Title

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Authors

Nitsche, H.
Lee, S.C.
Gatti, R.C.

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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

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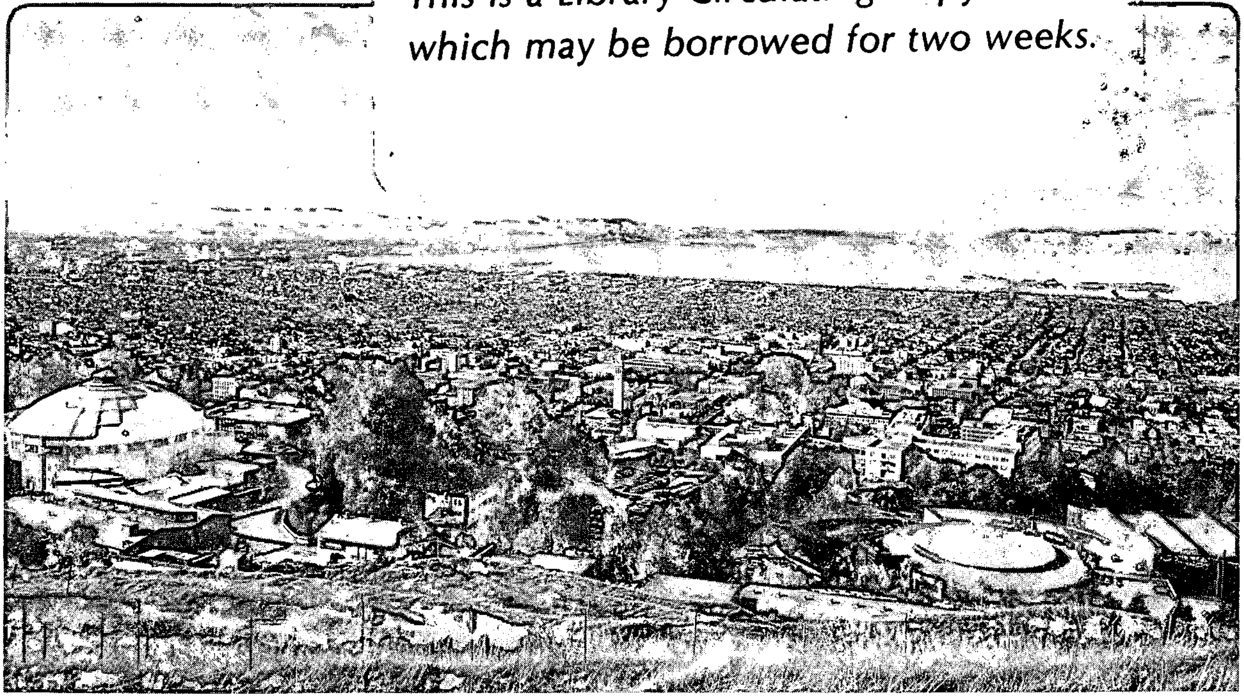

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Determination of Plutonium Oxidation States at Trace Levels Pertinent to Nuclear Waste Disposal

H. Nitsche, S. C. Lee, and R. C. Gatti

Lawrence Berkeley Laboratory
Earth Sciences Division
University of California
Berkeley, California 94720
(USA)

Abstract

A scheme was developed for the determination of oxidation states of plutonium in environmental samples. The method involves a combination of solvent extractions and coprecipitation. It was tested on solutions with both high-level and trace-level concentrations. The scheme was used to determine Pu oxidation states in solutions from solubility experiments in groundwater from a potential nuclear waste disposal site. At steady-state conditions, Pu was found to be soluble predominantly as Pu(V) and Pu(VI).

Introduction

The storage of radioactive waste in underground repositories is one possible means of permanent disposal. One of the safety assessments for a prospective repository site is the possible failure of the waste container. Although the likelihood of the release of radionuclides from the waste package is significantly reduced by the use of multiple man-made and geological barriers, the migration of contaminated groundwater must be considered as the principal mechanism for the transport of radionuclides from the storage location to the environment. The magnitude of the groundwater contamination will be controlled by a variety of factors. Factors of significant importance are the formation of solubility-controlling solids and the formation of soluble ions and complex species. The oxidation state of the radionuclide and the speciation, which describes both the nature and the charge of complexes formed, will influence the solubility in the groundwater and the migration rate through the geomedia.

Speciation studies for plutonium in groundwaters from the water table of a prospective repository site are made difficult by the low solubility of Pu. Typical low concentration levels between 10^{-6} **M** and 10^{-10} **M** are below the sensitivity range of methods such as absorption spectrophotometry or polarography, which would allow the direct measurement of the species present. Therefore, indirect methods for the determination of oxidation states must be employed. Solvent extraction, ion-exchange and adsorption chromatography, and coprecipitation, or combinations thereof are described in the literature to accomplish this analytical task.[1–9]

Ion exchange techniques were shown to be rather unsatisfactory at trace levels since most exchange resins exhibit reducing properties.[10] This can change the oxidation state distribution of the analytical Pu solution and will result in misleading data at trace levels. Solvent extraction and coprecipitation methods appear to be more reliable. However, some studies appear to overlook the fact that Pu solutions with several oxidation states present are governed by the rapid equilibrium[18]

$$\mathrm{Pu(IV)} + \mathrm{Pu(V)} \rightleftarrows \mathrm{Pu(III)} + \mathrm{Pu(VI)}.$$

Often Pu tracers of a specific oxidation state are added to monitor separation yields. For this technique the concentration of the tracer must be several orders of magnitude lower than the Pu concentration of the solution to be analyzed, in order to avoid disturbing the equilibrium significantly. This criterion seems to be difficult to fulfill for many environmental samples (10^{-13} **M** – 10^{-18} **M**) and for cases with even higher concentrations, when ^{242}Pu, with its rather long half-life, is used as the spiking isotope. Also, consecutive extractions on the same solution, if not performed extremely rapidly, can influence this equilibrium. We have found that more reproducible results can be obtained when only a single extraction step is performed at a time on several separate solutions in parallel instead of performing several sequential extractions on a single solution. Therefore, we have developed a scheme to determine quantitatively plutonium ions in the oxidation states III, IV, V, VI and Pu(IV) polymer at trace level concentrations using a variety of solvent extractions and one coprecipitation method. We have investigated thenoyl-trifluoro-acetone (TTA), methylisobutyl-ketone (Hexone), and di(2-ethylhexyl) phosphoric acid (HDEHP) as extractants and lanthanum fluoride as coprecipitant. The pH dependance of the extraction characteristics was investigated for TTA at pH 0 and 4, and for HDEHP at pH 0 and pH 1. Table 1 surveys the methods used and their selectivity for specific oxidation states. The scheme was used to determine the oxidation state distribution of plutonium solubility studies in J-13 groundwater from Yucca Mountain, Nevada, a potential nuclear waste disposal site.

Experimental

Extractions

TTA (Alfa Products, M. Thiokol, Inc.) was recrystallized twice from cyclohexane. It was dissolved in xylene to make a 0.5 M solution. The extractant was presaturated with 1 M HCl or pH 4 acetate buffer prior to its use. One half milliliter of the test solution was adjusted (HCl for pH 0, acetate buffer and HCl for pH 4) to make 1 ml, which was extracted for 5 min with an equal volume of TTA utilizing a vortex mixer (VWR scientific, model K-550-G). The phases were separated and subjected to a second extraction. The combined organic phases were "back-washed" with equal volumes of aqueous solution (1 M HCl for pH 0, acetate buffer for pH 4). After phase separation, the back-wash solution was combined with the remaining aqueous solutions. The organic raffinate and the aqueous solution were assayed.

The methyl isobutyl ketone used for the Hexone extractions was doubly distilled and acid presaturated (1 M HNO_3) prior to its use. Solid $Ca(NO_3)_2 \cdot 4H_2O$ and 1 M HNO_3 were added to 0.5 ml aliquots to make the solution 4 M in $Ca(NO_3)_2$. The extraction was done twice in the manner described for TTA; the back-wash was 4 M in $Ca(NO_3)_2$ and 1 M in HNO_3.

HDEHP (Alfa Products, M. Thiokol, Inc.) was diluted with toluene to make a 0.5 M solution. It was presaturated with 1 M HCl or 0.1 M HCl prior to its use. Aliquots of 0.5 ml of the test solution were acidified with HCl to make 1ml of solution of either pH 0 or pH 1. The extraction was performed twice with equal volumes of extractant. The unified organic raffinates were back-washed with HCl of appropriate concentration, and then the phases were separated.

Coprecipitation

The coprecipitation was performed as follows: 0.5 ml of the analyte solution was made 1 M in HNO_3, 0.5 M in H_2SO_4 and 0.02 M in $Na_2Cr_2O_7$. Then Zr^{4+}, as hold-back ion (1 mg/ml) and La^{3+} carrier (2 mg/ml) were added. A solution of 28 M HF, pretreated with a trace of $Na_2Cr_2O_7$ to oxidize possible reductants present, was added to precipitate the lanthanum fluoride from a solution 2 M in HF. The precipitate was digested, centrifuged, and washed three times, dissolved in 1 M HNO_3/saturated with H_3BO_3, and counted for activity. The supernatant and the wash solutions were combined and assayed.

Pu Solutions

^{242}Pu and ^{239}Pu stock solutions were prepared from oxide and metal, respectively. The materials were dissolved in 6 M HCl and converted to the perchlorate by fuming twice to near dryness with concentrateed $HClO_4$. The residues were taken up in 0.1 M $HClO_4$. Isotopic purity was determined by α and γ pulse-height analysis. The various Pu oxidation states were adjusted by controlled-potential coulometry. Purity control for each valence state was established by absorption spectrophotometry in the range 350-1250 nm (Varian Instr. Division, Cary Products, Model 17). For molar absorptivities with values below 100 M^{-1} cm^{-1}, cells of 100 mm pathlength were used; for solution ions with higher molar absorptivity (PuO_2^{2+}) 10 mm cuvettes were adequate. All measurements were referenced against solutions corresponding to the analytical one without Pu. Spectra obtained for each individual oxidation state were identical with published data.[12]

Nuclear assays

After separation, the individual solutions were assayed by either *L* X-ray[13] or liquid scintillation spectroscopy. Utmost care was exercised to properly set the α-energy window for liquid scintillation counting. Ecolite (Westchem) was used as the organic scintillator. Overall chemical yields (recoveries) were determined by summation of the concentrations from each individual fraction and comparing the total concentration to the concentration of an assay which was taken prior to each separation step. $^{241}Am^{3+}$, produced by the decay of ^{241}Pu, was present in very small quantities in the Pu-stock solutions. It was used as an internal gamma–tracer to monitor the effectiveness of each separation step. Both separated fractions were counted for ^{241}Am and, when a complete separation was achieved, the ^{241}Am was found only in the fraction which contained the oxidation state +3.

Results and Discussion

Extractions and coprecipitation

The TTA extractions were tested individually on a Pu^{4+} solution and on Pu oxidation state mixtures without Pu(IV) polymer present. Table 2 lists the test results for pH 0. Recoveries were excellent and the amount of Pu(IV) extracted agreed well with the spectrophotometric findings. The main absorption features for Pu(III), Pu(V) and Pu(IV) polymer are between 540 and 620 nm with molar absorptivities below 25 $M^{-1}cm^{-1}$. For this reason it is nearly impossible to discriminate properly between these oxidation states and only the sum of Pu(III, V, polymer) can be reported. This sum was calculated from the total Pu concentration derived from the assay before separation, minus the concentrations of Pu(IV) and Pu(VI), determined individually by spectrophotometry. Table 3 gives the results for pH 4. The overall material recoveries were still acceptable but not as good as for pH 0. However, the extraction for Pu(III, IV, VI) seems to work satisfactorily.

Hexone extractions were tested on a Pu(III), Pu(IV) mixture and on mixtures containing all oxidation states. Results are given in Table 4. The recoveries were very good and the extracted quantity of Pu(IV + VI) agreed well with the spectrophotometric results.

The results on LaF_3 coprecipitations are listed in Table 5. The method separates low-oxidation-state Pu from high-oxidation-state Pu with excellent material balance.

Oxidation state analysis scheme

Pu^{3+}, Pu^{4+}, Pu(IV) polymer, PuO_2^+, and PuO_2^{2+} mixtures were analyzed by the above-described methods at the 10^{-4} M and 10^{-7} M levels in an Ar-atmosphere glove box to determine whether the extraction methods tested at relatively high concentrations would be also effective at trace levels. Furthermore, it was important to see how rather large amounts of Pu(IV) polymer (~ 30%) might affect the separations. First, the concentration of a $Pu^{3+}/Pu^{4+}/PuO_2^+/PuO_2^{2+}$ mixture and Pu(IV) polymer were determined by spectrophotometry at 10^{-4} M and 10^{-3} M, respectively. Second, the two solutions were mixed to yield a total Pu concentration assayed as 1.88×10^{-4} M (mixture 1). Third, this solution was diluted with 1 M HCl to give a total Pu concentration of 9.89×10^{-8} M (mixture 2). Then both solutions underwent the oxidation state analysis. Each extraction and coprecipitation was done parallel for both concentrations, i.e. to exclude possible changes of the solution composition with time. It was impossible to analyze the amount of each individual oxidation state present in solution by spectrophotometry due to the presence of the large amounts of Pu(IV) polymer. The results in Table 6 show that the derived oxidation state determination scheme is indeed applicable to trace level concentrations. However, the hexone extractions at both concentrations did not extract IV and VI completely, although they were rather reproducible.

Therefore, a set of two other Pu oxidation state mixtures was prepared without Pu(IV) polymer. Mixture 1 (7.54×10^{-5} M) was analyzed spectrophotometrically and contained only Pu^{4+}, PuO_2^+, and PuO_2^{2+}. An aliquot of this mixture was diluted with 1 M $HClO_4$ to give mixture 2 with a total Pu concentration of 1.46×10^{-7} M. Also HDEHP extractions at pH 0 and pH 1 were introduced to the scheme as a possible alternative to Hexone and TTA at pH 4, respectively. The results of this oxidation state determination are shown in Table 7. Again, all separation results agreed at both concentration levels with each other and Hexone did not extract quantitatively. Table 8 shows the comparison of the results for each individual oxidation state with the findings from the absorption spectra. Individual oxidation states were calculated as the difference between two or more separation methods (i.e., HDEHP (pH 0) – TTA (pH 0) = PuO_2^{2+}; LaF_3 (supernatant) – $Pu0_2^{2+}$ = $Pu0_2^{+}$). These results demonstrate the usefulness of some liquid-liquid extractants and a coprecipitation method for studying the distribution of oxidation states in solutions containing trace amounts of Pu. An analysis scheme using a combination of TTA at pH 0, HDEHP at pH 0 and 1, and LaF_3 coprecipitation will provide a complete understanding of the oxidation states present in the supernatant solutions from plutonium solubility experiments.

Solubility experiments

Pu solubilities were studied in J-13 groundwater[14] from the water table at Yucca Mountain under a variety of different conditions in order to provide maximum possible release concentrations for the assessment of a potential high-level nuclear waste disposal site in Nevada.[15] The solubilities were studied starting with saturated solutions. Approaching solubility measurements in this way allows an upper limit to be determined for the material of interest. Experiments were typically run between 50 and 130 days to reach steady-state conditions. Efficient separation of solid and solution phase was achieved by ultrafiltration with Centricon Microconcentrators (Amicon Corp., MW cutoff 30,000, calculated pore size 4.1 nm). Previous studies on Pu(IV) polymer solutions have demonstrated[15] that after such filtration, virtually no polymer (< 0.5%) exists with particle sizes below 4.1 nm. This means that no Pu(IV) polymer was in the supernatant solution which was analyzed for its oxidation state distribution utilizing the outlined scheme.

The first set of experiments investigated the influence of the initial Pu oxidation state on the oxidation state distribution in solution at steady-state. At the beginning of the experiment, Pu was added to J-13 groundwater either as Pu^{4+}, PuO_2^+, or PuO_2^{2+}. Results of the oxidation state analysis are given in Table 9. Regardless of the initial oxidation state, the soluble plutonium at steady-state was converted almost completely to PuO_2^+ and PuO_2^{2+}. Starting with Pu^{4+}, PuO_2^{2+} could be produced by the disproportionation reaction [16]

$$3\,Pu^{4+} + 2H_2O \rightleftarrows 2Pu^{3+} + PuO_2^{2+} + 4H^+. \quad (1)$$

At the prevailing solution conditions (pH 7, Eh = 0.7 V), the equilibrium would be shifted towards the right and also Pu^{3+} would immediately be oxidized to Pu^{4+}. PuO_2^+ is known to disproportionate in acidic solution as[17]

$$PuO_2^+ + PuO_2^+ + 4H^+ \rightleftarrows Pu^{4+} + PuO_2^{2+} + 2H_2O. \quad (2)$$

According to reaction (2), PuO_2^+ is calculated to be stable at pH 7. Furthermore, the Pu equilibrium[18]

$$PuO_2^+ + Pu^{4+} \rightleftarrows Pu^{3+} + PuO_2^{2+} \quad (3)$$

must be maintained. Since virtually no Pu^{3+} or Pu^{4+} is present in the solution at steady state, the equilibrium is governed primarily by PuO_2^+ and PuO_2^{2+}. Furthermore, the influence of α-radiation on the solution equilibria must be considered directly (e.g., $PuO_2^{2+} + \alpha \rightarrow PuO_2^+$) and indirectly through the formation of peroxide from water radiolysis.

The second set of experiments investigated the effect of temperature on the oxidation state distribution. The Pu solubility was studied at 25°C and 60°C; Pu^{4+} was added at the start. As shown in Table 10, both solutions again contained predominantly Pu(V) and Pu(VI) and no significant change in distribution was found when the temperature was raised from 25°C to 60°C.

The third set of experiments studied the effect of pH on the distribution of oxidation states. The Pu was added initially as Pu^{4+}, and pH values of 6, 7, and 8.5 were maintained at 60°C. It can be seen from Table 11 that, as in the previous experiments, Pu(V) and Pu(VI) are the dominant oxidation states; as the amount of Pu(V) increases with pH, the Pu(VI) decreases. This phenomenon is in agreement with the predictions of equations (1) and (2).

The experiments have proven that the developed separation scheme provides a highly reliable and reproducible method for the determination of individual Pu oxidation states in solution at trace level concentrations.

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Table 1

Methods to determine the oxidation state in plutonium solutions

Method	Oxidation State Distribution	
	Organic Phase	Aqueous Phase
TTA extraction at pH 0	+4	+3, +5, +6, poly.[a]
TTA extraction at pH 4	+3, +4, +6	+5, poly.[a]
HDEHP extraction pH 0	+4, +6	+3, +5, poly.[a]
HDEHP extraction pH 1	+3, +4, +6	+5, poly.[a]
Hexone extraction	+4, +6	+3, +5, poly.[a]
LaF_3 precipitation[b]	+3, +4, poly.[a] in precipitate	+5, +6 in supernatant

(a) poly. = Pu(IV) polymer.

(b) method with "holding oxidant."

Table 2

Results for TTA extractions at pH 0 on simulated ^{242}Pu oxidation state mixtures with concentrations of ~ 10^{-4} M

Percentage	Test 1		Test 2		Test 3	
	Extraction	**Spectrum**	**Extraction**	**Spectrum**	**Extraction**	**Spectrum**
Pu(IV)	97 ± 3	100 ± 5	72 ± 4	63 ± 5	70 ± 3	63 ± 5
Pu(III,V,VI, poly.)	3 ± 3	–	28 ± 1	–	30 ± 1	–
Pu(VI)	–	0	–	10 ± 1	–	10 ± 1
Pu(III,V, poly.)$_{calc.}$	–	0	–	27 ± 5	–	27 ± 5
Recovered	98 ± 2	–	97 ± 5	–	96 ± 2	–

Table 3

Results for TTA extractions at pH 4 on simulated ^{242}Pu oxidation state mixtures with concentrations of ~ 10^{-4} M

Percentage	Test 1		Test 2		Test 3	
	Extraction	Spectrum	Extraction	Spectrum	Extraction	Spectrum
Pu(III,IV,VI)	100 ± 4	–	85 ± 4	–	94 ± 5	–
Pu(V, poly.)	0	–	15 ± 1	–	6 ± 1	–
Pu(III)	–	88 ± 4	–	–	–	0
Pu(IV)	–	12 ± 1	–	63 ± 4	–	100 ± 5
Pu (VI)	–	0	–	10 ± 1	–	0
$Pu(III,V, poly.)_{calc.}$	–	0	–	27 ± 5	–	0
Recovered	92 ± 4	–	95 ± 3	–	83 ± 3	–

Table 4

Results for hexone extractions at pH 0 on simulated ^{242}Pu oxidation state mixtures with concentrations of ~ 10^{-4} M

Percentage	Test 1		Test 2		Test 3	
	Extraction	Spectrum	Extraction	Spectrum	Extraction	Spectrum
Pu(IV,VI)	7 ± 1	–	74 ± 2	–	76 ± 3	–
Pu(III,V, poly.)	91 ± 3	–	26 ± 1	–	24 ± 1	–
Pu(III)	–	91 ± 5	–	–	–	–
Pu(IV)	–	9 ± 1	–	65 ± 4	–	63 ± 5
Pu (VI)	–	0	–	12 ± 1	–	10 ± 1
Pu(III,V, poly.)$_{calc.}$	–	–	–	23 ± 2	–	27 ± 5
Recovered	98 ± 3	–	100 ± 3	–	92 ± 3	–

Table 5

Results for LaF_3 coprecipitations (with holding oxidant) on simulated ^{242}Pu oxidation state mixtures with concentrations of ~ 10^{-4} M

Percentage	Test 1		Test 2	
	Precipitation	Spectrum	Precipitation	Spectrum
Pu(III,IV, poly.)	78 ± 4	–	77 ± 3	–
Pu(V,VI)	22 ± 1	–	23 ± 1	–
Pu(IV)	–	65 ± 4	–	63 ± 5
Pu(VI)	–	12 ± 1	–	10 ± 1
Pu(III,V, poly)$_{calc.}$	–	23 ± 2	–	27 ± 5
Recovered	102 ± 4	–	100 ± 2	–

Table 6

Test of speciation scheme at different Pu concentrations

Method	TTA, pH 0		TTA, pH 4		Hexone		LaF_3	
Mixture*	1	2	1	2	1	2	1	2
IV	60.3 ± 2.1	61.5 ± 7.3						
III,V,VI, poly.	39.7 ± 1.4	38.5 ± 4.8						
III,IV,VI			81.8 ± 2.7	81.6 ± 9.1				
V, poly.			19.2 ± 0.6	19.4 ± 2.2				
IV,VI					(50.8 ± 2.9)	(64.9 ± 3.2)		
III,V, poly.					(43.2 ± 2.5)	(35.1 ± 3.0)		
III,IV, poly.							90.7 ± 3.0	99.7 ± 12.2
V,VI							9.3 ± 0.5	0.3 ± 0.1

III,IV,V,VI = Pu oxidation states; poly. = Pu(IV) polymer

* = mixture 1 $(1.88 \pm 0.04) \times 10^{-4}$ M or mixture 2 $(9.89 \pm 0.69) \times 10^{-8}$ M.

Table 7

Test of speciation scheme at different Pu concentrations

Method	TTA, pH 0		HDEHP, pH 0		HDEHP, pH 1		Hexone		LaF_3	
Mixture*	1	2	1	2	1	2	1	2	1	2
IV	69.2 ± 4.8	74.0 ± 4.3								
III,V,VI, poly.	30.7 ± 2.3	26.8 ± 1.6								
IV,VI			93.6 ± 6.6	86.3 ± 5.1			(59.2 ± 4.1)	(64.5 ± 5.0)		
III,V, poly.			6.4 ± 5.0	14.3 ± 1.2			(40.8 ± 2.8)	(35.5 ± 2.4)		
III,IV,VI					92.3 ± 7.7	84.2 ± 7.4				
V, poly.					7.7 ± 0.9	15.8 ± 1.4				
III,IV, poly.									63.3 ± 3.2	62.3 ± 6.5
V,IV, poly.									36.7 ± 2.0	37.7 ± 2.8

III,IV,V,VI = Pu oxidation states; poly. = Pu(IV) polymer

* = mixture 1 (7.54 ± 0.28) × 10^{-5} M or mixture 2 (1.46 ± 0.05) × 10^{-7} M

Table 8

Comparison of results from speciation method at different Pu concentrations with absorption spectra

Oxidation States	Pu(Mixture 1)$_{spectrum}$	Pu(Mixture 1)$_{found}$	Pu(Mixture)$_{found}$
III	0	0 ± 12	0 ± 6
IV	74 ± 5	69 ± 5	74 ± 4
V	9 ± 5	12 ± 8	25 ± 7
VI	17 ± 1	24 ± 8	12 ± 7
polymer	0	0 ± 8	0 ± 7

Table 9

Influence of initial Pu oxidation state on the oxidation state distribution in J-13 groundwater (25°C, pH 7)

Initial State	Oxidation States (%)			
	Pu(IV)	Pu(V)	Pu(VI)	Pu(III + poly.)
Pu^{+4}	1.0 ± 0.1	39 ± 4	59 ± 2	1.0 ± 0.1
PuO_2^+	0.4 ± 0.1	63 ± 4	35 ± 1	1.2 ± 0.1
PuO_2^{++}	0.3 ± 0.1	68 ± 4	30 ± 1	2 ± 5

steady-state concentrations:

- Pu^{4+}, $(1.6 \pm 0.2) \times 10^{-6}$ M
- PuO_2^+, $(8 \pm 3) \times 10^{-6}$ M
- PuO_2^{2+}, $(3 \pm 2) \times 10^{-5}$ M

Table 10

Temperature effect on Pu oxidation state distribution in J-13 groundwater at pH 7

	Oxidation States (%)			
Temp. (°C)	Pu(IV)	Pu(V)	Pu(VI)	Pu(III + poly.)
25	1.0 ± 0.1	39 ± 4	59 ± 2	1.0 ± 0.1
60	1.5 ± 0.7	44 ± 9	52 ± 4	3.2 ± 0.8

steady-state concentrations:

at 25°C, $(1.6 \pm 0.2) \times 10^{-6}$ **M**

at 60°C, $(3.8 \pm 0.8) \times 10^{-8}$ **M**

Table 11

pH effect on Pu oxidation state distribution in J-13 groundwater at 60°C

pH	Oxidation States (%)			
	Pu(IV)	Pu(V)	Pu(VI)	Pu(III + poly.)
6	2 ± 1	17 ± 5	72 ± 5	10 ± 2
7	2 ± 1	44 ± 9	52 ± 4	3 ± 1
8.5	13 ± 1	58 ± 2	24 ± 1	5 ± 4

steady-state concentrations:

- pH 6, $(2.7 \pm 1.1) \times 10^{-8}$ M
- pH 7, $(3.8 \pm 0.8) \times 10^{-8}$ M
- pH 8.5, $(1.24 \pm 0.11) \times 10^{-7}$ M

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