

ACTINIDES IN PERSPECTIVE

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SOLUBILITIES OF ACTINIDES IN NEUTRAL OR BASIC SOLUTIONS

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ABSTRACT

The solubility of actinides in environmental waters is largely determined by complexes formed with inorganic anions (OH^- , CO_3^{2-} , HPO_4^{2-} , F^- , SO_4^{2-}) and organic complexing agents. Measured and estimated complex formation quotients have been summarized for the actinides, U, Np, Pu and Am. Speciation and solubility of these elements are largely determined by hydrolysis and formation of carbonate and possibly fluoride and phosphate complexes. Solubilities in the pH-range 5 - 11 have been calculated, considering formation of hydroxy and carbonate complexes only, and compared with data from the literature. Experimentally determined solubilities are rarely equal to values calculated from thermodynamic data. What appears to be oversaturated solutions can be obtained due to slow kinetics in the formation of e.g. thermodynamically stable oxides, or due to the existence of colloidal particulates not in true solutions. By the presence of oxide or silicate surfaces, on the other hand, species in solution will be adsorbed in certain pH-ranges, leading to a lower concentration in solution than predicted. Due to the lack of accurate thermodynamic data for some of the dominating reactions in environmental waters, calculated solubilities must in general be considered as somewhat speculative.

KEYWORDS

Actinides, uranium, neptunium, plutonium, americium, hydrolysis, hydroxide, carbonate, solubility, natural waters, neutral solutions, basic solutions.

INTRODUCTION

Long-lived actinides and their daughter products are among the radionuclides that would dominate the biological hazards from the nuclear fuel cycle. The actinide concentration levels in the environment and the mobility in aquifers would be related to the complexes formed with anions in the water and to some extent limited by the low solubility of certain compounds. Thus, it is of considerable interest to characterize the chemical behaviour of the actinides (complex formation and speciation, solubility, etc.) in neutral or slightly basic solutions and the influence of complexing agents that may be present in concentration levels representative of environmental waters.

The lower actinides actinium and thorium exist only as Ac(III) and Th(IV), respectively, in aqueous solutions. For protactinium the most stable oxidation

state is Pa(V), although also Pa(IV) can exist in aqueous solutions. For uranium, U(IV) and U(VI) can exist, and probably U(V), although it is prone to disproportionation. The lowest state U(III) is slowly oxidized by water with evolution of hydrogen. For neptunium and plutonium all the oxidation states III, IV, V, and VI can exist in aqueous solutions, although Np(III) is a strong reducing agent, and Pu(V) may disproportionate. Both neptunium and plutonium can exist as the strong oxidizing agents Np(VII) and Pu(VII). The higher actinides americium and curium are most stable as Am(III) and Cm(III). Less stable are Am(VI), which is a strong oxidizing agent, Am(V), which tends to disproportionate, and Am(IV), which cannot exist in solution except in the presence of high concentrations of complexing agents.

Thus, the following oxidation states for the actinides (here denoted by An) would be of environmental interest: An(III): Pu, Am, Cm; An(IV): Th, Pa, U, Np, Pu; An(V): Pa, U, Np, Pu; An(VI): U, Np, Pu. Only data for U, Np, Pu and Am, which have very similar chemical properties in the same oxidation state, will be discussed in this paper.

Natural waters contain a number of complexing agents such as HCO_3^- - CO_3^{2-} , H_2PO_4^- - HPO_4^{2-} - PO_4^{3-} , F^- , SO_4^{2-} and Cl^- as well as organic carboxylic acids (humic acids, fulvic acids, etc.).⁴ In non-saline waters (most groundwaters, lakes, rivers, etc.) the expected concentrations of the inorganic anions would be in the ranges 0.3 - 8 mM for total CO_3^{2-} , <0.001 mM for total PO_4^{3-} , 0.003 - 0.2 mM for F^- , 0.01 - 1 mM for SO_4^{2-} and 0.05 - 5 mM for Cl^- . (Stumm and Morgan, 1970). The solubility of actinides in waters of various redox potentials and containing these naturally occurring inorganic anions and the chemical species formed are discussed in this paper. Other recent discussions of actinide speciation and solubilities are given e.g. by Bondietti and Sweeton (1977), Langmuir (1978), Newton, Aguilar and Erdal (1980), Skytte Jensen (1980), Grenthe and Ferri (1981) and others.

ACTINIDE COMPLEXES WITH INORGANIC LIGANDS

The chemistry of actinides in solution reflects the peculiar electron configuration of these elements where the 5f and 6d shells are of similar energy. Since the 5f orbitals are less well shielded than the 4f orbitals of the lanthanides, they are prone to participate in bonding (Ahrland, Liljenzin and Rydberg, 1973). In the early part of the series the elements exhibit multiple oxidation states (from 3 to 7), but beyond plutonium the lower oxidation states (2 to 4) are predominant. The non-complexed ions normally formed at the oxidation states III to VI are M^{3+} , M^{4+} , MO_2^+ and MO_2^{2+} , respectively.

The actinides are generally classified as hard (class A) (Ahrland, 1972). Strong complexes are formed with the fluoride ions as well as ligands coordinating via oxygen (oxides, hydroxides, phosphates, sulfates). The affinity for sulfur and the heavy halides is weak. The complex strength increases in the order $\text{MO}_2^+ < \text{M}^{3+} < \text{MO}_2^{2+} < \text{M}^{4+}$, i.e. with the effective charge of the acceptor atom. The complexes are generally formed in endothermic reactions, and the high stability is due to a large gain of entropy which balances or more than compensates for the unfavourable enthalpy change.

A logical first step of analysing solubility and speciation of the actinides would be to describe the composition of systems in equilibrium, based on thermodynamic data. In order to explain observed solution properties the addition of kinetic information describing non-equilibrium conditions would be necessary (Grenthe and Ferri, 1981). It is of importance for an approach using thermodynamic data that all relevant equilibria and species are included in the model. It is therefore justified, and even necessary, to include estimated or extrapolated

stability data for species that are likely to be present, considering known properties of analogous elements, even if these species have in fact not been experimentally verified. It is also necessary to adjust what are reported as thermodynamic constants, possibly from experiments where some systematic error might have been overlooked, when these data contradict or apparently do not fit other experimental observations. Thus, the model discussed in this paper, is not strictly based on firmly established measured stability constants, since these are not determined for all the reactions of importance, but rather on a mixture of thermodynamic data, empirical experimental observations and extrapolated data from elements with similar properties.

There are several recent critical compilations of thermodynamic data for the formation of actinide complexes, e.g. by Smith and Martell (1976), Baes and Mesmer (1976), Rai and Serne (1977), Langmuir (1978), Lemire and Tremaine (1980), Langmuir and Herman (1980) and several others. The ranges of formation constants and solubility products for the inorganic actinide complexes of interest (at ionic strength $I=0$) are given in Table 1 and 2, with data taken from the references given above and from Sillán and Martell (1964). Based on these ranges for the various complexes a set of constants for a model actinide An has been assessed, Table 3. Considering the uncertainties in published stability constants, which usually correspond to a minimum of a factor of 2 - 3 and more often more than one order of magnitude for many of the high complexes, the data in Table 3 could in fact be valid for any of the actinides U, Np, Pu or Am, except for a few systems where substantial differences have been reported. The choice of constants for Table 3 in the present analysis is briefly discussed below.

TABLE 1 Ranges of Reported Complex Formation Constants for Actinide Complexes ($An + L \rightleftharpoons AnL$, K_1 ; $I=0$)

Ligand	$\log K_1$			
	An^{3+}	An^{4+}	AnO_2^+	AnO_2^{2+}
OH^-	5.7-6.3 ^a	12.5-13.8	4.0-5.1	8.1-8.9
CO_3^{2-}	4.6-6.3 ^b			9.8-10.5
HPO_4^{2-}		12.0-13.0		8.4
$H_2PO_4^-$	2.4-2.5	4.5		3.0
F^-	3.4-4.3	7.9-8.6	3.7	5.1-5.7
SO_4^{2-}	3.5-3.7	5.5-5.6	2.0	3.0-3.7
Cl^-	-1	-2		-2

^a For lanthanides

^b For lanthanides, $I=1-3$

Hydroxides

Hydrolysis of cations, including the actinides, is critically reviewed by Baes and Mesmer (1976). Much of the information on actinide hydrolysis stems in fact from quite early work (e.g. reviewed by Kraus, 1956). Hydrolysis products of actinides and similar elements that appear to be sufficiently well characterized are given in Table 4. (Baes and Mesmer, 1976).

TABLE 2 Ranges of Reported Solubility Products for Actinide Complexes ($xAn + yL \rightleftharpoons An_xL_y(s)$, (x,y) , K_s ; $I=0$)

Ligand	(x,y) -logK _s			
	An ³⁺	An ⁴⁺	AnO ₂ ⁺	AnO ₂ ²⁺
OH ⁻	(1,3) 22.0-24.5 ^a	(1,4) >47 ^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) 13.8-14.1
HPO ₄ ²⁻		(1,2) 26.8-27.6		(1,1) 12.6
PO ₄ ³⁻	(1,1) 23(?)	(3,4) <57(?)		(3,2) 23.5
F ⁻	(1,3) 10.2	(1,4) 23.5-27.6		

^a For lanthanides

^b Values between 47 and 63 are reported.

Similar hydrolysis products and complex formation constants would be expected for trivalent actinides and lanthanides. Reported values for AmOH²⁺ and CmOH²⁺, however, as obtained by solvent extraction techniques, appear to be too high, in comparison with corresponding constants for the lanthanides (e.g. for NdOH²⁺, Nd and Am having very similar ionic radius₁) (Désiré, Hussonnois and Guillaumont, 1969). For the fluorides LnF²⁺ and AnF²⁺ no similar large differences are reported. There are examples (for some lanthanide systems) that apparent hydrolysis constants obtained by solvent extraction technique can be too high, e.g. due to the formation of a significant fraction of soluble species other than with the studied ligand. Thus, data for Nd³⁺ are used in Table 3, as suggested by Baes and Mesmer (1976) and by Edelstein, Brown and Silva (1980). These data are in fair agreement with some recent solution studies of americium and europium (Lundqvist, 1981). All three of the 1,1-, 1,2- and 1,3-complexes are assumed to exist. The existence of a negatively charged species An(OH)₄⁻, as has been reported for some lanthanides, is assumed. Electromigration studies of americium by Staric and Ginzburg (1963), by Fried and coworkers (1975) and by Olofsson and coworkers (1981) indicate a formation of anionic species at high pH, although it is not clear whether those species are hydroxides or carbonates. Also for the solubility product the value for Nd(OH)₃(s) is used.

For tetravalent actinides reliable hydrolysis constants are available only for the first hydrolysis product AnOH³⁺. Baes and Mesmer (1976) predicts formation constants for the complexes An(OH)₂²⁺, An(OH)₃⁺ and An(OH)₄ largely based on reported pH-dependent solubility measurements of U(OH)₄, Gayer and Leider, (1957), indicating the formation of U(OH)₅⁻. However, considering the fact that traces of oxygen or carbon dioxide in the system could change the overall uranium solubility by several orders of magnitude (formation of U(VI)-CO₃²⁻-complexes) the proposed U(OH)₅⁻-species and calculated constants should be considered as tentative.

TABLE 3 Selected Complex Formation Constants for a Model
Actinide ($x\text{An} + y\text{L} \rightleftharpoons \text{An}_x\text{L}_y^z$, (x,y) , $K_{x,y}$; $I=0$)

Ligand	Reaction	$\log K_{x,y}$			
		An^{3+}	An^{4+}	AnO_2^+	AnO_2^{2+}
OH^-	(1,1)	6.0	13.5	4.6	8.3
	(1,2)	11.0	25.5		16.0
	(1,3)	15.5	36.0		
	(1,4)	19.0	45.5		
	(1,5)		50		
	(2,2)	14	27		22.5
	(3,5)	37			54.5
	(4,8)		(110)		
CO_3^{2-}	(6,15)		(210)		
	(1,1)	6.5		(5)	10.0
	(1,2)	11.0		(9)	16.7
	(1,3)	14.5		(14)	23.8
	(1,5)		(37)		
	(2,3)				
	(3,6)				60.5
	(1,1,2)	(12.5)			
HPO_4^{2-}	(1,3,1)		(42)		
	(3,3,1)				46
	(1,1)	(6)	13.0		8.4
	(1,2)		23.8		18.5
H_2PO_4^-	(1,3)		33.4		
	(1,1)	2.4	4.5		3.0
	(1,2)		8.9		5.5
F^-	(1,1)	4.3	8.6	3.7	5.7
	(1,2)	7.6	14.5		11.1
	(1,3)	10.8	19.1		15.9
	(1,4)		23.6		18.8
	(1,5)		25.3		
SO_4^{2-}	(1,1)	3.5	5.6	2	3.0
	(1,2)	5.2	10.3		4.3

Solubility products:

$\text{An}(\text{OH})_3(\text{s})$,	$\log K_S = -23.5$	$\text{An}(\text{HPO}_4)_2(\text{s})$,	$\log K_S = -27$
$\text{AnO}_2(\text{s})$,	$\log K_S = -54$	$\text{AnO}_2\text{HPO}_4(\text{s})$,	$\log K_S = -12.6$
$\text{AnO}_2(\text{OH})(\text{s})$,	$\log K_S = -8.8$	$\text{AnPO}_4(\text{s})$,	$\log K_S = -23$
$\text{AnO}_2(\text{OH})_2(\text{s})$,	$\log K_S = -23.0$	$(\text{AnO}_2)_3(\text{PO}_4)_2(\text{s})$,	$\log K_S = -23.5$
$\text{An}_2(\text{CO}_3)_3(\text{s})$,	$\log K_S = -31$	$\text{AnF}_3(\text{s})$,	$\log K_S = -10.2$
$\text{AnO}_2\text{CO}_3(\text{s})$,	$\log K_S = -13.8$	$\text{AnF}_4(\text{s})$,	$\log K_S = -24$

TABLE 4 Identified Hydroxide Species

M^{3+}	MOH^{2+} , $M(OH)_4^{-} (?)$ (Sc, Y, lanthanides) $M_2(OH)_2^{4+}$ (Sc, Y, lanthanides), $M_3(OH)_5^{4+}$ (Sc, Y, lanthanides)
M^{4+}	MOH^{3+} , $M(OH)_2^{2+}$ (Ce, Th, Pa), $M(OH)_3^{+}$ (Pa, Pu), $M(OH)_4$ (Zr, Th, Pu), $M(OH)_5^{-} (?)$ (Zr, U) $M_2(OH)_2^{6+}$ (Ce, Th), $M_4(OH)_8^{8+}$ (Zr, Th), $M_6(OH)_{15}^{9+}$ (Th, U(?))
MO_2^{+}	MO_2OH
MO_2^{2+}	MO_2OH^{+} , $MO_2(OH)_2$ $(MO_2)_2(OH)_2^{2+}$ (U, Np, Pu), $(MO_2)_3(OH)_5^{+}$ (U, Np, Pu)

In more recent studies of Pu(IV)- and Np(IV)-hydrolysis by Metivier and Guillaumont (1976) and by Duplessis and Guillaumont (1977), stability constants for the 1,1-, 1,2-, 1,3- and 1,4-complexes are calculated (for plutonium). No formation of $An(OH)_5^{-}$ -species are, however, reported, although electromigration studies by Fried and coworkers (1975) indicate a formation of anionic Pu(IV)-hydroxides at high pH. The reported constants are in reasonable agreement with the estimates by Baes and Mesmer (1976).

The high value suggested for the formation constant of $Pu(OH)_4$ is, however, not compatible with recent experimental observations by Rai, Serne and Swanson (1980) who conclude that predominantly Pu(V)-species would exist in solution in equilibrium with $PuO_2(s)$ or $Pu(OH)_4(s)$ at pH 3 - 6 under oxidic conditions. Since the plutonium study by Metivier and Guillaumont was performed under slightly oxidizing conditions, to prevent the reduction to Pu(III), a formation of Pu(V) can not be excluded, leading to progressively too high formation constants with increasing number of hydroxy ligands.

Recent measurements by Tremaine and coworkers (1981) on the solubility of $U(OH)_4(s)$ in alkaline solutions under controlled redox conditions and in the absence of carbon dioxide, do indicate a formation of a 1,5-hydroxide with a formation constant $\log K = -5.8 - \log K_s$. Considering recent solubility measurements on crystalline $UO_2(s)$ by Grenthe and Ferri (1981), giving a solubility product $\log K_s = -55.8$, a formation constant of $\log K = 50$ for the 1,5-complex would be obtained. Thus, the constants suggested in Table 3 for An(IV)-hydroxides are slightly lower than the estimated constants given by Baes and Mesmer (1976), and by Allard, Kipatsi and Liljenzin (1980), especially for the higher hydroxides. A formation of an anionic $An(OH)_5^{-}$ -species is assumed, according to the measurements by Tremaine and coworkers (1981).

Quite few experimental solubility measurements have been done on crystalline $AnO_2(s)$ under well defined conditions. Recently, Grenthe and Ferri (1981) reported $\log K_s = -55.8$ for $UO_2(s)$ (c.f. above) and Rai, Serne and Moore (1980) have suggested $\log K_s = -52$ for $PuO_2(s)$. These values are considerably higher than what can be estimated, either from thermochemical data (Langmuir, 1978, and Lemire and Tremaine, 1980) or from solubility-lattice correlations by Baes and Mesmer (1976), who estimates $\log K_s = -62.5$ for $PuO_2(s)$. For $Pu(OH)_4(s)$ reported solubility products $\log K_s$ vary from -47.3 to -56.3 (Perez-Bustamente, 1965). In the present study a value of $\log K_s = -54$ was selected for the hypothetical model actinide, supposed to be representative of the solubility of an oxide $AnO_2(s)$.

Evidently, and not surprisingly, the observed solubility of e.g. $\text{PuO}_2(\text{s})$ can vary substantially depending on crystallinity, stoichiometry, presence of lattice defects, presence of impurities, condition of formation and existence of various modifications, etc.

Polymeric species of well defined stoichiometry and in thermodynamic equilibrium with monomeric species or with a solid oxide/hydroxide would not be expected to exist in neutral or basic solutions (Baes and Mesmer, 1976) and are not considered in Table 3, except for thermodynamically stable complexes like the 2,2- and 3,5-complexes for An(III) and An(VI) and the 2,2-, 4,8- and 6,15-complexes for An(IV) which may exist in the low pH-range and at fairly high An-concentrations.

For the penta- and hexavalent state the estimates given by Baes and Mesmer (1976) or Allard, Kipatsi and Liljenzin (1980) have been adopted in Table 3. Anionic species like $\text{AnO}_2(\text{OH})_2^-$ and $\text{AnO}_2(\text{OH})_3^-$ are not included in Table 3, although it is possible that such species might exist. A formation of polymeric hydroxy anionic complexes has e.g. been reported for uranium at pH above 11 (Musikas, 1972). There are, however, no conclusive experimental indications of the existence of such species under the conditions discussed in this paper. Even traces of carbon dioxide in the system could explain any observed amphoteric behaviour due to the formation of An(V)- (or An(VI)-) CO_3^{2-} -complexes.

Carbonates

Carbonate complexes with actinides and lanthanides that appear to be sufficiently well characterized are summarized in Table 5.

TABLE 5 Identified Carbonate Species

M^{3+}	MCO_3^+ , $\text{M}(\text{CO}_3)_2^-$, $\text{M}(\text{CO}_3)_3^{3-}$, $\text{M}(\text{CO}_3)_4^{5-}$ (lanthanides) $\text{M}_2(\text{CO}_3)_2^{2+}$ (La) $\text{MOH}(\text{CO}_3)_2^{2-}$ (Eu) ^a
M^{4+}	$\text{M}(\text{CO}_3)_5^{6-}$ (U) $\text{M}(\text{OH})_x\text{CO}_3^{2-x}$ (?) (Pu) ^a
MO_2^+	MO_2CO_3^- (?) (Np)
MO_2^{2+}	MO_2CO_3 , $\text{MO}_2(\text{CO}_3)_2^{2-}$, $\text{MO}_2(\text{CO}_3)_3^{4-}$ (U, Pu) $(\text{MO}_2)_3(\text{CO}_3)_6^{6-}$ (U, Pu) $(\text{MO}_2)_3(\text{OH})_3\text{CO}_3^+$ (U)

^a Tentative; exact composition not known.

For the trivalent state experimental data are available for Ce, La, Eu and some other lanthanides as well as for Am, Table 6. Potentiometric data by Grenthe and Ferri (1981) are in fair agreement with solvent extraction data by Lundqvist (1981). The constants in Table 3 are largely based on the data by Grenthe and Ferri (1981), at an ionic strength of 3.0, however with no attempt to correct for

ionic strength effects. The existence of a mixed hydroxy-carbonate complex $(\text{EuOH}(\text{CO}_3)_2)^{2-}$ has been suggested by Avogadro and Girardi (1981). Solubility products for lanthanide carbonates $\text{M}_2(\text{CO}_3)_3(\text{s})$ were determined by Jordanov and Havezov (1966), and subsequent reports of lanthanide carbonate solubilities have given similar values. An identical solubility product has been assumed for the hypothetical actinide, Table 3.

TABLE 6 Carbonate Formation Constants (logK) for M^{3+}

MCO_3^+	6.5	(Ce, I=3)	a
	5.7	(La, I=3)	a
	6.2	(Eu, I=1)	b
	5.7	(Am, I=1)	b
	9.6	(Pu, est.)	c
$\text{M}(\text{CO}_3)_2^-$	10.95	(Ce, I=3)	a
	9.7	(Eu, I=1)	b
	7.9	(Eu, I?)	d
	9.4	(Am, I=1)	b
	12.9	(Pu, est.)	c
$\text{M}(\text{CO}_3)_3^{3-}$	14.5	(Ce, I=3)	a
	16.2	(Pu, est.)	c
$\text{M}(\text{CO}_3)_4^{5-}$	16.9	(Ho, I=0)	e
	16.9	(Er, I=0)	e
$\text{MOH}(\text{CO}_3)_2^{2-}$	12.5	(Eu, I?)	d

- a Hietanen (1979), Ciavatta and coworkers (1981) and Grenthe and Ferri (1981)
 b Lundqvist (1981)
 c Saltelli, Avogadro and Bertozzi (1979)
 d Avogadro and Girardi (1981)
 e Dumonceau and coworkers (1979)

There is very little experimental support for the formation of a tetravalent species PuCO_3^{2+} , as suggested by Moskvin and Gelman (1958), since formation of other species equally well explain the measurements. If the solubility of $\text{Pu}(\text{OH})_4(\text{s})$ in carbonate solutions can be ascribed to only one single species, $\text{Pu}(\text{OH})_i\text{CO}_3$, the constant $k_i = [\text{Pu}(\text{OH})_i\text{CO}_3^{2-}][\text{Pu}(\text{OH})_{4-i}]^{-1}[\text{CO}_3^{2-}]^{-1}$ can be estimated for various i , as suggested by Skytte Jensen (1981), since the formation constants for $\text{Pu}(\text{OH})_{4-i}$ are known or estimated. Using this method the formation constant for $\text{An}(\text{OH})_3\text{CO}_3^-$ given in Table 3 was calculated. A similar value may be obtained by using the method suggested by Dyrssen, Jagner and Wengelin (1968) for a constant describing the formation of a mixed complex $\text{M}(\text{OH})_y(\text{CO}_3)_z$:

$$K_{1,y,z} = \frac{(y+z)!}{y!z!} \sqrt[y+z]{K_{1,y+z,0}^y K_{1,0,y+z}^z}$$

Casadio and Orlandini (1972), however, suggested from polarographic studies that the complex $\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ would be the most probable species formed at high pH and high carbonate concentration. Thus, neither the exact composition (or even existence) of a mixed $\text{An}(\text{IV})\text{-OH}\text{-CO}_3^{2-}$ complex nor the formation constant are accurately known, and the estimated value given in Table 3 may be incorrect by orders of magnitude.

Convincing evidences that the tetravalent $\text{U}(\text{CO}_3)_5^{6-}$ species may be formed at high pH and high carbonate concentration have been given by Grenthe and Ferri (1981). The original constant (at ionic strength 3.0) has been corrected to zero ionic strength (Table 3) by the procedure described by Baes and Mesmer (1976). A complex with the composition $\text{An}(\text{CO}_3)_5^{6-}$ would be coordinatively saturated and probably quite stable. Similar solid compounds with thorium and cerium are known (Voliotis and coworkers, 1977). The stabilization of tetravalent cerium, praseodymium and terbium by carbonate at high pH has previously been demonstrated by Hobart and coworkers (1981).

The information on pentavalent actinide carbonate complexes is scarce in the literature. The formation of mixed $\text{An}(\text{V})\text{-OH}\text{-CO}_3^{2-}$ complexes are suggested by Moskvin (1971) for neptunium, although the exact composition of the complexes can not be unambiguously determined from the experimental data. The constants suggested in Table 3 are merely estimates, based on comparisons with corresponding hydroxy, carbonate and oxalate complexes of $\text{An}(\text{III})$, $\text{An}(\text{V})$ and $\text{An}(\text{VI})$. Recent measurements by Grenthe (1981) indicate, however, a formation constant $\log K = 15.3$ for $\text{UO}_2(\text{CO}_3)_3^{5-}$.

Numerous studies on the $\text{UO}_2^{2+}\text{-CO}_3^{2-}$ system are reported in the literature. Data in Table 3 (corrected for ionic strength effects) are largely based on recent studies by Ciavatta and coworkers (1979) and (1981), Ferri, Grenthe and Salvatore (1981) and Ferri and Grenthe (1981) and references cited therein. Generally, higher stability constants were found than previously given in the literature, especially for the species $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$. Both these complexes would be expected to be stabilized for geometric reasons, which may explain the high formation constants. Since the pentavalent AnO_2^+ -ion and the hexavalent AnO_2^{2+} -ion have almost identical geometries, it is likely that also for the AnO_2^+ -ion a stabilisation of at least the $\text{AnO}_2(\text{CO}_3)_3^{5-}$ complex would be possible.

From spectrophotometric and calorimetric data a formation of predominantly $\text{PuO}_2(\text{OH})_2(\text{HCO}_3)^-$ instead of PuO_2CO_3 has been suggested by Sullivan, Bertrand and Choppin (1981). However, the only mixed $\text{An}(\text{VI})\text{-OH}\text{-CO}_3^{2-}$ complex that appears to be unambiguously identified is probably $(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^+$, which is included in Table 3 (Ciavatta and coworkers, 1979).

Other complexes

Data for phosphates, fluorides and sulfates in Table 3 are largely taken from Smith and Martell (1976), Langmuir (1978), Patil (1978), and Lemire and Tremaine (1980).

ESTIMATED ACTINIDE SOLUBILITIES FOR DISCRETE OXIDATION STATES

From the reported ranges of stability constants in Table 1, 2 and 3 and considering the anion concentration ranges in natural waters, it is obvious that actinide solution chemistry in environmental waters would be dominated by hydroxide and carbonate complexation. This has previously been stated by Skytte Jensen (1980) and by Grenthe and Ferri (1981). Despite the fact that fluorides and possibly

phosphates may significantly affect the overall solubility of actinides in certain natural waters (high fluoride or phosphate concentrations, pH below 7) (Langmuir, 1978), only hydrolysis and carbonate complexation are considered in the following calculations and discussions.

The solubility of the model actinide, An, considering hydroxide and carbonate complexes according to Table 3, have been calculated for the following systems:

- a. $P(\text{CO}_2) = 0$
- b. $P(\text{CO}_2) = 10^{-3.5}$ atm (corresponding to water in equilibrium with air)
- c. $p(\Sigma\text{CO}_3) = 3.3$ (closed system; total carbonate of $10^{-3.3}$ M, corresponding to 30 ppm)
- d. $p(\Sigma\text{CO}_3) = 2.1$ (closed system; total carbonate of $10^{-2.1}$ M, corresponding to 485 ppm)

Thus, b would represent a system open to the air while c and d would represent groundwaters with very low and very high total carbonate concentration, respectively.

Trivalent state

In the absence of carbonate a significant hydrolysis is obtained above pH 6 - 6.5, and at pH above 10 - 10.5 the anionic 1,4-complex will dominate. In the low pH range (below 5.5) a significant fraction would be polynuclear. (Fig. 1).

For all carbonate systems carbonate species will dominate in solution already at pH above 7.5, and negatively charged carbonates will dominate at pH above 9 - 9.5. The solubility limiting species would be $\text{An}_2(\text{CO}_3)_3(\text{s})$ rather than $\text{An}(\text{OH})_3(\text{s})$ in the environmental pH-range.

Tetravalent state

Already at pH 5 the dominating species in solution would be the neutral $\text{An}(\text{OH})_4$ -complex, while the anionic 1,5-complex would dominate at pH above 9.5. (Fig. 2).

Carbonate in the water has very little influence on the solubility, except for the open system at high pH (above 9.5 - 10), where the $\text{An}(\text{CO}_3)_5^{6-}$ may be dominating species in solution. Solubility limiting species is the oxide $\text{AnO}_2(\text{s})$.

Pentavalent state

In the absence of carbonate non-hydrolyzed AnO_2^+ would dominate at pH up to 9 - 9.5. (Fig. 3).

In the presence of carbonate the solubility is largely determined by anionic carbonate complexes above pH 7.5 - 8, giving very high solubilities, especially at pH above 8.5 - 9 in the open (b) and high-carbonate (d) systems (dominating species $\text{AnO}_2(\text{CO}_3)_3^{5-}$).

Hexavalent state

Hydrolyzed species would dominate at pH above 5.5 - 6 in the absence of carbonate. (Fig. 4). Significant fractions of polynuclear species would be formed in the low pH-range up to pH 7 - 7.5.

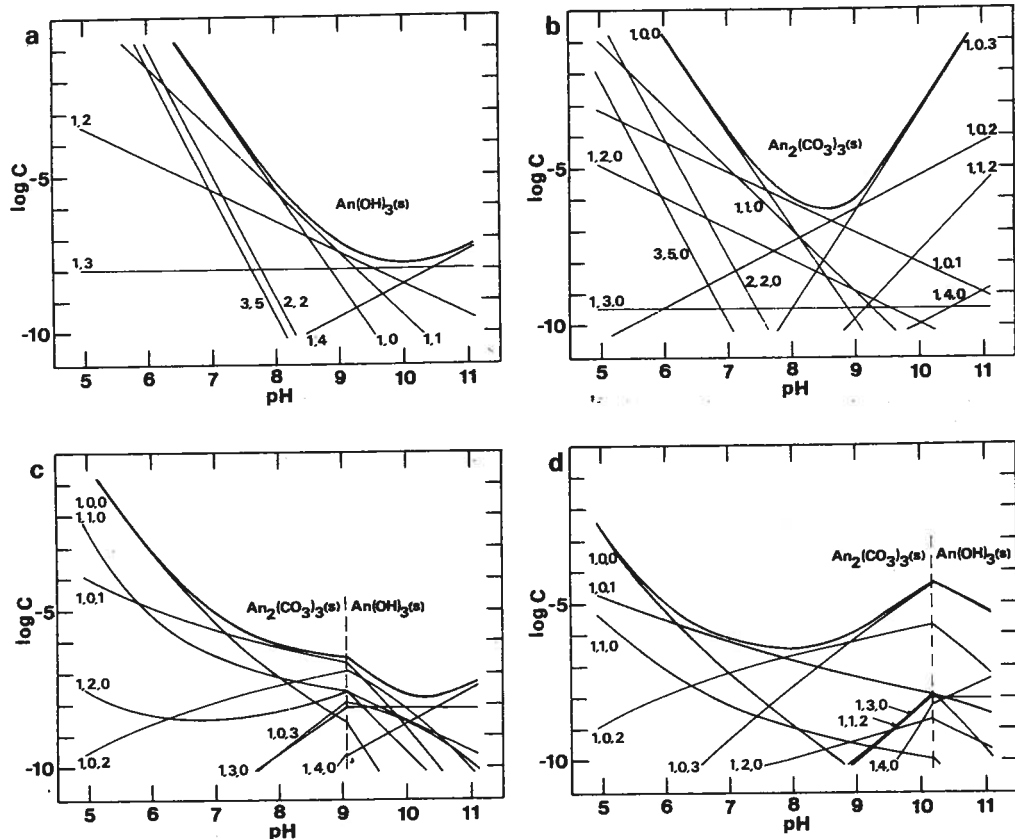


Fig. 1. An(III) solubilities (M); $(An_x(OH)_y(CO_3)_z)$; x, y, z
 a) $P(CO_2)=0$; b) $P(CO_2)=10^{-3.5}$ atm; c) $p(\Sigma CO_3)=3.3$; d) $p(\Sigma CO_3)=2.1$

Just as for the pentavalent state, the carbonate complexes would dominate entirely in solution in the carbonate systems, already at pH 5 in the closed systems. Above pH 7 negatively charged complexes would dominate, even as low as pH 5.5 $((AnO_2)_3(CO_3)_6^{6-})$ in the closed high-carbonate system (d). The solubilities in the open (b) and high-carbonate (d) systems would be very high.

ESTIMATED ACTINIDE SOLUBILITIES (U, Np, Pu, Am) IN ENVIRONMENTAL SYSTEMS

The solubilities of uranium, neptunium, plutonium and americium have been calculated for the following systems:

- $Eh = 0.8 - 0.06pH$; $P(CO_2) = 0$
- $Eh = 0.8 - 0.06pH$; $P(CO_2) = 10^{-3.5}$ atm
- $Eh = 0.8 - 0.06pH$; $p(\Sigma CO_3) = 3.3$
- $Eh = 0.8 - 0.06pH$; $p(\Sigma CO_3) = 2.1$
- $Eh = 0.2 - 0.06pH$; $p(\Sigma CO_3) = 3.3$
- $Eh = 0.2 - 0.06pH$; $p(\Sigma CO_3) = 2.1$

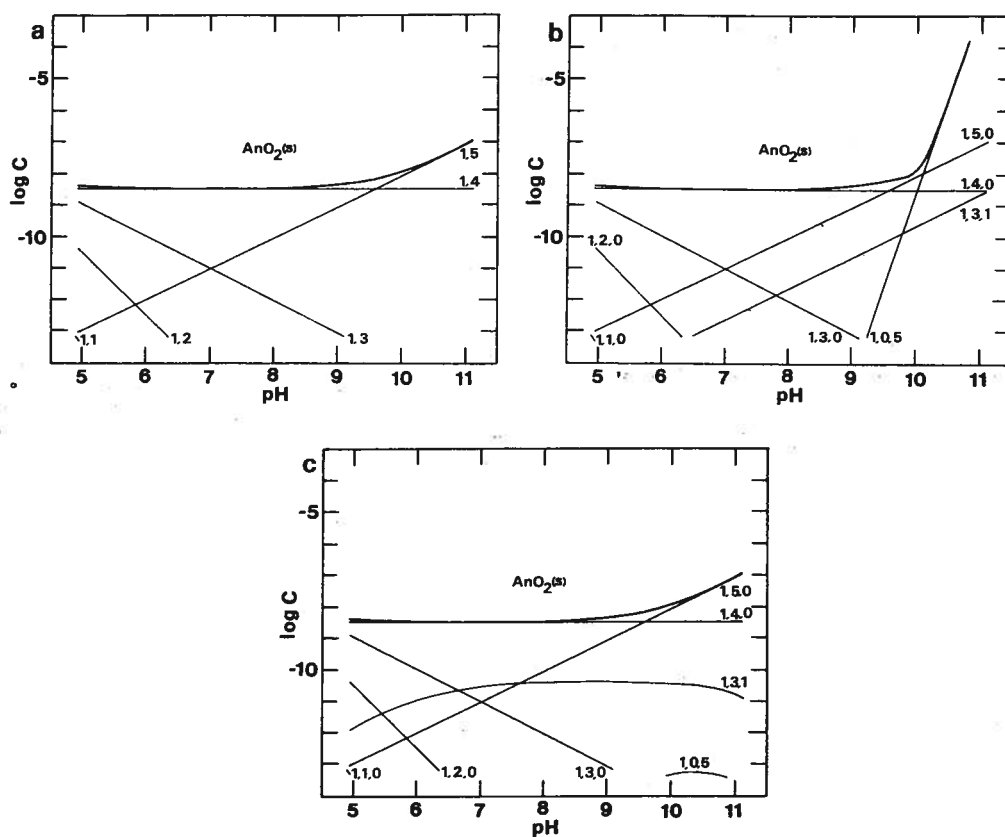


Fig. 2. An(IV) solubilities (M); $(\text{An}_x(\text{OH})_y(\text{CO}_3)_z)$; x, y, z
 a) $P(\text{CO}_2)=0$; b) $P(\text{CO}_2)=10^{-3.5}$ atm c) $p(\Sigma\text{CO}_3)=2.1$

The redox potential $E_h = 0.8 - 0.06\text{pH}$ (V) corresponds roughly to water in equilibrium with air. (Experimental values corresponding to $E_h = 0.73 - 0.055\text{pH}$ have been reported by Rai, Serne and Moore (1980), and a similar potential relationship is suggested by Garrels and Christ (1965) for oxic conditions). The redox potential $E_h = 0.2 - 0.06\text{pH}$ (V) could be representative of a system buffered by an Fe(III)(s)/Fe(II)(s)-equilibrium, simulating the conditions in an undisturbed groundwater in contact with ferrous minerals.

Total solubilities have been calculated as indicated in Table 8. The standard potentials (given in Table 7) are calculated from free energy data given by Fuger and Oetting (1976). The $E_{6,4}$ -value for uranium differs significantly from what is given in most other compilations. Original experimental values were recalculated by Fuger and Oetting, considering ionic strength effects.

The same constants, Table 3, have been used for all four of the actinides uranium, neptunium, plutonium and americium. For the hard complexes obtained

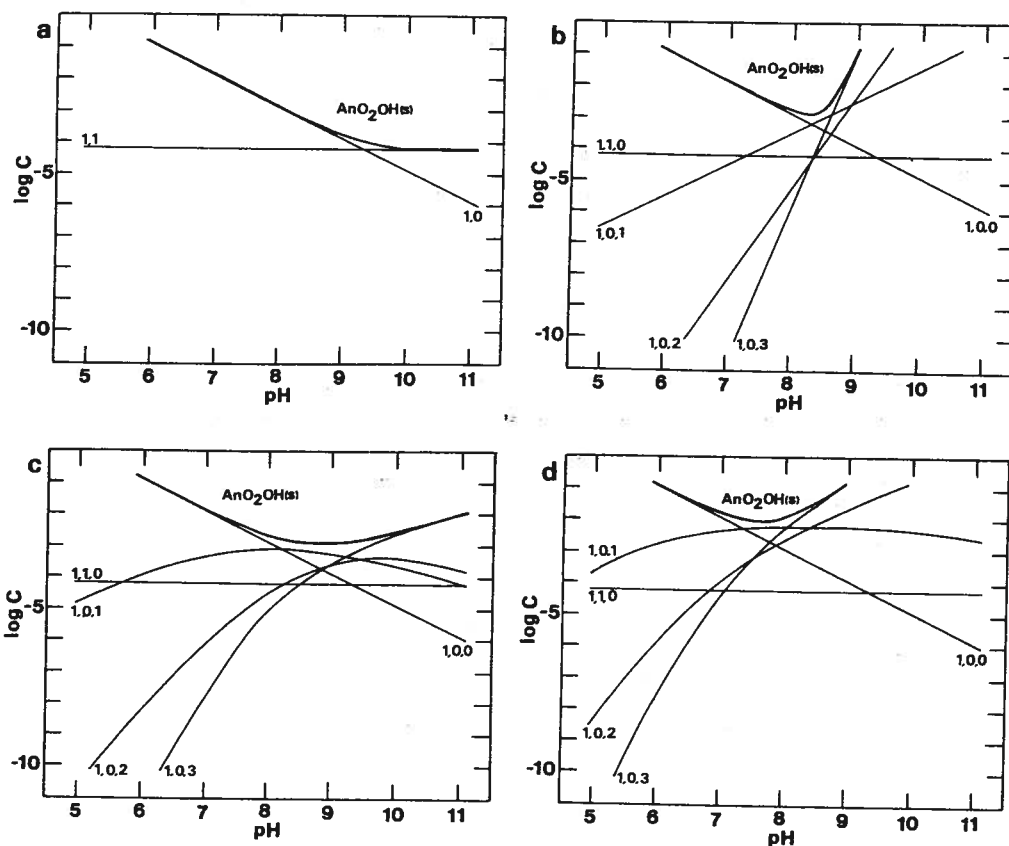


Fig. 3. An(V) solubilities (M); $((\text{AnO}_2)_x(\text{OH})_y(\text{CO}_3)_z)$; x, y, z
 a) $P(\text{CO}_2)=0$; b) $P(\text{CO}_2)=10^{-3.5}$ atm; c) $p(\Sigma\text{CO}_3)=3.3$; d) $p(\Sigma\text{CO}_3)=2.1$

between actinides and oxygen ligands the complex strength would largely be determined by the size and charge of the central atom. Thus, slightly increasing constants with decreasing radius (increasing atomic number) would be expected, similar to what is observed for the lanthanides. Not even for thoroughly studied systems (like An(IV)-OH⁻, An(VI)-CO₃²⁻ etc.) are the reported constants accurate enough to show significant differences and a trend in the series uranium, neptunium, plutonium and americium, although quite substantial differences between the individual systems (e.g. UO₂²⁺ and PuO₂²⁺) are reported in a few cases. Moreover, many of the formation constants for important species have to be estimated, leading to large uncertainties, which make any differentiation between the individual elements meaningless. Thus, since the purpose of this paper is to illustrate what species would dominate in solution under various conditions rather than giving absolute concentration data, it should be justified to use the same formation constants for all of the actinides for a given oxidation state and stoichiometry.

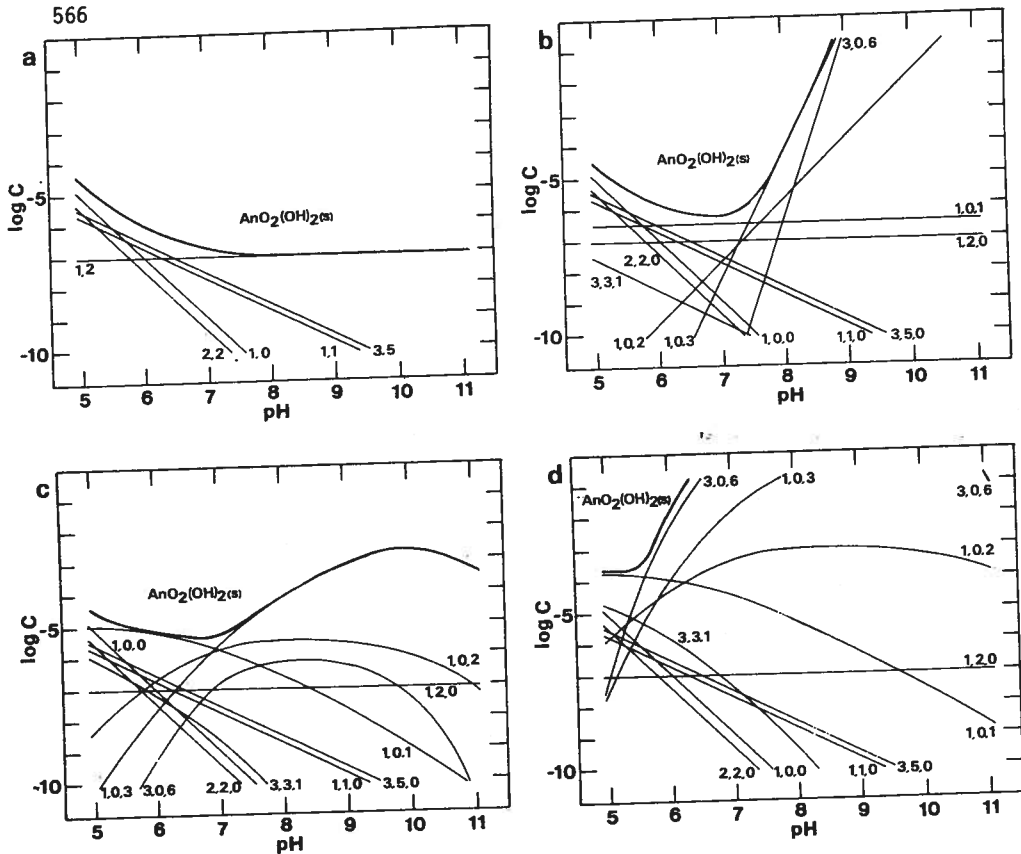


Fig. 4. An(VI) solubilities (M); $((\text{AnO}_2)_x(\text{OH})_y(\text{CO}_3)_z; x, y, z)$
 a) $p(\text{CO}_2)=0$; b) $p(\text{CO}_2)=10^{-3.5}$ atm; c) $p(\Sigma\text{CO}_3)=3.3$; d) $p(\Sigma\text{CO}_3)=2.1$

TABLE 7 Selected Standard Potentials (E^0) for Actinide
 Elements ($I=0$)

	E^0, V			
	U	Np	Pu	Am
$\text{An}^{4+} + e^- = \text{An}^{3+}$	-0.52	0.15	1.01	2.34
$\text{AnO}_2^+ + 4\text{H}^+ + e^- = \text{An}^{4+} + 2\text{H}_2\text{O}$	0.38	0.65	1.10	1.10
$\text{AnO}_2^{2+} + 4\text{H}^+ + 2e^- = \text{An}^{4+} + 2\text{H}_2\text{O}$	0.27	0.94	1.03	1.35
$\text{AnO}_2^{2+} + e^- = \text{AnO}_2^+$	0.16	1.23	0.96	1.60

TABLE 8 Equilibria Determining the Total Actinide Concentration C_{tot} in Aqueous Solutions at pH >4 (Only Hydroxides and Carbonates considered)

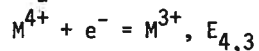
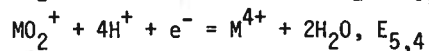
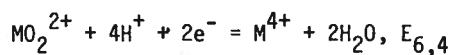
$$\begin{aligned}
 C_{\text{tot}} = & [M^{3+}] + [MOH^{2+}] + [M(OH)_2^+] + [M(OH)_3] + [M(OH)_4^-] + \\
 & + [MCO_3^+] + [M(CO_3)_2^-] + [M(CO_3)_3^{3-}] + \\
 & + [M(OH)_2^{2+}] + [M(OH)_3^+] + [M(OH)_4] + [M(OH)_5^-] + \\
 & + [M(CO_3)_5^{6-}] + [M(OH)_3CO_3^-(?)] + \\
 & + [MO_2^+] + [MO_2(OH)] + \\
 & + [MO_2CO_3^-] + [MO_2(CO_3)_2^{3-}] + [MO_2(CO_3)_3^{5-}] + \\
 & + [MO_2^{2+}] + [MO_2OH^+] + [MO_2(OH)_2] + [(MO_2)_2(OH)_2^{2+}] + [(MO_2)_3(OH)_5^+] + \\
 & + [MO_2CO_3] + [MO_2(CO_3)_2^{2-}] + [MO_2(CO_3)_3^{4-}] + [(MO_2)_3(CO_3)_6^{6-}]
 \end{aligned}$$

$$C_{\text{tot}} = \sum K_{x,y,z} [M]^x [OH]^y [CO_3]^z;$$

$$[OH] = \exp(\text{pH} - 14.0)$$

$$[CO_3] = \exp(2\text{pH} - 18.1 + \log P(\text{CO}_2)) \text{ (open system)}$$

Redox equilibria:



$$[M^{3+}] = [M^{4+}] \exp(E_{4,3} - E) / RT$$

$$[MO_2^+] = [M^{4+}] \exp(E - E_{5,4}) / RT + 4\text{pH}$$

$$[MO_2^{2+}] = [M^{4+}] \exp 2(E - E_{6,4}) / RT + 4\text{pH}$$

$$E = 0.8 - 0.059 \text{ pH (open system in contact with air)}$$

$$E = 0.20 - 0.059 \text{ pH (assessed for a reducing system).}$$

Solubility limiting species:

$$M_2CO_3(s) \quad [M^{3+}] = \exp(0.5 \log K_s + 1.5 \text{pCO}_3)$$

$$M(OH)_3(s) \quad [M^{3+}] = \exp(\log K_s + 42.0 - 3\text{pH})$$

$$MO_2(s) \quad [M^{4+}] = \exp(\log K_s + 56.0 - 4\text{pH})$$

$$MO_2OH(s) \quad [MO_2^+] = \exp(\log K_s + 14.0 - \text{pH})$$

$$MO_2(OH)_2(s) \quad [MO_2^{2+}] = \exp(\log K_s + 28.0 - 2\text{pH})$$

Uranium

The solubility limiting species in all the oxidic systems (a - d) is $\text{UO}_2(\text{OH})_2(\text{s})$, and hexavalent species dominate entirely over the whole pH-range 5 - 11 (Fig. 5). The overall solubility is drastically increased by the presence of carbonate above pH 6, even for the low-carbonate system (c). (C.f. Fig. 9). Carbonate species in solution are dominating already at pH above 5, leading to very high solubilities ($\text{UO}_2(\text{CO}_3)_3^{4-}$ and $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$) at pH above 7 - 8). Possibly other species than $\text{UO}_2(\text{OH})_2(\text{s})$ may be solubility limiting in such systems, e.g. like $\text{M}(\text{I})_4\text{UO}_2(\text{CO}_3)_3(\text{s})$, which have not been considered in Table 3.

Under reducing conditions (e, f) the solubility limiting solid phase would be $\text{UO}_2(\text{s})$. The somewhat surprising result that pentavalent UO_2^+ would dominate at pH below 6 - 7 is obtained and also that pentavalent carbonates might dominate at high pH and high carbonate concentrations. The conclusion that UO_2^+ may dominate in waters of intermediate or low redox potentials (+0.2 to -0.1 V) and pH-values of 1 - 7 has previously been drawn by Langmuir (1978). This is a result of using the revised $E_{6,4}$ -potential, Table 7, instead of the original somewhat higher value given in most compilations of actinide solution data, e.g. by Ahrlund, Liljenzin and Rydberg (1973). The formation of U(V)-species, as well as U(IV)-species, by electrolytic reduction of U(VI) in solution at high pH (above 10.5) and high carbonate concentration, has previously been indicated by Grenthe (1981). The formation of UO_2^+ under reducing conditions does not necessarily indicate a uranium release mechanism in nature since the concentration would be low, but is still of importance since UO_2^+ would interact with geologic media (sorption) to a less degree than e.g. tetra- or hexavalent hydrolysis products at the same pH (at low carbonate concentration). However, the existence of UO_2^+ under these conditions still has to be demonstrated experimentally.

On an intermediate pH-range, from pH 6 - 8 to 10 - 11, hexavalent carbonate species might dominate, even under reducing conditions, and tetravalent soluble species might be found only at low carbonate concentrations and in a narrow pH-range around 7 - 9.

The low solubility of many uranium compounds with common anions in nature can explain the formation of some of the principle ore minerals like uraninite (UO_2 to U_3O_8) and coffinite (USiO_4). The formation of secondary geochemical concentrations due to geological processes, including weathering and oxidation/reduction cycles, is well known through world wide prospecting for minable uranium deposits. Many such cycles have been analysed in detail, e.g. by Germanov and Panteleyev (1967), Paces (1969) and Dahl and Hagemeyer (1974) and others. A large amount of geologic observations suggest that tetravalent uranium remains immobile in the ground and is slowly mobilized if exposed to the atmosphere or oxygen/carbon dioxide-bearing natural waters.

Neptunium

The solubility limiting solid phase would be $\text{NpO}_2(\text{s})$ for all the systems (a - f), Fig. 6. Under oxidic conditions, however, pentavalent species would dominate entirely in solution. Carbonate species would dominate in carbonate systems above pH 7.5 - 8, leading to an increased solubility.

Under reducing conditions (e, f) only tetravalent species like $\text{Np}(\text{OH})_4$ (at pH between 5 and 9) would be expected. Pentavalent carbonate species might be of importance at high pH and very high carbonate concentrations (not found in nature). Thus, the overall solubility is drastically decreased under reducing conditions (c.f. Fig. 9).

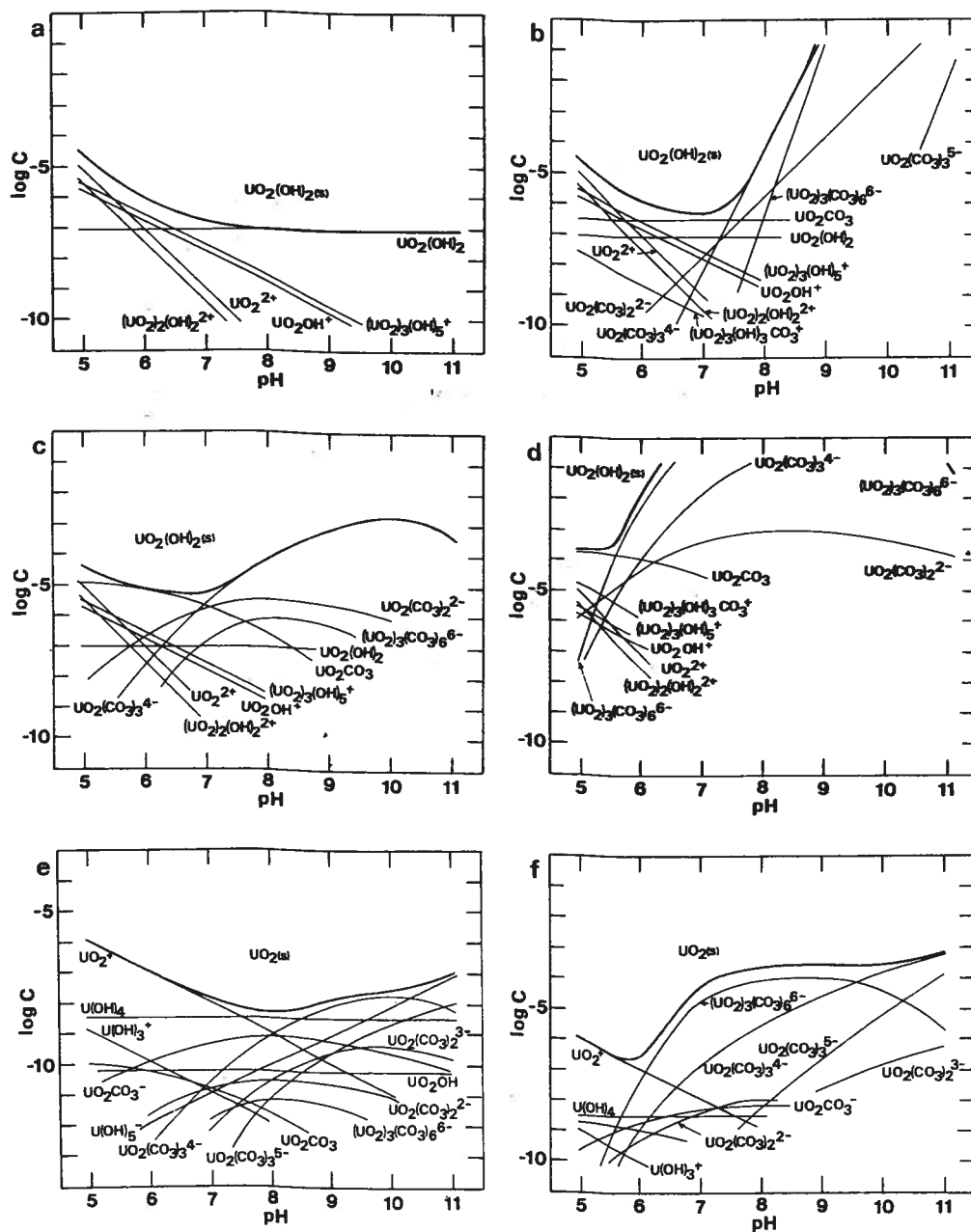


Fig. 5. Uranium solubilities (M) and species in solution
 a) $P(\text{CO}_2)=0$; b) $P(\text{CO}_2)=10^{-3.5}$ atm; c), e) $p(\Sigma\text{CO}_3)=3.3$; d), f) $p(\Sigma\text{CO}_3)=2.1$
 $E_h=0.8-0.06\text{pH}$ (a-d); $E_h=0.2-0.06\text{pH}$ (e, f)

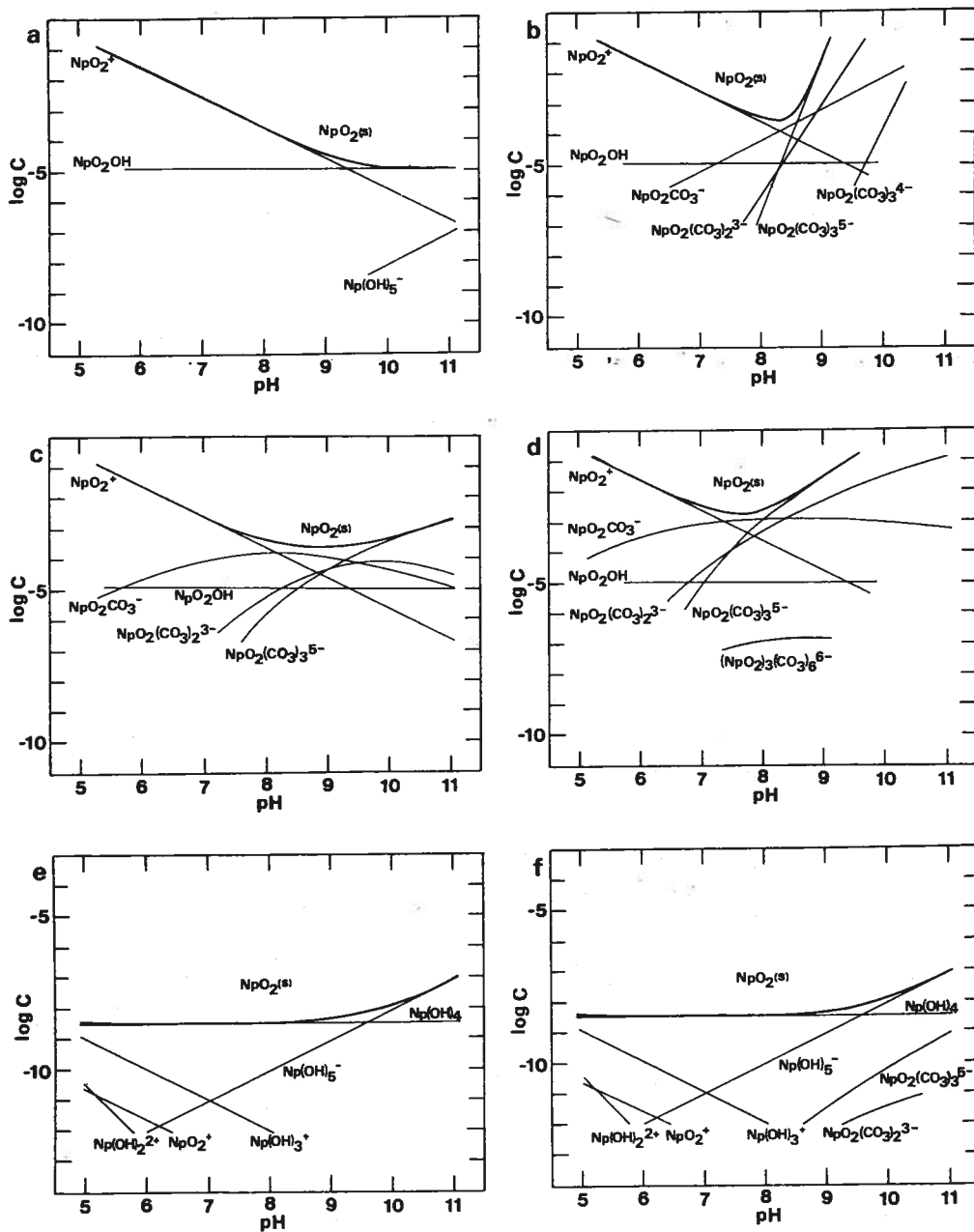


Fig. 6. Neptunium solubilities (M) and species in solution
 a) P(CO₂)=0; b) P(CO₂)=10^{-3.5} atm; c), e) p(ΣCO₃)=3.3; d), f) p(ΣCO₃)=2.1
 Eh=0.8-0.06pH (a-d); Eh=0.2-0.06pH (e, f)

Solubility measurements on $\text{NpO}_2(\text{s})$ under oxic conditions by Rai and Strickert (1980) have given much lower solubilities than indicated in Fig. 6, however after a fairly short time (54 d.).

Plutonium

Under oxic conditions (a - d), the solubility of plutonium is limited by $\text{PuO}_2(\text{s})$, giving low solubilities in the intermediate pH-range 6 - 9, with $\text{Pu}(\text{OH})_4$ as dominating species in solutions (Fig. 7). At pH below 5, the pentavalent PuO_2^+ would be the major species down to pH 4 or below, where Pu^{3+} would dominate. In the high pH-range (above 8.5 - 9), pentavalent carbonates ($\text{PuO}_2(\text{CO}_3)_3^{5-}$) would dominate in carbonate systems. Hexavalent species would not be expected to contribute significantly. At very high pH (above 11) and high carbonate concentrations a stabilization of the tetravalent state ($\text{Pu}(\text{CO}_3)_5^{6-}$) might be accomplished.

Under reducing conditions (e, f) trivalent species would dominate at pH below 9 - 10.5. The solubility limiting phase at pH below 7 - 8 would be $\text{Pu}_2(\text{CO}_3)_3(\text{s})$ rather than $\text{PuO}_2(\text{s})$. Thus, surprisingly enough, the overall solubility of plutonium would increase drastically under reducing conditions in the presence of carbonate and at pH below 8 - 9 (Fig. 9).

Several attempts have previously been made to characterize speciation and solubility of plutonium in environmental waters, e.g. by Andelman and Rozzell (1970), Polzer (1971), Silver (1971), Ames, Rai and Serne (1976), Rai and Serne (1977) and others. Rai and Serne predicted that $\text{PuO}_2(\text{s})$ would be comparatively stable in the pH and redox potential ranges found in terrestrial environments. Bondiotti and Reynolds (1976) observed that about 95% of the soluble plutonium in neutral carbonate solutions (0.1 mM total carbonate) containing $\text{PuO}_2(\text{s})$ as the solid phase was either Pu(V) or Pu(VI). It has also been found that Pu(V) is the dominating oxidation state in sea-water and that Pu(VI) is rapidly reduced to Pu(V) in lake water or bicarbonate solutions (Nelson, 1980). Solutions in equilibrium with $\text{Pu}(\text{OH})_4(\text{s})$ or $\text{PuO}_2(\text{s})$ contains PuO_2^+ as the dominating species under oxic conditions at pH below 6 - 7, according to recent experimental results by Rai, Serne and Swanson (1981). Also the possible reduction to the trivalent state in natural waters at low and intermediate pH-values has been indicated by Dahlman, Bondiotti and Eyman (1976).

The experimentally determined solubilities of $\text{PuO}_2(\text{s})$ at pH below 6 - 7 by Rai, Serne and Swanson (1981) are in fair agreement with the calculated curves (a - d, Fig. 7 and 9).

Americium

The only oxidation state that would be obtained under the present conditions (a - f) would be the trivalent state. In the absence of carbonate, the solubility is limited by $\text{Am}(\text{OH})_3(\text{s})$, Fig. 8.

In the presence of carbonate, the solubility would increase above pH 8.5 - 9, due to the formation of carbonate complexes that would dominate in solution from pH 7 - 7.5 and upwards. However, at pH below 8.5, the solubility would decrease in the carbonate system due to the formation of a new solubility limiting species $\text{Am}_2(\text{CO}_3)_3(\text{s})$ (below pH 9 - 10). (C.f. Fig. 9).

Experimental solubility data in the absence of carbon dioxide (Edelstein, Brown and Silva, 1980) and at low carbonate concentrations (Olofsson and coworkers, 1981) are in fair agreement with the calculated curves (a and c, Fig. 8 and 9).

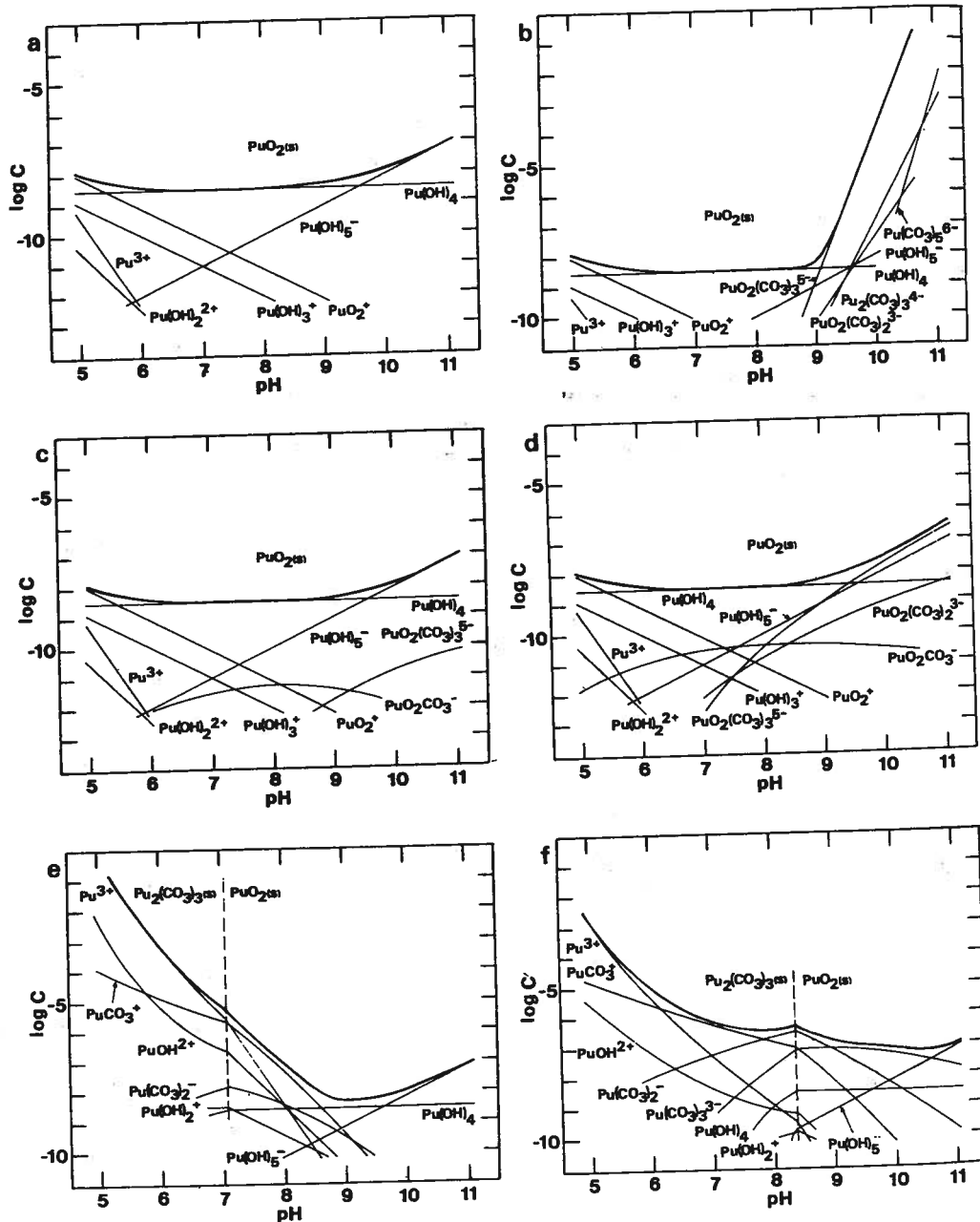


Fig. 7. Plutonium solubilities (M) and species in solution
 a) $p(\text{CO}_2) = 0$; b) $p(\text{CO}_2) = 10^{-3.5}$ atm; c), e) $p(\Sigma\text{CO}_3) = 3.3$; d), f) $p(\Sigma\text{CO}_3) = 2.1$
 $\text{Eh} = 0.8 - 0.06\text{pH}$ (a-d); $\text{Eh} = 0.2 - 0.06\text{pH}$ (e, f)

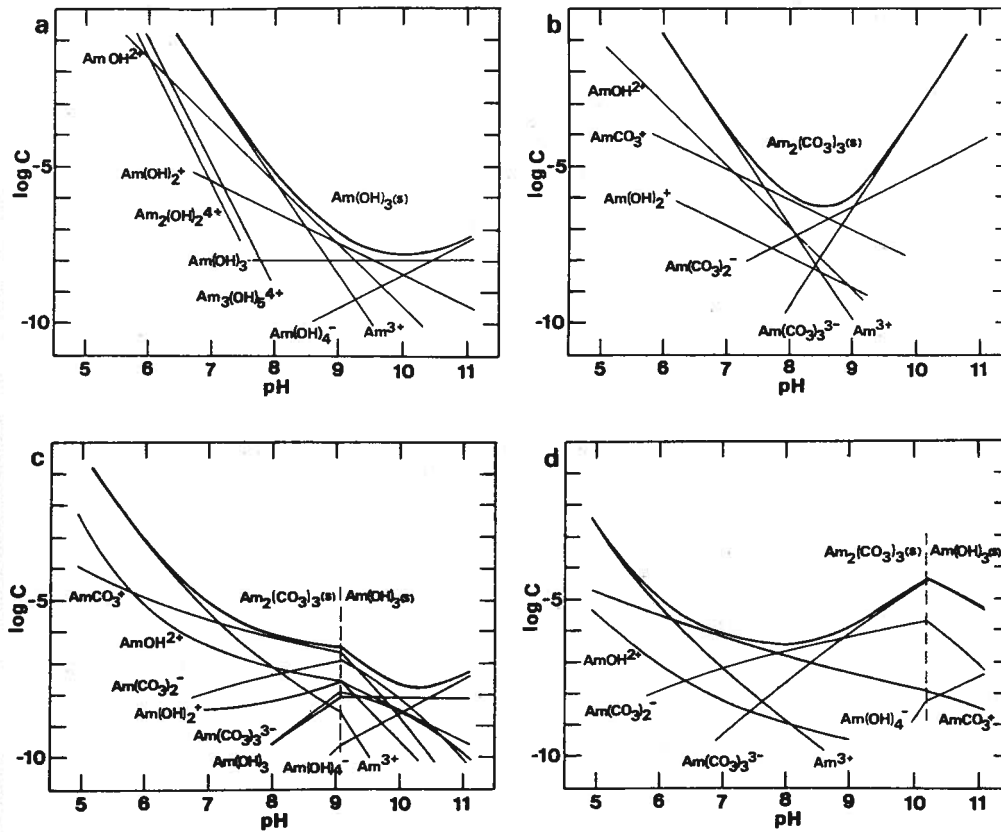


Fig. 8. Americium solubilities (M) and species in solution
 a) $P(\text{CO}_2)=0$; b) $P(\text{CO}_2)=10^{-3.5}$ atm; c) $p(\Sigma\text{CO}_3)=3.3$; d) $p(\Sigma\text{CO}_3)=2.1$
 $E_h=0.8-0.06\text{pH}$ and $E_h=0.2-0.06\text{pH}$

FORMATION OF COLLOIDS AND SORPTION PHENOMENA

Colloid formation

Many cations show a tendency to form polymeric hydroxides (c.f. Baes and Mesmer, 1976). This is particularly the case for tetravalent actinides. (C.f. the review by Johnson and Toth, 1978). Hydroxy colloids may be considered as highly polymerized hydroxy complexes with large residual charges, which prevent them from aggregation because of electrostatic repulsion. Thus, an apparent solubility which can exceed the solubility product by many orders of magnitude may be observed. However, since polymeric and colloidal species usually are formed under acidic or neutral conditions they possess a residual positive charge and would sorb strongly on e.g. exposed silicate or oxide surfaces, which would lead to a decreased concentration in solution not due to precipitation. These colloids should be considered as metastable forms and will slowly convert to thermodynamically stable species (Skytte Jensen, 1980).

A precipitation of the hydroxide of an actinide in the acidic pH-range, e.g. in a laboratory experiment, will for a tetravalent actinide lead to the formation of an amorphous solid of colloidal nature. (Precipitation in nature of e.g. uraninite at low temperatures also frequently gives minerals of a colloform nature). Most reported experimental studies of actinide polymerization have been done with tetravalent plutonium and at low pH (below 2) and high plutonium concentration (mM or larger) (see e.g. Costanzo, Biggers and Bell, 1973). Electron microscopy, electron diffraction and x-ray analysis on such colloidal plutonium hydroxide precipitates have shown that freshly precipitated material consists of essentially amorphous particles which, however, after aging become crystalline. These crystallites consist of $\text{PuO}_2(\text{s})$ (Lloyd and Haire, 1973, and Rai, Serne and Moore, 1981). Analogous to what is observed for thorium hydroxide precipitates, no formation of crystalline $\text{Pu}(\text{OH})_4(\text{s})$ has been indicated (Haire and coworkers, 1971). The oxide microcrystallites tend to further aggregate to form large colloidal particles, as have also been observed for thorium (Magini, Cabrini and Scibona, 1975).

The formation and stability of e.g. $\text{Pu}(\text{IV})$ -hydroxide colloids are very pH-dependent. Polymeric suspensions of $\text{Pu}(\text{IV})$ were found to be stable for several months at pH below 2, while more than 99% of the polymer or colloidal fraction settled in a matter of days at pH above 5 - 6 (Rai and Swanson, 1981). Also no evidences for the formation of $\text{Pu}(\text{IV})$ -polymers were found by the dissolution of $\text{Pu}(\text{IV})$ -hydroxide or PuO_2 in water at pH 3.4 - 7.7 (Rai, Serne and Moore, 1980). Experimentally determined solubilities of fresh $\text{Pu}(\text{IV})$ -polymer suspensions at intermediate pH were between the solubilities of amorphous $\text{Pu}(\text{OH})_4(\text{s})$ and crystalline $\text{PuO}_2(\text{s})$, after a short dissolution time (less than 45 d.) as reported by Rai and Swanson (1981). There were essentially no differences between pH-adjusted oversaturated and flocculated undersaturated polymers. A rapid and complete neutralization of acidic $\text{Pu}(\text{IV})$ -solutions is claimed to lead to a precipitation of essentially monomeric $\text{Pu}(\text{OH})_4$, according to Cleveland (1970).

Although it is a priori unlikely that polymeric species would be formed by the dissolution of a tetravalent metal oxide $\text{MO}_2(\text{s})$ in neutral solutions it can be possible that the crystallinity of e.g. $\text{PuO}_2(\text{s})$ is reduced due to alfa radiation leading to a solubility increase and formation of amorphous $\text{Pu}(\text{OH})_4$ or polymeric species.

Evidently the slow kinetics for the formation and alteration of colloidal hydroxide species, although not thermodynamically stable, as well as the large tendency for the colloids to sorb either on exposed macro surfaces or on other colloidal particles in solution (including dust particles, other metal hydroxides, silica from glass equipment, etc.) have largely prevented detailed characterization of colloidal actinide species. Much of the confusion concerning reported solubility products etc. for particularly tetravalent actinide hydroxides or oxides ($\text{An}(\text{OH})_4(\text{s})$ - $\text{AnO}_2(\text{s})$) can be ascribed to the difficulties in properly defining the solid phase as well as what is in true solution and colloidal form, respectively. Much reported solubility data probably do not represent equilibrium states, due to the slow kinetics of the hydroxide dissolution and transformation processes.

Sorption phenomena

Sorption of actinide species in true solution on exposed solid surfaces e.g. of oxides, silicates, etc. is another phenomenon that would lead to apparent solubilities not directly determined by a solubility product. The sorption of actinides in solution would be dependent on the composition of the solution (pH, ionic strength, complexing ions, redox potential; charge of species in solution).

concentration of the actinide, composition of the solid phase (e.g. presence of complexing counter ions in the solid lattice, ion exchange capacity) as well as experimental parameters such as contact time, surface properties of the solid etc. (see e.g. Allard, Beall and Krajewski, 1980, and others). Evidently these kind of reactions would largely influence experimental solubility studies and are other sources of errors. Also, sorption rather than true solubility limitations will determine concentrations in solution in many environmental aqueous systems, e.g. in groundwaters, where large solid surfaces are exposed. Adsorption of uranyl on inorganic and organic materials play a significant role in the transport and concentrating of uranium in nature. Much of the primary uraninite and coffinite are formed by reduction of uranyl species that are sorbed on to organic matter (Langmuir, 1978). Mechanisms and magnitudes of sorption phenomena are, however, beyond the scope of this paper and are not further discussed.

CONCLUSIONS

Although no distinction between formation constants for the various actinides has been made and a fairly arbitrary value for the important solubility product of $\text{AnO}_2(\text{s})$ was selected, some general conclusions can be drawn considering actinide solubilities and speciation in aqueous solutions representative of environmental waters.

1. The actinide solution chemistry in natural waters is largely determined by redox properties of the water, pH and the carbonate concentration.
2. The solubility of all the actinides except possibly for plutonium under oxic conditions is enhanced by the presence of carbonate (open system or closed with high carbonate concentration), not seldom several orders of magnitude in the environmental pH-range 8 - 9. Most of the dominating carbonate species in solution are negatively charged (dominating above pH 5 - 6 for uranium, 7.5 - 8 for neptunium, 8.5 - 9 for plutonium and 8 - 8.5 for americium). Thus, these species will have a high mobility in natural aquifers (low sorption on geologic media).
3. Previously given formation constants for especially the hexavalent complexes $\text{AnO}_2(\text{CO}_3)_3^{4-}$ and $(\text{AnO}_2)_3(\text{CO}_3)_6^{6-}$ are probably underestimated as well as the role of the corresponding pentavalent complex $\text{AnO}_2(\text{CO}_3)_3^{5-}$ and of $\text{An}(\text{III})\text{-CO}_3^{2-}$ -species.
4. Uranium would be hexavalent under oxic conditions. Under reducing conditions the solubility limiting species would be the tetravalent oxide $\text{UO}_2(\text{s})$, while species in solution would be pentavalent below pH 6 - 7, tetravalent at pH 7 - 9 (at low carbonate concentration only) and hexavalent above pH 6 - 8, depending on the carbonate concentration. Thus, even under reducing conditions, the uranium species in solution would be fairly mobile in geologic aquifers, although the solubility would be low.
5. Neptunium would be pentavalent under oxic conditions and tetravalent under reducing conditions. The solubility in both cases would be determined by the tetravalent oxide $\text{NpO}_2(\text{s})$.
6. Plutonium solubility would be limited by the tetravalent oxide $\text{PuO}_2(\text{s})$ under oxic conditions as well as reducing conditions at low carbonate-high pH. Species in solution under oxic conditions would be trivalent below pH 3 - 4, pentavalent at pH 4 - 6, tetravalent at pH 6 - 9 and pentavalent at pH above 8.5 - 9. Under reducing conditions trivalent species would dominate below pH 9 (mostly carbonates) with the solubility limiting solid phase $\text{Pu}_2(\text{CO}_3)_3(\text{s})$.

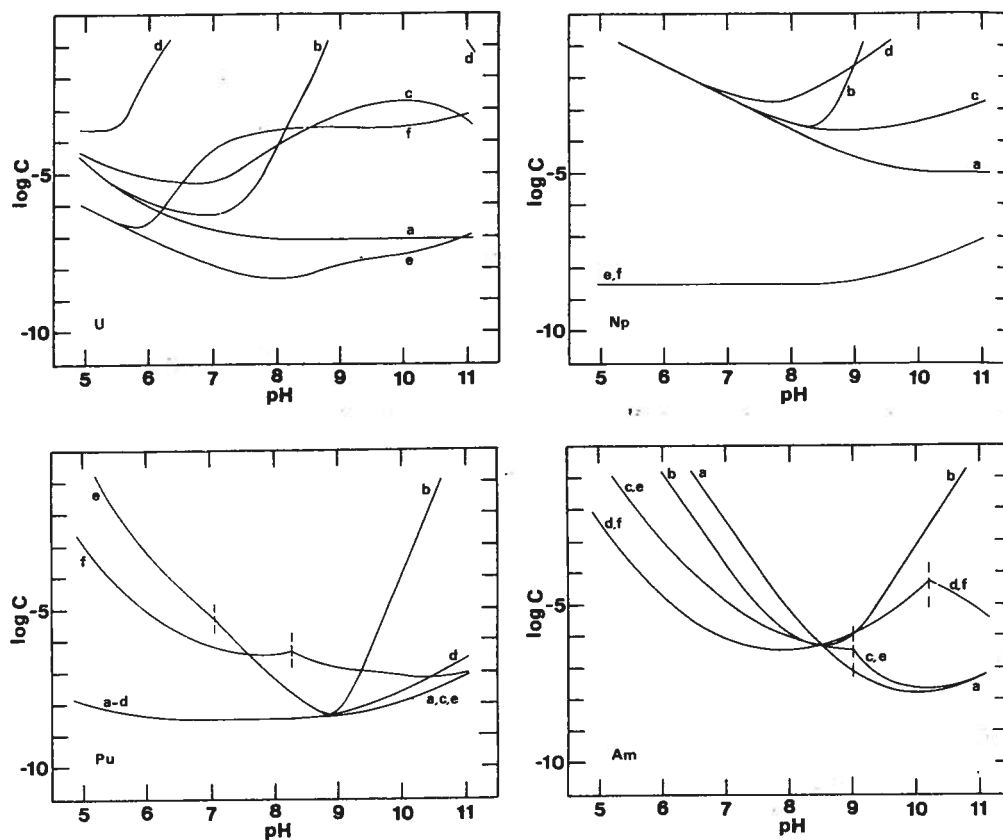


Fig. 9. Summary of actinide (U, Np, Pu, Am) solubilities (M)
 a) $P(\text{CO}_2)=0$; b) $P(\text{CO}_2)=10^{-3.5}$ atm; c),e) $p(\Sigma\text{CO}_3)=3.3$; d),f) $p(\Sigma\text{CO}_3)=2.1$
 $E_h=0.8-0.06\text{pH}$ (a-d); $E_h=0.2-0.06\text{pH}$ (e,f)

7. Americium would be trivalent under environmental conditions. Carbonates would dominate above pH 7.5 - 8 and $\text{Am}_2\text{CO}_3(\text{s})$ would be the solubility limiting solid phase except for high pH (above 9 - 10).

8. Species of crucial importance for the overall solubility are the tetravalent oxide $\text{AnO}_2(\text{s})$ as well as to some extent $\text{An}(\text{OH})_4$ - $\text{An}(\text{OH})_5^-$ as well as the penta- and hexavalent carbonate complexes. Solubility products and formation constants are not adequately known.

9. Conditions of formation, properties and stabilities of colloidal species and their role in e.g. actinide transport in nature, as well as sorption phenomena on low capacity solids of actinides in solution are not adequately characterized and understood.

As a general conclusion can be stated that accurate predictions of actinide solubility and behaviour in neutral solutions, especially in the environment, can

not yet be done solely based on available thermodynamic data. However, information in fair agreement with experimental observations can be obtained, using measured or estimated thermodynamic data, on species in solution and solubility limiting solid phases etc.

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