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A Review of the Environmental Behavior of Uranium Derived From Depleted Uranium Alloy Penetrators

R. L. Erikson
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January 1990

Prepared for
U.S. Army Combat Systems Test Activity
Aberdeen Proving Ground, Aberdeen, Maryland
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A REVIEW OF THE ENVIRONMENTAL BEHAVIOR OF URANIUM DERIVED FROM DEPLETED URANIUM ALLOY PENETRATORS

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SUMMARY

The use of depleted uranium (DU) penetrators as armor-piercing projectiles in the field results in the release of uranium into the environment. Elevated levels of uranium in the environment are of concern because of radioactivity and chemical toxicity. In addition to the direct contamination of the soil with uranium, the penetrators will also chemically react with rainwater and surface water. Uranium may be oxidized and leached into surface water or groundwater and may subsequently be transported. In this report, we review some of the factors affecting the oxidation of the DU metal and the factors influencing the leaching and mobility of uranium through surface water and groundwater pathways, and the uptake of uranium by plants growing in contaminated soils.

The uranium in the DU penetrators is in the form of uranium metal alloyed with 0.75 wt% Ti to reduce the overall corrosion rate and to improve mechanical properties of the penetrator. Because uranium metal is thermodynamically unstable relative to more oxidized forms of uranium [U(IV) and U(VI)], it will react to form oxides when in contact with the earth's atmosphere. The primary oxidation products are hyperstoichiometric U(IV) oxides of the form UO_{2+x}, where $0 < x < 0.4$. Further oxidation to mixed U(IV) and U(VI) oxides and to U(VI) oxides may also occur. A review of reaction rates suggest that the most rapid atmospheric oxidation of uranium metal occurs in contact with pure water vapor. The oxidation rates of uranium metal are much slower in dry air, CO_2, and O_2 and water vapor. Under some conditions, the addition of 0.75% Ti to uranium metal appears to slow the oxidation rate by a factor of approximately 16. Corrosion rates for uranium metal under aqueous conditions, such as might exist in surface-water pools, tend to be higher than atmospheric oxidation rates.

The potential for the migration of uranium depends on the chemistry of local soils and pore waters as well as on the oxidation products of the DU penetrator. The mobility of dissolved uranium will depend on the Eh, pH, and the presence of complexing ligands in local groundwaters. Uranium (VI) is more mobile than U(IV) because of aqueous complexation reactions involving ligands commonly found in natural waters; carbonate and phosphate are

considered the most important of these. The transport of dissolved uranium can also be affected by attenuation reactions that can reduce uranium concentrations in groundwater and surface waters. These reactions include ion exchange and specific adsorption of uranium on organic matter, clay minerals, and ferric oxides and oxyhydroxides commonly present in soils.

An evaluation of the potential for the migration and uptake of uranium from DU penetrators at a particular site requires detailed field characterization data for the chemical composition of the surface water, groundwater, and soil. Measurements for surface and pore waters should be made that include pH, Eh, and the concentrations of major cations, anions, selected trace metals, and organic compounds. In addition, the soils should be characterized for mineral type and content and for organic matter.

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INTRODUCTION

The addition of heavy metals to armor-piercing penetrators makes the penetrators more effective because of the higher kinetic energies on impact. Moreover, using uranium metal in a penetrator provides an additional pyrophoric quality, making it more effective on the battlefield. Depleted uranium (DU), because of its availability and its reduced radioactivity compared to natural uranium, has been put to this use in ammunition manufacture. However, test firing of DU alloy (DU - 0.75% Ti) penetrators in the field may cause contamination because uranium is released into the environment. Small particles may be dispersed and deposited on soils as a result of the impact of the penetrator. Alternatively, if the penetrator does not impact a downrange target, it may come to rest relatively intact on or near the soil surface or in shallow surface water. In any case, not only will there be direct contamination of the soil with uranium, but the penetrators will also be subject to chemical interactions that are associated with weathering (i.e., dissolution) reactions involving rainwater or surface water.

Elevated levels of uranium (U) in soil are of concern because of radioactivity and chemical toxicity (Hanson and Miera 1976; Loewenstein 1980). Uranium may be oxidized and leached into surface water or groundwater and may subsequently be transported. These processes could lead to direct exposure to humans who ingest the contaminated water. Potentially toxic groundwater concentrations could result from leaching of the DU, depending on the rate of leaching of U by rainwater. In addition, U could enter the food chain through plants growing in contaminated sediment or soil, animals consuming the contaminated vegetation, and humans then consuming either the contaminated vegetation or the contaminated animals. The potential dose from this exposure pathway would add to the dose from the direct ingestion exposure pathway. A final potential exposure pathway is from inhalation of contaminated soil particles. The relative importance of these exposure pathways will depend on the local environmental conditions.

In this report, we review some of the factors affecting conversion of the DU metal to oxide, factors influencing the leaching and mobility of U through surface water and groundwater pathways, and the uptake of U by plants growing in contaminated soils. The concentration of dissolved U entering the soil profile will be governed by the weathering reactions among the U metal particles, their oxidation products, and water. Therefore, the chemical kinetics of reactions involving the transformation of the U metal into U-oxides or other weathering products and the relative solubilities of those products in soil pore waters must be evaluated. In addition, both the presence of complexing ligands and the redox conditions of the pore waters affect the quantity of U leached from different U solids. These effects must also be evaluated. Reactions between the dissolved U and the minerals and mineral surfaces in the local soils may attenuate U concentrations in the soil profile. Such reactions include precipitation of secondary minerals and adsorption reactions that can reduce the concentrations of U in soil pore waters. In this review, three factors affecting the mobility of U from spent penetrators are discussed: 1) the oxidation of U and DU alloy metal into more stable oxides, 2) the effects of the chemical composition of the soil pore waters involved in the weathering process, and 3) the attenuation of dissolved U by local soils. Finally, we review the factors influencing the uptake of U by plants growing in contaminated soils.

PAST STUDIES

Several studies have measured U contamination in soils and groundwater that was a result of impacts of DU penetrators at target ranges. For example, observations at a DU-explosive testing site at the Los Alamos Scientific Laboratory (LASL) have found U concentrations in standing water in the detonation crater in the range of 87 to 280 ppm (Hanson and Miera 1977). After a rainstorm, concentrations in runoff water 100 and 250 m from the site were 52 and 37 ppb U, respectively. Thus, migration of dissolved U in surface water is an important factor in U transport at the LASL site. Concentrations of U in the soils at the LASL testing site were highest (average of 4500 ppm) in the uppermost 2.5 cm of soil at a distance of 0 to 10 m from the detonation point. The concentration of U decreased to about 700 ppm at a distance of 50 to 200 m from the detonation point. However, the U had also penetrated the soil to depths of 30 cm. A value of about 50 ppm U in the soil is considered chemically toxic to plants (Hanson 1974).

Stoetzel et al. (1983) have reported soil and surface water measurements of uranium concentrations for two target areas (the B-3 and Ford's Farm ranges) at the Aberdeen Proving Grounds in Maryland. Average concentrations of U in the soils ranged from 1.3 ppm at the B-3 range (open-air soft target range) and 3.6 ppm at the Ford's Farm site (open-air hard target area).(a) These concentrations are only slightly higher than those in several U.S. soils in which the natural U concentration is expected to be "normal," that is, uranium concentrations in the range of 0.6 to 1.6 ppm (Hanson and Miera 1976, 1977).

Water samples collected from the B-3 range and the Ford's Farm site contained U concentrations between 0.03 and 43 ppb and between 0.13 and 59 ppb, respectively. Typical river waters, contacting igneous rocks and clay, contain about 0.5 ppb, while waters in contact with carbonates can be higher. Normal maxima are around 0.2 ppm (Hanson 1974). Thus the U concentrations at the Aberdeen Proving Ground are somewhat high. However, in general, the total U concentrations in both the soil and local waters measured at the Aberdeen Proving Grounds are considerably less than the concentrations reported for the LASL site. Clearly, the variations in the environmental conditions at testing sites are reflected by the differences in mobility of dissolved DU. As will be discussed in the following sections, the mobility of DU in the environment is influenced by environmental conditions and complex processes, such as oxidation, aqueous complexation, precipitation, and adsorption.

OXIDATION OF URANIUM AND DU - 0.75% Ti ALLOY

The U in the DU penetrators is in the form of U metal alloyed with 0.75 wt% Ti to reduce the overall corrosion rate and to improve mechanical properties of the penetrator. Because U metal is thermodynamically unstable

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(a) Open-air testing at Ford's Farm was discontinued in 1980, and subsequent test firing was conducted in an enclosure. All test firing of DU penetrators at Ford's Farm was discontinued in 1985.

with respect to more oxidized forms of U [U(IV) and U(VI)], it will react to form them when in contact with the earth's atmosphere. The ability of water to dissolve U depends on the oxidation state of the U.

Published work on the oxidation of U metal has primarily focussed on oxidation at the relatively high temperatures found in reactor environments or in fires (approximately 100°C to 1,000°C). However, some data are available for the oxidation of U metal in contact with dry air, moist air, water vapor, and carbon dioxide at temperatures less than 100°C (Ritchie 1981; Tyzack and Cowen 1976). The primary oxidation products are hyperstoichiometric U(IV) oxides of the form UO_{2+x}, where $0 < x < 0.4$. The oxidation reactions are:

$$U + [(2+x)/2]O_2 = UO_{2+x} \tag{1}$$

$$U + (2+x)H_2O = UO_{2+x} + (2+x)H_2 \tag{2}$$

$$U + 2CO_2 = UO_2 + 2CO \tag{3}$$

Further oxidation to mixed U(IV) and U(VI) oxides (e.g., U_4O_9, U_3O_7, and U_3O_8) and to U(VI) oxides ($UO_3 \cdot nH_2O$) may also occur (Ritchie 1981; Bloch et al. 1982; Aronson et al. 1957).

Two limiting cases bound the rate of oxidation of the U metal contained in a penetrator following a test firing: either 1) the U metal oxidizes immediately and completely upon target impact, or 2) none of the U metal oxidizes until it is on the ground. The first case most closely represents the impact of a penetrator on a hard target (such as at the Ford's Farm site). The second case most closely represents the landing of an intact penetrator, or large pieces of a penetrator, on the soil of a soft target range (such as at the B-3 range). The actual behavior (with oxidation occurring before and following deposition) depends on the details of the impact (whether with a target, other materials, or the ground), including the temperatures reached during impact and the size/frequency distribution of the dispersed particles. For the purposes of this review, we consider the bounding case in which oxidation does not occur until after impact or deposition onto the soil. Our calculations provide a lower estimate of the rate at which U(IV) and U(VI) become available for leaching into water.

The mass loading (amount of mass present in a particle per unit surface area) and the oxidation rate (mass oxidized per unit surface area per unit time) govern the rate at which U metal is converted into U(IV). The mass loading can be calculated from the size/frequency distribution of dispersed particles or pieces of a penetrator. In the absence of adequate information regarding size/frequency distributions, we provide trial calculations for 1 kg of U metal divided into N spheres of equal mass. The choice of spherical geometry is arbitrary and will affect the results of the calculation by only a factor of approximately 2. Uranium metal has a molecular weight of 238,029 mg/mole, and a molar volume of 12.497 cm^3/mole (Robie et al. 1978). Table 1 shows the mass (M), surface area (A), and mass loading (M/A) of each U metal sphere.

Note that as the particle size decreases, the same amount of mass has more surface area. For example, the combined surface area of 1 million spheres each of 1 mg mass and 0.00678 cm^2 surface area is 6,780 cm^2. Thus, for a given oxidation rate, greater amounts of U metal will be oxidized per unit time as the average particle size becomes smaller. For example, hypothetical DU penetrators that are 5/8 in. (1.59 cm) in diameter and 14 in.

TABLE 1. Mass Loading of Spherical U Metal Particles

N	Mass (mg)	Area (cm^2)	M/A (mg/cm^2)
1	1,000,000	67.6	14,800
10	100,000	14.6	6,850
100	10,000	3.15	3,180
1,000	1,000	0.678	1,470
10,000	100	0.146	685
100,000	10	0.0315	318
1,000,000	1	0.00678	148

(35.56 cm) long have a mass of 1,345,000 mg, a surface area of 181.6 cm^2, and the surface loading ratio is 7406 mg/cm^2.

Atmospheric Oxidation

Oxidation rates are given in units of milligrams of U metal oxidized per square centimeter per hour (mg/cm^2-h). Table 2 lists oxidation rates for U metal (Ritchie 1981) under various conditions. A review of reaction rates suggest that the most rapid oxidation of U metal occurs when U metal is in contact with pure water vapor (Ritchie 1981; Tyzack and Cowen 1976). At 25°C, this rate is approximately 0.024 mg U/cm^2-h. The oxidation rates are much slower in dry air (0.000026), CO_2 (0.000001), and O_2 and water vapor (0.00041). The reaction rates are exponential functions of temperature, approximately doubling as the temperature increases from 25°C to 35°C. Note that in Table 2 we used the approximation that the rate law applies below 40°C to extrapolate rates for the oxidation of U at 25°C in the U-dry air and U-O_2-water vapor systems. The oxidation rate of U - 0.75% Ti alloy has been measured at 74°C and 75% relative humidity as 3.3×10^{-4} mg U/cm^2-h (Loewenstein 1980). Under such conditions, the addition of 0.75% Ti to U metal appears to slow the oxidation rate by a factor of approximately 16.

TABLE 2. Atmospheric Oxidation Rates of U Metal

System	Temp (°C)	Rate Law	Rate at 25°C (mg/cm^2-h)
U-dry air	$40 \leq T \leq 300$	$(6.9 \times 10^8)\exp(-18{,}300/RT)$	2.6×10^{-5}
U-water vapor (100% RH)	$20 \leq T \leq 100$	$(3.2 \times 10^8)\exp(-13{,}800/RT)$	2.4×10^{-2}
U-O_2-water vapor (100% RH)	$25 \leq T \leq 100$	$(4.6 \times 10^9)\exp(-17{,}800/RT)$	4.1×10^{-4}
U-O_2-water vapor (2 to 90% RH)	$40 \leq T \leq 130$	$(4.8 \times 10^{13})\exp(-25{,}000/RT)$	2.2×10^{-5}

For the rate laws, T is temperature in degrees Kelvin, and R is the gas constant in cal/mol·deg.

These data illustrate the importance of the presence of oxygen and relative humidity on the corrosion rate of U metal. If the relative humidity is less than 90%, the oxidation rate is significantly reduced to nearly that of water-free air. The effect of water vapor on the corrosion rate between 50 and 75°C has also been found to be small (Bennett and Price 1981). The higher oxidation rate in wet, oxygen-free environments is believed to be a result of the structural disruption of the metal caused by the formation of uranium hydride, which in turn is a result of the absorption and reaction of hydrogen that is produced by the reaction that exposes additional surface. In the presence of oxygen, the oxide film formed is more protective and the base metal is not disrupted.

Using the data provided in the Tables 1 and 2, the availability of U(IV) can be calculated using the mass of U metal oxidized to UO_2 per unit time. For example, if 1000 pieces from a 1-kg disrupted penetrator average 1 g each in mass (Table 1), and if the reaction rate in the presence of O_2 and water vapor at 100% relative humidity is appropriate (0.00041 mg U/cm^2-h; Table 2), then 0.28 mg of U metal will be oxidized each hour. The estimated lifetime of 1 kg of U metal under these conditions will be about 410 years. In making that estimate, it is assumed that the surface of the metal is uniformly exposed in a humid air environment and that atmospheric oxidation dominates. For an intact DU penetrator having a mass of 1.345 kg, 0.075 mg of U metal would be oxidized to UO_2 each hour, and the estimated lifetime of the penetrator would be around 2100 years. In either case, within a matter of hours the amount of UO_2 available to be leached by rainwater exceeds several milligrams. Under some environmental conditions, the solubility of UO_2 in water is on the order of a few micrograms of U per liter of water. Therefore, the rate at which U metal is oxidized to U(IV) oxide probably does not limit the mobility of U in the subsurface pathway.

Aqueous Corrosion

For aqueous conditions, such as might exist in surface-water pools or along a shoreline, corrosion rates tend to be higher than atmospheric oxidation rates. For instance, in contrast to the rates given for atmospheric reactions in Table 2, the corrosion rate of U in 5% NaCl solution was observed to be 27 mils/year (mpy, or 0.15 mg/cm^2-hr) and that of U - 0.75% Ti to be 9.1 mpy or 0.05 mg/cm^2-hr (McIntyre et al. 1988). Crevice areas (which have low oxygen concentrations) promoted U - 0.75% Ti corrosion to rates of 30 mpy. The presence of chloride is important because concentrations as low as 0.005 M (178 ppm chloride) can destroy passivity and cause pitting (Levy et al. 1973). Once pitting has begun, areas with low oxygen content and an acidic environment will develop and accelerate the corrosion rate.

The reaction products of U metal in water are probably similar to the oxidation products in water vapor (equation 2), and hydrogen would be produced in the absence of oxygen. The corrosion resistance of metals can be measured as the electrode potential relative to the standard calomel electrode (SCE). Large negative potentials are associated with high corrosion rates. Table 3 lists the electrode potentials of various metals in deionized water and in a NaCl solution at 29°C. Although U metal is anodic to AISI 4340 carbon steel in the NaCl solution, the net corrosion rate for the U metal is lower (8 mpy), possibly because more adherent films have formed (McIntyre et al. 1988). Aluminum is normally anodic to U - 0.75% Ti in chloride-free solutions, but in chloride solutions the potentials reverse. However, even in this case, the corrosion rate of the U alloy is low, near 3 mpy (McIntyre et al. 1988).

TABLE 3. Electrode Potentials for Metals (in V) at 29°C (Briggs 1985)

5.0% NaCl at pH 6.8		Deaerated, Distilled water at pH 5.8	
304 SS	+0.234	Ag	+0.126
Ag	-0.084	304 SS	+0.102
Cu	-0.276	Cu	+0.070
Sn	-0.482	Sn	-0.142
4340 steel	-0.678	DU	-0.163
DU	-0.768	U-.75 Ti	-0.206
5083 Al	-0.770	4340 steel	-0.442
U-.75 Ti	-0.838	Zn	-0.658
Zn	-1.050	5083 Al	-0.820

FACTORS AFFECTING SOURCE-TERM URANIUM CONCENTRATIONS

Most published information about the occurrence and mobility of U in the natural environment has focussed on the geochemical conditions of formation of uranium ore deposits, the adsorption and ion-exchange of uranium on soil minerals, and the aqueous solubilities of uranium minerals. The calculation of uranium concentrations resulting from either solubility equilibrium with any uranium solid or adsorption of uranium on soil minerals is dependent on the set of thermodynamic data used in the calculation. Langmuir (1978a,b) has critically reviewed the thermodynamic properties of dissolved U and the mineral-solution equilibria relevant to the formation of U ore deposits. Since 1978, more recent thermodynamic data have been re-evaluated and compiled, and alternative viewpoints relevant to the aqueous behavior of U(IV) or U(VI) have been presented in other reviews by Krupka et al. (1983, 1985) and Tripathi (1984). Krupka et al. (1983, 1985) reviewed thermodynamic data for the aqueous behavior of U(IV) and U(VI) and evaluated experimental data for the solubilities of some uranium minerals. A review of thermodynamic data for U(VI) was also discussed by Tripathi (1984) who used the data to model experimental measurements of the adsorption of U(VI) on goethite.

Although the speciation scheme used by Langmuir (1978a,b) differs from the later reviews of the speciation behavior of U(IV) and U(VI), the field descriptions and calculations relevant to the occurrence of uranium in nature presented by Langmuir (1978a,b) are still useful as a guide to the possible weathering reactions that may occur between soil pore waters and corrosion products of spent DU penetrators. Therefore, much of the following discussion is based upon the calculations presented by Langmuir (1978a,b). The reader should be aware, however, that the calculations shown in the subsequent section of the report may differ substantially if another speciation scheme for the aqueous behavior of uranium is used to calculate the mineral solubility equilibria.

Uranium occurs in solids and in groundwater in two primary oxidation states, U(IV) and U(VI). Redox conditions therefore determine the form of dissolved U in groundwater and the type of U solids formed. The chemical composition of soil pore waters also determines which U solid will be thermodynamically stable and the source-term concentration of dissolved U, because dissolved uranium concentrations are affected by the presence of complexing ligands, such as OH^-, Cl^-, CO_3^{2-}, PO_4^{3-}, F^-, $H_4SiO_4^0$, SO_4^{2-}, and soil organic acids.

The stability of various U solids and the resulting U concentrations in groundwater have been described by Langmuir (1978a,b) in terms of mineral solubility equilibria. An assumption made here is that the source-term concentrations of U are solubility-limited by the interactions of near-surface waters and U-oxide corrosion products of DU. A review of the solubilities of U solids as a function of relevant geochemical parameters will provide information on the range of U concentrations that can be expected from the leaching of the oxidation products of the weathering of DU penetrators.

The most common U ore minerals in reduced environments are the U(IV) minerals, which include uraninite (UO_2), coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$], and (in some ore deposits in Japan that contain a source of phosphate) ningyoite [$(U,Ca,Ce)_2(PO_4)_2 \cdot 1\text{-}2H_2O$] (Muto 1965). Uranium (IV) in solution exists as the uranous ion (U^{4+}) and is complexed in reduced groundwater mainly in the form of several hydrolysis species, sulfate, chloride, and phosphate, and it is complexed by fluoride at pH values less than 4 (Langmuir 1978a). Figure 1 shows the distribution of these species for typical groundwater ligand concentrations, as calculated by Langmuir (1978a). Uranium (IV) complexes involving chloride, sulfate, and phosphate are insignificant over the pH range shown. Between pH values of 5 and 8, the important U(IV) complexes include the $U(OH)_4^0$ and $U(OH)_5^-$ hydrolysis species. At a pH of less than 3, the U(IV) fluoride complexes are dominant.

As discussed in the previous section, one of the first products expected from oxidation of spent DU penetrators is UO_2. Figure 2 shows the change in uranium concentrations versus pH, calculated for the solubility of uraninite in water (Langmuir 1978a). In the range of pH values common to most reduced groundwaters (pH 5 to 8), the solubility of uraninite is very low and dissolved U concentrations are generally below 0.1 ppb (Figure 2). Figure 2 also shows the effect of fluoride complexation on uraninite solubility at low pH values. More recent review and recalculation of the thermodynamic data

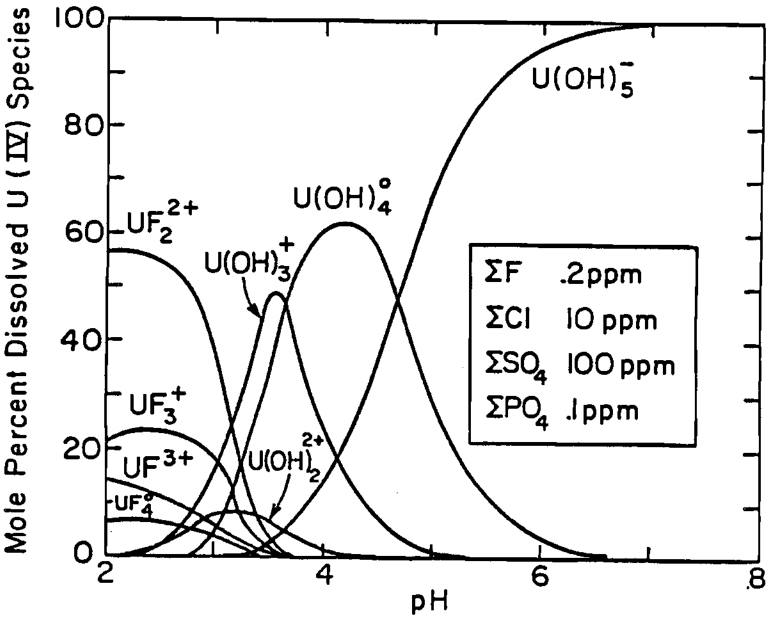

Figure 1. Distribution of the significant U(IV) complexes as a function of pH at 25°C calculated for the ligand concentrations shown (Reprinted with permission, from Langmuir 1978a).

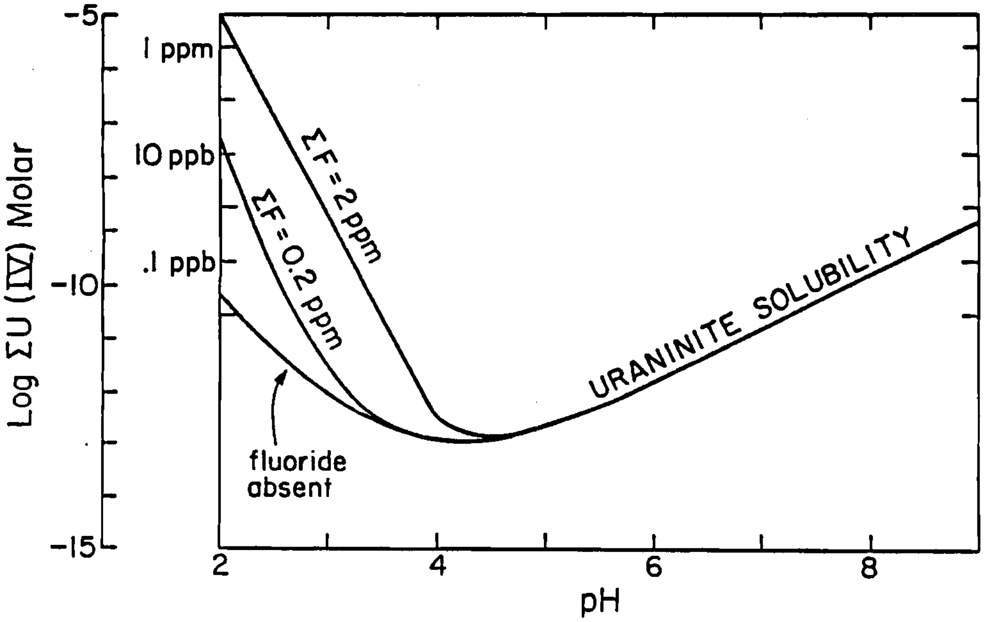

Figure 2. The solubility of uraninite (UO_2) as a function of pH at 25°C, showing the effect of dissolved fluoride (Reprinted with permission, from Langmuir 1978a).

involving U(IV) aqueous species and calculations of uraninite solubility has shown that above pH 6 the solubility of uraninite may be as much as two orders of magnitude smaller than that shown in Figure 2 (Krupka et al. 1983). Thus, in a reduced environment where UO_2 is a stable solid, source-term concentrations of U at typical groundwater pH values and ligand concentrations would be expected to be very small.

Because soil pore waters interacting with DU penetrators may be oxidizing, the stability of UO_2 must be examined as a function of redox potential (Eh). In addition, the oxidation of U to form U(VI) oxides, their relative solubilities, and the aqueous complexation scheme for U(VI) must also be reviewed. The oxidation of U(IV) to U(VI) may modify the source-term concentrations and mobility of dissolved U entering a soil profile, both because U(VI) is strongly complexed by ligands commonly found in groundwater and because the solubilities of U(VI) minerals are generally larger than that of UO_2.

Dissolved U(VI) exists in solution as the uranyl ion (UO_2^{2+}), and forms complexes with OH-, CO_3^{2-}, F^-, PO_4^{3-}, SO_4^{2-}, and organic ligands. In Figure 3, the distribution of the significant uranyl species calculated by Langmuir (1978a) is shown for ligand concentrations typical of the Wind River Formation (primarily sandstone units located in Wyoming). The uranyl ion is complexed primarily by fluoride at pH less than 4, and it is strongly complexed by phosphate between pH values of 4 and 7.5. At higher pH, dissolved uranium is present predominantly as the uranyl carbonate complexes shown in Figure 3. More recent work by Maya (1981) and Maya and Begun (1981) has shown evidence for additional hydroxocarbonato species that were not included in the calculations by Langmuir (1978a). The effects of the additional species on the U(VI) speciation scheme and on the adsorption of U(VI) were further evaluated by Tripathi (1984).

Both the proportion of the total dissolved U that is divided into U(IV) and U(VI) aqueous complexes and the effect of the speciation scheme on the relative stabilities of the U(IV) and U(VI) minerals will depend on the Eh and the ligand concentrations in the soil pore water. Of the complexing ligands known to affect the concentrations of uranium in oxidized

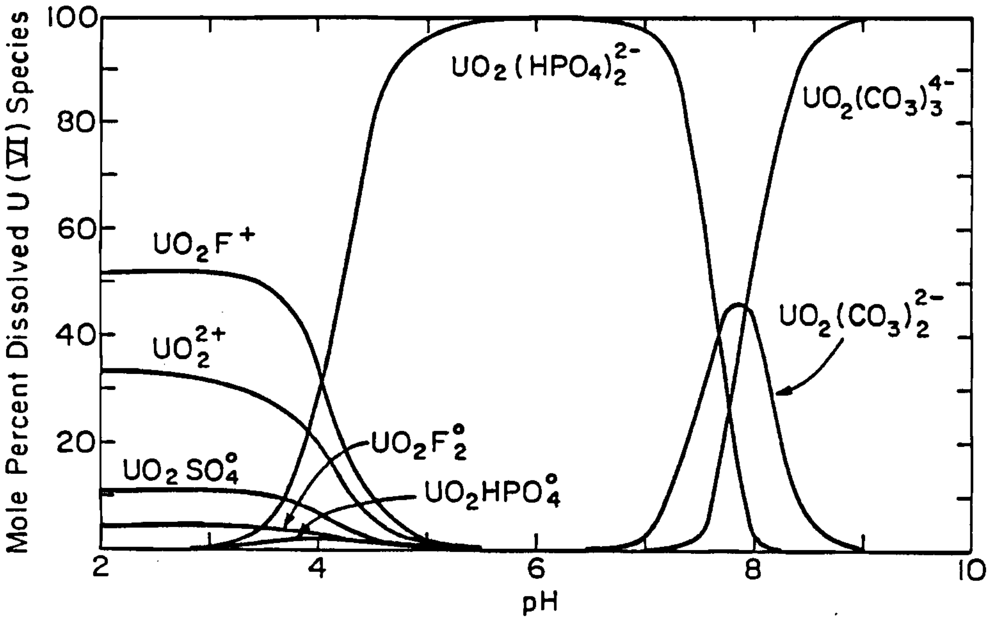

Figure 3. Distribution of significant U(VI) complexes at 25°C as a function of pH for a groundwater having the following composition: $pCO_2=10^{-2.5}$ atm, F=0.3 ppm, Cl=10 ppm, SO_4=100 ppm, PO_4=0.1 ppm, SiO_2=30 ppm (Reprinted with permission, from Langmuir 1978a).

ground-water, dissolved carbonate and phosphate are considered the most important (Langmuir 1978a). The examples in Figures 4 through 6 illustrate some of the effects that the Eh and complexing ligands have on dissolved U concentrations involving UO_2 solubility.

Figure 4 is an Eh-pH diagram showing the stability fields for uraninite and for the dominant U(IV) and U(VI) aqueous species at a CO_2 partial pressure (pCO_2) of 10^{-2} atm (the atmosphere has a pCO_2 of $10^{-3.5}$ atm) and a total U concentration of 10^{-6} M (0.24 ppm). The diagram shows the dominance of the uranyl carbonate species at pH values above 6 and that uraninite is stable up to Eh values of about +100 mV in the neutral pH range at this U concentration. The effect of dissolved carbonate on U concentrations resulting from the solubility of UO_2 is shown in Figure 5 at a pH of 8 for two CO_2 partial pressures. In more oxidized groundwater, the increase in UO_2 solubility is a

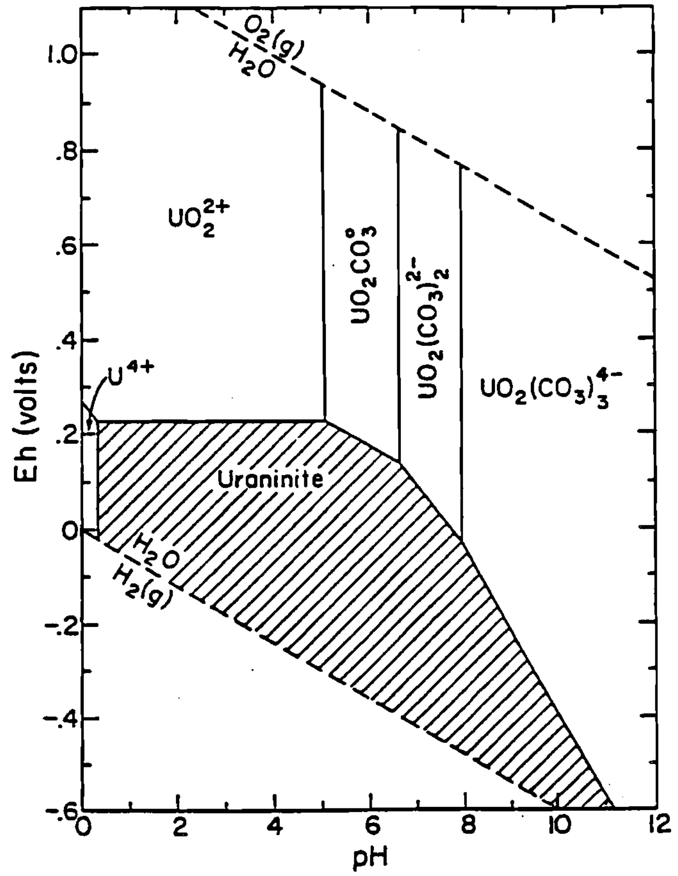

Figure 4. Eh-pH diagram in the system U - O_2 - CO_2 - H_2O at 25°C, showing the stability field of UO_2 for a total U concentration of 0.24 ppm and a pCO_2 of 0.01 atm (Reprinted with permission, from Langmuir 1978a).

result of the complexation of the uranyl ion by dissolved carbonate. At any Eh value above -200 mV, an increase in pCO_2 results in a larger uraninite solubility. A similar plot (Figure 6) for two phosphate concentrations shows the increase in uraninite solubility at high Eh values that occurs because of complexation of uranyl ion by phosphate. Therefore, source-term concentrations of U resulting from UO_2 solubility will depend on the Eh, pH, and concentration of complexing ligands in the near-surface waters. Typical surface waters in equilibrium with the atmosphere have Eh values between +250 and +500 mV, suggesting UO_2 is likely to be more soluble than U(VI) minerals. Under these conditions, U(VI) minerals may be more stable and consequently may control aqueous U concentrations at lower values.

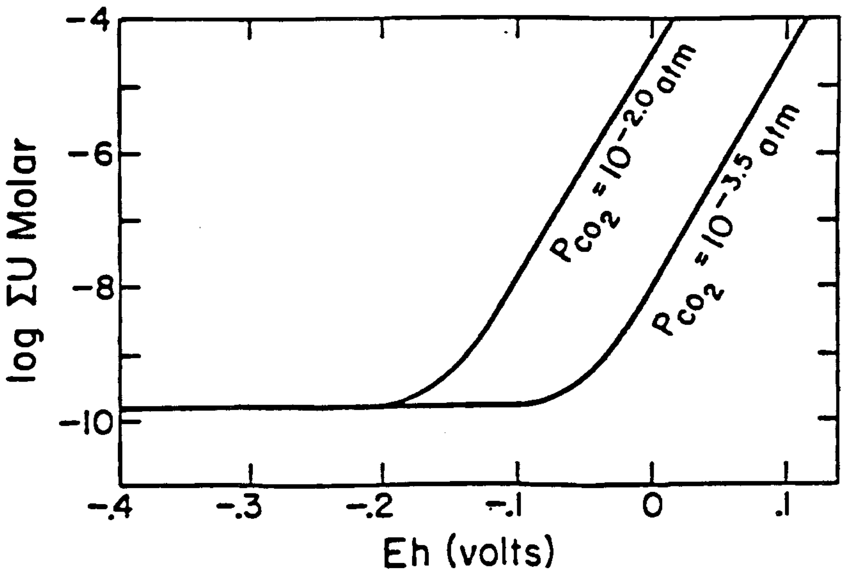

Figure 5. The solubility of UO_2 at 25°C and pH 8 as a function of Eh and pCO_2 (Reprinted with permission, from Langmuir 1978a).

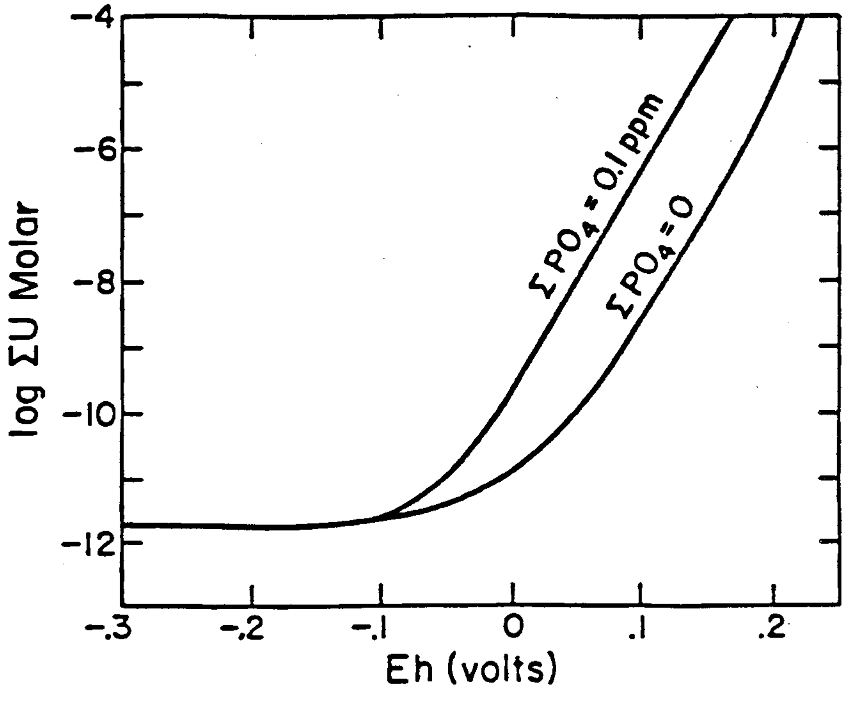

Figure 6. The solubility of UO_2 at pH 6, pCO_2=0.01 atm, and 25°C for two phosphate concentrations (Reprinted with permission, from Langmuir 1978a).

ATTENUATION BEHAVIOR OF URANIUM

Other reactions between local soils and groundwater may also affect the concentrations of U transported through a soil profile. These reactions include precipitation of secondary U minerals, ion exchange of U on clay minerals, and specific-ion adsorption of U on mineral surfaces. All three types of mass-transfer reactions could decrease the concentration of U in groundwater migrating through a soil profile.

The precipitation of U(VI) minerals from an oxidized groundwater containing uranium that has been leached from corroded DU penetrators is one mechanism that could attenuate the subsurface migration of U. Which U(VI) minerals precipitate will depend on the pH and ligand concentrations in the groundwater. Some of the more common U(VI) minerals found in oxidized zones near uranium ore deposits are carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$], tyuyamunite [$Ca(UO_2)_2(VO_4)_2 \cdot 2.5\text{-}8H_2O$], autunite [$Ca(UO_2)_2(PO_4)_2 \cdot 10\text{-}12H_2O$], and uranophane [$Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$] (Langmuir 1978a). Of these U(VI) minerals, carnotite and tyuyamunite are the least soluble in groundwater containing small quantities of dissolved vanadium. Figures 7 and 8 show the solubilities of carnotite and tyuyamunite as a function of pH, as calculated by Langmuir (1978a). In the pH range from 5 to 8, either solid could limit the total concentration of dissolved U to levels less than 10^{-8} molar (~2 ppb U) at atmospheric pCO_2 ($10^{-3.5}$ atm). The uppermost curves in Figures 7 and 8 show the effect of increasing the partial pressure of CO_2 gas. The higher solubility at any pH value illustrates the effect of complexation of the uranyl ion by dissolved carbonate.

For groundwater that does not contain vanadium but does contain dissolved phosphate, autunite is the least soluble U(VI) mineral that could limit the concentration of U (Langmuir 1978a). Figure 9 shows the solubility of autunite as a function of pH and pCO_2. In the pH range shown at either of the pCO_2 values, autunite is more soluble than the uranyl vanadate minerals (Figures 7 and 8). The mineral uranophane is more soluble than any of the uranyl vanadate or phosphate minerals discussed above at the vanadium and

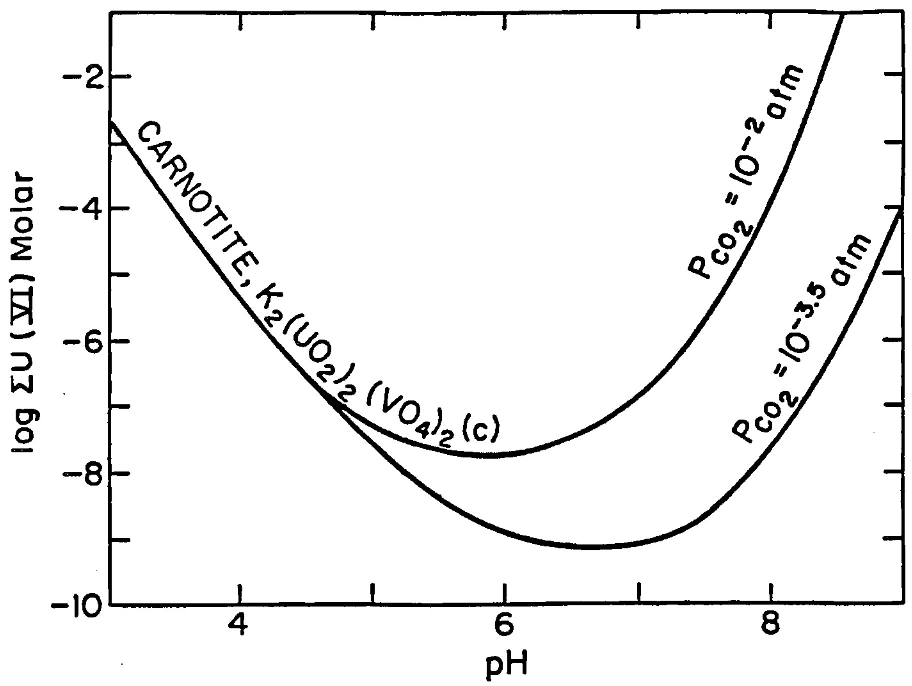

Figure 7. The solubility of carnotite at 25°C as a function of pH and pCO_2 for concentrations of K = 39 ppm and VO_4 = 0.1 ppm (Reprinted with permission, from Langmuir 1978a).

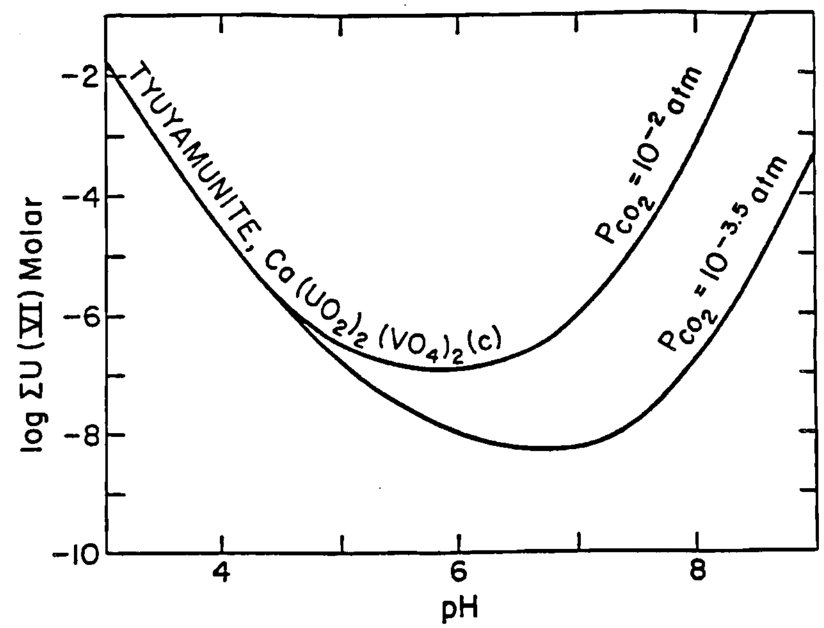

Figure 8. The solubility of tyuyamunite at 25°C as a function of pH and pCO_2 for concentrations of Ca = 80 ppm and VO_4 = 0.1 ppm (Reprinted with permission, from Langmuir 1978a).

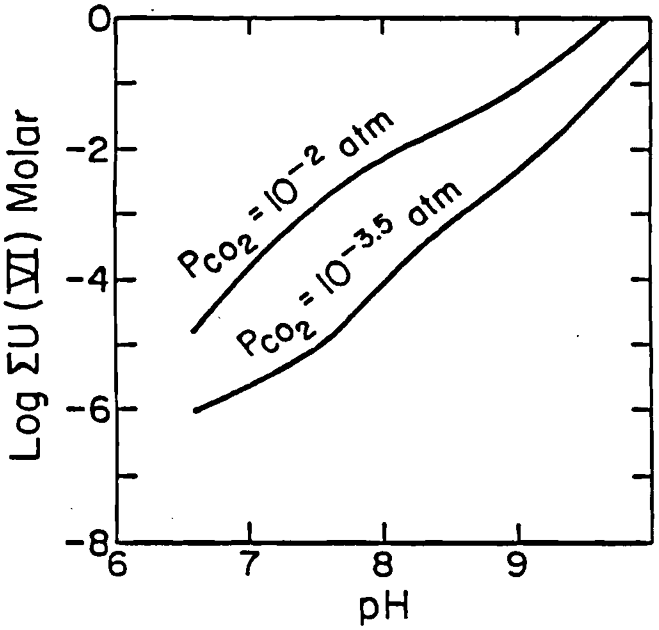

Figure 9. The solubility of autunite at 25°C as a function of pH and pCO_2 for concentrations of Ca = 80 ppm and PO_4 = 0.1 ppm (Reprinted with permission, from Langmuir 1978a).

phosphorus concentrations expected in groundwater (Langmuir 1978a). Therefore, if groundwater source-term concentrations of U leached from DU penetrators enter a soil profile above the solubility limits of the U(VI) minerals, precipitation of the U(VI) minerals could lower the concentration of dissolved U. The relative stabilities of these minerals will depend primarily on the concentrations of dissolved vanadate and phosphate in the groundwater. The solubility-limited concentration of U transported through the soil profile will also depend on the groundwater pH, Eh, and carbonate concentration.

A second mechanism that can attenuate the transport of U through sediments is the adsorption of dissolved U on mineral surfaces, by either ion exchange or specific adsorption reactions. The adsorption of the uranyl ion has been studied experimentally on a variety of surfaces including organic matter (peat), clay minerals, and ferric oxides and oxyhydroxides that are common in soils.

In their description of the mineralization of U ore deposits in Japan, Doi et al. (1975) suggested that adsorption of U on organic matter was the most important factor in concentrating U on solid surfaces. Doi et al. (1975) reported that in suspensions of 1 g of peat per 100 ml uranyl perchloride acid solution (4 ppm U) between pH values of 3 and 8.5 up to 100% adsorption of uranium occurred. Above pH 8.5, the U was desorbed because $NaHCO_3$ was used to adjust the pH of the solutions, resulting in increased carbonate complexation of the uranyl ion.

Several experimental studies have measured the affinity of the uranyl ion for different clay mineral surfaces commonly found in soils. Borovec (1981) measured the distribution coefficients (Kd) of U on kaolinite, illite, and montmorillonite in chloride solutions containing between 10^{-2} and 10^{-5} molar (2400-2 ppm) U(VI) at pH 6. For dissolved U concentrations less than 10^{-4} molar, the Kd values measured increased from 50 to about 1000 ml/g in the order kaolinite < illite < montmorillonite. Ames et al. (1983a) performed similar measurements for the same clay minerals at pH 7 in NaCl solutions and pH 8-9 in $NaHCO_3$ solutions. Maximum Kd values in the NaCl solutions for illite, montmorillonite, and kaolinite were 500, 650, and 700 ml/g, respectively. In the carbonate solutions, the cation exchange of uranyl ion on the clays was reduced because aqueous complexation reactions formed uranyl carbonate species. As a result, the maximum Kds for illite and montmorillonite decreased to 110 and 2, respectively. This pattern is consistent with the decreased affinity of clay mineral surfaces for the uranyl ion. Similar measurements were made by Ames et al. (1983b) for several mica minerals (biotite, phlogopite, muscovite) that are less prominent in weathered soils.

Perhaps the most important soil mineral surfaces with a strong affinity for adsorbing dissolved solutes are the surfaces of iron oxides and oxyhydroxides. Ames et al. (1983c) measured the adsorption of uranyl ion on amorphous ferric hydroxide in NaCl solution at pH 7 and in $NaHCO_3$ solution at pH 8.7. Calculations from the measurements suggest that the Kd for U(VI) is greater than 2×10^6 ml/g in NaCl solution and 3×10^4 ml/g in $NaHCO_3$ solution. More comprehensive studies of uranyl adsorption by iron oxides and oxyhydroxides have since been published by Hsi and Langmuir (1985) and by

Tripathi (1984). These studies discuss the adsorption of U(VI) over a wider range of pH values with and without dissolved carbonate present. For example, Hsi and Langmuir (1985) showed that uranyl ion is strongly adsorbed by hematite, goethite, and amorphous ferric oxyhydroxide at pH values greater than 5 to 6 (Figure 10). Adsorption was greatest on the amorphous

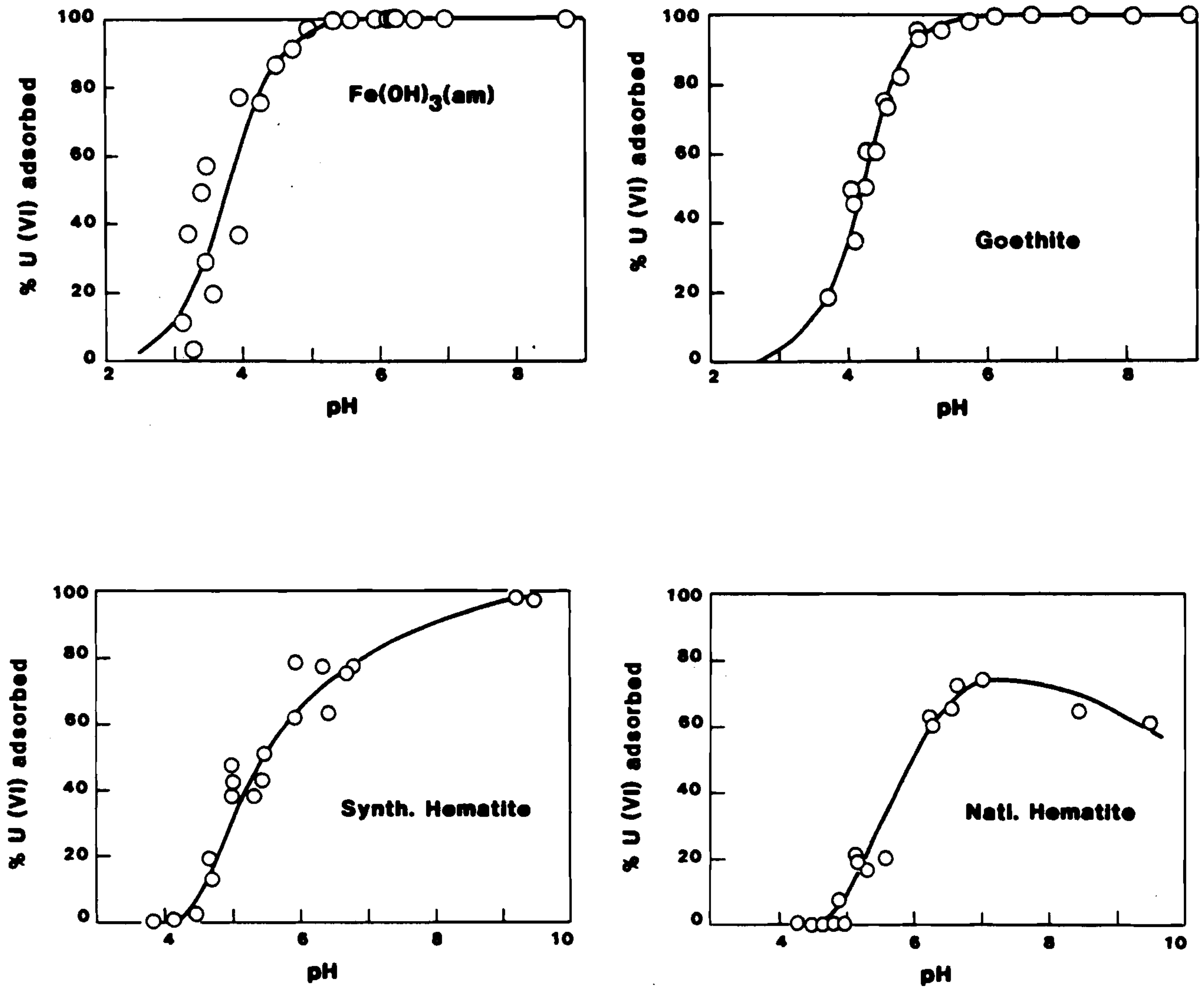

Figure 10. Adsorption of uranyl ion versus pH at a total U concentration of 10^{-5} molar (2.4 ppm) onto 1 g/L suspensions of ferric oxyhydroxides in 0.1 M $NaNO_3$ solutions at 25°C (Reprinted with permission, from Hsi and Langmuir (1985).

oxyhydroxide and least on hematite. At total U concentrations of 10^{-5} molar (2.4 ppm), essentially all U(VI) is adsorbed by 1 g/L of goethite and amorphous ferric oxyhydroxide above pH 5 in the carbonate-free system. Hematite adsorbed only about 80% of the U over the same pH range. In the presence of dissolved carbonate at concentrations of 10^{-3} to 10^{-2} molar (60-600 ppm), U adsorption was inhibited on all of the ferric oxide surfaces above pH 6.5.

The results of the adsorption studies of dissolved U on common mineral surfaces show that the iron oxides and oxyhydroxides have the strongest affinity for U(VI) adsorption. The affinity of these surfaces for the uranyl ion could reduce the concentrations of dissolved U in groundwater and thus attenuate its subsurface transport. The data also show that dissolved carbonate present at concentrations common in most groundwater could inhibit the attenuation of dissolved uranium because of complexation effects. As a result, an accurate assessment of the potential for the attenuation of the subsurface transport of uranium requires site-specific field characterization data relevant to the groundwater chemistry and to the types and quantities of minerals present in local subsurface soils.

UPTAKE OF URANIUM BY PLANTS

The uptake of radionuclides by plants from soils has been modeled using element-specific plant/soil concentration ratios (CR). In a review of CR values for U, Th, and Pb, Sheppard and Evenden (1988) recommended appropriate values for U to be used in environmental assessments. The mobility of U in the soil is an important factor governing the uptake by plants and is dependent on U solution species and on the particle size of the soil, which affects the soil adsorption/retention characteristics. The mobility of U is increased through complexation with the carbonate anion and, in some cases, by soil organic matter. It was suggested by Sheppard and Evenden (1988) that the uptake of radionuclides by plants is correlated with radionuclide concentrations in the soil pore waters more strongly than with total concentrations in the soil. Existing CR data for radionuclides have limited application because such ancillary data as the soil pH and concentrations of organic and carbonate ligands are usually not reported (Sheppard and Evenden 1988). It is therefore difficult to interpret and categorize the CR data based on the chemical composition of the soils and soil pore waters. These same limitations also apply to the environmental sampling data discussed above for the LASL site and for the ranges on the Aberdeen Proving Grounds.

CONCLUSIONS

The results of this review suggest there is a potential for U from spent DU penetrators that is dispersed in soils to become mobilized and travel through the groundwater and surface water pathways. The oxidation of U metal to U(IV) oxide probably will not limit the mobility of U in the surface or subsurface water pathways. The potential for U migration depends on the oxidation products of the depleted U and on the chemistry of local soils and pore waters. Uranium (VI) is more mobile than U(IV) because of complexation reactions involving ligands commonly found in natural waters; carbonate and phosphate are generally considered the most important of these. The mobility of U in the environment therefore depends on Eh, pH, and the presence of complexing ligands. The transport of U may also be affected by attenuation reactions that could reduce U concentrations in local groundwater and surface water. These reactions include ion exchange and specific adsorption of U on organic matter, clay minerals, and ferric oxides and oxyhydroxides commonly present in soils.

Evaluating the potential for U migration and uptake from spent DU penetrators at a particular location requires detailed field characterization data for the chemical composition of surface water, and groundwater, and soil. We have shown that the concentrations of U to be expected in groundwater are strongly dependent on the chemical compositions of both the groundwater and local soils. The results of Sheppard and Evenden (1988) suggest that these same factors are also important to the uptake of U by plants. Because concentrations of total U in contaminated soils and groundwater were the only chemical measurements reported for the LASL and Aberdeen target ranges, it was not possible to develop a quantitative understanding of the differences between the measured U concentrations in the local groundwater at these sites.

Interpretation of aqueous and soil U concentrations in terms of specific geochemical mechanisms is not possible without supporting data. It is not sufficient to report only U concentrations in surface water, groundwater, or soils. To develop an understanding of the processes controlling the corrosion rate and the subsequent U migration requires additional measurements. Measurements for surface and pore waters should (at a minimum) include pH, Eh, and the concentrations of major cations, anions, specific trace elements (e.g., V and P), and dissolved organic compounds. The soils should be characterized for mineral type and content, organic matter, and amorphous iron hydroxide contents. Further site-specific soil experiments should be performed to quantify U attenuation.

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