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Dependence of Actinide Solubility and Speciation on Carbonate Concentration and Ionic Strength in Groundwater

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Abstract

Yucca Mountain, Nevada, USA, is being investigated for its potential suitability as a geologic nuclear waste repository. As part of the site characterization studies, actinide solubilities and speciations were studied at pH 6, 7, and 8.5 in two different groundwaters coming from the vicinity of Yucca Mountain.

The groundwaters differ substantially in total dissolved carbonate concentration, and to a lesser extent in ionic strength. The solubilities of neptunium(V) decreased, whereas those of americium(III) increased in the water with the higher carbonate content. The solids formed were sodium neptunium carbonates and americium hydroxycarbonates. Plutonium solubilities did not significantly change with changing water composition, because the solubility-controlling solids were mostly amorphous Pu(IV) polymers that contained only small amounts of carbonate.

1. Introduction

Yucca Mountain, Nevada, has been designated by the U.S. Department of Energy (DOE) for site characterization as a potential site for a geologic high-level nuclear waste repository. As a worst case scenario, intrusion of water into the repository must be considered for risk assessment. Water moving through the emplacement area towards the accessible environment can transport radionuclides in two ways: either as dissolved species in the water or as particulate material carried by the water. The Site Characterization Plan (SCP) requires "Studies to Provide the Information Required on Radionuclide Retardation by Precipitation Processes along Flow Paths to the Accessible Environment" before licensing and construction of the repository [1].

The purpose of this study is to supply data for calculating radionuclide transport along potential transport pathways from the repository to the accessible environment. Data derived from solubility studies are important for validating geochemical codes that are part of predictive radionuclide transport models. Such codes should be capable of predicting the results of solubility experiments. Furthermore, agreement between geochemical calculations and experimental results can validate the thermodynamic data base used with the modeling calculation.

In addition, experimental solubility data also provide the source terms or the starting concentrations for experimental sorption studies, in order to study sorption in the absence of precipitation processes.

Neptunium, plutonium, and americium are expected to be sparingly soluble with solubility-limited dissolution rates. Water samples with compositions that bracket the range of waters expected in the vicinity of Yucca Mountain were chosen for solubility measurements [2]. These samples come from two sources. Water from Well J-13 is expected to be representative of the water composition of the unsaturated zone near the proposed emplacement area. Well UE25p#1 taps the carbonate aquifer that underlies the emplacement horizon. This water has an ionic strength and total carbonate content higher by approximately a factor of four than Well J-13 water. Well J-13 water represents natural water with the highest concentrations of dissolved species expected in the vicinity of Yucca Mountain. The water from both wells is oxidizing. Generally, radionuclide solubility studies under oxidizing conditions lead to higher solubilities for a number of radionuclides than would occur under mildly or strongly reducing conditions. These experiments will therefore provide conservative upper limits.

We are comparing in this paper the results of solubility studies of neptunium, plutonium, and americium in Well J-13 water and Well UE25p#1 water at 25°C.

2. Experimental

The principles for complete and reliable solubility experiments were described earlier [3]. We followed these principles in our study. We studied the solubilities of $^{237}NpO_2^+$, $^{239}Pu^{4+}$, and $^{241}Am^{3+}/Nd^{3+}$ in two different groundwaters from the Yucca Mountain region at 25°C and respective pH values of 6.0, 7.0, and 8.5. The solubilities were studied from oversaturation by injecting a small amount, usually between 0.5 and 1 ml, of actinide stock solution into 80 ml of groundwater obtained from Well J-13 or Well UE25p#1. The analyses of the water compositions are listed in Table 1 [4, 5]. The well waters' total dissolved carbonate was preserved at each individual pH and temperature by equilibrating the solution with mixtures of CO_2 in argon. The amount of CO_2 at a given pH was calculated from Henry's constant and the

Table 1. Water compositions at Yucca Mountain [4, 5]

	J-13	UE-25p#1
Na^+ (mM)	9.96	7.43
K^+ (mM)	0.14	0.34
Ca^{2+} (mM)	0.29	2.19
Mg^{2+} (mM)	0.07	1.31
SiO_2(aq) (mM)	1.07	0.62
Carbonate (tot.) (mM)	2.81	11.44
Cl^- (mM)	0.18	1.04
SO_4^{2-} (mM)	0.19	1.34
F^- (mM)	0.11	0.18
PO_4^{3-} (μM)	1.25	—
pH	7.0	6.7
Eh (mV)	700	360
Ionic strength (mM)	~3	~20

dissociation constants of carbonic acid from literature data [6]. The concentrations of the equilibration gas mixtures are given in Table 2. A computer-operated control system (pH-stat) was used to maintain the aqueous actinide solutions at constant pH values not exceeding 0.1 pH unit for the duration of the solubility experiment [7].

The actinide stock solutions were prepared by using established methods [8] ^{237}Np(V) and ^{241}Am(III) stock solutions were prepared by dissolving their oxides in HCl. Stable neodymium(III) was used on several occasions as an analogue for americium(III). It was prepared by dissolving Nd_2O_3 in $HClO_4$. The solution was then spiked with purified ^{241}Am(III) tracer to enable the use of nuclear counting for the determination of the neodymium solution concentrations. The use of the neodymium spike with ^{241}Am tracer reduced the alpha-radiation level to 21% of the radiation that would have been present if we had used pure ^{243}Am instead. In a different experiment, we determined that the substitution of americium with the neodymium analogue is acceptable [9]. The results of this study showed that neodymium is indeed a good stand-in element for americium.

^{239}Pu(IV) stock was prepared from plutonium metal. The actinide solutions were purified from possible metal contaminants by ion exchange chromatography. For neptunium and plutonium, anion exchange was used, whereas cation exchange was employed for americium. The purity of these stock solutions was tested by spark emission spectroscopy, and no contaminants were found above the detection limits of the method. The solutions were converted to a non-complexing perchlorate system. The neptunium and plutonium stock solutions were in the oxidation state +6 after their conversion to perchlorate and were reduced electrolytically to NpO_2^+ and Pu^{4+}, respectively [10–12]. Valence purity was established by absorption spectrophotometry [13, 14].

The groundwaters were filtered through 0.05 μm filters (Nuclepore Corp., Pleasanton, CA). The actinide stock solutions, and all other solutions utilized in this experiment were filtered through 0.22 μm polyvinylidene difluoride syringe filter units (Millipore Corp., Bedford, MA). Filtration was used to remove suspended particulate material, e.g., dust or silica, that could absorb the actinide ions to form pseudocolloids. Before the addition of actinide stock solutions to the well water, a small amount of CO_2-free sodium hydroxide solution was added in order to keep the pH values at or above the desired solution pH. Letting the pH drop below the target value would necessitate addition of concentrated base to the system while the actinide ion is already present in the solution. Addition of strong base can result in unpredictable micro-precipitation and formation of microcolloids.

Table 2. Concentrations (in percent) of carbon dioxide gas in argon to maintain a constant total dissolved carbonate concentration in J-13 and UE-25p#1 groundwaters at different pH and 25°C

	J-13	UE-25p#1
pH 6.0	6.06	28.44
pH 7.0	1.57	6.36
pH 8.5	0.0573	0.24

Achievement of steady-state conditions for the solubility measurements was monitored by sampling aliquots of the solution phases and analyzing for the respective radioisotope as a function of time. We used Centricon-30 centrifugal filters (Amicon Corp., Danvers, MA) for separating the liquid from the solid phase. To ascertain that we achieved complete phase separation and minimal adsorption on the filters during the preparation of the solution assays, we conducted a series of filtration tests. For each solution, these tests were done at different times during the equilibration period. We used one filter per solution and filtered consecutive portions of 500 μl solution through it. Each filtrate was acidified to minimize sorption in the filtrate-collection container and an assay was taken. Then another 500 μl were filtered through the same filter, collected in a new container, and assayed. This is repeated until the assays show a constant concentration. The volume necessary to saturate the filter was the cumulative amount of volumes used until the assay concentration remained constant. The presaturation volume was radionuclide-dependent and varied between 500 and 2500 μl.

Concentration measurements of the supernatants were made by counting liquid aliquots with a generation low-energy counting system (LBL design). For ^{237}Np and ^{241}Am the 29.38 keV and 59.54 keV γ-ray lines were used respectively. ^{239}Pu was analyzed by utilizing the U*L* X-rays coming from the α-decay of the plutonium. Possible contributions to the *L* X-rays from the decays of other radionuclides, also present in small amounts, were corrected by subtraction [15]. The solids were analyzed by X-ray powder diffraction measurements.

Table 3. Results for NpO_2^+ solubility experiments in J-13 and UE-25p#1 groundwaters

pH	Concentration (M)		Np Speciation (±5%)				Eh vs. NHE (±15 mV)	
	J-13	UE-25p#1	J-13		UE-25p#1		J-13	UE-25p#1
			NpO_2^+	$NpO_2(CO_3)_n^{1-2n}$ + $NpO_2(OH)_n^{1-n}$	NpO_2^+	$NpO_2(CO_3)_n^{1-2n}$ + $NpO_2(OH)_n^{1-n}$		
6	$(5.32\pm0.28)\times10^{-3}$	$(2.88\pm0.63)\times10^{-3}$	91	9	100	0	588	877
7	$(1.27\pm0.18)\times10^{-4}$	$(4.7\ \pm1.1)\times10^{-5}$	46	54	42	58	482	438
8.5	$(4.4\ \pm0.7)\times10^{-5}$	$(7.0\ \pm0.6)\times10^{-6}$	38	62	0	100	497	259

At the end of each solubility experiment, we measured the Eh with a platinum electrode versus a Ag/AgCl/sat. NaCl reference. The platinum electrode was cleaned with 6 M HNO_3 before each measurement. Readings were stable within 30 to 60 minutes. The electrode setup was checked with "Zobell's Solution" before and after each measurement [16, 17]. We list the Eh values for completeness. They are, however, only of limited value because they may represent a combination of many different redox reactions for each individual solution.

3. Results and discussion

3.1. Neptunium

Results of the neptunium solubility studies, the solutions' Eh values, and the speciation results are given in Table 3. The neptunium solubility in each groundwater decreased with increasing pH. At each individual pH, the neptunium was less soluble in UE-25p#1 water than in J-13 water. The difference becomes more pronounced with increasing pH values: 1.9 times less at pH 6, 2.7 times less at pH 7, and 6.3 times less at pH 8.5. This behavior appears to depend on the nature of the solubility-controlling solid phases. The solids were identified by comparing their X-ray powder diffraction patterns with published patterns of $Na_{0.6}NpO_2(CO_3)_{0.8} \cdot 2.5\,H_2O$, $Na_{0.6}NpO_2(CO_3)_{0.8} \cdot nH_2O$, $NaNpO_2CO_3 \cdot 2\,H_2O$, $NaNpO_2CO_3 \cdot 3.5\,H_2O$, and $Na_3NpO_2(CO_3)_2 \cdot nH_2O$ [18–21]. From the relatively good agreement with the literature patterns, all solids formed in both waters were identified as $Na_{0.6}NpO_2(CO_3)_{0.8} \cdot 2.5H_2O$, except the solid formed in J-13 groundwater at pH 7 which was $NaNpO_2CO_3 \cdot 2H_2O$. The influence of the different carbonate concentrations on the neptunium species distribution is shown in Table 3. In both waters at pH 6 and pH 7, the distributions between free neptunium(V) and neptunium(V) hydrolysis products and carbonate complexes are about the same within the error of the spectrophotometric detection method. At pH 8.5, however, in J-13 water 38% of the species was uncomplexed NpO_2^+ and 62% hydrolytic and carbonate complexed species. Due to the much higher concentration of free carbonate, the UE-25p#1 solution at pH 8.5 contained no uncomplexed neptunium; all the neptunium was present in the form of hydrolysis products and carbonate complexes.

3.2. Plutonium

Results for plutonium, steady-state concentration and Eh measurements are listed in Table 4. No clear trend of changing solubility with pH was observed. The precipitates in both groundwaters had a dark green appearance similar to that of Pu(IV) polymer. Most of the few X-ray diffraction lines observed were rather diffuse, indicating at most a low degree of crystallinity. All patterns have several lines in common, but we found no reference pattern in the literature to assign the lines. They were compared to patterns of crystalline PuO_2 [22], $PuO_3 \cdot 0.8H_2O$, PuO_2CO_3 [23], $NH_4PuO_2CO_3$ [24], and PuO_2CO_3 [25].

Dissolution tests of the solids with 1 M HCl showed partial evolution of CO_2-gas, increasing amounts for the pH 6, 7, and 8.5 precipitates. Further dissolution with 6 M HCl/NaF and spectrophotometric analyses showed the presence of Pu(IV) polymer. FTIR spectra on the solids showed absorptions that can be assigned to carbonate-containing aged Pu(IV) polymer [26]. Pu(IV) polymer is known to absorb CO_2, which converts on the polymer surface to carbonate. Although aged Pu(IV) polymer is known to produce an X-ray pattern with diffuse lines at the same spacings as PuO_2 [22], we can conclude from our experimental results that the solids are mainly made from Pu(IV) polymer that contain increasing amounts of carbonate with increasing pH. The predominance of Pu(IV) polymer explains why the plutonium solution concentrations are relatively unaffected by changes in groundwater composition and pH in the near-neutral region. The somewhat higher solubility in UE-25p#1 at pH 8.5 compared to J-13 groundwater may come from a significantly larger formation of plutonium carbonate that is due to the much higher concentration of CO_3^{2-} at that pH.

The plutonium oxidation state distribution was determined by a combination of solvent extractions and coprecipitation [27]. The results are shown in Figures 1, 2, and 3. The observed valence distributions cannot be explained by disproportionation equilibria and complex stabilization [28]. It is possible that oxidation products formed by α-radiolysis of the water

Table 4. Results for Pu^{4+} solubility experiments in J-13 and UE-25p#1 groundwaters

pH	Concentration (M)		Eh vs. NHE (±15 mV)	
	J-13	UE-25p#1	J-13	UE-25p#1
6	$(1.1\pm0.4)\times10^{-6}$	$(8.3\pm0.4)\times10^{-7}$	342	348
7	$(2.3\pm1.4)\times10^{-7}$	$(4.5\pm0.4)\times10^{-7}$	126	282
8.5	$(2.9\pm0.8)\times10^{-7}$	$(1.1\pm0.1)\times10^{-6}$	259	273

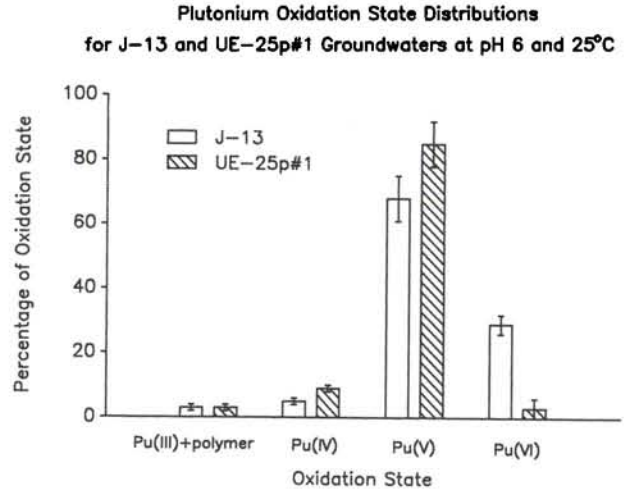

Fig. 1. Plutonium oxidation state distributions of the supernatant at steady-state for Pu^{4+} solubility experiments in J-13 and UE-25p#1 groundwater at pH 6 and 25°C.

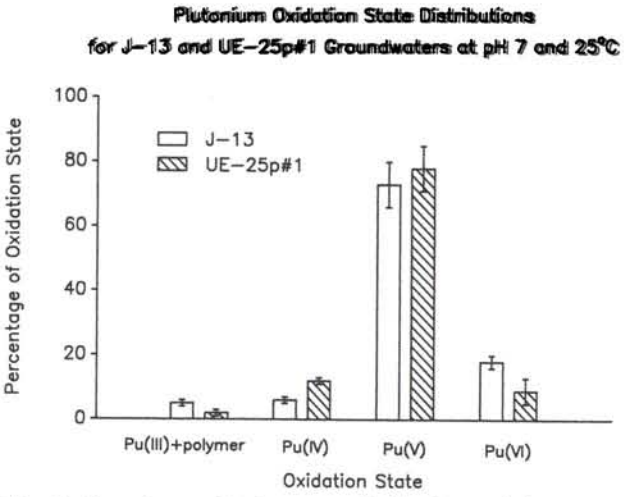

Fig. 2. Plutonium oxidation state distributions of the supernatant at steady-state for Pu^{4+} solubility experiments in J-13 and UE-25p#1 groundwater at pH 7 and 25°C.

may cause the predominance of high oxidation states in the plutonium solutions. It is noteworthy that the solutions were filtered through a 4.1-nm filter prior to the oxidation state determination because we wanted to determine only the true soluble plutonium fraction. Therefore, we refer to Pu(IV) polymer in the context of this determination only to the fraction that is smaller than 4.1 nm. Both groundwaters contained predominantly Pu(V). Smaller fractions were found of

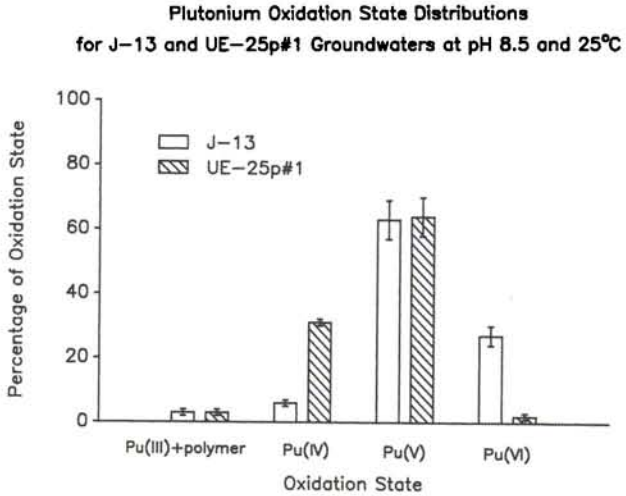

Fig. 3. Plutonium oxidation state distributions of the supernatant at steady-state for Pu^{4+} solubility experiments in J-13 and UE-25p#1 groundwater at pH 8.5 and 25°C.

Pu(VI) in J-13, and of Pu(IV) in UE-25p#1 groundwater. The higher carbonate concentration in UE-25p#1 water seems to somewhat stabilize the oxidation state +4.

3.3. Americium/Neodymium

Steady-state solubility concentrations and Eh measurements are listed in Table 5. The neodymium/americium solubility difference between the two waters is significant. The solubility in UE-25p#1 groundwater is about 172, 267, and 1,292 times larger than in J-13 water for pH 6, 7, and 8.5, respectively. The solids in both waters at pH 6 are hexagonal $AmOHCO_3$ [29]. The pH 7 and pH 8.5 solids in J-13 water are orthorhombic $AmOHCO_3$ [30], whereas the corresponding UE-25p#1 solids contain carbonate but remain unidentified. Their X-ray diffraction powder patterns were compared to literature patterns of $AmOHCO_3$, $Nd_2(CO_3)_2 \cdot 2H_2O$ [30] and $KAmCO_3$ [31].

Direct speciation measurements could not be carried out because of the low solution concentrations. The trivalent neodymium, however, cannot change its oxidation state. By using a combined extraction and coprecipitation procedure we were able to establish that the trivalent americium tracer did not change its oxidation state during the experiment.

Table 5. Results for $Nd^{3+}/^{241}Am^{3+}$ solubility experiments in J-13 and UE-25p#1 groundwaters

pH	Concentration (M)		Eh vs. NHE (±15 mV)	
	J-13	UE-25p#1	J-13	UE-25p#1
6	$(1.8\pm0.6)\times10^{-9}$	$(3.1\pm1.1)\times10^{-7}$	331	111
7	$(1.2\pm0.3)\times10^{-9}$	$(3.2\pm1.6)\times10^{-7}$	361	358
8.5	$(2.4\pm1.9)\times10^{-9}$	$(3.1\pm0.8)\times10^{-6}$	182	376

4. Conclusion

Neptunium and americium showed different solubilities in J-13 groundwater compared to UE-25p#1 groundwater. Neptunium solubilities were lower and americium solubilities were higher in UE25p#1 than in J-13 water. Plutonium solubilities did not significantly change with changing water composition. These solubility effects are a result of the different carbonate content of the water. The difference in ionic strengths appears to have a much lesser noticeable influence on the solubility, because both waters are very dilute.

We are currently assembling a thermodynamic data set, including solubility product and complex equilibrium constants, that will allow us to compare our experimental results with modeling calculations [32].

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Appendix

The data used to write this publication are recorded in the following YMP Laboratory Record Books

TWS-LBL-02-91-01, pp. 13–35
TWS-LBL-02-90-04, pp. 190–213
TWS-LBL-07-89-01, pp. 11–108
TWS-LBL-01-89-01, pp. 1–293
TWS-LBL-01-89-02, pp. 18–303
TWS-LBL-05-88-01, pp. 33–301
TWS-LBL-05-88-02, pp. 9–249
TWS-LBL-10-88-01, pp. 191–291
TWS-LBL-06-86-01, pp. 253–259

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