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## Actinide solution equilibria and solubilities in geologic systems

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# SUMMARY

Stability constants and solubility products for actinide (Th, U, Np, Pu and Am) hydroxide and carbonate complexes have been collected, and total solubilities have been calculated under conditions representative of deep granitic groundwaters (pH 7-9.5; high total carbonate concentration according to log $[CO_3]$ = 0.76pH-10.83; redox potentials corresponding to oxic systems, Eh$\gtrsim$0.8-0.06pH, and reducing systems, Eh<0.3-0.06pH). The solubility limiting species under reducing systems are $ThO_2(s)$, $UO_2(s)$, $NpO_2(s)$, $PuO_2(s)$ and $Am_2(CO_3)_3(s)$, respectively, and the corresponding calculated maximum solubilities are $3\times10^{-10}$ M (0.07 µg/l) for Th, $0.3-250\times10^{-10}$ M (0.01-6 µg/l) for U (depending on the carbonate concentration), $1\times10^{-10}$ M (0.03 µg/l) for Np, $1-3\times10^{-9}$ M (0.2-0.7 µg/l) for Pu and $0.6-2\times10^{-7}$ M (15-50 µg/l) for Am. The calculated solubilities for U are in fair agreement with observed uranium concentrations in natural deep groundwaters. Hexavalent uranium carbonate species would dominate in solution except under highly reducing conditions (Eh<0.2-0.06pH) and low total carbonate concentrations. Under oxic conditions the concentrations of U and Np would be larger than $10^{-5}-10^{-6}$ M (mg/l-level).

TABLE OF CONTENTS                                          Page

## 1. INTRODUCTION

Long-lived actinides, such as $^{237}$Np, $^{239}$Pu, $^{240}$Pu, $^{241}$Am and $^{243}$Am as well as the daughter products $^{226}$Ra and $^{230}$Th (from $^{238}$U), $^{229}$Th (from $^{241}$Am-$^{237}$Np) and $^{231}$Pa (from $^{235}$U) will largely dominate the biological hazards from the nuclear fuel cycle, e.g. from spent fuel or reprocessing waste, from some 100 years after the discharge from a nuclear reactor and onwards. The actinide concentration levels and mobility in natural aquifers would largely be related to the chemical behaviour in terms of speciation (formation of complexes) and solubility. Thus, it is essential to characterize and model the chemical behaviour of the individual actinides in aqueous systems representative of natural waters.

In this report some calculations of actinide solubilities and speciation in deep groundwaters are presented (for Th, U, Np, Pu and Am), considering pH, redox potentials and carbonate concentrations of these waters. Necessary input data (complex formation constants) are either taken from the literature (c.f. Appendix 1) or determined within the current Swedish nuclear waste program. Most of the calculations and conclusions in this report have previously been presented elsewhere, particularly in ref. 1.

## 2. ACTINIDE SOLUTION CHEMISTRY

### 2.1. General properties and oxidation states

The chemistry of the actinides (here denoted by An) in solution reflects the peculiar electron configuration of these elements, where the 5f and 6d electron shells are of similar energy (2). Since the 5f orbitals are less well shielded than the 4f orbitals of the lanthanides they are prone to participate in bonding.

In the early part of the series (Th, Pa, U, Np, Pu, Am) the elements exhibit multiple oxidation states (from 3 to 7), but

beyond plutonium (Am, Cm, etc.) the lower oxidation states (2 to 4) are predominant.

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 both U(IV) and U(VI) can exist in aqueous systems, and under certain conditions also 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 easily oxidized and Pu(V) tend to disproportionate. Both neptunium and plutonium can also exist as the easily reduced Np(VII) and Pu(VII). Americium is most stable as Am(III), although the easily reduced Am(VI) and Am(V), which tends to disproportionate, also can exist in aqueous systems, as well as Am(IV) in the presence of high concentrations of strong complexing agents.

The non-complexed ions normally formed at the oxidation states III to VI are $An^{3+}$, $An^{4+}$, $AnO_2^+$ and $AnO_2^{2+}$, respectively.

## 2.2. Complex formation with inorganic ligands

The actinides are generally classified as hard (3). Strong complexes are formed with the fluoride ion $F^-$ as well as with oxygen containing ligands (oxide, $O^{2-}$; hydroxide, $OH^-$; carbonate, $CO_3^{2-}$; phosphate, $PO_4^{3-}$; to some extent sulfate, $SO_4^{2-}$). The affinity for sulfur (e.g. sulfide, $S^{2-}$) or the heavy halides ($Cl^-$, $Br^-$, $I^-$) is weak. The complex strength generally increases in the order $AnO_2^+ < An^{3+} \lesssim AnO_2^{2+} < An^{4+}$, i.e. with the effective charge of the acceptor atom. The complexes are generally formed in endothermic reactions. The high stability is due to a large gain of entropy which balances or more than compensates for the unfavourable enthalpy change.

There are several recent compilations of thermodynamic data for actinide complex formation (c.f. Appendix 1). Ranges of reported formation constants and solubility products for inorganic complexes of interest are given in Table 1 and 2, which indicate the relative importance of complex formation with $OH^-$, $CO_3^{2-}$ and phosphates in particular.

## 2.2.1. Hydroxides

Much of the information on actinide hydrolysis stems from fairly early work (c.f. reviews in ref. 4 and 5). Hydrolysis products of actinides and similar elements that appear to be identified and well characterized are given in Table 3.

Similar hydrolysis products and complex formation constants would be expected for trivalent actinides and lanthanides. However, most of the published data for e.g. $AmOH^{2+}$ and $CmOH^{2+}$ (obtained by solvent extraction technique and electromigration techniques) appear to be too high, in comparison with the corresponding constants for the lanthanides. No similar large differences e.g. between lanthanide and actinide fluorides have been reported. Calculations based on constants for $Nd^{3+}$ as a model for the trivalent actinides seem to be in a fair agreement with measured solubility curves. Several recent papers indicate the expected similar hydrolysis behaviour for trivalent actindes and lanthanides (6-8).

All three of the (1,1)-, (1,2)- and (1,3)-complexes are assumed to exist, as well as an anionic species $An(OH)_4^-$, as has been reported for the lanthanides. Anionic species have in fact been observed at high pH for $Am^{3+}$, but it is not clear whether those species are hydroxides or carbonates (1). Just as for the hydrolysis constants similar solubility products would be expected for the trivalent lanthanide and actinide hydroxides.

For the tetravalent actinides reliable hydrolysis constants are available for the (1,1)-complex only. Measured data for $Np^{4+}$ and

Table 1    Ranges of reported complex formation constants for
inorganic (1,1)-complex (I = 0, 25°C) (c.f. Appendix 1)

| Ligands | $logK_1$ | | | |
|---|---|---|---|---|
| | $An^{3+}$ | $An^{4+}$ [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 2    Ranges of reported solubility products for $An_xL_y(s)$
(I = 0, 25°C) (c.f. Appendix 1)

| Ligand | $(x,y)$ $-logK_s$ | | | |
|---|---|---|---|---|
| | $An^{3+}$ | $An^{4+}$ [c] | $AnO_2^+$ | $AnO_2^{2+}$ |
| $OH^-$ | (1,3) | (1,4) | (1,1) | (1,2) |
| | 22.0-24.5[a] | >46[b] | 8.5-9.3 | 22.2-24.5 |
| $CO_3^{2-}$ | (2,3) | | | (1,1) |
| | 30.6-33.0[a] | | | 10.5-14.5 |
| $HPO_4^{2-}$ | | (1,2) | | (1,1) |
| | | 26.8-27-7 | | 10.7-12.6 |
| $PO_4^{3-}$ | (1,1) | (3,4) | | |
| | 23(?) | <57(?) | | |
| $F^-$ | (1,3) | (1,4) | | |
| | 10.2-15 | 18.5-24 | | |

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

$Pu^{4+}$ seem to have yielded too high constants, partly because of poor control of the oxidation state (for Pu). Reported estimated constants for the (1,2)-, (1,3)- and (1,4)-complexes (e.g. in ref. 5) are largely based on some early solubility measurements on $U(OH)_4(s)$, which indicate the presence of $U(OH)_5^-$. More recent data on this system give log K = -5.8 - log $K_s$ for the (1,5)-complex (9), which would in fact indicate lower values for the formation constants for the (1,2)-, (1,3)- and (1,4)-complexes as well as for the (1,5)-complex than given in ref. 5.

Despite the fact that the corresponding (1,5)-complex has not been identified for $Th^{4+}$, it is assumed that such a complex might exist for $U^{4+}$, $Np^{4+}$ and $Pu^{4+}$, just as indicated in ref. 9 (for $U^{4+}$). The existence of an anionic (1,5)-complex has been claimed for $Zr^{4+}$.

Quite few experimental solubility measurements have been made on crystalline $AnO_2(s)$ under well-defined conditions. From thermo-chemical data or from lattice considerations values of the solubility product of log $K_s$ = -60 or below have been suggested (c.f. Appendix 1). However, experimental studies have indicated values as high as log $K_s$ = -46 (for $Pu(OH)_4(s)$). Recent measurements have given a value of log $K_s$ = -52, as estimated from the overall solubility of $PuO_2(s)$ (10). Evidently, the observed solubility of a tetravalent oxide $AnO_2(s)$ can vary substantially depending on the crystallinity of the product, presence of lattice defects, presence of impurities, existence of various modifications, etc. In a recent study log $K_s$ = -55.8 is given for $UO_2(s)$ (11), and subsequent measurements have given even lower values (log $K_s$ = -56.6) (12).

For hexavalent uranium all of the (1,1)-, (1,2)- and probably (1,3)-complexes exist. However, even traces of carbon dioxide in the system at high pH may lead to the formation of carbonate complexes. Thus, a poor carbon dioxide control would explain the observed amphoteric behaviour and would largely prevent any evaluation of stability constants for higher hydroxy complexes.

Similar penta- and hexavalent species can be assumed, at least for the (1,1)-complex.

Polymeric species with well defined stoichiometry and in thermodynamic equilibrium with monomeric species or with a solid phase would not be expected in neutral or basic solutions, except possibly for the hexavalent state (13). However, in the low pH-range the (2,2)- and (3,5)-complexes seem to exist for tri- and hexavalent actinides as well as the (2,2)-, (4,8)- and (6,15)-complex and possibly others for the tetravalent state (5).

### 2.2.2. Carbonates

Carbonate complexes with actinides and lanthanides that appear to be identified and well characterized are summarized in Table 4.

For the trivalent state data are available both for lanthanides as well as actinides (Am). All the (1,1)-, (1,2)- and (1,3)-complexes seem to exist. Solubility products have been determined for some lanthanide complexes. The evidences for mixed hydroxy-carbonate complexes, however, are not convincing.

The proposed stability of a tetravalent $PuCO_3^{2+}$-species reported in the literature seems most likely to be based on incorrect calculations, and instead the possible existence of mixed hydroxy-carbonate complexes of the type $(An(IV)(OH)_xCO_3^{2-x}$ has been suggested (14). Convincing evidences that the complex $U(CO_3)_5^{6-}$ exists have been presented (11). It has also been shown, that tetravalent Ce, Pr, Tb, and Am can be achieved and stabilized in the presence of high carbonate concentrations (15).

The hexavalent state has been thoroughly studied, and the existence of the (1,1)-, (1,2)- and (1,3)- as well as the (3,6)-carbonate complexes is well known. For hexavalent uranium and plutonium some mixed hydroxy-carbonate-species have been proposed under suitable pH-conditions (16-18).

Table 3   Identified hydroxide species ($\underline{1}$)

$M^{3+}$     $MOH^{2+}$, $M(OH)_4^-(?)$ (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)

$M^{3+}$     $MCO_3^+$, $M(CO_3)_2^-$, $M(CO_3)_3^{3-}$, $M(CO_3)_4^{5-}$ (lanthanides)
$M_2(CO_3)_2^{2+}$ (La)
$MOH(CO_3)_2^{2-}$ (Eu)[a]

$M^{4+}$     $M(CO_3)_5^{6-}$ (U)
$M(OH)_xCO_3^{2-x}(?)$ (Pu)[a]

$MO_2^+$     $MO_2CO_3^-$, $MO_2(CO_3)_2^{3-}$, $MO_2(CO_3)_3^{5-}$ (Np)

$MO_2^{2+}$     $MO_2CO_3$, $MO_2(CO_3)_2^{2-}$, $MO_2(CO_3)_3^{4-}$ (U,Pu)
$(MO_2)_3(CO_3)_6^{6-}$ (U,Pu)
$MO_2(OH)_3CO_3^{3-}$, $(MO_2)_2(OH)_3CO_3^-$, $(MO_2)_3(OH)_3CO_3^+$ (U)

[a] Tentative; exact composition not known.

Just as for the hexavalent state fairly strong <u>pentavalent</u> carbonates would be expected, at least the (1,1)-complex, and most likely also the (1,2)- and (1,3)-complex (<u>19</u>,<u>20</u>).

### 2.2.3. <u>Other complexes</u>

Data on the formation of other actinide complexes are summarized in Table 1 and 2 as well as in Appendix 1 and are not further discussed.

### 2.3. <u>Redox equilibria</u>

Selected standard potentials for equilibria between actinides in different oxidation states are given in Table 5. The values in ref <u>21</u> have been used except the potential for the U(VI)/U(V)- couple, where the previously suggested value has been adopted (<u>2</u>), in agreement with recent measurements (<u>22</u>). The uncertainty is substantial (as high 0.05 V for some systems) for many of the reactions of environmental importance.

### 3.  ACTINIDE SOLUBILITIES AND SPECIATION IN NATURAL WATERS

A first step in analyzing actinide solubilities and speciation would be to describe the composition of a system in <u>equilibrium</u>, on the basis of thermodynamic data. Also <u>kinetic</u> information, describing non-equilibrium conditions, would be required to explain observed solution properties. It is imperative that all relevant species and equilibria are included in the model. This means that it is justified, and sometimes necessary, to include extrapolated or even estimated data for species that are likely to be formed, considering known properties of similar elements, even if these species have not even been firmly verified experi- mentally. For the same reason it can sometimes be better to assess an estimated formation constant, based on analogy with a similar element or compound, than to use a poorly determined value that is based on experimental results. There are numerous published data from experiments with poor control of important

chemical parameters, or based on misinterpretations or erroneous calculations. Thus, the calculations presented here are based on a mixture of accurately measured thermodynamic constants and extrapolations, or estimations in cases where reliable data are completely lacking.

## 3.1.  Conditions in natural waters

Natural waters contain a number of inorganic complexing agents such as $OH^-$, $HCO_3^- - CO_3^{2-}$, $H_2PO_4^- - HPO_4^{2-} - PO_4^{3-}$, $F^-$, $SO_4^2$ and $Cl^-$. The expected concentrations in e.g. non-saline groundwaters would usually 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 0.05-1 mM for $Cl^-$. Moreover, there are complexing organics (humic acids, fulvic acids, etc.) in natural waters. The role of these organics is discussed elsewhere ([23]).

The concentrations of the complexing anions as well as the dominating cations in surface waters and groundwaters representative of Scandinavian granitic environments are summarized in Table 6 ([24],[25]).

## 3.2.  Actinide solubilities and speciation

Considering the anion concentrations in deep groundwaters (c.f. Table 6) and the stability constants for actinide complexes with these ligands (c.f. Appendix 1), it is evident that actinide solution chemistry in environmental waters is almost entirely defined by

o    the redoxpotential, determining the oxidation state
o    the pH, determining the degree of hydrolysis, and
o    the total carbonate concentration, defining carbonate complexation.

Despite the fact that fluorides and possibly phosphates may significantly affect the overall solubility and speciation in certain waters, these conditions would not be expected in e.g.

Table 5   Selected standard potentials ($E^O$) ($I = 0$, $25^O C$)

| | $E^O$, 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 |

Table 6   Composition (mg/l) of some various natural waters
(24,25)

| | 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.

deep undisturbed groundwaters in crystalline rock, and only the three parameters the redoxpotential, pH and the carbonate concentration will be further considered.

Selected formation constants and solubility products for actinide hydroxide and carbonate complexes are given in Table 7.

Considering the uncertainties in published stability constants, as well as in the extrapolated constants (c.f. Appendix 1), which usually correspond to a minimum of a factor of 2-3 and more often one order of magnitude or more for many of the high complexes, a set of constants (hydrolysis and carbonate complexation) could in fact be assessed which would be valid for any of the actinides U, Np, Pu or Am in the same oxidation states. Such a model system has previously been discussed (1). In the subsequent discussion of the individual actinides, constants from Table 5 and 7 have been used. The total solubility and speciation etc. are derived from the equations in Table 8. The concentrations are set equal to the activities (unity activity coefficients). The uncertainty introduced by this is small compared to the errors resulting from uncertainties in the thermodynamic data.

In the calculations of actinide solubilities the following limiting conditions have been assumed:
(1)  pH: 7-9.5
(2)  Redoxpotential according to Fig. 1:
     $Eh = 0.8-0.06pH$ (oxic system; the potential set by the oxygen in the air) (1)
     $Eh = 0.24-0.06pH\pm0.06$ (reducing system; the potential set by Fe(III)/Fe(II)-equilibria. This would be representative of a reducing granitic environment, (25,26).
(3)  Total $CO_3^{2-}$-concentration according to Fig. 2:
     $\log [CO_3^{2-}] = 0.76pH-10.83$
     This would be representative of a deep groundwater with a high carbonate concentration (27).

Table 7    Selected formation constants and solubility products for actinide hydroxide and carbonate complexes ($I=0$, $25^{\circ}C$).

$$xAn+yOH+zCO_3=An_x(OH)_y(CO_3)_z,$$
$$K=[An_x(OH)_y(CO_3)_z]/[An]^x[OH]^y[CO_3]^z;$$

$$xAn+yOH+zCO_3=An_x(OH)_y(CO_3)_z(s),$$
$$K=[An]^x[OH]^y[CO_3]^z$$
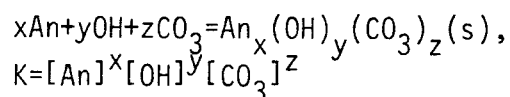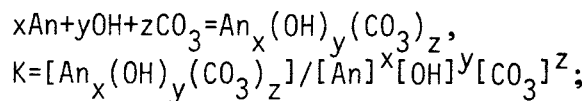
Values within paranthesis are estimated or extrapolated.

| xyz | An$^{3+}$ | | An$^{4+}$ | | | | AnO$_2{}^+$ | | | 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.

Table 8   Equilibria determining total actinide concentrations
($C_{tot}$) in aqueous solutions (pH 7-9.5; only hydroxides
and carbonates considered)

Significant species in solution; $An_x(OH)_y(CO_3)_z$;
complex equilibria:

$C_{tot}$ = $[An^{3+}]+[AnOH^{2+}]+[An(OH)_2^+]+[An(OH)_3]+[An(OH)_4^-]+$

$+ [AnCO_3^+]+[An(CO_3)_2^-]+[An(CO_3)_3^{3-}]+$

$+ [An(OH)_2^{2+}]+[An(OH)_3^+]+[An(OH)_4]+[An(OH)_5^-]+$

$+ [An(CO_3)_5^{6-}]+[An(OH)_3CO_3](?) +$

$+ [AnO_2^+]+[AnO_2(OH)]+$

$+ [AnO_2CO_3^-]+[AnO_2(CO_3)_2^{3-}]+[AnO_2(CO_3)_3^{5-}]$

$+ [AnO_2^{2+}]+[AnO_2OH^+]+[AnO_2(OH)_2]+[(AnO_2)_2(OH)_2^{2+}]+[(AnO_2)_3(OH)_5^+]+$

$+ [AnO_2CO_3]+[AnO_2(CO_3)_2^{2-}]+[AnO_2(CO_3)_3^{4-}]+[(AnO_2)_3(CO_3)_6^{6-}]$

$C_{tot}$ = $\Sigma K_{x,y,z}[An]^x[OH]^y[CO_3]^z$;

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

$[CO_3^{2-}] = \exp(0.76pH - 10.83)$ (closed system saturated with

$CaCO_3(s)$).

Redox equilibria:

$AnO_2^{2+} + 4H^+ + 2e^- = An^{4+} + 2H_2O$, $E_{6,4}$

$AnO_2^+ + 4H^+ + e^- = An^{4+} + 2H_2O$, $E_{5,4}$

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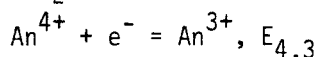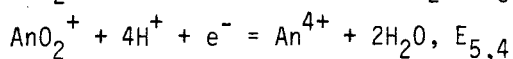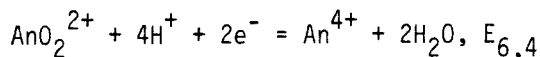
$[An^{3+}] = An^{4+} \exp(E_{4,3}-E)/RT$

$[AnO_2^+] - An^{4+} \exp(E-E_{5,4})/RT+4pH$

$[AnO_2^{2+}] = An^{4+} \exp 2(E-E_{6,4})/RT+4pH$

$E = 0.8 - 0.06$ pH (open system in contact with air)

$E = 0.24 - 0.06$ pH (assessed for a system defined by an

Fe(II)/Fe(III)-equilibrium)

Solubility limiting species:

$An_2CO_3(s)$     $[An^{3+}]= \exp(0.5\log K_s - 1.5\log CO_3 )$

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

$AnO_2(s)$     $[An^{4+}]= \exp(\log K_s + 56.0-4pH)$

$AnO_2OH(s)$     $[AnO_2^+]= \exp(\log K_s + 14.0-pH)$

$AnO_2(OH)_2(s)$     $[AnO_2^{2+}]= \exp(\log K_s + 28.0-2pH)$
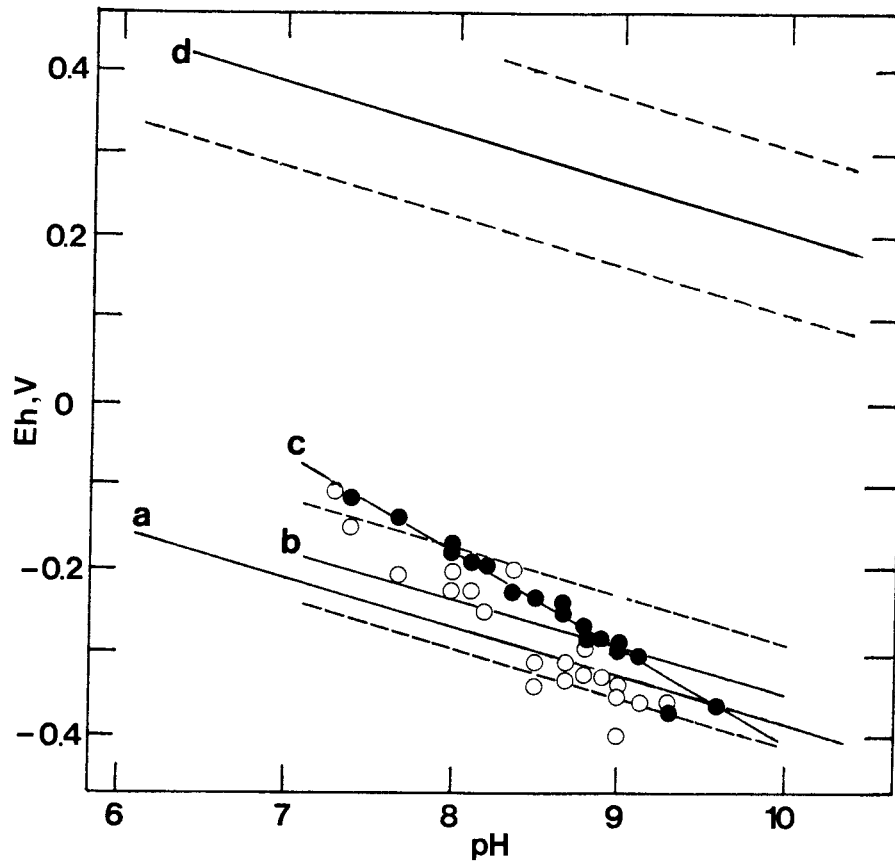
Figure 1    Calculated Eh/pH-values for deep granitic ground-
            waters (25,26). The experimental points represent
            calculated Eh-values based on measured Fe(II)-con-
            centrations and assuming equilibrium with goethite
            or goethite/siderite

            (a) Eh = 0.21-0.06pH; $Fe_2O_3/Fe_3O_4$-equilibrium

            (b) Eh = 0.24-0.06pH$\pm$0.06 (V)

            (c) Eh = 0.68-0.115pH (V)

            (d) Eh = 0.8-0.06pH$\pm$0.1 (V); open system in contact
                with air.
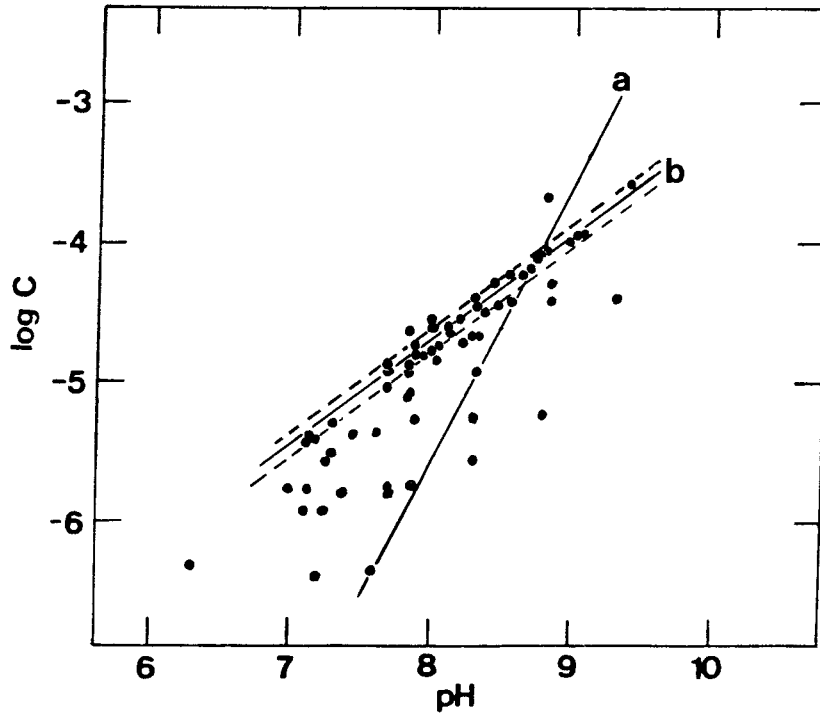
Figure 2    Measured $CO_3^{2-}$-concentrations and corresponding
pH-values in deep granitic groundwaters (27).
(a) log $[CO_3]$ = 2pH-18.1 + logP($CO_2$); open system in
equilibrium with air
(b) log $[CO_3]$ = 0.76pH-10.83$\pm$0.08; closed system,
saturation with respect to $CaCO_3$(s).

Thus, these conditions would roughly represent the range of
conditions in terms of pH, Eh and carbonate concentrations to be
expected in deep granitic groundwaters.

3.2.1. Thorium

Thorium exists solely in the tetravalent state in aqueous solu-
tions. The solubility limiting solid phase is $ThO_2$(s). Dominating
species in solution would be Th(OH)$_4$, Fig. 3. The solubility
would not be affected by the carbonate concentration within the
concentration ranges of granitic groundwaters.
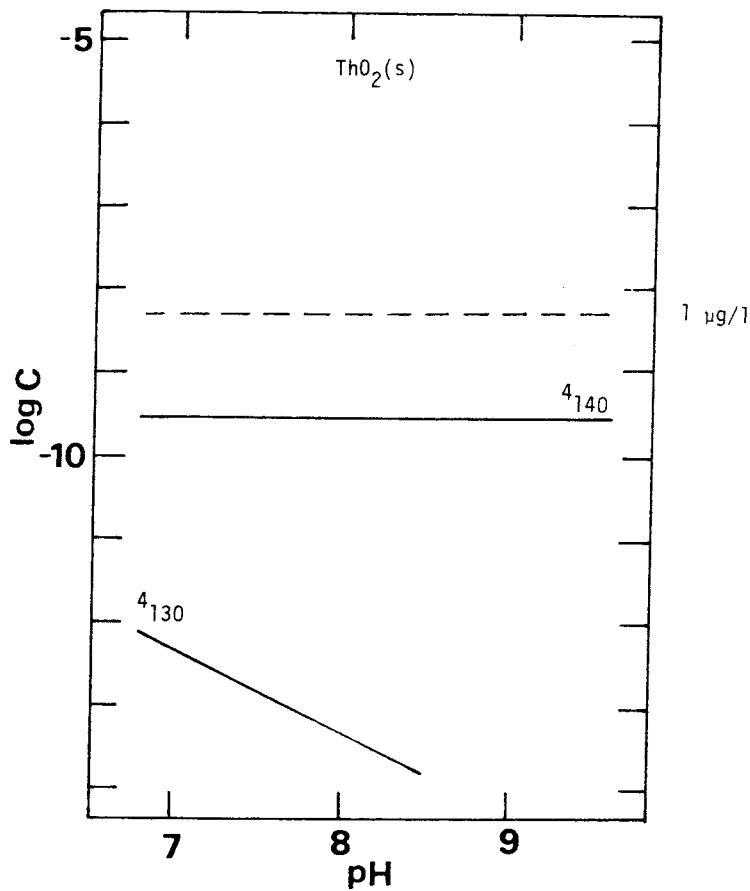
Figure 3    Calculated thorium solubility
            (Reducing or oxic system)

## 3.2.2. Uranium

Under strongly reducing conditions the solubility limiting solid phase would be $UO_2(s)$, with $U(OH)_4$ and possibly $U(OH)_5^-$ as dominating species in solution at low total carbonate concentrations, Fig. 4. At high carbonate concentrations or only mildly reducing conditions, the hexavalent species $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ would be the dominating species in solution, still in equilibrium with the solid tetravalent oxide. A dominance of the pentavalent $UO_2^+$ is possible, however, at pH far below the range 7-9.5 expected for deep groundwaters.
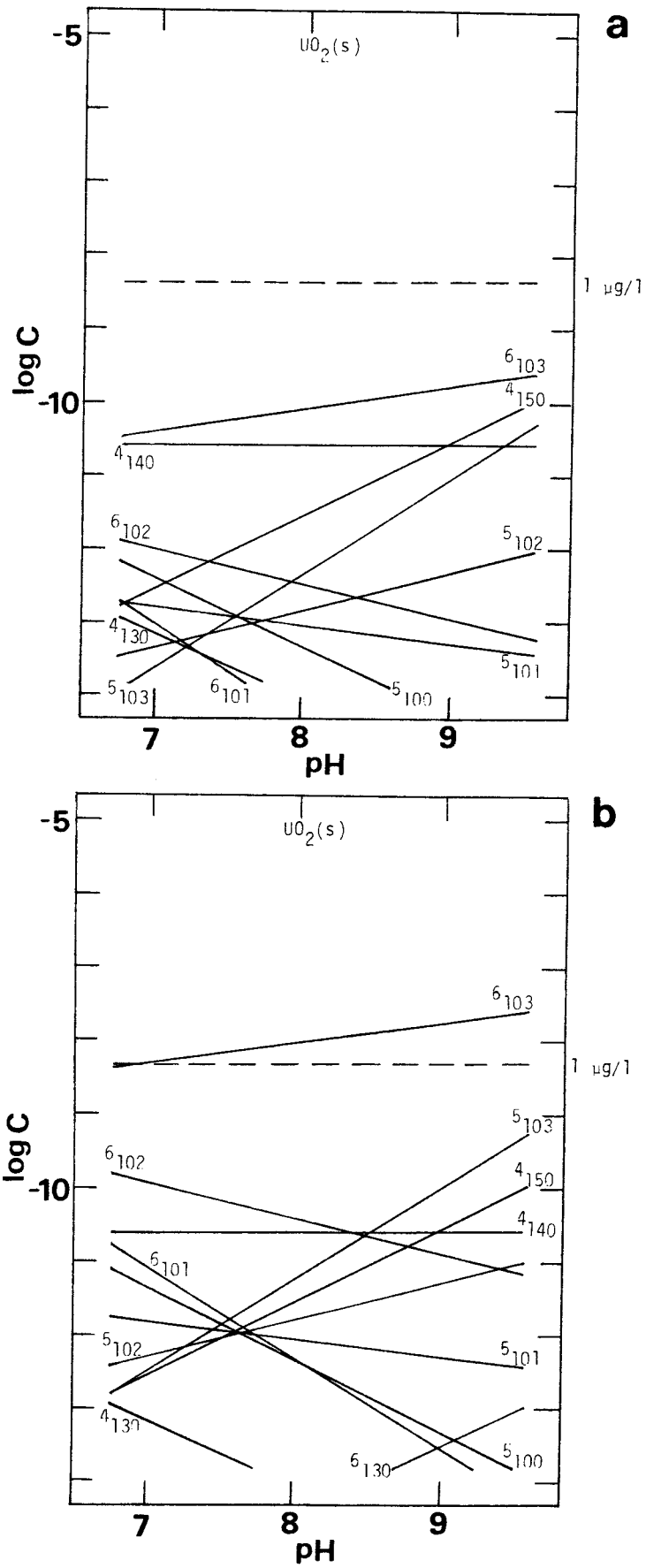
Figure 4    Calculated uranium solubilities
(a) Eh = 0.18-0.06pH
(b) Eh = 0.24-0.06pH
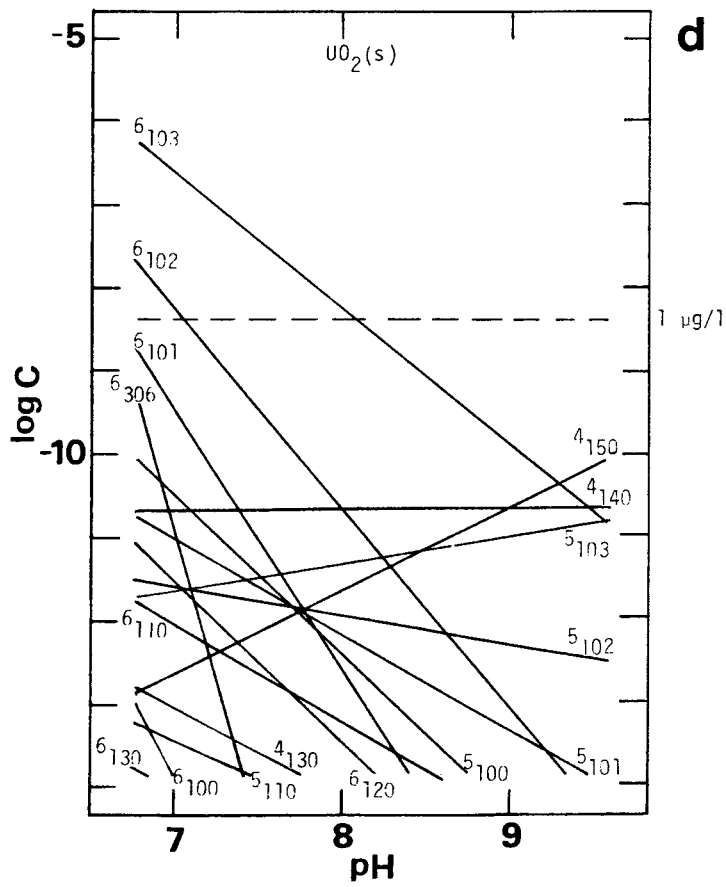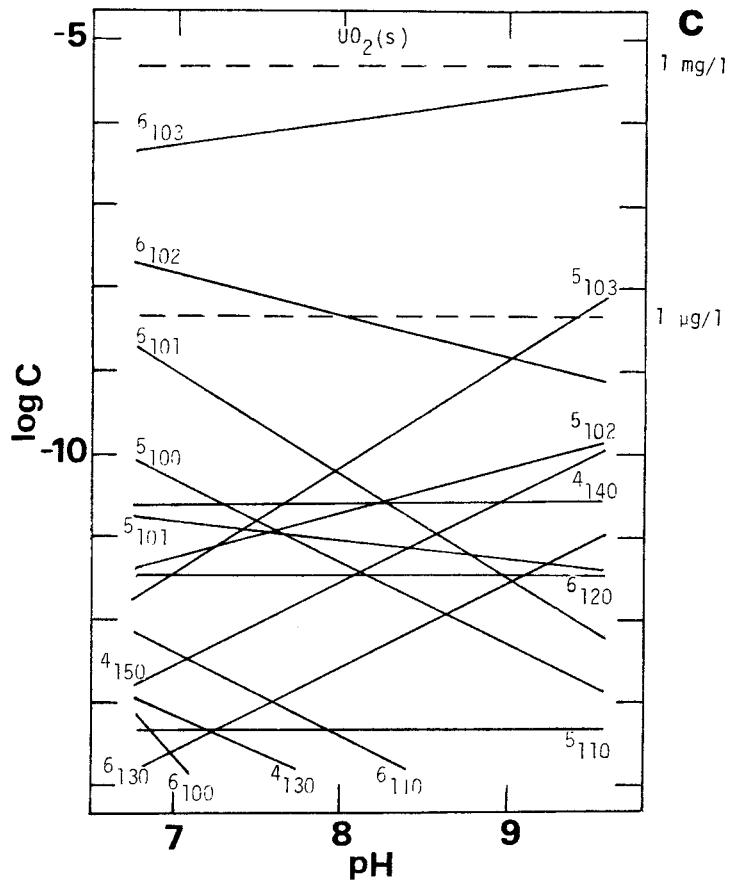
Figure 4    (c)  Eh = 0.30-0.06pH
            (d)  Eh = 0.68-0.115pH

Under mildly reducing or slightly oxic conditions (Eh above 0.4-0.06pH, V) the hexavalent state dominates entirely in solution, even at low carbonate concentrations. Solubility limiting solid phases are (with increasing Eh) $U_4O_9$, $U_3O_8$ and $UO_2(OH)_2$ (at Eh above 0.7-0.06pH, V). The solubility would be high in aerated systems (e.g. in the mM-range or higher), largely limited by the total amount of carbonate available for complexation. However, the formation of various fairly poorly defined solid phases (besides the oxides $U_4O_9(s)$ and $U_3O_8(s)$ under mildly reducing conditions) such as $Na_2U_2O_7(s)$, $NaUO_3(s)$ and others, as well as phosphates under environmental conditions, would be possible. These solid phases would limit the solubility to less than $10^{-5}$ M (mg/l-range) (28).

The existence of U(V) and U(VI) in environmental waters under reducing conditions does not necessarily indicate a uranium release mechanism in nature since the concentration would be low. Still it would be of interest whether uranium is penta-, hexa- or tetravalent in solution, since the sorption behaviour of U(V), U(VI) and U(IV) would be entirely different. This would be of importance for the transport of uranium under conditions when one of the oxidation states dominate entirely over the others in solution. The possible dominance of U(V) at low pH has not been demonstrated experimentally.

The low solubility of many uranium compounds can explain the formation of some of the principle ore minerals like uraninite ($UO_2$-$U_3O_8$) and coffinite ($USiO_4$) (29). The formation of secondary uranium minerals due to weathering and oxidation/reduction cycles is well-known. Geologic observations largely indicate that tetravalent uranium remains immobile in the ground and slowly mobilizes by the exposure to atmospheric conditions or oxygen/ carbon dioxide bearing natural waters.

The calculated uranium solubilities, Fig. 4, are in reasonable agreement with observed solubilities in deep reducing ground-waters, Fig. 5 (26,30), which indicate a total solubility of

$10^{-7}$-$10^{-8}$ M (10-1 µg/l) or less. The data in Fig. 1, 2 and 5 are all from the same sampling places. High isotopic ratios ($^{234}$U)/$^{238}$U), which are generally indicative of saturated systems in equilibrium with a solubility limiting phase (most likely $UO_2(s)$), are usually only observed in natural waters with total uranium concentrations below $10^{-8}$-$10^{-9}$ M (µg/l-level or below) (31). Since the observed uranium concentrations in Fig. 5 are of the same order of magnitude it is likely that these waters do represent systems near saturation. Significantly higher uranium concentrations are reported from shallow groundwaters in similar bedrock (32). These systems are not necessarily reducing, and the low observed isotopic ratio indicate non-equilibrium systems.
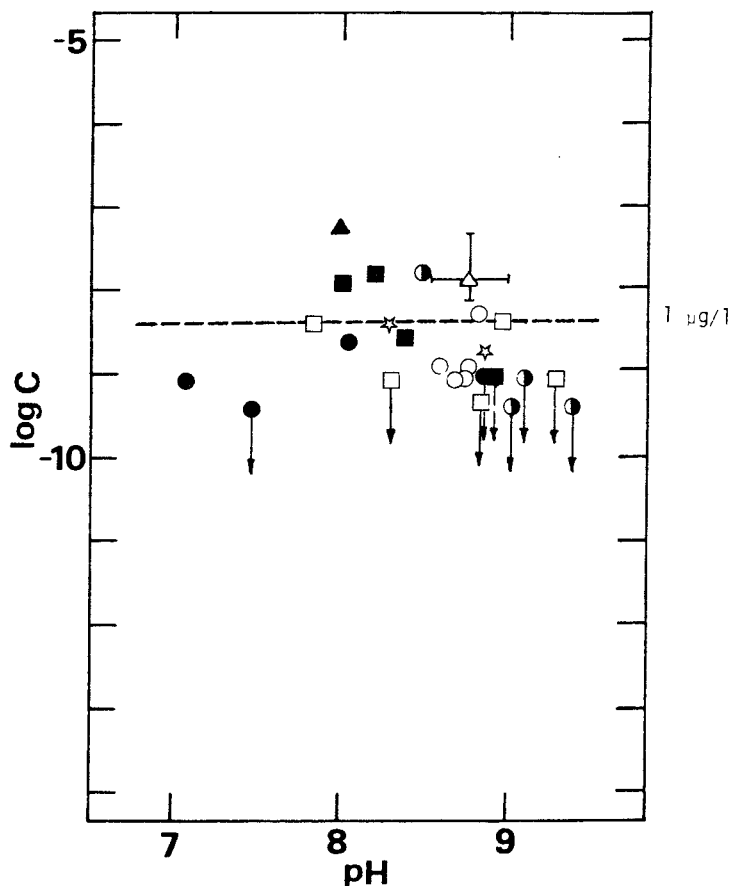


Figure 5    Measured uranium concentrations in deep granitic groundwaters (26,30).

◑ Svartboberget 4,  ○ Gideå 2,    □ Gideå 4,

● Fjällveden 2,  ■ Fjällveden 4,  ☆ Fjällveden 8,

▲ Kamlunge 2 (106m),  △ Kamlunge 2 (376m).

### 3.2.3. Neptunium

The solubility limiting solid phase would be $NpO_2(s)$, both under reducing and mildly oxidizing conditions.

Under reducing conditions tetravalent species, largely $Np(OH)_4$, would dominate, Fig. 6. At Eh above 0.4-0.06pH (V), pentavalent carbonate species like $NpO_2(CO_3)_3^{5-}$ and $NpO_2(CO_3)_2^{3-}$ would become important, and the pentavalent carbonates, as well as the non-complexed $NpO_2^+$ at low pH, would dominate entirely under oxic conditions.

Solubility limiting phases under oxic conditions would be species like $Na_{2x-1}NpO_2(CO)_x(s)$, e.g. with x=0.8-1 (12,20). Considering the sodium concentrations in most groundwaters, the maximum solubility is likely to be less than $10^{-5}$ M (in the mg/l-range) even under oxic conditions.

### 3.2.4. Plutonium

The plutonium solubility is limited by the solid phase $PuO_2(s)$ both under reducing and oxic conditions. Under highly reducing conditions and at high total carbonate concentrations and low pH the formation of $Pu_2(CO_3)_3(s)$ is also possible.

Under reducing conditions (Eh below 0.3-0.06pH, V) trivalent species like $PuCO_3^+$, $Pu^{3+}$ and $PuOH^{2+}$ would dominate, particularly at low pH, Fig. 7. At higher potentials, up to Eh = 0.8-0.06pH (V), the tetravalent state prevails, with $Pu(OH)_4$ as the dominating species in solution. At still higher potentials, which could be obtained in the presence of oxidizing agents, or possibly as a result of radiolysis, pentavalent carbonates like $PuO_2(CO_3)_3^{5-}$ and $PuO_2(CO_3)_2^{3-}$ would dominate at high pH and the non-complexed $PuO_2^+$ at low pH. The formation of hexavalent plutonium species is unlikely.
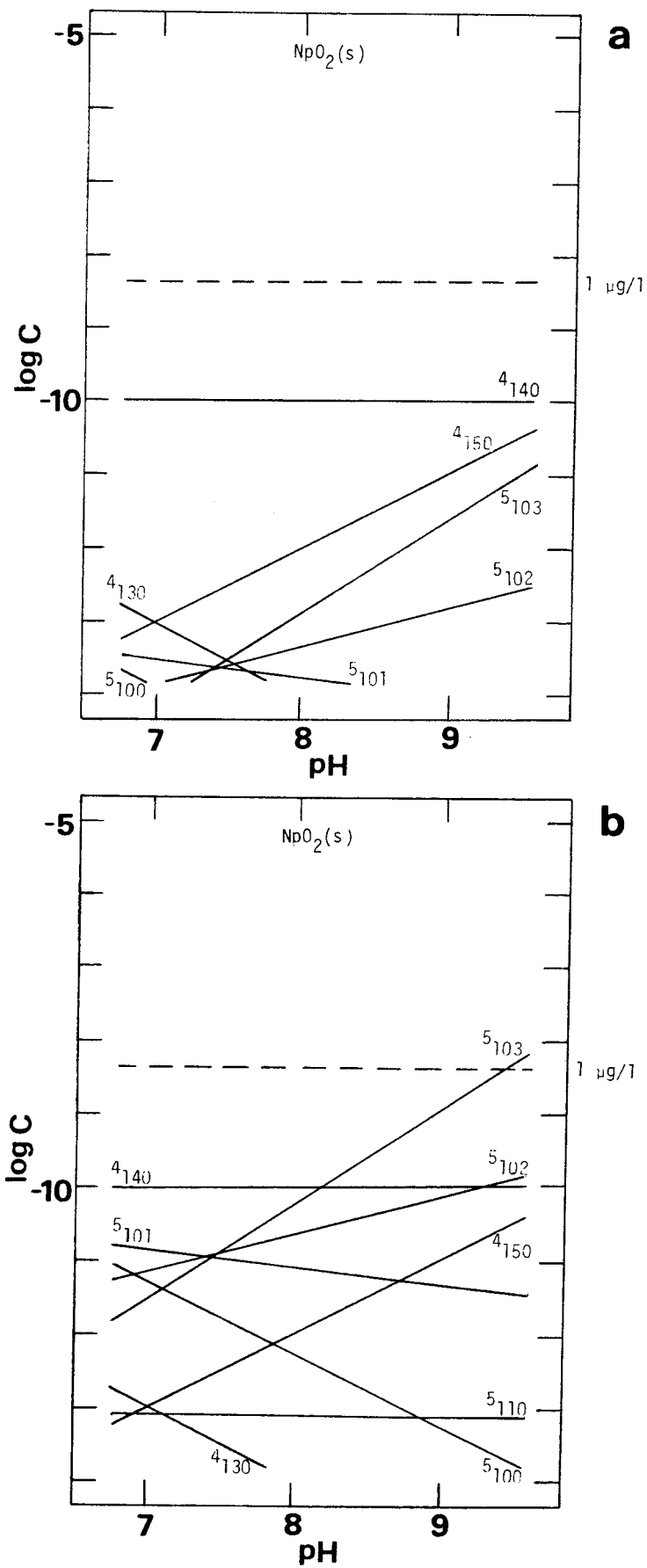
Figure 6    Calculated neptunium solubilities
            (a) Eh = 0.24-0.06pH
            (b) Eh = 0.40-0.06pH
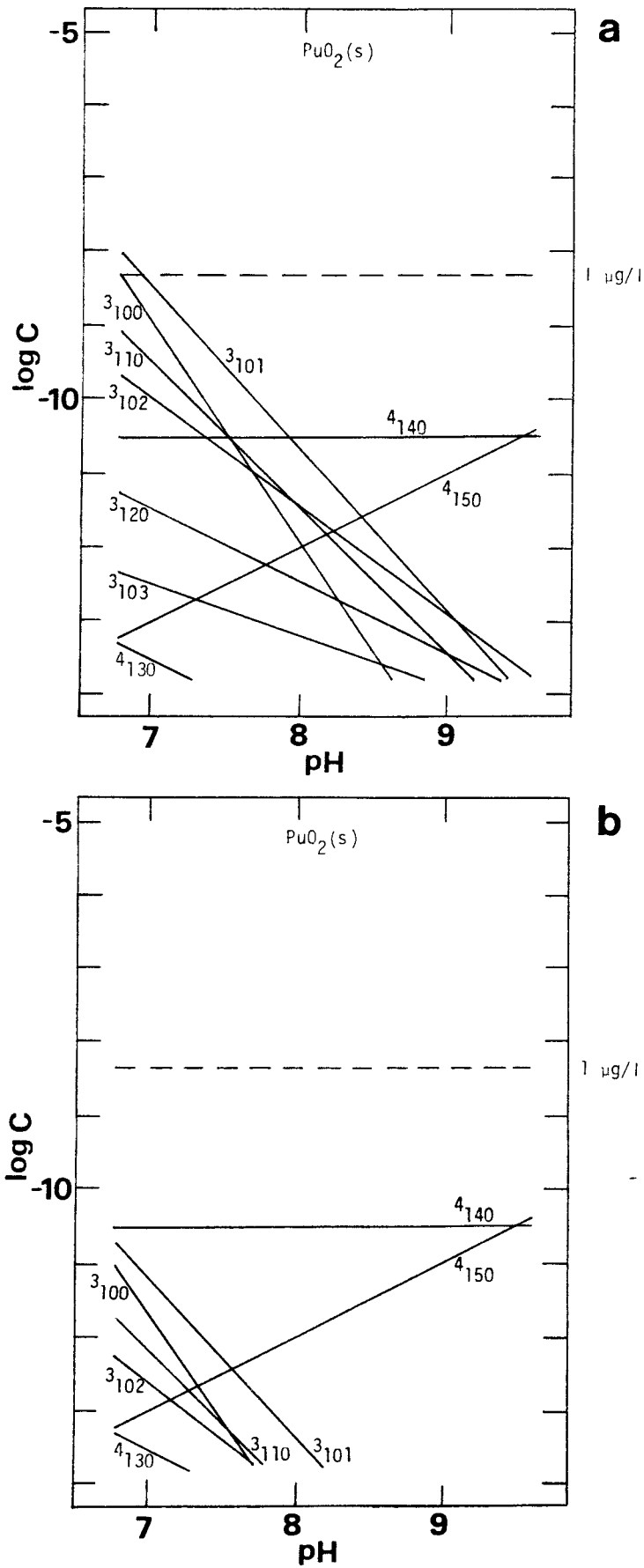
Figure 7    Calculated plutonium solubilities

(a) Eh = 0.24-0.06pH

(b) Eh = 0.40-0.06pH
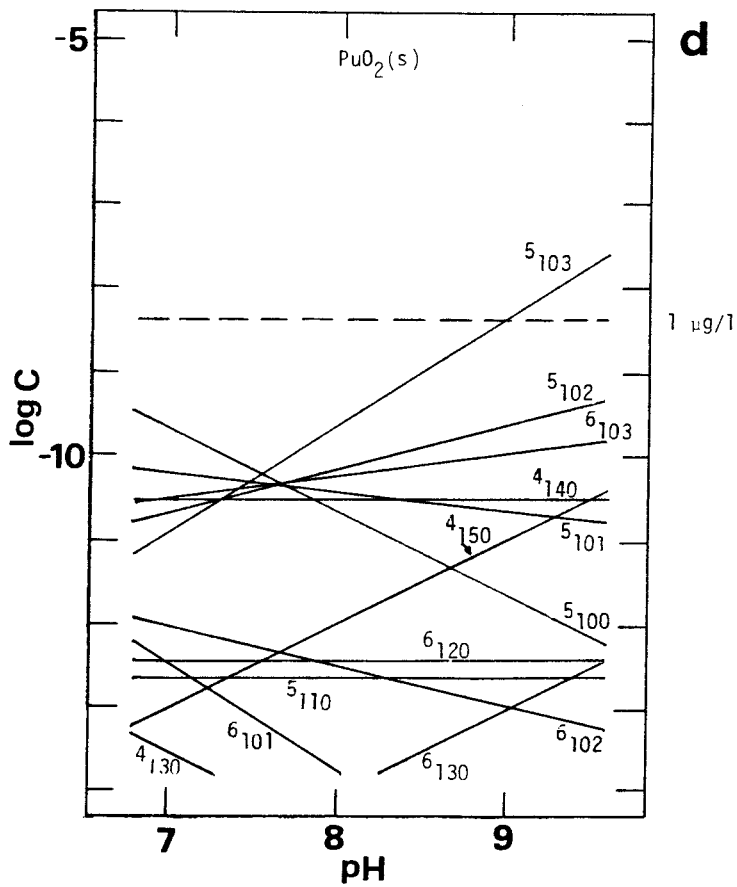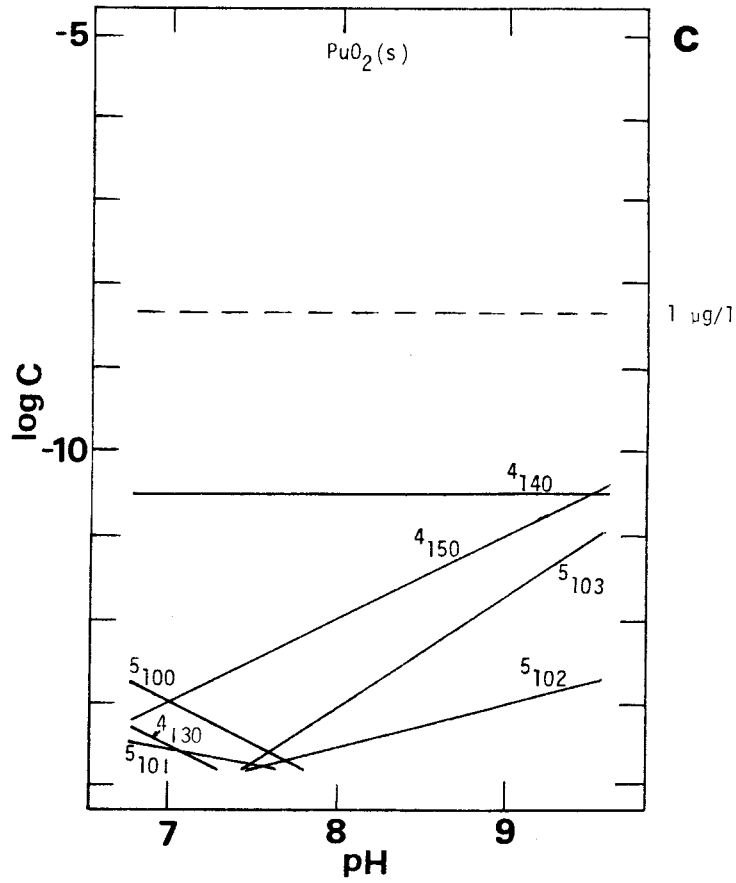
Figure 7    (c) Eh = 0.8-0.06pH

(d) Eh = 1.0-0.06pH

The seasonal variations of the redox conditions e.g. in biologically active shallow waters might be within the redox potential range that would shift the plutonium equilibrium from the tetra- to the pentavalent state. Thus, since the sorption behaviour of these two oxidation states would be entirely different (33), the observable apparent concentrations could vary considerably depending on the season. Such variations of the apparent plutonium concentrations have in fact been observed in natural aerated aquifers (34).

The somewhat unexpected total plutonium solubilities reported for aerated aqueous solutions in contact with $PuO_2(s)$ (10) are in reasonable agreement with predicted concentrations and speciation in Fig. 7, assuming a redox potential of 0.9-0.06pH or above. Otherwise, a shift in the Pu(V)/Pu(IV)-potential of Table 5 has to be assumed, in order to explain the reported redox behaviour.

### 3.2.5. Americium

Americium is trivalent both under reducing and oxidizing conditions. 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 dominating species in solution, Fig. 8.

Experimental solubility data in the absence of carbon dioxide (6) and at low carbonate concentrations (35) are in fair agreement with the calculated curves in Fig. 8.

### 3.3.  Formation of colloidal and metastable species

The tetravalent and to some extent the trivalent actinides have a tendency to form polymeric colloidal hydroxides (36). These species could be composed of highly polymerized hydroxy complexes with large residual charges, which prevent them from aggregation
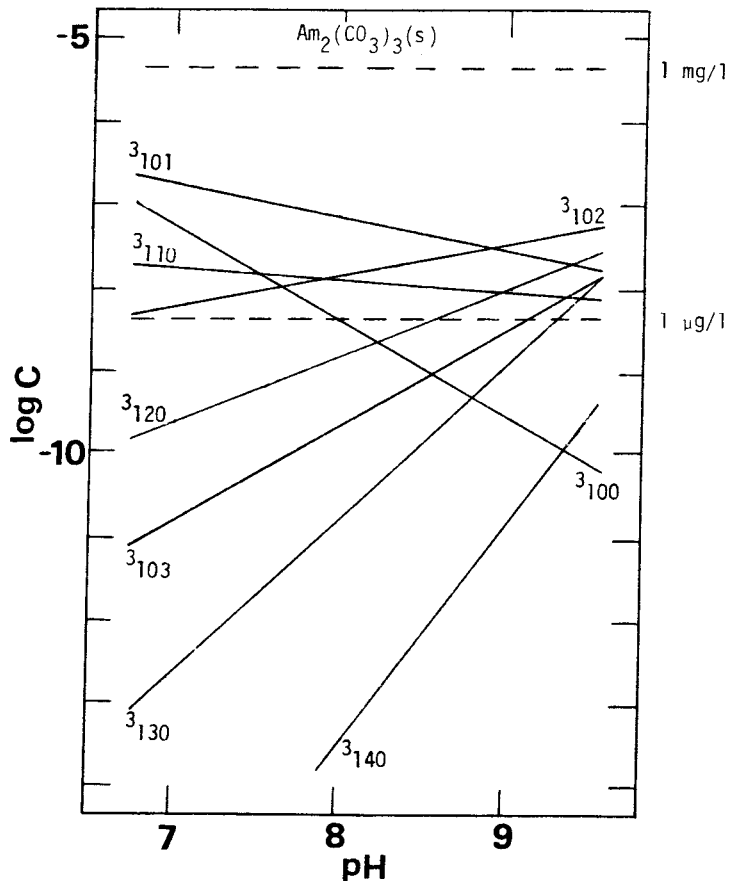
Figure 8    Calculated americium solubility
(Reducing or oxic conditions)

because of electrostatic repulsion. Thus, an apparent solubility
which may exceed the expected equilibrium solubility by many
orders of magnitude can be achieved. These colloids should be
considered as metastable forms which will slowly convert to
thermodynamically stable species (14). However, stable polymeric
species could in fact also exist, particularly at low pH and high
actinide concentrations. These species would carry a positive net
charge.

The precipitation of the hydroxide of e.g. a tetravalent actinide
will generally lead to the formation of an amorphous solid of
colloidal nature. The formation and stability of the precipitate
is highly pH-dependent. Freshly precipitated material consists
essentially of amorphous particles, which after aging becomes
crystalline, as indicated from electron microscopy, electron
diffraction, and X-ray diffraction. These crystallites consist of

the oxide (e.g. $PuO_2(s)$). The corresponding neutral hydroxide
(e.g. $Pu(OH)_4(s)$) is non-crystalline. The apparent solubility
product of the amorphous tetrahydroxide is at least two orders of
magnitude higher than of the corresponding oxide (see. e.g. ref.
10 and Appendix 1). However, the neutral hydroxides should be
considered as metastable species which slowly dehydrate and
become crystalline, leading to a reduced total solubility.

The properties of actinide colloids are further discussed e.g. in
ref. 35-38.

Much of the confusion concerning reported solubilities and
solubility products of the actinide hydroxides, particularly for
the tetravalent state, can be ascribed to the difficulties in
properly defining the solid phase as well as what is in true
solution and colloidal state, respectively. The slow kinetics of
hydroxide dissolution and transformation and the strong tendency
for hydroxy species and colloids to sorb strongly on exposed
macro surfaces as well as on colloidal particles in solution
(metal hydroxides, silica, etc.) can lead to experimental diffi-
culties and possibly misinterpretations of experimental observa-
tions.

## 3.4.   Sorption on geologic media

Sorption of actinides on exposed solid geologic material, e.g.
oxides, silicates, etc., would lead to apparent solubilities not
predictable from thermodynamic complex formation data. The
sorption would be dependent on the composition of the solution
(e.g. pH, redox potential, ionic strength, presence of complexing
agents), the total actinide concentration, and the composition of
the solid sorbent (e.g. ion exchange capacity, presence of
complexing counter ions in the lattice). Sorption, rather than
true solubility limitations will determine actinide concentra-
tions at trace levels in environmental aqueous systems.

Actinide sorption phenomena are further discussed in detail
elsewhere (33,39).

4.    CONCLUSIONS


4.1.    Actinide chemistry in aqueous geosystems


Some general conclusions can be stated concerning the chemical properties and solubilities of actinides in aqueous geosystems.


o    The actinides solution chemistry in natural waters is largely determined by redox properties, pH and the carbonate concentration of the aqueous system.


o    The solubility of all actinides, except for tetravalent species, is enhanced by the presence of carbonate.


o    Under reducing conditions, e.g. in deep granitic ground-waters, the oxidation states $Th(IV)$, $U(IV)$ ($+U(VI)$), $Np(IV)$, $Pu(III)$ ($+Pu(IV)$) and $Am(III)$ would dominate; in aerated systems an oxidation to $U(VI)$, $Np(V)$ and $Pu(IV)$ ($+Pu(V)$ would be expected.


o    The tetravalent dioxide would be the solubility limiting species for all of Th, U, Np and Pu within a large pH-Eh-range of environmental interest. Metastable amorphous tetravalent tetrahydroxides would, however, be formed at the precipitation of these actindies under proper conditions. These hydroxides have a larger solubility product than the oxides, but they will slowly be transformed to the corresponding oxides.


The calculated maximum solubilities in granitic groundwaters (pH 7-9.5) are summarized in Table 9.


4.2.    Current problems concerning actinide geochemistry


Among problems connected to actinide solution chemistry in natural water systems are the following ones:

Table 9    Calculated maximum actinide solubilities in the pH-range 7-9.5 assuming equilibrium with with $ThO_2(s)$, $UO_2(s)$, $NpO_2(s)$, $PuO_2(s)$ and $Am_2(CO_3)_3(s)$, respectively.

| | Max. concentrations, $Mx10^{10}$ | | | |
|---|---|---|---|---|
| | Reducing conditions[a] | | Oxidizing conditions[b] | |
| | Low $[CO_3^{2-}]$ [c] | High $[CO_3^{2-}]$ [d] | Low $[CO_3^{2-}]$ [c] | High $[CO_3^{2-}]$ [d] |
| Th | 3 | 3 | 3 | 3 |
| U | 0.3 | 250 | c | e |
| Np | 1 | 1 | e | e |
| Pu | 10 | 30 | 0.3 | $0.3^f$ |
| Am | 600 | $2x10^3$ | 600 | $2x10^3$ |

[a] $Eh < 0.24-0.06pH$ (V)

[b] $Eh = 0.8-0.06pH$ (V)

[c] $\log [CO_3] = pH-14$

[d] $\log [CO_3] = 0.76pH-10.83$

[e] Solubility of the order $10^{-5}-10^{-6}$ M or higher are expected. The solubility is limited by other phases than the oxides $UO_2(s)$ and $NpO_2(s)$, respectively; c.f. 3.2.

[f] 200 at $Eh = 1.0-0.06pH$ (V)

o   Many of the available stability constants for actinide complexes of environmental interest are either lacking or not measured under proper conditions. Reliable thermodynamic data are needed particularly for the hydrolysis of the tri- and tetravalent actinides $(An(OH_2)^+$, $An(OH)_3$, $An(OH)_4$, $An(OH)_5^-)$; carbonate complexation of the pentavalent actinides $(AnO_2(CO_3)_3^{5-}$, $AnO_2(CO_3)_2^{3-})$ and solubility products $(AnO_2(s)$, other oxide phases in the uranium system, $M_xAnO_2(CO_3)_y(s))$.

o   Methods for the extrapolation of constants from one ionic strength to another are not adequate.

o   The uncertainty in many redox potentials is too large
    (~0.05 V) (e.g. U(VI)/U(V), U(VI)/U(IV), possibly Pu(V)/Pu(IV),
    etc.).

o   The kinetics of the transfer from hydroxide to oxide $(An(OH)_4(s)$-
    $AnO_2(s))$ is not adequately known. The possibility of a
    solubility increase due to the reverse reaction (as a result
    of radiolysis?) should be looked into, as well as the
    possible long-term existence of metastable polymeric hydrox-
    ides in solution.

Other problem areas, not specifically discussed in this report,
are

o   formation and properties of organic complexes
o   formation and properties of colloids
o   sorption phenomena.

## 5.   ACKNOWLEDGEMENTS

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SELECTED ACTINIDE COMPLEX FORMATION CONSTANTS
GIVEN IN THE LITERATURE

Selected complex formation constants for actinide complexes with
inorganic ligands are given in Table 1-1. These constants, which
are taken from some recent compilations and critical evaluations
of available thermodynamic data (ref. A-K) also include extrapola-
ted and estimated values for reactions where no measured data are
available. Values which are specifically denoted as estimated or
otherwise stated as uncertain are given within parentheses. The
constants (log K) in Table 1-1 refer to the reaction (at $25^{\circ}C$,
ionic strength 0)

$$xAn + yL = An_xL_y, \ (x,y); \ \log K = [An_xL_y]/[An]^x[L]^y$$

or

$$xAn + yL = An_xL_y(s), \ (x,y)(s); \ \log K = [An]^x[L]^y$$
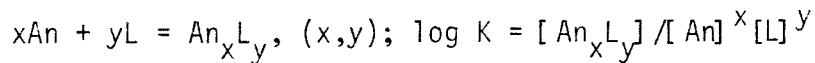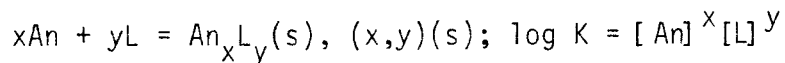
where An denotes the actinide, L the ligand and the brackets
activities.

Table 1-1     Selected actinide complex formation constants (log K).

(a) Trivalent actinides.

| | | Np(III) | | Pu(III) | | Am(III) | | An(III) | |
|---|---|---|---|---|---|---|---|---|---|
| OH⁻ | (1,1) | (6.6±0.5) | (F) | 6.7[a] | (A) | 7.9[a] | (A) | 6.0 | (J) |
| | | (6.6) | (K) | 6.0±0.5 | (B) | 8.0[b] | (C) | | |
| | | | | 7.05 | (C) | (8.2) | (D) | | |
| | | | | (7.2) | (D) | 7.9 | (I) | | |
| | | | | 7.2±0.5 | (F) | 6.0 | (K) | | |
| | | | | 6.0±0.2 | (G) | | | | |
| | | | | 6.7 | (I) | | | | |
| | | | | 7.2 | (K) | | | | |
| | (1,2) | (11±1) | (F) | (12.1±1.0) | (F) | (15) | (D) | 11.0 | (J) |
| | | (11) | (K) | (12.1) | (K) | (11.1) | (K) | | |
| | (1,3) | (15±2) | (F) | (16.7±1.5) | (F) | (21) | (D) | 15.5 | (J) |
| | | (15) | (K) | (16.7) | (K) | (15.5) | (K) | | |
| | (1,4) | (18±2) | (F) | (20.2±2.0) | (F) | (25) | (D) | 19.0 | (J) |
| | | (18) | (K) | (20.2) | (K) | (18.9) | (K) | | |
| | (2,2) | (15±2) | (F) | (16±2) | (F) | (19) | (D) | 14 | (J) |
| | | (15) | (K) | (16) | (K) | 14.14 | (K) | | |
| | (3,5) | | | | | (46) | (D) | 37 | (J) |
| | | | | | | 41.5 | (I) | | |
| | (1,3)(s) | (-24±2) | (F) | -19.7 | (B) | -19.57 | (C) | -23.3 | (B) |
| | | | | -19.7 | (C) | (-28) | (D) | -23.1[c] | (I) |
| | | | | -25±2 | (F) | -19.6 | (I) | -23.5 | (J) |
| | | | | -19.5±1.2 | (G) | | | | |
| | | | | -19.7 | (I) | | | | |
| CO₃²⁻ | (1,1) | | | 9.6 | (I) | | | 6.5 | (J) |
| | (1,2) | | | 12.9 | (I) | | | 11.0 | (J) |
| | (1,3) | | | 16.2 | (I) | | | 14.5 | (J) |
| | (1,4) | | | | | (11) | (D) | | |
| | AnOH(CO₃)₂²⁻ | | | | | | | 12.5[d] | (J) |
| | (2,3)(s) | | | | | (-33) | (D) | -32[d] | (I) |
| | | | | | | | | -31 | (J) |
| NO₃⁻ | (1,1) | | | | | 0.26[e] | (A) | | |
| | | | | | | 0.26[e] | (C) | | |
| | | | | | | (-1) | (D) | | |

| | | Np(III) | Pu(III) | | Am(III) | | An(III) | |
|---|---|---|---|---|---|---|---|---|
| $H_2PO_4^-$ | (1,1) | | 2.5±0.7 | (G) | 2.51 | (A) | 2.4 | (J) |
| | | | | | 2.51 | (C) | | |
| | | | | | (2.5) | (D) | | |
| | | | | | 2.73 | (K) | | |
| | (1,2) | | | | 3.72 | (K) | | |
| $HPO_4^{2-}$ | (1,1) | | | | | | (6) | (J) |
| $PO_4^{3-}$ | (1,1)(s) | | | | (-23) | (D) | -23 | (J) |
| $SO_4^{2-}$ | (1,1) | | 1.26[e] | (A) | 1,86[f] | (A) | 3.5 | (J) |
| | | | 1.26[e] | (C) | 3.68 | (C) | | |
| | | | (3.7) | (D) | (3.6) | (D) | | |
| | | | 3.5±0.6 | (G) | 1.57 | (I) | | |
| | | | 1.26 | (I) | 3.6 | (K) | | |
| | | | 3.5 | (K) | | | | |
| | (1,2) | | | | 2.82[f] | (A) | 5.2 | (J) |
| | | | | | (5.6) | (D) | | |
| | | | | | 2.66 | (I) | | |
| | | | | | 5.0 | (K) | | |
| $F^-$ | (1,1) | | 4.0±2.3 | (G) | 3.39[f] | (A) | 4.3 | (J) |
| | | | | | 3.39 | (C) | | |
| | | | | | (4.3) | (D) | | |
| | | | | | 3.39 | (I) | | |
| | | | | | 4.3 | (K) | | |
| | (1,2) | | | | 6.11[f] | (A) | 7.6 | (J) |
| | | | | | 6.11 | (C) | | |
| | | | | | (7.5) | (D) | | |
| | | | | | 6.11 | (I) | | |
| | | | | | 7.4 | (K) | | |
| | (1,3) | | | | 9.0[f] | (A) | 10.8 | (J) |
| | | | | | (10.8) | (D) | | |
| | | | | | 9.0 | (I) | | |
| | | | | | 10.6 | (K) | | |
| | (1,3)(s) | | -15.6 | (C) | -15.11 | (C) | -10.2 | (J) |
| | | | -10.2±2.3 | (G) | (-15) | (D) | | |
| $Cl^-$ | (1,1) | | -0.1[g] | (A) | -0.1[g] | (A) | | |
| | | | (1.1) | (D) | 1.17 | (C) | | |
| | | | -0.1 | (I) | (1.0) | (D) | | |
| | | | | | -0.1 | (I) | | |
| | | | | | 1.1 | (K) | | |
| | (1,2) | | | | (0.5) | (D) | | |

(b) Tetravalent actinides

| | | Th(IV) | U(IV) | Np(IV) | Pu(IV) | An(IV) |
|---|---|---|---|---|---|---|
| OH⁻ | (1,1) | 10.8 (A)<br>10.8±0.2 (B)<br>10.8 (C)<br>10.8 (D)<br>10.8±0.3 (F)<br>10.8 (H)<br>10.8 (K) | 13.3 (A)<br>13.35±0.04 (B)<br>13.00 (C)<br>13.3 (D)<br>13.34 (E)<br>13.4±0.4 (F)<br>13.3±1.3 (G)<br>12.2 (I)<br>13.35 (K) | 12.5 (A)<br>12.51±0.05 (B)<br>11.95 (C)<br>12.5 (D)<br>13.2±0.4 (F)<br>11.7 (I)<br>12.51 (K) | 12.14 (A)<br>13.5±0.1 (B)<br>(13.2) (D)<br>13.7±0.3 (F)<br>13.5±0.5 (G)<br>13.6 (I)<br>13.5 (K) | 13.5 (J) |
| | (1,2) | 21.1 (A)<br>21.1±0.2 (B)<br>21.07 (C)<br>21.1 (D)<br>22.2 (F)<br>21.0 (H)<br>21.07 (K) | (25.4) (B)<br>23.7 (C)<br>(25) (D)<br>(25.7) (E)<br>(25.5±0.8) (F)<br>(25.7±3.5) (G)<br>25.5 (I)<br>(25.4) (K) | (24) (D)<br>(25.2±0.7) (F)<br>(25.2) (K) | (25.7) (B)<br>(25) (D)<br>(25.7±0.6) (F)<br>26.7±3.5 (G)<br>26.8 (I)<br>(25.7) (K) | 25.5 (J) |
| | (1,3) | <30.3 (B)<br><30.3 (C)<br>(30) (D)<br>(30.3) (E)<br>30.3 (K) | (36.2) (B)<br>(36) (D)<br>(37.08) (E)<br>(36.6±1.2) (F)<br>(37.0±3.5) (G)<br>(36.2) (K) | (34) (D)<br>(36.4±1.1) (F)<br>(36.7) (K) | (36.7) (B)<br>(36) (D)<br>(36.7±0.9) (F)<br>37.0±3.5 (G)<br>37.5 (I)<br>(36.7) (K) | 36.0 (J) |
| | (1,4) | 40.1±0.3 (B)<br>40.1 (C)<br>(37) (D)<br>40.1 (F)<br>40.1 (G)<br>40.1 (K) | (45.7) (B)<br>(46) (D)<br>(47.4) (E)<br>(46.3±1.6) (F)<br>(47.4±3.5) (G)<br>(45.7) (K) | (43) (D)<br>(46.1±1.4) (F)<br>(46.1) (K) | 46.5±0.2 (B)<br>(45) (D)<br>46.5±1.2 (F)<br>46.4±3.5 (G)<br>46.5 (K) | 45.5 (J) |
| | (1,5) | (44) (D) | 54.0 (A)<br>54.0±0.1 (B)<br>54.0 (D)<br>(56.8) (E)<br>54.0±2 (F)<br>56.8±1.4 (G)<br>54 (F)<br>54.0 (K) | (50) (D)<br>(53±2) (F)<br>(53) (K) | (55.0) (B)<br>(52) (D)<br>(55±2) (F)<br>55.0±3.5 (G)<br>(55) (K) | 50 (J) |
| | (2,2) | (21.9) (A)<br>21.86±0.06 (B)<br>21.86 (C)<br>(23) (D)<br>21.9±0.06 (F)<br>21.84 (H)<br>21.86 (K) | (27) (D)<br>(27±3) (F)<br>(27) (K) | (26) (D)<br>(26±3) (F)<br>(26) (K) | (27) (D)<br>(27±3) (F)<br>(27) (K) | 27 (J) |

| | | Th(IV) | | U(IV) | | Np(IV) | | Pu(IV) | | An(IV) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | (4,8) | (90.9) | (A) | | | | | | | (210) | (J) |
| | | 90.9±0.1 | (B) | | | | | | | | |
| | | (91) | (D) | | | | | | | | |
| | | 90.9±0.1 | (F) | | | | | | | | |
| | | 90.8 | (G) | | | | | | | | |
| | | 90.9 | (K) | | | | | | | | |
| | (6,15) | 173.2 | (A) | 192.8 | (A) | | | | | | |
| | | 173.24±0.06 | (B) | 192.81 | (B) | | | | | | |
| | | 173.2 | (D) | 192.8 | (D) | | | | | | |
| | | 173.1 | (E) | 192.6 | (E) | | | | | | |
| | | 173.24 | (K) | 196 | (K) | | | | | | |
| | (1,4)(s) | -44.7[h] | (A) | -46.23 | (C) | -55.22 | (C) | -47.3 | (A) | | |
| | | -43.17 | (C) | (-48) | (D) | (-46) | (D) | -55.15 | (C) | | |
| | | -44.7 | (D) | (-55.0) | (E) | (-53±2) | (F) | (-47.3) | (D) | | |
| | | -44.7 | (F) | (-54±2) | (F) | | | -55.2±1.2 | (F) | | |
| | | | | | | | | -55.2±5.1 | (G) | | |
| | AnO$_2$(s) | -49.7 | (A) | -56.2 | (A) | -60 | (B) | -62.0 | (B) | -54 | (J) |
| | | -49.7±0.5 | (B) | -57.8 | (B) | (-51) | (D) | -62.5 | (C) | | |
| | | -49.7 | (C) | -52.37 | (C) | -58.7±2 | (F) | (-55) | (D) | | |
| | | -49.7 | (D) | (-56.2) | (D) | -55.4 | (I) | -62.5±1.2 | (F) | | |
| | | -49.7 | (F) | -60.6 | (E) | | | -63.3±0.1 | (G) | | |
| | | -49.67 | (G) | -57.8±2 | (F) | | | | | | |
| | | | | -60.6±0.4 | (G) | | | | | | |
| | | | | -56.2 | (I) | | | | | | |
| CO$_3^{2-}$ | (1,1) | 11.03 | (K) | | | | | 40.7±3.7 | (G) | (42)[i] | (J) |
| | | | | | | | | 41[i] | (I) | | |
| | | | | | | | | 40.7 | (K) | | |
| | (1,5) | | | | | | | | | (37) | (J) |
| NO$_3^-$ | (1,1) | 0.67[f] | (A) | 1.6 | (A) | 1.7[j] | (A) | 1.8 | (A) | | |
| | | (1.8) | (D) | 1.6 | (D) | 0.38[a] | (C) | 0.72[a] | (C) | | |
| | | | | | | 1.7 | (D) | 1.8 | (D) | | |
| | (1,2) | (1.5) | (D) | (1.6) | (D) | 0.08[a] | (C) | (2.4) | (D) | | |
| | | | | | | (1.6) | (D) | | | | |
| | (1,3) | (2) | (D) | (1.5) | (D) | (1.0) | (D) | (2.3) | (D) | | |
| | (1,4) | (1) | (D) | (1.1) | (D) | (1) | (D) | (1) | (D) | | |
| H$_2$PO$_4^-$ | (1,1) | 3.96[k] | (A) | (5) | (D) | (5) | (D) | (5) | (D) | 4.5 | (J) |
| | | (4.7) | (D) | | | | | | | | |
| | | 4.64 | (H) | | | | | | | | |
| | | 4.52 | (K) | | | | | | | | |

| | | Th(IV) | | U(IV) | | Np(IV) | | Pu(IV) | | An(IV) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | (1,2) | $7.5^k$ | (A) | (8) | (D) | (8) | (D) | (8) | (D) | 8.9 | (J) |
| | | (8.2) | (D) | | | | | | | | |
| | | 8.91 | (H) | | | | | | | | |
| | | 8.88 | (K) | | | | | | | | |
| $HPO_4^{2-}$ | (1,1) | 10.8 | (H) | 12.0 | (E) | | | 13.0±1.4 | (G) | 13.0 | (J) |
| | | 12.9 | (K) | 12.1±3.7 | (G) | | | 13 | (K) | | |
| | | | | 12 | (K) | | | | | | |
| | (1,2) | 22.8 | (H) | 22.0 | (E) | | | 23.8±1.4 | (G) | 23.8 | (J) |
| | | 28.0 | (K) | 22.0±3.7 | (G) | | | 24 | (K) | | |
| | | | | 22 | (K) | | | | | | |
| | (1,3) | 31.3 | (H) | 30.6 | (E) | | | 33.4±1.4 | (G) | 33.4 | (J) |
| | | 34.5 | (K) | 30.7±3.7 | (G) | | | 33 | (K) | | |
| | | | | 31 | (K) | | | | | | |
| | (1,4) | | | 38.7 | (E) | | | 43.1±1.4 | (G) | | |
| | | | | 38.7±3.7 | (G) | | | 43 | (K) | | |
| | | | | 39 | (K) | | | | | | |
| | (1,2)(s) | -19.92 | (C) | -26.8 | (E) | | | -27.7 | (C) | -27 | (J) |
| | | -26.9 | (H) | -26.8±0.4 | (G) | | | -27.6±1.4 | (G) | | |
| $PO_4^{3-}$ | (3,4)(s) | -78.6 | (H) | (-90) | (D) | | | | | | |
| $SO_4^{2-}$ | (1,1) | $3.22^k$ | (A) | $3.42^k$ | (A) | $3.51^k$ | (A) | (5.8) | (D) | 5.6 | (J) |
| | | (5.5) | (D) | (5.6) | (D) | (5.7) | (D) | 5.8±1.4 | (G) | | |
| | | 5.46 | (H) | 5.46 | (E) | 3.41 | (I) | 3.66 | (I) | | |
| | | 5.45 | (K) | 5.5±1.4 | (G) | | | 5.8 | (K) | | |
| | | | | 3.42 | (I) | | | | | | |
| | | | | 5.47 | (K) | | | | | | |
| | (1,2) | $5.53^k$ | (A) | $5.82^k$ | (A) | (9) | (D) | (9) | (D) | 10.3 | (J) |
| | | (9) | (D) | (9) | (D) | 5.42 | (I) | 10.3±3.0 | (G) | | |
| | | 9.75 | (H) | 9.75 | (E) | | | 7.4 | (K) | | |
| | | 9.73 | (K) | 9.8±3.0 | (G) | | | | | | |
| | | | | 9.72 | (K) | | | | | | |
| | (1,3) | (10) | (D) | | | | | | | | |
| | | 10.52 | (H) | | | | | | | | |
| | | 10.50 | (K) | | | | | | | | |
| | (1,4) | 8.50 | (H) | | | | | | | | |
| | | 8.48 | (K) | | | | | | | | |
| $F^-$ | (1,1) | 8.44±0.2 | (A) | $7.15^l$ | (C) | (8.5) | (D) | $6.77^a$ | (A) | 8.6 | (J) |
| | | 8.65 | (C) | (9.2) | (D) | 8.3 | (I) | 7.94 | (C) | | |
| | | 8.44 | (D) | 8.6 | (E) | | | (8) | (D) | | |
| | | 8.03 | (H) | 8.6±1.4 | (G) | | | 8.0±1.4 | (G) | | |
| | | 8.03 | (K) | 9.0 | (I) | | | 6.77 | (I) | | |
| | | | | 8.6 | (K) | | | 8.0 | (K) | | |

|  |  | Th(IV) |  | U(IV) |  | Np(IV) |  | Pu(IV) |  | An(IV) |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | (1,2) | 15.1±0.2 | (A) | 12.40[1] | (C) | (14.8) | (D) | (15) | (D) | 14.5 | (J) |
|  |  | 15.08 | (D) | (16.0) | (D) | 14.5 | (I) |  |  |  |  |
|  |  | 14.25 | (H) | 14.5 | (E) |  |  |  |  |  |  |
|  |  | 14.25 | (K) | 14.5±1.4 | (G) |  |  |  |  |  |  |
|  |  |  |  | 15.7 | (I) |  |  |  |  |  |  |
|  |  |  |  | 14.4 | (K) |  |  |  |  |  |  |
|  | (1,3) | 19.8±0.4 | (A) | 17.30[1] | (C) | (20) | (D) | (20) | (D) | 19.1 | (J) |
|  |  | 19.8 | (D) | (21) | (D) | 20.3 | (I) |  |  |  |  |
|  |  | 18.90 | (H) | 19.1 | (E) |  |  |  |  |  |  |
|  |  | 18.93 | (K) | 19.1±2.3 | (G) |  |  |  |  |  |  |
|  |  |  |  | 21.2 | (I) |  |  |  |  |  |  |
|  |  |  |  | 19.1 | (K) |  |  |  |  |  |  |
|  | (1,4) | 23.2 | (A) | (26) | (D) | (25) | (D) | (25) | (D) | 23.6 | (J) |
|  |  | 23.2 | (D) | 23.6 | (E) | 25.1 | (I) |  |  |  |  |
|  |  | 22.31 | (H) | 23.7±2.3 | (G) |  |  |  |  |  |  |
|  |  | 22.31 | (K) | 23.6 | (K) |  |  |  |  |  |  |
|  | (1,5) |  |  | 25.2 | (E) |  |  |  |  | 25.3 | (J) |
|  |  |  |  | 25.3±3.0 | (G) |  |  |  |  |  |  |
|  |  |  |  | 25.2 | (K) |  |  |  |  |  |  |
|  | (1,6) |  |  | 27.7 | (E) |  |  |  |  |  |  |
|  |  |  |  | 27.6±3.0 | (G) |  |  |  |  |  |  |
|  |  |  |  | 27.7 | (K) |  |  |  |  |  |  |
|  | (1,4)(s) | -25.3 | (C) | -21.24 | (C) | (-28) | (D) | -19.22 | (C) | -24 | (J) |
|  |  | (-27) | (D) | (-28) | (D) |  |  | (-28) | (D) |  |  |
|  |  | -30.2 | (H) | -18.5 | (E) |  |  | -13.2±5.8 | (G) |  |  |
|  |  |  |  | -23.5±3.7 | (G) |  |  |  |  |  |  |
|  |  |  |  | -27.6[m] | (E) |  |  |  |  |  |  |
|  |  |  |  | -27.5±2.3[m] | (G) |  |  |  |  |  |  |
| Cl⁻ | (1,1) | 1.38 | (A) | 0.30 | (A) | 0.15 | (A) | 0.14[a] | (A) |  |  |
|  |  | 1.38 | (C) | 0.8 | (C) | -0.04[a] | (C) | 0.15[a] | (C) |  |  |
|  |  | 1.38 | (D) | (1.5) | (D) | (1.2) | (D) | (1.3) | (D) |  |  |
|  |  | 1.11 | (H) | (1.33) | (E) | 0.15 | (I) | 0.9±0.7 | (G) |  |  |
|  |  | 1.09 | (K) | 2.5±1.4 | (G) |  |  | 0.14 | (I) |  |  |
|  |  |  |  | 0.26 | (I) |  |  | 0.9 | (K) |  |  |
|  |  |  |  | 1.46 | (K) |  |  |  |  |  |  |
|  | (1,2) | (0.4) | (D) | (1) | (D) | -0.24[a] | (C) | -0.17[a] | (A) |  |  |
|  |  | 0.84 | (H) |  |  | (0.91) | (D) | (1.0) | (D) |  |  |
|  |  | 0.80 | (K) |  |  | -0.24 | (I) | -0.17 | (I) |  |  |
|  | (1,3) | 1.66 | (H) |  |  |  |  |  |  |  |  |
|  |  | 1.65 | (K) |  |  |  |  |  |  |  |  |
|  | (1,4) | 1.23 | (H) |  |  |  |  |  |  |  |  |
|  |  | 1.26 | (K) |  |  |  |  |  |  |  |  |

(c) Pentavalent actinides

| | | U(V) | | Np(V) | | Pu(V) | | An(V) | |
|---|---|---|---|---|---|---|---|---|---|
| $OH^-$ | (1,1) | (4±1) | (D) | 5.15 | (B) | 4.8 | (B) | 4.6 | (J) |
| | | | | 4.01 | (C) | 4.3 | (C) | | |
| | | | | 5.0±0.8 | (F) | 4.3±0.8 | (F) | | |
| | | | | 4.0 | (I) | 4.3±2.3 | (G) | | |
| | | | | 5.15 | (K) | 4.3 | (I) | | |
| | | | | | | 4.3 | (K) | | |
| | (1,2) | (8±2) | (D) | (10±2) | (F) | (9±2) | (F) | | |
| | | | | (10) | (K) | (9) | (K) | | |
| | (1,1)(s) | | | <-9.3 | (B) | <-8.6 | (B) | -8.8 | (J) |
| | | | | -9.09 | (C) | -9.30 | (C) | | |
| | | | | -9.1±1.0 | (F) | -9.3±1.0 | (F) | | |
| | | | | -9.1 | (I) | -8.5±1.4 | (G) | | |
| | | | | | | -9.3 | (I) | | |
| $CO_3^{2-}$ | (1,1) | | | 5.9 | (K) | | | (5) | (J) |
| | (1,2) | | | | | | | (9) | (J) |
| | (1,3) | | | 16.3 | (K) | | | (14) | (J) |
| $NO_3^-$ | (1,1) | (0.1) | (D) | (1.1) | (D) | | | | |
| $HPO_4^-$ | (1,1) | | | 3.38 | (C) | 2.8 | (K) | | |
| | | | | 3.3 | (K) | | | | |
| $SO_4^{2-}$ | (1,1) | (2.0) | (D) | | | | | 2 | (J) |
| $F^-$ | (1,1) | (3.7) | (D) | | | | | 3.7 | (J) |
| | (1,2) | (6.3) | (D) | | | | | | |
| | (1.3) | (7.6) | (D) | | | | | | |
| | (1,4) | (7.7) | (D) | | | | | | |
| $Cl^-$ | (1,1) | -0.1 | (I) | -0.3 | (I) | -0.17 | (C) | | |
| | | | | 0.3 | (K) | -0.17 | (I) | | |
| | | | | | | -0.17 | (K) | | |

(d) Hexavalent actinides

| | | U(VI) | | Np(VI) | | Pu(VI) | | An(VI) | |
|---|---|---|---|---|---|---|---|---|---|
| OH⁻ | (1,1) | 8.2 | (A) | 8.9 | (A) | 8.4 | (A) | 8.3 | (J) |
| | | 8.2±0.2 | (B) | 8.85±0.09 | (B) | 8.4±0.2 | (B) | | |
| | | 9.86 | (C) | 10.63 | (C) | 8.70 | (C) | | |
| | | 8.2 | (D) | 8.9 | (D) | 8.4 | (D) | | |
| | | 8.2 | (E) | 9.1±0.5 | (F) | 8.9±0.3 | (F) | | |
| | | 8.1±0.2 | (F) | 8.6 | (I) | 8.4±1.4 | (G) | | |
| | | 8.2±0.5 | (G) | 8.85 | (K) | 7.9 | (I) | | |
| | | 8.1 | (I) | | | 8.4 | (K) | | |
| | | 8.9 | (K) | | | | | | |
| | (1,2) | 15.98 | (C) | 18 | (D) | 16.99 | (C) | 16.0 | (J) |
| | | (18) | (D) | (17.8±0.8) | (F) | (16) | (D) | | |
| | | (17.2±0.8) | (F) | (17.8) | (K) | 17.6±0.5 | (F) | | |
| | | 16.1±0.9 | (G) | | | 17 | (I) | | |
| | | 16 | (I) | | | 17.6 | (K) | | |
| | | (17.2) | (K) | | | | | | |
| | (1,3) | 18.36 | (C) | (23±2) | (D) | 21.29 | (C) | | |
| | | (22) | (D) | (23) | (K) | 22±2 | (F) | | |
| | | (21±2) | (F) | | | 21.3 | (I) | | |
| | | 18.2 | (I) | | | 22 | (K) | | |
| | | 21 | (K) | | | | | | |
| | (2,2) | 22.4 | (A) | 21.6 | (A) | 19.6 | (A) | 22.5 | (J) |
| | | 22.38±0.02 | (B) | 21.61±0.06 | (B) | 19.64±0.15 | (B) | | |
| | | 22.94 | (C) | 21.6 | (D) | 19.49[a] | (C) | | |
| | | 22.4 | (D) | 21.6±0.8 | (F) | 19.6 | (D) | | |
| | | 22.35 | (E) | 20.9 | (I) | 20.3±0.3 | (F) | | |
| | | 22.4±0.2 | (F) | 21.61 | (K) | 19.7±2.3 | (G) | | |
| | | 22.4±0.9 | (G) | | | 20.1 | (I) | | |
| | | 21.6 | (I) | | | 19.64 | (K) | | |
| | | 22.38 | (K) | | | | | | |
| | (3,5) | 54.4 | (A) | 52.5 | (A) | 48.4 | (A) | 54.5 | (J) |
| | | 54.37±0.03 | (B) | 52.51±0.06 | (B) | 48.35±0.09 | (B) | | |
| | | 54.4 | (D) | 52.5 | (D) | 48.4 | (D) | | |
| | | 54.38 | (E) | 53±1 | (F) | 50±0.5 | (F) | | |
| | | 55±1 | (F) | 50.7 | (I) | 48.3±3.7 | (G) | | |
| | | 54.3±1.2 | (G) | 52.51 | (K) | 49.3 | (F) | | |
| | | 52.6 | (I) | | | 48.35 | (K) | | |
| | | 54.4 | (K) | | | | | | |
| | (1,2)(s) | -22.4 | (A) | <-21.4 | (B) | -24.52 | (C) | -23.0 | (J) |
| | | -22.4±0.2 | (B) | -22.70 | (C) | -22.8±1 | (F) | | |
| | | -23.03 | (C) | (-22) | (D) | -24.4±1.4 | (G) | | |
| | | -22.4 | (D) | -22.7±1.2 | (F) | -24.5 | (I) | | |
| | | -22.4 | (E) | -22.7 | (I) | | | | |
| | | -22.4 | (F) | | | | | | |
| | | -22.2 | (G) | | | | | | |
| | | -22.4 | (I) | | | | | | |

|  |  | U(VI) |  | Np(VI) |  | Pu(VI) |  | An(VI) |  |
|---|---|---|---|---|---|---|---|---|---|
| $CO_3^{2-}$ | (1,1) | (12) | (D) |  |  | $12.0^a$ | (C) | 10.0 | (J) |
|  |  | 10.06 | (E) |  |  | 12 | (I) |  |  |
|  |  | 10.1±0.4 | (G) |  |  |  |  |  |  |
|  |  | 10.1 | (I) |  |  |  |  |  |  |
|  |  | 9.9 | (K) |  |  |  |  |  |  |
|  | (1,2) | 14.6 | (C) |  |  | 15.04 | (C) | 16.7 | (J) |
|  |  | (14.7) | (D) |  |  | 14.9±2.3 | (G) |  |  |
|  |  | 16.98 | (E) |  |  | 15 | (I) |  |  |
|  |  | 17.1±0.4 | (G) |  |  | 15 | (K) |  |  |
|  |  | 17.1 | (I) |  |  |  |  |  |  |
|  |  | 16.7 | (K) |  |  |  |  |  |  |
|  | (1,3) | 18.3 | (C) |  |  | 18.3 | (I) | 23.8 | (J) |
|  |  | (18.9) | (D) |  |  |  |  |  |  |
|  |  | 21.40 | (E) |  |  |  |  |  |  |
|  |  | 21.4±0.4 | (G) |  |  |  |  |  |  |
|  |  | 21.4 | (I) |  |  |  |  |  |  |
|  |  | 21.4 | (K) |  |  |  |  |  |  |
|  | (3,6) |  |  |  |  |  |  | 60.5 | (J) |
|  | $(AnO_2)_3(OH)_3CO_3^+$ |  |  |  |  |  |  | 46 | (J) |
|  | (1,1)(s) | -10.54 | (C) |  |  | $-12.77^a$ | (C) | -13.8 | (J) |
|  |  | -14.46 | (E) |  |  |  |  |  |  |
|  |  | -14.2±0.2 | (G) |  |  |  |  |  |  |
|  |  | -14.4 | (I) |  |  |  |  |  |  |
| $NO_3^-$ | (1,1) | (0.8) | (D) | $-0.9^a$ | (A) |  |  |  |  |
|  |  |  |  | (1.0) | (D) |  |  |  |  |
| $H_2PO_4^-$ | (1,1) | 3.03 | (E) |  |  | $3.93^n$ | (C) | 3.0 | (J) |
|  |  | 2.9±0.5 | (G) |  |  | 4.0±2.2 | (G) |  |  |
|  |  | 3.0 | (K) |  |  | 11 | (K) |  |  |
|  | (1,2) | 5.47 | (E) |  |  |  |  | 5.5 | (J) |
|  |  | 5.5±0.7 | (G) |  |  |  |  |  |  |
|  | (1,3) | 7.18 | (E) |  |  |  |  |  |  |
|  |  | 7.2±0.7 | (G) |  |  |  |  |  |  |
| $HPO_4^{2-}$ | (1,1) | 8.40 | (E) |  |  |  |  | 8.4 | (J) |
|  |  | 8.4±7.3 | (G) |  |  |  |  |  |  |
|  |  | 8.43 | (K) |  |  |  |  |  |  |
|  | (1,2) | 18.6 | (E) |  |  |  |  | 18.5 | (J) |
|  |  | 18.5±7.3 | (G) |  |  |  |  |  |  |
|  |  | 18.8 | (K) |  |  |  |  |  |  |
|  | (1,1)(s) | $-12.17^o$ | (A) | (-13) | (D) | -12.6±2.3 | (G) | -12.6 | (J) |
|  |  | -10.67 | (C) |  |  |  |  |  |  |
|  |  | (-13) | (D) |  |  |  |  |  |  |

| | | U(VI) | | Np(VI) | | Pu(VI) | | An(VI) | |
|---|---|---|---|---|---|---|---|---|---|
| | (2,2)(s) | $-23.5\pm2.3$ | (G) | | | | | | |
| $PO_4^{3-}$ | (3,2)(s) | $-49.7$ | (A) | $(-50)$ | (D) | | | $-23.5$ | (J) |
| | | $-46.33$ | (C) | | | | | | |
| | | $(-51)$ | (D) | | | | | | |
| | | $-49.0$ | (E) | | | | | | |
| | | $-49.1\pm3.0$ | (G) | | | | | | |
| $SO_4^{2-}$ | (1,1) | $2.95$ | (A) | $3.27$ | (A) | $3.3\pm1.6$ | (G) | $3.0$ | (J) |
| | | $2.95$ | (D) | $1.90^a$ | (C) | $3$ | (K) | | |
| | | $2.75$ | (E) | $3.27$ | (D) | | | | |
| | | $3.0\pm0.7$ | (G) | $1.82$ | (I) | | | | |
| | | $1.81$ | (I) | $3.27$ | (K) | | | | |
| | | $2.95$ | (K) | | | | | | |
| | (1,2) | $4.0$ | (A) | $2.77^a$ | (C) | | | $4.3$ | (J) |
| | | $4.0$ | (D) | $(4.1)$ | (D) | | | | |
| | | $4.25$ | (E) | $2.62$ | (I) | | | | |
| | | $2.5$ | (I) | | | | | | |
| | | $4.3$ | (K) | | | | | | |
| | (1,3) | $3.7$ | (A) | $(5)$ | (D) | | | | |
| | | $(5.2)$ | (D) | | | | | | |
| | | $3.7$ | (F) | | | | | | |
| | | $4.7$ | (K) | | | | | | |
| $F^-$ | (1,1) | $4.3^f$ | (A) | $4.6$ | (A) | $5.7\pm0.7$ | (G) | $5.7$ | (J) |
| | | $4.54^g$ | (C) | $3.96^a$ | (C) | $5.6$ | (K) | | |
| | | $(4.8)$ | (D) | $4.6$ | (D) | | | | |
| | | $5.10$ | (E) | $3.85$ | (I) | | | | |
| | | $5.1\pm0.3$ | (G) | $4.6$ | (K) | | | | |
| | | $4.54$ | (I) | | | | | | |
| | | $5.16$ | (K) | | | | | | |
| | (1,2) | $7.97^a$ | (A) | $7.00^f$ | (A) | $11.0\pm0.7$ | (G) | $11.1$ | (J) |
| | | $(8.3)$ | (D) | $6.97^a$ | (C) | $11.0$ | (K) | | |
| | | $8.96$ | (E) | $(7.5)$ | (D) | | | | |
| | | $9.0\pm0.4$ | (G) | $6.97$ | (I) | | | | |
| | | $7.97$ | (I) | $7.7$ | (K) | | | | |
| | | $8.85$ | (K) | | | | | | |
| | (1,3) | $10.55^a$ | (A) | $(10)$ | (D) | $15.9\pm0.7$ | (G) | $15.9$ | (J) |
| | | $(10.9)$ | (D) | | | $15.9$ | (K) | | |
| | | $11.35$ | (E) | | | | | | |
| | | $11.3\pm0.4$ | (G) | | | | | | |
| | | $10.55$ | (I) | | | | | | |
| | | $11.42$ | (K) | | | | | | |
| | (1,4) | $12.0^a$ | (A) | $(11)$ | (D) | $18.8\pm0.7$ | (G) | $18.8$ | (J) |
| | | $(12.3)$ | (D) | | | $18.8$ | (K) | | |
| | | $12.56$ | (E) | | | | | | |
| | | $12.6\pm0.4$ | (G) | | | | | | |
| | | $12$ | (I) | | | | | | |
| | | $11.97$ | (K) | | | | | | |

|  |  | U(VI) |  | Np(VI) |  | Pu(VI) |  | An(VI) |
|---|---|---|---|---|---|---|---|---|
| $Cl^-$ | (1,1) | 0.21 | (A) | $0.3^f$ | (A) | (0.4) | (D) |  |
|  |  | 0.21 | (C) | $-0.35^f$ | (C) | $-0.3\pm0.7$ | (G) |  |
|  |  | 0.21 | (D) | (0.2) | (D) | 0.1 | (I) |  |
|  |  | 0.24 | (E) | -0.1 | (I) | -0.3 | (K) |  |
|  |  | $1.8\pm1.4$ | (G) |  |  |  |  |  |
|  |  | 0.21 | (K) |  |  |  |  |  |

[a] $I=0.1$    [e] $I=1.0$    [i] $An(OH)_3CO_3^-$    [m] $AnF_4\times2.5H_2O(s)$

[b] $I=0.1$, $23^oC$    [f] $I=0.5$    [j] $20^oC$    [n] $I<0.2$

[c] Data for Nd    [g] $I=1$, $20^oC$    [k] $I=2$    [o] $I=0.3$, $20^oC$

[d] Data for Eu    [h] $22^oC$    [l] $I=0.12$    [p] $I=0.4$

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3   BWR Channels in Concrete
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