FINAL REPORT

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RESEARCH PROGRAM TO DETERMINE REDOX REACTIONS AND THEIR EFFECTS ON
SPECIATION AND MOBILITY OF PLUTONIUM IN DOE WASTES

Principle Investigators: Gregory R. Choppin
Florida State University
and
Dhanpat Rai
Pacific Northwest National Laboratory

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I. Executive Summary

Plutonium is one of the major contaminants at many DOE sites where plutonium containing solutions have been released to soils and sediments. Plutonium is present in the soils and sediments at half of the DOE sites and in the groundwater at even more of these. The plutonium-bearing wastes stored at DOE sites often contain organics (e.g., EDTA, NTA, DTPA) as residues from separation processes. The soils at these sites vary greatly in pH, soluble inorganic and organic electrolytes, Eh, and plutonium concentration. This plutonium can be present in multiple oxidation states (III, IV, V, and VI) and, in these oxidation states, forms aqueous complexes of varying stability and solid phases of varying solubility. The dominant oxidation state in solid and in the aqueous phase may differ; e.g., Pu(IV) solids are in equilibrium with aqueous PuO_2^+ . As a result, plutonium in these geologic matrices undergoes a variety of complex reactions which complicate its environmental behavior. These complexities in plutonium chemistry whereby a large variety of precipitation, dissolution, adsorption/desorption, and redox reactions control plutonium speciation and concentrations, result in the need for a rather large amount of reliable, fundamental data to predict Pu behavior in geologic media.. These data are also needed for evaluation of remediation strategies that involve removing most of the contaminants by selective methods, followed by in-situ immobilization of residual contaminants.

Two areas were studied during this EMSP project: 1) thermodynamic data for Th(IV) and Pu(IV) complexes of EDTA and for Pu(V) interactions with chloride; 2) kinetic data for redox reactions of Pu in the presence of common redox agents (e.g., H_2O_2 , MnO_2 , and NaOCl) encountered under waste disposal conditions. These studies are relevant to understanding Pu behavior in wastes disposed of in diverse geologic conditions (e.g., at the WIPP and YUCCA Mountain repositories and in contaminated sediments at many different DOE sites) and also for developing effective remediation strategies (e.g., processing of high level waste tanks).

During this 3 year period, reliable thermodynamic data for Pu(IV) complexes with EDTA and for Pu(V) with chloride were obtained (Rai et al. 2000a and 2000b). These studies, especially those with Pu(IV), have provided a methodology for studying Pu(IV) behavior where the concentration of the simple, hydrated ion, Pu^{4+} can be determined as this is needed for accurate measurement of equilibrium constants (Rai et al. 2000a). It was not possible in previous studies reported in the literature to determine reliably the concentration of Pu^{4+} , even in very acidic conditions, due to hydrolytic interference and the lack of reliable hydrolysis constants. Our methodology can be used to study

systems involving EDTA and other ligands, (e.g., DTPA, HEDTA, and NTA) which were used in separations and, consequently, are present in the wastes.

A number of studies (Nelson and Lovett 1978, Nelson et al. 1984, Bondietti and Trabalka 1980, Fukai et al. 1987, Choppin et al. 1986, Choppin and Stout 1989) have shown that Pu(V) is the dominant soluble Pu species in natural waters (Pacific Ocean, Irish Sea, Mediterranean Sea, Lake Michigan, Gulf of Mexico, and in alkaline freshwater ponds). Despite the reported stability of Pu(V) in these systems, little data are available for important Pu(V) reactions. Under this EMSP contract, we showed that thermodynamic data for Np(V) can be used to reliably predict Pu(V) behavior (Rai et al. 2000b). We also demonstrated the need for research on the effects of reducing agents generally present in geologic environments to reduce plutonyl species to the lower oxidation states (Choppin 1999). We have also studied the effect of H₂O₂, NaClO, and MnO₂ on the reduction of Pu(V) in this research period and have in the past studied the reduction kinetics of U(VI) and Np(VI) by organic compounds of environmental importance (Choppin and Rao 1992, Choppin 1991, Rao and Choppin 1991a, 1991b). In summary, these studies have yielded data to address redox reactions of plutonium in the presence of environmentally important agents (e.g. organic and inorganic oxidants/reductants).

II. Research Objectives

The stored USDOE tank wastes contain plutonium as well as organic co-contaminants (e.g., EDTA, NTA, DTPA) in alkaline media. Most of these organic contaminants strongly complex Pu and can make Pu(IV) (which is otherwise fairly insoluble) soluble and, therefore, mobile. However, reliable values for stability constants for these Pu(IV) complexes, which are necessary to predict Pu behavior in the presence of these organic ligands, are not available. In addition, if released to the environment by accidents, leaks, etc, the plutonium would be in complex geologic matrices which vary greatly in pH, soluble inorganic and organic electrolytes, Eh, and plutonium concentration. Plutonium in these geologic matrices can undergo a variety of complex reactions that control its environmental behavior. Because of the complexities in plutonium chemistry (four different oxidation states that show differing behavior) and in disposal conditions where a large variety of precipitation/dissolution, adsorption/desorption, and redox reactions can control plutonium oxidation states and concentrations, there is a pressing need for a fundamental approach to obtain data capable of reliably predicting plutonium behavior in these extremely complex and diverse matrices. These data are also needed for remediation strategies which

involve removing the contaminants by selective leaching followed by ex-situ treatment for removal or in-situ retention of contaminants for immobilization.

To contribute to the development of a fundamental model for reliably predicting the geochemical behavior of Pu in diverse geologic environments, the emphasis of these studies was placed on only the important aspects of Pu chemistry for which reliable data are not available. Therefore, our studies dealt with developing 1) thermodynamic data for Pu(IV)-EDTA complexes and methodology for developing thermodynamic data for other ligands, such as NTA and DTPA, that strongly complex Pu(IV), 2) thermodynamic data for Pu(V) systems and demonstration that thermodynamic data for Np(V), an analog for Pu(V), can be used to describe Pu(V) behavior, and 3) fundamental data on Pu oxidation state transformation reactions in the presence of environmentally important oxidants and reductants.

III. Research Results

III-1 Thermodynamic Model for the Solubility of PuO₂(am) in the Aqueous Na⁺-H⁺-OH⁻-Cl⁻-H₂O-ethylenediaminetetraacetate System

Soils contaminated with plutonium are present at a number of USDOE sites (e.g., Oak Ridge, Hanford, Savannah River, Los Alamos, Rocky Flats, the Nevada Test Site) and are of concern due to the long half-life and high toxicity of plutonium (ORNL 1993, Riley et al. 1992)..

Ethylenediaminetetraacetic acid (H₄EDTA), which was co-disposed with radionuclides at several sites, has been reported to enhance the solubility and transport of Pu, ⁶⁰Co, and other radionuclides in groundwater at Oak Ridge, Chalk River, and Maxey Flats (Riley et al. 1992, Cleveland and Rees 1981, Means et al. 1978, Champ and Robertson 1986, Killey et al. 1984). Despite the reported impact of organic complexants on Pu solubility and mobility in geologic environments, limited reliable, experimental thermodynamic data exist on complexation with these ligands (Foreman and Smith 1957a and 1957b, Cauchetier and Guichard 1973). For example, the reported equilibrium constants for Pu(IV) formation of PuEDTA(aq) vary over nine orders of magnitude. Moreover, these values are based on data obtained in relatively acidic conditions (pH < 4), which may not be applicable to the range in pH values expected in most environmental conditions. Foreman and Smith (1957b) reported a difference of over seven orders of magnitude between the equilibrium constants they obtained for PuEDTA formation at pH 3.3 (log K of 17.1) and in 1.0 M HNO₃ (log K of 24.2). This value was later revised by Klygin et al. (1959) to 26.15 and by Krot et al. (1962) to 26.75 because the authors did not

consider H_5EDTA^+ and $\text{H}_6\text{EDTA}^{2+}$, which are important in these acidic solutions. Our studies, described later, show that none of these values are applicable to the range of pH values encountered in geologic environments.

A major difficulty in calculating reliable values of complexation constants for strongly complexing ligands [e.g., EDTA, DTPA, and NTA] by the techniques (spectrophotometric, polarography, and ion exchange) and pH values used in past studies is that the concentration of Pu^{4+} needed to calculate these constants is very difficult to measure reliably. This is due to the very strong hydrolysis of Pu^{4+} which is further complicated by the redox behavior of Pu. It is relatively easy to control plutonium in the highest, Pu(VI), or lowest, Pu(III), oxidation states by adding strong oxidizing or reducing agents but it is more difficult to maintain it in the Pu(IV) and Pu(V) states, especially under conditions relevant to geologic environments.

Some of the major difficulties encountered in the past can be overcome by studies of the solubility of plutonium in equilibrium with a Pu(IV) solid of known solubility product as this can provide reliable values of Pu^{4+} concentration as a function of pH. We, therefore, studied the solubility of $\text{PuO}_2(\text{am})$ in solutions of 0.001 M and 0.0001 M total EDTA concentration for pH values ranging from 1 to 13.5. Another set of experiments were done at a pH of approximately 9 and with EDTA concentrations ranging from 0.00001 to 0.093 M. The solubility studies were carried out as a function of time. The oxidation states were determined by x-ray absorption near edge spectroscopy and solvent extraction.

Significant Results

The comparison of the experimental solubility with the predictions based on literature data (Cauchetier and Guichard 1973) showed that the predicted concentrations are orders of magnitude lower (e.g. at pH 8, the difference is approximately six orders of magnitude) and this difference increases with the increased pH. This indicated that the existing models were inadequate to represent complexation behavior of Pu(IV) with EDTA at pH values >4 (Figure 1). Our data were interpreted using the Pitzer ion-interaction model (Pitzer 1991) that is applicable to dilute as well as concentrated electrolytes. Our model was developed based on the solubility of $\text{PuO}_2(\text{am})$ at 0.0001 M EDTA concentrations and as a function of pH. The assumption of $\text{Pu}(\text{OH})_x\text{EDTA}$, instead of $\text{PuEDTA}(\text{aq})$, in the model successfully simulated the observed plutonium concentrations as a function of pH in the entire pH region (Figure 1). This is consistent with the absence of a significant formation of PuEDTA in favor of the ternary complexes $\text{Pu}(\text{OH})_n\text{EDTA}^{-n}$.

The reliability of the model developed from the data for $\text{PuO}_2(\text{am})$ equilibrated with 0.0001 M EDTA at different pH values for 7 days, using the modeling parameters given in Tables 1 and 2, was tested against $\text{PuO}_2(\text{am})$ solubility in 0.001 M EDTA over a wide range in pH values and against EDTA concentrations ranging from very low to 0.093 M at a fixed pH. Close agreement between the experimental and predicted Pu concentrations in these different sets indicates that this model is consistent with the experimental data over the full range of conditions. The model included $\text{Pu}(\text{OH})\text{EDTA}^-$, $\text{Pu}(\text{OH})_2\text{EDTA}^{2-}$, $\text{Pu}(\text{OH})_3\text{EDTA}^{3-}$, and the Pitzer ion-interaction parameters for the bulk electrolyte ions and for the different EDTA species (Table 2). These modeling parameters provide $\log K^0$ values for the $\text{PuO}_2(\text{am})$ dissolution reactions of 21.58, 15.92, and 6.95 for the formation of $\text{Pu}(\text{OH})\text{EDTA}^-$, $\text{Pu}(\text{OH})_2\text{EDTA}^{2-}$, and $\text{Pu}(\text{OH})_3\text{EDTA}^{3-}$, respectively according to the reaction $[\text{PuO}_2(\text{am}) + \text{EDTA}^{4-} + (4 - x)\text{H}^+ = \text{Pu}(\text{OH})_x\text{EDTA}^{-x} + (2 - x)\text{H}_2\text{O}]$. The combination of the log of the solubility product value of B56.85 (Rai 1984) for $[\text{PuO}_2(\text{am}) + 2\text{H}_2\text{O} = \text{Pu}^{4+} + 4\text{OH}^-]$ combined with the equilibrium constant of the above reaction provides $\log K^0$ values of 36.44, 44.78, and 49.80 for the formation of $\text{Pu}(\text{OH})\text{EDTA}^-$, $\text{Pu}(\text{OH})_2\text{EDTA}^{2-}$, and $\text{Pu}(\text{OH})_3\text{EDTA}^{3-}$, respectively, according to the reaction $[\text{Pu}^{4+} + x\text{OH}^- + \text{EDTA}^{4-} = \text{Pu}(\text{OH})_x\text{EDTA}^{-x}]$. The different complexes are dominant in different pH regions.

The stability constants from this EMSP study were used to predict Pu(IV) behavior in the presence of EDTA and the results indicated that EDTA complexes of Pu(IV) are not important in the high-level waste tanks as the calculated concentrations in the presence of 0.001 M EDTA are extremely low due to hydrolytic competition at the high pH values of the wastes. We have developed, also, a method for reliably determining Pu(IV) stability constants with other strongly complexing ligands such as HEDTA, DTPA, and NTA.

A manuscript based on the data developed in this study was prepared and is in press in *Radiochimica Acta*. (Rai et al 2000a).

III-2. Thermodynamics of the PuO_2^{+} - Na^+ - OH^- - Cl^- - ClO_4^- - H_2O System: Use of NpO_2^{+} Pitzer Parameters for PuO_2^{+}

Reliable thermodynamic data for all the oxidation states of plutonium are required to develop comprehensive models for prediction of its behavior in different environments. The difficulty in obtaining reliable thermodynamic data for Pu(V) due to its redox and/or disproportionation reactions in aqueous systems has resulted in very limited data for Pu(V)

Figure 1. Aqueous Pu(IV) concentrations contacting $\text{PuO}_2(\text{am})$ suspensions in 0.0001 M EDTA adjusted to a range in pH values and equilibrated for 7 days. Lines represent predicted total and species concentrations, as designated. Modeling species and parameters are reported in Tables 1 and 2. C&G 1973 represents predicted concentrations based on $\text{PuEDTA}(\text{aq})$ complexation constant value reported by Cauchetier and Guichard 1973.

Table 1. Dimensionless standard^a molar Gibbs free energies of formation ($\Delta G_f^0/RT$)

Species	$\Delta G_f^0/RT$	Reference
Pu ⁴⁺	-194.279	[Fuger and Oetting 1976]
Pu(OH)EDTA ⁻	-288.566 $\pm$ 0.81	This study ^b
Pu(OH) ₂ EDTA ²⁻	-371.219 $\pm$ 0.81	This study ^b
Pu(OH) ₃ EDTA ³⁻	-446.197 $\pm$ 0.81	This study ^b
PuO ₂ (am)	-387.594	[Rai 1984]
H ₆ EDTA ²⁺	-3.09	This study, calculated ^c
H ₅ EDTA ⁺	-3.47	This study, calculated ^c
H ₄ EDTA(aq)	0.00	[Pokrovsky et al. 1998]
H ₃ EDTA ⁻	5.76	[Pokrovsky et al. 1998]
H ₂ EDTA ²⁻	12.87	[Pokrovsky et al. 1998]
HEDTA ³⁻	28.71	[Pokrovsky et al. 1998]
EDTA ⁴⁻	53.05	[Pokrovsky et al. 1998]
H ₂ O (R)	-95.663	[Harvie et al. 1984]
OH ⁻	-63.435	[Harvie et al. 1984]
Na ⁺	-105.651	[Harvie et al. 1984]
Cl ⁻	-52.955	[Harvie et al. 1984]

a. The values for all species involving EDTA are only relative to each other, calculated with the assumption that H₄EDTA(aq) = 0.0.

b. Based on 7-day equilibration period data for 0.0001 M EDTA set (Table A.1).

c. Calculated from log K_n values reported by Krot et al. [1962], using the Davies equation to extrapolate the values to zero ionic strength and combining this information with other data reported in this table. Although these species were included for completeness, they do not significantly impact the calculations reported in this paper.

Table 2. Pitzer ion-interaction parameters used in this study^a

Binary parameters					
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^N	Reference
$\text{Pu}^{4+}\text{-Cl}^-$	1.644	15.5	0.00	0.1	^b
$\text{Na}^+\text{-EDTA}^{4-}$	1.016	11.60	0.00	0.001	[Pokrovsky et al. 1998]
$\text{Na}^+\text{-HEDTA}^{3+}$	0.5458	5.22	0.00	-0.048	[Pokrovsky et al. 1998]
$\text{Na}^+\text{ H}_2\text{EDTA}^{2-}$	-0.1262	1.74	0.00	0.054	[Pokrovsky et al. 1998]
$\text{Na}^+\text{ H}_3\text{EDTA}^-$	-0.2345	0.29	0.00	0.059	[Pokrovsky et al. 1998]
$\text{Na}^+\text{-OH}^-$	0.0864	0.253	0.00	0.0044	[Harvie et al. 1984]
$\text{Na}^+\text{-Cl}^-$	0.0765	0.2664	0.00	0.00127	[Harvie et al. 1984]
$\text{H}^+\text{-Cl}^-$	0.1775	0.2945	0.00	0.0008	[Harvie et al. 1984]
Ternary parameters					
$\text{H}^+\text{-Na}^+$	0.036				[Harvie et al. 1984]
$\text{H}^+\text{-Na}^+\text{-Cl}^-$	-0.004				[Harvie et al. 1984]
$\text{Cl}^-\text{-OH}^-$	-0.05				[Harvie et al. 1984]
$\text{Cl}^-\text{-OH}^-\text{-Na}^+$	-0.006				[Harvie et al. 1984]

a. Because the chloride concentrations in most of the samples are low, primarily from the HCl used in adjusting pH values, the parameters involving Cl^- do not figure significantly in calculations, but were included in the model for completeness.

b. Based on analogy to corresponding U(IV) system [Rai et al. 1997].

chemistry. Because of this paucity of data specifically for Pu(V), it is generally accepted that Np(V) can be used as an analog for Pu(V). However, more extensive verification of this concept over a wide range of conditions is desirable.

The objectives of this study were to determine the solubility of PuO₂(am) in air-equilibrated suspensions, where Pu(V) is known to be the dominant oxidation state (Rai et al. 1980a, Rai 1984) over a range of NaCl and NaClO₄ concentrations and to determine whether the ion-interaction parameters for Np(V) with Cl⁻ or ClO₄⁻ reported in the literature (Neck et al. 1995) can be used to reliably predict the corresponding Pu(V) behavior. The goal is to verify the extent to which Np(V) can be used as an analog for Pu(V) in studies of the speciation and environmental modeling of Pu. Two different methods were used to analyze the data. One method used estimated values of the pe, and the other assumed constant effective oxygen fugacities. The results from both of these methods show that Pu(V) indeed does behave in an analogous fashion to Np(V).

Significant Results

The aqueous Pu concentrations in contact with PuO₂(am) suspensions at different concentrations of NaClO₄ or NaCl (with the exception of 4.36 m NaCl) are similar at the different equilibration periods (Figures 2 and 3), indicating that the steady-state concentrations are reached rapidly. The observed increase in Pu concentration with the increase in equilibration period for the 4.36 m NaCl system is not due to slow kinetics of dissolution of PuO₂(am), but rather is due to oxidative dissolution as a result of the production of oxidizing species by alpha radiolysis in the chloride media. The experimental data indicate that the dominant aqueous Pu oxidation state is Pu(V).

Ion-interaction parameters for the bulk electrolyte ions in this study are available (Table 3), but they are not available for PuO₂⁺. However, parameters for NpO₂⁺ (which is used often as an analog for PuO₂⁺) with Cl⁻ and ClO₄⁻, are available (Neck et al. 1995) and were used to compare how closely these NpO₂⁺ parameters, in conjunction with log K⁰ value of -18.85 (similar to -19.45 reported by Rai 1984) for the reaction [PuO₂(am) = PuO₂⁺ + e⁻] along with the estimated pe values, described the PuO₂⁺ system. Close agreement exists between the predicted and observed PuO₂⁺ concentration in all of the systems investigated (0.4 and 4.0 M NaClO₄ or NaCl; Figures 2 and 3), with the exception of a 110-day equilibration period for 4.0 M NaCl. Significant increases in solubility in 4.0 M NaCl observed at longer equilibration periods (Figure 3) are most likely due to conversion of NaCl to NaOCl through alpha radiolysis (Buppelmann et al 1988). The close agreement demonstrates that the modeling parameters (Table 3) used in this

Figure 2. Plutonium concentrations in 0.0018-: m filtrates from PuO₂(am) suspensions in NaClO₄ and equilibrated for different periods. Solid line represents model predictions based on ion-interaction parameters reported in Table 3 and assumptions discussed in the text.

Figure 3. Plutonium concentrations in 0.0018-: m filtrates from $\text{PuO}_2(\text{am})$ suspensions in NaCl and equilibrated for different periods. Solid line represents model predictions based on ion-interaction parameters reported in Table 3 and assumptions discussed in the text.

Table 3. Pitzer ion-interaction parameters used in this study.

Binary parameters					
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^N	Reference
$\text{Na}^+ - \text{Cl}^-$	0.0765	0.2644	0.00	0.00127	Harvie et al. [1984]
$\text{Na}^+ - \text{ClO}_4^-$	0.0554	0.2755	0.00	-0.00118	Pitzer and Mayorga [1973]
$\text{Na}^+ - \text{OH}^-$	0.0864	0.2530	0.00	0.00440	Harvie et al. [1984]
$\text{H}^+ - \text{Cl}^-$	0.1775	0.2945	0.00	0.00080	Harvie et al. [1984]
$\text{H}^+ - \text{ClO}_4^-$	0.1747	0.2931	0.00	0.00819	Pitzer and Mayorga [1973]
$\text{Ca}^{2+} - \text{OH}^-$	0.1747	-0.2303	-5.72	0.00	Harvie et al. [1984]
$\text{Ca}^{2+} - \text{Cl}^-$	0.3159	1.614	0.00	-0.00034	Harvie et al. [1984]
$\text{PuO}_2^+ - \text{Cl}^-$	0.1415	0.2810	0.00	0.00	This study ^a
$\text{PuO}_2^+ - \text{ClO}_4^-$	0.257	0.180	0.00	0.0081	This study ^a
Common ternary parameters					
Species	Value			Reference	
$\text{Na}^+ - \text{H}^+$	0.036			Harvie et al. [1984]	
$\text{Na}^+ - \text{H}^+ - \text{Cl}^-$	-0.004			Harvie et al. [1984]	
$\text{Cl}^- - \text{OH}^-$	-0.050			Harvie et al. [1984]	
$\text{Cl}^- - \text{OH}^- - \text{Na}^+$	-0.006			Harvie et al. [1984]	
$\text{Ca}^{2+} - \text{H}^+$	0.092			Harvie et al. [1984]	
$\text{Ca}^{2+} - \text{H}^+ - \text{Cl}^-$	-0.015			Harvie et al. [1984]	
$\text{H}^+ - \text{Na}^+ - \text{ClO}_4^-$	-0.016			Pitzer [1991]	

a. Assumed to be identical to the corresponding NpO_2^+ parameters reported by Neck et al. [1995]

study are reasonable, and that the NpO_2^+ ion interaction parameters with Cl^- and ClO_4^- are equally applicable to the corresponding PuO_2^+ system. Changes in pe would increase or decrease the solubility curves up and down. However, the difference between the PuO_2^+ concentrations in 0.4 and 4.0 M solutions, the direction of change, and the shape of the curves depends on the aqueous species and the ion interaction parameters used in calculations. Therefore, a pe independent approach can be used to test how well the Np(V) parameters describe the observed Pu(V) behavior. Such analyses and the experimental data showed that: 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 difference between the concentrations in 0.4 and 4.0 M solutions for the observed as well as for the predicted concentrations are similar; and 3) the inclusion of Pitzer ion-interaction parameters for PuO_2^+ correctly predicts 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. These results show that ion-interaction parameters for PuO_2^+ with Cl^- and ClO_4^- are required to accurately predict the effects of changes in the concentrations of the bulk electrolytes, and that the NpO_2^+ parameters can be used to model satisfactorily the PuO_2^+ behavior.

In summary, the solubility of $\text{PuO}_2(\text{am})$ was determined in air-equilibrated suspensions as a function of pH, time, and concentrations of NaCl or NaClO_4 . With the exception of 4.0 M NaCl at longer equilibration periods (≈ 106 days), the data support Pu(V) as the dominant aqueous species in all of the systems investigated. In agreement with the data reported in the literature, Pu(VI) was a result of oxidants produced by alpha radiolysis and was found to be the dominant oxidation state only in 4.0 M NaCl suspensions equilibrated for ca. 106 days. The predicted Pu concentrations, using available thermodynamic data and Pitzer ion-interaction parameters for Np(V) with Cl^- or ClO_4^- were in good agreement with the observed Pu concentrations as a function of pC_{H^+} for all of the systems investigated (synthetic WIPP brine, and 0.4 and 4.0 M NaClO_4 and NaCl). This confirms that NpO_2^+ and PuO_2^+ systems behave in an analogous fashion.

It is also of value to develop the capability for predicting $\text{PuO}_2(\text{am})$ solubility behavior in geologic repositories. For this purpose, $\text{PuO}_2(\text{am})$ solubility was determined for samples under $\text{N}_2(\text{gas})$ atmosphere in a synthetic solution of which 5.31 m NaCl is the major component (described by Rao et al 1999) and which is representative of a brine from the Waste Isolation Pilot Project (WIPP). A close agreement exists between our predicted value, using the data in Table 1 in the above reference and

other assumptions discussed in that paper, and the measured Pu concentrations [$\log C_{\text{Pu(V)}}$ /mol kg⁻¹] values of -5.94 and -5.83 measured, and -5.93 and -5.78 predicted for pC_{H^+} values of 6.46 and 6.38, respectively, indicating the usefulness of the model developed in this study for predicting Pu(V) behavior in repository environments.

A manuscript detailing the results of this study has been submitted to *Radiochimica Acta*. (Rai et al 2000b).

III-3 Plutonium species with / without Reducing Agents

Reliable thermodynamic data for all the oxidation states of plutonium are required to develop comprehensive models for prediction of its behavior in different environments. The difficulty in obtaining reliable thermodynamic data for Pu(V) due to its redox and/or disproportionation reactions in aqueous systems has resulted in very limited data for Pu(V) chemistry.

The known stability of soluble Pu(V) in slightly acidic to near neutral solutions in which $\text{PuO}_2(\text{am})$ is suspended (Rai et al 1980, Rai 1984) was used to study the solubility of plutonium in 0.4 and 4.0 M NaCl or NaClO_4 solutions ranging in pC_{H^+} values from 4 to 9 as a function of time. The close agreement between the observed solubility and the predicted solubility using Pitzer ion-interaction parameters of Np(V) with Cl or ClO_4^- indicates that Pu(V), as expected, behaves in an analogous fashion to Np(V) and confirms the value of using Np(V) data to model Pu(V) behavior.

Although Pu(V) is the dominant oxidation state in most natural waters (Nitsche et al 1984, Rai et al 2000b, Nelson and Lovett 1978, Nelson et al 1984, Bendiatti and Trabalka 1980, Fukai et al 1987, Choppin and Stout 1989) there are reductants in many geologic environments that might reduce the PuO_2^+ species to the tri- or tetravalent states. In redox studies, the reduction of PuO_2^+ by hydrogen peroxide was measured to have an inverse dependence on the H^+ concentration with a half-life for reduction (10^{-10} M Pu(V), 0.001 M H_2O_2) of about 8 days (Morgenstern and Choppin 1999). Similar studies showed a fast oxidation of Pu(IV) to Pu(V) and Pu(VI) by MnO_2 : Since this may be an important factor in Pu redox in the tank wastes, measurement of the rate equation in high alkaline conditions could provide very useful data for evaluating the best remediation systems. Initial experiments with NaOCl (also present in tank wastes) confirmed that it oxidized Pu(IV) to Pu(V) and Pu(VI).

IV. Detailed Results

IV-1 Th(IV) Complexation with Citrate and EDTA

The high stability of the An(IV)EDTA and An(IV)DTPA complexes results in extremely small concentrations of free metal in solutions of excess ligand in solution ($< 10^{-10}$ M), so indirect competitive methods are necessary to measure the equilibrium concentrations in solution.

Citric acid (2-hydroxypropane-1, 2, 3-tricarboxylic acid) was chosen as a competing ligand. Th(IV) was studied initially as an analog of Pu(IV) to avoid redox problems. Using literature values for the stability constants of the Th(Cit)_n (n = 1-3) complexes (Raymond et al 1987) and thorium hydrolysis constants (Moon 1989), the speciation of solutions containing Th(IV), citric acid, and EDTA was calculated as a function of pH. The speciation diagrams were generated using HySS with the results shown in Figure 4. The results of the speciation calculations indicate that citric acid should be able to compete effectively with Th(IV) for EDTA binding and can minimize hydrolysis of the free thorium cation. In addition, only two species, ThEDTA and Th(Cit)₃, are predicted to be present in solution over the pH range of 6 - 8.

The competitive equilibrium between citric acid and EDTA for Th(IV) complexation was monitored by ¹H NMR spectroscopy as the ¹H NMR spectra of citric acid and EDTA are easily resolved. The ¹H NMR spectrum of free EDTA showed a downfield singlet corresponding to the eight acetate protons and an upfield singlet of the four ethylenic protons of the EDTA backbone. The citric acid ¹H NMR spectrum exhibited two doublets upfield of the ethylenic singlet of free EDTA. Based upon the symmetry of the molecule, the ¹H NMR spectrum of citric acid would be expected to exhibit a single singlet corresponding to the protons of the three acetate groups. However, a pair of doublets was observed which we assign to hindered rotation of the acetate groups. No variation in the ¹H NMR spectra of citrate anion was observed as function of pH.

The formation of ThEDTA and Th(Cit)₃ in solution resulted in changes in the observed ¹H NMR spectra. The singlets due to the acetate and ethylenic groups of EDTA shifted upfield. The resonance due to the acetate proton showed further splitting, the extent of which depends upon the degree of metal

binding. The ethylenic resonance remained a singlet. The ^1H NMR of citric acid was broadened by complexation with thorium, but no new resonances attributable to $\text{Th}(\text{Cit})_n$ were evident.

Figure 4. Th(IV)-Citrate-EDTA, I = 0.1 M.

The concentration of ThEDTA in the competition experiments was determined by integration of the singlet, due to the ethylenic protons of the bound EDTA and of the free EDTA. The Th(Cit)_n stability constants have been determined at I= 0.1 m NaCl, 0.3 m NaCl, 0.5 m NaCl, and 1.0 m NaCl, 3.0 NaCl by potentiometric titration. The Th(Cit)_n stability constants calculations were performed by independent analysis of the data by BEST and Hyperquad2000. The values are presented in Table 4.

The Th-EDTA stability constant was determined by using the citrate anion as a competing ligand at pcH = 6.0. From the calculation of speciation using estimated constants, at pH = 6.0 only ThEDTA and Th(Cit)₃ have significant concentrations in solution. The magnitude of the Th-EDTA stability constant was calculated using the equation:

$$\beta_{\text{ThEDTA}} = \beta_{\text{Th(cit)}_3} \frac{[\text{ThEDTA}][\text{cit}]^3}{[\text{Th(cit)}_3][\text{EDTA}]} \quad (1)$$

where [ThEDTA] is calculated from the concentration of free EDTA determined by ¹H NMR and the total mass balance for EDTA and citric acid, and [Th(Cit)₃] is assumed equal to [EDTA].

The stability constants calculated using the above equation are listed in Table 4 as a function of ionic strength.

A publication reporting these results is in preparation.

IV-2 Solubility measurements of PuO₂(am)

Another set of solubility experiments involved samples of PuO₂ (282.5 g/L) stirred in 0.40 and 4.00 M solutions of NaCl and of NaClO₄ over a pH range of 3 to 10. The samples were centrifuged and analyzed for pH, Eh, and plutonium oxidation state distribution, as described previously. Because the studies were conducted in air and over a very large range in pH values, extending to the alkaline region, we calculated the importance of hydroxo and/or carbonato complexes of PuO₂⁺ in these solutions. Modeling (Pitzer) calculations, assuming (a) hydroxo and carbonato complexes and (b) the ion-interaction parameters for the Np(V) system apply to the Pu(V) system, showed that the hydroxo and carbonato complexes of PuO₂⁺ contribute much less than 1% to the total soluble Pu, and, therefore, these complexes need not be included in the final model.

Table 4. Stability constants of Th-Citrate and Th-EDTA at complexes at 25 C

Ionic Strength (m)	a. Th-Cit					Th-EDTA
	$\log \beta_{101}$	$\log \beta_{102}$	$\log \beta_{112}$	$\log \beta_{103}$	$\log \beta_{113}$	$\log \beta_{101}$
0.1 NaCl	11.66 ± 0.09	20.89 ± 0.18	23.79 ± 0.18	26.26 ± 0.18	30.52 ± 0.19	22.8 ± 0.5
0.3 NaCl	11.53 ± 0.05	20.35 ± 0.02	22.56 ± 0.04	25.45 ± 0.06	29.39 ± 0.07	22.0 ± 0.3
0.5 NaCl	10.12 ± 0.05	19.19 ± 0.02	21.42 ± 0.04	24.32 ± 0.04	28.43 ± 0.04	20.6 ± 0.7
1.0 NaCl	9.46 ± 0.37	19.13 ± 0.01	21.70 ± 0.01	24.15 ± 0.03	28.50 ± 0.02	20.7 ± 0.3
3.0 NaCl	15.81 ± 0.14	22.43 ± 0.08	*****	25.59 ± 0.13	30.95 ± 0.04	22.1 ± 0.1

Significant increases in solubility in 4.0 M NaCl were observed at longer equilibration periods. These increases are most likely due to conversion of NaCl to NaOCl through alpha radiolysis. Although the measured redox potentials in these systems may not be reliable, the increases in p_e values at the 110-day equilibration period as compared with a 7-day period for 4 M NaCl and 7- and 106-day equilibration periods for 0.4 M NaCl are consistent with the above conclusion. In the presence of this NaOCl, Pu(VI) would be the stable oxidation state, which would account for the high aqueous Pu concentrations. Spectrophotometric analyses of the dissolved solids from 4.0 M NaCl suspensions equilibrated for 425 days showed the presence of Pu(VI) and the absence of other oxidation states. The increase in p_e , the presence of Pu(VI) at longer equilibration periods, and the observed increases in p_{cH+} are consistent with published data (Buppelmann et al 1988). Because of the lack of information on the solid phases and the aqueous species in these concentrated chloride solutions equilibrated for long periods, further interpretation of these results is not possible. It is also important to note that the effects of radiolysis can be complicated and are dependent upon the ionic media. For example: 1) the formation of Pu(VI), and an increase in p_e and solubility were observed in 4.0 M NaCl, but were not observed in NaClO₄ solutions of similar ionic strength, even at long equilibration times, (553 days); 2) for PuO₂(am) suspensions in concentrated Cl, an increase in p_{cH+} and the production of NaOCl were observed; for PuO₂(am) suspensions in 0.0015 M CaCl₂, a continuous decrease in pH was observed with increasing in equilibration time which is probably due to radiolytic oxidation of dissolved nitrogen to HNO₃.

IV-3 PuO₂⁺ Reduction by H₂O₂

In this area of the research program, we studied the kinetics of the reduction of pentavalent plutonium, PuO₂⁺ by hydrogen peroxide, which is known to be a product of radiolysis in high-level liquid wastes and which may influence the oxidation state of plutonium in such wastes (Sullivan 1983). There is also evidence for the formation of hydrogen peroxide through photolysis of organic matter in surface waters (Cooper and Zika 1983), (Zika et al 1985). As Pu(V) is the predominant oxidation state of dissolved plutonium in natural waters (Choppin et al 1986), (Orlandini et al 1986), (Choppin 1991), the interaction between PuO₂⁺ and hydrogen peroxide may be of major importance in the environmental behavior of plutonium. Our review of relevant journals failed to find any studies of the redox kinetics of tracer level PuO₂⁺ with hydrogen peroxide in alkaline media.

In this study a combined ultrafiltration and solvent extraction procedure using TTA as extractant was employed to monitor the change in plutonium oxidation state with time. This method was found to be relatively simple and fast, allowing experimental data points to be recorded within short time intervals. The major disadvantage of this method lies in the necessity to change the solution pH from its original value between, 7.9 and 10.8, to pH 4.5 prior to ultrafiltration and solvent extraction. Such changes possibly can perturb the oxidation state distribution in solution. Consequently, a second independent solvent extraction procedure using dibenzoylmethane, DBM, as an extractant was used to validate the experimental results. This procedure allows separation of Pu(III) and Pu(VI) from Pu(IV) and Pu(V) without changing the sample pH but it does require more time between data points, (Figure 5).

Based on the experimental data the rate equation for the reduction of Pu(V) with hydrogen peroxide can be described by:

$$R = -d[\text{Pu(V)}]/dt \quad (2a)$$

$$= k[\text{Pu(V)}]^1 [\text{H}_2\text{O}_2]^m [\text{H}^+]^{-n} \quad (2b)$$

A dependence of the apparent first-order rate constant on the reciprocal of the proton concentration indicates a correlation between the reduction rate and the deprotonation of the reducing agent, hydrogen peroxide. This observation suggests the formation of $\text{PuO}_2^+ \cdot \text{O}_2\text{H}^-$ in an activated complex.

Assuming first order kinetics with respect to the concentration of $[\text{Pu(V)}]$, the reduction of PuO_2^+ by hydrogen peroxide can be described by the following rate equations:

$$R = (3.59 \times 10^{-9} \pm 1.79 \times 10^{-9})\text{min}^{-1} [\text{Pu(V)}] [\text{H}_2\text{O}_2] [\text{H}^+]^{-1} \quad (3)$$

Using this equation, the redox half-life of Pu(V) under various conditions can be calculated. In seawater conditions at pH 8.0 with a typical concentration of hydrogen peroxide of 1.0×10^{-7} M, 50% of the pentavalent plutonium is reduced within approximately 55 years. In waste storage tanks, however, pH values are sometimes higher and the concentration of hydrogen peroxide might reach higher levels due to water radiolysis. Under these conditions, the redox half-life of Pu(V) would be shortened significantly; e.g., at pH 11 and in presence of millimolar levels of hydrogen peroxide, it decreases to 4 min. (Figure 6).

These results are reported in an article in *Radiochimica Acta*, 86, pp. 109-113 (1999).

Figure 5. (a) Combined ultrafiltration and TTA extraction procedure for plutonium oxidation state analysis.

(b) DBM procedure for plutonium oxidation state analysis.

IV-4 Pu(IV) Oxidation by MnO₂

The kinetics of oxidation of Pu(IV) by manganese dioxide has been investigated. MnO₂ is a component in some of the tank wastes of the USDOE and is also a common component of natural waters. Consequently, it may contribute to the kinetics of oxidation of Pu(IV) to the more soluble PuO₂⁺ and PuO₂²⁺ species. The same techniques used in the studies of oxidation by H₂O₂ were employed. A set of data on the oxidation state distribution of plutonium after 7 days reaction with varying amounts of a suspension MnO₂ at pH 8.1 are given in Table 5.

In acid solution (pH 2.0 B 3.5), the rate equation was found to be:

$$R = -d[\text{Pu(IV)}]/dt = 3.72(\pm 0.13) \times 10^{-3} [\text{Pu(IV)}] [\text{MnO}_2] [\text{H}^+]^{-0.21} \quad (4)$$

Experiments in neutral pH range showed rapid oxidation kinetics but a lower fraction of oxidized species, due to strong hydrolysis and stabilization of tetravalent state. The conclusion is that MnO₂ may contribute to remobilization of Pu(IV) through oxidation to more soluble and mobile Pu(V) and Pu(VI).

A manuscript on this study is in the final stage of preparation. A poster was presented at the Pu Futures B 2000 Conference (Santa Fe, N.M., 7/00).

IV-5 Pu(IV) Oxidation by NaOCl

The oxidation of Pu(IV) to higher states by NaOCl was also investigated. As noted earlier in this Report, OCl⁻ is formed in aqueous saline systems by radiolyses. It has been reported (Buppleman et al 1988) that hypochlorite oxidizes Pu(IV) to Pu(VI) but no data on rates or intermediates are available. Since OCl⁻ would be present in stored radioactive wastes or in environmental waters subjected to radiation, its quantitative effect on Pu(IV) redox speciation is an important question in such systems.

The kinetics of the oxidation of Pu(IV) with sodium hypochlorite were investigated in the pH range 7.7-8.3 in 1.0 M NaNO₃. The oxidation state distribution of plutonium was monitored by two parallel extraction steps using TTA and HDEHP as extractants. The oxidation of Pu (IV) by sodium hypochlorite was found to proceed to Pu(V) and Pu(VI), with the relative amounts of oxidized species being dependent on the concentration of sodium hypochlorite. The stability of Pu (VI) in the presence of sodium hypochlorite was studied in separate experiments.

Figure 6. $T_{1/2}$ of reduction of PuO_2^+ by peroxide as a function of pH.

Table 5. Oxidation of Pu(IV) by MnO_{2(s)} : pH 8.1, t = 7 days

MnO ₂ (mmoles / L)	[Pu(IV)] (%)	[Pu(V)] (%)	[Pu(VI)] (%)	k= (10 ⁴ min ⁻¹)
-	86.2 ± 0.1	7.2 ± 1.1	6.6 ± 1.0	-
9.58 q 10 ⁻³	69.6 ± 0.8	15.7 ± 0.8	14.7 ± 1.1	8.39 ± 1.80
2.05 q 10 ⁻²	72.3 ± 2.3	20.4 ± 2.7	7.4 ± 1.0	-
5.15 q 10 ⁻²	61.6 ± 0.5	28.0 ± 0.4	10.5 ± 0.1	-
5.14 q 10 ⁻¹	54.6 ± 1.7	-	-	-
1.02	51.4	-	-	-
4.97	50.1 ± 1.2	-	-	-

The reaction reaches a stable oxidation state distribution of plutonium after ca. 2 days for higher concentration of NaOCl (0.02 M) but requires longer times for lower concentrations. The oxidation of Pu(IV) with 0.02 M NaOCl at pH 8.2 leads to the formation of 27% Pu(IV), 21% Pu(V) and 52% after 12 days. Decreasing the concentration of sodium hypochlorite to the submillimolar concentration range decreases the amount of oxidized species formed. The relative amounts of Pu(IV), (V) and (VI) formed after 2 days are summarized in Table 6. Since the rate of the oxidation reaction is relatively fast, the reaction rates could not be evaluated by these techniques.

Addition of Pu(VI) to a solution containing 0.02 M NaOCL resulted in a fast decrease of the concentration of Pu(VI) to ca. 47% of its initial concentration while 22% Pu(V) and 31% Pu(IV) were formed. The observed oxidation state distribution resembles very closely the results for identical experimental conditions in which, initially, Pu(VI) was added. These results indicate that the same equilibrium distribution of oxidation states is obtained, regardless of the original oxidation state, Pu(IV) or Pu(VI), that is added to the solution.

Lowering the concentration of sodium hypochlorite to 10^{-4} M resulted in an even sharper drop in the concentration of Pu(VI). The amount of Pu(VI) present was reduced to ca. 11% of its initial concentration within 1 hour. Only 10% Pu(V) was formed while Pu(IV) constituted the predominant oxidation state, with a relative concentration of nearly 80%. Again, these results are comparable to the results summarized in column 1 of Table 6, where, starting with Pu(IV) a similar oxidation state distribution was obtained in the presence of 1.6×10^{-4} M NaOCl after 2 days reaction time.

In summary, hypochlorite oxidizes Pu(IV) to Pu(V) and Pu(VI) with the fraction of these oxidation states increasing (at fixed time) with the OCl concentration. However, at these concentrations and pH, the systems reach an equilibrium state in which all three states are present after several (2-12) days.

It is planned to prepare a manuscript on this system. A poster was presented at Pu Futures 2000 Conference (Santa Fe, 7/00).

Table 6: Oxidation of Pu(IV) with various concentrations of sodium hypochlorite; Relative fractions of Pu(IV), Pu(V) and Pu(VI) after 2 days reaction time.

[NaOCl](mol/L)	1.0×10^{-4}	1.6×10^{-4}	3.2×10^{-4}	7.8×10^{-4}	2.0×10^{-2}
[Pu(IV)] (%)	7.9	64	57	52	30
[Pu(V)] (%)	10	22	20	22	22
[Pu(VI)] (%)	11	14	24	26	48

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VI. Publications from this EMSP Grant

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3. Rai, D., Moore, Felmy, R.A., Choppin, G.R., and Moore, R.C., Thermodynamics of the $\text{PuO}_2^+ - \text{Na}^+ - \text{OH}^- - \text{Cl}^- - \text{ClO}_4^- - \text{H}_2\text{O}$ System: Use of NpO_2^+ Pitzer Parameters for PuO_2^+ ; *Radiochim. Acta*, in press
4. Morgenstern, A., and Choppin, G. R.: Kinetics of the reduction of Pu(V)O_2^+ Hydrogen Peroxide. *Radiochim. Acta* **86**, 109-113 (1999)
5. Choppin, G. R.: Actinide Behavior in Neutral Media. *Symposium for EMSP at the 218th Meeting of the American Chemical Society*, New Orleans, August 22-26, 1999, in press as Am. Chem. Soc. book.
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VII. Personnel

1996-2000

A. Principal Investigators.

Professor Gregory R. Choppin, Lawton Distinguished Professor of Chemistry, Florida State University.

Dr. Dhapat Rai, Senior Staff Scientist, Pacific Northwest National Laboratory.

B. Research Scientists (PNNL)

Drs. H. Bolton, D. A. Moore, N. J. Hess, R. A. Felmy

C. Post-Doctoral Research Associates (FSU)

Dr. Kath Morris, Ph.D., U. Manchester (England), presently, Lecturer, Leeds University (England).

Dr. Alfred Morgenstern, Ph.D., U. of Munich (Germany); presently, Research Chemist, Tranuranium Institute, Karlsruhe (Germany).

Dr. Dean R. Peterman, Ph. D., U. of Cincinnati, presently, Research Scientist at Idaho National engineering Energy Laboratory.

Dr. J. N. Mathur, Visiting Scientist (2 mos), Behabba Atom. Energy Res. Center, India

D. Research Affiliate

Dr. Robert C. Moore, Sandia National Laboratory.