Thermodynamic and Oxidation/Reduction Reactions and Their Effects on Speciation and Mobility of Plutonium in DOE Wastes

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PuEDTA COMPLEXES

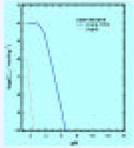
Reasons for Studying Pu(IV) EDTA

- EDTA forms strong complexes with Pu(IV) and co -disposed with Pu
- EDTA is reported to enhance Pu(IV) mobility
- Only limited data available for Pu(IV) EDTA system
- Reported equilibrium constants vary over many orders of magnitude
- Complexation constant data not available for environmental rangein pH values and highly alkaline conditions
- Existing thermodynamic data at odds with field studies
- Reliable predictions of Pu(IV) behavior in the presence of EDTA not possible

Equilibrium Constants for the Formation of PuEDTA(aq) Complexes [$Pu^{4+} + EDTA^{4-} \rightleftharpoons$ PuEDTA(aq)] Reported in the Literature

log K	Ionic Strength	pH	Method	Reference
17.66	0.1	3.3	Ion exchange	Foreman and Smith [1957a]
17.1	0.1	3.3	Spectrophotometric	Foreman and Smith [1957b]
24.2	1.0	0	Spectrophotometric	Foreman and Smith [1957b]
26.14	1.0	0	Calculated [a]	Klygin et al. [1959] from data of Foreman and Smith [1957b]
26.75	1.0	0	Calculated [b]	Krot et al. [1962] from data of Foreman and Smith [1957b]
25.6	0.1	2.2	Polarography	Caucheitier and Guichard [1973]
28.2	0.1	1.6-4.6	Spectrophotometric	Caucheitier and Guichard [1973]
2.6[a]	0.1		Polarography	Caucheitier and Guichard [1973]

[a] Constant for the Reaction [PuEDTA (aq) + $H^+ \rightleftharpoons$ $HPuEDTA^+$]



Note: In conflict with field studies (Cleveland and Rees 1981; Rees and Cleveland 1982) which show Pu(IV)EDTA complexes important in as highpHas12

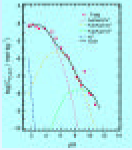
Predicted PuO2(am) Solubility from Literature Thermodynamic Data

Pitzer Ion-interaction Parameters Used in This Study

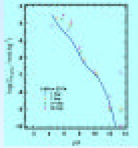
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Reference
		Binary parameters			
Pu^{4+}-Cl^-	1.644	15.5	0.00	0.1	Analogy to U(IV), Rai et al. [1997]
Na^+-$EDTA^{4-}$	1.016	11.60	0.00	0.001	Pokrovsky et al. [1998]
Na^+-$HEDTA^{3-}$	0.5458	5.22	0.00	-0.048	Pokrovsky et al. [1998]
Na^+-H_2EDTA^{2-}	-0.1262	1.74	0.00	0.054	Pokrovsky et al. [1998]
Na^+-H_3EDTA^-	-0.2345	0.29	0.00	0.059	Pokrovsky et al. [1998]
Na^+-OH^-	0.0864	0.253	0.00	0.0044	Harvie et al. [1984]
Na^+-Cl^-	0.0765	0.2664	0.00	0.00127	Harvie et al. [1984]
H^+- Cl^-	0.1775	0.2945	0.00	0.0008	Harvie et al. [1984]
		Ternary parameters			
OH^--Na^+	0.036				Harvie et al. [1984]
H^+- Na^+-Cl^-	-0.004				Harvie et al. [1984]
Cl^--OH^-	-0.05				Harvie et al. [1984]
Cl^--OH^--Na^+	-0.006				Harvie et al. [1984]

Results

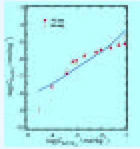
Solubility of PuO_2(am) was determined as a function of pH and EDTA concentrations. Aqueous species/oxidation-states were characterized using a combination of techniques involving XAS, solvent extraction, and UV- Vis- NIR. Pitzer model was developed from PuO_2(am) solubility in 0.0001 M EDTA and as a function of pH and was tested against all of the other data. The close agreement between the observed and predicted concentrations overa wide range in pH (4-14) and EDTA concentrations (0.0001-1.0 M) demonstrates the reliability of the model.



PuO_2(am) Solubility in 0.0001 M EDTA



PuO_2(am) Solubility in 0.001 M EDTA



PuO_2(am) Solubility in EDTA at pH ~ 9

Thermodynamic Data

Reaction	log K°	Reference
$Pu^{4+} + OH^- + EDTA^{4-} \rightleftharpoons Pu(OH)EDTA^-$	36.39	This study
$Pu^{4+} + 2OH^- + EDTA^{4-} \rightleftharpoons Pu(OH)_2EDTA^{2-}$	44.74	This study
$Pu^{4+} + 3OH^- + EDTA^{4-} \rightleftharpoons Pu(OH)_3EDTA^{3-}$	49.64	This study
$PuO_2(am) + 2H_2O \rightleftharpoons Pu^{4+} + 4OH^-$	-56.85	Rai (1984)

Conclusions

- Pu(IV) makes strong complexes with EDTA
- Ternary Pu^{4+}- OH^--$EDTA^{4-}$ complexes important in highly acidic to highly alkaline conditions
- Pu(IV) solubility, thus potential mobility, increases with the decrease in pH and increase in EDTA concentrations
- Processes that directly on indirectly lower EDTA concentrations will lessen the impact of Pu, for example
  - Microbial degradation (direct)
  - Metal competition for EDTA (indirect)
- Pu(IV)- EDTA complexes not expected to be important under highly alkaline conditions

OVERALL OBJECTIVE

Need for This Study

- Pu is a major contaminant at many DOE sites
  - Intentionally or inadvertently released to sediments
  - Generally contain strongly complexing ligands as co -contaminants
  - Concentrated electrolytes
- Reliable fundamental data are lacking, especially for
  - Pu(IV) with strongly complexing ligands
  - Redox reactions
- Fundamental data are required for predicting Pu environmental behavior and developing waste processing technologies

Objectives

Develop fundamental data for important Pu reactions for predicting Pu behavior in environmental/waste systems

Pu(V) MODEL DEVELOPMENT

Reasons for This Study

- Pu(V) can undergo disproportionation reactions making it difficult to obtain thermodynamic data
- Knowledge of Pu(V) behavior important
  - Dominant species in natural waters
  - Dominant oxidation state in air-equilibrated PuO_2(am) suspensions
- Data needed for predicting Pu behavior in oxygenated systems

Results

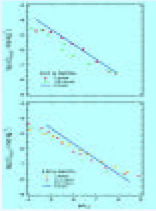
The objectives of this study were to determine the solubility of PuO_2 (am) in air -equilibrated suspensions, where Pu(V) is known to be the dominant oxidation state (Rai et al. 1980, Rai 1984), and to determine whether the ion-interaction parameters for Np(V) with Cl^- or ClO_4^- reported in the literature (Neck et al. 1995) can be used to reliably predict the corresponding Pu(V) behavior. Two different methods were used to analyze the data. One of these methods used estimated values of the pe, and the other assumed the same effective oxygen fugacities. The results from both of these methods show that Pu(V) indeed does behave in an analogous fashion to Np(V).

Methods Used to Analyze the Data

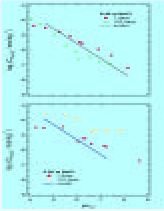
- Pe Dependent Method
  $PuO_2(am) \rightleftharpoons PuO_2^+ + e$
- Pe Independent Method

[illegible]

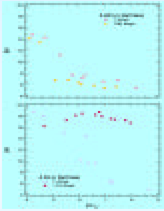
Where x = 0.4 M and y = 4.0 M for the given quantities. The calculated values of log ($m_{PuO_2^+}^{y}/m_{PuO_2^+}^{x}$) are –0.12 for $NaClO_4$ and 0.28 for NaCl systems.



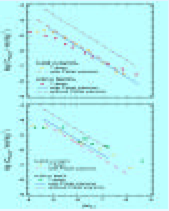
PuO_2(am) Solubility in $NaClO_4$



PuO_2(am) Solubility in NaCl



Effect of Time and NaCl Concentrations on pe During PuO_2(am) Solubility



Comparison of Predicted and Observed PuO_2(am) Solubility

Pitzer Ion-Interaction Parameters[a] and Thermodynamic Data Used in This Study

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Reference
		Binary parameters			
Na^+-Cl^-	0.0765	0.2644	0.00	0.00127	84 HAR/MOL
Na^+-ClO_4^-	0.0554	0.2755	0.00	-0.00118	73 PIT
Na^+-OH^-	0.0864	0.2530	0.00	0.00440	84 HAR/ML
H^+- Cl^-	0.1755	0.2945	0.00	0.00080	86 HAR/ML
H^+- ClO_4^-	0.1747	0.2931	0.00	0.00819	73 PIT
Ca^{2+}- OH^-	0.1747	-0.2303	-5.72	0.00	84 HAR/MOL
Ca^{2+}-Cl^-	0.3159	1.614	0.00	-0.00034	84 HAR/MOL
PuO_2^+- Cl^-	0.1415	0.2810	0.00	0.00	This study[b]
PuO_2^+- ClO_4^-	0.257	0.180	0.00	0.0081	This study[b]
$PuO_2(am) \rightleftharpoons PuO_2^+ + e$			log K° = -18.85		This study

[a]Common ion ternary parameters were also used for these systems but are not reported here.

[b]Assumed to be identical to the corresponding Np parameters reported by Neck et al. (1995).

Several observations can be made from these data: 1) the predicted concentrations in 4.0 M NaCl and $NaClO_4$ solutions without the inclusion of parameters for PuO_2^+ with Cl^- and ClO_4^- are approximately an order of magnitude higher than with the inclusion of these parameters, 2) the absolute difference between the concentrations in 0.4 and 4.0 M solutions for the observed as well as the predicted concentrations are similar, and 3) the inclusion of Pitzer ion-interaction parameters for PuO_2^+ correctly predicted a decrease and an increase in observed PuO_2^+ concentrations in $NaClO_4$ and NaCl solutions, respectively, when the concentrations of the electrolytes were changed from 0.4 to 4.0 M.

Pu(V) Reduction Reactions

Experiments were conducted over a range of pH (7.9-10.8) and H_2O_2 (0.00001-0.04 M), and in the presence of Pu(V) (log M = -9.82) and 1.0 M NaCl at 19±2°C to determine the rate of reduction of Pu(V) by H_2O_2. The reduction of PuO_2^+ was found to be first order with respect to H_2O_2 concentration and inverse first order with respect to H^+ concentration. With these results and assuming a first order dependence with respect to the concentration of PuO_2^+, the reaction can be described by the following rate equation:

$$d[Pu(V)]/dt = k \times [Pu(V)] \times [H_2O_2]/[H^+],$$

with k = $3.59 \times 10^{-9} \pm 1.79 \times 10^{-9}$ min^{-1}. Using this equation, the redox half life of PuO_2^+ has been calculated for a range of environmentally relevant conditions.

NOTE: Details about these studies are not presented because the results have been published in the open literature (Radiochimica Acta 86:109-113).

Overall Summary

- Developed data on Pu(IV)-EDTA complexes
- Developed Pu(V) model for concentrated Cl and ClO_4 systems
- Developed data for predicting PuO_2^+ reduction in the presence of H_2O_2
- Summarized thermodynamic data for different Pu oxidation states
- Data and models help
  - Predict Pu(IV)- EDTA behavior under environmental condition
  - Show that Pu(IV)- EDTA complexes are not expected to be important in tank wastes
  - Show that Np(V) can be used as an analog for Pu(V)
  - Provide methodology to study Pu(IV) complexes with other strongly complexing ligands

Publications

- Rai, D., H. Bolton, D. A. Moore, N. J. Hess, G. R. Choppin. 2000. Thermodynamic Model for the Solubility of PuO_2(am) in the Aqueous Na^+- H^+-OH^- -Cl^-- H_2O- Ethylenediaminetetraacetate System. *Radiochimica Acta* (submitted).
- Rai, D., D. A. Moore, A. R. Felmy, , G. R. Choppin, R. C. Moore. 2000. Thermodynamics of PuO_2^+- Na^+- Cl^--ClO_4^--OH^-- H_2O System: Use of NpO_2^+ Pitzer Ion-Interaction Parameters for PuO_2^+. *Radiochimica Acta* (submitted).
- Morgenstern, A., G. R. Choppin. 1999. Kinetics of the reduction of Pu(V)O_2^+ by Hydrogen Peroxide. *Radiochimica Acta* 86:109-113.
- Three publicly available technical reports summarizing Pu(III), Pu(IV), Pu(V), and Pu(VI) thermodynamic data

Acknowledgements

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