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XXXIV. FIFTY YEARS WITH
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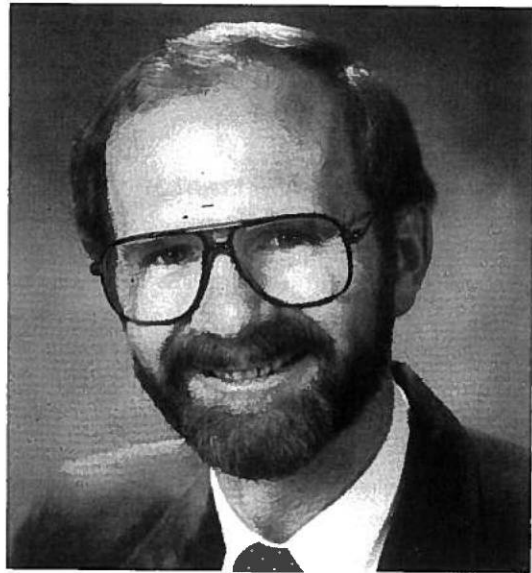
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CHAPTER XIII

ACTINIDES IN THE ENVIRONMENT*

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I. INTRODUCTION

It was evident early on that mankind could have a significant impact on the quality of his life by upsetting the natural order of the environment. But man's active concern for his environment started only a few decades ago. It began when Apollo astronauts returned from space with photographs of a unique and precious small blue planet. It was a dramatic new view and the beginning of a new attitude. One of our most serious environmental concerns is the safe disposal of nuclear waste. It is increasingly obvious that we cannot continue to rely on dwindling fossil fuel resources to meet our ever-increasing energy demands. Nuclear power promises to be the long term answer to our energy needs, provided the problems associated with nuclear waste disposal are solved. The approach to these problems lies in understanding the fundamental physical and chemical behavior in the environment of the key radionuclides in nuclear waste, the actinides.

"Growing worldwide interest and a natural desire to protect man and his environment have led to increasing concern in public, scientific, and government sectors about the release of such radionuclides into the environment...It is essential, in view of their long half-lives and high relative radiotoxicities, that their fate in the environment be understood well enough to permit associated potential impacts to be assessed and hence effective control to be provided." [1]

There is a vast body of literature on the chemical behavior of actinide elements in the environment and, therefore, it is not possible to provide a comprehensive review of all aspects of the field. Consequently, this review should be regarded as a survey rather than a comprehensive treatise. This author's intention is to lead the interested reader to more detailed works in the chemical literature. Historical reports are cited for completeness, but for the most part, emphasis has been placed on some of the most recent reports available at the time of writing. Extensive use has been made of a number of recent reviews. [1-8]

A. Our Nuclear Legacy

The actinides are the fourteen 5-*f* elements following actinium in the Periodic Table. Naturally occurring actinide elements, thorium, protactinium, and uranium, have been

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known for some time [2]. Thorium and uranium occur in vast quantities in the Earth's crust, while protactinium is available in lesser amounts. Native transuranium elements have been detected in trace amounts in nature [9, 10]. An excellent review of transuranium elements in nature is presented by Prof. G. Herrmann in the chapter preceding this one [11].

This year, 1990, we commemorate the Fiftieth Anniversary of the discovery of the synthetic transuranium elements. Neptunium, was discovered in 1940 by McMillan and Abelson [12] and later that year, plutonium was discovered by Seaborg, McMillan, Kennedy, and Wahl [13]. The other transuranium elements were discovered in successive years: americium and curium in 1944/45; berkelium and californium in 1949/50; einsteinium and fermium in 1952; mendelevium in 1955; nobelium in 1957; and lawrencium in 1961 [2]. The discovery of the transuranium elements and the dawn of the Nuclear Age provided mankind with a double-edged sword. Nuclear power can provide us with an unlimited energy source through peaceful applications, or we can use it to devastate this planet in a matter of minutes with thermonuclear weapons. The threat of all-out nuclear war has diminished somewhat in recent years, but perhaps more threatening now is the proliferation of nuclear waste. Mankind has been living on this planet with its natural radioactivity background for millennia without significant harmful effects. The improper treatment and disposal of nuclear waste has the potential to significantly increase radiation exposure to man. The Earth's environment is a very complex system which has evolved over billions of years. If we manage to avoid destroying it in only a few minutes with nuclear weapons, we may still destroy it in only a few decades through lack of knowledge, improper attitudes, and disregard for safe nuclear waste disposal.

B. Sources of Actinides

The development of a large scale nuclear power industry and the detonation of nuclear weapons in the atmosphere and underground have contributed to the present vast inventories of nuclear waste. Reentry and disintegration of nuclear powered satellites, nuclear reactor releases, and incidents involving aircraft armed with nuclear weapons have added to the problem. The major source of world-wide radioactive contamination is by far from atmospheric nuclear weapons testing. [14]

On July 16, 1945, the first injection of transuranium elements into the atmosphere occurred with the detonation of the first nuclear explosion (Figure 1) at Trinity Site near Alamogordo, NM. Between 1945 and 1952 further nuclear detonations resulted in additional radioactive contamination of the atmosphere, but these were all low-yield (kilo-ton) *fission* devices and contamination was confined to the troposphere. On November 1, 1952, the first thermonuclear *fusion* device (code-named Mike) was detonated on Eniwetok Island, a remote location in the South Pacific. This 14 mega-ton explosion injected large quantities of radioactive debris into the stratosphere, causing global fallout [8]. The high neutron flux resulting from the Mike test greatly increased the production of transuranium elements and resulted in the discovery of two new elements, einsteinium and fermium [15]. Since then, the majority of all of the actinide elements and radioactive debris that has been injected into the atmosphere is the result of atmospheric nuclear weapons tests by the U.S. and the U.S.S.R. in 1961 and 1962. This includes the largest atmospheric detonation to date

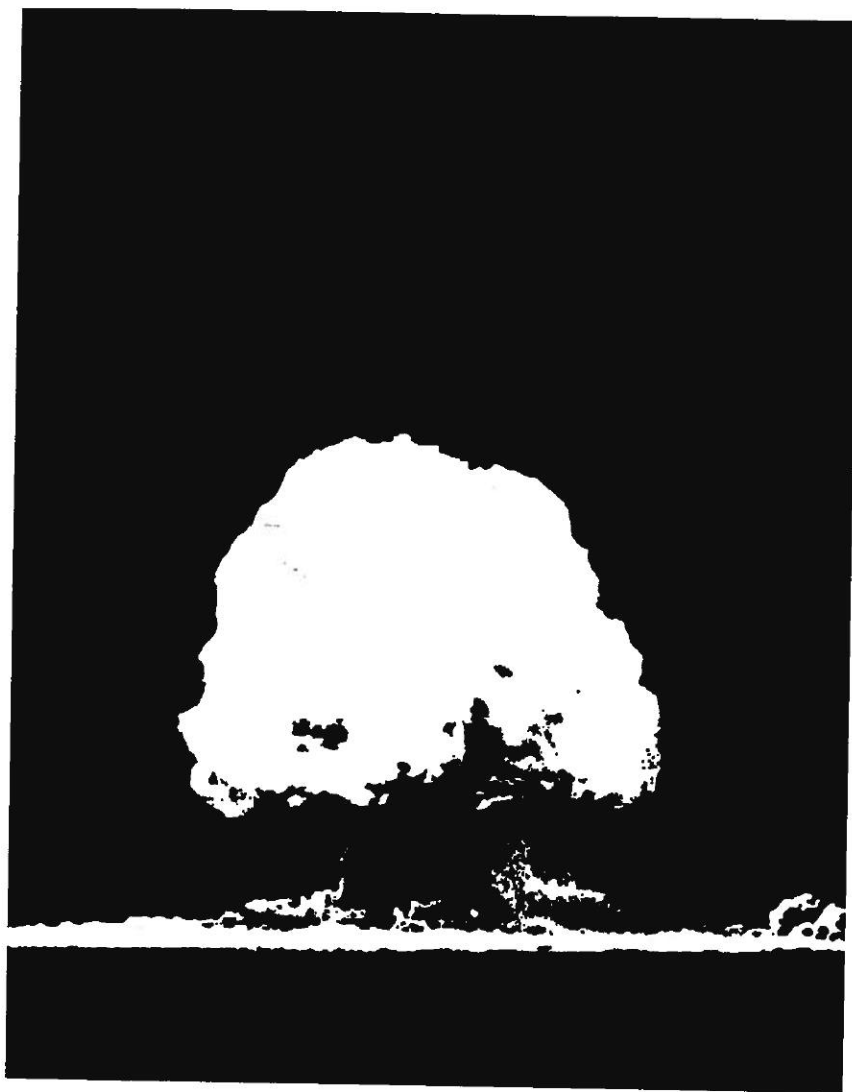


FIGURE 1

The first injection of transuranium elements into the atmosphere occurred with the detonation of the first nuclear explosion on July 16, 1945 at Trinity Site near Alamogordo, New Mexico. (Photo courtesy of Los Alamos National Laboratory Archives)

conducted by the Soviets on October 30, 1961 on the island of Novaya Zemlya in the Barents Sea. This explosion was estimated at 58 mega-tons! [16]

Finally, early in 1963, atmospheric testing of nuclear weapons was banned by agreement between the U.S., United Kingdom, and the U.S.S.R. Unfortunately, all countries did not sign the test-ban agreement and atmospheric testing was resumed by the Chinese and French in 1964. In recent years, third world countries have conducted tests in the atmosphere adding to the global fallout inventory. To date, approximately 360 kCi (~4400 kg) of plutonium-239 and plutonium-240 have been injected into the atmosphere. Smaller amounts of americium-241 (~95 kg) show up in global fallout from β^- decay of short-lived plutonium-241 [5,14]. In addition, 17 kCi of plutonium-238 entered the atmosphere in 1964 as a result of the high altitude disintegration of a SNAP-9 navigational satellite which failed to achieve a stable Earth orbit [5, 14, 17, 18]. The U.S. National Council on Radiation Protection and Measurements reported that in 1962, global fallout accounted for 7% of the annual mean dose of radiation, whereas in 1989, this amount dropped to 1%. Other radiation sources are listed in Table I.

Release of actinide elements from nuclear reactor plants is another source of environmental contamination. Now quite famous (or infamous as the case may be) is the 1986 Chernobyl Reactor incident in the U.S.S.R. [19, 20]. Nuclear power reactors generate substantial amounts of actinides because of long term neutron irradiation of nuclear fuels. Consequently, plutonium-238, americium-241, and curium isotopes are the principal actinides from reactors. Incidents involving nuclear power plants and those involving air transport of nuclear weapons can be quite severe on the local level, but do not effect global fallout levels. On the local level, contamination of the Irish Sea is the result of releases from the United Kingdom's Windscale reprocessing plant. Additionally, there are a number of U.S. Department of Energy sites which have severe local actinide contamination of soils and groundwaters. Most of the radioactive material from the nuclear power industry is presently contained in above ground, temporary storage. The waste from underground nuclear weapons testing is presumably confined *in situ* and amounts to greater than 1,270 kg. Greater than 272 Mg of plutonium are presently stored in nuclear weapons. It is predicted that by the year 2000, plutonium accumulation will amount to 2,177 Mg (2400 tons)! [3]

II. ACTINIDES OF ENVIRONMENTAL CONCERN

The radioactivity and toxicity of the actinide elements and the long half-lives of many of their radionuclides provides sufficient cause for concern if they are indiscriminately released to the environment. Plutonium-239, for example, is intensely radioactive, emitting 1.4×10^8 α particles per milligram per minute. Since most α particles can be stopped by 1 cm of air or a sheet of paper, isolation of plutonium is not necessarily mandated because of external α radiation. It is, however, the consequences of ingestion of plutonium and other actinides which offer the greatest toxic threat to man. Plutonium-239 inhaled into the lungs as fine particulate matter could remain there and could cause lung cancer. Alternately, the inhaled plutonium could be transported to the bone and, in time, could cause a number of complications including leukemia, and bone cancer, to name a few [2]. Comprehensive reviews of the toxicology of the actinide elements can be found elsewhere [1,2].

**TABLE I.
SOURCES OF RADIATION***

Annual Mean Dose	
Radon emission	55%
Medical sources	15%
Natural internal	11%
Cosmic rays	8%
Geological	8%
Professional	2%
Global fallout (1989)	1%
Global fallout (1962)	7%

*Nat. Council on Rad. Protection and Measurements

A. Short Term and Long Term Concerns

The residence time of a detrimental substance in the environment determines how important the concern should be and what prevention or remediation steps, if any, need be taken. It is convenient to divide actinide environmental contamination into two categories of concern: short term and long term.

Short term concern involves actinide nuclides which may be very radioactive, but have very short half-lives. Alternately, the nuclides may only be produced in minute quantities at any one time or they may be widely diluted or disseminated in nature; dilution will effectively make actinide contamination problems disappear. Radioactive decay follows a first order reaction law:

$$A = A_0 e^{-\lambda t} \quad (1)$$

Where "A" is the activity of the radioisotope, " A_0 " is the initial activity present, "e" is the base of the natural logarithm, " λ " is the characteristic decay constant of the particular isotope, and "t" is time. Activity is directly proportional to the number of atoms of the radionuclide. The half-life ($t_{1/2}$) of a radionuclide is the time required for half of the original amount of atoms present to decay:

$$t_{1/2} = (\ln 2)/\lambda. \quad (2)$$

For first order exponential decay, after 5 half-lives, essentially 97% of the radionuclide has decayed away. Protactinium-233, for example, has a short (27 day) half-life. If this nuclide were released to the environment today, less than 3% of the original quantity would be present after 135 days. In ten half-lives (270 days), 0.1% of the protactinium-233 remains. There is a caveat, however, in dealing with actinide nuclides with short half-lives (short term concern); they may decay to form daughter nuclides which may be of long term concern. Again using protactinium as an example, protactinium-233 ($t_{1/2} = 27$ d) β^- decays to produce long-lived uranium-233 ($t_{1/2} = 1.6 \times 10^5$ y). Consequently, inventories in stored nuclear waste may increase with time (rather than decay away) due to ingrowth from short-lived parents! This has been quantified recently by Allard *et al.* [7] and Oversby [21] who have compiled tables listing high-level waste radionuclide inventories as a function of time for up to 1000 years. In any case, the short term problem will generally take care of itself by radioactive decay or dilution, but the result may be formation of daughter nuclides of long-term concern with potentially quite different chemical properties than those of the parent.

Long term environmental concerns involve long-lived actinide isotopes produced in large quantities that require extreme precautions in handling, isolation, and safe disposal. Not all of the 14 actinide elements pose a long term threat to man and the environment. In the discussion following, an assessment will be made to determine which actinides are of greatest long term environmental concern, based on nuclear properties, availability, and distribution.

B. Nuclear Properties

The actinide elements have unstable nuclei and statistically decay to form daughter products with the simultaneous release of considerable amounts of energy in the form of ionizing radiation: particles (α , β , or neutrons) and/or electromagnetic radiation (x -rays and γ -rays). Alternately, many of the actinide radionuclides may spontaneously fission, releasing huge amounts of energy as neutrons and γ radiation. The nuclear properties and availability of common isotopes of the *weighable* actinide elements (thorium - einsteinium) are listed in Table II [2]. The heavier actinide elements, fermium through lawrencium, have very short half-lives and low production yields. These transeinsteinium actinides are only available in quantities of from picograms for fermium to tens of atoms at a time for lawrencium! Consequently, these elements do not pose a threat to the environment and will not be considered further. Inspection of Table II will show that additional elements can be eliminated from the list of environmentally relevant actinides by virtue of their short half-lives, scarcity, and/or distribution. Thorium has a number of naturally occurring isotopes and some of these are available in large quantities. This, combined with long half-lives of many of the isotopes, makes thorium an element of concern. In contrast, protactinium has two isotopes listed in Table II with very short half-lives. The long half-life of protactinium-231 is compensated by the fact that it is widely disseminated in nature. Consequently, we can exclude protactinium from our list of relevant key actinides. Uranium, neptunium, plutonium, americium, and curium have many isotopes with long half-lives that are available in kilogram quantities. These nuclear fuel cycle elements are of major long term environmental concern. The remaining weighable actinides, berkelium, californium, and einsteinium, are of short term environmental concern. Berkelium and einsteinium isotopes are short-lived and are only available in minute quantities. Californium-249 has a moderately long half-life of 351 years, but it is only available in minute quantities.

Of the fourteen actinide elements, it has been shown above by virtue of their nuclear properties, availability, and/or distribution, that only six of these elements (thorium, uranium, neptunium, plutonium, americium, and curium) are of long term environmental concern [21, 22]. Consequently, the main focus of the remainder of this review will be on these environmentally relevant actinides.

C. Consequences of Electronic Structure

Like their lanthanide counterparts, the actinides are a subseries of the *d*-transition metals. Both series result from the consecutive filling of electrons into *4f* orbitals of the lanthanides and *5f* orbitals of the actinides. The shielding of *5f* electrons by outer electrons is less effective than that of *4f* electrons and consequently, the actinides exhibit a richer chemistry than do the lanthanides. This is particularly true for the lighter actinides, as evidenced by the wide range of accessible oxidation states exhibited by these elements. The shielding of *5f* electrons becomes more effective in the heavier half of the actinide series and thus, the transamericium elements exhibit a more lanthanide-like chemical behavior, with the trivalent state dominating their chemistry. Table III lists the known oxidation states of the weighable actinide elements. The elements protactinium, berkelium, californium, and einsteinium are, as outlined previously, not of long term environmental

TABLE II.
Nuclear Properties of Selected Actinide Isotopes [2]

Nuclide	Mode of Decay	Half-life	Availability	Source
Th-227	α	18.7 d	trace	nature
Th-228	α	1.9 y	trace	nature
Th-229	α	7.3×10^3 yr	g	^{233}U daughter
Th-230	α	8.0×10^4 yr	g	nature
Th-232	α	1.41×10^{10} yr	Kg	nature
	SF	$>1 \times 10^{21}$ yr		
Th-234	β^-	24.10 d	trace	nature
Pa-231	α	3.28×10^4 yr	g	nature
Pa-233	β^-	27.0 d	g	^{233}Th daughter ^{237}Np daughter
Pa-234	β^-	6.75 h	trace	nature
U-232	α	68.9 yr	g	^{232}Th daughter
	SF	8×10^{13} yr		
U-233	α	1.59×10^5 yr	Kg	^{233}Pa daughter
	SF	1.2×10^{17} yr		
U-234	α	2.45×10^5 yr	g	nature
	SF	2×10^{16} yr		
U-235	α	7.0×10^8 yr	Kg	nature
	SF	3.5×10^{17} yr		
U-238	α	4.47×10^9 yr	Kg	nature
	SF	8.19×10^{15} yr		
Np-237	α	2.14×10^6 y	Kg	nature(?)
	SF	$>1 \times 10^{18}$ y		^{237}U daughter ^{241}Am daughter $^{237}\text{Np}(n,\gamma)$
Np-238	β^-	2.1 d	trace	nature(?)
Np-239	β^-	2.35 d	μg	nature(?)
				^{243}Am daughter ^{239}U daughter ^{242}Cm daughter ^{238}Np daughter
Pu-238	α	87.7 y	Kg	nature(?)
	SF	4.8×10^{10} y		
Pu-239	α	2.41×10^4 y	Kg	nature(?)
	SF	5.5×10^{15} y		^{239}Np daughter n capture
Pu-240	α	6.56×10^3 y	g	multi n capture
	SF	1.34×10^{11} y	g	
Pu-241	β^- (>99%) α (<0.002%)	14.4 y	g	multi n capture
Pu-242	α	3.76×10^5 y	g	multi n capture
	SF	6.8×10^{10} y		
Pu-244	α	8.26×10^7 y	g	nature(?)
	SF	6.6×10^{10} y		multi n capture

TABLE II.
Nuclear Properties of Selected Actinide Isotopes [2]
 (continued)

Nuclide	Mode of Decay	Half-life	Availability	Source
Am-241	α	432.7 y	Kg	^{241}Pu daughter
	SF	1.15×10^{14} y		multi n capture
Am-242	β^- (82.7%)	16.01 h	g	$^{241}\text{Am}(n,\gamma)$
	EC (17.3%)			
Am-242m	IT (99.5%)	141 y	g	$^{241}\text{Am}(n,\gamma)$
	α (0.48%)			
Am-243	SF (0.02%)	9.5×10^{11} y	Kg	multi n capture
	α	7.38×10^3 y		
Cm-242	SF	2.0×10^{14} y	g	$^{239}\text{Pu}(\alpha,n)$
	α	162.9 d		
Cm-244	SF	6.1×10^6 y	Kg	^{242}Am daughter
	α	18.11 y		
Cm-245	SF	1.35×10^7 y	g	^{244}Am daughter
	α	8.5×10^3 y		
Cm-246	SF	4.73×10^3 y	g	multi n capture
	α	1.8×10^7 y		
Cm-247	SF	1.56×10^7 y	g	multi n capture
	α	3.4×10^5 y		
Cm-248	α (91.74%)	320 d	mg	multi n capture
	SF (8.26%)			
Bk-249	β^- (>99%)	320 d	mg	multi n capture
	α (<0.002%)			
Bk-250	β^-	3.217 h	trace	^{254}Es daughter
Cf-249	α	351 y	mg	^{249}Bk daughter
	SF	6.9×10^{10} y		
Cf-252	α (96.91%)	2.645 y	mg	multi n capture
	SF (3.09%)			
Es-253	α	20.47 d	μg	multi n capture
	SF	6.3×10^5 y		
Es-245g	α	275.7 d	μg	multi n capture
	SF	$>2.5 \times 10^7$ y		
Es-254m	β^- (99.6%)	39.3 h	μg	$^{253}\text{Es}(n,\gamma)$
	SF (0.33%)			
Es-255	β^- (92.0%)	$>1 \times 10^5$ y	trace	multi n capture
	α (8.0%)			
	SF ($4 \times 10^{-3}\%$)			

α = helium nucleus (^4He) SF = Spontaneous Fission
 β^- = negative electron (e^-) IT = Internal Conversion
 n = neutron EC = Electron Capture

TABLE III.
Oxidation States of Selected Actinide Elements

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
					II			II	II
III	III	III	III	III	III	III	III	III	III
IV	IV	IV	IV	IV	IV	IV	IV	IV	
	V	V	V	V	V				
		VI	VI	VI	VI				
			VII	VII	VII				

*Boldface indicates most stable state

concern, however, they have been included in Table III for completeness and to show general trends. The dominance of the trivalent oxidation state in the transcurium elements allows one to extrapolate to the chemical behavior of berkelium, californium, and einsteinium. Thus the study of trivalent americium and curium facilitates examination of the transcurium elements by proxy.

The variety of accessible oxidation states, particularly of the lighter actinides, makes the environmental chemistry of the actinides quite complicated. Furthermore, multiple oxidation states of the same element may exist simultaneously. Plutonium, for example, may exist in four oxidation states (III, IV, V, and VI) under the same environmental conditions. On the other hand, a number of oxidation states of the long term environmentally significant actinides will be eliminated from consideration in subsequent discussion by virtue of their lack of stability in the environment.

III. ACTINIDES IN NATURAL WATERS

There is a high probability that actinides released to the atmosphere, geosphere, or biosphere will eventually (if not immediately) come into contact with water in the form of rain, snow, surface fresh water, groundwater, ocean, brines, etc. Consequently, knowledge of the solution chemistry of the actinides is most important in understanding and predicting the fate of these elements in the environment. There is a lack of sufficient data on the chemistry of actinides in natural waters. After fifty years of transuranium elements, this may seem somewhat surprising, however, traditional actinide solution chemistry involved strongly acidic or strongly basic media (to ensure sufficient actinide solubilities). Most of the chemistry involved nuclear fuel reprocessing technology, with nitric acid as the classic solvent. In contrast, most natural waters have near-neutral pH conditions and the traditional actinide chemistry data are not particularly relevant. It has only been recently that environmentally relevant actinide solution studies have appeared in the literature to any extent.

A. Characteristics of Natural Waters

Natural groundwaters, seawaters, and brines may contain a wide variety of native soluble species that can significantly affect the chemical behavior of actinide ions through pH effects, redox reactions, complexation, etc. Table IV. [3, 23, 24] lists various natural waters and their compositions. Actinide ions are "hard" acids and consequently form strong complexes with highly ionic ligands. In natural fresh waters, the most common inorganic actinide-complexing ligands include hydroxide, carbonate, phosphate, fluoride, chloride, and sulfate. Silicate ions are also important ligands for actinides in natural waters that are in intimate contact with silicate rocks and minerals. The most common inorganic actinide-complexing agents in seawaters are hydroxide, carbonate, phosphate, chloride, and sulfate ions. Because of the relatively high concentrations of hydroxide and carbonate in both fresh and seawaters, hydrolysis and carbonate complexation are expected to be the most important factors influencing actinide behavior in these waters [5, 6]. At high pH values (>9) in concentrated brines, carbonate ions predominate along with relatively high chloride and sulfate ion concentrations [25, 27]. Bio-organic complexants, including natural humic acids

TABLE IV.
Characteristics of Natural Waters [3.23,24]

Analysis	Rainwater	Surface Water (a)	Bedrock Water (b)	YMP g J-13 Water	YMP g UE-25p#1 Water	Ocean	Mono Lake Brine
Depth (meters)	0	0.50	≤500			0-20	
Age (years)	0	≤10	≥100				
pH	4-6	7.3-8.4(7.9)	7-10	6.9	6.7	.8-1	
Eh (Volts)	0.9	0.0-0.3	-0.05	0.1	0.36	0.8	
O ₂ (mg/liter) ^c	10	1-10	<0.1	5.7		≤9	
Na ⁺	0.3-20	1-20(12)	10-100(d)	45	171	10,766	22,000
K ⁺	0.1-4	0.3-8 (4)	1-5	5.3	13.4	399	
Ca ²⁺	0.5-5	2-100(25)	20-60	11.5	87.8	413	
Mg ²⁺	0.1-0.5	3-30(10)	15-30	1.76	31.9	1292	
Fe (total)		0.1-1	5-30	0.04	<0.1	<0.02	1
F ⁻		≤0.1	0.5-2	2.1	3.5	1.4	48
Cl ⁻	0.1-20	0.5-90(10)	5-50(d)	6.4	37	19,353	
Br ⁻						67	
CO ₃ ²⁻ (total) (d)	≤1	60-200	5-400	118-143	960	~140	28,300
NO ₃ ⁻	0.1-4	≤10	<1	10.1	<0.1	<0.7	
PO ₄ ³⁻ (total)	0	≤0.1	≤0.1			≤0.1	20
SO ₄ ²⁻ (total)	≤20(1-5)	3-300(20)	1-15	18.1	129	2712	8300
SiO ₂ (total)	0	3-15	5-30	66	66	0.01-7	
SH ⁻ (e)	0	0	<1				
NH ₃ (e)	£0.5	<0.1	<0.5			<0.05	
Organic carbon		1-50	<1	0.15		~1	

(a) Lakes, rivers, and shallow wells; typical values within parenthesis, (b) Swedish granite, (c) all concentrations in mg/liter, (d) Mainly as HCO₃⁻, (e) For relict water, the value may be 500-3000 mg/liter, (f) SH⁻ and NH₃ only occur in reducing waters (Eh<0), except for surface waters in industrial areas, (g) Yucca Mountain, Nevada wells.

and a variety of common organic contaminants, can effect the speciation and transport of actinides to a large extent in natural waters [5, 6].

B. Speciation of Actinides

Speciation is an important factor influencing the physical and chemical behavior of actinides in environmental waters. Solution conditions (e.g., pH, Eh, ionic strength, redox reagents, complexing ligands, actinide concentration, etc.) can significantly affect the relative stabilities of the various oxidation state species in natural waters.

Speciation is defined as:

- (1) The identify of the element or radionuclide.
- (2) The determination of its oxidation state.
- (3) The formula of the ionic or neutral complex.
- (4) The detailed structure of the complex.

The actinide III and IV oxidation states can exist as simple hydrated cations, whereas the V and VI states form the dioxo cations AnO_2^+ and AnO_2^{2+} , respectively. As mentioned previously, the speciation of the lighter actinides is complicated by the coexistence of multiple oxidation states of the same element.

1. Redox Behavior

a. Redox Potentials

Not all oxidation states of the key actinides of long term concern listed in Table III are stable in environmental waters. The *standard* reduction potentials for the key actinide elements (in Volts versus the Normal Hydrogen Electrode (NHE)) are displayed in Figure 2 [2]. Standard potentials are measured or calculated for non-complexing, *standard*-state conditions, but they can still serve as a guideline when discussing environmentally relevant *formal* redox potentials for actinide couples. Formal redox potentials change as a function of ionic strength, temperature, hydrolysis, complexation, pH, etc. The potential (Eh) values of natural waters listed in Table IV range from about + 0.7 V to 0.0 V at pH 6 to near + 0.6 V to -0.4 V at pH 10.

In Figure 2, the redox potential for the Th(IV)/Th(III) couple is given as -3.8 V [28]. This extremely reducing potential is not found in natural waters. Consequently, Th(IV) is the only oxidation state encountered in such waters. The potential values in Figure 2 indicate that U(III) is more stable than Th(III). However, U(III) is still too unstable to exist in natural waters, whereas, U(VI), (V), and (IV), are expected in natural waters. The redox potentials also show that U(V) is unstable to disproportionation. Therefore, only U(VI) and U(IV) are of long term concern in environmental waters. The potential for the Np(IV)/Np(III) couple is close to that for stability in natural waters, but neptunium(III) is on the edge of stability only in strongly reducing natural waters at low pH. Figure 3 is a potential versus pH (Pourbaix) diagram for a number of actinide redox couples [29] and should be referred to for the remainder of this discussion of redox potentials. (Allard *et al.* [30] have also constructed Pourbaix diagrams for actinide redox couples in natural waters. Paquette and Lemire [31] published Pourbaix diagrams for uranium and plutonium up to

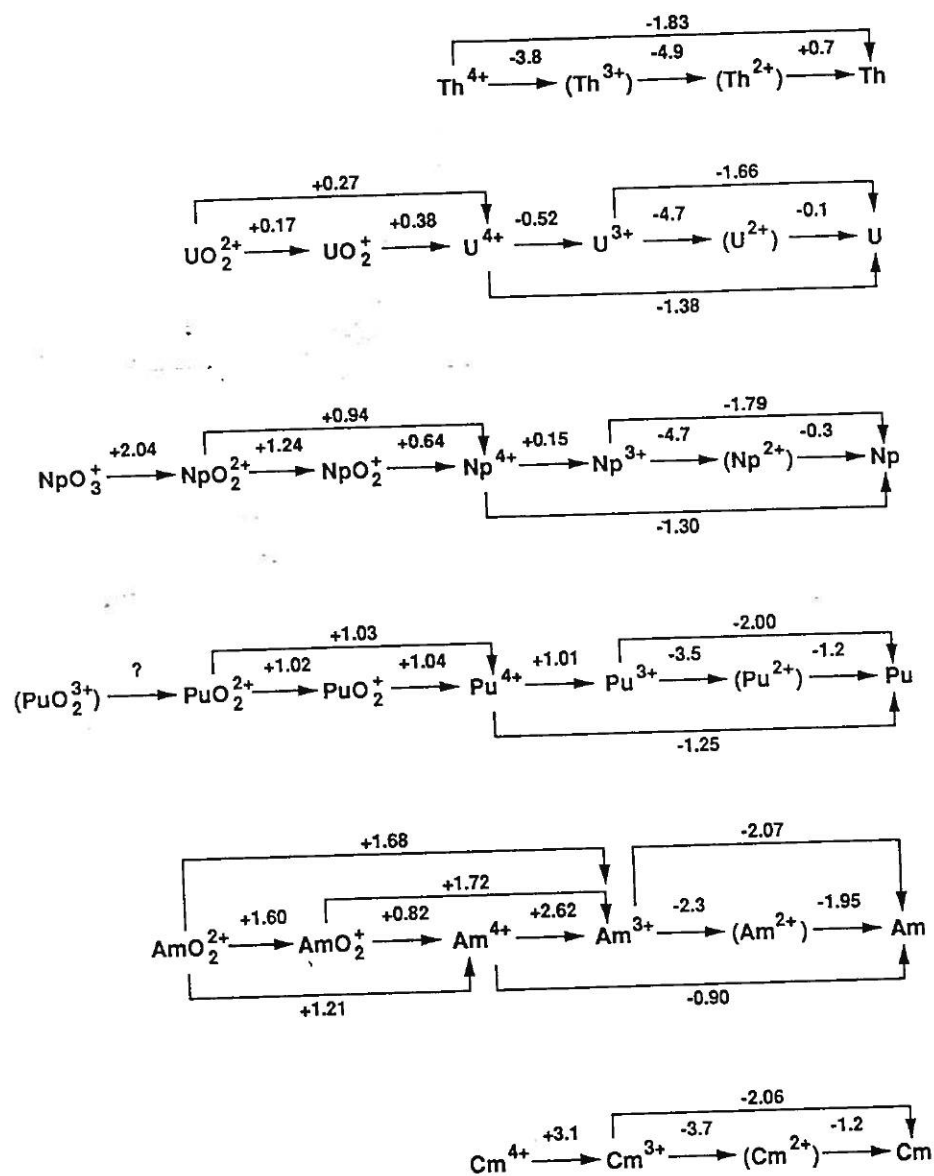


FIGURE 2

Standard reduction potentials in Volts vs. NHE for redox couples of selected actinide elements. [2]

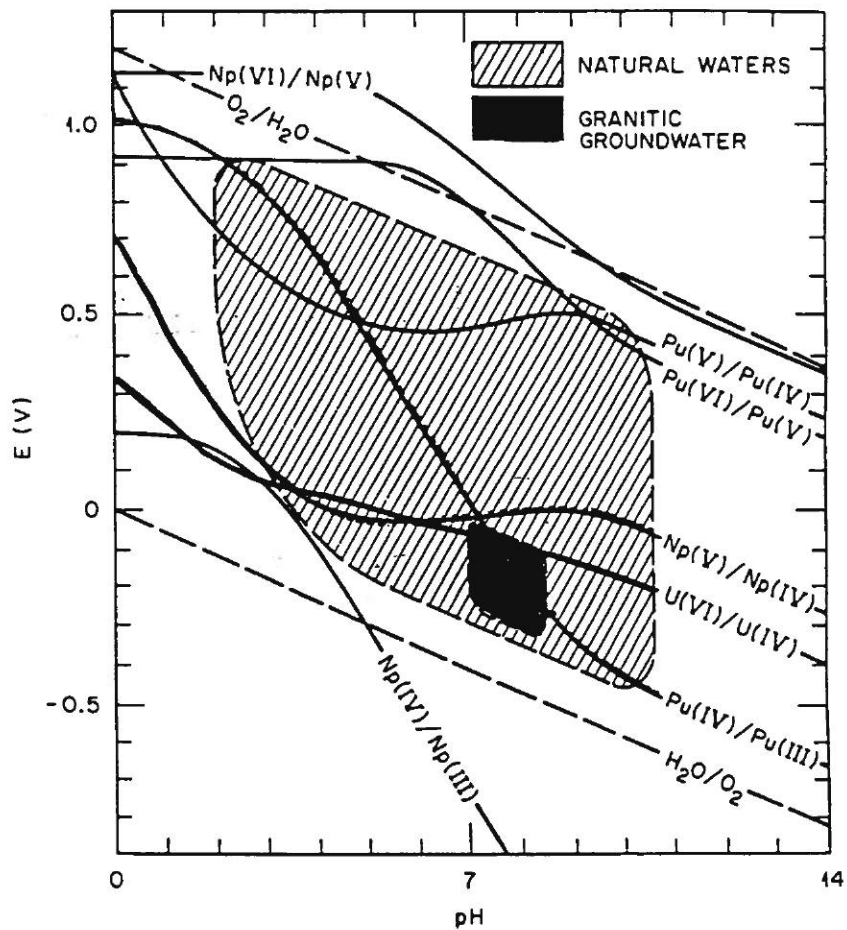


FIGURE 3

Potential versus pH diagram for uranium, neptunium, and plutonium redox couples at low metal concentration with consideration of hydrolysis reactions. [29]

200°C). Note how, in Figure 3, that the line for Np(IV)/Np(III) couple just approaches the range of potentials for stability in natural waters. At a potential of + 0.64 V for the Np(V)/Np(IV) couple, both Np(IV) and Np(V) are expected oxidation states in aquatic systems. The potential for the Np(V)/Np(VI) couple is much too high (+ 1.16 V [32]) to permit Np(VI) to be a stable species in such waters.

For plutonium, note that all of the potentials for Pu(III), (IV), (V), and (VI) couples are all around 1.0 V [32, 33]. Thus, all four oxidation states can exist simultaneously in natural water systems. Pu(V) is prone to disproportionation, but at low concentrations in natural waters it is known to be quite stable [34]. The potentials for reduction of Am(III) to Am(II) and for oxidation of Am(III) to Am(IV) are quite large, -2.3 V [35] and + 2.62 V [36, 37], respectively. Therefore, Am(III) is the only oxidation state expected under normal environmental conditions. The same argument can be given for oxidation or reduction of Cm(III) [38]. The kinetics of redox reactions for actinides are important in natural water systems. A comprehensive review of actinide redox kinetics was published by Newton [39].

In summary, based solely on redox potentials, the following key actinide elements and their oxidation states are deemed to be of significant environmental concern: Th(IV), U(IV,VI), Np(IV, V), Pu(III, IV, V, VI), Am(III), and Cm(III). Other oxidation states of these elements may exist under unusual conditions (redox reagents, radiolysis, elevated temperatures, etc.), but they are not expected to remain stable under normal environmental conditions.

b. Redox Reactions

Humic materials are probably the most common redox reagents for actinides in natural groundwaters. Pu(VI) and Pu(IV) can be reduced by soil fulvic acids and by humic acids. U(VI) and Am(III) would not be reduced, but Np(VI) and Np(V) may be reduced to Np(IV) by humic acids [40]. The common inorganic redox reagents in natural water systems include Fe(II) and Mn(II) in some reducing waters and in minerals and rocks in contact with groundwaters. These natural redox systems are not well studied for actinide redox reactions.

c. Radiolysis

Radiolysis of water can generate some rather potent redox reagents that can generate some unusual actinide oxidation states. Radiation of water can generate small steady-state concentrations of H₂, O₂, and H₂O₂. In addition short-lived radicals of H, OH, and O can exist. Stradler and Kim [41] found that Am(III) was oxidized to Am(V) via radiolysis in concentrated carbonate-free saline solutions.

Christensen and Bjergbakke [42] have published data on alpha-radiolysis of aqueous solutions. These researchers also studied the effects of radiolysis in the presence of iron. Based on the proposal that an excess of oxidizing radicals from radiolysis of groundwater may cause a migrating front of radionuclides, soluble actinides coming in contact with Fe(II) may reduce and precipitate [43]. These experiments were continued by Eriksen *et al.* [44]. Redox reactions of radiolytically produced OH radicals with U(III) [45], Pu(III) [46], and Am(III) [47] have been studied. Buppelmann *et al.* [48] studied the redox behavior of plutonium in saline solutions under radiolysis effects.

2. Solubility

Solubility is defined thermodynamically as the concentration of an ion in solution *in equilibrium* with the corresponding solid phase. An example is the dissolution of plutonium(IV) hydroxide (Eq. 3). The expression for the thermodynamic solubility product constant, K_{sp} for this reaction is given in Eq. 4.



$$K_{sp} = [\text{Pu}^{4+}] [\text{OH}^-]^4 \quad (4)$$

This at first appearance seems like rather straightforward chemistry, but, in reality, it is not. First of all, reported estimates for K_{sp} for Equation 3 are about 10^{-57} [49, 50]. This corresponds to a very low concentration ($< 10^{-29}$ M) of Pu^{4+} in near-neutral solution. Low concentrations are difficult to quantify with any confidence without extremely sensitive analysis techniques (nuclear counting methods are sensitive, but they do not provide speciation information). Secondly, in natural waters where there is a variety of soluble species existing in contact with many different solid phases, it is important to determine which solid phase is the solubility-limiting solid for a particular ion. In addition, aquo Pu^{4+} readily hydrolyzes above pH 1 to form colloids. More complications arise when one considers that natural waters may have a number of ligands which strongly complex Pu^{4+} and will affect the equilibrium in Equation 3. With regard to equilibrium, recall that the common plutonium isotope, plutonium-239, is highly radioactive and emits intense ionizing radiation. This radiation may form any number of radiolysis products that may oxidize or reduce plutonium(IV). It has been reported by Newton *et al.* [50] that, because of radiation effects, equilibrium is not attained for Equation 3 even after two years! Thermodynamic equilibrium calculations are the preferred approach to solubility determinations for actinides in natural water, but for the above reasons, this approach is not always practical. A more practical approach uses a somewhat more empirical solution to the problem. *Apparent* solubilities of key radionuclides are determined directly in actual samples of natural waters. In order to bracket the *true* equilibrium value, it is useful to approach the solubility from both oversaturated and undersaturated conditions. In the oversaturated case, well-characterized actinide "spike" solutions are added to natural waters and samples are analyzed at various time intervals until an *apparent constant concentration* is attained. Solid compounds which form in these solutions (presumably the solubility limiting solid) are collected and analyzed for structure and identity. Once the identity is determined, the compound can be prepared and equilibrated with natural water until an *apparent constant concentration* is reached. It is very important in solubility experiments that an effective solid-solution phase separation be performed, especially if colloids are formed. Usually, filtration through a $0.45 \mu\text{m}$ filter is sufficient for phase separation [5]. Another pitfall is that, often times, the solid formed in the oversaturated case is amorphous and cannot be characterized. In this situation, approach from oversaturation is the only route to determining solubility and only an upper limit can be established.

Nitsche and Edelstein [51] have published a report on the solubility and speciation of key radionuclides for a site specific investigation using the empirical approach outlined

above. The solubilities and speciation of neptunium, plutonium, and americium were determined at 25°C at pH 7 in J-13 well water from the Yucca Mountain Site. (Yucca Mountain, Nevada, is being considered for the Nation's first high level radioactive waste disposal site, and J-13 well water is used as a natural water typical of that in the proposed waste repository horizon in the unsaturated (vadose) zone. The Yucca Mountain Site Characterization Project (YMP) is the responsible agency for determining site suitability.) Simultaneous solubility experiments were performed in dilute perchlorate solutions and the well water results were compared. It was determined that some complexing ligands in the well waters had a significant effect on the solubilities of plutonium and americium. The solubility of neptunium showed little difference in the various solutions. The Np(V) ion is the least affected by complexing ligands. These workers also reported that, regardless of the initial oxidation states, the states present at attainment of apparent constant concentration were V for neptunium, and V and VI for plutonium. Americium remained in the III state. These results have significance in that, once again, Pu(V) is the surprising prominent oxidation state in natural waters and, in lieu of thermodynamic solubility values, upper limits for solubility have been provided for geochemical modeling calculations. It is interesting to note that these oversaturation experiments resulted in the first identification of orthorhombic [52] and hexagonal [53] americium hydroxy-carbonates.

Nitsche and coworkers [54-56] are continuing solubility investigations of the key actinide radionuclides in J-13 well water and in UE-25p#1 well water at 25, 60, and 90°C at pH values maintained at 6, 7, and 8.5. Yucca Mountain UE-25p#1 well water taps the carbonaceous aquifer below the proposed repository horizon and differs from J-13 in ionic strength and carbonate ion concentration (see Table IV). A plot of concentration versus time for solubility experiments with Am(III) is shown in Figure 4. It is clear from this plot that apparent constant concentration conditions are not reached in a short time and experiments must be continued to ensure a closer approach to equilibrium. Results of Pu(IV) solubility experiments in J-13 water at various temperatures are shown in Figure 5. These data show that Pu(IV) solubility decreases with increasing temperature. This is undoubtedly due to the improved conditions for colloid formation at higher temperatures (peptization). As a function of pH, Pu(IV) solubility first drops between pH 5.9 and pH 7 and then slightly increases at pH 8.5. This latter effect is probably the result of carbonate complexation of Pu(IV). [54-56]

Choppin and Stout [5] have summarized measured and calculated solubilities and reviewed identities of solubility limiting solids for thorium and uranium in seawater. With thorianite (ThO₂) assumed to be the solubility limiting solid, a solubility of 8×10^{-15} M was calculated for Th(IV) solubility. This value is two orders of magnitude lower than the value measured in seawater. These workers suggest that, based on the high values for solubility of Th(IV) in Mono Lake [57], carbonate complexation should be considered in the calculation. The calculated value for the solubility of uranyl(VI) ion of 1.8×10^{-14} M (based on haiweeite, Ca(UO₂)₂Si₂O₅·5H₂O as the solubility limiting solid) are an order of magnitude higher than those measured, even when taking into account a multiplication factor for complexation. Reasons for this are attributed to lack of accurate thermodynamic data, or in not accounting for possible sorption processes.

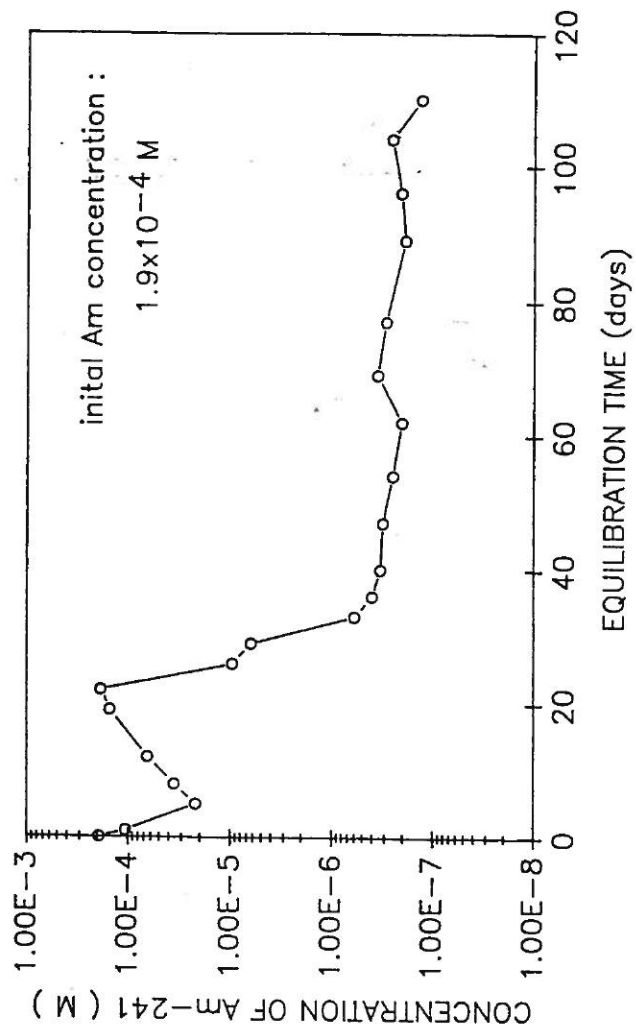


FIGURE 4

Approach to apparent constant concentration for americium(III) at pH 6 and 25°C in Yucca Mountain UE-25p#1 well water. [54]

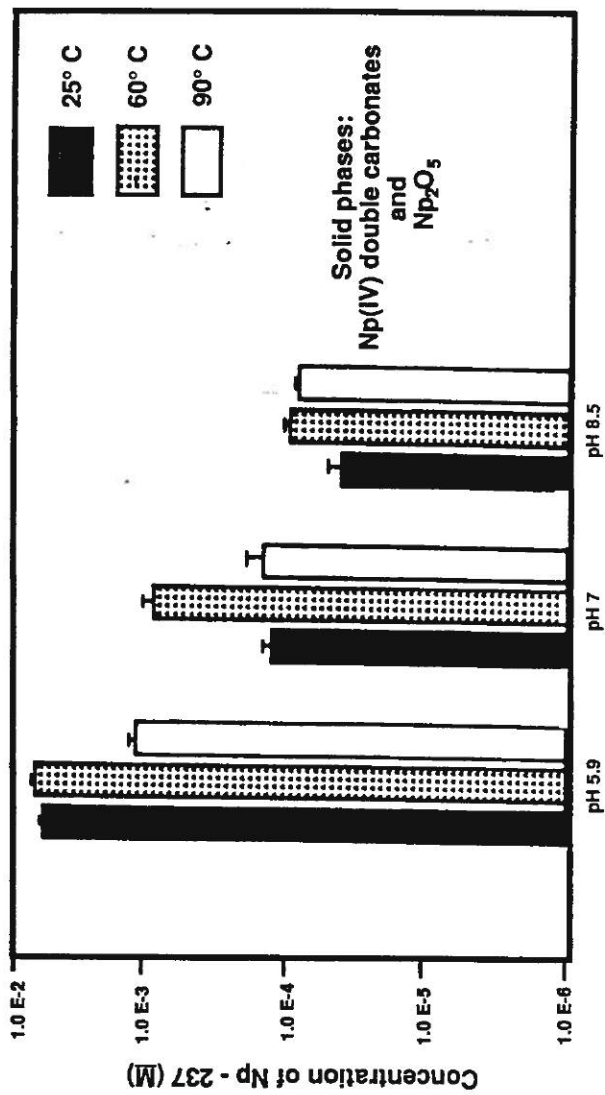
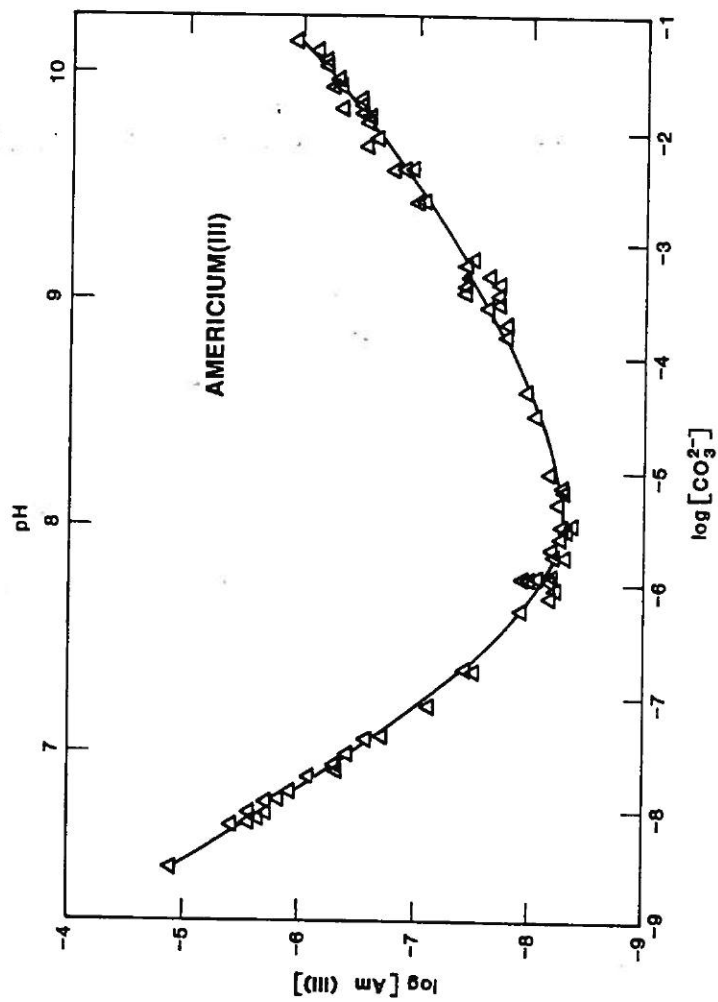


FIGURE 5
Solubility of neptunium(V) in Yucca Mountain J-13 well water as a function of pH and temperature. [54]



AMERICIUM(III)

FIGURE 6
Solubility of americium(III) in carbonate solution. [58]

Bernkopf and Kim [58] studied the carbonate complexation of Am(III) in natural waters via solubility. The solubility curve shown in Figure 6 is plotted versus carbonate ion concentration and pH. Note that at high pH values, carbonate complexation increases the solubility. Also note that the low point in the curve corresponds to 10^{-8} M in Am(III). Species-specific analytical probes are under development (e.g., laser induced photothermal and fluorescence spectroscopies), however, there are no off-the-shelf technologies for such low concentrations and, therefore, non-species-specific radioactive counting techniques are often employed.

3. Sorption

Sorption of actinide solutes on solid geologic media, such as rock and mineral surfaces and natural inorganic and organic colloids, can significantly affect the apparent solubility and mobility/retardation of actinide nuclides in natural waters. Actinide ions in solution can interact with solid materials in basically three ways: (1) *physical adsorption*, (2) *electrostatic adsorption*, and (3) *chemisorption*. Physical adsorption is a non-specific adsorption of the solute onto a sorbent. Electrostatic adsorption is an ion exchange mechanism which is the result of a coulombic attraction between solute and sorbent. This process is rapid and reversible and is dependent on a number of solution parameters, including pH, ionic strength, etc. Chemisorption, or specific adsorption, is the result of chemical forces (bonding) between solute and sorbent. Anions of the solid may form complexes with the solute. Typical strong complexing agents for actinides are hydroxide, fluoride, carbonate, etc. These anions, affixed to solid surfaces or as an intrinsic component of the solid on the surface, can act as chemical sorption agents [6, 59, 60]. It is most important in laboratory sorption studies to ensure that the actinide concentration in solution does not exceed the solubility limit. If the solubility limit is exceeded, the phenomenon attributed to sorption may simply be precipitation. This is usually not a problem when performing experiments with natural waters, since actinide concentrations are quite low.

Quantitative measurements of sorption are expressed in terms of *sorption isotherms* as total concentration in solution versus total concentration in the sorbent, or as a distribution ratio:

$$R_d = \frac{[An]_{solid}}{[An]_{soln}} \quad (5)$$

where $[An]_{solid}$ is the radioactivity in the solid phase per unit mass and $[An]_{soln}$ is the activity in solution per unit volume. R_d is expressed in milliliters per gram and applies only to carefully specified experimental conditions. A more rigorous distribution ratio, defined as K_d , is expressed in terms of true thermodynamic equilibrium activities and is valid for all experimental conditions. Since reversible equilibrium conditions are not often attained and activity coefficients are not known under environmental conditions, R_d values are frequently reported.

At one time, the United States was considering a nuclear waste disposal site in Washington state (Hanford) basaltic rocks. Basalts are usually dark, fine-grained aluminosilicate rocks. Perry and Tsao [61] studied thorium(IV) sorption on Hanford basalt via

photoelectron spectroscopy. These workers found that at the high pH values at which they were working (pH 10-12), Th(IV) not only chemisorbed on the surface, but also penetrated greater than 20 Å into the surface of the basalt. Furthermore, the data were consistent with a process involving the chemisorption of CO₂ onto and reaction with the sorbed hydrated thorium oxide, thus forming a mixed oxide/hydroxide-carbonate. This phenomenon has been reported previously for plutonium(IV) colloid [62].

O'Kelley *et al.* [63] used auto radiographics methods to investigate the sorption of uranium, neptunium, plutonium, and americium in synthetic groundwater on Climax stock granite. The sorption observed on specific mineral sites was correlated with that on pure mineral phases. It was observed that the actinides sorbed in a general manner on the granite with some specificity for the Fe(II)-containing minerals, pyrite and biotite. This work has significance in the study of nuclear waste disposal in deep granitic repositories.

Sorption measurements have been and are continuing to be performed with actinides in natural well waters on Yucca Mountain tuffs for the YMP project. A summary of these sorption measurements performed at Los Alamos National Laboratory from 1977 to 1985 have been published by Thomas [64]. Tuff is a rock resulting from consolidation of volcanic ash fall and is the native rock of the proposed repository site. This tuff often contains zeolites (hydrated alkali metal aluminosilicates) that have strong ion-exchange capacities for actinide cations. There is a vast body of experimental data for sorption of actinides on numerous whole rock samples in the summary report and a number of generalizations can be made from the data. For the most part, however, this Edisonian approach to sorption has not been particularly satisfying from a theoretical point of view. Consequently, the focus at Los Alamos has been shifted to studying actinide sorption on well-characterized pure mineral phases. It is expected that the results from pure mineral phases can be extended to encompass composite whole rock. It has been suggested that trace minerals lining cracks and fissures in Yucca Mountain tuff rocks may play an important role in the sorption of actinide ions [65]. Although trace minerals may be a very minor component in the tuff rock, it can be envisioned that actinides flowing in groundwater or being transported in the unsaturated regions in the ground may have ample opportunity to react with trace minerals over the long time period (>10,000 years) being considered for safe underground disposal of nuclear waste.

Calcium carbonate is a trace mineral in tuff, and actinides form strong complexes with hard oxygen donor ligands such as carbonate. Some preliminary experiments by Newton *et al.*, with neptunium(V) on pure crushed calcium carbonate (optically clear calcite crystals collected from the Harding Pegmatite Mine, Taos Co., NM) have shown that the sorption of NpO₂⁺ on calcite is very dependent on the pH of the solution, and that carbonate complexation is a major factor in determining the fate of radionuclides in the environment [66].

A number of iron and manganese oxide minerals are present as coatings on some minerals and rocks in Yucca Mountain tuffs. These oxides provide a high area reactive surface for actinide ion interactions. Kohler *et al.* [67] studied Np(V) sorption on hematite (α-Fe₂O₃). A schematic diagram of the interaction of Np(V) ions, for example, with a metal oxide mineral surface is shown in Figure 7. The neptunyl ion (NpO₂⁺) may (a) react with an oxygen of the oxide surface to form a generic surface complex, (b) the ligands in

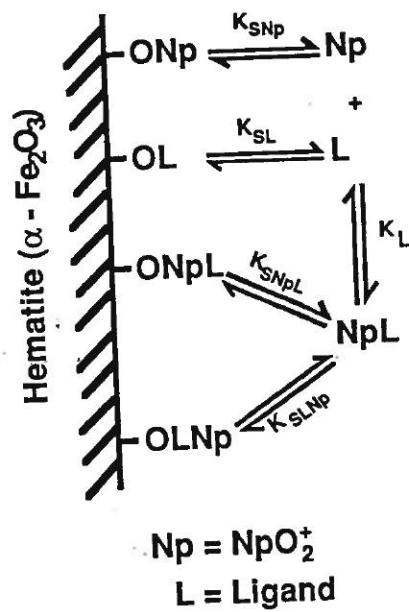


FIGURE 7

Schematic diagram of possible interactions of neptunium(V) with a solid hematite surface in a complexing solution. [67]

solution may compete with neptunium in occupying surface sites, (c) ligands in solution may complex the neptunium, (d) the resultant Np-Ligand complex may sorb via the Np ion, and/or (e) complex via the Ligand ion.

A molecular level analysis is required to determine the true nature of the sorption of neptunyl(V) ions on metal oxides. Combes *et al.* [68] have reported the use of synchrotron-based x-ray absorption fine structure spectroscopy (EXAFS) for investigation of the sorption of Np(V) on crystalline α -FeOOH (goethite). EXAFS is particularly useful for studying solution/surface interfaces on the molecular level. The sorption of Np(V) on goethite as a function of pH is shown in Figure 8. Sorption does not start until pH 2 and at pH values > 7, the sorption is nearly 100%. This typical S-shaped curve is a reflection of the charge properties of the surface of the goethite, i.e., the *point of zero charge* for goethite is near pH 6. This is where the surface changes from a net positive charge to a net negative charge and consequently can strongly bind actinide cations. Fourier transformed EXAFS spectra for Np(V) in NpO_2 solid, NpO_2^+ in solution, and NpO_2^+ sorbed on goethite are displayed in Figure 9. The spectra indicate that the molecular level structure of Np(V) is very little changed (when sorbed on goethite) from its structure in aqueous solution. These workers concluded that Np(V) was not precipitated, but bound to the surface of goethite. The conclusions reached in this work were that NpO_2^+ sorbs on goethite as a mononuclear species with a local geometry similar to that of the free aquo ion [68].

Nelson *et al.* [69] used sorption of actinide elements on calcium carbonate to develop an oxidation state analysis method. The method was used to distinguish between the III and IV states of plutonium in Mono Lake water.

Balukovia *et al.* [70] reported sorption experiments for neptunium, plutonium, americium, and curium ions in various solutions equilibrated with alumino-silicate rocks. In addition to studying solutions of actinides in nitrate, some solutions included polyphenyl organic complexant, which are not found in nature, but could result from mixed waste (radioactive/reactive organic) pollution.

4. Complexation

Complexation is a dominant factor influencing actinide speciation in natural waters. Complexation by natural ligands may significantly increase actinide solubility and affect actinide sorption properties to a large extent. The complexation strength is a measure of how effectively a ligand can compete with water in the hydration shell of the aquo actinide ion. In most cases, complex formation involves an exchange of the water molecules in the hydrate shell by complexing ligands to form *inner-sphere* complexes. In this case, both ligand and any remaining water molecules are bound directly to the central metal atom. These kinds of interactions form very strong complexes. Weaker complexes result when a ligand is bound to the central metal atom *via* the waters of hydration. These are called *outer-sphere* complexes. Actinide ions are "hard" acids and consequently form strong (inner sphere) complexes with highly ionic ligands, such as fluoride, and hard oxygen donor ligands, such as hydroxide, carbonate, phosphate, silicate, etc., all of which are common in natural waters. Actinide ions form complexes of moderate strength with nitrogen donors and weak (outer-sphere) complexes with sulfur donor ligands. Consequently, humic acids (which contain many functional groups) form strong actinide complexes via interactions with

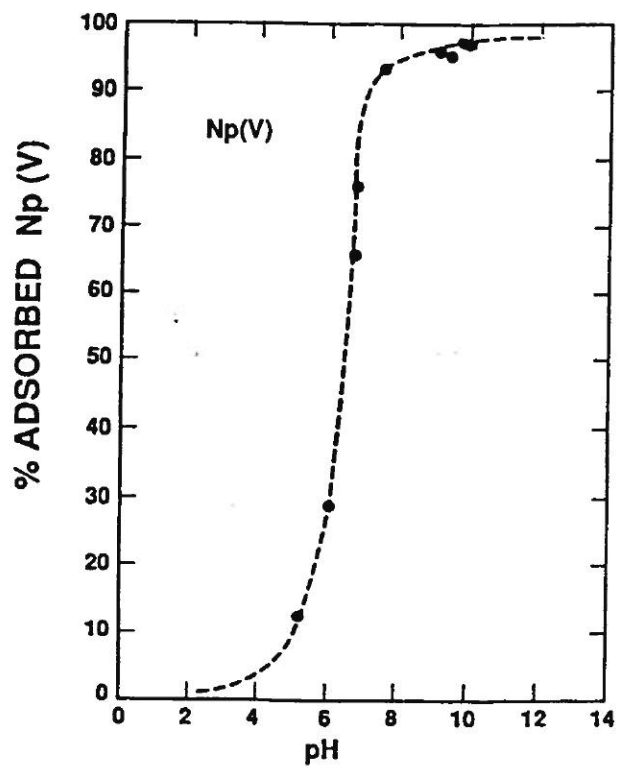


FIGURE 8
Sorption of neptunium(V) on goethite. [68]

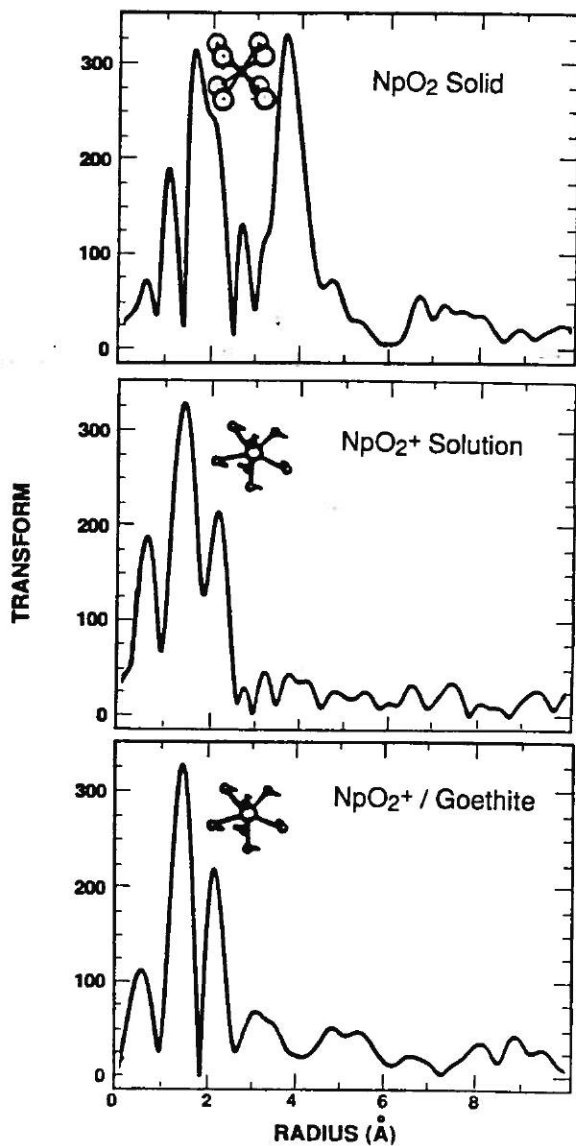
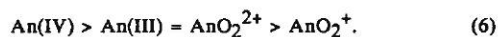


FIGURE 9

Fourier transform x-ray absorption fine structure spectra of neptunium(V) in various environments. [68]

humate carboxylate groups at near-neutral pH values. Ligands such as oxalate, citrate, EDTA, HDEHP, and others which strongly complex actinides are not normally found in natural waters, however, they may be present in mixed (radioactive/reactive) wastes. These important ligands are not reviewed in detail here.

The relative affinity for actinides to form complexes generally follows the sequence:



Consequently, An(IV) ions (as An^{4+}) form the strongest complexes and the An(V) actinyl ions (AnO_2^+) form the weakest. It should be noted that the actinyl ions, AnO_2^+ and AnO_2^{2+} , form stronger complexes than would be expected when compared to those of divalent and monovalent cations of lighter main block elements. Because the actinides have quite similar ionic radii for a given oxidation state, it is possible to make generalizations concerning their complexation. For example, the formation quotients for americium(III) and curium(III) with the same ligand should have quite similar values.

A general equation for a typical trivalent actinide complexation reaction with a ligand, L^- , and the stability quotient expression are given below.



$$Q = \frac{[\text{AnL}^{2+}]}{[\text{An}^{3+}][\text{L}^-]} \quad (8)$$

For a general discussion of the methods used to determine stability quotients for complexation reactions, the reader is referred to Rossotti and Rossotti [71] and Ahrland *et al.* [72].

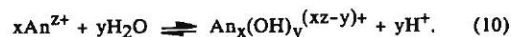
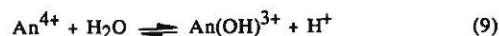
Since hydrolysis and carbonate complexation of actinide ions are dominant factors in most natural waters, these two inorganic complexing ligands will be discussed in more detail than the other actinide complexing ligands. Hydroxide and carbonate are strong actinide complexants in significant concentrations in the environment. The other inorganic ligands (phosphate, silicate, and fluoride) which strongly complex actinide ions and those ligands which moderately complex actinide ions (sulfate and chloride) as well as organic complexants (humics) will be discussed briefly.

a. Hydrolysis

Hydrolysis is the formation of new ionic species or precipitates by the action of water. The hydroxide ion is always present in water solutions and can form strong inner sphere complexes with many cations. For the actinides, hydrolysis results in soluble complexes of hydroxides or oxides and precipitates of hydroxides, oxides, or basic salts. Hydrolysis reactions are significant for all of the actinide oxidation state species at pH values found in natural waters with the exception of the V state.

The actinide(IV) ions have a high charge-to-radius ratio and readily hydrolyze. The reaction for the formation of the first hydrolysis product of a typical tetravalent actinide

cation, An(IV), is shown in equation 9. The generalized reaction for additional hydrolysis products is given in equation 10.



The formation quotients for the above reactions are expressed as follows:

$$Q_{1,1} = \frac{[\text{AnOH}^{3+}][\text{H}^+]}{[\text{An}^{4+}]} \quad (11)$$

$$Q_{x,y} = \frac{[\text{An}_x(\text{OH})_y^{(xz-y)+}][\text{H}^+]^y}{[\text{An}^{z+}]^x} \quad (12)$$

Pentavalent actinyl ions, AnO_2^+ , do not readily hydrolyze until higher pH values (> 9) and the hexavalent actinyl ions, AnO_2^{2+} , do not appreciably hydrolyze until near-neutral pH values are attained.

Thorium. Thorium(IV) is the largest tetravalent cation (ionic radius of 0.99 Å versus 0.93 and 0.90 Å for U(IV) and Pu(IV), respectively) [73] and is the actinide(IV) ion most resistant to hydrolysis. However, hydrolysis does occur between pH 2 and 3 with the formation of $\text{Th}(\text{OH})^{3+}$ (log Q = -3.2) and $\text{Th}(\text{OH})_2^{2+}$ (log Q = -6.93). Further hydrolysis produces $\text{Th}(\text{OH})_3^0$ and $\text{Th}(\text{OH})_4^0$, with estimated log Q values of ≤ -11.7 and -15.9 , respectively [74]. In perchlorate solutions near pH 4, thorium(IV) may undergo irreversible hydrolysis in solution or hydrous ThO_2 may precipitate. Polynuclear species exist for Th(IV) which include the dimer, $\text{Th}_2(\text{OH})_2^{6+}$, and the hexamer, $\text{Th}_6(\text{OH})_{14}^{10+}$ or $\text{Th}_6(\text{OH})_{15}^{9+}$. These polynuclear complexes are common in chloride and nitrate solutions [74]. It seems somewhat curious that these polynuclear hydrolysis products have only been reported for thorium and not for any other tetravalent actinide ions.

Uranium. U(IV) and U(VI) are the oxidation states expected under environmental conditions. The hydrolysis of uranium(IV) begins at acid concentrations greater than 0.1 M. Qualitatively, the hydrolysis of U(IV) is similar to that of Th(IV). Conclusive identification of individual species is uncertain, but it is most likely that the important hydrolysis species are UOH^{3+} , $\text{U}(\text{OH})_2^{2+}$, $\text{U}(\text{OH})_3^+$, $\text{U}(\text{OH})_4^0$, and $\text{U}(\text{OH})_5^-$. Estimates of the hydrolysis quotients for the formation of these species have been published by Baes and Mesmer [74].

Hydrolysis of aquo UO_2^{2+} begins at about pH 3. The first hydrolysis product is $\text{UO}_2(\text{OH})^+$ (log Q = -5.8) at uranium concentrations less than 10^{-5} M. At higher U concentrations, the dimer, $(\text{UO}_2)_2(\text{OH})_2^{2+}$ (-2.6) is the first hydrolysis product, followed by $(\text{UO}_2)_3(\text{OH})_5^+$ (-15.63). After this, hydrous uranyl hydroxide precipitate is the stable species [74].

Neptunium. Np(IV) is expected to be the dominant oxidation state under reducing conditions in natural groundwaters. Sullivan and Hindman [75] studied the hydrolysis of Np(IV) spectrophotometrically. They reported the formation constant of the first hydrolysis product, NpOH^{3+} , to be $\log Q = -2.30$ at ionic strength of 2 M and room temperature. Np(V) is the most common oxidation state in oxygen rich natural waters and it does not hydrolyze readily.

Plutonium. Pu(III) hydrolysis is not well known because of its rapid oxidation to Pu(IV) in anything but strong acid solutions. The first hydrolysis product, PuOH^{2+} , was studied by Kraus and Dam who estimated a $\log Q$ value of -7.0 [76]. In solutions greater than 0.05 M acid and unit ionic strength, Pu(IV) is predominantly Pu^{4+} aquo ion. In 0.05 M acid solutions, $\text{Pu}(\text{OH})^{3+}$ and $\text{Pu}^{4+}(\text{aq})$ have about equal concentrations. At lower acid concentrations, further hydrolysis is expected to give the ions $\text{Pu}(\text{OH})_2^{2+}$ and $\text{Pu}(\text{OH})_3^+$, and neutral species such as $\text{Pu}(\text{OH})_4^0$. Formation constants have been estimated for these species [74], but measurements have been made only for the first hydrolysis product, $\text{Pu}(\text{OH})^{3+}$ ($\log Q$ values range from -0.5 to -1.72) [77]. The lack of data for the higher hydrolysis quotients is due to the formation of colloids under the required solution conditions for existence of these soluble hydrolyzed species. Pu(V) does not appreciably hydrolyze, particularly at low environmentally relevant Pu(V) concentrations. Pu(VI) exists mainly as PuO_2^{2+} at low concentrations in acid solutions. At higher pH values, the following species have been identified: $\text{PuO}_2(\text{OH})^+$ ($\log Q = -5.6$), $\text{PuO}_2(\text{OH})_2^{2+}$ (-8.36), and $(\text{PuO}_2)_3(\text{OH})_5^+$ (-21.65) [77].

Americium. Am(III) is expected to be the dominant oxidation state in natural waters. Hydrolysis reactions of Am(III) are not appreciable even at near-neutral pH values. The first hydrolysis quotient for formation of AmOH^{2+} was calculated by Désiré *et al.* [78] to be $\log Q = -5.92$ and by Shalinets and Stepanov [79] who reported $\log Q = -3.3$. More recently, Stradler and Kim [41] investigated the hydrolysis of Am(III) in noncomplexing aqueous perchlorate solutions and in carbonate-free saline solutions using solubility data. Their results displayed as a speciation diagram are shown in Figure 10. An interesting aspect of this work is that in concentrated NaCl solutions ($\mu \leq 3$, $\text{pH} > 7$), alpha radiolysis generated substantial amounts of oxidized chlorine species which subsequently oxidized Am(III) to Am(V). This reference also provides a thorough literature review of previous americium hydrolysis studies.

Curium. Cm(III) is the only oxidation state that can exist in environmental waters. The first hydrolysis quotient for formation of CmOH^{2+} was reported by Désiré *et al.* [78] as $\log Q = -5.92$, quite similar to the value for Am(III), as expected. In studies related to hydrolysis, Piotrowiak *et al.* [80] investigated the exchange rates between the molecules of water in the primary coordination sphere of Cm(III) and the bulk solvent using oxygen-17 NMR. These workers determined that Gd(III) is not a perfect model for Cm(III).

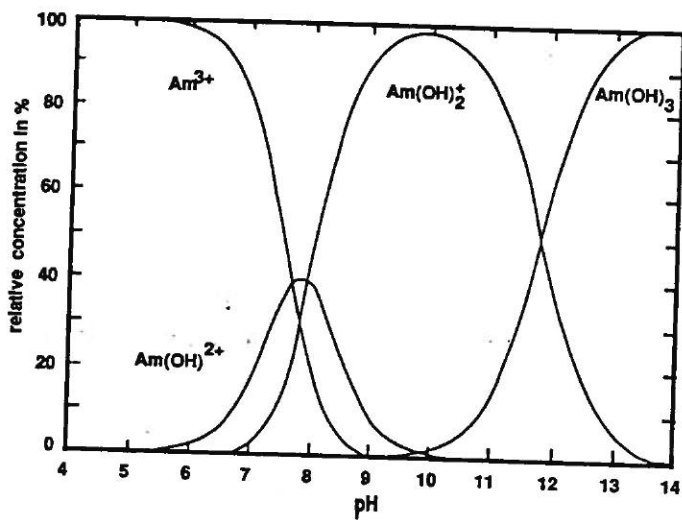


FIGURE 10

Speciation diagram for hydrolysis of americium(III) in 0.1 M sodium perchlorate solution.

[41]

b. Carbonate Complexes

Carbonate and bicarbonate ions are very common in natural waters (see Table IV). Knowledge of their complexes with actinides is critical to understanding actinide behavior in the environment. The environmental chemistry of actinide carbonate complexes is particularly important at low ligand concentrations. However, because of experimental difficulties, most studies have been performed at relatively high ligand concentrations and attempts are made to extrapolate this information to lower, more relevant concentration regimes. A comprehensive and critical review of actinide carbonate complexes has been published by Newton and Sullivan [81]. The association quotients for key actinide carbonate complexes are listed in Table V [81].

Solid thorium hydroxide absorbs carbon dioxide readily and solid thorium(IV) oxycarbonates dissolve in an excess of alkali carbonate solution. Thus, ample evidence exists for formation of $\text{Th}(\text{CO}_3)_4^{4-}$, $\text{Th}(\text{CO}_3)_5^{6-}$, and $\text{Th}(\text{CO}_3)_6^{8-}$ in solution [28, 98].

Uranium(IV) carbonate complexes were studied by Ciavatta *et al.* [82] who identified the complex $\text{U}(\text{CO}_3)_5^{6-}$ with a log Q value of 40 ($\mu = 3 \text{ M}$). No evidence for complexes with lower ligand numbers were found in the solutions studied and apparently no recent work has been performed in this area. The uranyl(VI) carbonate system is economically important because of carbonate leaching of uranium ores and in the preparation of actinide oxide ceramics [99]. Uranium(VI) carbonate complexes have been studied quantitatively for the past 30 years and, to date, the system is still not completely characterized. Uranium(VI) carbonate complexes, formation quotients, and references are listed in Table V [81].

Recent studies of neptunium(V) carbonate complexes have been reported by Nitsche *et al.* [100]. These workers determined the formation constant of $\text{NpO}_2\text{CO}_3^-$ in 0.1 M NaClO_4 solution by remote fiber-optic absorption spectrophotometry. The advantage in this study is a direct observation of the species for determination of the formation quotient, $\log Q = 4.69 \pm 0.13$. This value is in excellent agreement with Maya's value of 4.49 ± 0.09 [92] (see Table V). The absorption spectra of Np(V) carbonate solutions recorded by Nitsche *et al.* [100] are displayed in Figure 11.

Plutonium(IV) carbonate complexation was investigated by Silva and Nitsche [101]. They found a log Q value of > 13 for the formation of PuCO_3^{2+} using spectrophotometry and a complex competition method. This value is 2 orders of magnitude greater than that reported in Table V. This result implies that Pu(IV) concentrations in carbonate waters are dominated by this complex. Hobart *et al.* [102] attempted to use a complex-competition method to determine the carbonate complexation of Pu(IV) using citrate ion. The equilibria were quite complicated and multiple mixed ligand complexes were detected. Figure 12 shows spectral evidence of the carbonate complexation of Pu(IV) [102].

The reaction rates for the exchange of actinyl(VI) triscarbonate complexes, $\text{AnO}_2(\text{CO}_3)_3^{4-}$, (An = U, Np, and Pu) with the carbonate ion have been studied by Stout *et al.* [103] using variable temperature carbon-13 NMR. This method permits direct observation of the individual species present. At the same pH, it was observed that the exchange rate increases in the sequence $\text{UO}_2^{2+} < \text{NpO}_2^{2+} < \text{PuO}_2^{2+}$. Interestingly, these workers found no evidence for the trimer, $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, or mixed hydroxy complexes or mixed bicarbonate-carbonate complexes under the conditions of their experiments [103]. Experiments are presently in progress to extend this study to include the americyl(VI) ion in

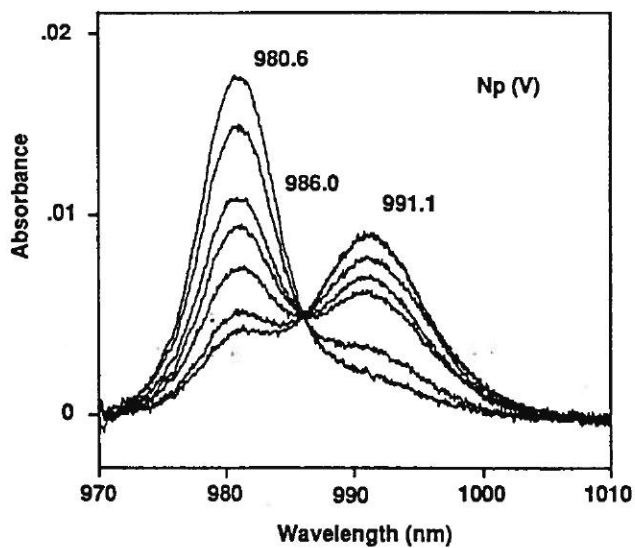


FIGURE 11

Absorption spectra of neptunium(V) carbonate solutions. $[\text{Np(V)}] = 5.56 \times 10^{-5} \text{ M}$ and $[\text{CO}_3^{2-}] = 3.39 \times 10^{-6}$ to $1.45 \times 10^{-4} \text{ M}$ [100]. (Reproduced with permission from the authors and Kluwer Academic Publishers).

TABLE V.
Association Quotients for Actinide Carbonate Complexes [81]

Oxidation State	Species	Ionic Strength (M)	log Q ^a	Reference
VI	UO ₂ CO ₃ (aq)	3.0	8.60 ^b	[82]
		0	9.87	[82]
	UO ₂ (CO ₃) ₂ ²⁻	0.1 ^f	16.22 ± 0.03	[83]
		0.1	16.2 ± 0.3	[84]
		0.1 - 0.5	14.6 - 16.7	[82]
	(UO ₂) ₃ (CO ₃) ₆ ⁶⁻	3.0	60.6 ^b	[85]
				[86]
	UO ₂ (CO ₃) ₃ ⁴⁻	0.1 ^f	21.54	[87]
		0.1	21.8 ± 0.05	[88]
		3.0	24	[86]
		0.1 - 1.0	18.3 - 23	[82]
	(UO ₂) ₃ (OH) ₃ CO ₃	3.0	43 ^b	[82]
	(UO ₂) ₂ (OH) ₃ CO ₃ ⁻	0.1	41 ^b	[88]
	(UO ₂) ₁₁ (OH) ₁₂ (CO ₃) ₆ ²⁻	3.0	202 ^b	[82]
	PuO ₂ (CO ₃) ₂ ²⁻	var. ^{e,g}	(16) ^c	[89]
	PuO ₂ (OH)CO ₃ ⁻	var. ^{e,g}	(23) ^c	[89]
	PuO ₂ (OH) ₂ CO ₂ ²⁻	var. ^{e,g}	(22) ^c	[89]
PuO ₂ (CO ₃) ₃ ⁴⁻	0.15	(20) ^d	[90]	
PuO ₂ (OH) ₂ (HCO ₃) ⁻	0.1	(20) ^b	[91]	
PuO ₂ (CO ₃) ₂ ²⁻	0.1	13.1 ± 0.1 ^d	[91]	
V	NpO ₂ (CO ₃) ₃ ⁵⁻	1.0	8.53 ± 0.06	[92]
	NpO ₂ (CO ₃) ₂ ³⁻	1.0	7.11 ± 0.07	[92]
	NpO ₂ CO ₃ ⁻	1.0	4.49 ± 0.09	[92]
IV	U(CO ₃) ₅ ⁶⁻	3.0	40	[86]
	Np(OH) ₄ CO ₃ ²⁻	var. ^{e,g}	(53.1 ± 0.01) ^c	[93]
	PuCO ₃ ²⁺	7 - 10	(42) ^{b, d}	[94]
	PuCO ₃ ²⁺	1.0	(47.1 ± 3.0) ^d	[95]
	Pu(CO ₃) ₂ (aq)	1.0	(55.0 ± 2.5) ^d	[95]
	Pu(CO ₃) ₃ ²⁻	1.0	(57.9 ± 2.7) ^d	[95]
	Pu(CO ₃) ₄ ⁴⁻	1.0	(59.6 ± 2.9) ^d	[95]
	Pu(CO ₃) ₅ ⁶⁻	1.0	(62.4 ± 2.4) ^d	[95]
	Pu(OH)CO ₃ ⁺	1.0	(55.2 ± 2.3) ^d	[95]
III	AmCO ₃ ⁺	1.0	5.81 ± 0.04	[96]
	Am(CO ₃) ₂ ⁻	1.0	9.72 ± 0.1	[96]
	Am(HCO ₃) ₂ ⁺	0.2	4.79 ± 0.07	[97]
	Am(HCO ₃) ₂ ⁺	0.2	8.15 ± 0.08	[97]
	Am(CO ₃) ₂ ⁻	0.2	11.45 ± 0.07	[97]
	AmOH(CO ₃) ₂ ²⁻	0.2	15.57 ± 0.08	[97]

^a 25° C unless otherwise indicated.

^b Calculated from the actinide aquo ions, CO₃²⁻ and OH⁻ if required.

^c Value not considered to be reliable by [81]

^d Based on uncertain assumptions.

^e Ionic strength allowed to vary.

^f 20°C.

^g Temperature not stated.

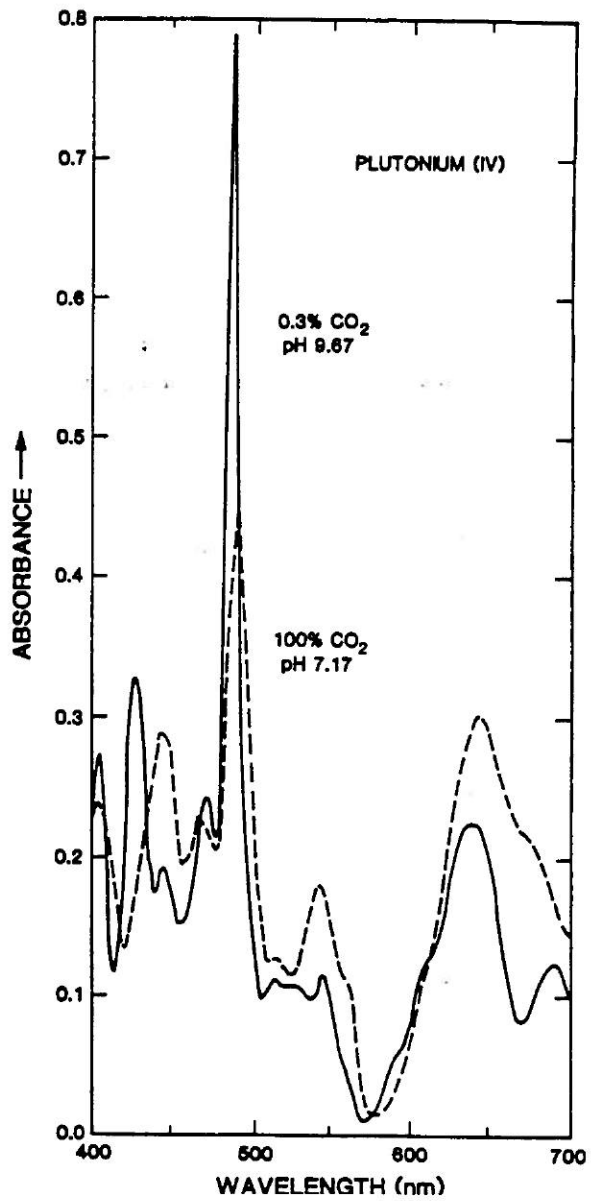


FIGURE 12

Absorption spectra of plutonium(IV) in carbonate solutions as a function of carbon dioxide pressure (pH). [102]

a collaboration between the University of Cincinnati and Argonne and Los Alamos National Laboratories.

Americium(III) carbonate complexation studies have been reported recently by Moulin *et al.* [104] and Nitsche *et al.* [105]. Moulin *et al.* considered carbonate complexation in granitic groundwaters and in interstitial concrete (waste form) waters. Hydrolysis of Am(III) was the only effect observed in the concrete waters ($p\text{CO}_2 = 10^{-13}$ atm), but Am(III) carbonate was present in the granitic waters ($10^{-3.5} < p\text{CO}_2 < 10^{-1}$ atm). No mixed americium hydroxy-carbonate species were found and a species, $\text{Am}(\text{CO}_3)_3^{3-}$, was reported with $\log Q = 11.3$ at $\mu = 0.1$ M [104]. Nitsche *et al.* [105] used fiber-optic absorption spectrophotometry and determined a $\log Q$ value of 6.69 ± 0.15 for the formation of AmCO_3^+ at $\mu = 0.1$ M. These workers found no evidence for a bicarbonate complex.

Considerable uncertainty exists in the literature for both the hydrolysis and carbonate complexation data for Am(III). The inconsistencies are unresolvable without new experiments with highly sensitive direct speciation methods. Kerrisk and Silva [106] compiled a consistent set of data for modeling purposes. Bernkopf and Kim [58] studied carbonate complexation of Am(III) carbonate using solubility data (from Figure 6). The speciation diagram resulting from treatment of their data is shown in Figure 13. It can be seen that in the presence of carbonate ion the solubility and speciation of Am(III) are dominated by carbonate complexation at pH values > 8 .

c. Fluoride, Chloride, Phosphate, and Silicate Complexes

The actinide fluoride complexes are more stable than the comparable chloride complexes (see Table VI). An^{4+} ions form stronger fluoride complexes than the AnO_2^{2+} or An^{3+} ions. Trivalent ions of plutonium, americium, and curium exhibit similar complexation quotient values with fluoride ions. Actinide tri- and tetravalent ions form relatively insoluble compounds with fluoride ion. Actinide(IV) ions are readily hydrolyzed, and consequently, when studying actinide fluoride complexation, high acid (HF) conditions are required to avoid hydrolysis and maintain detectable limits of actinide ion concentration. These rather harsh experimental conditions makes it difficult to extend this data to environmentally relevant regimes of near neutral pH and low actinide concentrations. Selected actinide fluoride complexes are listed in Table VI along with their stability quotients [107].

The fluoride complexes of plutonium(IV) were investigated by Nash and Cleveland [24] in an effort to explain the high solubility of Pu(IV) in certain fluoride-rich groundwaters. The reported fluoride ion concentration was 52 mg/L (2.74×10^{-3} M) at pH 9.3 with a Pu(IV) concentration of from 10^{-7} to 10^{-9} M. The complexes PuF_3^+ and PuF_2^{2+} were studied and their stability quotients, along with the enthalpy and entropy for the complexation reactions, were reported. The thermodynamic values determined in this work agreed reasonably well with previously determined enthalpy and entropy values for the AnF_3^+ complexation reactions of Th(IV), U(IV), and Np(IV) [108,109]. Nash and Cleveland concluded that simple fluoride complexes could not explain the relatively high solubility of plutonium in these fluoride-rich groundwaters, and they suggested that nonequilibrium conditions or unknown equilibria involving mixed-ligand or anionic complexes may be the solubility determining factor(s) [24].

TABLE VI.
Stability Quotients of Selected Actinide
Halide Complexes*

Ion	Fluoride		Chloride	
	μ (M)	log Q_1	μ (M)	log Q_1
Am ³⁺	1	2.93	1	-0.01
Cm ³⁺	0.5	3.34	0.5	0.18
Th ⁴⁺	0.5	7.56	1	0.18
U ⁴⁺	4	8.97	1	0.30
Np ⁴⁺	4	8.26	1	-0.04
Pu ⁴⁺	0	8.4	1	0.14
UO ₂ ²⁺	1	4.54	1	-0.01
NpO ₂ ²⁺	1	4.27	2	-0.21
PuO ₂ ²⁺	1	4.22	4	0.02

* From [107] and references therein.

Phosphate complexes of uranium(IV) and (VI) are tabulated by Weigel [99]. Complexes with $\text{Pu}^{4+}:\text{PO}_4^{3-}$ ratios of 1:5 were reported by King [110] as early as 1949. Electromigration [111] and solubility experiments [112, 113] were performed to study these complexes as well. Moskvina [114] studied the phosphate complexes of Am(III) and reported identification of the following species: $\text{Am}(\text{H}_2\text{PO}_4)^{2+}$ ($\log Q = 1.48$), $\text{Am}(\text{H}_2\text{PO}_4)_2^+$ (2.10), $\text{Am}(\text{H}_2\text{PO}_4)_3^0$ (2.85), and $\text{Am}(\text{H}_2\text{PO}_4)_4^-$ (3.4). Lebedev *et al.* [115] found $\log Q = 4.61$ for formation of $[\text{AmO}_2(\text{H}_2\text{O})_x-2(\text{H}_2\text{PO}_4)_2]^0$.

Actinide silicate complexes are expected to be important in the environment. Silicate ions are the major component of many rock-forming minerals which may be in contact with groundwaters. Many natural waters contain appreciable soluble silicate (see Table IV). Actinide silicates may be prepared in the laboratory using a hydrothermal technique. This method involves coprecipitation of an actinide hydroxide with some form of soluble silicate. The resultant coprecipitated gel is adjusted to a pH value between 8 to 9 and placed in a heated pressure vessel (250°C, 30 atmospheres) [116]. Although these are not typical conditions found in the environment, these conditions may be expected in the near-field of an underground nuclear waste repository as a result of radiation heating [117]. There are little data on actinide silicate compounds and even less data on soluble complexes. Fortunately, a number of naturally occurring thorium and uranium silicate minerals are available for study. Information from these compounds as well as from transuranium compounds may provide information on the type of bonding expected in the soluble complexes. This study is presently underway at Los Alamos National Laboratory utilizing a host of spectroscopic characterization techniques [118].

d. Humic Complexes

Humic materials are ubiquitous throughout the environment. Through redox reactions, complexation, and colloid formation, humic materials can have a dramatic influence on the speciation and migration of actinides in the ecosystem. Humic substances are organic polyelectrolytes with a variable structure, formula, molecular weight, etc. and may possess a wide variety of functional groups [40]. A proposed structure for a generic humic acid was published by Stevenson [119] and is shown in Figure 14. In reality, this structure should be viewed as representative of a portion of a humic acid molecule. Although all molecules might have a similar pattern, each individual molecule may have its own unique structure. This variability in the actual structure of these important actinide complexants makes it difficult to characterize their actinide complexing behavior. The general classes of humic substances include humic and fulvic acids and humin. The differences among these are defined operationally. Fulvic acids are soluble at all pH values, whereas humic acids are soluble above a pH of 3.5. Humins are insoluble at all pH values. In general, fulvic acids have more aliphatic and less aromatic character than humic acids and lower molecular weights [6, 40]. The humate composition of natural waters is usually reported as "dissolved organic carbon" (DOC). As shown in Table IV, DOC may vary considerably in surface waters; from 1 mg/L on the surface of the ocean to 50 mg/L in dark water swamps [120].

There is strong evidence for complexation of all actinides by humates at ambient concentrations in many natural waters. Distribution experiments with ^{241}Am tracer in moist

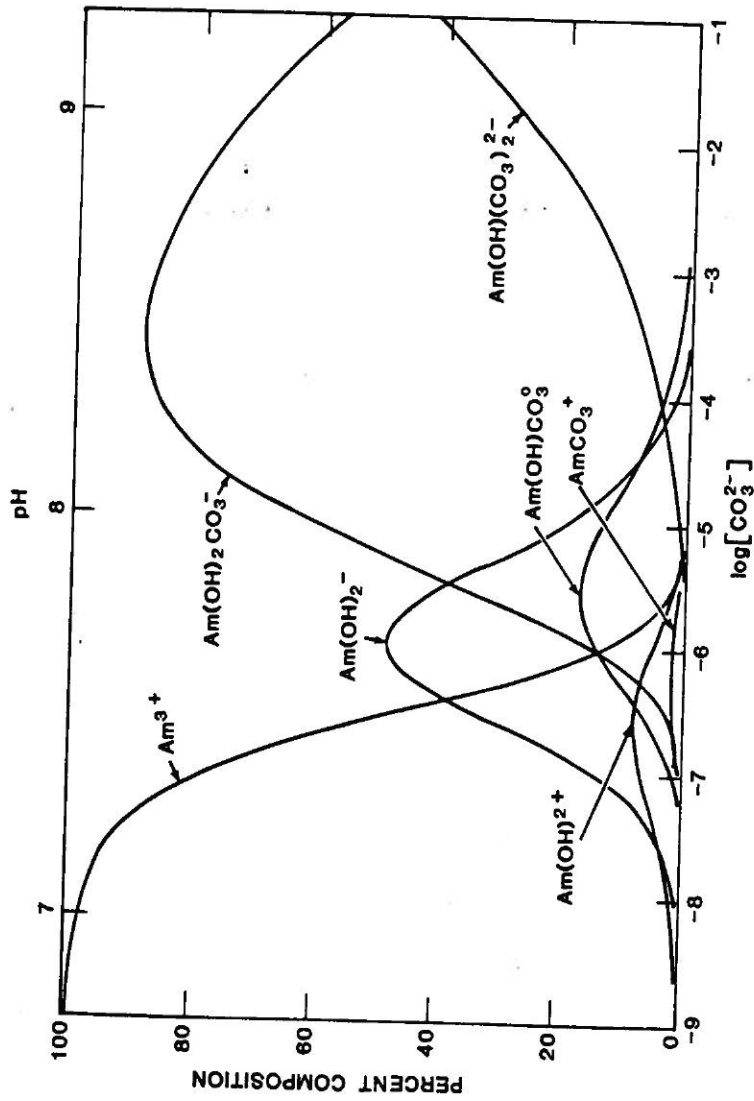


FIGURE 13
 Speciation diagram for americium(III) in carbonate solution derived from solubility data. [58]

TABLE VII
Actinide Association Quotients with Natural Organic
Complexing Agents*

Element	Agent	pK _a	log Q ₁ **	log Q ₂ **
Am(III)	HA	4.67	8.9 ± 0.2	12.9 ± 0.2
Th(IV)	HA	4.85	12.9 ± 0.1	18.0 ± 0.2
Th(IV)	HA	4.45	11.8 ± 0.1	16.8 ± 0.2
Th(IV)	HA	4.44	11.8 ± 0.1	17.3 ± 0.2
Th(IV)	FA	4.02	8.3 ± 0.2	11.5 ± 0.4
U(IV)	HA		7.0	11.5
U(IV)	FA		6.6	11.6
Pu(IV)	X		9.6	18.3
U(VI)	HA	4.19	4.11 ± 0.02	8.94 ± 0.03
U(VI)	HA		6.7	11.5
U(VI)	FA		7.4	13.0
U(VI)	X		8.9	16.1

*Ref. [6] and references therein.

**Stability constants for actinide humates and fulvates (25°C, ionic strength 0.01 M and degree of dissociation 0.5 unless otherwise noted).

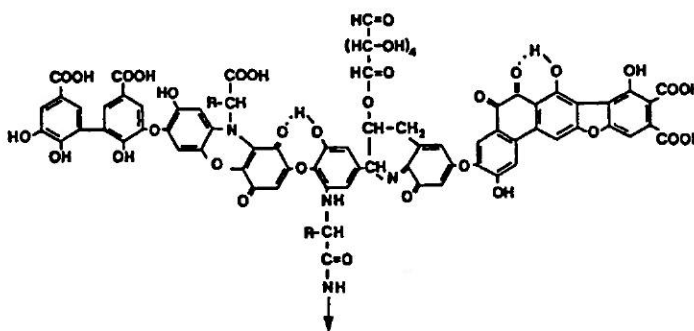


FIGURE 14

A proposed structure for a "generic" humic acid molecule. [119]

soils indicated that Am(III) forms very strong humic acid complexes with formation quotients of approximately 10^5 [121]. Some data for different actinide humate complexes are shown in Table VII. The stability constants listed in Table VII were calculated on the basis of the number of equivalents of carboxylic acid groups in the dissolved humic per liter of solution.

A concise summary of actinide complexation by humic materials was published by Choppin and Allard [6].

"Organic macromolecules could dominate the solution chemistry of trivalent actinides even at moderately low concentrations and even in the presence of carbonate. Organic macromolecules are unlikely to be of importance for the solution chemistry of the tetravalent actinides even at high concentrations since hydrolysis would be dominant in most natural water systems. Pentavalent actinides form complexes with organic macromolecules, but carbonate complexation may be more significant than organic complexation in most environments. Carbonate complexation is likely to dominate over that with organic macromolecules for the hexavalent actinides." [6]

For additional information on humate complexation of actinides, the following references are cited [6, 40, 121-123].

5. Colloid Formation

Colloids represent a unique form of matter intermediate between true solids and true solutions and having characteristics of both. For the most part, colloid particles contain about 10^3 to 10^9 atoms, which corresponds to particle sizes from about $0.01 \mu\text{m}$ up to about $1 \mu\text{m}$ (or up to about several μm in the case of macromolecular organic compounds). Colloids have a very low settling velocity and may be suspended indefinitely and transported over long distances in environmental systems. *Natural* colloids are naturally occurring inorganic or organic particulates (e.g., hydroxides and hydrated oxides of iron, aluminum, silicon, chromium, titanium, etc., fine clay particles, and bio-organic, humic materials, etc.) [124]. In general, inorganic natural colloids result from decomposition of geologic media.

Several of the lighter actinides are known to form *radiocolloids* under conditions found in typical environmental waters. Radiocolloids are very fine, well dispersed, intrinsic particles of actinide compounds. A radiocolloid or a soluble actinide species may combine with a natural colloid to form a third class of colloids. These "piggy-back" colloids have been called "pseudocolloids" or "carrier colloids." Both terms are misleading and this author chooses the term *associative colloids* to describe this third class of colloids. Many complexing ligands have the ability to enhance the adsorption of actinides onto natural colloid surfaces. Humic acids are known to modify substantially the sorption properties of natural colloids [125].

The actinide IV ions have a high charge-to-radius ratio and readily hydrolyze to form hydroxide complexes, colloids, and colloidal *sols*. Radiocolloid formation of

actinide(IV) ions is believed to proceed through a series of nucleation and growth processes resulting in formation of hydrous oxide or hydroxide according to the scheme shown in Figure 15. The ultimate dehydration product in this scheme is the actinide(IV) dioxide. Actinide III, IV, V, and VI ions have a strong affinity for forming associative colloids by combination with natural colloids.

Thorium. Colloidal Th(IV) results from polymeric hydroxyl and oxygen bridge formation between monomers. Sols can be prepared by peptization of colloidal Th(OH)₄ [2, 126]. The potential for radionuclide migration of colloidal thorium was investigated by Olofsson and coworkers [4].

Neptunium. A slow change in the pH of a Np(IV) solution with time was observed by Sullivan and Hindman [75]. They suggested that this could be the result of colloid formation. Sokhina and coworkers [127], using spectrophotometry and dialysis, reported that colloidal Np(IV) could be formed by dissolution of Np(IV) hydroxide in dilute nitric acid at an elevated temperature (50°C) and by dilution of acidic concentrated solutions of Np(IV) with hot water. Moriyama and coworkers [128] studied Np(IV) radiocolloids in 0.01 M sodium dithionite (Na₂S₂O₄) holding reductant solutions at pH values from 2 to 10. After initial hydrolysis of Np(IV), amorphous Np(OH)₄ reacted further to form radiocolloids at pH values greater than 8. Above pH 8, carbonate complexation of Np(IV) became the most important factor.

Column experiments with Np(IV) solutions in natural groundwaters flowing through sediments have been performed by Lieser and Mühlenweg [129]. They observed the presence of neptunium(IV) associative colloids under anaerobic conditions. Colloid formation was favored at low concentrations of the radionuclide, near the standard redox potential (E°), and at low ionic strength. The groundwater used had substantial amounts of humic acid present and it was concluded that Np(IV) was bound to colloidal forms of humic acid.

Plutonium. Tetravalent plutonium readily forms radiocolloids above pH 1. Pu(IV) colloid can be prepared by a number of methods including: dilution of aquo Pu⁴⁺ solutions, precipitation of Pu(IV) hydroxide followed by peptization, auto oxidation of near-neutral pH solutions of Pu(III), etc. Pu(IV) sols are green, optically clear, display a characteristic absorption spectrum (see Figure 16), and may remain suspended indefinitely [130-132]. By elimination of water, the hydrolyzed forms of Pu(IV) may undergo stepwise formation of oxygen and/or hydroxy bridges that result in colloidal sols, precipitates, and ultimately in crystalline plutonium dioxide (see Figure 15) [49].

The characterization of plutonium(IV) colloid has met with only limited success since its identification by Kraus [133]. Colloids are almost certainly not in thermodynamic equilibrium and, as such, their formation, composition, size, and stability may vary to a large extent [124]. This variability in all of the important characteristics of colloids makes successful research results elusive indeed. Weigel [33] provides a comprehensive historical treatment of Pu(IV) radiocolloid formation and behavior.

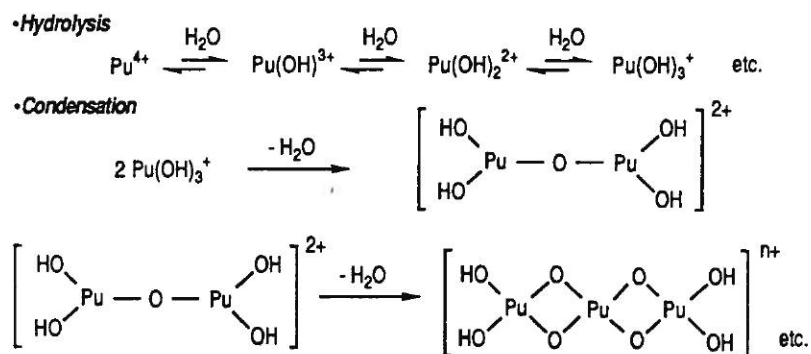


FIGURE 15
Stepwise formation of plutonium(IV) colloid.

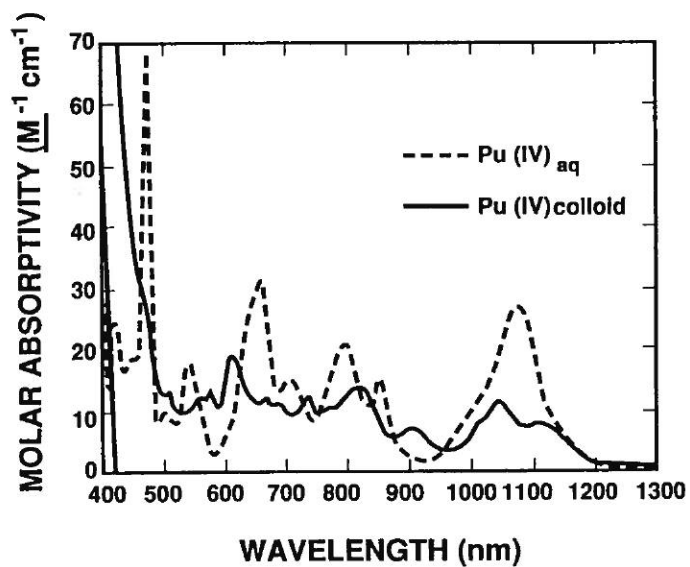


FIGURE 16
Solution absorption spectra of plutonium(IV) aquo ion and plutonium(IV) colloid. [134]

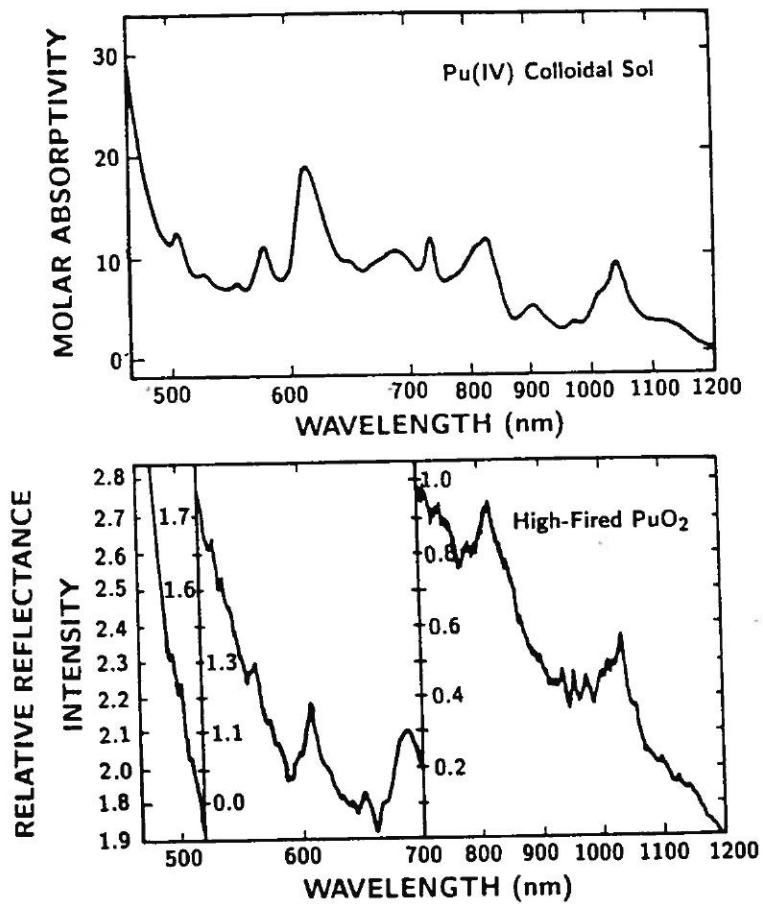


FIGURE 17
 Comparison of the absorption spectrum of plutonium(IV) colloid with the diffuse reflectance spectrum of high-fired plutonium dioxide solid. [134]

A recent report reviews the literature on the formation, characterization, and stability of plutonium(IV) radiocolloid [134]. Spectroscopic and electrochemical methods have been applied to determining the structure of Pu(IV) colloid. Further evidence was obtained which suggests that the structure of Pu(IV) colloid is closely related to that of high-fired plutonium dioxide. The solid state diffuse reflectance spectrum of plutonium dioxide, shown in Figure 17, bears a strong resemblance to the absorption spectrum of Pu(IV) colloidal sol. This provides evidence that plutonium ions in both the high-fired oxide and the colloidal sol have similar electronic environments. It was also found that Pu(IV) colloid is reactive at an electrode surface [135]. Autocorrelation photon spectroscopy was used to determine colloid particle size. The smallest size measured with this method was reported to be 1.5 nm in diameter [136].

Complexation of plutonyl(V) and (VI) ions by humics can result in reduction to Pu(IV), followed by hydrolysis to form radiocolloids in natural waters. In the presence of humates, these Pu(IV) radiocolloids could combine with colloidal humic material to form associative colloids [40, 137].

Americium. Since Am(III) does not readily hydrolyze even at near-neutral pH values, americium colloids are, in general, not radiocolloids but associative colloids. Am(III) in near-neutral pH solution is notorious for adsorbing on all surfaces encountered, including Teflon [56]. This effect is most pronounced in very dilute americium solutions since all of the Am(III) seems to totally disappear during the experiment.

Nash *et al.* [27] suggest that the apparent low solubility of americium in natural groundwaters and seawaters may be explained by the formation of americium radiocolloids and associative colloids. Suffice it to say that the exact nature of americium colloids is not well known.

Understanding the role of colloids in the release of radionuclides and their migration in the environment is of increasing importance. In the event of a breach in an underground nuclear waste repository, for example, colloids represent a source of radionuclide transport to the far field environment in parallel with the transport of dissolved actinide species. Furthermore, these colloids may decompose or disaggregate into soluble ionic species [50]. Actinide colloids must be taken into account when determining such fundamental chemical properties as solubility and sorption in natural waters. The filtration of colloids by geologic media in groundwaters may also play a significant role in migration/retardation and may act to limit the release of actinide radionuclides to the accessible environment. An excellent review of all three classes of colloids can be found in a recent publication by Lieser *et al.* [124].

IV. ACTINIDES IN THE ATMOSPHERE

A. Physical Description

As a result of the intense heat of their birth in nuclear explosions or burning reactor cores, it is assumed that actinide fallout in the atmosphere is in the form of intrinsic particulates of high-fired oxides and/or adsorbed on to non-radioactive particulates. These non-radioactive carrier particles could be calcium oxides/carbonates resulting from detonation of nuclear devices on coral islands [138] or they could be soot from burning

graphite reactor cores [19]. In investigating the 1986 Chernobyl reactor accident, Khodakovsky and Mironenko [19] determined that actinide carbidization was possible under the conditions of high temperature in the presence of burning graphite. It is suspected that a significant fraction of the plutonium deposited on Earth was produced by an (n, γ) reaction with ^{238}U and the subsequent decay of ^{239}U through ^{239}Np to ^{239}Pu . Thus, a significant fraction of the plutonium in the environment was formed by transmutation long after the explosion and was never involved in refractory heating. It must be kept in mind, however, that the plutonium progenitors were involved in the matrix heating process and the chemical consequences of radioactive decay must be considered [139]. The chemical consequences of radioactive decay of selected transplutonium elements has been investigated by Young and coworkers [140]. The form of actinides released in small quantities from nuclear fuel processing facilities may range from relatively insoluble particles to quite soluble inorganic and organic complexes, which may be in the form of solid or liquid wastes [141].

B. Distribution of Fallout

In the troposphere, the residence time for fallout is reasonably short (on the order of from 20 to 40 days) and as a result, the deposition rate is quite rapid. The radioactive debris is mainly deposited in the hemisphere of the test, with higher deposition in the test latitude. The movement of radioactive particulates in the troposphere is influenced by all forms of weather. Rain and snow will scavenge particulates, causing uneven distributions on the Earth's surface [14].

In the stratosphere, the situation is quite different from that in the troposphere. The debris leaving the stratosphere passes through the tropopause discontinuity, which occurs near the midlatitudes. Consequently, deposition of the debris is nearly independent of the latitude of detonation [14].

Some very interesting studies are involved with the transfer phenomena of actinides from natural waters to the atmosphere by bubble bursting [142] and sea spray [143]. Mechanisms for returning even small quantities of radioactive material to land as a consequence of low-level discharge in coastal waters should be investigated to determine acceptable limits. It has been shown that trace ionic solutes can be enriched when sea spray forms. Thus maritime aerosol may be an important, overlooked mechanism for radionuclide transport [141]. Additional information on actinides in the atmosphere can be found elsewhere [1, 2, 8, 17]. In any case, radioactive debris in the atmosphere eventually deposits on the Earth's water or land surfaces, where new mechanisms and interactions will dominate.

V. ACTINIDES IN THE GEOSPHERE

Radioactive fallout is deposited on land surfaces from the atmosphere in the form of relatively insoluble particulates. As a consequence of this, more than 99% of the plutonium inventory is found in the soil component of most ecosystems, with a majority of the contamination in the first few cm of the surface. Most plutonium exists strongly adsorbed on surface soils. Even after a considerable amount of water (many years of rain and snow fall) has percolated through the soil column, the contamination remains in the first 10 cm [141]. Essington *et al.* [144] in investigating soil samples from the Nevada Test Site, found

that for half of the samples studied, 95% of the total amount of plutonium was concentrated in the uppermost 5 cm of soil. Nyhan *et al.* [145] determined that after 28 years, little downward soil migration was noted at the Trinity Site in New Mexico. Half of the material was retained in the upper 5 cm, with the remainder between 5 and 20 cm. The mobility of plutonium in soils is low because of fixation to soil colloids and particularly to clay minerals. Plutonium is sorbed strongly to kaolinite and illite and to a lesser degree on montmorillonite [146].

Whenever a considerable migration of actinides is noted in soils, it is usually caused by mechanical processes, such as frost/thaw and wet-dry phenomenon, erosion, biological activity, tilling, etc. [147]. A mechanism which may effect plutonium migration in soils is the phenomenon of flaking of colloidal material from the surface of particles via the action of radiation damage. This phenomenon has been of concern in the storage and disposal of high-fired actinide oxide fuel elements. Soils in water may retain actinides to a large degree even when in intimate contact with these waters. Cochran [148] has published a discussion of the study by Colley and Thompson [149] of uranium in deep sea sediments. The redox conditions of the sediments determine the oxidation state of the uranium and the relative mobility. The results indicate that, for the most part, natural uranium has been immobilized in these sediments for up to 500,000 years! This determination was made by studying uranium-238-series equilibrium in a sediment dated at this time period [149]. As in the case with atmospheric contamination, soil radionuclides will remain immobile or may come into contact with near-neutral pH natural waters, and aqueous chemistry will come into play. The reader is referred to a number of reviews for more information on the behavior of actinides in soils [1, 8, 147].

VI. NUCLEAR WASTE DISPOSAL

A number of proposals have been considered, if only briefly, for the long-term disposal of high-level nuclear waste. These have included (a) deep space disposal, (b) emplacement in subsiding tectonic plates, (c) deep sea bed emplacement, (d) solar injection, (e) transmutation, (f) deep geological disposal, etc. There is a worldwide scientific consensus, however, that deep geologic disposal (the approach being followed by the United States, Sweden, Germany, and other countries) is the best option for disposal of high-level nuclear waste. If packaged and placed in carefully designed and engineered underground facilities, where the site has been carefully selected, it may be possible to ensure isolation of the waste from the far-field environment for tens of thousands of years or longer. Summary reports on the topic of geological nuclear waste disposal have appeared in the recent literature [151-153].

The United States Congress first reviewed five locations for siting a high level nuclear waste repository and decided to investigate three sites with three bedrock forms: Deaf Smith County, Texas (salt); near Hanford, Washington (basalt); and Yucca Mountain, Nevada (tuff). In 1987, Congress selected Yucca Mountain as the only location designated for site characterization.

Yucca Mountain is located approximately 100 miles NNE of Las Vegas, Nevada. The proposed repository horizon is in a zone of densely welded, devitrified tuff in the lower part of the Topopah Spring member of the Miocene Paintbrush tuff, 200 to 400 meters

above the water table in the unsaturated (vadose) zone. With the present philosophy of minimal engineered barriers, it is expected that the selection of a suitable indigenous geologic formation will provide an adequate natural barrier to prevent movement of radionuclides from a repository to the accessible environment. A major mechanism for migration of actinides from such a repository is transport by water. Under the current climate conditions at Yucca Mountain, water flow is thought to occur mainly in the matrix of the tuff units, but it may occur locally or intermittently in fractures and faults [151]. The tuff itself provides certain desirable properties for containment of radionuclides. Although the devitrified tuff units contain predominantly quartz and feldspars, the fractures contain zeolites which have high sorption affinity for actinides. The surrounding vitrified tuff units contain significant amounts of zeolites within the matrix and lining the fractures. A summary of the sorption properties of Yucca Mountain tuffs has been cited earlier in this report [64]. In addition, a number of earlier Los Alamos reports provide more details on radionuclide sorption on Yucca Mountain tuff [154-156] and on the geochemistry of the Yucca Mountain area [157].

The potential for Nevada tuff to retard actinide radionuclide migration in the ground can be inferred from studies conducted at the Nevada Test Site, adjacent to Yucca Mountain. For many years, researchers have been studying the migration of radionuclides away from explosion cavities formed by underground nuclear tests carried out at this location. To date, these workers have not found evidence suggesting that actinide elements have migrated away from the cavities under the influence of groundwater movement [158].

Many more detailed investigations of the Yucca Mountain site are required to fully characterize the location in order to meet licensing requirements and to alleviate public concern for the potential for contamination of man and the environment. The nation's inventory of high-level radioactive waste is presently stored at the surface, mostly located at the point of origin, in many major metropolitan areas near the reactor facilities. The problems associated with nuclear waste disposal must be addressed expeditiously. The present danger is not to take any action at all. It is hoped that sound judgement and hard scientific data will be used to make responsible decisions on this issue. In any case, knowledge of actinide element behavior in the environment will be valuable in the assessment of potential repository locations to ensure safe disposal and isolation of nuclear waste from man and the environment.

VII. CONCLUSIONS

The mobility and distribution of actinides in the environment are directly correlated to redox conditions, actinide solubility, complexing agents (speciation), and to the presence of solid surfaces (sorbing surfaces including colloids). The net effect of the sorption process is the slow removal of actinides from the aqueous phase. The adsorption on solids follows the same trend as hydrolysis and complexation, i.e., $An(IV) > An(III) = An(VI) > An(V)$. (It is interesting to note that the uptake of actinides by plants follows the reverse order of hydrolysis [123].) Organic and inorganic particles in soils and natural waters constitute a major mode of actinide transportation in flowing environmental water systems [7]. Adsorption of actinides on particles may also be the main reason for retardation of actinides in geological groundwaters by action of filtration and settling.

A fundamental understanding of actinide chemistry under environmental conditions is needed to define the nature of the contaminants, to learn how they move in the environment, to determine their effects on health, safety, and society, and to find alternative methods for control of effluents, disposal of waste, and methods for decontamination and reclaiming of lands. In this manner, we can preserve, protect, and enhance the quality of the environment while at the same time allowing for production of the energy which we so urgently need [159].

The photographs of Earth from space remind us that, as far as radioactive contamination is concerned, there is no such thing as a remote location on this planet. It is also apparent that the naive and unsafe practices of the past are unacceptable. Furthermore, the solution to the problems associated with long term disposal of nuclear waste cannot be solved by engineering alone. Sound scientific investigation tempered by proper socio-economic and political insight will help us to solve one of the most difficult problems facing man in the 21st century.

"We live in a unique time in the history of our planet. For the first time, one species, man, now has the capacity to change the environment for life on a global scale - from pole to pole - from the heights of the stratosphere to the depths of the ocean... But, at the same time, we have developed the capacity to think about what we do. To observe the subtle changes and interactions that occur between the ocean, the biosphere, and the atmosphere. Our challenge now is to apply our knowledge and wisdom to chart a wise course to the future, to live in harmony with our planet, while maintaining the quality of life for all living things on this planet." [160]

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INTRODUCTION AND DISCUSSION

Dr. Lester R. Morss, (Discussion Leader), Argonne National Laboratory: I am pleased to introduce Dr. David Hobart. As I indicated before the last talk, we are shifting from one topic to another, but both are of great interest. The last presentation was how to find transuranic elements in nature. The next one is how to keep them out of nature, which is an issue of increasing importance.

Dave Hobart received his Ph.D. from Professor Joe Peterson, who was to have been the first speaker this morning, at the University of Tennessee about 10 years ago. His scientific grandfather is Burris Cunningham, Joe's mentor, who was my scientific father. So, we are connected there, and we all go back scientifically to Glenn Seaborg. One way or another we are all connected.

Dave's research specialty is in actinides in near neutral solution, particularly in solution and heterogeneous systems that involve complexation. His talk this afternoon will be actinides in the environment.

[The following discussion took place after Dr. Hobart's address.]

Dr. Morss: Please let us take a few minutes to discuss this most important and challenging topic. I will open the floor for questions.

Dr. Charles Hudson, Texas A&M University: In a conference held about 12 years ago here, sponsored by the Welch Foundation, one of the speakers or discussion leaders made the statement that the problem of disposal of nuclear waste was a solved problem. He said that those nuclides of very short half life could be separated out and simply stored on site until they decayed. Those of very long half life could be separated and together would form a waste less than 5 percent as radioactive as certainly naturally-occurring rocks, incorporated into ceramic and buried deeply. The remainder of the nuclides of intermediate half life could be put back in the reactor and converted into the other two.

I would like to know whether you agree with that assessment that was made here 12 years ago, and if not, why?

Dr. Hobart: That is totally correct, in my opinion. One problem is cost. We have made a decision in this country that we will not reprocess or separate nuclear waste. Unless you want your tax money to go up, there is a considerable expense and cost in separating out the waste and storing it in separate areas, and I agree with you.

Dr. Hudson: My understanding was that the reason for not reprocessing nuclear waste was not one of economics, but one of the danger of transport and the possibility of seizure by terrorists.

Dr. Hobart: This is always a concern. Darleane, do you have a comment on that?

Dr. Darleane C. Hoffman, University of California, Berkeley: The reason that we do not reprocess commercial waste is proliferation, and during the Carter Administration that decision was made, and it still holds, and so, we are not allowed to reprocess waste. It isn't just dollars. That is a political problem.

Anon: Reagan rescinded that, didn't he?

Dr. Hoffman: No, it hasn't been rescinded, so far as I know. I, personally, think we could reprocess waste safely without the fear of proliferation. There are certain methods for doing that, but we still cannot do commercial waste in this country. We can do military waste. He may have espoused the idea, but it has not been changed so far as I know.

Dr. Morss: May I ask a question? One of the biggest concerns in my mind as well as that of the public is our wastes that are in so-called "interim storage," such as reprocessing wastes that are sludges, solutions, solids that have not been sent to a permanent repository. Keeping these out of the environment is maybe as big a challenge as worrying about actinides already in the environment, and I wonder how you would put into perspective the relative priorities of handling interim wastes compared to worrying about transuranium elements that are in the environment?

Dr. Hobart: There are only a few severely contaminated sites, particularly reprocessing facilities that are problems in that immediate area, but not on a global scale. So, I think your point is well taken that in this case we need to concern ourselves with release of these interim materials as a priority. In other words, we could create a much bigger problem if we don't pay attention to what we are doing with these particular materials. I hope that answers your question, Lester.

I apologize that I covered a great deal of chemistry very briefly. Feel free to peruse the manuscript. It goes into much more detail and will provide you with many more references than I was able to provide today.

Dr. Richard Wilde, Texas Tech University: Do you foresee the construction of breeder reactors in the future, and if so, approximately how much plutonium will be in the core of the typical breeder reactor?

Dr. Hobart: This is not my area of expertise, but I think I have a feeling for the political situation here. The government is definitely not planning at the present time to construct breeder reactors in the United States. I suspect that in the future we may be required to buy our nuclear fuel from France or other countries. I think the environmentalists are certainly on the bandwagon to prevent breeders from happening in this country. And as far as additional quantities, it depends on how many reactors. If you read some of the literature from 1975, when they had the nuclear conference on radionuclides in the environment in San Francisco, they were projecting how many more reactors we were going to have operating in 1990. You know what happened. We had some accidents. Reactor construction has been cut back a great deal, and there are less reactors than anticipated. So, it is hard to predict the future like that, and I hope that answers your question.

Dr. Morss: Are there any other questions of Dave?

If not, let us thank him once again.