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Utility of Oxidation State Analogs in the Study of Plutonium Behavior*

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Oxidation / Plutonium / Analogs / Stability constants

Summary

Plutonium can exist in several oxidation states simultaneously which can complicate interpretation of the behavior of Pu in separation, processing and environmental systems. To assist in obtaining data on the behavior of the separate oxidation states, it is useful to use redox stable cations which have very similar chemical behavior to Pu in the same oxidation state. For example, such analogs are Eu(III) and Am(III) for Pu(III), Th(IV) for Pu(IV), Np(V)O$_2^+$ for Pu(V)O$_2^+$ and U(VI)O$_2^{2+}$ for Pu(VI)O$_2^{2+}$. The degree of similarity and the advantages and the limitations of the use of such analogs is assessed. The agreement in chemical properties is very good for the trivalent and pentavalent analogs, and acceptable for the hexavalent analogs. The tetravalent analogs require adjustments be made to the analog data to make the values agree more closely with those of Pu(IV). Such adjustments as well as equations for obtaining estimates of Pu(IV) data from trivalent and hexavalent analogs are discussed. A brief discussion is given on the use of data from natural analog sites.

Introduction

Plutonium may be unmatched among metallic elements in the diversity of its chemical behavior. In large part this is due to the existence of six oxidation states — the 0, III, IV, V, VI and VII. In all but the Pu(0) state, it is found as cations. In aqueous systems, while Pu(III) and Pu(IV) are simple monotonic cations, Pu(V) and Pu(VI) form linear dioxo species Pu(V)O$_2^+$ and Pu(VI))O$_2^+$. As indicated in the similar values of the reduction potentials of redox pairs of plutonium in Fig. 1, in strongly acidic solutions plutonium can exist in equilibrium in all four states although only two or three states may be present in macro concentrations. By contrast the potential values of uranium and neptunium indicate that a single oxidation state is more stable at different sets of conditions. Plutonium does show normal behavior in an increased stability of the higher oxidation states as the pH of the solution increases; in neutral/basic solutions, Pu(III) is not observable [1].

The similarity in redox potentials of the various plutonium couples seen in Fig. 1 suggest that the distribution of plutonium among its oxidation states can be relatively easily perturbed. This ease of redox change between the plutonium couples is associated
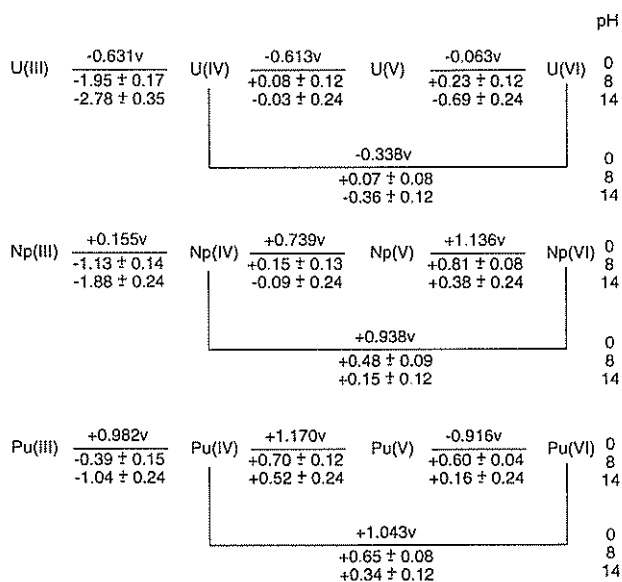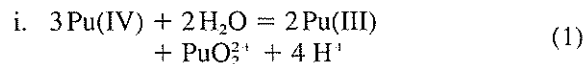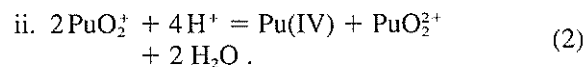
Fig. 1. Reduction potential at pH = 0, 8 and 14 for actinide cations from reference 1, Ch. 22.

with a rapid rate of redox reaction between the III and IV states and the V and VI states.

However, the interchange between the III, IV states and the V, VI states is slower due to the need to make or break the Pu–O bonds. Disproportion reactions also are relatively slow as arrangement/rupture of metal-oxo bonds is involved as seen in the reactions:

i. $\quad 3\,Pu(IV) + 2\,H_2O = 2\,Pu(III)$
$\qquad\qquad + PuO_2^{2+} + 4\,H^+ \qquad\qquad (1)$

and

ii. $\quad 2\,PuO_2^+ + 4\,H^+ = Pu(IV) + PuO_2^{2+}$
$\qquad\qquad + 2\,H_2O . \qquad\qquad\qquad\quad (2)$

The disproportionation of Pu(V) keeps it at very low concentrations in acid solutions relative to the other three states. However, in basic solutions, the fourth power dependence on the H$^+$ concentration prevents this as a path for PuO$_2^+$ reaction and Pu(V) is the dominant solution phase species in neutral and basic waters.

The slow kinetics of the conversion of the reduced Pu(III) and Pu(IV) and the oxidized Pu(V) and Pu(VI) has been used in separation processes of these species. For example, the precipitation of PuF$_3$ + PuF$_4$ with LaF$_3$ carrier in acid solution has been a standard method of separation of Pu(III) + Pu(IV) from PuO$_2^+$ and PuO$_2^{2+}$ (which remain in solution) [2].

This lability of plutonium in the variation of its oxidation state distribution greatly complicates its study as the distribution can be very different in matrices which may be only slightly different. This difficulty is a major problem in tracer level studies where it is not possible to use spectroscopic signatures to measure the relative concentrations of the different oxidation states.

The major factors influencing the oxidation state distribution of plutonium in aqueous solution include the E_h and pH, the presence of complexing ligands and radiolytic effects in high activity solutions. A limiting factor of the concentration of plutonium in neutral/basic solutions is the very strong hydrolysis of Pu(IV). For example, in such solutions, the most stable oxidation state for the dissolved plutonium is IV; however, the insolubility of $Pu(OH)_4$ (log $K_{sp} \leq -54$) results in such a very low concentration of Pu^{4+} that the resulting redox equilibrium limits PuO_2^+ to concentrations of $\leq 10^{-8}$ M [3].

Oxidation state analogs

In order to develop new and improved methods for separation of plutonium or for treatment of nuclear waste which includes plutonium, it is necessary to have a good understanding of the initial distribution of oxidation states and of any perturbations of these which may occur during the separation/treatment. It is also important in environmental systems in which plutonium has been released to natural waters to understand the role of the different oxidation states. Unfortunately, the complexity of the redox reactions of plutonium greatly complicates the interpretation of data in terms of redox speciation of plutonium.

To gain better insight into these systems, many research groups have used oxidation state analogs in which metal ions with similar chemical behavior to the plutonium species of interest are used to mimic the plutonium behavior. Hopefully, the chemical behavior would be almost identical for a particular plutonium state and its oxidation state analog. In this review, the degree of similarity that can be obtained by careful choice of oxidation state analog is discussed. Validation that the study of particular analogs can provide acceptable data for use in modeling the chemical behavior of plutonium in its different oxidation states would be of major value in performance evaluation assessments of nuclear storage sites, separation processes, remediation of contamined areas, etc. A major advantage associated with the oxidation state analogs is that macro concentrations of the analogs can be studied, allowing use of such techniques as Raman, luminescence, UV-vis and NMR spectroscopies. For non-radioactive analogs, a further advantage is the absence of redox perturbation due to radiolytic effects. This is valuable in using analog data to model plutonium behavior at tracer levels.

The basis for the similarity in chemical properties for plutonium and the oxidation state analogs is the predominantly ionic nature of the bonding [4, 5]. Plutonium in all four oxidation states of interest and the analog cations are hard acid species and interact preferentially with hard base donor atoms. As a result, within a specific oxidation state, the strength of the resulting ionic bonds between the cation and the ligand is primarily dependent on the cationic radius for any particular hard donor. Thus, the primary requirements for choice of the cations used as oxidation state analogs are the same oxidation state and similar radius as the ion of the plutonium oxidation state of interest.

The properties of the analogs are compared with those of the associated plutonium cation in the following sections. The various techniques which can be used to study the various analogs also are briefly discussed.

Analogs for Pu(III)

For oxidation state III there is very good correlation in the behavior of Pu(III) and that of other trivalent 4f and 5f elements such as Am(III), Cm(III), Nd(III), Sm(III), Eu(III) and Gd(III) [6]. These analogs can be obtained as radioisotopes for use in tracer studies but, particularly the 4f element cations allow a variety of other techniques to be employed at higher concentrations. For example, Nd(III) has hypersensitive spectral absorption bands (17167, 19103 cm^{-1}) which are sensitive to changes in complexation, symmetry, etc. [7]. Eu(III) has excellent luminescence characteristics which can be used to monitor the number of coordinating donor sites on a ligand from the shift in wavelength of the $^5D_0 - ^7D_0$ transition at 17276 cm^{-1} for the hydrated Eu(III) ion [8]. The residual number of waters of hydration in the inner sphere can be calculated from the half-life of the luminescence decay and the number of species present can be obtained from the number lines in the $^5D_0 - ^7F_0$ excitation spectrum of Eu(III) [9]. Gd(III) is commonly used as a relaxation agent in NMR studies and both shifts and relaxation spectra induced by the paramagnetism of Eu(III) and Gd(III), respectively, can provide valuable information on the structural characteristics of ligands bound to the lanthanide ion on the residual hydration [10]. Using such oxidation stable analogs is important as studies with plutonium at such millimolar or higher concentrations is difficult as plutonium may be present in more than a single oxidation state. Also, Pu(III) cannot be studied by many of the techniques mentioned.

Am(III) and Cm(III) are also useful analogs. [241]Am is a gamma emitting radionuclide which simplifies sample preparation and counting. [248]Cm is a relatively long-lived nuclide with excellent luminescence properties. Even at $10^{-12} - 10^{-8}$ M concentrations, the luminescence half-life can be used to measure the number of water molecules bound to the Cm(III) in a complex [11, 12].

Tables 1 and 2 have data on inorganic (Cl^-, SO_4^{2-}) and organic ($acetate^{-1}$, $EDTA^{4-}$) stability constants for trivalent ions [13]. Data for Pu(III) is not listed but the

Table 1. Comparison of stability constants [13] of inorganic complexes of M(III)

Metal	log β_{101}	log β_{102}	I (M)
		a) Chloride	
Pu	−0.04		1.0
Am	−0.05		1.0
	+0.1		1.0
	0.02	−0.37	1.0
Cm	0.22	−0.03	1.0
Sm	0.13		1.0
		b) Sulfate	
Pu	1.99	3.04	0.5
Am	1.86	2.79	0.5
	1.43	1.85	2.0
Cm	1.85	2.70	0.5
	1.34	1.86	2.0
Sm	1.30	1.91	2.0

Table 2. Comparison of stability constants [13] of organic complexes of M(III)

Metal	log β_{101}	log β_{102}	log β_{103}	I (M)
		a) Acetate		
Pu	2.1			1.0
	2.02	3.34		2.0
Am	1.99	3.28	3.9	0.5
	1.96			2.0
Cm	2.06	3.09		0.5
Nd	1.95			2.0

Metal	b) Citrate (log β_{101})	c) EDTA, (log β_{101})	
	I = 0.1 M	I = 0.1 M	0.5 M
Am	7.73	17.8	16.4
Cm	7.73	18.1	16.7
Nd	7.85	16.60	15.75
Sm	7.93	17.09	16.20
Eu	7.77	17.29	16.23

Table 3. Comparison of stability constants [13] of M(IV).
a) Sulfate (I = 2.0 M)

Metal	log β_{101}	log β_{102}
Th	3.23	5.58
	3.21	5.47
	3.27	5.58
U	3.43	5.75
	3.53	5.89
	3.54	5.95
Np	3.44	5.49
	3.54	6.06
	3.51	6.05

b) EDTA

Metal	I (M)	log β_{101}
Th	0.1	23.2
	0.5	22.3
U	0.1	25.7
	0.5	25.8
	1.0	23.2
Np	1.0	24.6

Am(III) and Cm(III) values can be compared with the lanthanide values as a measure of the similarity in trivalent lanthanide and actinide complexation. The chloro complexes have an outer sphere structure (i.e., the anion is bound to a water molecule in the primary coordination sphere of the cation); the sulfate complexation is inner sphere (i.e., direct metal ion-anion binding); the acetate complexation is inner sphere via the single carboxylate group; the EDTA complexation is hexadentate with the metal ion binding to the four carboxylate and two amine groups of the ligand. Thus, the values reflect the agreement among these 4f and 5f (including Pu(III)) cations in four quite diverse complexation systems.

Analogs for Pu(IV)

The tetravalent plutonium species is the one for which the oxidation state analog approach is most problem-

atic. In general, Th(IV) is the best oxidation state analog for Pu(IV) but for Th(IV), the complexation is somewhat weaker, as is the hydrolytic tendency. The use of Th(IV) as a model requires some adjustment to fit Pu(IV) behavior as the ionic radii [6] are relatively different (1.048 Å for Th(IV) vs. 0.962 Å for Pu(IV). U(IV), Np(IV) and Ce(IV) are closer in radii to Pu(IV)) but control of their tetravalent oxidation state can be a problem in their use as an analog. Unfortunately, very little reliable data are available on stability constants for Pu(IV) but the data in Table 3 on other An(IV) ions reflect the effect of radii. Th(IV) has no useful spectroscopic properties but its complexes can be studied by potentiometry and NMR (^{1}H and ^{13}C spectra of ligands).

Analogs for PuO_2^+ and PuO_2^{2+}

PuO_2^+ and PuO_2^{2+} are closely related to the chemical behavior of the much more stable species NpO_2^+ and UO_2^{2+}. The lower specific activity of U isotopes and ^{237}Np allows use of a much broader variety of spectroscopic and other techniques which require $10^{-4}-10^{-3}$ M concentrations, providing more information on the systems under study. These analog cations also can be used at tracer level concentrations without concern that their oxidation state speciation may be modified. Both NpO_2^+ and UO_2^{2+} can be studied by Raman spectroscopy (at 970 cm^{-1} for NpO_2^+ and 484 cm^{-1} for UO_2^{2+}). In addition, the fluorescence of UO_2^{2+} provides a useful spectroscopic tool.

Since PuO_2^+ is limited to tracer concentrations in acid systems by its disproportionation reaction and in neutral and basic systems by the redox equilibrium with extremely insoluble $Pu(OH)_4$, little data has been reported to provide comparison with analogous NpO_2^+ data. The available data for 1:1 complexation does

Table 4. Comparative data of oxidation analogs (I = 2.0 M)

	III		IV		VI	
	Sm	Am	Th	Np	U	Pu
	$\log \beta_{101}$		$\log \beta_{101}$		$\log \beta_{101}$	
	a) Inorganic					
SO_4^{2-}	1.3	1.4	3.3	3.5	1.7	1.9
OH^-	−7.3	−7.5	−3.2	−1.5	−5.8	−6.0
F^-	3.1	2.9	4.5	4.7	4.7	4.3
	b) Organic					
Acetate	2.0	2.0			2.4	2.2
EDTA	16.2	16.4	23	24		

Table 5. Correction of radii, $An^{4+} + nSO_4^{2-} \rightleftharpoons M(SO_4)_n^{4-2n}$ (I = 2.0 M)

Metal	$\log \beta_{101}^{exp}$	$\log \beta_{102}^{exp}$	$\log \beta_{101}$ (Pu)	$\log \beta_{102}$ (Pu)
Th^{4+}	3.25	5.54	3.38	5.76
U^{4+}	3.50	5.82	3.54	5.95
Np^{4+}	3.50	6.06	3.50	6.16
Avg.		3.5 ± 0.1	6.2 ± 0.2	

show good agreement; e.g., $\log \beta_{101}$ values with NTA in 0.1 M ($NaClO_4$) solution are 6.80 for NpO_2^+ and 6.91 for PuO_2^+. However, lack of analogs is not a major problem as PuO_2^+ is a weakly complexing cation whose concentration is predominantly determined by its redox equilibrium with the III, IV and VI oxidation states and in both acidic and basic solutions, it is present only in tracer level concentrations.

Evaluation of analogs

In summary, the available data supports the validity of use of oxidation state analogs, as reflected in Table 4, in which, in addition to acetate and EDTA complexation, data is given for $\log \beta_{101}$ values for fluoride, sulfate and hydroxide complexation. The analogs have very similar chemistry to that of Pu(III) and allow use of a variety of techniques to study a number of prop-
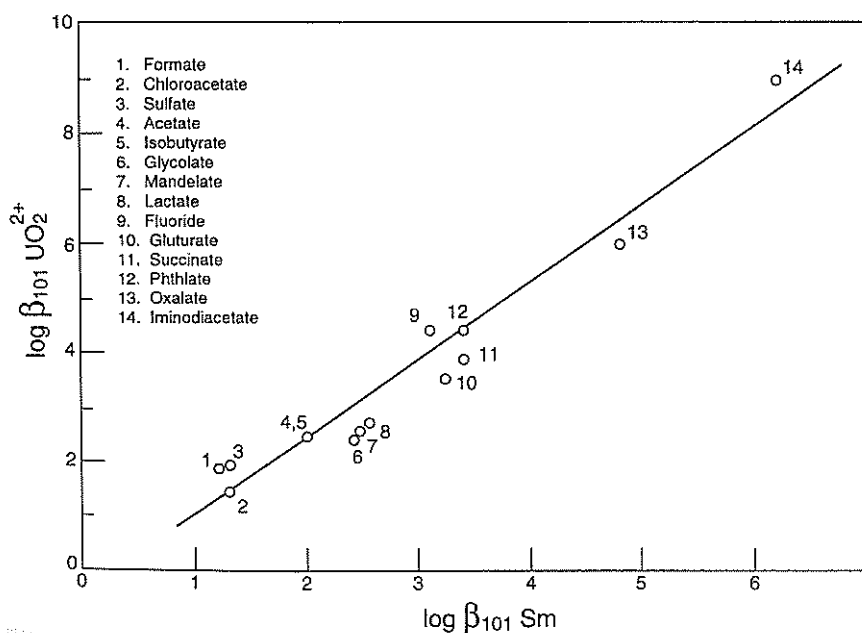
erties of Pu(III) chemistry. The analogs of PuO_2^+ and PuO_2^{2+} seem to mimic their chemistry well enough to be used and to allow use of analog stability constants in Pu(V) and Pu(VI) modeling. The analogs of tetravalent plutonium do not replicate its chemistry as well and the stability constants, etc. of the principle analog, Th(IV), require adjustments before use in modeling to accurately predict Pu(IV) behavior. However, values for Th(IV) can be used in conservative modeling of Pu(IV) chemical behavior.

Corrections in use of Th(IV) data

As discussed previously, the radius of Th(IV) is about 9% greater than that of Pu(IV) for CN = 8, the most common coordination number. Since the metal-donor is ionic, this difference should be reflected directly in the stability constants. Assuming a radius of 1.28 Å for the donor oxygen of sulfate, the stability constants of the Th(IV), U(IV) and Np(IV) monosulfate complexes were corrected by the equation:

$$\log \beta_{101}^{corr} = \log \beta_{101}^{exp} [d_{Pu(IV)L}/d_{Am(IV)L}] . \tag{3}$$

The $\log K_2$ values were corrected in the same manner and added to $\log \beta_1$ to get the value for $\log \beta_2^{corr}$. The corrected values are listed in Table 5 and reflect the

1.	Formate
2.	Chloroacetate
3.	Sulfate
4.	Acetate
5.	Isobutyrate
6.	Glycolate
7.	Mandelate
8.	Lactate
9.	Fluoride
10.	Gluturate
11.	Succinate
12.	Phthlate
13.	Oxalate
14.	Iminodiacetate

Fig. 2. Correlation of values of $\log \beta_{101}$ for SmL and UO_2L complexes (I = 1.0 M ($NaClO_4$)).
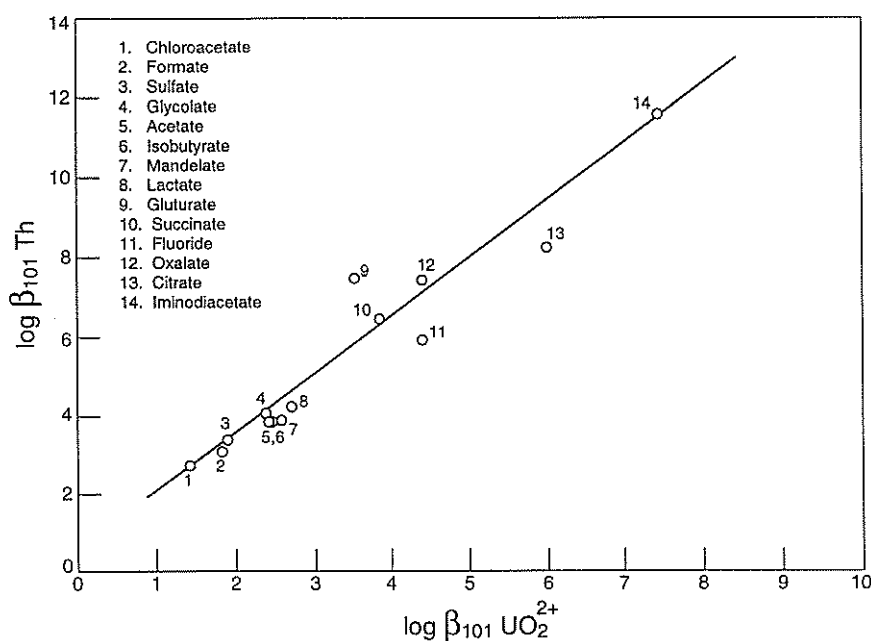
Fig. 3. Correlation of values of log β_{101} for UO_2L and ThL complexes (I = 1.0 M ($NaClO_4$).

Approaches to estimated values

A more extensive approach to estimation of the stability constants which allows use of experimental values for analog ions in different oxidation states takes advantage of the linear free energy relationships which results from the common ionic nature of the cation-anion bond. Figs. 2 and 3 show the linear relation between the stability constants of Sm(III) and $U(V)O_2^+$ and of $U(VI)O_2^{2+}$ and Th(IV) for a number of inorganic and organic ligands.

The strongly ionic nature of the bonding has been shown to allow use of a modified Born equation to estimate stability constants (14). However, this requires some understanding of structural factors, etc. An approach which avoids some of these uncertainties is to use values from chemical analogs and to modify those values by the modified Born equation. The modification is accomplished with the equation:

$$\log \beta_n(A) = \log \beta_n(B) \cdot (Z_A/Z_B) \cdot (D_B/D_A)(d_{B/d}) \qquad (4)$$

where: Z_i = "effective" charge on ion i;
$\quad\quad\quad D_i$ = "effective" dielectric constant for ion i;
$\quad\quad\quad d_i$ = Shannon radius for ion i [15].

The effective charges are $+3$ for M(III), $+4$ for M(IV), $+2.2$ for $M(V)O_2^+$ and $+3.3$ for $M(VI)O_2^{2+}$ [16]. The effective dielectric constants which have been used successfully in the Born equation to estimate stability constants are equal to 65 for MO_2^+, 57 for M(III), 55 for MO_2^{2+} and 40 for M(IV) systems (16). The radii used were for a coordination number of 8 for M(III) and M(IV) and of 6 for MO_2^+ and

MO_2^{2+}. The values are listed in Table 6. Table 7 lists the values of log β_{101} calculated by this approach compared to the reported experimental values when the

Table 6. Parameters used in Eq. (4)

Cation	Z(An)	D(An)	R(An-F) Å	R(An-O) Å
Sm(III)	+3	57	2.63	2.40
Pu(III)	+3	57	2.40	2.45
Am(III)	+3	57	2.37	2.44
Th(IV)	+4	50	2.22	2.26
U(IV)	+4	50	2.17	2.21
Np(IV)	+4	50	2.15	2.19
Pu(IV)	+4	50	2.14	2.18
$Np(V)O_2^+$	+2.2	65	2.03	2.07
$Pu(V)O_2^+$	+2.2	65	2.02	2.06
$U(VI)O_2^{2+}$	+3.3	55	1.99	2.03
$Np(VI)O_2^{2+}$	+3.3	55	2.00	2.04
$Pu(VI)O_2^{2+}$	+3.3	55	1.99	2.03

Table 7. Estimates from Eq. (4)

$$\log \beta (An(x)) = \log \beta (Ln(III)) \frac{Z_x d(III)}{Z_{III} d(x)} = 1.9 \log \beta(IV)$$
$$= 1.3 \log \beta(VI)$$
$$= 0.53 \log \beta(V)$$

	log β_1: Estimates vs. Experimental		
Ligand	Th(IV)	U(VI)	Np(V)
Acetate	3.8 vs. 3.9	2.5 vs. 2.5	1.1 vs. 0.9
Oxalate	9.5 vs. 8.2	6.3 vs. 6.0	2.7 vs. 6.3
Citrate	15 vs. 12	8.8 vs. 7.4	3.5 vs. 2.5
NTA	22 vs. 13	14 vs. 10	6.0 vs. 6.8

Values from reference 13.

Table 8. Values of log β_i^0 estimated from Eq. (4)

a). An(III) and An(IV) (based on Sm(III))

	F⁻	Cl⁻	NO₃⁻	OH⁻	CO₃²⁻	SO₄²⁻	H₂PO₄⁻	HPO₄²⁻
Sm(III)	4.2	0.3	1.2	6.1	7.3	3.7	5.23	5.35
Pu(III)	4.1	0.3	1.2	6.0	7.2	3.6	2.2	5.2
Am(III)	4.2	0.3	1.2	6.0	7.2	3.6	2.2	5.2
Th(IV)	6.8	0.5	1.9	9.9	11.8	5.9	3.6	8.6
U (IV)	6.9	0.5	2.0	10.1	12.1	6.1	3.7	8.8
Np(IV)	7.0	0.5	2.0	10.2	12.2	6.1	3.7	8.9
Pu(IV)	7.0	0.5	2.0	10.2	12.2	6.1	3.7	9.0

b) AnO_2^+ and AnO_2^{2+} (based on UO_2^{2+})

	F⁻	Cl⁻	NO₃⁻	OH⁻	CO₃²⁻	SO₄²⁻	H₂PO₄⁻	HPO₄²⁻	PO₄³⁻
UO_2^{2+}	5.09	0.17	0.3	8.8	9.68	3.15	3.26	7.24	13.23
NpO_2^+	2.8	0.09	0.17	4.9	5.4	1.8	1.8	4.0	7.4
PuO_2^+	2.8	0.09	0.17	4.9	5.4	1.8	1.8	4.0	7.4
NpO_2^{2+}	5.1	0.17	0.3	8.8	9.6	3.1	3.2	7.2	13.2
PuO_2^{2+}	5.1	0.17	0.3	8.8	9.7	3.2	3.3	7.2	13.2

values of Sm(III) were used for the base set in the equation.

Table 8 lists the values calculated for trivalent and tetravalent ions in 1:1 complexation with a variety of inorganic ligands based on Sm(III) values. In (b) of Table 8, the values calculated for NpO_2^+, PuO_2^+, NpO_2^{2+} and PuO_2^{2+}, based on UO_2^{2+} values, are listed.

A primary use of these values would be in screening values reported in the literature which may be incorrect due to the researchers' failure to consider adequately experimental problems due to redox, sorption, precipitation, ternary complexation, etc. In lieu of directly measured stability constants, these values may have use in preliminary modeling to assess the need for research to obtain such constants.

Use of natural analogs

Plutonium, due to its relatively short half-life, is not present in ore deposits, soils, etc. from geologic times. A major concern is to validate present modeling estimates of plutonium behavior of $10^3 - 10^6$ year time periods although such behavioral records are absent in present day geologic systems due to the total decay of any primordial plutonium. One approach is to use comparisons of the calculated values with those measured in appropriate geologic sites known as natural analogues. These natural analogue sites are areas in which uranium or thorium ores have been present for geologic time periods; if these sites have not been affected by human activities, the record of geological, long-term effects should be well preserved. A number of such sites are being studied around the world. In these natural analogue sites, the mobilization and fixation of uranium involves complexation while that of thorium is almost exclusively due to hydrolysis by carbonate and humics. The redox potential is strongly buffered if significant amount of organic substances

are present. The value of use of data from natural analog sites in which the major "oxidized" species is $U(VI)O_2^{2+}$ and the major "reduced" species are U(IV) and Th(IV) depend on the similarity in chemical behavior of these species with $Pu(VI)O_2^{2+}$ and Pu(IV), respectively.

In the Pocos de Caldas formation in Brazil in which the water is reduced, most of the thorium, the rare earths, and, to a lesser extent, the uranium, is associated with goethite (FeOOH) particles and transport by organic colloids is much less important [17]. In another region of this formation, the thorium and rare earths are associated with organic (humic) colloids and have a higher mobility. The uranium as UO_2^{2+} is more soluble in this region as carbonate and humic complexes.

At an analogue site in Scotland, the liquid from the ore passes into a peat bog in which the uranium becomes associated predominantly with humic material. The Th is found on Fe/Al oxyhydroxide colloids and particles [18]. In many clay deposits, the organic material is most significant in maintaining a reducing potential which restricts actinide migration and provides a sorption source of the mobilized fraction, confirming the value of such material as the backfill in the near field of nuclear repositories. An important observation in these sites is the role of the humic type organics which can reduce the species or interact with them to result in increased migration or in increased sorption (decreased migration) on repository surfaces. With proper regard for the differences in sites, the information from natural analog studies can be of significant value in validating the calculations of probable radionuclide migration from nuclear repositories when such releases can be attributed to normal conditions (i.e., no unusual natural events such as earthquakes, volcanic activity, flooding, etc.). By contrast, there is evidence for significant dissolution of minerals at the

Oklo natural nuclear reactor sites in Gabon, Africa due to the radiation and high temperatures present during and after the fission processes [19]. As a result, conditions were considerably more perturbed in Oklo and much less favorable for radionuclide retention. However, the uranium and rare earth elements show evidence of a rather small amount of localized redistribution, but the majority of these elements was retained within the reactor zone. Essentially 100% of the Pu and 85−100% of the Nd were retained within the reactor zones. The migration fission products were held within a few tens of meters of these zones. The water leaving the reactor zones had 2×10^{-5} M concentrations of Tc, Ru and Nd at a flow rate of 5 m y^{-1}. Thermodynamic calculations of the temperature dependent solubilities indicate that the loss of the fission products was diffusion controlled, whereas retention in the surrounding rocks was due to temperature dependent deposition from an aqueous solution.

In summary, data from natural analog studies can provide useful tests of the modeling predictions. For example, insight into the data base used in modeling as well as into the assumptions used can be gained. The natural analog approach can identify the significant aqueous species and the solid phases which control solubility. It may also provide a measure of leaching to the aqueous phase and of the tendency of plutonium to sorb to surfaces. In general, modeling may oversimplify and/or omit processes, they may assume equilibrium processes when the natural systems may be in a steady state mode, the solid phases in nature may be non-stoichoimetric and the models may not be able to estimate transportation of colloids.

Conclusions

Values of the stability constants of the appropriate oxidation state analogs of Pu(III), PuO_2^+ and PuO_2^{2+} can be used in modeling the behavior of plutonium in natural waters. The use of Th(IV) values generally underestimates the strength of Pu(IV) complexation. However, corrections based on the difference in radii can result in values which approach closely that of Pu(IV) and can be used in modeling the solution behavior of Pu(IV). It is also possible to estimate useful values for all four oxidation states from the Born equation with appropriate radius, dielectric constant, and effective charge. Data from natural analog sites can provide information on the factors which effect migration or retention of plutonium in geologic sites.

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