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Environmental Actinide Chemistry

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Introduction

The large production of actinides in the generation of nuclear fission energy, and the widespread handling of these elements in connection with the nuclear fuel cycle (waste from nuclear reactors, reprocessing, transport and storage of spent fuel and radioactive waste, permanent disposal of high-level waste, etc.) have increased the risk of accidental releases of actinides to the environment. Substantial amounts of actinides have already been spread as fallout products from weapon testing and from reprocessing facilities, and also from the use of radionuclide batteries. The presence of actinides at significant concentrations in ecosystems would present a major health hazard. Consequently, it is of prime importance to characterize and model the chemical behaviour of the actinides in terrestrial and aquatic environments, particularly for neptunium, plutonium and americium, which do not normally exist in nature. In this review, which is largely based on some previous papers [1–14], aspects of actinide chemistry (up to curium) pertinent to distribution and transport in the environment are given.

Actinide Sources and Environmental Distribution

Both thorium and uranium are relatively common elements in the earth's crust, Table I [15]. Uranium concentrations in soil, sediments and rocks are usually in the range 1000–10^4 μg/kg, but can be substantially higher in igneous rocks, and particularly in sediments rich in organic material ('black shales'). Thorium concentrations in crystalline rock (granite, basalt etc.) are usually somewhat higher (5000–2 × 10^4 μg/kg) than for uranium.

Uranium concentrations in water are usually in the range 0.01–10 μg/l, locally up to 500 μg/l, while thorium concentrations usually are below the μg/l-level [16–18].

Small amounts of transuranium elements, primarily ^{239}Pu, are continuously formed in nature due to neutron capture in uranium [19, 20] (*cf.* Table I), but the major amounts of these elements come from nuclear activities of human origin. The total amount of transuranium elements in spent UO_2-fuel corresponds to 0.8–1 weight %, and the dominating element is plutonium (more than 90%). The annual global production of plutonium in the nuclear power industry is approximately 50 tonnes, and the accumulated plutonium amount is estimated to be 250 tonnes (2400 tonnes by the year 2000) [21].

TABLE I. Naturally Occurring Long-lived Actinides.

Nuclide	Half-life, y	Abundance, %	Concentration	
			Earth's crust, μg/kg	Ocean, μg/l
^{232}Th	1.41×10^{10}	100	10^4–1.2×10^4	6×10^{-4}
^{233}U	1.59×10^5	0.0054		
^{235}U	7.04×10^8	0.720		
^{238}U	4.47×10^9	99.275	2000–5000	3.3
^{239}Pu	2.41×10^4		a	

[a] $^{239}Pu/^{238}U = 3 \times 10^{-12}$.

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TABLE II. Long-lived Actinides in Spent Fuel (PWR, 38 000 MWd/tU) [22].

Nuclide	Half-life, y	Activity, GBq/tU, after		
		40 y	100 y	1000 y
^{229}Th	7.3×10^3	–	–	0.006
^{230}Th	8.0×10^4	0.018	0.048	0.74
^{231}Pa	3.28×10^4	0.001	0.002	0.011
^{232}U	72	0.78	0.44	–
^{233}U	1.59×10^5	0.003	0.007	0.15
^{234}U	2.45×10^5	52	67	89
^{235}U	7.04×10^8	0.52	0.52	0.52
^{236}U	2.34×10^7	10	10	10
^{238}U	4.47×10^9	12	12	12
^{237}Np	2.14×10^6	16	19	48
^{239}Pu	2.41×10^4	1.1×10^4	1.1×10^4	1.1×10^4
^{240}Pu	6.57×10^3	1.4×10^4	1.4×10^4	1.3×10^4
^{241}Pu	14.4	9.3×10^5	5.2×10^4	12
^{242}Pu	3.76×10^5	110	110	110
^{241}Am	433	1.8×10^5	1.9×10^5	4.4×10^4
^{243}Am	7.37×10^3	0.0012	0.0012	0.0011

The distribution of long-lived actinides in irradiated PWR UO_2-fuel is given in Table II [22]. Many of these nuclides are members of decay chains, such as:

$$^{245}\mathrm{Cm} \rightarrow {}^{241}\mathrm{Pu} \rightarrow {}^{241}\mathrm{Am} \rightarrow {}^{237}\mathrm{Np} \rightarrow {}^{233}\mathrm{U} \rightarrow {}^{229}\mathrm{Th} \rightarrow$$

$$^{242}\mathrm{Am} \rightarrow {}^{242}\mathrm{Cm} \rightarrow {}^{238}\mathrm{Pu} \rightarrow {}^{234}\mathrm{U} \rightarrow {}^{230}\mathrm{Th} \rightarrow {}^{226}\mathrm{Ra} \rightarrow$$

$$^{243}\mathrm{Am} \rightarrow {}^{239}\mathrm{Pu} \rightarrow {}^{235}\mathrm{U} \rightarrow {}^{231}\mathrm{Pa} \rightarrow {}^{227}\mathrm{Ac} \rightarrow$$

Thus, the activity of some of the long-lived nuclides will in fact increase with time after discharge from the reactor. The total biological hazards from spent fuel will be dominated by ^{241}Am from some 10 to 10^3–10^4 years after discharge, and thereafter by ^{239,240}Pu and ^{243}Am (up to 10^4–10^5 years) and eventually by ^{237}Np with contribution from ^{229}Th (up to 10^6–10^7 years). The importance of the various elements in Table II as environmental contaminants and potential health problems is of course highly related to their chemical properties, modes of dispersion and distribution, as well as biological availability.

A uranium breeder cycle, using a mixed UO_2-PuO_2-fuel, would give substantially higher yields of transuranium elements than indicated in Table II. The isotopes ^{232}U and ^{233}U may constitute major environmental contaminants in the thorium breeder cycle [23].

The actinides produced in the nuclear fuel cycle must be prevented from spreading into the environment. It is presently believed that storage in underground facilities would be the safest way to isolate spent fuel or high-level nuclear waste. However, future releases of various sizes must be anticipated, considering the large amounts of actinides being handled and the time required before the biological hazard has been reduced to acceptable levels through natural decay (more than 10^6 years).

Substantial amounts of transuranium elements have been distributed in the environment as the result of nuclear weapon testing, Table III. Most of the fallout from atmospheric tests has been deposited on the northern hemisphere. The total amount of plutonium injected in the atmosphere is about 4.2 tonnes, corresponding to a cumulative fallout of ^{239,240}Pu of 4–80 MBq/km^2 (maximum at latitude 40–50° north; somewhat lower in the Antarctic region) [21, 24, 25]. Another 1.4 tonnes of plutonium have been directly deposited in the ground through surface and subsurface tests. Minor amounts have been spread in accidents involving aircraft carrying nuclear weapons (Spain, 1956 and Greenland, 1968). About 300 tonnes of plutonium is presently stored in nuclear weapons [21].

Releases from reprocessing facilities and disposal sites have resulted in localized contamination in the environment, *e.g.* at Oak Ridge, Los Alamos, Rocky Flats, the Irish Sea *etc.* Some disposal of transuranic elements in low-level effluents into

TABLE III. Transuranium Elements Released to the Atmosphere [24].

Nuclide	Amount, TBq
^{238}Pu[a]	890[b]
^{239}Pu	5.7×10^3
^{240}Pu	7.7×10^3
^{241}Pu	3.6×10^5 [c]
^{241}Am	1.2×10^4 [d]

[a] Half-life 87.7 y. [b] Including 590 TBq from a SNAP 9A radionuclide battery in a satellite which vaporized upon reentring the atmosphere. [c] Largely decayed to ^{241}Am. [d] Largely from ^{241}Pu.

aquatic environments occurs in accordance with national guidelines. The global amount of plutonium entering the sea through low-level effluents is probably below 0.1 kg/y (0.3 TBq/y), and some 100 kg may end up in various waste streams in the reprocessing [26].

Plutonium concentration ranges in water, soils and sediments representative of global fallout and locally contaminated areas are given in Table IV and V [27]. The plutonium is generally distributed towards the solid phase, *e.g.* in the Irish Sea.

Actinide Solution Chemistry

The solution chemistry of the actinides reflects the electron configuration of this group of elements with the 5f and 6d shells having similar energies [28]. In the first part of the actinide series the elements exhibit multiple oxidation states (from 3 to 7), but beyond plutonium the lower oxidation states (from 2 to 4) are predominant. Thorium exists only in the IV state in aqueous solutions, while protactinium can exist both in the IV and V states. All of the oxidation states III, IV, V and VI can exist for uranium, neptunium, plutonium and americium, although U(III) and Np(III) are easily oxidized. Neptunium and plutonium in the VII state have also been identified. For americium the IV state requires high concentrations of a stabilizing complexing agent, the V state is prone to disproportionation and the VI state is easily reduced, leaving the III state as the most stable. The following oxidation states for the actinides (here denoted by An) could conceivably exist in environmental systems: An(III): Pu, Am and Cm; An(IV): Th, Pa, U, Np and Pu; An(V): Pa, U, Np and Pu; An(VI): U, Np and Pu.

TABLE IV. Plutonium (^{239,240}Pu) in Water [27].

Source and location	Amount, Bq/l
Nuclear weapon testing	
Enewetak Atoll (groundwater)	7×10^{-6}–0.03
Lake Michigan	7×10^{-6}–10^{-5}
Atlantic Ocean	4×10^{-6}
Chemical reprocessing	
Los Alamos (treated effluent, surface and groundwater)	0.005–0.6
Irish Sea	0.002–0.02
Savannah River	4×10^{-6}–7×10^{-5}

TABLE V. Plutonium (^{239,240}Pu) in Soils and Sediments [27].

Source and location	Amount, Bq/kg
Nuclear weapon testing	
Nevada Test Site debris (soil)	3000–2×10^6
Bikini Atoll (soil)	20–10^4
Trinity Site fallout (soil)	0.7–10
Lake Michigan (sediment)	3–10
Global fallout (soil)	0.02–0.7
Chemical reprocessing	
Los Alamos (alluvium)	40–10^4
Irish Sea (sediment)	10–2000
Rocky Flats (soil)	0.1–3000
Hanford (soil)	0.1–30
Savannah River (soil)	0.2–100

The actinides are classified as hard, *i.e.* strong complexes are generally formed with oxygen-containing ligands (oxides, hydroxides, phosphates, carbonates, sulfates) and fluoride, whereas the affinity for sulfur and heavy halides is weak (*cf.* Table VI and VII). The elements exhibit similar behaviour when they are in the same oxidation state, and the differences in complex formation constants for inorganic complexes of environmental interest between the actinides uranium, neptunium, plutonium and americium in the same oxidation state are often within experimental error. The chemical properties are, however, markedly different between the various oxidation states. The complex strength increases with the effective charge of the acceptor ion, *i.e.* in the order An(V) (as AnO_2^{+}) < An(III) (as An^{3+}) ⩽ An(VI) (as AnO_2^{2+}) < An(IV) (as An^{4+}) (*cf.* Table VI and VII).

TABLE VI. Ranges of Reported Complex Formation Constants for Actinide Complexes ($An + L = AnL$, K_1; $I = 0$) [5, 13].

Ligands	$\log K_1$			
	An^{3+}	An^{4+} [c]	AnO_2^+	AnO_2^{2+}
OH^-	5.7–6.3[a]	12.5–13.7	4.0–5.1	8.1–9.1
CO_3^{2-}	4.6–6.3[b]		5–5.9	9.9–12
HPO_4^{2-}		12.0–13.0	2.8–3.4	8.4
$H_2PO_4^-$	2.4–2.7	4.5–5		2.9–4.0
F^-	3.4–4.3	7.9–8.6	3.7	5.1–5.7
SO_4^{2-}	3.5–3.7	5.5–5.8	2.0	2.8–3.3
Cl^-	<1	<2	<0	<2

[a] For lanthanides. [b] For lanthanides, I = 1–3. [c] Excluding Th(IV).

TABLE VII. Ranges of Reported Solubility Products for Actinide Complexes ($xAn + yL = An_xL_y(s)$, (x,y), K_s; $I = 0$) [5, 13].

Ligand	$(x, y) - \log K_s$			
	An^{3+}	An^{4+} [c]	AnO_2^+	AnO_2^{2+}
OH^-	(1,3) 22.0–24.5[a]	(1,4) >46[b]	(1,1) 8.5–9.3	(1,2) 22.2–24.5
CO_3^{2-}	(2,3) 30.6–33.0[a]			(1,1) 10.5–14.5
HPO_4^{2-}		(1,2) 26.8–27.7		(1,1) 10.7–12.6
PO_4^{3-}	(1,1) 23(?)	(3,4) <57(?)		
F^-	(1,3) 10.2–15	(1,4) 18.5–24		

[a] For lanthanides. [b] Values between 46 and 63 are reported. [c] Excluding Th(IV).

Actinide Solubilities and Species in Environmental Waters

Natural waters in environmental systems contain complexing inorganic anions such as OH^- (pH 4–10), HCO_3^-–CO_3^{2-} (0.3–8 m*M*), $H_2PO_4^-$–HPO_4^{2-}–PO_4^{3-} (<0.001 m*M*), F^- (0.003–0.2 m*M*), SO_4^{2-} (0.01–1 m*M*) and Cl^- (0.05–5 m*M*) (common concentration ranges for non-saline groundwaters in parentheses [29]; in saline waters the concentration of particularly Cl^- and SO_4^{2-} can be up to orders of magnitude higher; *cf.* Table VIII). Moreover, most waters also contain organic complexing agents of natural origin (humic and fulvic acids, usually 10^{-5}–10^{-6} meq/l or higher even in deep undisturbed groundwaters) [30].

An analysis of actinide solubilities and speciation should primarily be related to the composition of a system at equilibrium, on the basis of thermodynamic data. Also kinetic information, describing

TABLE VIII. Inorganic Constituents (mg/l) in Natural Waters [13].

	Rain water	Shallow groundwaters	Deep granitic groundwaters	Sea water
HCO_3^-	<1	60–250	90–275[a]	140
SO_4^{2-}	0.1–5	0.5–25	0.5–15[c]	2650–2712
HPO_4^{2-}		0.01–0.1	0.01–0.2	<0.1
NO_3^-	0.1–4	0.1–5	0.01–0.05	<0.7
F^-	0–0.2	0.5–2	0.5–5	1.4
Cl^-	0.1–20	4–25	4–15[c]	18980–19353
HS^-			<0.05	
Ca^{2+}	0.5–5	5–50	10–40[c]	380–399
Mg^{2+}	0.1–0.5	0.5–10	1–10[c]	1272–1292
Na^+	0.3–20	2–25	10–100	10560–10766
K^+	0.1–4	0.5–5	1–5	380–399
Fe^{2+}			0.02–5	
Fe(tot)		0–0.5	1–5	<0.02
SiO_2(tot)		3–30	3–14	0.01–7
pH	4–6	5–8.5	7–9[b]	8.1

[a] Max. value 400 mg/l. [b] Max. value around 10. [c] Saline waters dominated by NaCl, but with enhanced concentrations of Mg, Ca or SO_4^{2-} are common at great depth or in certain areas.

TABLE IX. Selected Formation Constants and Solubility Products for Actinide Hydroxide and Carbonate Complexes [13] ($I = 0$, 25 °C). $x\mathrm{An} + y\mathrm{OH} + z\mathrm{CO_3} = \mathrm{An}_x(\mathrm{OH})_y(\mathrm{CO_3})_z$; $K = [\mathrm{An}_x(\mathrm{OH})_y(\mathrm{CO_3})_z/[\mathrm{An}]^x[\mathrm{OH}]^y[\mathrm{CO_3}]^z$; $x\mathrm{An} + y\mathrm{OH} + z\mathrm{OH} + z\mathrm{CO_3} = \mathrm{An}_x\text{-}(\mathrm{OH})_y(\mathrm{CO_3})_z(\mathrm{s})$; $K = [\mathrm{An}]^x[\mathrm{OH}]^y[\mathrm{CO_3}]^z$. Values within Parentheses are Estimated or Extrapolated.

xyz	log K											
	An^{3+}		An^{4+}				$\mathrm{AnO_2}^+$			$\mathrm{AnO_2}^{2+}$		
	Pu	Am	Th	U	Np	Pu	U	Np	Pu	U	Np	Pu
110	a	6.5	10.8	13.4	12.5	13.5	(4)	5.1	4.3	8.2	8.9	8.4
120	a	11.5	21.1	25.5	25	25.5				16.1	(17.8)	(17.6)
130	a	(15.5)	30.3	36.5	36	36.5				(21)	(23)	(22)
140	a	(19)	40.1	46	46	46.5						
150			?	(51)	(50)	(51)						
220	a	(14)		(27)	(26)	(27)				22.4	21.6	19.7
350	a	(37)								54.4	(53)	48.4
110(s)							(−9)	−9.1	−9			
120(s)										−22.4	−22.7	−23
130(s)	a	(−23.5)										
140(s)			−49.7	−56.6	−56	−57						
101	a	6					(5)	5.9	b	10.1	b	(9)
102	a	10					(10)	11.1	b	16.7	b	(15)
103	a	(13)					15.3	16.3	b	23.8	b	(22)
105				36.5	b	b						
306										60.1	b	b
101(s)										−13.8	b	b
203(s)	a	−31										
131				c	c	(42)						
231										41	b	b
331										43	b	b

[a] Same as for Am assumed. [b] Same as for U assumed. [c] Same as for Pu assumed.

non-equilibrium conditions, is needed to explain observed solution behaviour. It is necessary to consider all relevant species involving all possible complexing agents present in the water. Thus, the analysis must also take into account estimated or extrapolated stability data for species that are likely to exist based on the similarity with other elements, even though experimental data are scarce and thermodynamic data not available.

Reported ranges of formation constants and solubility products for inorganic complexes of environmental interest are given in Tables VI and VII [5, 13]. From these constants and the concentrations of the corresponding anions in natural waters, Table VIII, it is clear that the chemistry of the actinides in environmental aqueous systems is largely dominated by hydroxide and carbonate complexation, considering inorganic systems only. A set of formation constants for hydroxide and carbonate complexes with uranium, neptunium, plutonium and americium has been assessed, Table IX, as well as redox potentials, Table X [13]. Calculated solubilities and speciations for these actinides are given in Figs. 1–4, based on the data in Tables IX and X, for the following systems:

a. Closed anoxic systems; pH 5–10, Eh = 0.21 – 0.06 pH (V), assessed for systems defined by $\mathrm{Fe_2O_3(s)/Fe_3O_4(s)}$ equilibria [32].

(1) log $[\mathrm{CO_3}^{2-}]$ = pH – 14, assessed as a minimum value representative of deep groundwaters, based on empirical data [32];

(2) log $[\mathrm{CO_3}^{2-}]$ = 0.76 pH – 10.83, assessed as a maximum value representative of deep groundwaters, based on empirical data [32].

b. Open systems in equilibrium with air or closed oxic systems; pH 5–10, Eh = 0.8–0.06 pH (V), assessed for systems defined by $\mathrm{O_2/H_2O_2}$ equilibria due to contact with oxygen [31].

(1) log $[\mathrm{CO_3}^{2-}]$ = pH – 14; see above;

(2) log $[\mathrm{CO_3}^{2-}]$ = 2pH – 18.1 + log$P(\mathrm{CO_2})$, assessed for open systems in equilibrium with $\mathrm{CO_2}$; $P(\mathrm{CO})_2 = 10^{-3.5}$ atm has been assumed.

TABLE X. Selected Standard Potentials for Actinide Elements (I = 0) [13].

	Standard potential, V			
	U	Np	Pu	Am
$An^{4+} + e^- = An^{3+}$	−0.52	0.15	1.01	2.34
$AnO_2^+ + 4H^+ + e^- = An^{4+} + 2H_2O$	0.46	0.65	1.10	1.10
$AnO_2^{2+} + 4H^+ + 2e^- = An^{4+} + 2H_2O$	0.27	0.94	1.03	1.35
$AnO_2^{2+} + e^- = AnO_2^+$	0.08	1.23	0.96	1.60

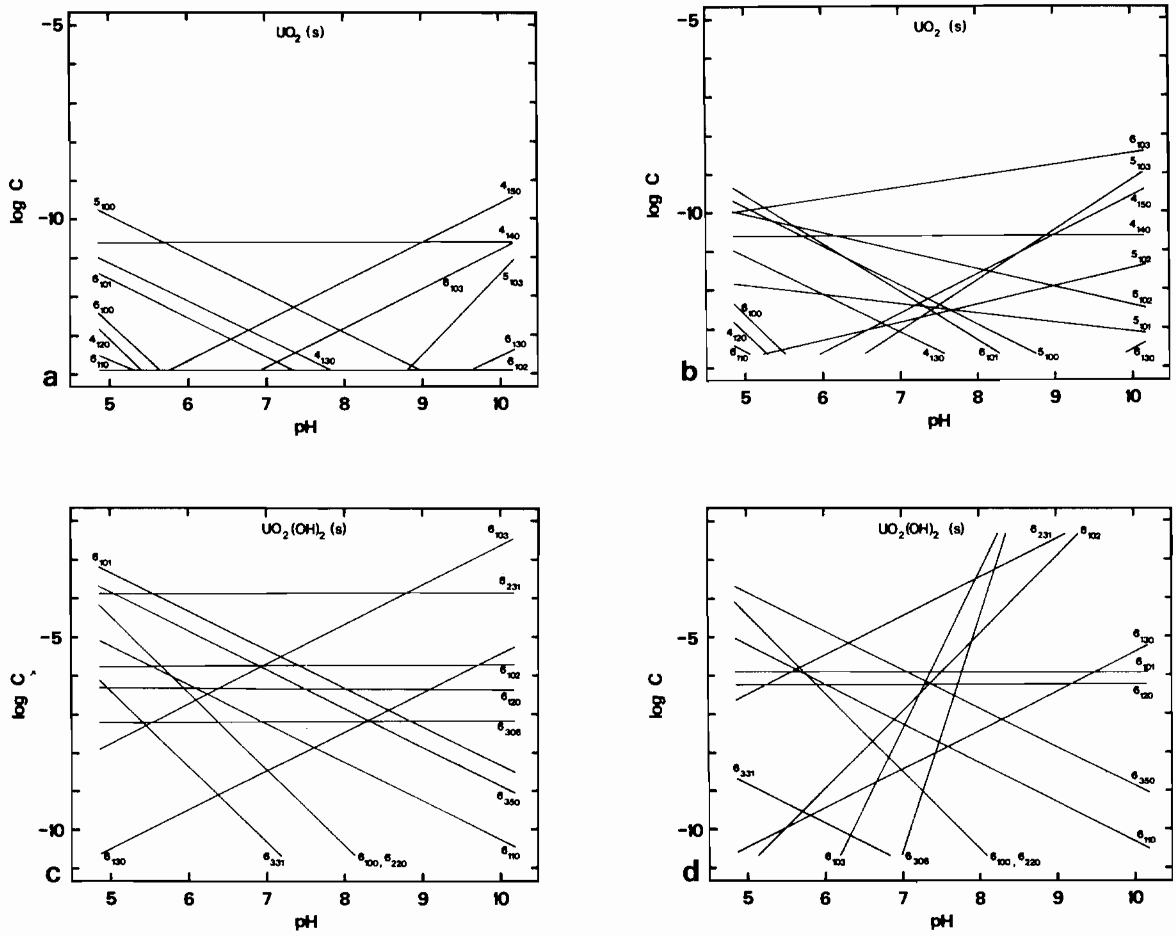

Fig. 1. Calculated uranium speciation and solubility. a) Eh = 0.21–0.06 pH, log $[CO_3^{2-}]$ = pH – 14; b) Eh = 0.21–0.06 pH, log $[CO_3^{2-}]$ = 0.76 pH – 10.83; c) Eh = 0.8–0.06 pH, log $[CO_3^{2-}]$ = pH – 14; d) Eh = 0.8–0.06 pH, log $[CO_3^{2-}]$ = 2 pH – 21.6.

Thus, the selected reference systems represent extreme combinations of pH, Eh and $[CO_3^{2-}]$.

Uranium

The dominating species under strongly reducing conditions ($E^\circ \leqslant 0.2$ V)* and low total carbonate concentration are the tetravalent hydroxides $U(OH)_4$, and possibly $U(OH)_5^-$ with $UO_2(s)$ as the solubility limiting solid phase, giving total concentration of less than 10^{-10} *M* (below 0.1 μg/l). The hexavalent species $UO_2(CO_3)_3^{4-}$ is the dominating soluble species at high carbonate concentrations or at only

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*Here E° denotes the pH-independent contribution to the redox potential, expressed as Eh = E° – 0.06 pH.

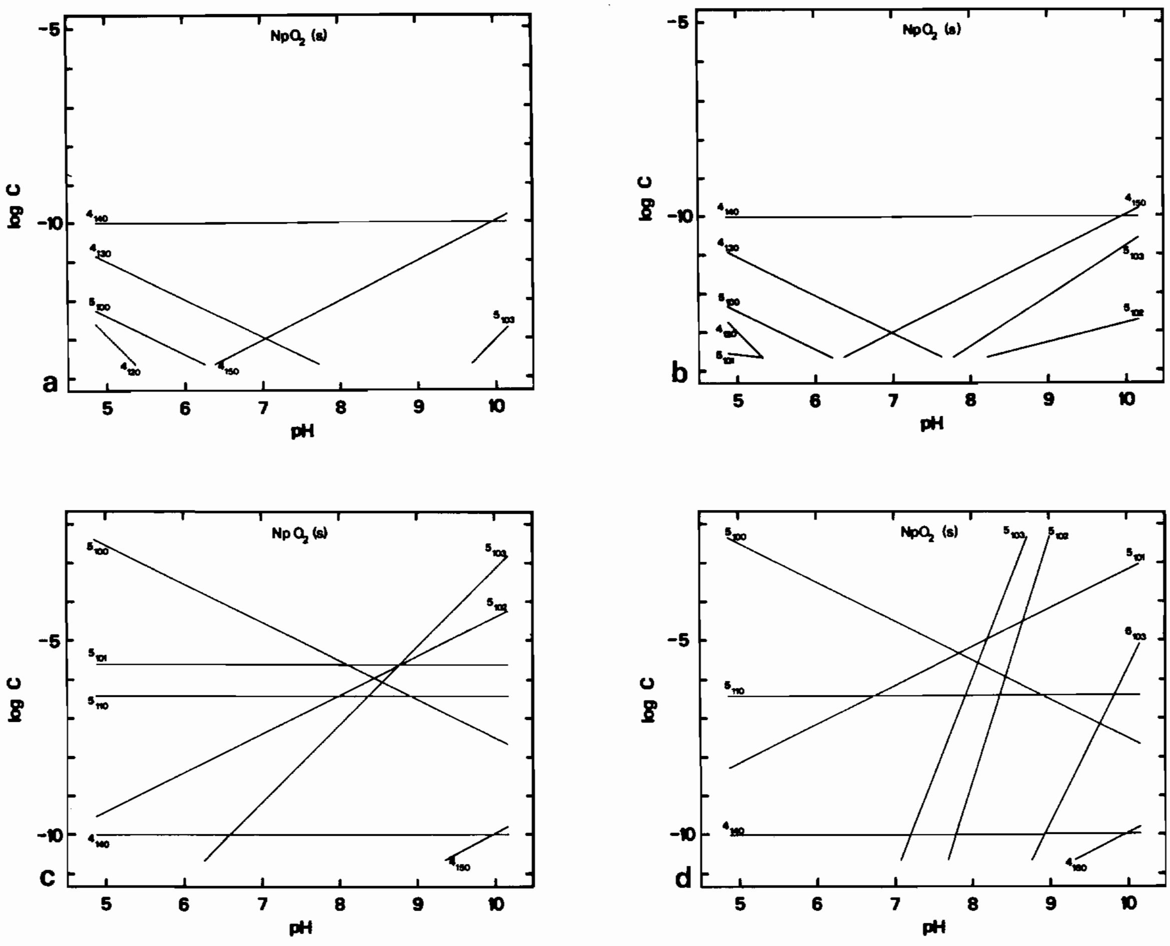

Fig. 2. Calculated neptunium speciation and solubility. a–d as in Fig. 1.

mildly reducing conditions, still in equilibrium with UO_2(s). A dominance of the pentavalent UO_2^+ is possible at low pH.

Under mildly reducing or slightly oxic conditions ($E^\circ > 0.4$ V) the hexavalent state dominates entirely in solution, even at low carbonate concentrations. Solubility limiting phases are (with increasing Eh) U_4O_9(s), U_3O_8(s) and $UO_2(OH)_2$(s) (at E° above 0.7 V). The formation of poorly-defined solid oxide phases at intermediate or high pH ($Na_2U_2O_7$(s), $NaUO_3$(s) and others) would also be possible under environmental conditions, limiting the total solubility to less than 10^{-5} M (mg/l-range) [31].

The existence of U(V) and U(VI) in environmental waters under reducing conditions would provide a uranium release mechanism due to the enhanced mobility of penta- and hexavalent species in comparison with tetravalent hydroxides. This could be of importance under conditions when one of the oxidation states V or VI dominates entirely over IV. The possible existence of U(V) in equilibrium with UO_2(s) at low pH in natural waters has not been verified experimentally.

Uranium solubilities calculated from Table IX and X are in reasonable agreement with observed solubilities in environmental waters, at least for anoxic conditions. Total concentrations in saturated solutions (as indicated from $^{234}U/^{238}U$-ratios) in natural waters under reducing conditions are usually below 10^{-9}–10^{-10} M (below μg/l) [16].

Neptunium

Tetravalent species, largely $Np(OH)_4$, dominate under reducing conditions with NpO_2(s) as the solubility-limiting solid phase and total concentrations not above 10^{-9}–10^{-10} M (below 0.1 μg/l). Pentavalent species like $NpO_2(CO_3)_3^{5-}$ and $NpO_2(CO_3)_2^{3-}$ become important under mildly oxic conditions ($E^\circ > 0.4$ V) and at high carbonate concentrations, as well as NpO_2^+ at low pH.

Pentavalent species dominate entirely under oxic conditions, when solubility-limiting phases can be

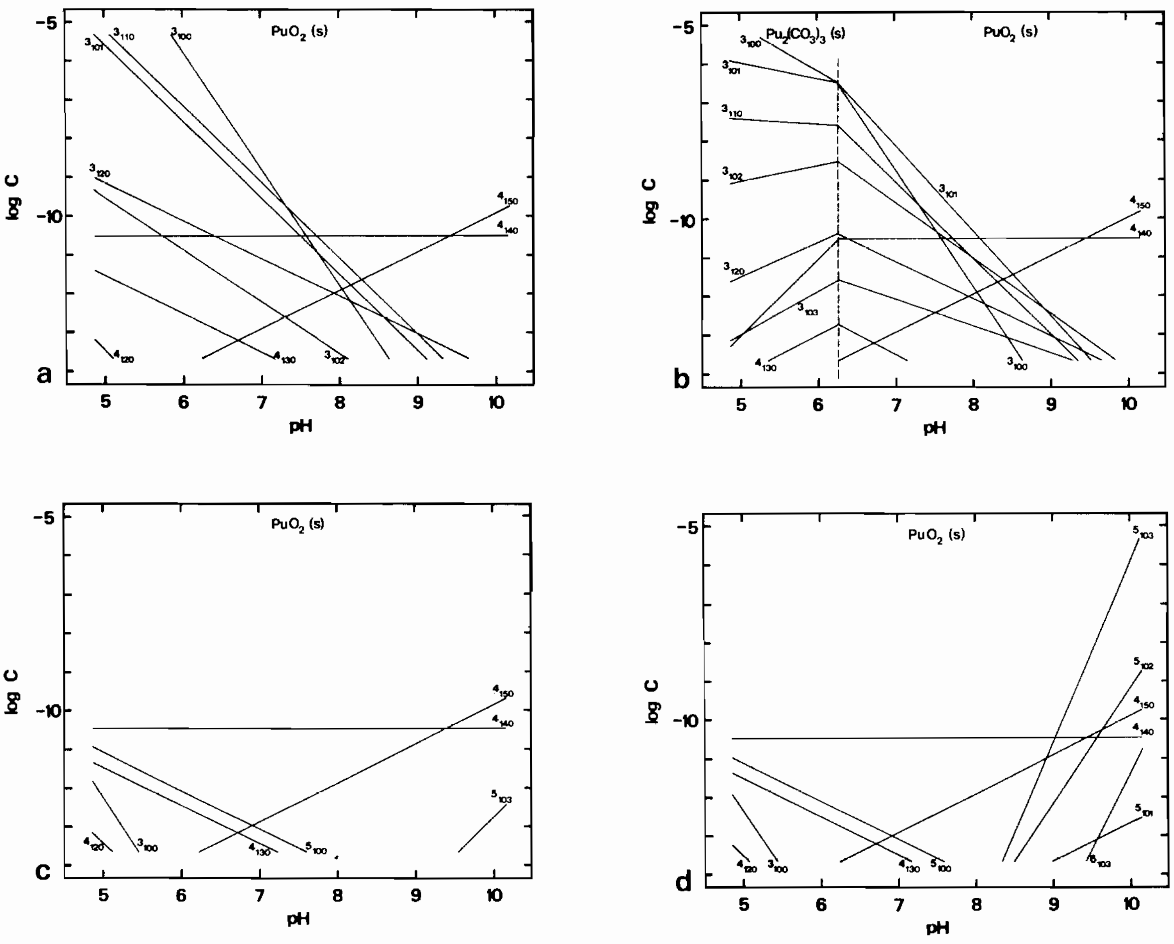

Fig. 3. Calculated plutonium speciation and solubility. a–d as in Fig. 1.

either $NpO_2(s)$ or species like $Na_{2x-1}NpO_2(CO_3)_x(s)$, x = 0.8–1 [33, 34]. The maximum solubility is likely to be less than 10^{-5} *M* (mg/l-range), considering the sodium concentrations in most environmental waters.

Plutonium

The solubility-limiting solid phase is $PuO_2(s)$, both under reducing and oxic conditions. Under highly reducing conditions ($E^\circ < 0.2$ V) and/or at high total carbonate concentrations the formation of $Pu_2(CO_3)_3(s)$ is also possible, especially at low pH.

Trivalent species like $PuCO_3^+$, Pu^{3+} and $PuOH^{2+}$ dominate in solution under reducing conditions ($E^\circ < 0.3$ V), with total solubilities not above 10^{-7}–10^{-8} *M* at pH 7–9 (μg/l-level). At higher potentials ($E^\circ = 0.3$–0.8 V) the tetravalent state prevails, with $Pu(OH)_4$ as dominating soluble species. At still higher potentials, which can be obtained in the presence of oxidizing agents or possibly as the result of radiolysis, or at very high carbonate concentrations (open systems), the pentavalent carbonates $PuO_2(CO_3)_3^{5-}$ and $PuO_2(CO_3)_2^{3-}$ would be expected to dominate, as well as the non-complexed PuO_2^+ at low pH. Thus, a solubility minimum can be expected at pH 7–8 and $E^\circ = 0.4 - 0.8$ V. The formation of hexavalent plutonium is unlikely under environmental conditions.

The predicted shift in oxidation state with pH under oxic conditions ($E^\circ \geqslant 0.8$–0.9 V) as well as the calculated total concentrations are in fair agreement with laboratory studies [35, 36], considering the uncertainties in redox potentials and in the solubility products for $PuO_2(s)$ (see below).

A change from predominantly tetravalent to pentavalent state would be feasible around the redox potential normally encountered in natural systems (at pH 7–9) with moderate or high total carbonate concentrations. Seasonal variations of the redox conditions, *e.g.* in biologically-active shallow waters could cause such a change of the predominant oxidation state. The change of oxidation state from IV to V

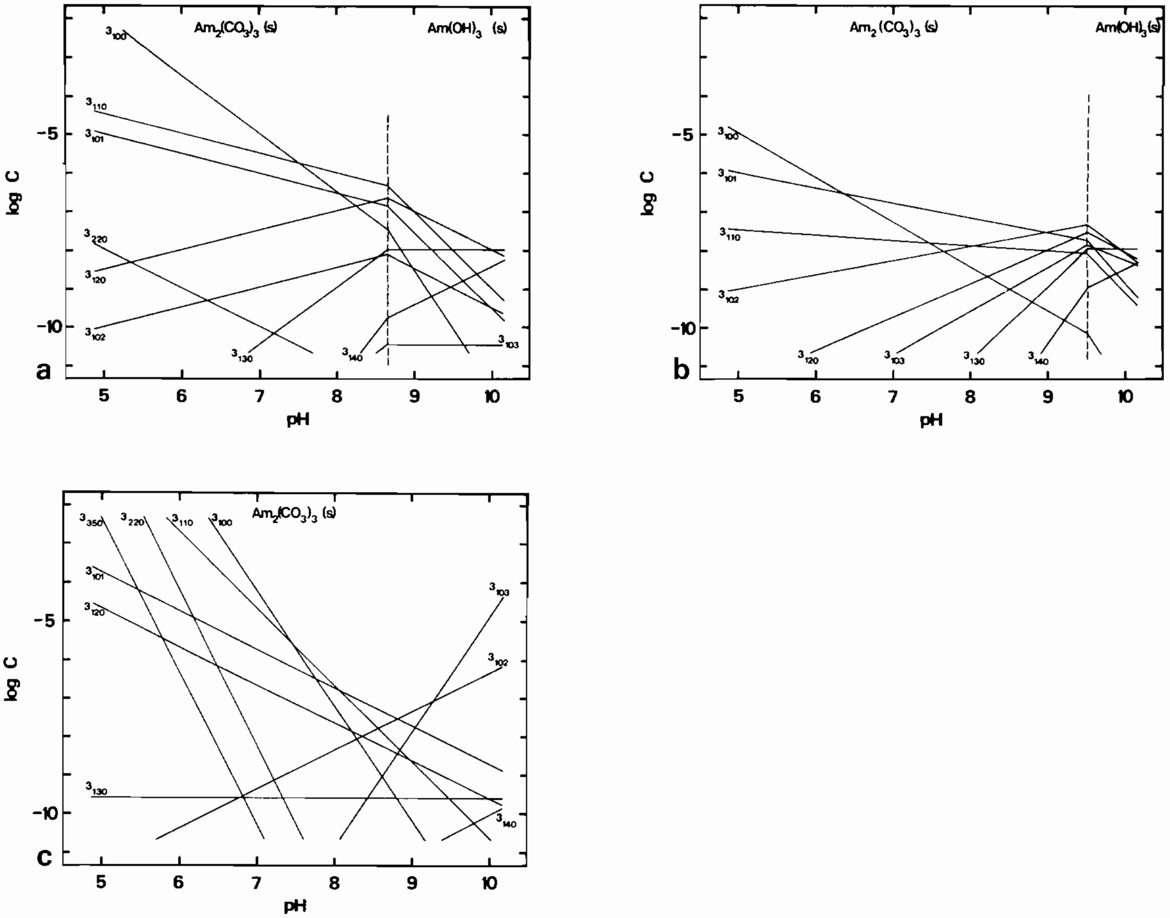

Fig. 4. Calculated americium speciation and solubility. a) log $[CO_3{}^{2-}]$ = pH − 14; b) log $[CO_3{}^{2-}]$ = 0.76 pH − 10.83; c) log $[CO_3{}^{2-}]$ = 2 pH − 21.6. Eh between 0.2−0.06 pH and 0.8−0.06 pH in all cases.

would lead to an enhanced mobility (and total solubility) and reduced sorption (see below) of plutonium, which could account for the observed fluctuations in plutonium concentration in natural aerated aquifers [37–39]. These shifts may also be related to sorption-desorption processes on solid materials as well as changes in pH and carbonate concentrations.

Both the V/IV- and IV/III-equilibria will be significantly influenced by the presence of organics. A reduction, possibly to Pu(III), has been observed in the presence of macromolecular organic acids [40].

Americium

Americium is trivalent both under reducing and oxidizing conditions in the environment. The solubility limiting phase is $Am_2(CO_3)_3(s)$ and possibly $Am(OH)_3(s)$, at low carbonate concentrations and high pH.

Carbonate complexes like $AmCO_3{}^+$ and $Am(CO_3)_2{}^-$ as well as the hydroxides $AmOH^{2+}$ and $Am(OH)^{2+}$ (at low carbonate concentrations) are the dominating species in solution. The total solubility would have a minimum of about 10^{-7}–10^{-8} M (below 0.1 mg/l) in the pH-range 7–9. Experimental solubility data are in fair agreement with these calculations [41, 42].

Some of the uncertainties in the constants given in Table IX and X, which would have a significant impact on the calculated solubilities and speciation should be pointed out:

– The tetravalent oxide $AnO_2(s)$ is the solubility-limiting species for U, Np and (largely) Pu under reducing conditions. Values of the solubility product (log K_s) between −47 and −63 have been reported. The constants in Table IX are based on a recent study on U(IV) [43]. Higher solubilities would be expected for fresh amorphous precipitates and probably much lower for highly crystalline compounds, such as natural uraninite [17].

– The dominating tetravalent species at environmental pH are $An(OH)_4$ and $An(OH)_5^-$; the uncertainty in the corresponding formation constants are at least one order of magnitude, and it is not verified unambiguously that species like $An(OH)_5^-$ would exist (*e.g.* not identified for Th(IV)).

– The possible existence of mixed OH^-–CO_3^{2-}-complexes with tetravalent actinides has been neglected.

– Recently formation constants have been suggested for the NpO_2^+ – CO_3^{2-}-system (the 101-, 102- and 103-complexes), which are several orders of magnitude lower than what is suggested in Table IX [33, 34].

– The formation constant for $UO_2(CO_3)_3^{4-}$, which would dominate even under reducing conditions in the presence of high carbonate concentrations, is obtained from a recent study [43]; however, constants about two orders of magnitude lower have been suggested previously [17].

– The uncertainty in the redox potentials are usually of the order of 50 mV or more. An increase of the suggested U(VI)/U(IV) potential by 50 mV and assuming a correct U(VI)/U(V)-potential would significantly change the predicted oxidation state distribution in Fig. 1 (increased stability of U(IV); decreased stability of U(V) and U(VI) under reducing conditions). A decrease of the Pu(VI)/Pu(V)-potential by 50 mV would change the predicted Pu(V)/Pu(IV)-distribution in favour of Pu(V), *etc.*

– Oxide phases other than $UO_2(s)$ and $UO_2(OH)_2(s)$ can be solubility-limiting phases at intermediate or high redox potentials ($Eh > 0.4 - 0.06$ pH), *e.g.* $U_4O_9(s)$, $U_3O_8(s)$, $Na_2U_2O_7(s)$, $NaUO_3(s)$ *etc.* [31].

– The pentavalent carbonate, $Na_{2x-1}NpO_2(CO_3)_x(s)$, $x = 0.8$–1, can probably be the solubility-limiting phase for neptunium under oxic conditions [33].

– Other ligands exist in nature that would form sparingly soluble phases under certain environmental conditions (F^-, PO_4^{3-}, SiO_4^- *etc.*) [17, 18, 31].

– Formation of organic complexes with humic and fulvic acids can modify the calculated distribution of species in Fig. 1–4 in certain waters, especially for trivalent actinides (Pu(III), Am(III)) [30].

Actinide Sorption Phenomena in Geologic Systems

The interaction of trace elements in aqueous solutions with solid surfaces can generally be described in terms of three basic kinds of sorption mechanisms [10, 44].

Physical adsorption is due to non-specific forces of attraction between solute and sorbent. This is a rapid, reversible and fairly concentration independent process, since the binding of the solute takes place on non-specific positions and can result in the formation of successive layers. The composition of the solid sorbent phase is of minor importance in comparison with the influence of the speciation of the solute (*e.g.* degree of hydrolysis, complexation *etc.*).

Electrostatic adsorption (ion exchange processes) is due to coulombic attraction between charged solute species and the solid sorbents, which usually would carry a net charge (dependent on pH and the ionic strength). This is a rapid, often reversible, concentration dependent process which also is dependent on properties of the solid (exchange capacity) as well as concentrations of competing ions in solution (ionic strength dependence).

Chemisorption is caused by the action of chemical forces between solute and sorbent, *e.g.* when the anions of the solid lattice could form strong complexes with the solute. This is a fairly slow. partly irreversible and concentration-dependent process that requires a certain composition of the solid sorbent.

All three of these basic sorption mechanisms can be observed for the actinides in aqueous environmental systems. Examples of some laboratory sorption studies are given in Fig. 5, showing distribution coefficients, K_d, *i.e.* the concentration in the solid (mol/kg) divided by the concentration in solution (mol/kg), *vs.* pH under well defined conditions [4, 10]. The distribution coefficient is highly dependent on a number of physical and chemical parameters of the system, as well as of the experimental methodology and is not a thermodynamic or even an element-specific quantity. Some of the observations for actinide systems are summarized below (*cf.* Fig. 5).

Uranium is generally fairly poorly sorbed on geologic media under oxic conditions (in the hexavalent state), especially at moderate and high concentrations and in the presence of high carbonate concentrations. A significant sorption is observed at pH above 5–6, corresponding to the beginning of hydrolysis (physical adsorption). The sorption reaches a maximum around pH 8 followed by a decrease with increasing pH, due to the formation of anionic low-sorbing carbonate complexes. Certain minerals (*e.g.* phosphates) would enhance the uptake due to chemisorption phenomena. A reduction to the tetravalent state would increase the sorption by several orders of magnitude (in terms of the distribution coefficient) in the environmental pH-range.

Neptunium is poorly sorbed on most geologic media under oxic conditions (in the pentavalent state) at pH below 8–9. Chemisorption effects would be obtained in the presence of certain minerals (*e.g.* phosphates), just as for hexavalent uranium.

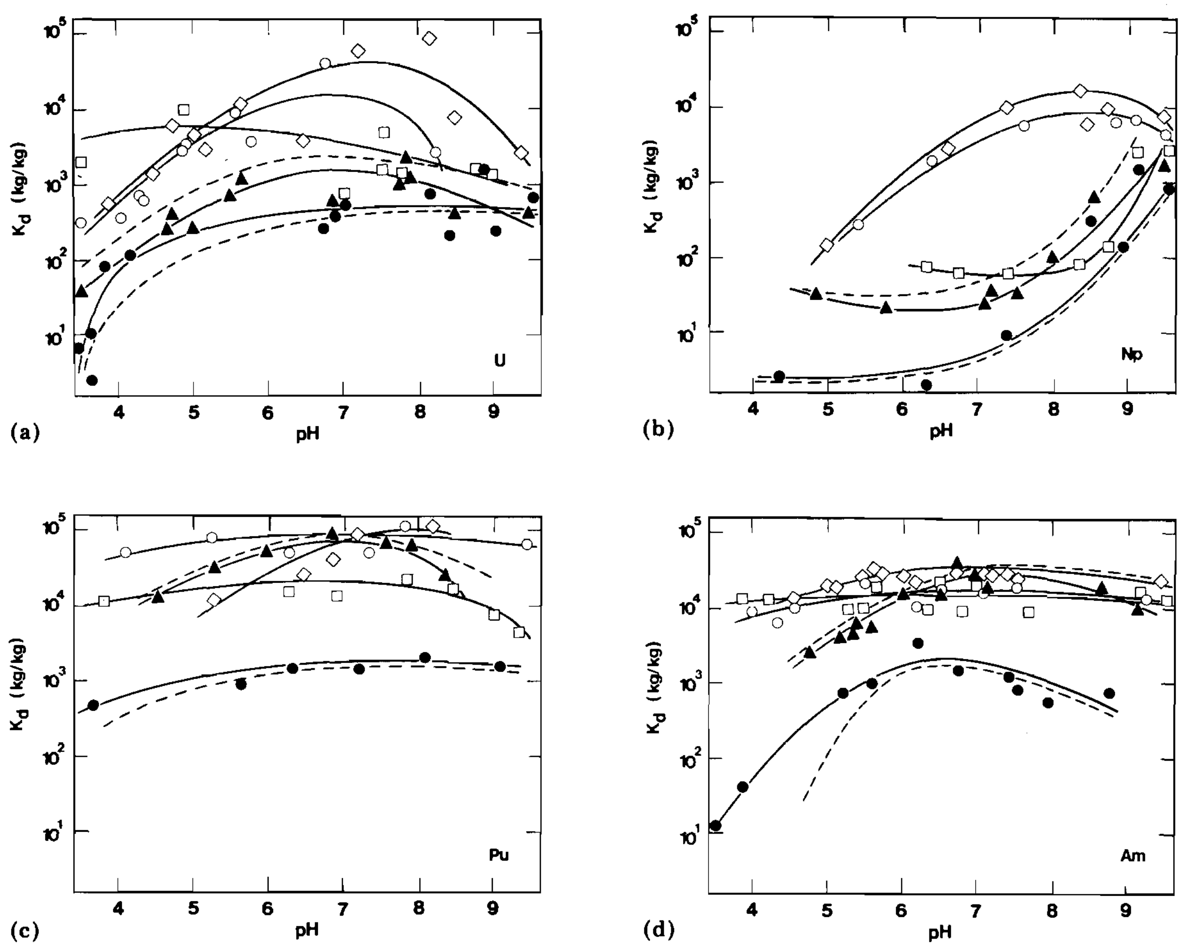

Fig. 5. Measured distribution coefficients (K_d, kg/kg) for uranium(VI), neptunium(V), plutonium and americium(III) [4]. Aqueous phase: Artificial groundwater. Solid phase: ● quartz, ▲ biotite, ○ apatite, ◇ attapulgite, □ montmorillonite. Dashed lines indicate the range for major minerals in igneous rock. One week contact time, equilibrium with air. [U], [Np], [Pu]: 1–5 × 10^{-11} M, [Am]: 1–2 × 10^{-9} M.

A reduction to the tetravalent state would increase the sorption by up to three orders of magnitude.

Plutonium is strongly sorbed on most geologic materials in the environmental pH-range, both under oxic and reducing conditions. The uptake would be reduced under the conditions when pentavalent species are formed, *i.e.* under highly oxidizing conditions at intermediate or high pH and high carbonate concentrations.

Americium is strongly sorbed at pH above 5–6 with a maximum around pH 7–8 (physical adsorption).

The uptake of actinides is further illustrated in Fig. 6, showing autoradiographs of a polished granite surface exposed to a groundwater spiked with actinides [3]. A general distribution on all the minerals is observed for Am(III) and Pu(IV) in Fig. 6c,d, with a certain preference for biotite and pyrite as well as for a filled fracture. This is in accordance with observations in batch-type distribution studies, Fig. 5. The sorption of Np(V), U(VI) and Pu(VI) is poor except on the biotite grains, the fracture filling and the pyrite vein (for Np(V) and Pu(VI)), Fig. 6e–g. Possibly the enhanced sorption on the pyrite indicates a reduction to the tetravalent state on the mineral surface. This is not observed for U(VI), which would be expected to require a more reducing environment and total exclusion of air to be reduced to the tetravalent state. No preferential sorption of Np(V) on Fe(II)-containing minerals was observed when the rock surface was oxidized with O_3 prior to the sorption experiment, Fig. 6h (longer exposure time than 6c–g).

The sorption behaviour of all the lower actinides (thorium, protactinium, uranium, neptunium, plutonium, americium) is highly related to the degree of hydrolysis, determined by pH, and the oxidation state, determined by Eh [8, 10]. Sorption maxima are generally observed in the pH-range where neutral hydroxy species would dominate in solution, while

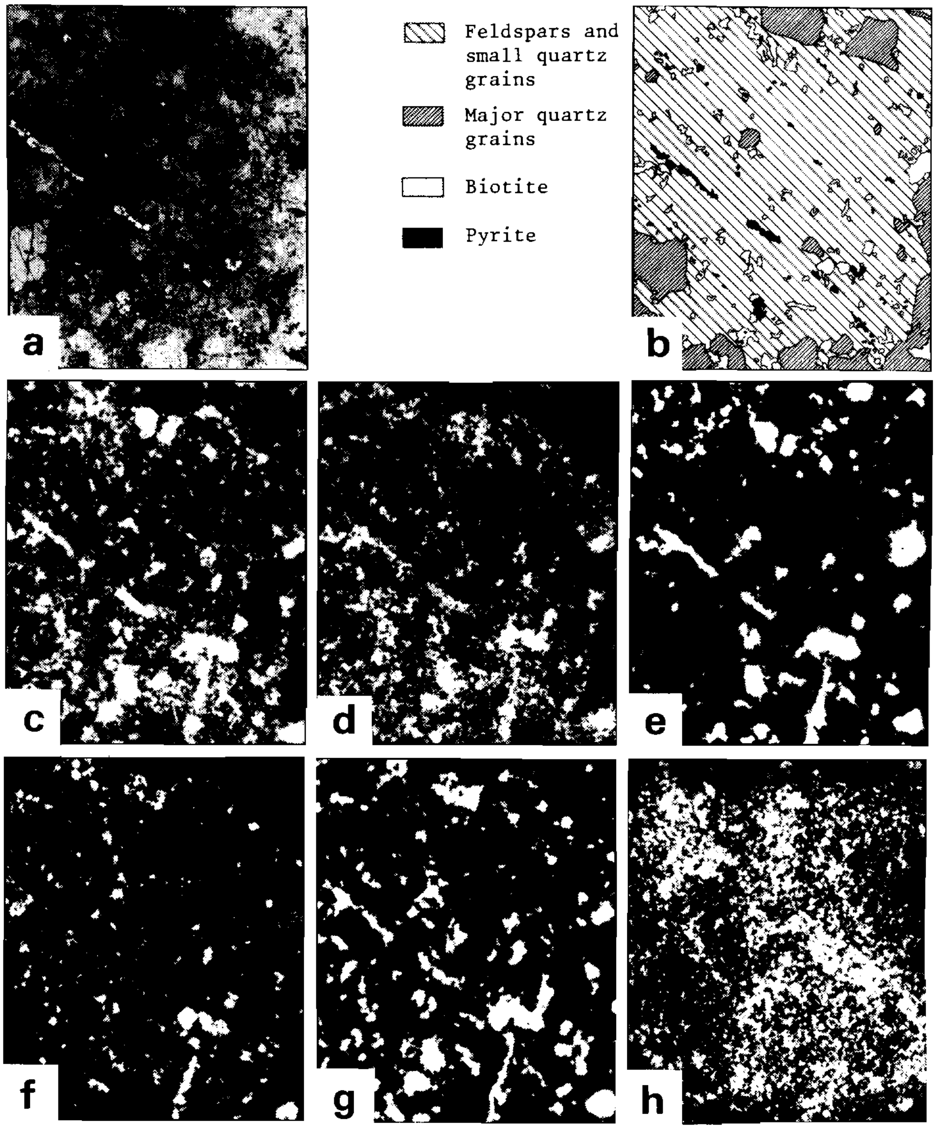

Fig. 6. Sorption of actinides on a polished 3 × 3 cm granite surface [3]. a. Photograph; b. Mineralogic composition; c–g. Autoradiographs, fresh surface; c, Am(III), d, Pu(IV), e, Np(V), f, U(VI), g, Pu(V,VI); h, Autoradiograph, altered surface (oxidized with O_3), Np(V).

the formation of anionic complexes (*e.g.* with carbonate) seems to reduce the sorption. The properties of the solid (*e.g.* exchange capacity) as well as the total salt concentration of the aqueous phase (cations and non-complexing anions like Cl^-) have relatively little influence on the magnitude of the sorption, except in the pH-range where non-hydrolyzed species would dominate (electrostatic interactions) or when the solid phase has specific complexing properties (chemisorption).

Actinide Colloid Formation

Many cations, like the actinides in their lower oxidation states, have a tendency to form polymeric hydroxides [45–48]. These species may carry a large residual charge which prevents them from aggregation because of electrostatic repulsion. Thus, metastable species can be formed, giving an apparent solubility which exceeds the thermodynamic solubility product.

Polymeric hydroxy species formed at low and intermediate pH generally carry a positive residual charge. Some of these polymeric species should in fact be considered as thermodynamically stable complexes. They are strongly sorbed on exposed surfaces of geologic materials (silicates, oxides), as well as on natural colloidal particles in the aqueous phase (clay particles, metal hydroxides *etc.*).

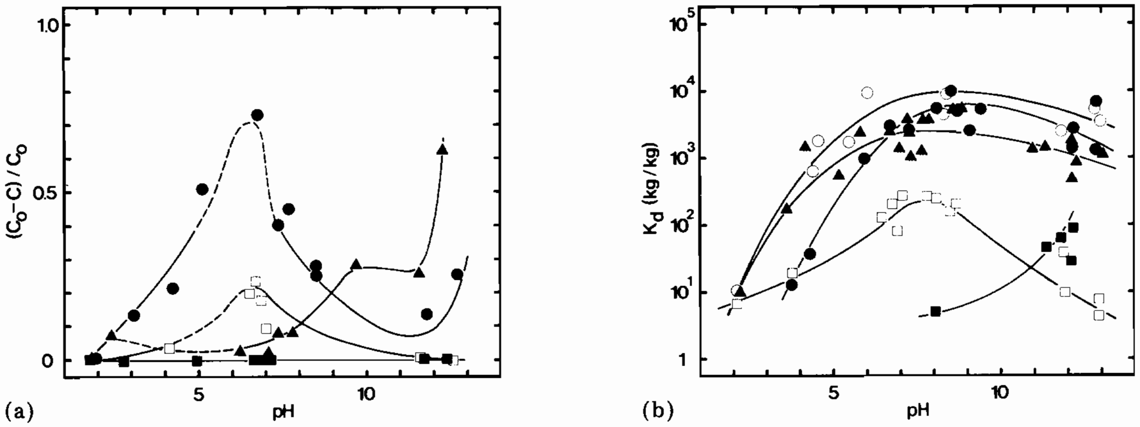

Fig. 7. Formation and sorption of actinide particle fractions [8, 45]. Left: Formation of a centrifugable fraction (r > 20 nm). Aqueous pahse: 0.01 *M* $NaClO_4$, storage time: 6 weeks. Equilibrium with air. Right: Sorption on Al_2O_3 in the same system. ○ Th(IV), □ U(VI), ■ Np(V), ▲ Pu (essentially IV), ● Am(III); concentrations 2×10^{-9}–6×10^{-10} *M*.

Another type of species with colloidal properties are formed in the course of precipitation of solid metal hydroxides. These particulates, which can carry a negative net charge or be neutral, gradually change with time from an amorphous to a crystalline state. A transfer from the hydroxide to the corresponding oxide, particularly for tetravalent species like $Th(OH)_4$ and $Pu(OH)_4$ (giving ThO_2, PuO_2) is a spontaneous but slow process.

There is a formation of a significant particle fraction for Am(III) and Pu(IV), even at low concentrations. For U(VI) the formation of such a fraction is minor, and for Np(V) totally absent, Fig. 7 [45]. The particle fractions (r > 20 nm) formed at high pH for Am(III) and Pu(IV) probably illustrate the formation of hydroxy colloids, while the particle fractions for Am(III) and U(VI) around pH 6–8 possibly represent the formation of pseudocolloids (sorption on $Fe(OH)_3$ present as an impurity in the active stock solutions?).

The introduction of a solid sorbent (Al_2O_3) to the systems is also illustrated in Fig. 7 [8]. Evidently the sorption on the solid surface is pronounced even in the pH-range where a particle fraction would be formed in a pure aqueous phase. The decrease in sorption for U(VI) at pH above 8 can be attributed to the formation of anionic carbonate complexes. The slight decrease in sorption observed for Am(III) and Pu at pH above 8–9 would also be due to the formation of anionic species, both in true solution (hydroxides and carbonates for Am(III), hydroxides for Pu) and in the colloidal state, and could possibly also indicate an increased fraction of Pu(V) in the plutonium system.

Slow kinetics of transfer from metastable states to thermodynamically stable species, difficulties in establishing stoichiometric compositions, as well as the mechanisms for polymerisation and dehydration and the strong tendency for aggregates with high residual charges to interact with solid surfaces (both in laboratory experiments as well as under natural conditions) have largely prevented detailed quantitative studies of the properties of colloidal actinide systems. However, the transport of actinides as pseudocolloidal species (sorbed on mobile natural colloids or particles) is undoubtedly one major migration mechanism in the aqueous environment, especially for the lower oxidation states (*e.g.* Th(IV), Pu(IV) and Am(III) under oxic conditions).

Actinide Distribution and Mobility in Environmental Systems

The mobility and distribution of actinides in the environment is highly related to the solution chemistry (determining the chemical state in terms of oxidation state and complexation) and to the presence of solid material (sorbing surfaces, including natural colloidal particles). The overall effect of sorption processes is that the actinides at trace concentrations generally are slowly eliminated from aqueous phases. This is exemplified in Table XI, showing distribution coefficients, K_d, and transfer coefficients (concentration factors), defined as amounts per kg product divided by amount per kg source (here also denoted by K_d). The uptake on solids reflects the order of hydrolysis, *i.e.* Pu(IV) $\geqslant$ Am(III) > U(VI) > Np(V). This would in fact lead to variations in the distribution of *e.g.* Pu(V)/Pu(IV) between surface waters and water near the bottom where interactions with solid phases are possible. The assimilation in plants usually declines in the order Np(V) > U(VI) > Am(III) $\geqslant$ Pu(IV), Np(IV) [27]. This order of uptake is almost the reverse of the order of hydrolysis.

TABLE XI. Distribution (K_d) of Actinides (Th, U, Np, Pu, Am) between Water, Solid Phases and Biota in Natural Environments [11, 27].

Equilibrium between	logK_d (kg/kg)				
	Am(III)	Pu	Th(IV)	Np(V)	U(VI)
Water–sediment					
Laboratory measurements[a]					
Pure minerals	2.5–4.5	2.5–5		0.5–4	2.2–4.5
Granite	4.0	3.7	4.3	1.6	2.9
Pacific Ocean (Enewetak)		5.0 ± 1.5			
Irish Sea (Windscale)		4.8 ± 0.6			
Lake Michigan		5.5			
White Oak Lake (Tennessee)		4.7 ± 0.8			
Hudson River		4.8			
Marine environment	6.4	6.4	>7	3.7	3
Water–organisms					
Lake Michigan–					
Phytoplankton	4.2	4.0; 3.7	<3.9; 4.3		2.2; 1.6
Zooplankton	2.7	2.5; 3.0	3.5; 4.1		1.4; 1.1
Planktivorous fish	≤2.2	1.4	<3.6		–0.4
Piscivorous fish	≤1.7	0.6	<3.6		–0.3
Coastal plants	4.2	3.7			1.6
Marine waters –					
Phytoplankton		3.4			
Zooplankton		3.4			
Fish		0.5			

[a] Ranges of values for some 35–40 minerals, pH 7–9, are given as well as values representative of granitic rock [10].

TABLE XII. Distribution (K_d) of actinides (Th, U, Np, Pu, Am) between solid phases and biota [11, 27].

Equilibrium between	logK_d (kg/kg)				
	Am(III)	Pu	Th(IV)	Np(V)	U(VI)
Sediments–organisms					
Lake Michigan–					
Phytoplankton	–2.2	–1.5			
Zooplankton	–3.4	–3.0			–0.8
Planktivorous fish	≤–4.1	–4.1			–1.8
Piscivorous fish	≤–4.6	–4.9			
Sediments–plants					
Lake Michigan–					
Coastal plants	–2.1	–1.8			–1.1[a]
Fruit, vegetable or seed	–3.4	–4.3	–3.6		–3
Food–animal					
Rat	<–3.5	–4.2[b] –4.8[c]	<–2.5	–2.9	
Man (An as oxide or hydroxide)	–3.3	–5	–3.7		–2.7
Man (An in other common forms)	–3.3	–4	–3.7		–1.3

[a] Value from Lake Issyk-Kul. [b] Plutonium as Pu(III). [c] Plutonium as Pu(IV).

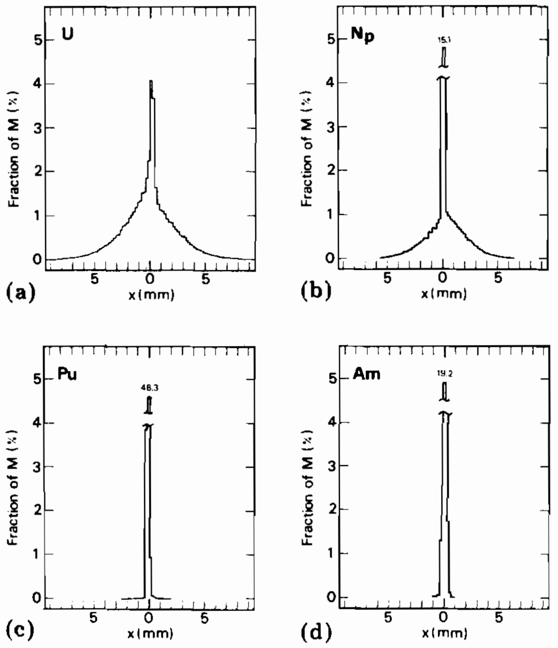

Fig. 8. Concentration profiles of uranium(VI), neptunium(V), plutonium and americium(III) in water-saturated compacted bentonite illustrating transport by diffusion from a flat source [49]. Transport time 2–3 months.

The uptake of actinides by organisms from solid phases is minor, as well as the uptake by man through food, Table XII. Evidently, only a minor fraction of *e.g.* plutonium would reach man. An example of this is that out of the 4.2 tonnes of plutonium deposited on earth after atmospheric nuclear explosions the total amount in man (whole world population) is estimated to be less than 1 g [21].

One may deduce from Table XI and XII, that the concentration of *e.g.* plutonium accumulated in man in equilibrium with the environment would not likely exceed the concentration in natural waters, independently of the mode of ingestion [11].

The organic and inorganic particles in soils and waters constitute a major mode of actinide transportation in flowing environmental water systems. The amount of particulate matter (clay, silt, metal hydroxides etc. as well as organic material) in natural waters varies from very high values in silt carrying rivers (more than 1000 mg/l) to practically zero (0.05 mg/l) in the ocean. A typical value may be 1–10 mg/l. Considering the variety of sources for organic material, a great diversity in the concentration of particulate organic matter is observed. A typical value for estuarine waters would be 5 mg/l of particulate organic matter [11].

Thus, factors like particle size distribution and discharge rates would be important in combination with the chemical factors influencing speciation and sorption in the transport process at sediment–water interfaces. Particulate transport and distribution and uptake in organisms are outside the scope of this review and are not further discussed.

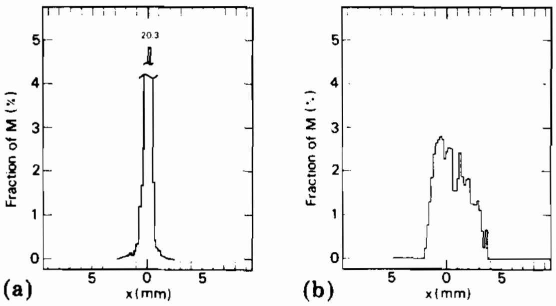

Fig. 9. Concentration profiles of uranium in water-saturated compacted bentonite, illustrating reduction from U(VI) to U(IV) [49]. (*Cf.* Fig. 8). Left: Clay + 0.5% Fe. Right: Clay + 0.5% Fe in half of the sample (left half in the figure).

The transport of actinides in *e.g.* water-saturated clay formations and sediments *etc.* would be by molecular diffusion. Examples of actinide mobility measurements in compacted clay (bentonite) are given in Fig. 8, showing the migration uf U(VI), Np(V), Pu and Am(III) from a flat source in a water saturated medium [49]. The apparent diffusivities are of the order of 10^{-14} m^2/s for the low-valent actinides (Am(III) and Pu which is evidently predominantly in the tetravalent state) and 10–100 times higher for U(VI) and Np(V).

The addition of a reducing agent to the clay can reduce *e.g.* U(VI) to U(IV), Fig. 9, which would decrease the apparent uranium diffusivity. This demonstrates one mechanism of uranium immobilization in nature, when mobile U(VI)-species encounters a reducing environment. The time required for the actinides in their lower oxidation state to penetrate *e.g.* 1 m of compact water-saturated clay or sediment would be 10^4 years or more.

Generally, retention factors (water velocity divided by nuclide velocity) would be in the range of 10^4–10^5 or even larger for actinides in the lower oxidation states (III and IV), when transported by water in fractured rock or in porous media [22].

Summary and Conclusions

Some general conclusions can be drawn concerning the chemical behaviour of actinides in natural environments.

– Both thorium and uranium are common elements in the earth's crust and in environmental waters.

– The major amounts of transuranium elements come from nuclear activities of human origin. Most of these elements in the environment are constituents of the fallouts from testing nuclear weapons (plutonium, americium).

– Actinide chemistry in environmental waters is largely determined by redox conditions and the presence of complexing agents (OH^-, CO_3^{2-}, organic acids, possibly F^- and PO_4^{3-}).

– The dominating oxidation states are Th(IV), U(IV), Np(IV), Pu(III,IV) and Am(III) under reducing conditions ($AnO_2(s)$ and $An_2(CO_3)_3(s)$ solubility limiting phases) and Th(IV), U(VI), Np(V), Pu(IV,V) and Am(III) under oxic conditions.

– Dominating species in solution under most environmental conditions are for An(III): An^{3+}, $AnOH^{2+}$, $AnCO_3^+$, $An(CO_3)_2^-$ and possibly organic complexes; for An(IV): $An(OH)_4$, ($An(OH)_5^-$); for An(V): $AnO_2(CO_3)_2^{3-}$, $AnO_2(CO_3)_3^{5-}$; for An(VI): $AnO_2(CO_3)_2^{2-}$, $AnO_2(CO_3)_3^{4-}$.

– Dominating actinide species in a given aqueous phase can often be predicted from thermodynamic data. The uncertainties in some of these data are, however, too large to allow reliable quantitative predictions.

– Colloidal species can be formed, particularly for actinides in the lower oxidation states (III and IV). These species could represent thermodynamically stable hydroxy polymers but also metastable species formed in the course of hydroxide precipitation.

– Sorption of actinides on solid geologic material starts when hydrolysis reactions become significant and reach a maximum in the pH-range where neutral species would dominate (physical adsorption). Thus, the actinides in their lower oxidation states are strongly sorbed on exposed geologic media under most environmental conditions.

– Formation of anionic species (molecular or colloidal) tends to reduce the sorption (*e.g.* of U(VI) in the presence of CO_3^{2-}).

– Solids containing anions that would form sparingly soluble compounds (*e.g.* PO_4^{3-}) would enhance the sorption of actinides (chemisorption).

– Transport of dissolved actinides in the lower oxidation states (flow in porous media or fractured rock, diffusion in sediments and clay *etc.*) is very slow.

– Particles of geologic or organic materials and natural colloids would constitute major actinide transport mechanisms in flowing water systems. Thus, physical rather than chemical processes largely dominate in the transport of actinides in the environment. Exceptions are the transport of anionic species (*e.g.* penta- and hexavalent carbonate complexes) and possibly organic complexes.

– The enrichment of actinides from water to food appears to be fairly well compensated for by metabolic discriminations against these elements (*e.g.* plutonium) in higher trophic levels, including man.

Some important problems connected with environmental actinide chemistry should be mentioned:

– Many of the available stability constants for actinide complexes of environmental interest are either extrapolated or not measured under proper conditions.

– The formation of colloidal species (mechanisms, kinetics) is not adequately understood.

– Information on the formation and transport of complexes between actinides and natural organics is scarce.

– Detailed knowledge about the mechanisms of actinide sorption on geologic material is lacking.

– The mechanisms for redox reactions in the environment, *e.g.* in the plutonium system, are not fully understood.

– Direct chemical studies of actinides at trace concentration levels cannot yet be accomplished on a routine basis.

– Very few data are available concerning the behaviour of transuranium elements in nature, other than for plutonium.

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