.1 at 23°C	- 5.92	Keller (1971)
$\text{Am}^{3+} + \text{Cl}^- \rightleftharpoons \text{AmCl}^{2+}$	0	1.17	Sillen and Martell (1964)
$\text{Am}^{3+} + \text{F}^- \rightleftharpoons \text{AmF}^{2+}$	0.5	3.39	Keller (1971)
$\text{Am}^{3+} + 2\text{F}^- \rightleftharpoons \text{AmF}_2^+$	0.5	6.11	"
$\text{AmF}_2^+ + \text{F}^- \rightleftharpoons \text{AmF}_3^\circ$	0.1 (HClO_4) at 23°C	4.13	Sillen and Martell (1964)
$\text{Am}^{3+} + \text{NO}_3^- \rightleftharpoons \text{AmNO}_3^{2+}$	1.0 $\text{H}(\text{ClO}_4)$	0.26	"
$\text{Am}^{3+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{AmH}_2\text{PO}_4^{2+}$	0	2.51	Keller (1971)
$\text{Am}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{AmSO}_4^+$	0	3.68	Sillen and Martell (1964)
$\text{AmSO}_4^+ + \text{SO}_4^{2-} \rightleftharpoons \text{Am}(\text{SO}_4)_2^-$	1.5	0.35	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO_4) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO_4 - constant concentration of the substance stated (1.0 moles/liter HClO_4).

FIGURE 3. The Relative Stability of Various Americium Solids in an Oxidizing Environment ($pO_2 = 0.68 \text{ atm}$)

FIGURE 4. The Activity of Various Americium Species in Equilibrium with AmO₂ in an Oxidizing Soil Environment [$pO_2(g) = 0.68 \text{ atm}$], $pSO_4^{2-} = pCl^- = 3.0$ and $pH_2PO_4^- = 5.0$

PREDICTED VS. OBSERVED BEHAVIOR OF AMERICIUM

Information regarding the possible solid phases of americium in soil and rock environments is lacking.

It can be seen from Figure 4 that the predominant solution species of americium are all cationic, thus americium would be expected to enter into exchange reactions with soil minerals. This prediction is supported by the laboratory results. Americium adsorption (K_d values) on various soils and rocks have been correlated with 1) cation exchange capacity of soils (Sheppard, Kittrick and Hart, 1976; Glover, Miner, and Polzer, 1977), and 2) the concentration of the competing cations (Na^+ , Ca^{2+} , Sr^{2+} , La^{3+} and Zr^{4+}) so that the adsorption of americium decreases with an increase in concentration of competing cations (Fried, Friedman and Quarterman, 1974; Fried, Friedman and Weeber, 1974; Routson, Jansen and Robinson, 1975; Sheppard, Kittrick and Hart, 1976; Fried, 1977). Although none of the workers have tried to distinguish the contributions of polymer adsorption, cation exchange, hydrolysis and precipitation to the K_d value, the laboratory data indicate that americium removal from solution may be predominantly via an ion exchange mechanism.

ANTIMONY

The selected thermodynamic data for various antimony solids are reported in Table 4 and are plotted in Figure 5 to determine the relative stability of these solid phases. This figure represents a highly oxidizing environment ($O_2 = 10^{-0.68}$). Under these conditions $SbCl_3$, SbF_3 , and Sb_2S_3 are very soluble and therefore are not shown in the figure.

Under these oxidizing conditions ($O_2 = 10^{-0.68}$ atm) the minerals in increasing order of stability throughout the pH range can be arranged as follows: orthorhombic Sb_2O_3 , cubic Sb_2O_3 , orthorhombic Sb_4O_6 , cubic Sb_4O_6 , $Sb(OH)_3$, Sb_2O_4 , and Sb_2O_5 . Solids containing antimony in a +5 state (Sb_2O_5 and Sb_2O_4) and the Sb_2S_3 would change their relative positions with changes in the oxidation-reduction conditions, whereas the other solids will retain their relative positions. Sb_2O_5 and Sb_2O_4 will become less stable with an increase in reducing conditions, while Sb_2S_3 will become the most stable solid phase in extremely reducing conditions. Sb_2S_3 is very soluble in an oxidizing environment because of the oxidation of sulfur to sulfate, which is the stable solution species (Garrels and Christ, 1965). Under extremely reducing conditions and total sulfur levels of approximately $10^{-3}M$ where the dominant sulfur species is no longer the SO_4^{2-} , the most stable mineral will be Sb_2S_3 . In oxidation-reduction conditions corresponding to oxygen pressures of $<10^{-35}$ atmospheres, $Sb(OH)_3$ would be the most stable solid.

The selected thermodynamic data for solution species is reported in Table 4. The relative activity of various solution species in equilibrium with $Sb_2O_3(s)$ is given in Figure 6. If equilibrium with $Sb(OH)_3(s)$ is assumed, the activity of all the species would be approximately 2.9 log units lower with the lines still parallel to the lines given in Figure 4. In the environmental pH range of interest (4 to 8), it can be seen that $HSbO_2^\circ$ and $Sb(OH)_3^\circ$ are the species that would govern the total activity of antimony present in solution. The other species [$SbOF^\circ$, $Sb(OH)_2^+$, SbO^+ , $Sb(OH)_4^-$ or SbO_2^- and $NH_4SbO_2^\circ$] do not contribute significantly to the total antimony present in the solution and hence can be ignored. Since the predominant solution species [$HSbO_2^\circ$, $Sb(OH)_3^\circ$] are neutral, ion exchange as an antimony adsorption mechanism is not expected to be important.

TABLE 4. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Antimony

Reaction	Medium	Log K	Reference
<u>Solid Compounds</u>			
$\text{Sb}_2\text{O}_3 \text{ (cubic)} + 2\text{H}^+ \rightleftharpoons 2\text{SbO}^+ + \text{H}_2\text{O}$	0	- 3.05	Sillen and Martell (1964)
$\text{Sb}_2\text{O}_3 \text{ (orthorhombic)} + 2\text{H}^+ \rightleftharpoons 2\text{SbO}^+ + \text{H}_2\text{O}$	0	- 2.32	"
$\text{Sb}_2\text{O}_4 + 2\text{H}^+ \rightleftharpoons 2\text{SbO}^+ + 0.5 \text{ O}_2 + \text{H}_2\text{O}$	0	- 18.56	Charlot (1958); Wagman et al. (1968)
$\text{Sb}_4\text{O}_6 + 4\text{H}^+ \rightleftharpoons 4\text{SbO}^+ + 2\text{H}_2\text{O}$	0	- 14.96	Wagman et al. (1968)
$\text{Sb(OH)}_3 + \text{H}^+ \rightleftharpoons \text{SbO}^+ + 2\text{H}_2\text{O}$	0	- 5.93	"
$\text{Sb}_2\text{O}_5 + 2\text{H}^+ \rightleftharpoons 2\text{SbO}^+ + \text{H}_2\text{O} + \text{O}_2$	0	- 41.66	"
$\text{Sb}_3\text{S}_3 + 2\text{H}_2\text{O} + 6\text{O}_2 \rightleftharpoons 2\text{SbO}^+ + 3\text{SO}_4^{2-} + 4\text{H}^+$	0	339.95	"
$\text{SbCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SbO}^+ + 3\text{Cl}^- + 2\text{H}^+$	0	1.74	"
$\text{SbF}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SbO}^+ + 3\text{F}^- + 2\text{H}^+$	0	- 10.44	Garrels and Christ (1965)
<u>Oxidation-Reduction Reactions</u>			
$\text{Sb(s)} + \text{H}_2\text{O} \rightleftharpoons \text{SbO}^+ + 2\text{H}^+ + 3\text{e}^-$	0	- 10.53	Wagman et al. (1968)
$\text{SbO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{HSbO}_2^\circ + \text{H}^+$	0	- 1.19	"
$\text{HSbO}_2^\circ \rightleftharpoons \text{SbO}_2^- + \text{H}^+$	0	- 11.79	"
<u>Hydrolysis and Other Reactions</u>			
$\text{SbO}^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{Sb(OH)}_3^\circ + \text{H}^+$	0	- 1.18	Wagman et al. (1968)
$\text{SbO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Sb(OH)}_2^+$	0	0.20	Baes and Mesmer (1976); Wagman et al. (1968)
$\text{SbO}^+ + \text{H}_2\text{O} + \text{NH}_4^+ \rightleftharpoons \text{NH}_4\text{SbO}_2^\circ + 2\text{H}^+$	0	- 12.98	Wagman et al. (1968)
$\text{SbO}^+ + \text{F}^- \rightleftharpoons \text{SbOF}^\circ$	0	5.51	"

FIGURE 5. The Activity of SbO^+ in Equilibrium with Various Antimony Solids in an Oxidizing Soil Solution Environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$]

FIGURE 6. The Activity of Various Antimony Species in Equilibrium with $\text{Sb}_2\text{O}_3(\text{s})$ (cubic) with $\text{pNH}_4^+ = 3.0$ and $\text{pF}^- = 4.5$. Oxidation-reduction changes do not affect the concentration of species reports in this figure.

PREDICTED VS. OBSERVED BEHAVIOR OF ANTIMONY

The principal aspect of antimony chemistry that governs its adsorption reactions with soils and rocks over the pH range 4 to 8 is the prevalence of neutral and complexed species (Figure 6). Low K_d values are found in high salt, high pH solutions as well (Serne, 1973), with relatively rapid migration through soils (Haney and Linderoth, 1959; Haney, 1967; Anonymous, 1973) and surface waters (Magno et al., 1970). There are indications that antimony can be precipitated or coprecipitated in solids even at low pH values (Jackson, 1976). In low redox conditions ($O_2 < 10^{-35}$ atmospheres), antimony trihydroxide may precipitate and may be a stable compound that controls antimony concentrations (Figure 5). Many of the antimony species associated with organo-pollutants are water soluble (Saas and Grauby, 1973) and migrate readily with the water. Thermodynamic data on the antimony complexes formed with soil organic materials do not exist at present because the complexes are chemically poorly defined, and in many cases, unknown.

CERIUM

The relative stability of various cerium solid phases is shown in Figure 7. The thermodynamic data of the compounds used in Figure 7 are reported in Table 5. Among the solids depicted in Figure 5, CeO_2 is the only one that changes its position with a change in oxidation-reduction conditions. In an oxidizing environment ($p\text{O}_2 < 23.68 \text{ atm}$), the solids in increasing order of stability are Ce_2O_3 , $\text{Ce}(\text{OH})_3$, CePO_4 , and CeO_2 . Ce_2S_3 is too soluble to plot in Figure 3 in an oxidation-reduction environment where SO_4^{2-} will be the most dominant sulfur species. In oxidation-reduction conditions corresponding to $p\text{O}_2$ of > 23.68 , CePO_4 would be the most stable solid phase.

The activity of various solution species of cerium in equilibrium with CePO_4 (solid) and under such concentrations of F^- , Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-} as commonly found in the environment is shown in Figure 8. The thermodynamic data for the species presented in Figure 8 are reported in Table 5. Since Figure 8 is based on solution complexes in equilibrium with $\text{Ce}(\text{III})$ as CePO_4 , $\text{Ce}(\text{IV})$ ions and complexes would decrease in activity with increase in reducing conditions. In the environmental pH range of interest the $\text{Ce}(\text{IV})$ ions and complexes do not contribute significantly to the total cerium concentration in solution.

Trivalent cerium species in increasing order of importance are CeCl^{2+} , CeNO_3^{2+} , CeF^{2+} , Ce^{3+} , and CeSO_4^+ . Thus, CeSO_4^+ would be the most dominant solution species in the environmental pH range of interest (pH 4 to 8).

FIGURE 7. The Activity of Ce^{3+} in Equilibrium with Phosphate Levels from Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP)

TABLE 5. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Cerium

Reaction	Medium ^(a)	Log K	Reference
<u>Solid Compounds</u>			
$\text{Ce}_2\text{O}_3 + 6\text{H}^+ \rightleftharpoons 2\text{Ce}^{3+} + 3\text{H}_2\text{O}$	0	61.20	Schumm et al. (1973)
$\text{Ce}(\text{OH})_3 + 3\text{H}^+ \rightleftharpoons \text{Ce}^{3+} + 3\text{H}_2\text{O}$	0	19.9	Baes and Mesmer (1976)
$\text{CePO}_4 \rightleftharpoons \text{Ce}^{3+} + \text{PO}_4^{3-}$	dil	- 21.3	Sillen and Martell (1964)
$\text{CeO}_2 + 3\text{H}^+ \rightleftharpoons \text{Ce}^{3+} + 1.5 \text{H}_2\text{O} + 0.25 \text{O}_2$	0	0.47	Schumm et al. (1973)
$\text{Ce}_2\text{S}_3 \rightleftharpoons 2\text{Ce}^{3+} + 3\text{S}^{2-}$	0	- 10.22	Sillen and Martell (1964)
<u>Oxidation-Reduction Reactions</u>			
$\text{Ce(s)} \rightleftharpoons \text{Ce}^{3+} + 3\text{e}^-$	0	117.7	Schumm et al. (1973)
$\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+} + \text{e}^-$	0	29.5	"
<u>Hydrolysis and Other Reactions</u>			
$\text{Ce}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{CeOH}^{3+} + \text{H}^+$	3ClO_4^-	1.1	Baes and Mesmer (1976)
$\text{Ce}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ce}(\text{OH})_2^{2+} + 2\text{H}^+$	3ClO_4^-	0.3	"
$2\text{Ce}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ce}_2(\text{OH})_2^{6+} + 2\text{H}^+$	3ClO_4^-	3.6	"
$2\text{Ce}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Ce}_3(\text{OH})_3^{5+} + 3\text{H}^+$	3ClO_4^-	4.1	"
$2\text{Ce}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Ce}_2(\text{OH})_4^{4+} + 4\text{H}^+$	3ClO_4^-	3.5	"
$2\text{Ce}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ce}_2(\text{OH})_2^{4+} + 2\text{H}^+$	0	- 15.5	"
$3\text{Ce}^{3+} + 5\text{H}_2\text{O} \rightleftharpoons \text{Ce}_3(\text{OH})_5^{4+} + 5\text{H}^+$	0	- 33.5	"
$\text{Ce}^{3+} + \text{F}^- \rightleftharpoons \text{CeF}^{2+}$	0	4.0	Sillen and Martell (1964)
$\text{Ce}^{3+} + \text{Cl}^- \rightleftharpoons \text{CeCl}^{2+}$	0	- 0.78	Schumm et al. (1973)
$\text{Ce}^{3+} + \text{NO}_3^- \rightleftharpoons \text{CeNO}_3^{2+}$	0	1.09	Sillen and Martell (1964)
$\text{Ce}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{CeSO}_4^+$	0	3.47	Schumm et al. (1973)

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, $2(\text{HClO}_4)$ - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0HClO_4 - constant concentration of the substance stated (1.0 moles/liter HClO_4).

FIGURE 8. The Activity of Various Cerium Species in Equilibrium with CePO₄(s) in an Oxidizing Soil Environment [$p_{O_2(g)} = 0.68 \text{ atm}$], $pF^- = 4.5$, $pCl^- = pSO_4^{2-} = 2.5$, $pNO_3^- = 3.0$ and $pH_2PO_4 = 5.0$

PREDICTED VS. OBSERVED BEHAVIOR OF CERIUM

No information is available on solid compounds of cerium that may be present in soils and sediments. It appears that CePO_4 (Figures 7 and 8), especially in alkaline conditions, may form in soils and sediments and may control cerium concentrations.

In all terrestrial environments Ce(IV) and its complexes would have insignificant effects on cerium concentration (Figure 8). Thus, cerium would be expected to be present as Ce(III) (Figure 8 and Ahrens, 1952; Bensen, 1960). In the absence of strong complexing ligands, and especially in acidic environments, cerium would be expected to be present as Ce^{3+} (Figure 8; Bensen, 1960) and ion exchangeable. The increase in pH has been shown to increase the cerium adsorption (Rhodes, 1957; Bensen, 1960; Nishita, et al., 1956; Kokotov, et al., 1962; Kampbell, 1964). As expected, the presence of complexing ligands such as DTPA increases cerium concentration in solution and reduces adsorption (Kampbell, 1964). In slightly acidic (pH 6.5) to alkaline conditions, cerium is thought to be present as radiocolloid which has been shown to increase adsorption (Rhodes, 1957; Brown, et al., 1969). Kampbell (1964) reported that kaolinite, montmorillonite, and illite have a strong affinity for cerium. Cerium adsorbed on suspended solids has been shown to migrate in field and laboratory studies (Magno, et al., 1970; Eichholz, et al., 1967). However, this type of movement would be expected to be dependent upon the particle size of the suspended solids and the pore size distribution of soils and rocks.

CESIUM

Thermodynamic data was collected for the following solid phases of cesium: $\text{Cs}(\text{OH})$, Cs_2O , CsCl , CsClO_4 , Cs_2SO_4 , Cs_2CO_3 , CsHCO_3 , CsNO_3 , CsF . All are highly soluble and, therefore, solid phase diagrams for cesium are not presented.

Baes and Mesmer (1976) report that cesium may be associated with OH^- ions in solution and that the extent of this association cannot be estimated accurately. Charlott (1957) reported that cesium rarely forms solution complexes. Therefore, cesium would be expected to appear in solutions predominantly as Cs^+ . Only 1.5% of the cesium from underground nuclear explosions was found (Izrael et al., 1969) to be colloidal, which may have been adsorbed on other colloids. The main soil and rock reactions with cesium is expected to be ion exchange.

PREDICTED VS. OBSERVED BEHAVIOR OF CESIUM

Cesium mainly exists in solutions as Cs^+ . Therefore, the principal reaction mechanism of cesium adsorption on soils and rocks is expected to be cation exchange. In some instances cesium shows a direct K_d -cation exchange capacity relationship (Routson, 1973), and in other instances, no relation between K_d and exchange capacity (Jacobs, 1962). At trace cesium concentrations competing cation effects are minor (McHenry, 1954), while at 10% or more of the exchange capacity occupied by cesium, the K_d value begins to fall off (Prout, 1958). Potassium is better than sodium or calcium for desorbing cesium (Davis, 1961). There is a tendency for cesium to become "fixed" in 10Å mica-like minerals (Tamura and Jacobs, 1961; Jacobs, 1962; Tamura, 1963; Coleman et al., 1963; Lomenick, 1967), which may be due to a slow desorption rate rather than fixation (Levi and Miekeley, 1967; Routson, 1973). The secondary silicate minerals such as zeolites and clay minerals generally show much higher cesium K_d values than the primary silicate minerals found in igneous rocks (Berak, 1963).

The migration rate of cesium in the groundwater is faster at lower pH values but slower through clays than through sands due to larger clay K_d values (Baetsle et al., 1964). Much of the cesium that migrates in surface waters does so adsorbed on suspended solids (Eichholz et al., 1967; Magno et al., 1970).

Occasionally cesium can migrate through the soil column adsorbed on suspended solids (Carlile and Hajek, 1967). Chelating agents and organic soil materials have little effect on cesium migration through soils (Nishita and Essington, 1967; Knoll, 1969; Salo and Saxen, 1974).

COBALT

The thermodynamic data and their sources for various solid phases of Cobalt are reported in Table 6 and these data are plotted in Figure 9. The stability of cobalt solid phases depends on the pH and the oxidation-reduction environment. For example, in acidic (pH 6) and oxidizing (pO_2 0.68) environments, the solids in increasing order of stability are: $Co(OH)_3$, CoO , $CoHPO_4$, $Co_3(PO_4)_2$, $CoCO_3$, Co_3O_4 , and $CoOOH$ as shown in Figure 9. With the change in oxidation-reduction environment, all the minerals except $Co(OH)_3$, Co_3O_4 , and $CoOOH$ would stay in their relative positions. The latter minerals would decrease in stability. With the change in oxidation-reduction conditions from the extremely oxidizing condition to moderately well oxidized or reducing conditions ($pO_2 > 20$), $CoCO_3$ would be the most stable mineral. Under extremely reducing conditions such as $pO_2 80$, CoS would be the most stable mineral. Cobalt sulfide (CoS) is the chief cobalt ore mineral. In general, the stability of all the cobalt minerals increases with an increase in pH.

Cobalt exists as Co^{2+} and Co^{3+} and forms solution complexes with common soil anions (OH^- , Cl^- , SO_4^{2-} , NO_3^-). The thermodynamic data for different solution species are reported in Table 6. The relative concentration of these solution species in equilibrium with $CoCO_3$ and in an oxidizing environment (pO_2 0.68) is depicted in Figure 10. If a solid phase other than $CoCO_3$ or a constant concentration of Co is chosen for the diagram, the lines will shift up and down, while the relative concentration of various solution species would stay the same.

It can be seen from the Figure 10 that cobaltinuous ion (Co^{2+}) and its solution complexes are the most stable and dominant solution species in the oxidizing environment. The most dominant solution species up to a pH value of approximately 9.5 is Co^{2+} . Beyond pH 9.5, $Co(OH)^{\circ}$ becomes dominant. The activity of Co^{2+} ion in solution decreases 100-fold with an increase of a pH unit, whereas the activity of $Co(OH)^{\circ}_2$ does not change with the pH. These predictions are similar to Baes and Mesmer (1975). If $CoCO_3$ was the solid phase that controlled the solubility, the total cobalt concentration in solution at pH 7 would be approximately $10^{-7}M$ and approximately $10^{-12}M$ at pH 9.5.

TABLE 6. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Cobalt

Reaction	Medium	Log K	Reference
<u>Solid Compounds</u>			
$\text{CoO} + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+} + \text{H}_2\text{O}$	0	13.59	Chase et al. (1975)
$\text{Co}_3\text{O}_4 + 6\text{H}^+ \rightleftharpoons 3\text{Co}^{2+} + 3\text{H}_2\text{O} + 0.5\text{O}_2$	0	13.99	"
$\text{CoOOH} + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+} + 1.5\text{H}_2\text{O} + 0.25\text{O}_2$	0	2.03	Sillen and Martell (1964)
$\text{Co(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+} + 2.5\text{H}_2\text{O} + 0.25\text{O}_2$	0	13.73	"
$\text{Co(OH)}_2(\text{pink}) + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+} + 2\text{H}_2\text{O}$	0	13.04	Wagman et al. (1969)
$\text{Co(OH)}_2(\text{pink aged}) + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+} + 2\text{H}_2\text{O}$	0	12.34	"
$\text{Co(OH)}_2(\text{blue}) + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+} + 2\text{H}_2\text{O}$	0	13.77	"
$\text{CoHPO}_4 \rightleftharpoons \text{Co}^{2+} + \text{PO}_4^{3-} + \text{H}^+$	0	- 18.70	"
$\text{Co}_3(\text{P}_4^0)_2 \rightleftharpoons 3\text{Co}^{2+} + 2\text{PO}_4^{3-}$	0	- 33.94	"
$\text{CoCO}_3 \rightleftharpoons \text{Co}^{2+} + \text{CO}_3^{2-}$	0	- 12.84	Sillen and Martell (1964)
$\text{CoS} + 2\text{O}_2 \rightleftharpoons \text{Co}^{2+} + \text{SO}_4^{2-}$	0	-125.49	Wagman et al. (1969)
<u>Oxidation-Reduction Reactions</u>			
$\text{Co(s)} \rightleftharpoons \text{Co}^{2+} + 2\bar{e}$	0	9.53	Wagman et al. (1969)
$\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+} + \bar{e}$	0	- 32.99	"
<u>Hydrolysis and Other Reactions</u>			
$\text{Co}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CoOH}^+ + \text{H}^+$	0	- 9.65	Baes and Mesmer (1976)
$\text{Co}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_2^0 + 2\text{H}^+$	0	- 18.8	"
$\text{Co}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_3^- + 3\text{H}^+$	0	- 31.5	"
$\text{Co}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Co(OH)}_4^{2-} + 4\text{H}^+$	0	- 46.5	"
$\text{Co}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{CoCl}_2^0$	0	- 0.03	Wagman et al. (1969)
$\text{Co}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CoSO}_4^0$	0	+ 0.02	"
$\text{Co}^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{Co(NO}_3)_2^0$	0	- 0.015	"
$\text{Co}^{2+} + \text{P}_2\text{O}_7^{4-} \rightleftharpoons \text{CoP}_2\text{O}_7^{2-}$	Variable	3.02	Sillen and Martell (1964)
$\text{Co}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{CoSO}_4^+$	2.7(NaClO ₄)	1.34	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO₄) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO₄ - constant concentration of the substance stated (1.0 moles/liter HClO₄).

FIGURE 9. The Relative Stability of Cobalt Solids in an Oxidizing Environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$], $p\text{Ca}^{2+} = 2.5$ and Phosphate Levels in Equilibrium with Variscite and Gibbsite (V and G), Dicalcium and Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP)

FIGURE 10. The Activity of Various Cobalt Ions in Equilibrium with CoCO₃(s) in an Oxidizing Soil Environment [pO₂(g) = 0.68 atm], pCO₂(g) = 1.52 atm, pCl⁻ = pSO₄²⁻ = 2.5, pNO₃⁻ = 3.0 and pH₂PO₄⁻ = 5.0

PREDICTED VS. OBSERVED BEHAVIOR OF COBALT

Discrete cobalt minerals have not been identified in soils. High concentrations of cobalt are required to precipitate cobalt minerals presented in Figure 9 under acidic pH values. It is not likely that any of the minerals would exist in the acidic soil environment. However, in highly alkaline conditions, CoCO_3 would maintain fairly low concentrations of Co in solution and thus could exist in the soil environment.

The thermodynamic data indicates that through a wide pH range ($\text{pH} < 9.5$), cobalt would predominantly exist as Co^{2+} and with the increase in pH it hydrolyzes to CoOH^+ and Co(OH)_2 (Figure 10). These predictions are consistent with the laboratory results as are outlined below. Among the various soil components, Fe_2O_3 (Gonzales and Gomez, 1961) and illite (Friend, 1963; Sorathesn et al., 1960) have been shown to have a strong affinity for cobalt. The adsorption of cobalt by soil minerals have been attributed to mainly an ion exchange phenomenon (Hawkins, 1964; Basu and Mukherjee, 1965). With the increase in pH (especially 6 to 9) the adsorption of cobalt increases (James and Healy, 1972; Tewari, Campbell and Lee, 1972). This increase in adsorption with pH has generally been explained as due to the formation of cobalt colloids (Sorathesn et al., 1960) and hydrolysis of Co^{2+} (Tewari et al., 1972). The presence of various complexing ions such as EDTA, cyanide, and fulvic acids have been shown to reduce the adsorption by soil minerals (Wilding and Rhodes, 1963; Rhodes and Nelson, 1957; Dunigan and Francis, 1972).

Cobalt is apparently relatively easily complexed by natural organics (Duguid, 1976; Means et al., 1976) and by synthetically-produced organics (Haney, 1967; Saas and Grauby, 1973), and as such is able to migrate with relative ease through the soil column with which it would normally react by adsorption.

CURIUM

Curium forms hydride, hydroxide, halides, oxides, and organometallic compounds (Keller, 1971). Except for CmF_3 , a search for thermodynamic data for these compounds was unsuccessful. Therefore, predictions regarding the stability of formation of various compounds of curium in soils cannot be made at this time.

Curium is found in two oxidation states [Cm(III) and Cm(IV)] in aqueous solution (Keller, 1971). Curium (IV) is not stable in solutions because of self-radiation and rapid changes to Cm(III) . Only trivalent curium is stable in aqueous solutions. Keller (1971) reports that the behavior of Cm^{3+} in solution is similar to lanthanide elements. Most of the lanthanides form trivalent hydroxides in natural waters with solubility products of $<10^{-19}$ (Vickery, 1953). Thomas and Jacobs (1969) found that the activity of curium in 0.1M NaCl solutions which contained approximately 10^{-11} m/l of curium decreased at pH values above 3. They attributed this decrease in activity in pure solutions to either precipitation or adsorption on walls. If this is assumed to be due to precipitation, the solubility product of curium hydroxide would be at least as low as the lanthanides, and probably much lower.

Since thermodynamic data for the curium compounds is not available, it was decided to plot the solution species in equilibrium with Cm(OH)_3 with an assumed $\log K^\circ$ of Z for the dissolution of Cm(OH)_3 [$\text{Cm(OH)}_3 + 3\text{H}^+ \rightleftharpoons \text{Cm}^{3+} + 3\text{H}_2\text{O}$] in order to show the relative activity of various solution species of curium with the changes in pH. Keller (1971) reviewed the curium data and stated that little work has been performed on the complex chemistry of curium and since a wide variation occurs in stability constants determined by various authors, these values should be regarded as relative rather than absolute. The thermodynamic data used to develop Figure 11 are reported in Table 7.

It can be seen from Figure 11 that curium forms various solution complexes with OH^- , F^- , Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} . The activity of all the complexes decreases with the increase in pH. The solution complexes of PO_4^{3-} , Cl^- , NO_3^- , do not contribute significantly to the total curium concentration in solutions. The most dominant solution species in pH ranges of <3.3, 3.3-5.7, 5.7 and up are Cm^{3+} , $\text{Cm}(\text{OH})^{2+}$, and $\text{Cm}(\text{OH})_2^+$, respectively.

FIGURE 11. The Activity of Various Curium Ion Species in Equilibrium with $\text{Cm(OH)}_3(\text{s})$ with $\text{pF}^- = 4.5$, $\text{pCl}^- = \text{pSO}_4^{2-} = 2.5$, $\text{pNO}_3^- = 3.0$ and $\text{pH}_2\text{PO}_4^- = 5.0$

TABLE 7. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Curium

Reaction	Medium ^(a)	Log K	Reference
<u>Oxidation-Reduction Reactions</u>			
$\text{Cm}_{(s)} \rightleftharpoons \text{Cm}^{3+} + 3\bar{e}$	0	117.15	Keller (1971)
$\text{Cm}^{3+} \rightleftharpoons \text{Cm}^{4+} + \bar{e}$	0	- 52.40	"
$\text{Cm}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{CmO}_2^+ + 4\text{H}^+ + 2\bar{e}$	0	- 98.05	Nugent (1975)
$\text{Cm}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{CmO}_2^{2+} + 4\text{H}^+ + 3\bar{e}$	0	-131.86	"
<u>Hydrolysis and Other Reactions</u>			
$\text{Cm}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{CmOH}^{2+} + \text{H}^+$	0	- 3.40	Shalinets and Stepanov (1972)
$\text{Cm}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cm}(\text{OH})_2^+ + 2\text{H}^+$	0	- 9.10	"
$\text{Cm}^{3+} + \text{Cl}^- \rightleftharpoons \text{CmCl}^{2+}$	0.5 HClO_4	0.18	Trotman-Dickinson (1973)
$\text{Cm}^{3+} + \text{F}^- \rightleftharpoons \text{CmF}^{2+}$	0.5 HClO_4	3.34	"
$\text{Cm}^{3+} + 2\text{F}^- \rightleftharpoons \text{CmF}_2^+$	0.5 HClO_4	3.34	"
$\text{Cm}^{3+} + 3\text{F}^- \rightleftharpoons \text{CmF}_3^0$	0.5 HClO_4	9.08	"
$\text{Cm}^{3+} + \text{NO}_3^- \rightleftharpoons \text{CmNO}_3^{2+}$	1.0 Na_4ClO_4	0.57	Jones et al. (1969)
$\text{Cm}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{CmSO}_4^+$	0.5 HClO_4	1.86	Trotman-Dickinson (1973)
$\text{Cm}^{3+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{CmH}_2\text{PO}_4^{2+}$	0	2.40	Moskin (1969)
$\text{Cm}^{3+} + \text{PO}_4^{3-} \rightleftharpoons \text{CmPO}_4^0$	0	20.2	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO_4) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO_4 - constant concentration of the substance stated (1.0 moles/liter HClO_4).

PREDICTED VS. OBSERVED BEHAVIOR OF CURIUM

No information is available on possible curium compounds in soils and sediments. It appears that curium precipitation as $\text{Cm}(\text{OH})_3$ in alkaline solutions may control curium concentrations in those solutions. Theoretical calculations (Figure 11) indicate that Cm^{3+} hydrolyzes even in acidic solutions (pH 3.3 and above). Very little reliable information is available on interactions of curium with soils and sediments, and none on curium interactions with rocks. What little data are available indicate that curium adsorption is not a function of ion exchange capacity of the soil (Thomas and Jacobs, 1969; Jacobs et al., 1966), and that precipitation and/or formation of radiocolloids may predominately influence curium adsorption reactions (Thomas and Jacobs, 1969; Sheppard et al., 1976).

EUROPIUM

Europium forms oxides, hydroxides, and salts with chlorides and sulfates [EuO , Eu_2O_3 , Eu_3O_4 , $\text{Eu}(\text{OH})_3$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$]. Thermodynamic data (Table 6) for these solid phases were used to plot the stability of the minerals (Figure 12). It can be seen that, except for the hydroxides [$\text{Eu}(\text{OH})_3$], all the other minerals considered are too soluble in environmental pH ranges of interest (pH 4-10). In Figure 12, $\text{Eu}(\text{OH})_3$, Eu_2O_3 , $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ are the only solids shown. The other solids were too soluble and fall beyond the graph boundaries. Of all the solids considered in Figure 12, $\text{Eu}(\text{OH})_3$ is the most stable in alkaline environments.

Europium can exist as Eu^{2+} and Eu^{3+} . However, Eu^{3+} is the only state which is stable in water (Baes and Mesmer, 1976). The thermodynamic data for various solution species are reported in Table 8. The activity of various solution species of europium in equilibrium with $\text{Eu}(\text{OH})_3$ and at assumed concentrations of various anions commonly found in soils is given in Figure 13.

In a general way the solution complexes of europium in decreasing order of importance can be arranged as follows: $\text{Eu}_2\text{P}_2\text{O}_7^{2+}$, EuSO_4^+ , $\text{Eu}(\text{SO}_4)_2^+$, EuF^{2+} , EuCl^{2+} , and EuNO_3^{2+} . Under the conditions assumed in Figure 13, the predominant solution species in pH ranges of <4.5, 4.5-7.75, 7.5-8.85, and >8.85 will be EuSO_4^+ , $\text{Eu}_2\text{P}_2\text{O}_7^{2+}$, EuSO_4^+ , and EuOH^{2+} , respectively. Thus, significant quantities of uncomplexed europium (Eu^{3+}) can only be expected in soils with very low levels of sulfate and phosphate. The solution complexes of europium with fluoride, chloride, and nitrate do not contribute significantly to total europium concentration in solution and hence can be ignored.

Serne and Rai (1976, unpublished data, Battelle Northwest, Richland, Washington 99352) studied the adsorption-precipitation behavior of europium in soils and pure solutions. The pH of the various europium solutions (0.15M CaCl_2 plus trace to 50 mg Eu/l) was increased in 0.05 pH increments until precipitation was observed by the Tyndall Beam method. At the point of $\text{Eu}(\text{OH})_3$ precipitation, the europium activity and pH was determined. The results are plotted in Figure 14 along with the theoretical $\text{Eu}(\text{OH})_3$ solubility line. The results indicate that:

- 1) the kinetics of precipitation of $\text{Eu}(\text{OH})_3$ is rapid
- 2) the laboratory results agree well with the theoretical $\text{Eu}(\text{OH})_3$ solubility
- 3) Eu^{3+} does not appear to hydrolyze appreciably and does not appear to form strong complexes with chloride, because total europium activity in equilibrium with $\text{Eu}(\text{OH})_3$ is similar to the calculated Eu^{3+} activity
- 4) for meaningful K_d values, the theoretical solubility of $\text{Eu}(\text{OH})_3$ should not be exceeded

Europium adsorption experiments where $\text{Eu}(\text{OH})_3$ did not precipitate were conducted (Serne and Rai, 1976), as shown in Table 9. The results show that the europium K_d increases with an increase in pH and decreases with increasing europium concentration, below the point of $\text{Eu}(\text{OH})_3$ precipitation. These reactions suggest that ion exchange is an active mechanism below the point of $\text{Eu}(\text{OH})_3$ precipitation.

FIGURE 12. The Relative Stability of Various Europium Solids at $p\text{SO}_4^{2-} = 2.5$

TABLE 8. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Europium

Reaction	Medium ^(a)	Log K	Reference
<u>Solid Compounds</u>			
$\text{Eu}(\text{OH})_3 + 3\text{H}^+ \rightleftharpoons \text{Eu}^{3+} + 3\text{H}_2\text{O}$	0	15.92	Schumm et al. (1973)
$\text{Eu}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} \rightleftharpoons \text{Eu}^{3+} + 3\text{SO}_4^{2-} + 8\text{H}_2\text{O}$	0	- 9.80	Latimer (1952)
$\text{EuO} \rightleftharpoons \text{Eu}^{3+} + 0.5\text{O}_2 + 3\text{e}^-$	0	3.01	Schumm et al. (1973)
$\text{Eu}_2\text{O}_3 + 6\text{H}^+ \rightleftharpoons 2\text{Eu}^{3+} + 3\text{H}_2\text{O}$	0	53.02	"
$\text{Eu}_3\text{O}_4 + 8\text{H}^+ \rightleftharpoons 3\text{Eu}^{3+} + 4\text{H}_2\text{O} + \text{e}^-$	0	92.42	"
<u>Oxidation-Reduction Reactions</u>			
$\text{Eu(s)} \rightleftharpoons \text{Eu}^{2+} + 2\text{e}^-$	0	94.65	Schumm et al. (1973)
$\text{Eu}^{2+} \rightleftharpoons \text{Eu}^{3+} + \text{e}^-$	0	5.94	"
<u>Hydrolysis and Other Reactions</u>			
$\text{Eu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{EuOH}^{2+} + \text{H}^+$	0	- 7.8	Baes and Mesmer (1976)
$\text{Eu}^{3+} + \text{Cl}^- \rightleftharpoons \text{EuCl}^{2+}$	0	0.90	Schumm et al. (1973)
$\text{Eu}^{3+} + 2\text{Cl}^- \rightleftharpoons \text{EuCl}_2^+$	0	0.19	"
$\text{Eu}^{3+} + \text{F}^- \rightleftharpoons \text{EuF}^{2+}$	1M(NaClO ₄)	3.19	Walker and Choppin (1971)
$\text{Eu}^{3+} + \text{NO}_3^- \rightleftharpoons \text{EuNO}_3^{2+}$	0	0.31	Schumm et al. (1973)
$\text{Eu}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{EuSO}_4^+$	0	3.55	"
$\text{Eu}^{3+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Eu}(\text{SO}_4)_2^-$	0	5.32	"
$2\text{Eu}^{3+} + 2\text{PO}_4^{3-} \rightleftharpoons \text{Eu}_2\text{P}_2\text{O}_7^{2+} + 0.5\text{O}_2 + 2\text{e}^-$	0	- 0.51	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO₄) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO₄ - constant concentration of the substance stated (1.0 moles/liter HClO₄).

FIGURE 13. The Activity of Various Europium Species in Equilibrium with $\text{Eu}(\text{OH})_3(\text{s})$. Other conditions include $\text{pSO}_4^{2-} = \text{pCl}^- = 2.5$, $\text{pNO}_3^- = 3.0$, $\text{pF}^- = 4.5$ and phosphate levels in equilibrium with variscite and gibbsite (V and G), dicalcium phosphate dihydrate (DCPD), and Octacalcium phosphate (OCP)

FIGURE 14. The Influence of pH on the Activity of Europium in Solution (Serne and Rai, 1976, Unpublished data)

TABLE 9. Effect of pH and Europium Concentration on Europium Kd by Burbank Sand(a) (Serne and Rai, 1976)

Eu, ppm ^(b)	Final pH	Kd, mg/l	Eu, ppm ^(b)	Final pH	Kd, mg/l	Eu, ppm ^(b)	Final pH	Kd, mg/l
0	4.82	46	0.05	5.25	73	5.0	5.20	17.7
0	4.82	48	0.05	5.30	83	5.0	5.20	15.9
0	4.90	51	0.05	5.30	82	5.0	5.25	17.0
0	5.00	75	0.05	5.30	84	5.0	5.32	20.0
0	5.05	70	0.05	5.35	98	50.0	4.70	6.9
0	5.05	69	0.5	4.75	28	50.0	4.70	6.9
0	5.08	75	0.5	4.80	26	50.0	4.73	6.5
0	5.10	84	0.5	4.80	27	50.0	4.88	5.8
0	5.10	78	0.5	5.00	35	50.0	4.90	5.8
0	5.10	78	0.5	5.05	35	50.0	4.90	5.9
0	5.10	82	0.5	5.05	41	50.0	4.90	6.3
0	5.10	75	0.5	5.10	42	50.0	4.90	6.2
0	5.15	93	0.5	5.10	41	50.0	4.90	6.2
0	5.15	90	0.5	5.10	42	50.0	5.00	7.2
0	5.15	81	0.5	5.15	43	50.0	5.00	7.0
0	5.15	93	0.5	5.15	45	50.0	5.00	7.1
0	5.20	94	0.5	5.20	53	50.0	5.15	8.2
0	5.20	98	0.5	5.20	48	50.0	5.15	8.2
0	5.20	98	0.5	5.20	45	50.0	5.20	7.9
0	5.25	107	0.5	5.25	48			
0	5.30	106	0.5	5.25	57			
0	5.30	97	0.5	5.30	54			
0	5.50	153	0.5	5.35	60			
0.05	4.75	32	5.0	4.80	12.4			
0.05	4.75	38	5.0	4.80	11.3			
0.05	4.80	38	5.0	4.80	12.4			
0.05	5.00	63	5.0	4.95	16.9			
0.05	5.00	53	5.0	5.00	18.4			
0.05	5.00	53	5.0	5.05	15.7			
0.05	5.08	56	5.0	5.05	14.8			
0.05	5.08	62	5.0	5.10	15.9			
0.05	5.10	67	5.0	5.10	18.7			
0.05	5.25	71	5.0	5.15	16.4			

(a) One gram samples free of CaCO₃ and soluble salts were used.

(b) Various concentrations of Eu were added to 0.15M CaCl₂ solutions spiked with Eu¹⁵². Samples were equilibrated first for 48 hr and then for 24 hr after adjusting the pH.

PREDICTED VS. OBSERVED BEHAVIOR OF EUROPIUM

No information on possible europium compounds in soils and sediments is available. Serne and Rai (1976) have shown that the kinetics of precipitation of $\text{Eu}(\text{OH})_3$ from pure solutions is rapid. The concentration of europium in equilibrium with $\text{Eu}(\text{OH})_3$ decreases 1000-fold with an increase of one pH unit. The activity of europium in equilibrium with $\text{Eu}(\text{OH})_3$ is low under highly alkaline conditions and $\text{Eu}(\text{OH})_3$ may control europium concentration in alkaline soils and sediments.

Bensen (1960) and Baetsle and Dejonghe (1962) reported that europium appears to be taken up principally by ion exchange below pH 3. Baetsle and Dejonghe (1962) suggested that ion exchange was not the adsorption mechanism above pH 3 because of europium hydrolysis. However, data presented in Figure 13 and the results of Serne and Rai (1976) are at variance with the above conclusion. Serne and Rai (1976) have shown that for meaningful determination of K_d values in soils, one must be below the solubility line of $\text{Eu}(\text{OH})_3$. Their results, thus obtained, showed that between pH 4.7 and 5.5 the K_d decreases with an increase in pH and K_d decreases as europium concentration increases, which suggests an ion exchange as an adsorption mechanism.

IODINE

Most of the compounds of iodine are very soluble. Some of the insoluble or sparingly soluble compounds include the iodides of Pb and Pd, the hypiodites of Ag and Hg, and Ba periodates (Pourbaix, 1966). In normal soils the concentration of most of these elements (Pb, Pd, As, Hg and Ba) with which iodine forms insoluble compounds with is very low. Therefore, they would not be expected to be present in soils.

Iodine can exist in -1, +1, +3, +5, and +7 oxidation states. Out of all of these oxidation states, -1 (I^- , iodide) is the most important and its domain of predominance extends all along the pH scale, almost completely covering a large part of the stability domain of water (Pourbaix, 1966). Thus, it is not surprising that iodine in aqueous solutions free from oxidizing agents generally exists as iodide.

PREDICTED VS. OBSERVED BEHAVIOR OF IODINE

Discrete iodine compounds would not be expected to be present in soils. Iodine in soil solutions would be present as iodide (I^-). Because the anion exchange capacities of most soils are minimal over a normal pH range of 6 to 8, the adsorption of iodide (I^-), iodate (IO_3^-) and organic-iodine molecules is normally also minimal (Wildung et al., 1975). However, with soils of low pH (4 to 6), the iodide K_d value can rise to 50 ml/g. Wildung et al. (1975) reported no statistical correlation between organic content and iodide K_d , as they did for methyl iodide. The range of methyl iodide K_d values was from 0.1 to 3.1, much lower than the iodide ion K_d range, even though the correlation between methyl iodide K_d values and soil organic content was statistically significant. Others (Sinitskaya, 1969; Irinevich et al., 1970; Pennington and Lishman, 1971) have shown a positive correlation between iodine content and organic material in the soil where the iodine is apparently covalently bonded to carbon (Walters and Winchester, 1971). It should be kept in mind that iodine, especially when present as an organic-iodine molecule, can change to a vapor phase and migrate much more rapidly than in an aqueous phase.

NEPTUNIUM

The thermodynamic data are lacking for neptunium compounds other than oxide and hydroxides (Table 10). Figure 15 relates the activity of NpO_2^+ to pH under an oxidizing environment ($p\text{O}_2$ 0.68) in equilibrium with neptunium oxide and hydroxides. Since Figure 15 was made using Np(V) (NpO_2^+) as the y axis, the solubility of Np(IV) minerals would decrease and Np(VI) minerals would increase with an increase in reducing conditions. In an oxidizing environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$] the solids in an increasing order of stability are Np(OH)_4 , NpO_2 , NpO_2OH , $\text{NpO}_2(\text{OH})_2$. Under the oxidation-reduction conditions represented by $p\text{O}_2(\text{g}) > 3.8 \text{ atm}$, NpO_2 would be the most stable compound. Since NpO_2 maintains very high concentrations of neptunium in solution, especially in acidic and very oxidizing environments, it is unlikely that NpO_2 would be found as a discrete solid in such terrestrial environments. It may exist in very reducing conditions.

The activity of various solution complexes of neptunium in equilibrium with $\text{NpO}_2(\text{s})$ under an oxidizing environment ($p\text{O}_2 = 0.68$) and assumed weathering environment is given in Figure 16. Thermodynamic data for different solution complexes of Np are given in Table 10. The solution complexes of Np(IV) , Np(V) , and Np(VI) in order of increasing importance are Np(IV) , Np(VI) , and Np(V) . The activity of Np(IV) and Np(VI) complexes is so small that these complexes can be safely ignored since they would not contribute significantly to the total activity of Np in solution (Burney and Harbour, 1974). The lines of Np(V) and Np(VI) complexes will shift downward with the increase in reducing environment but still be parallel to the present lines. Under the conditions assumed in Figure 16, NpO_2^+ is the most dominant solution species in a pH range of 0 to approximately 9. Beyond pH 9, $\text{NpO}_2\text{HPO}_4^-$ and $\text{NpO}_2\text{HCO}_3^-$ would control the total concentration of neptunium in solution.

NpO_2^+ is the usual form of charged neptunium species up to pH 9. Above pH 9, an uncharged bicarbonate complex is formed. According to Keller (1971) and the data presented in Figure 16, neptunium (V) does not hydrolyze below a pH of 7. Hence, a singly charged neptunyl ion would be expected to control geologic media interactions with neptunium.

TABLE 10. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Neptunium

Reaction	Medium ^(a)	Log K	Reference
<u>SOLID COMPOUNDS</u>			
$\text{Np}(\text{OH})_3 + 3\text{e}^- \rightleftharpoons \text{Np}(\text{s}) + 3\text{OH}^-$	1.0 NaOH	-114.11	Burney and Harbour (1974)
$\text{Np}(\text{OH})_4 \rightleftharpoons \text{Np}^{4+} + 4\text{OH}^-$	0	- 55.22	"
$\text{NpO}_2(\text{OH}) \rightleftharpoons \text{NpO}_2^+ + \text{OH}^-$	0	- 9.09	"
$\text{NpO}_2(\text{OH})_2 \rightleftharpoons \text{NpO}_2^{2+} + 2\text{OH}^-$	0	- 22.70	"
$\text{NpO}_2 + 4\text{H}^+ \rightleftharpoons \text{Np}^{4+} + 2\text{H}_2\text{O}$	0	- 2.68	Keller (1971)
<u>OXIDATION-REDUCTION REACTIONS</u>			
$\text{Np}^{3+} + 3\text{e}^- \rightleftharpoons \text{Np}(\text{s})$	0	- 94.13	Burney and Harbour (1974)
$\text{Np}^{4+} + \text{e}^- \rightleftharpoons \text{Np}^{3+}$	0	2.57	"
$\text{NpO}_2^+ + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{Np}^{4+} + 2\text{H}_2\text{O}$	0	12.66	"
$\text{NpO}_2^{2+} + \text{e}^- \rightleftharpoons \text{NpO}_2^+$	0	19.42	"
$\text{NpO}_2^{3+} + \text{e}^- \rightleftharpoons \text{NpO}_2^{2+}$	1.0 KOH	10.31	Keller (1971)
<u>HYDROLYSIS REACTIONS</u>			
$\text{Np}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{NpOH}^{3+} + \text{H}^+$	0	- 2.05	Burney and Harbour (1974)
$\text{NpO}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2\text{OH}^+ + \text{H}^+$	0	- 10.0	"
$\text{NpO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2\text{OH}^+ + \text{H}^+$	0	- 3.37	"
<u>OTHER REACTIONS</u>			
$\text{NpO}_2^+ + \text{HCO}_3^- \rightleftharpoons \text{NpO}_2\text{HCO}_3^\circ$	0	2.43	Burney and Harbour (1974)
$\text{Np}^{4+} + \text{Cl}^- \rightleftharpoons \text{NpCl}^{3+}$	1.0 HClO ₄	- 0.04	"
$\text{Np}^{4+} + 2\text{Cl}^- \rightleftharpoons \text{NpCl}_2^{2+}$	1.0 HClO ₄	- 0.24	"
$\text{NpO}_2^+ + \text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}^\circ$	2.0 HCl	- 0.30	"
$\text{NpO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}^+$	0.4 NaClO ₄	- 0.35	"
$\text{Np}^{4+} + \text{F}^- \rightleftharpoons \text{NpF}^{3+}$	4.0 HClO ₄	4.82	"
$\text{NpO}_2^{2+} + \text{F}^- \rightleftharpoons \text{NpO}_2\text{F}^+$	1.0 HClO ₄	3.86	"
$\text{NpO}_2^{2+} + 2\text{F}^- \rightleftharpoons \text{NpO}_2\text{F}_2^\circ$	1.0 HClO ₄	6.97	"
$\text{Np}^{4+} + \text{NO}_3^- \rightleftharpoons \text{NpNO}_3^{3+}$	1.0 HClO ₄	0.38	"
$\text{Np}^{4+} + 2\text{NO}_3^- \rightleftharpoons \text{Np}(\text{NO}_3)_2^{2+}$	1.0 HClO ₄	0.08	"
$\text{NpO}_2^+ + \text{NO}_3^- \rightleftharpoons \text{NpO}_2\text{NO}_3^\circ$	2.0 HClO ₄	- 0.25	"
$\text{NpO}_2^{2+} + \text{NO}_3^- \rightleftharpoons \text{NpO}_2\text{NO}_3^+$	0.4 HClO ₄	- 0.98	"
$\text{NpO}_2^+ + \text{HPO}_4^{2-} \rightleftharpoons \text{NpO}_2\text{HPO}_4^-$	0	3.38	Sillen and Martell (1964)
$\text{Np}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{NpSO}_4^{2+}$	2.0 HClO ₄	2.43	Burney and Harbour (1974)
$\text{Np}^{4+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Np}(\text{SO}_4)_2^\circ$	2.0 HClO ₄	3.47	"
$\text{NpO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{NpO}_2\text{SO}_4^\circ$	1.0 HClO ₄	1.90	"
$\text{NpO}_2^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{NpO}_2(\text{SO}_4)_2^{2-}$	1.0 HClO ₄	2.77	"

(a) The nature of the medium to which the equilibrium constants refer; for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO₄) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO₄ - constant concentration of the substance stated (1.0 moles/liter HClO₄).

FIGURE 15. The Relative Stability of Various Neptunium Solids in an Oxidizing Soil Environment [$p\text{O}_2(\text{g}) = 0.68 \text{ atm}$]

FIGURE 16. The Activity of Various Neptunium Species in Equilibrium with NpO₂(s) under pO₂ = 0.68, pCl⁻ = pSO₄²⁻ = 2.5, pNO₃⁻ = 3.0, pF⁻ = 4.5 and pH₂PO₄⁻ = 5.0

PREDICTED VS. OBSERVED BEHAVIOR OF NEPTUNIUM

The existing thermodynamic data (Figure 16) show that neptunium should exist in an oxidizing soil environment as Np(V) in the form of NpO_2^+ . However, existing adsorption results, essentially only a study by Routson et al. (1975, 1976) and Sheppard et al. (1976), inferred that there is little evidence of NpO_2^+ ion exchange as a neptunium adsorption mechanism. Sheppard et al. (1976) reported neptunium colloids present in the soil-solution environment, while Routson et al. (1975, 1976) specifically showed that they were absent from his solutions that had contacted soils. It is fairly certain that neptunium K_d values are generally low. Little more can be said based on the adsorption and migration studies now available in the literature. Additional research is required on neptunium-soil and rock reactions.

PLUTONIUM

The selected thermodynamic data for Plutonium compounds and solution species are reported in Table 11. Figure 17 relates the activity of Pu^{4+} to pH in an oxidizing environment [$p\text{O}_{2(g)} = 0.68 \text{ atm}$] in equilibrium with various Pu solid phases. Any solid in Figure 17 that lies below another solid, at a given pH, is the more stable. Thus, for any two solid phases at a specific pH, the solid that maintains lower Pu^{4+} activity is more stable. Under the assumptions outlined in Figure 17 and at pH 6, the plutonium compounds in order of increasing stability are: $\text{Pu}(\text{OH})_3$; $\beta\text{Pu}_2\text{O}_3$; PuF_4 ; PuF_3 ; $\text{Pu}(\text{HPO}_4)_2$; PuO_2OH ; PuO_2CO_3 ; $\text{Pu}(\text{OH})_4$; $\text{PuO}_2(\text{OH})_2$; and PuO_2 . Among the solids reported in Figure 15, PuO_2 is the most stable mineral under oxidizing conditions at all pH values.

The stabilities of plutonium solid compounds in a reducing environment [$p\text{O}_{2(g)} = 80 \text{ atm}$] are represented in Figure 18. In general, the reducing environment substantially changes the stabilities of the solids. Comparing Figures 17 and 18, it can be seen that the Pu(IV) solids remain unchanged, while Pu(III) solids increase and Pu(V and VI) solids decrease in their stabilities with the decrease in the oxygen pressure. Plutonium solids in the reducing environment at pH 6 can be arranged in order of increasing stability as follows: $\text{PuO}_2(\text{OH})_2$; PuO_2OH ; PuF_4 ; $\text{Pu}(\text{HPO}_4)_2$; $\text{Pu}(\text{OH})_3$; $\beta\text{Pu}_2\text{O}_3$; $\text{PuO}_2(\text{OH})_2$; PuF_3 ; and PuO_2 . PuF_3 would be the most stable solid compound below pH 4. Above this pH value, PuO_2 would be the most stable solid (Figure 18). Based upon the Eh-pH diagrams for plutonium oxides, and hydroxides, Polzer (1971) predicted $\text{PuO}_2(\text{s})$ to be the most stable solid phase under conditions generally found in the environment. However, the relative stabilities of Pu compounds other than hydroxides and oxides, and predictions regarding weathering sequences, were not considered by Polzer (1971).

Knowledge of the most stable compound present in the soil is necessary in order to predict the behavior or fate of the element in the soil. An extensive review on actinides indicated that numerous workers have studied the plutonium concentration and distribution with depth in soils. However, with the exception of Price and Ames (1975), none have made any attempt to

identify the solid phases of plutonium present in soils. Price and Ames (1975) reported the presence of PuO_2 under both alkaline and acidic oxidizing environments. Their observations were made approximately 20 years after the acidic radioactive waste was disposed to the alkaline soils. Tamura (1974) inferred the presence of PuO_2 in aridisols or entisols from the Nevada Test Site. Thus, the Price and Ames, and Tamura results confirm theoretical predictions regarding the most stable plutonium compound expected to be present in soils. However, if the soil solution activity of plutonium is lower than the solubility product of PuO_2 and any other possible compound, the final solution activities will depend mainly on the cation exchange processes and the coprecipitation of plutonium with other soil minerals.

Figure 19 demonstrates the activity of various plutonium species expected in equilibrium with $\text{PuO}_2(\text{s})$ and in an oxidizing environment ($p\text{O}_2$ 16 atm). Plutonium in solution exists in four oxidation states (Pu^{3+} , Pu^{4+} , PuO_2^+ , PuO_2^{2+}) and forms complexes with OH^- , Cl^- , F^- , SO_4^{2-} , H_2PO_4^- and CO_3^{2-} ions. In general, the activity of all positively charged ions and ion-complexes and a few neutral ion-pairs decreases with the increase in pH, while the activity of all negatively charged ion-complexes increases with the increase in pH. In an oxidizing environment, Pu^{3+} and Pu^{4+} and their ion-pairs have an insignificant effect on the total activity of plutonium in solution. At any given pH, the total activity of plutonium in solution can be obtained by adding the appropriate activities of various plutonium species. Since the lines for some plutonium species are based on concentration constants, the position of the lines may change when converted to thermodynamic equilibrium constants. Figures 19 and 20 were constructed by assuming a weathering environment ($p\text{CO}_2 = 3.52$; $p\text{Cl}^- = p\text{SO}_4^{2-} = 2.5$; $p\text{F}^- = 3.5$) and $\text{PuO}_2(\text{s})$ as the compound that may be present in the soil at equilibrium. When diagrams are constructed for an actual weathering environment of a given soil, all the organic and inorganic ligands present in the soil solution should be considered. Figures 19 and 20 were developed for selected inorganic ligands only.

Figure 20 relates the activities (a_i , moles/liter) of various solution species at pH 8 to the oxidation potential as represented by the various oxygen pressures. In general, with a decrease in oxygen pressure (increase in reducing conditions), the kind of activity of the solution species changes: 1) Pu^{3+} species increase in activity; 2) Pu^{4+} species are unaffected; and 3) PuO_2^+ and PuO_2^{2+} species decrease in activity. However, in doing so, the total activity of plutonium in solution at any given pH would not change significantly because the activity of species for which thermodynamic equilibrium constants are known is very large as compared to the others. When the concentration constants are converted to thermodynamic constants, the new lines would shift downward or upward but remain parallel to the present lines. The activities of various species would still vary in the same direction with the changes in pH as reported in Figure 19.

A few of the reactions are not plotted in the figures because either the activities of the species fall beyond the graph boundaries or the equilibrium constant data are not reliable. Cleveland (1970) suggested that the values for the formation constants of PuCO_3^{2+} and $\text{Pu}(\text{OH})_4^\circ$ were suspect; the values for $\text{PuO}_2(\text{OH})_3$, $\text{PuO}_2(\text{O})_2^\circ$, and PuO_2OH^+ should be viewed with skepticism; and the value for $\text{PuO}_2\text{OH}^\circ$ should be considered only approximate. Under the assumptions of Figure 19, the lines for $\text{Pu}(\text{OH})_4^\circ$ and $\text{PuO}_2(\text{OH})_2^\circ$ would be parallel to the X-axis with $10^{-12.51}$ and $10^{-19.16}$ moles/l activity, respectively. Many researchers (Andelman and Rozzell, 1970; Fukai and Murray, 1974; Grebenshchikova and Davydov, 1961, 1965; Sheidina and Kovarskaya, 1970) have reported that plutonium in solution also exists as colloidal species over a wide pH range. Colloidal species and neutral ion-complexes [$\text{Pu}(\text{OH})_4^\circ$, $\text{PuO}_2(\text{OH})_2^\circ$] are not reported in Figures 19 and 20. If present in large quantities, these species would significantly influence the nature of the species and the total concentration of plutonium in solutions.

For the conditions specified in Figure 19, the dominant plutonium species in low and high pH ranges are PuO_2^+ and $\text{PuO}_2\text{CO}_3\text{OH}^-$, respectively. The colloid complex of soils is mainly negatively charged. Therefore, positively charged species are usually absorbed by soils in cation exchange processes. Since positively charged PuO_2^+ species predominate only in solutions of pH values

<6, cation exchange adsorption of plutonium by soils would be limited to acidic soils (pH <6). The negatively charged $\text{PuO}_2\text{CO}_3\text{OH}^-$ complex that predominates above pH 8 [even when the activity of $\text{PuO}_2\text{CO}_3\text{OH}^-$ is compared to $\text{Pu}(\text{OH})^\circ_4$] should not be readily adsorbed by the soils. Thus, the activity of plutonium in soil solutions of pH >8 would be relatively high because of: 1) little soil adsorption of negatively charged ions; and 2) increases in the activities of negatively charged ions with the increase in pH. Similarly, under extremely low pH conditions the activity of plutonium in soil solutions in equilibrium with $\text{PuO}_2(\text{s})$ may also be high. Rhodes (1957a) found low adsorption of plutonium by soils in the pH range of approximately <2 and 8 to 13. Thus, his results confirm part of the predictions based on Figure 19; continuous decrease in adsorption is predicted with the increase in pH above 8, whereas Rhodes' data indicated first a decrease in adsorption to pH 12 and then an unexplained continuous increase in adsorption above pH 12.

TABLE 11. Selected Equilibrium Constants (K) at 25°C and 1 atm Pressure for Reactions Involving Plutonium

Reaction	Medium ^(a)	Log K	Reference
<u>Solid Compounds</u>			
$\text{PuO}_2 + 4\text{H}^+ \rightleftharpoons \text{Pu}^{4+} + 2\text{H}_2\text{O}$	0	- 6.50 ^(b)	Cleveland (1970)
$\text{Pu}_2\text{O}_3(\beta) + 6\text{H}^+ \rightleftharpoons 2\text{Pu}^{4+} + 3\text{H}_2\text{O} + 2\bar{e}$	0	11.59 ^(b)	Cleveland (1970); and Keller (1971)
$\text{Pu}(\text{OH})_3 \cdot x\text{H}_2\text{O} \rightleftharpoons \text{Pu}^{3+} + 3\text{OH}^- + x\text{H}_2\text{O}$	0	- 19.7	Cleveland (1970)
$\text{Pu}(\text{OH})_4 \cdot x\text{H}_2\text{O} \rightleftharpoons \text{Pu}^{4+} + 4\text{OH}^- + x\text{H}_2\text{O}$	0	- 55.15	Sillen and Martell (1964)
$\text{PuO}_2\text{OH} \rightleftharpoons \text{PuO}_2^+ + \text{OH}^-$	0	- 9.30	Cleveland (1970)
$\text{PuO}_2(\text{OH})_2 \rightleftharpoons \text{PuO}_2^{2+} + 2\text{OH}^-$	0	- 24.52	"
$\text{PuCl}_3 \rightleftharpoons \text{Pu}^{3+} + 3\text{Cl}^-$	0	11.44 ^(b)	"
$\text{PuO}_2\text{CO}_3 \rightleftharpoons \text{PuO}_2^{2+} + \text{CO}_3^{2-}$	1.0	- 12.77	Sillen and Martell (1964)
$(\text{NH}_4)_2\text{PuO}_2(\text{CO}_3)_2 \rightleftharpoons 2\text{NH}_4^+ + \text{PuO}_2^{2+} + 2\text{CO}_3^{2-}$	1.0	- 1.33	"
$\text{PuF}_3 \rightleftharpoons \text{Pu}^{3+} + 3\text{F}^-$	0	- 15.6	"
$\text{PuF}_4 \rightleftharpoons \text{Pu}^{4+} + 4\text{F}^-$	0	- 19.22	Cleveland (1970)
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O} \rightleftharpoons \text{Pu}^{4+} + 2\text{HPO}_4^{2-} + x\text{H}_2\text{O}$	0	- 27.7	"
$\text{K}_4\text{Pu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons 4\text{K}^+ + \text{Pu}^{4+} + 4\text{SO}_4^{2-} + 2\text{H}_2\text{O}$	0	- 18.0	Keller (1971)
<u>Oxidation-Reduction Reactions</u>			
$\text{Pu}^{3+} + 3\bar{e} \rightleftharpoons \text{Pu}(\text{s})$	0	-103.0	Sillen and Martell (1964)
$\text{Pu}^{4+} + \bar{e} \rightleftharpoons \text{Pu}^{3+}$	0	16.37	"
$\text{PuO}_2^+ + 4\text{H}^+ + \bar{e} \rightleftharpoons \text{Pu}^{4+} + 2\text{H}_2\text{O}$	0	19.50 ^(b)	"
$\text{PuO}_2^{2+} + \bar{e} \rightleftharpoons \text{PuO}_2^+$	0	15.7	"
<u>Hydrolysis Reactions</u>			
$\text{Pu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{PuOH}^{2+} + \text{H}^+$	0	- 6.95	Sillen and Martell (1964)
$\text{Pu}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{PuOH}^{3+} + \text{H}^+$	2.0 (ClO ₄ ⁻)	- 1.27	"
$\text{Pu}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})_4^\circ + 4\text{H}^+$	3.5 (KCl) at 20°C	- 6.01 ^(b)	"
$\text{PuO}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2\text{OH}^\circ + \text{H}^+$	0	- 9.7	"
$\text{PuO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2\text{OH}^+ + \text{H}^+$	0	- 5.30	Cleveland (1970)
$\text{PuO}_2\text{OH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2(\text{OH})_2^\circ + \text{H}^+$	0	- 5.71	"
$\text{PuO}_2(\text{OH})_2^\circ + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2(\text{OH})_3^- + \text{H}^+$	0	- 9.70	"
$2\text{PuO}_2^{2+} + 3\text{H}_2\text{O} \rightleftharpoons (\text{PuO}_2)_2(\text{OH})_3^+ + 3\text{H}^+$	Var at 20°C	- 6.28	Sillen and Martell (1964)
$2\text{PuO}_2^{2+} + 5\text{H}_2\text{O} \rightleftharpoons (\text{PuO}_2)_2(\text{OH})_5^- + 5\text{H}^+$	Var at 20°C	- 22.10	"
$2\text{PuO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{PuO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	1.0 (Na)ClO ₄	- 8.51	Cassol et al. (1972)

TABLE 11. (Continued)

Reaction	Medium ^(a)	Log K	Reference
<u>Other Reactions</u>			
$\text{Pu}^{4+} + \text{CO}_3^{2-} \rightleftharpoons \text{PuCO}_3^{2+}$	10.0 (KCl) at 20°C	46.96	Sillen and Martell (1964)
$\text{PuO}_2^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2\text{CO}_3^0$	1.0	12.0	"
$\text{PuO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2(\text{CO}_3)_2^{2-}$	0	15.04	Cleveland (1970)
$\text{PuO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2(\text{CO}_3)_3^{4-}$	1.0	2.09	Sillen and Martell (1964)
$\text{PuO}_2^{2+} + \text{CO}_3^{2-} + \text{OH}^- \rightleftharpoons \text{PuO}_2\text{CO}_3\text{OH}^-$	0	23.85	Cleveland (1970)
$\text{PuO}_2^{2+} + \text{CO}_3^{2-} + 2\text{OH}^- \rightleftharpoons \text{PuO}_2\text{CO}_3(\text{OH})_2^{2-}$	0	23.0	"
$\text{Pu}^{3+} + \text{HCl} \rightleftharpoons \text{PuCl}^{2+} + \text{H}^+$	0	- 2.4	"
$\text{Pu}^{4+} + \text{Cl}^- \rightleftharpoons \text{PuCl}^{3+}$	1.0	0.15	Keller (1971)
$\text{PuO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{PuO}_2\text{Cl}^0$	0	- 0.17	Sillen and Martell (1964)
$\text{PuO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{PuO}_2\text{Cl}^+$	2.0	0.10	Cleveland (1970)
$\text{PuO}_2\text{Cl}^+ + \text{Cl}^- \rightleftharpoons \text{PuO}_2\text{Cl}_2^0$	2.0	- 0.45	"
$\text{Pu}^{4+} + \text{F}^- \rightleftharpoons \text{PuF}^{3+}$	0	7.94	Sillen and Martell (1964)
$\text{Pu}^{4+} + \text{NO}_3^- \rightleftharpoons \text{PuNO}_3^{3+}$	1.02	0.72	Keller (1971)
$\text{Pu}^{4+} + \text{HPO}_4^{2-} \rightleftharpoons \text{PuHPO}_4^{2+}$	2.0 HNO_3	12.92	Sillen and Martell (1964)
$\text{PuHPO}_4^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{Pu}(\text{HPO}_4)_2^0$	2.0 HNO_3	10.82	"
$\text{PuO}_2^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{PuO}_2(\text{H}_2\text{PO}_4)^+$	Var(0.02-0.206)	3.93	Cleveland (1970)
$\text{Pu}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{PuSO}_4^+$	1.0 (H^+)	1.26	"
$\text{Pu}^{3+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{HSO}_4)_2^+$	1.0 (H^+)	1.0	"
$\text{Pu}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{PuSO}_4^{2+} + \text{H}^+$	0.5	0.98	"
$\text{Pu}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_2^0 + 2\text{H}^+$	0.5	1.30	"
$\text{Pu}^{4+} + 3\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_3^{2-} + 3\text{H}^+$	0.5	2.10	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO_4) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO_4 - constant concentration of the substance stated (1.0 moles/liter HClO_4).

(b) These equilibrium constants were calculated from the data in the given reference and the other appropriate data included in the tables or given in standard references.

FIGURE 17. The Relative Stability of Plutonium Solids Under $pO_2 = 0.68$, $pCO_2 = 3.52$, $pF^- = 3.5$ and Phosphate Levels in Equilibrium with Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP) (Rai and Serne, 1977)

FIGURE 18. The Relative Stability of Various Plutonium Solids in Reducing Environments ($pO_2 = 80$), $pCO_2 = 3.52$, $pF^- = 3.5$, and Phosphate Levels in Equilibrium with Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP) (Rai and Serne, 1977)

FIGURE 19. The Activity of Various Plutonium Species in Equilibrium with $\text{PuO}_2(\text{s})$ Under $p\text{O}_2 = 16$, $p\text{CO}_2 = 3.52$, $p\text{Cl}^- = 2.5$, $p\text{F}^- = 3.5$, and $p\text{H}_2\text{PO}_4^- = 5.0$ (Rai and Serne, 1977)

FIGURE 20. The Activity of Various Plutonium Species in Equilibrium with $\text{PuO}_2(\text{s})$ at $\text{pH } 8$, $\text{pCO}_2 = 3.52$, $\text{pCl}^- = \text{pSO}_4^{2-} = 2.5$, and $\text{pH}_2\text{PO}_4 = 5.0$ (Rai and Serne, 1977)

PREDICTED VS. OBSERVED BEHAVIOR OF PLUTONIUM

In most oxidizing environments, ionic plutonium is expected to be present in solution predominantly as Pu(V) or Pu(VI) (Figures 19 and 20). With high plutonium concentrations, PuO_2 could be expected as a stable solid phase (Figures 17 and 18). The plutonium adsorption data indicate that more than one mechanism is operating during reactions with rocks and soils. There is a direct correlation of plutonium adsorption results with soil cation exchange capacities (Thorburn, 1950; Evans, 1956; Rhodes, 1952, 1957a, 1957b; Van Dalen et al., 1975; Glover et al., 1977) indicating that part of the adsorption is due to ion exchange. However, little effect on adsorption was obvious from competing cation concentrations that were very high (Rhodes, 1957a; Mo and Lowman, 1975). Perhaps the principal correlation of plutonium adsorption is with pH (Rhodes, 1952, 1957a, 1957b; Knoll, 1965; Hajek and Knoll, 1966; Knoll, 1969). A relatively rapid soil column breakthrough of plutonium was obtained with a low pH (<1) solution (Knoll, 1965). Strong adsorption occurs over the pH range of from 4 to 8 (Prout, 1958, 1959), but above pH 8 the formation of negative complexes or polymers with low charge densities can cause lowered adsorption (Thorburn, 1950; Rhodes, 1957a; Polzer and Miner, 1977). In addition, plutonium is easily complexed with humic acids (Desai and Ganguly, 1970; Bondietti et al., 1975) and with oxalate (Bensen, 1960), acetate (Rhodes, 1957a) and a large number of phosphorus-bearing organics used in the nuclear fuels reprocessing industry (Knoll, 1969). Complexed plutonium also can result from soil fungal or microbial activities (Wildung et al., 1973, 1977; Au, 1974) all of which result in more mobile plutonium. Even the precipitated or adsorbed plutonium can be readily moved through the aqueous environments in the form of particulates or suspended sediments (Magno et al., 1970; Emery et al., 1974a, 1974b, 1975; Meyer, 1975; Montgomery et al., 1977). If the Eh environment allows it, Pu(IV) can be oxidized to Pu(V) or (VI), with much lower plutonium adsorption values resulting (Bondietti, 1974). The plutonium polymers usually are adsorbed readily, but can migrate more rapidly than soluble plutonium in some instances where the surface charge density is low (Friedman et al., 1977). Much experimental

work remains to be done to separate and understand the several reactions mechanisms occurring in plutonium adsorption on rocks or soils. A controlled Eh environment for the adsorption work is important as an experimental condition when an element disproportionates as readily as plutonium.

PROMETHIUM

Promethium forms crystalline compounds with F^- , Cl^- , Br^- , I^- , OH^- , PO_4^{3-} , AsO_4^{3-} , BO_3^{3-} , CrO_4 , CrO_3 , MoO_4^{2-} , WO_4^{2-} , VO_4^{3-} , ScO_3^{3-} (Lavrukhina and Pozdnyakov, 1970; Wheelwright, 1973). However, the thermodynamic data are only available for $Pm(OH)_3 \rightleftharpoons Pm^{3+} + 3OH^-$ with $\log K^\circ$ of -34 (Sillen and Martell, 1964) and for $Pm_2O_3 + 6H^+ \rightleftharpoons 2Pm^{3+} + 3H_2O$ with $\log K^\circ$ of 42.04 (Pourbaix, 1966). It is evident that $Pm(OH)_3$ is more stable than Pm_2O_3 (Figure 21). The Pm^{3+} activity in equilibrium with $Pm(OH)_3$ decreases a thousand-fold with a one unit increase in pH.

Promethium is a lanthanide and like most lanthanides exists in a trivalent state (Pm^{3+}). No data were found on solution species of promethium except for $PmNO_3^{2+}$ ($Pm^{3+} + NO_3^- \rightleftharpoons PmNO_3^{2+}$, $\log K^\circ$ at $I = 1$ is 2.48) (Lavrukhina and Pozdnyakov, 1970). The solution species is probably predominantly Pm^{3+} , much like europium. If it is assumed that promethium does not form any other complexes, then the concentration of promethium in solution will be governed mainly by Pm^{3+} . Under these conditions, ion exchange can be an important promethium removal mechanism in acidic environments and at trace promethium concentrations.

FIGURE 21. The Relative Stability of Various Promethium Solids

PREDICTED VS. OBSERVED BEHAVIOR OF PROMETHIUM

Low concentrations of promethium are expected in equilibrium with $\text{Pm}(\text{OH})_3$ in slightly acidic to slightly alkaline conditions (Figure 21) so that $\text{Pm}(\text{OH})_3$ precipitation may control promethium concentrations in soil and sediment solutions. Promethium, like europium, would be expected to be ion exchangeable below the concentration required for $\text{Pm}(\text{OH})_3$ precipitation. Only limited data are available on promethium adsorption on soils and sediments, but these data tend to support the above predictions.

The removal of promethium is nearly complete on soils and rocks above pH 6 (Bensen, 1960). The effect of competing cations on promethium adsorption above pH 7 is minimal. Below pH 3, the adsorption of all rare earths including promethium are similarly depressed by competing salts. Charged polymers can form under the proper conditions during $\text{Pm}(\text{OH})_3$ precipitation (Starik et al., 1959; Bensen, 1960). Citrate, acetate and carbonate ions inhibited rare earth adsorption on soils, probably due to the formation of complex ion species. Over 90% of the promethium discharged to a lagoon system remained in the lagoon (Magno et al., 1970) as strongly adsorbed on clay particles or present as an insoluble hydroxide (Schulz, 1965). Promethium can be removed from solution during replacement reactions (Ames, 1960).

RADIUM

The thermodynamic data for radium compounds are available only for radium nitrate, chloride, iodate and sulfate (Parker et al., 1971). However, all of the compounds except sulfate are very soluble. Therefore, solid phase diagrams are not presented for radium compounds. The solubility product for RaSO_4 is $10^{-10.37}$ compared to $10^{-9.96}$ for BaSO_4 .

No thermodynamic data were located for radium hydrolysis or complex ion species. It is expected the radium will behave in the soil solution much like strontium does. The species Ra^{2+} is expected to be the most important over the normal soil pH range from 4 to 8.

PREDICTED VS. OBSERVED BEHAVIOR OF RADIUM

Radium is present as Ra^{2+} over the normal soil pH range (4 to 8) and shows little tendency to form complex species (Schubert et al., 1950). Radium would be expected to substitute for other divalent cations during replacement or precipitation reactions (Granger et al., 1961; Granger, 1963). A direct correlation of cation exchange capacity with adsorption (Arnold and Crouse, 1965) and leaching studies with different types of competing cations (Starik and Polevaya, 1958; Starik and Lazerev, 1960; Shearer, 1962; Shearer and Lee, 1964; Havlik et al., 1968b) suggests that an important reaction mechanism for radium adsorption is cation exchange. Radium could be expected to migrate in much the same manner as strontium.

RUTHENIUM

Ruthenium is generally present in association with platinum group metals. It forms discrete solid compounds such as RuO_2 , RuO_4 , $\text{Ru}(\text{OH})_3$, $\text{Ru}(\text{OH})_4$, RuCl_3 , and RuS_2 . The relative stability of the discrete solids in oxidizing conditions ($p\text{O}_{2(\text{g})} = 0.68 \text{ atm}$) is given in Figure 22. The selected thermodynamic data are reported in Table 12. The solids in increasing order of stability for the conditions outlined in Figure 22 are: $\text{Ru}(\text{OH})_3$, RuO_4 , $\text{Ru}(\text{OH})_4$, and RuO_2 (amorphous, hydrated). RuCl_3 and RuS_2 do not appear in Figure 22 because they are too soluble and fall beyond the boundaries of the figure. From Figure 22 it can be ascertained that RuO_2 (amorphous, hydrated) would be most stable over the pH range and up to reducing environments equivalent to $p\text{O}_2$ of 50. In extremely reducing conditions ($p\text{O}_2 = 80$) where $\text{H}_2\text{S}(\text{aq})$ would be the most stable sulfur species, RuS_2 would maintain lower activities than RuO_2 and hence would be the most stable.

The activity of various solution complexes of ruthenium in equilibrium with RuO_2 (amorphous, hydrated) in oxidizing ($p\text{O}_2$ 0.68) and other conditions spelled out in the graph are given in Figure 23. The thermodynamic data used to construct Figure 23 were selected from several sources and are reported in Table 12. Baes and Mesmer (1976) indicate that the thermodynamic data on ruthenium complexes are either not available or are not very accurate. However, it was decided to construct Figure 23 using the existing data to estimate the nature of the species that may be present in solution.

Figure 23 indicates that in an oxidizing environment, significant activity of uncomplexed Ru^{4+} will be present only in very acidic conditions ($\text{pH} < 2$). Some of the ruthenium species which may be present in solution are RuO_4^- , RuO_4^{2-} , RuO_4° , $\text{Ru}(\text{OH})_2^{2+}$, $\text{RuO}_4(\text{OH})^-$, $\text{RuCl}_5(\text{OH})^{2-}$, Ru^{4+} , and Ru^{3+} . Among these species, Ru^{4+} would be predominant in $\text{pH} < 2$, $\text{Ru}(\text{OH})_2^{2+}$ in pH 2 to 5.2, RuO_4^- in pH 5.2 to 10.5, and RuO_4^{2-} in $\text{pH} > 10.5$. With an increase in reducing conditions, the activity of Ru^{3+} would increase, the activity of RuO_4° , RuO_4^{2-} and RuO_4OH^- would decrease and the rest of the species would remain unchanged in activity. The nature of the predominant solution species is highly dependent upon the oxidation-reduction conditions, as is

the most stable solid compound. The predominant ruthenium species are cationic below pH 5 and anionic above pH 5. Hence, ion exchange on soils and rocks, mainly cation exchange, would be of importance only below pH 5 under these conditions.

FIGURE 22. The Relative Stability of Various Ruthenium Solids in an Oxidizing Soil Environment [$pO_2(g) = 0.68 \text{ atm}$], $pCl^- = pSO_4^{2-} = 2.5$

TABLE 12. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Ruthenium

Reaction	Medium	Log K	Reference
<u>SOLID COMPOUNDS</u>			
$\text{RuO}_2(\text{amorphous hydrated}) + 4\text{H}^+ \rightleftharpoons \text{Ru}^{4+} + 2\text{H}_2\text{O}$	0	4.51	Wagman et al. (1969); Pourbaix (1966); and Sillen and Martell (1964)
$\text{RuO}_4 + 4\text{H}^+ \rightleftharpoons \text{Ru}^{4+} + 2\text{H}_2\text{O} + \text{O}_2$	0	15.43	"
$\text{Ru}(\text{OH})_3 + 3\text{H}^+ \rightleftharpoons \text{Ru}^{3+} + 3\text{H}_2\text{O}$	0	7.8	Sillen and Martell (1964)
$\text{Ru}(\text{OH})_4 + 4\text{H}^+ \rightleftharpoons \text{Ru}^{4+} + 4\text{H}_2\text{O}$	0	12.30	"
$\text{RuCl}_3 \rightleftharpoons \text{Ru}^{3+} + 3\text{Cl}^-$	0	4.96	Trotman-Dickinson (1973)
$\text{RuS}_2 + 4\text{O}_2 \rightleftharpoons \text{Ru}^{4+} + 2\text{SO}_4^{2-}$	0	187.62	Trotman-Dickinson (1973); Sillen and Martell (1964); and Pourbaix (1966)
<u>OXIDATION-REDUCTION REACTIONS</u>			
$\text{RuO}_4^- + \text{e}^- \rightleftharpoons \text{RuO}_4^{2-}$	0	10.19	Wagman et al. (1969)
$\text{RuO}_4^{\circ} + \text{e}^- \rightleftharpoons \text{RuO}_4^-$	0	17.23	"
$\text{Ru}^{4+} + \text{e}^- \rightleftharpoons \text{Ru}^{3+}$	0	11.35	Sillen and Martell (1964); and Pourbaix (1966)
$\text{RuO}_4^- \rightleftharpoons \text{Ru}^{4+} + 2\text{O}_2 + 5\text{e}^-$	0	- 84.04	Pourbaix (1966); Sillen and Martell (1964); and Wagman et al. (1969)
<u>OTHER REACTIONS</u>			
$\text{RuO}_4^{\circ} + \text{H}_2\text{O} \rightleftharpoons \text{RuO}_4\text{OH}^- + \text{H}^+$	0	- 11.9	Baes and Mesmer (1976)
$\text{Ru}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ru}(\text{OH})_2^{2+} + 2\text{H}^+$	0	- 4.73	Wagman et al. (1969); Sillen and Martell (1964); and Pourbaix (1966)
$\text{Ru}^{4+} + 5\text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{RuCl}_5(\text{OH})^{2-} + \text{H}^+$	0	8.13	"

FIGURE 23. The Activity of Various Ruthenium Species in Equilibrium with RuO_2 (Amorphous Hydrate) in an Oxidizing Soil Environment [$p_{\text{O}_2}(\text{g}) = 0.68 \text{ atm}$], $p_{\text{Cl}^-} = 2.5$

PREDICTED VS. OBSERVED BEHAVIOR OF RUTHENIUM

Most of the thermodynamic data for the ruthenium complexes with common solution ions of sulfate, nitrate, carbonate, chloride, and organic ligands do not exist. Thus an estimation of their relative importance in waste disposal operations or spills is difficult, requiring experimental studies for evaluation in each case. Based upon data of other species (Figure 23), it can be stated that the adsorption of anionic species that predominate above a pH of approximately 5 would be minimal.

Adsorption of Ru^{3+} peaks at pH 6.6 and 14, with a definite correlation between pH and ruthenium Kd for all ruthenium species (Rhodes, 1957; Eichholz et al., 1967; Amy, 1971). Adsorption of all ruthenium species is low at low pH, and little if any adsorption of anionic species occurs at any pH (Spitsyn et al., 1958; Haney et al., 1962; Brown and Haney, 1964; Raymond, 1964, 1965; Brown, 1967; Magno et al., 1970; Schulz, 1965). Some instances of migration on suspended solids have been noted (Champlin and Eichholz, 1976; Eichholz et al., 1967). Hydrated ferric oxide is a good adsorbent for ruthenium (Kepak, 1966). Low ruthenium Kd values have been reported in high salt solutions (Anonymous, 1973), probably as a result of nitrate complexing. Migration of most ruthenium complexes through the soil column is relatively rapid (Pickering et al., 1966; Izrael and Rovinskii, 1970; Amy, 1971).

STRONTIUM

Strontium is an alkaline earth and forms several salts. Thermodynamic data for various strontium compounds [SrO , $\text{Sr}(\text{OH})_2$, SrF_2 , SrCl_2 , $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 3\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot \text{H}_2\text{O}$, SrHPO_4 , $\text{Sr}_3(\text{PO}_4)_2$, SrSO_4 , $\text{Sr}(\text{NO}_3)_2$, SrCO_3 , SrSiO_3 , SrSiO_4] were considered in order to determine their stability (Table 13). Except for SrSiO_3 , SrHPO_4 , $\text{Sr}_3(\text{PO}_4)_2$, SrCO_3 , and SrSO_4 , the strontium solid phases are too soluble to show in Figure 24. In an acidic environment, most of the strontium solids will be highly soluble, and if the activity of Sr^{2+} in solution exceeds 10^{-4} moles/liter, SrSO_4 can precipitate and would be a stable phase. However, in alkaline conditions, SrCO_3 would be the stable phase and the compound that may maintain strontium activity in soil solutions.

The activity of various solution species in equilibrium with SrCO_3 and at anionic activities of $\text{pCl}^- = \text{pSO}_4^{2-} = 2.5$, $\text{pNO}_3^- = 3.0$, $\text{pF}^- = 4.5$, $\text{pH}_2\text{PO}_4^- = 5$ and $\text{pCO}_2(\text{g}) = 1.52$ atm are plotted in Figure 25. Although strontium forms complexes with the various anions listed above (Table 13), the solution complexes do not contribute significantly to the total strontium activity in solution. Sr^{2+} would be the dominant solution species over the environmental pH range of interest and would be expected to be adsorbed via an ion exchange reaction.

TABLE 13. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Strontium

Reaction	Medium ^(a)	Log K	Reference
<u>Solid Compounds</u>			
$\text{SrCO}_3 \rightleftharpoons \text{Sr}^{2+} + \text{CO}_3^{2-}$	0	- 9.25	Parker et al. (1971); Wagman et al. (1968)
$\text{SrHPO}_4 \rightleftharpoons \text{Sr}^{2+} + \text{H}^+ + \text{PO}_4^{3-}$	0	-19.35	"
$\text{Sr}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Sr}^{2+} + 2\text{PO}_4^{3-}$	0	-27.8	Sillen and Martell (1964)
$\text{SrO} + 2\text{H}^+ \rightleftharpoons \text{Sr}^{2+} + \text{H}_2\text{O}$	0	41.13	Parker et al. (1971)
$\text{SrSO}_4 \rightleftharpoons \text{Sr}^{2+} + \text{SO}_4^{2-}$	0	- 6.47	Parker et al. (1971); Wagman et al. (1968)
$\text{SrSiO}_3 + \text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{Sr}^{2+} + \text{H}_4\text{SiO}_4$	0	14.07	Parker et al. (1971); Helgeson (1969)
$\text{SrSiO}_4 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Sr}^{2+} + \text{H}_4\text{SiO}_4$	0	-56.76	Parker et al. (1971); Wagman et al. (1968)
<u>Hydrolysis and Other Reactions</u>			
$\text{Sr}^{2+} + \text{OH}^- \rightleftharpoons \text{SrOH}^+$	0	0.81	Parker et al. (1971)
$\text{Sr}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Sr}(\text{OH})_2^\circ + 2\text{H}^+$	0	-28.51	Wagman et al. (1968); Parker et al. (1971)
$\text{Sr}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{SrCl}_2^\circ$	0	0.00	Parker et al. (1971)
$\text{Sr}^{2+} + 2\text{F}^- \rightleftharpoons \text{SrF}_2^\circ$	0	2.02	Chase et al. (1975)
$\text{Sr}^{2+} + \text{NO}_3^- \rightleftharpoons \text{SrNO}_3^+$	0	0.82	Sillen and Martell (1964)
$\text{Sr}^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{Sr}(\text{NO}_3)_2^\circ$	0	0.00	Parker et al. (1971)
$\text{Sr}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{SrSO}_4^\circ$	0	0.00	"
$\text{Sr}^{2+} + \text{PO}_4^{3-} \rightleftharpoons \text{SrPO}_4^-$	0.15 (NaCl)	4.18	Sillen and Martell (1964)

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO₄) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO₄ - constant concentration of the substance stated (1.0 moles/liter HClO₄).

FIGURE 24. The Relative Stability of Strontium Solids at $\text{pCa}^{2+} = \text{pSO}_4^{2-} = 2.5$, $\text{pH}_4\text{SiO}_4 = 3.1$, $\text{pCO}_2 = 1.52$ and Phosphate Levels in Equilibrium with Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD), and Octacalcium Phosphate (OCP)

FIGURE 25. The Activities of Various Strontium Species in Equilibrium with $\text{SrCO}_3(\text{s})$ in the Soil at $\text{pCl}^- = \text{pSO}_4^{2-} = 2.5$, $\text{pNO}_3^- = 3.0$, $\text{pF}^- = 4.5$, $\text{pCO}_2 = 1.52$ and $\text{pH}_2\text{PO}_4^- = 5.0$

PREDICTED VS. OBSERVED BEHAVIOR OF STRONTIUM

Most of the strontium chemical compounds for which data are available are very soluble (Figure 24). Only in highly alkaline soils could SrCO_3 control strontium activity in solutions. Strontium in solution is expected to be predominantly present as Sr^{2+} (Figure 25) and to be exchangeable on soils. Laboratory studies show that ion exchange is the principal mechanism of strontium adsorption by soils and rocks (McHenry, 1955, 1958; Rhodes and Nelson, 1957; Klechovsky et al., 1958; Prout, 1958, 1959; Baker and Beetem, 1961). Strontium Kd values are usually directly correlated with cation exchange capacity of the soil or rock, but not invariably (McHenry, 1958). A direct correlation between solution pH and strontium Kd has also been reported (Rhodes, 1957; Prout, 1958, 1959; Baetsle et al., 1964; Juo and Barber, 1970), which suggests hydrogen ion competition with Sr^{2+} for exchange sites. Strontium Kd values fall rapidly from 100 to 200 ml/g or more in low ionic strength salt solutions to less than 5 ml/g in high ionic strength salt solutions (Rhodes, 1957). Strontium and calcium most readily replace trace strontium (Kokotov et al., 1961, 1962; Schulz, 1965) and cause strontium radioisotopes to migrate rapidly when present in groundwater with the strontium (Spitsyn et al., 1960). Low pH also results in a relatively high strontium migration velocity in groundwater (Parsons, 1963; Baetsle et al., 1964) with the strontium and groundwater velocity identical at pH 3. Calcium competition is the probable cause of the 90% soluble strontium migration from the lagoons of the Nuclear Fuel Services plant (Magno et al., 1970), although strontium also migrates on soil particulates (Carlile and Hajek, 1967). The many strontium Kd values determined by Berak (1963) demonstrated that secondary minerals such as clays and zeolites are much better strontium adsorbers and are more selective for strontium from solutions containing strontium and calcium than are the primary minerals such as quartz, feldspars and pyroxenes. Another mechanism for strontium removal from solution is its coprecipitation with calcite (Jenne and Wahlberg, 1968; Varga and Jacobs, 1970) or adsorption during phosphate or oxalate replacement of carbonate in calcite (McHenry, 1958; Ames, 1958). Strontium organic complexes are known that result in a strontium fixation (Mortensen and Marcusiu, 1963) or enhanced migration rates (Himes and Shufeldt, 1970).

TECHNETIUM

Baes and Mesmer (1976) reported that technetium (VII) forms strong peracids (HMO_4), and that its oxides are very soluble. No information is available concerning the soluble complexes of technetium or the solubility of its salts (Pourbaix, 1966). Pertechnetate ion, TcO_4^- , is the most stable species of the element in aqueous solutions (Boyd, 1959).

PREDICTED VS. OBSERVED BEHAVIOR OF TECHNETIUM

Pertechnetate ion, TcO_4^- , is the most stable species of technetium in aqueous solutions (Boyd, 1959). A major portion of the ion exchange capacity of soils and sediments exhibit cation exchange capacity at the usual near-neutral pH conditions. Therefore a negatively charged TcO_4^- would hardly be exchanged, and hence show little adsorption by soils and rocks (Routson et al., 1976, 1977). Gast (1975) reported high K_d values (800 to 900) for soils with high organic matter. He also reported the presence of H_2S in his equilibrating samples, and suggested that the high K_d values were due to precipitation of technetium as Tc_2S_7 in the presence of H_2S (Kotegov, 1968). In conditions where the soil contains appreciable organic matter, the Tc(VII) may be reduced to Tc(IV) and adsorbed (Wildung et al., 1975). Tc(IV) can coprecipitate with ferric hydroxide (Anders, 1960). With the exception of some sedimentary rocks, most rocks contain very little organic matter. Hence, technetium K_d values of close to zero would normally be encountered in oxidizing conditions and in rocks and soils that are relatively low in organic matter. More study is required to determine the nature of the organic matter-pertechnetate ion reaction, and the influence of redox conditions on adsorption of technetium by soils and rocks.

THORIUM

Figure 26 relates the activity of Th^{4+} to pH under an assumed weathering environment in equilibrium with various thorium solid phases. The thermodynamic data for various compounds are reported in Table 14. Under the assumptions outlined in Figure 26, all thorium compounds except ThF_4 can be arranged in an increasing order of stability throughout the pH range as follows: $\text{Th}(\text{HPO}_4)_2$, $\text{Th}_3(\text{PO}_4)_4$, $\text{Th}(\text{OH})_4$, and ThO_2 . ThF_4 would be least stable in a pH of approximately >7 and most stable approximately in $\text{pH} < 4$.

The relative activity of solution species of thorium in equilibrium with $\text{ThO}_2(\text{s})$ at assumed activities of various ions is plotted in Figure 27. The thermodynamic data for various solution species is reported in Table 14. In general, the total concentration of thorium in solution decreases with an increase of pH from zero to 5. Above 5, pH does not affect thorium concentration in solution due to the formation of $\text{Th}(\text{OH})_4$. The activity of all positively charged species decreases with an increase in pH, while the activity of the negatively charged species increases with the increase in pH. Under the conditions assumed for Figure 27, the total activity of thorium in solution would be expected to be approximately $10^{-9.6}$ moles/liter above pH 5.

In addition to OH^- , thorium forms various complexes with SO_4^{2-} , PO_4^{3-} , Cl^- , NO_3^- , and F^- . Various anions in increasing order of their importance to forming complexes are: NO_3^- , Cl^- , H_2PO_4^- , SO_4^{2-} , and F^- . Figure 27 shows that thorium exists as Th^{4+} only in very acidic solutions ($\text{pH} < 3$). Above pH 3, Th^{4+} hydrolyzes very rapidly and it does not contribute significantly to the total thorium concentration. Under the conditions assumed for Figure 27, ThF^{3+} would be a dominant solution species at $\text{pH} < 5$, and $\text{Th}(\text{OH})_4$ would be a dominant solution species at $\text{pH} > 5$. If fluoride ion is absent from the solution, or its concentration is extremely low, $\text{Th}(\text{OH})_2^{2+}$ would mainly control the thorium concentration in solution at $\text{pH} < 5$.

FIGURE 26. The Relative Stability of Various Thorium Solids in Equilibrium with Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD)

TABLE 14. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Various Reactions Involving Thorium

Reaction	Medium ^(a)	Log K	Reference
<u>Solid Compounds</u>			
$\text{ThF}_4 \rightleftharpoons \text{Th}^{4+} + 4\text{OH}^-$	Var	- 25.3	Sillen and Martell (1964)
$\text{Th}(\text{OH})_4 \rightleftharpoons \text{Th}^{4+} + 4\text{OH}^-$	0	- 43.17	"
$\text{ThO}_2 + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + 2\text{H}_2\text{O}$	0	6.3	Baes and Mesmer (1976)
$\text{Th}(\text{HPO}_4)_2 \rightleftharpoons \text{Th}^{4+} + 2\text{HPO}_4^{2-}$	Var at 20°C	- 19.92	Sillen and Martell (1964)
$\text{Th}_3(\text{PO}_4)_4 \rightleftharpoons 3\text{Th}^{4+} + 4\text{PO}_4^{3-}$	Var at 20°C	- 78.59	"
<u>Oxidation-Reduction Reactions</u>			
$\text{Th}^{4+} - \text{e}^- \rightleftharpoons \text{Th}^{3+}$	0	- 59.17	Keller (1971)
$\text{Th}^{4+} + 4\text{e}^- \rightleftharpoons \text{Th}(\text{s})$	0	-128.40	Sillen and Martell (1964)
<u>Hydrolysis Reactions</u>			
$\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ThOH}^{3+} + \text{H}^+$	0	- 3.20	Baes and Mesmer (1976)
$\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_2^{2+} + 2\text{H}^+$	0	- 6.93	"
$\text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_3^+ + 3\text{H}^+$	0	<<- 11.7	"
$\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_4^0 + 4\text{H}^+$	0	- 15.9	"
$\text{Th}(\text{OH})_4 + 2\text{OH}^- \rightleftharpoons \text{Th}(\text{OH})_6^{2-}$	0	- 5.80	Sillen and Martell (1964)
$2\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}_2(\text{OH})_2^{6+} + 2\text{H}^+$	0	- 6.14	Baes and Mesmer (1976)
<u>Other Reactions</u>			
$\text{Th}^{4+} + \text{Cl}^- \rightleftharpoons \text{ThCl}^{3+}$	0	1.38	Sillen and Martell (1964)
$\text{Th}^{4+} + \text{F}^- \rightleftharpoons \text{ThF}^{3+}$	0	8.65	"
$\text{Th}^{4+} + \text{NO}_3^- \rightleftharpoons \text{ThNO}_3^{3+}$	2.0 (HClO ₄) at 20°C	0.78	"
$\text{ThNO}_3^{3+} + \text{NO}_3^- \rightleftharpoons \text{Th}(\text{NO}_3)_2^{2+}$	2.0 (HClO ₄) at 20°C	0.33	"
$\text{Th}^{4+} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{ThH}_3\text{PO}_4^{4+}$	2.0 (NaClO ₄)	1.89	"
$\text{Th}^{4+} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{ThH}_2\text{PO}_4^{3+} + \text{H}^+$	2.0 (NaClO ₄)	2.18	"
$\text{Th}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{ThHSO}_4^{3+}$	1.7 (NaClO ₄)	2.3	"
$\text{ThHSO}_4^{3+} + \text{HSO}_4^- \rightleftharpoons \text{Th}(\text{HSO}_4)_2^{2+}$	1.7 (NaClO ₄)	1.1	"
$\text{Th}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{ThSO}_4^{2+}$	2.0 (NaClO ₄)	3.32	"
$\text{ThSO}_4^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{Th}(\text{SO}_4)_2^0$	2.0 (NaClO ₄)	2.38	"
$\text{Th}(\text{SO}_4)_2^0 + \text{SO}_4^{2-} \rightleftharpoons \text{Th}(\text{SO}_4)_3^{2-}$	0	0.76	"
$\text{Th}(\text{SO}_4)_3^{2-} + \text{SO}_4^{2-} \rightleftharpoons \text{Th}(\text{SO}_4)_4^{4-}$	0	- 2.02	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO₄) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO₄ - constant concentration of the substance stated (1.0 moles/liter HClO₄).

FIGURE 27. Activity of Various Thorium Species in Equilibrium with $\text{ThO}_2(\text{s})$, $\text{pCl}^- = \text{pNO}_3^- = \text{pSO}_4^{2-} = 3.0$, $\text{pF}^- = 4.5$ and $\text{pH}_2\text{PO}_4^- = 5.0$

PREDICTED VS. OBSERVED BEHAVIOR OF THORIUM

Under alkaline conditions, $\text{Th}(\text{OH})_4$ and ThO_2 maintain low activities in soil solutions (Figures 26 and 27) and these compounds could form and govern thorium concentration. Thorium hydrolyzes readily even in moderately acidic environments (Figure 27) so that the Th^{4+} would be present only in very acidic solutions. Laboratory studies also show that thorium tends to precipitate as thorium hydroxide and hydrated thorium oxide in soils (Schulz, 1965; Rancon, 1973).

An increase in thorium content with increase in CaCO_3 , phosphate and humus content of soils and sediments has been reported (Kuznetsov et al., 1968; Pashneva et al., 1965; Menzel, 1968; Yakobenchuck, 1968; Hansen and Huntington, 1969; Pokidin et al., 1972). However, Tyuryukanova and Kalugina (1971) reported low thorium concentrations in high humus soils (peats and forest podzols) compared with alluvial soils. Thorium adsorption increases with increase in pH (Rancon, 1973) and decrease in soil particle size (Hansen and Huntington, 1969; Hansen, 1970; Nishiwaki et al., 1972; Rubtsov, 1966, 1972; Bondietti, 1974). Strong humic and fulvic acid complexes with thorium occur in the neutral to acidic range (Rancon, 1973; Bondietti, 1974) which are noncationic (Desai and Ganguly, 1970) and mobile. It has been reported also that thorium migrates primarily in the colloidal form (polymeric) in the natural environment (Baranov et al., 1956; Lazarev et al., 1961; Kimura et al., 1968).

TRITIUM

Tritium (H^3) is a radioactive isotope of hydrogen. Thus, tritium behavior in soils would be expected to be similar to hydrogen and thus could exist as an ion, gas and liquid (tritiated water). Except for the slight differences in vapor pressure, tritiated water behaves the same as ordinary water (Jacobs, 1968). Although no discrete solid phases of tritium are expected in soils, it could associate itself with soil organic compounds containing hydrogen or with some soil minerals as mobile water, water of hydration, or as part of structural hydroxyl groups (Jacobs, 1968; Stewart, 1967).

Tritium rapidly travels at about the same velocity as the soil water or groundwater in the form of HTO . Some replacement of nontritiated water on clays and other hydrated soil constituents occurs, but the reaction is of marginal value as far as tritium retention is concerned. Tritium can move in a vapor phase through the soil under certain conditions as well.

PREDICTED VS. OBSERVED BEHAVIOR OF TRITIUM

Tritium substitutes readily for the hydrogen in water and thus becomes a part of the hydrological cycle (Jacobs, 1968). Migration of tritium through the groundwater takes place at the same velocity as the groundwater through sandy soils (Haney, 1963, 1964; Haney et al., 1962; Brown and Haney, 1964; Brown, 1967). Some investigators have reported the selective fixation of tritiated water on clays and other hydrated minerals (Rosenqvist, 1963; Koranda, 1965; Clayton et al., 1966; Savin, 1967; Stewart, 1967; Rabinowitz, 1969; Rabinowitz et al., 1973) while other investigators have considered tritium fixation to be minimal (Higgins, 1959; Halevy, 1964; Corey and Horton, 1968; Teller et al., 1968). However, all of the field studies have indicated that tritium movement is synonymous with water movement (Brown, 1967).

URANIUM

The thermodynamic data for different uranium compounds are reported in Table 15. The relative stability of several uranium solid phases, in terms of the uranyl ion activity produced by each, is shown in Figure 28. Since all the compounds shown in Figure 28 are of U(VI), and are plotted as a function of UO_2^{2+} , their curves would not move with changes in oxidation-reduction conditions. U(IV) compounds, such as UO_2 , are very soluble in an oxidizing environment and fall outside the boundary of Figure 28. With an increase in reducing conditions, U(IV) compounds would become more stable. At a $p\text{O}_2$ of >71 , the UO_2 curve would fall just below the $\text{UO}_2\text{NH}_4\text{PO}_4$ curve. U(VI) compounds are stable in an oxidizing environment and U(IV) compounds are stable in a reducing environment. Consistent with the thermodynamic data is the observation that carnotite, a U(VI) mineral is found in the oxidized zones of uranium ore deposits and uraninite, a U(IV) mineral is a primary mineral in reducing ore zones.

The thermodynamic data for solution species of uranium are reported in Table 15. All the species except UO_2^+ shown in Figure 29 are of U(VI). Since equilibrium is assumed with Na_2UO_4 , a U(VI) compound, a change in oxidation-reduction conditions will affect the position of the curves. In an oxidizing environment ($p\text{O}_2 = 0.68 \text{ atm}$), the U(IV) species are very low in concentration ($\log a_i < 38$) and fall outside of the boundaries of Figure 29.

Figure 29 shows that U(VI) species will control the solution concentration in an oxidizing environment. UO_2^{2+} is the predominant solution species up to a pH of approximately 6. The predominant solution species over pH ranges of from 6 to 8 and >8 are $\text{UO}_2(\text{OH})_2^0$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, respectively.

TABLE 15. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Uranium

Reaction	Medium	Log K	Reference
<u>Uranium (III & IV) Compounds</u>			
$\text{U(OH)}_3 \rightleftharpoons \text{U}^{3+} + 3\text{OH}^-$	0	-19.29	Latimer (1952)
$\text{U(OH)}_4 \rightleftharpoons \text{U}^{4+} + 4\text{OH}^-$	0	-46.23	"
$\text{UF}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{U}^{4+} + 4\text{F}^- + 2\text{H}_2\text{O}$	Var	-21.24	Sillen and Martell (1964)
$\text{UO}_2 + 4\text{H}^+ \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	0	3.63	Garrels and Christ (1965)
$\text{U(HPo}_4)_2 \rightleftharpoons \text{U}^{4+} + 2\text{HPo}_4^{2-}$	0	-17.51	Palei (1962)
$\text{U(OH)}_2\text{SO}_4 \rightleftharpoons \text{U}^{4+} + 2\text{OH}^- + \text{SO}_4^{2-}$	0	-31.17	Sillen and Martell (1964)
<u>Uranium (VI) Compounds</u>			
$\text{UO}_2\text{KAsO}_4 \rightleftharpoons \text{UO}_2^{2+} + \text{K}^+ + \text{AsO}_4^{3-}$	0	-22.60	Palei (1962)
$\text{UO}_2\text{NaAsO}_4 \rightleftharpoons \text{UO}_2^{2+} + \text{Na}^+ + \text{AsO}_4^{3-}$	0	-21.87	"
$\text{UO}_2\text{NH}_4\text{AsO}_4 \rightleftharpoons \text{UO}_2^{2+} + \text{NH}_4^+ + \text{AsO}_4^{3-}$	0	-23.77	"
$\text{UO}_3 + 2\text{H}^+ \rightleftharpoons \text{UO}_2^{2+} + \text{H}_2\text{O}$	0	14.77	Garrels and Christ (1965)
$\text{UO}_3\text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{UO}_2^{2+} + 2\text{H}_2\text{O}$	0	5.01	Latimer (1952)
$\text{UO}_2(\text{OH})_2 + 2\text{H}^+ \rightleftharpoons \text{UO}_2^{2+} + 2\text{H}_2\text{O}$	0	4.97	Sillen and Martell (1964)
$\text{UO}_2(\text{OH})_2\text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{UO}_2^{2+} + 3\text{H}_2\text{O}$	0	5.6	"
$\text{Na}_2\text{UO}_4 + 4\text{H}^+ \rightleftharpoons \text{UO}_2^{2+} + 2\text{H}_2\text{O} + 2\text{Na}^+$	0	-0.07	Latimer (1952)
$\text{UO}_2\text{CO}_3 \rightleftharpoons \text{UO}_2^{2+} + 2\text{CO}_3^{2-}$	0	-10.54	Garrels and Christ (1965)
$\text{Na}_4\text{UO}_2(\text{CO}_3)_3 \rightleftharpoons \text{UO}_2^{2+} + 4\text{Na}^+ + 3\text{CO}_3^{2-}$	0	-21.1	Sillen and Martell (1964)
$(\text{UO}_2)_3(\text{PO}_4)_2 \rightleftharpoons 3\text{UO}_2^{2+} + 2\text{PO}_4^{3-}$	0	-46.33	Palei (1962)
$\text{UO}_2\text{HPO}_4 \rightleftharpoons \text{UO}_2^{2+} + \text{HPO}_4^{2-}$	0	-10.67	"
$\text{UO}_2\text{KPO}_4 \rightleftharpoons \text{UO}_2^{2+} + \text{K}^+ + \text{PO}_4^{3-}$	0	-23.11	"
$\text{UO}_2\text{NH}_4\text{PO}_4 \rightleftharpoons \text{UO}_2^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-}$	0	-26.36	"
$\text{UO}_2(\text{SO}_4)3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2^{2+} + \text{SO}_4^{2-} + 3\text{H}_2\text{O}$	0	-1.57	Latimer (1952)
<u>Oxidation-Reduction Reactions</u>			
$\text{U}^{3+} + 3\text{e}^- \rightleftharpoons \text{U(s)}$	0	-91.0	Sillen and Martell (1964)
$\text{U}^{4+} + \text{e}^- \rightleftharpoons \text{U}^{3+}$	0	-10.3	"
$\text{UO}_2^+ + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	0	10.19	"
$\text{UO}_2^{2+} + \text{e}^- \rightleftharpoons \text{UO}_2^+$	0	0.88	"
$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	0	11.07	"

TABLE 15. (Continued)

Reaction	Medium ^(a)	Log K	Reference
<u>Hydrolysis Reactions</u>			
$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$	0	- 1.00	Garrels and Christ (1965)
$U^{4+} + 2H_2O \rightleftharpoons U(OH)_2^{2+} + 2H^+$	Var	- 2.30	Sillen and Martell (1964)
$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$	0	- 4.14	"
$UO_2^{2+} + 2H_2O \rightleftharpoons UO_2(OH)_2^0 + 2H^+$	0	-12.02	"
$UO_2^{2+} + 3H_2O \rightleftharpoons UO_2(OH)_3^- + 3H^+$	0	-23.64	"
$UO_2^{2+} + 4H_2O \rightleftharpoons UO_2(OH)_4^{2-} + 4H^+$	0	-37.81	"
$2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$	0	- 5.06	"
<u>Other Reactions</u>			
$UO_2^{2+} + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_2^{2-}$	0	14.6	Sillen and Martell (1964)
$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$	0	18.3	"
$U^{4+} + Cl^- \rightleftharpoons UCl^{3+}$	0	0.8	"
$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+$	0	0.21	"
$U^{4+} + F^- \rightleftharpoons UF^{3+}$	0.12(HClO ₄)	7.15	"
$U^4 + 2F^- \rightleftharpoons UF_2^{2+}$	0.12(HClO ₄)	12.40	"
$U^4 + 3F^- \rightleftharpoons UF_3^+$	0.12(HClO ₄)	17.30	"
$UO_2^{2+} + F^- \rightleftharpoons UO_2F^+$	1.0 at 20°C	4.54	Palei (1962)
$UO_2^{2+} + H_3PO_4 \rightleftharpoons UO_2H_2PO_4^+ + H^+$	1.06	1.19	"
$U^{4+} + HSO_4^- \rightleftharpoons USO_4^{2+} + H^+$	0	2.41	Sillen and Martell (1964)
$U^{4+} + 2HSO_4^- \rightleftharpoons U(SO_4)_2^0 + 2H^+$	0	3.73	"
$UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4^0$	0	2.76	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO₄) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO₄ - constant concentration of the substance stated (1.0 moles/liter HClO₄).

FIGURE 28. The Relative Stability of Various Solids in an Oxidizing Environment [$p\text{O}_2 = 0.68$], $p\text{CO}_2 = 3.52$, $\text{pK}^+ = \text{pNa}^+ = 3.0$ and Phosphate Levels in Equilibrium with Variscite and Gibbsite

FIGURE 29. Activity of Various Uranium Species in Equilibrium with Na_2UO_4 in Oxidizing Soil Environment ($p\text{O}_2 = 0.68$), $p\text{CO}_2 = 3.52$, $p\text{Cl}^- = p\text{SO}_4^{2-} = 3.0$, $p\text{F}^- = 4.5$ and $p\text{H}_2\text{PO}_4 = 5.0$

PREDICTED VS. OBSERVED BEHAVIOR OF URANIUM

The common oxidation states of uranium are U(III), U(IV), U(V), and U(VI) (Udaltsova, 1963). However, in the geologic environment U(IV) and U(VI) are the most important oxidation states. In oxidizing environments U(VI) compounds such as KUO_2VO_4 (Garrels and Christ, 1965), $\text{UO}_2\text{NH}_4\text{PO}_4$, Na_2UO_4 and UO_2KPO_4 (Figure 28) are stable and can precipitate. U(IV) would precipitate as UO_2 in a reducing environment. U(VI) solution species govern uranium concentrations and movement in oxidizing environments (Figure 29). Uranium retention by soils and rocks in alkaline conditions is poor because the predominant uranium species at $\text{pH} > 6$ in oxidizing environments (Figure 29) are either neutral or negatively charged. An increase in CO_2 pressure in soil solutions reduces uranium adsorption and can increase uranium concentration. The cation exchange properties of soils could contribute to the adsorption of uranium in the neutral to acidic pH range due to the presence of UO_2^{2+} . Oxidation-reduction conditions and pH would be important parameters of uranium mobilization and immobilization.

The above theoretically based predictions are substantiated by experimental results. Uranium has been reported to be solubilized and highly mobile in carbonate-containing waters (Brown and Keller, 1952; Naumov, 1961; Ermolaev et al., 1965; Legin et al., 1966; Haglund, 1968; Haglund et al., 1969). Soluble uranium [U(VI)] can:

1. precipitate in the presence of phosphorus as evidenced by a direct correlation of uranium and phosphate content in soils and rocks (Bell, 1960; Sakanoue, 1960; Habashi, 1962; Kuznetsov et al., 1968)
2. be adsorbed by the soil organic component and/or reduced to U(IV) followed by precipitation (Breger et al., 1955; Kolodny, 1969; Kolodny and Kaplan, 1970; Baturin, 1971; Dall'Aglia, 1971; Dorta and Rona, 1971; Gabelman, 1971; Baturin and Kochenov, 1973; Mo et al., 1973)

An increase in uranium content with a decrease in soil or sediment particle size was reported by several workers (Kovalevskii, 1967; Mizuno and Mochizuki, 1970; Ritchie et al., 1972).

ZIRCONIUM

The selected thermodynamic data for zirconium minerals are reported in Table 16. The solubility of different zirconium minerals with the changes in pH is shown in Figure 30. The zirconium minerals in increasing order of stability are: $\text{Zr}(\text{OH})_4$, ZrO_2 , and ZrSiO_4 , as shown in Figure 30. The most stable mineral throughout the pH range is zircon (ZrSiO_4). This is consistent with the empirical observations of many geologists and soil scientists who find that zircon (ZrSiO_4) is ubiquitous in soils and is very stable even compared to other common soil minerals.

The activity of various solution species with the change in pH and in equilibrium with zircon (ZrSiO_4) and soil SiO_2 is given in Figure 31. The thermodynamic data for solution species are reported in Table 16. Zirconium forms complexes with the common soil anions (F^- , Cl^- , SO_4^{2-} , NO_3^-). The significance of complexation of zirconium with these anions decreases in the following order: F^- , SO_4^{2-} , Cl^- , NO_3^- . Although zirconium forms complexes with common soil anions, ZrF^{3+} complex would be the only one which could contribute significantly in acidic environments (pH 3.5) to the total zirconium in solution. It can be seen from the diagram that the uncomplexed zirconium (Zr^{4+}) would exist in significant amounts only in very acidic solutions (pH < 1). The zirconium ions are hydrolyzed in solutions with pH values of greater than 1.0. The most dominant zirconium solution species with the conditions assumed in Figure 31 are ZrF^{3+} , $\text{Zr}(\text{OH})_4^0$, and $\text{Zr}(\text{OH})_5^-$ in pH ranges of <3.5, 3.5-6.25, and >6.25, respectively.

If a waste solution containing zirconium is assumed to be in equilibrium with zircon and the conditions assumed in Figure 31, then the total activity of zirconium in solution would be lower than 10^{-14} over a pH range of 3.5 to 8.

The Zr^{4+} ion becomes increasingly hydrolyzed above pH 1 (Figure 31). The Zr^{4+} content of the soil solution falls rapidly, as does the content of fluoride complex ZrF^{3+} , in favor of hydrolyzed species at higher pH values. Only at relatively low pH values of less than 4 do positively charged species

of zirconium predominate. Because most soils and rocks buffer waters contacting them to pH 5 or higher, ion exchange probably plays a relatively minor role in zirconium retention by soils and rocks. Because of the formation of negatively charged complexes in solutions of pH >6.5 (Figure 31), zirconium adsorption would be expected to decrease with an increase in pH above 6.5.

TABLE 16. Selected Equilibrium Constants (K) at 25°C and One Atmosphere Pressure for Reactions Involving Zirconium

Reaction	Medium ^(a)	Log K	Reference
<u>Solid Compounds</u>			
$\text{Zr(OH)}_4 \rightleftharpoons \text{Zr}^{4+} + 4\text{OH}^-$	Variable	-52.0	Sillen and Martell (1964)
$\text{ZrO}_2 + 4\text{H}^+ \rightleftharpoons \text{Zr}^{4+} + 2\text{H}_2\text{O}$	0	- 1.9	Baes and Mesmer (1976)
$\text{ZrSiO}_4 + 4\text{H}^+ \rightleftharpoons \text{Zr}^{4+} + \text{H}_4\text{SiO}_4$	0	- 3.59	Wagman et al. (1971); and Helgeson (1969)
<u>Hydrolysis and Other Reactions</u>			
$\text{Zr}^{4+} + \text{F}^- \rightleftharpoons \text{ZrF}^{3+}$	0	9.80	Sillen and Martell (1964)
$\text{Zr}^{4+} + \text{Cl}^- \rightleftharpoons \text{ZrCl}^{3+}$	(2 HClO_4)	0.30	"
$\text{Zr}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{ZrSO}_4^{2+}$	(2 HClO_4)	3.79	"
$\text{Zr}^{4+} + \text{NO}_3^- \rightleftharpoons \text{ZrNO}_3^{3+}$	(2 HClO_4)	0.3	"
$\text{Zr}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{ZrOH}^{3+} + \text{H}^+$	0	0.3	Baes and Mesmer (1976)
$\text{Zr}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_2^{2+} + 2\text{H}^+$	0	- 1.7	"
$\text{Zr}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_3^+ + 3\text{H}^+$	0	- 5.1	"
$\text{Zr}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_4^0 + 4\text{H}^+$	0	- 9.7	"
$\text{Zr}^{4+} + 5\text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_5^- + 5\text{H}^+$	0	-16.0	"
$3\text{Zr}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Zr}_3(\text{OH})_4^{8+} + 4\text{H}^+$	0	- 0.6	"
$3\text{Zr}^{4+} + 5\text{H}_2\text{O} \rightleftharpoons \text{Zr}_3(\text{OH})_5^{7+} + 5\text{H}^+$	0	3.7	"

(a) The nature of the medium to which the equilibrium constants refer, for example, 0 - zero ionic strength, var - ionic medium varied, 2(HClO_4) - ionic strength held constant at the value stated (2 moles/liter) by the addition of the chemical shown in parentheses, 1.0 HClO_4 - constant concentration of the substance stated (1.0 moles/liter HClO_4).

FIGURE 30. The Stability of Zirconium Solids in Equilibrium with Soil Silica ($pH_4SiO_4 = 3.1$)

FIGURE 31. The Activity of Various Zirconium Species in Equilibrium with Soil Silica ($pH_4SiO_4 = 3.1$) and at $pCl^- = pSO_4^{2-} = 2.5$, $pNO_3^- = 3.0$, $pF^- = 4.5$

PREDICTED VS. OBSERVED BEHAVIOR OF ZIRCONIUM

Trace concentrations of zirconium are strongly adsorbed on soils at pH 1 or higher with a dip in K_d values between pH 8 to 12 (Rhodes, 1957), probably due to the prevalence of uncharged or anionic zirconium species over this pH range (Figure 31). There is some evidence for affects caused by competing cations at near-neutral pH, suggesting at least partial removal by an ion exchange mechanism of polymerized or colloidal species (Eichholz et al., 1967; Harrison, 1969). Zirconium is well-adsorbed by the soil over the normal pH range of 4 to 8 (Spitsyn et al., 1958; Schulz, 1965; Magno et al., 1970). Carbonate, oxalate and citrate complexes of zirconium have been reported to migrate rapidly through soil columns (Bensen, 1960).

SUMMARY AND CONCLUSIONS

Among the factors that determine the fate of a given element in the environment, the solid phases, the total concentration and the type of solution species are the most important. Laboratory information on possible solid phases and solution species of elements of interest (Am, Sb, Ce, Cs, Co, Cm, Eu, I, Np, Pm, Ra, Ru, Sr, Tc, Th, ^3H , Zr) in radioactive waste is almost nonexistent (Ames and Rai, 1978). Therefore, thermodynamic data for these elements were used to predict the stable species and the degree of adsorption of these species by the solid matrix. The limitations of these predictions are discussed. These predictions are also compared with observations reported in literature.

The solid compounds of different elements that are considered in this report are those for which thermodynamic data are available. Among the compounds for which thermodynamic data are available, there are many that are very soluble. These compounds are unlikely to occur under environmental conditions. Some of the most stable compounds of different elements that 1) may occur in geologic environments, or 2) those that would be helpful in selecting radionuclide concentrations for adsorption experiments, include Sb_2O_5 , Sb_2S_3 , CePO_4 , CoOOH , CoCO_3 , $\text{Cm}(\text{OH})_3$, $\text{Eu}(\text{OH})_3$, NpO_2 , PuO_2 , $\text{Pu}(\text{OH})_4$, $\text{Pm}(\text{OH})_3$, RuO_2 , SrCO_3 , ThO_2 , $\text{Th}(\text{OH})_4$, $\text{UO}_2\text{NH}_4\text{PO}_4$, $\text{K}_2\text{UO}_2\text{VO}_4$, UO_2 , ZrSiO_4 , ZrO_2 , $\text{Zr}(\text{OH})_4$.

The predicted nature of the predominant solution species of various elements are reported in Table 17. The environmental conditions assumed for Table 17 data include a pH range of 4 to 9, $p\text{O}_2$ range of 0.68 to 80 atmospheres, $p\text{CO}_2$ of 1.52 to 3.52 atmospheres, $p\text{Cl}^- = p\text{NO}_3^- = p\text{SO}_4^{2-} = 3.0$, $p\text{F}^- 4.5$, and $p\text{H}_2\text{PO}_4^- 5.0$. It should be pointed out that a change in these environmental conditions, in addition to the ligands not considered in the above assumptions, may change the nature of the solution species. Depending upon the given chemical environment, several species of an element can exist in solution. Cesium, cobalt, promethium, radium, strontium, and tritium would be expected to exist predominantly as uncomplexed solution species: Cs^+ , Co^{2+} , Pm^{3+} , Ra^{2+} , Sr^{2+} and $^3\text{H}^+$ (or T). Certain elements such as plutonium, neptunium

and uranium can exist in acidic solutions in an oxidizing environment as uncomplexed solution ions (PuO_2^+ , PuO_2^{2+} , NpO_2^+ , UO_2^{2+}). Some of the elements such as curium, thorium and zirconium hydrolyze very readily even in acidic environments, so they mainly exist as hydrolyzed species [CmOH^{2+} , $\text{Cm}(\text{OH})_2^+$, $\text{Th}(\text{OH})_3^+$, $\text{Zr}(\text{OH})_4^0$, $\text{Zr}(\text{OH})_5^-$]. Some of the common soil ligands (CO_3^{2-} , SO_4^{2-}) form strong complexes with americium, curium, europium, neptunium, plutonium and uranium so that these ligands would influence the concentration of these elements in solutions. Oxidation-reduction conditions would predominantly influence the nature of the solution species of antimony, neptunium, plutonium, technetium, and uranium.

Based upon the nature of the predominant solution species, qualitative predictions regarding the adsorption and movement of various elements can be made. Soils and sediments mainly show cation exchange capacities (since these materials carry a large net negative charge) and to a limited extent, anion exchange capacities. Thus, most cations migrate through the soil or rock column at speeds slower than the groundwater. Relative to each other, the trivalent cations generally move the slowest, the divalent cations at intermediate velocities and the monovalent cations most rapidly. Tritium is unique in that it readily substitutes for hydrogen in water and migrates, therefore, at the same velocity as water. Complicating factors include a higher selectivity of a soil or rock component for a given cation or a more successful hydrogen ion competition with one cation relative to another. The relative mobilities of strontium and cesium at low pH is a good example of the latter effect. Strontium is much more mobile at low pH than is cesium.

The simple anions tend to migrate through soils and rocks with little reaction because usually a pH of less than 4 is required to activate a significant soil anion exchange capacity. However, both Tc (in oxidizing environment) and I which exist predominantly as anions (I^- , TcO_4^-) undergo other reactions with organic ligands that can greatly slow their migration.

The migration and retention of inorganic complex species (mononuclear and polynuclear) would also be dependent upon the charge and size of the species. Positively charged species would move slower than the negatively

charged species. The highly charged metal ions tend to polymerize or form colloidal size, charged precipitates. The trivalent metal ions (Am, Cm, Sb, Ru) and quadrivalent or higher charged metal ions (Pu, Th, U, Zr) are known to form polymers. Initially, at lower pH, the polymers are positively charged and at pH 8 become increasingly negatively charged. The result is good adsorption and very slow movement at acidic to neutral pH, and greatly lessened adsorption and rapid migration from pH 8 upward.

The behavior of organic complexed species of elements is difficult to predict because of the lack of knowledge regarding the exact nature of the organic ligands, a wide variation in amounts and types of organic ligands, and the size and solubility of these organics. These organic materials can either retain the element or complex it in a form that migrates readily. The source of these organic ligands can be the radioactive waste solutions containing the synthetic organic ligands such as TBP and/or the organic ligands produced by soil flora.

TABLE 17. Predominant Solution Species of Elements in a pH 4 to 9, pO_2 0.68 to 80, pCO_2 1.52 to 3.52, $pCl^- = pNO_3^- = pSO_4^{2-} = 3.0$, pF^- 4.5 and $pH_2PO_4^-$ 5.0 Environment Without Organic Ligands

Elements	Predominant Solution Species of Elements		
	Little Affected by Oxidation-Reduction	In An Oxidizing Environment	In A Reducing Environment
Am	Am^{3+} , $AmSO_4^+$, $Am(OH)^{2+}$		
Sb		$HSbO_2^\circ$, $Sb(OH)_3^\circ$, $SbOF^\circ$, $Sb(OH)_4^-$	SbO^+
Ce	Ce^{3+} , $CeSO_4^+$		
Cs	Cs^+		
Co	Co^{2+} , $Co(OH)_2^+$		
Cm	Cm^{3+} , $CmOH^{2+}$, $Cm(OH)_2^+$		
Eu	Eu^{3+} , $EuSO_4^+$, $Eu_2P_2O_7^{2+}$		
I	I^- , IO_3^-		
Np		NpO_2^+ , $NpO_2HPO_4^-$, NpO_2HCO_3	$NpOH^{3+}$, Np^{4+}
Pu		PuO_2^{2+} , $PuO_2(CO_3)(OH)_2^{2-}$, PuO_2^+	$PuOH^{2+}$, Pu^{3+}
Pm	Pm^{3+}		
Ra	Ra^{2+}		
Ru		$Ru(OH)_2^{2+}$, RuO_4^- , RuO_4^{2-}	RuO_4^-
Sr	Sr^{2+}		
Tc		TcO_4^-	Tc^{2+}
Th	ThF^{3+} , $Th(OH)_3^+$		
3H	H^+ , $^3H-O-H$		
U		UO_2^{2+} , UO_2F^+ , $UO_2(OH_2)^\circ$, $UO_2(CO_3)_3^{4-}$	UO_2^{2+} , UOH^{3+} , UO_2^+ , $UO_2(CO_3)_3^{4-}$
Zr	$Zr(OH)_4^\circ$, $Zr(OH)_5^-$, ZrF^{3+}		

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