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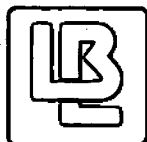
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**Radionuclide Solubility and Speciation Studies for the  
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# RADIONUCLIDE SOLUBILITY AND SPECIATION STUDIES FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

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## ABSTRACT

Yucca Mountain, Nevada, U.S.A., is being investigated for its suitability as a potential site for 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 at 25° and 60°C in two different groundwaters from the vicinity of Yucca Mountain.

The groundwaters differ substantially in total dissolved carbonate concentration, and to a lesser extent in ionic strength. In the waters with higher carbonate content, the solubilities of neptunium(V) decreased, whereas those of americium(III) increased at 25°C and decreased at 60°C. 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.

## 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 when preparing the 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 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.<sup>1</sup>

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

In addition, results of solubility experiments also provide the source terms and starting concentrations used for studies of 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.<sup>2</sup> These samples

come from two sources: Water from Well J-13 from the tuff aquifer may be representative of the water composition of the unsaturated zone near the proposed emplacement area, and well UE-25p #1 taps the carbonate aquifer that underlies the emplacement horizon.

Table I shows the chemical composition obtained from the analysis of both groundwaters.<sup>3</sup> The UE-25p #1 water has an ionic strength and total carbonate content higher by approximately a factor of five 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, and, in this paper, we will compare the results of solubility studies of neptunium, plutonium, and americium in Well J-13 water and Well UE-25p #1 water at 25° and 60°C.

**Table I. Analyzed chemical composition of J-13 and UE-25p #1 well water<sup>3</sup>**

Species	Well J-13 Concentration (mM)	Well UE-25p #1 Concentration (mM)
Na <sup>+</sup>	1.96	7.43
K <sup>+</sup>	0.14	0.34
Ca <sup>2+</sup>	0.29	2.19
Mg <sup>2+</sup>	0.07	1.31
SiO <sub>2</sub> (aq)	1.07	0.62
Cl <sup>-</sup>	0.18	1.04
SO <sub>4</sub> <sup>2-</sup>	0.19	1.34
F <sup>-</sup>	0.11	0.18
Total Carbonate	2.81	15.31
Ionic Strength	~3	~20
pH	7.0	6.7
Total Alkalinity	2.34 mequiv./L	11.44 mequiv./L
Eh	700 mV	360 mV

## EXPERIMENTAL

We followed the principles for complete and reliable solubility experiments which have been described earlier.<sup>4</sup> We studied the solubilities of  $^{237}\text{NpO}_2^+$ ,  $^{239}\text{Pu}^{4+}$ , and  $^{241}\text{Am}^{3+}/\text{Nd}^{3+}$  in two different groundwaters from the Yucca Mountain region at 25° and 60°C and respective pH values of 6.0, 7.0, and 8.5. The solubilities were studied from oversaturation and undersaturation 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 UE-25p #1. The well waters' total dissolved carbonate was preserved at each individual pH and temperature by equilibrating the solution with mixtures of  $\text{CO}_2$  in argon at one atmosphere.

The concentrations of the equilibration gas mixtures are given in Table II. Because the solubilities are highly sensitive to pH and temperature changes, close control of these parameters is necessary. We controlled the solutions' pH within 0.1 unit, and the temperature within 1°C. 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. Depending on the radionuclide and temperature, the solubility experiments were monitored for between 55 and 308 days. Concentration measurements of the supernatants were made by counting liquid aliquots with a germanium low-energy counting system.

**Table II. Concentrations (in percent) of  $\text{CO}_2$  gas in argon to maintain a total dissolved carbonate concentration of  $1.531 \times 10^{-2}$  M in UE-25p #1 and  $2.81 \times 10^{-3}$  M in J-13 water at 1 atm and at different pH and temperatures**

	J-13		UE-25p #1	
	25° C	60° C	25° C	60° C
pH 6	6.06	9.67	28.44	52.03
pH 7	1.57	2.35	6.555	11.22
pH 8.5	0.0573	0.0877	0.2353	0.3909

## RESULTS AND DISCUSSION

### Neptunium

Results of the neptunium solubility studies are given in Table III.

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. In J-13 well water, neptunium solubility increased with temperature at all three pH values. The opposite trend was found in UE-25p #1 well water except at pH 8.5 where the neptunium solubility also

increased with temperature. All solids formed in both waters were identified by x-ray powder diffraction as sodium neptunium carbonates,  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ . With this study, we established that the solubility controlling solids in these two Yucca Mountain groundwaters are ternary sodium neptunium carbonates, and not binary compounds such as amorphous  $\text{NpO}_2\text{OH}$  or crystalline  $\text{NpO}_2$ , as was assumed in modeling exercises.<sup>5</sup> The neptunium species in solution were free neptunium(V) and neptunium(V) hydrolysis products at pH 6, with increasing amount of carbonate complexes forming at pH 7 and 8.5.



Because of 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.

**Table III. Results for  $\text{NpO}_2^+$  solubility experiments in J-13 and UE-25p #1 groundwaters at 25° and 60° C**

pH	Concentration (M)			
	J-13		UE-25p #1	
	25° C	60° C	25° C	60° C
6	$(5.3 \pm 0.3) \times 10^{-3}$	$(6.4 \pm 0.4) \times 10^{-3}$	$(2.9 \pm 0.6) \times 10^{-3}$	$(2.5 \pm 0.2) \times 10^{-3}$
7	$(1.3 \pm 0.2) \times 10^{-4}$	$(9.8 \pm 1.0) \times 10^{-4}$	$(4.7 \pm 1.1) \times 10^{-5}$	$(3.4 \pm 1.0) \times 10^{-5}$
8.5	$(4.4 \pm 0.7) \times 10^{-5}$	$(1.0 \pm 0.1) \times 10^{-4}$	$(7.0 \pm 0.6) \times 10^{-6}$	$(1.4 \pm 0.6) \times 10^{-5}$

### Plutonium

Results for plutonium steady-state concentrations are listed in Table IV. No clear trend of changing solubility with pH was observed. The solubility decreased significantly with increasing temperature. At corresponding pH values, plutonium solubility was slightly lower in J-13 water than in UE-25p #1 water except at pH 6 and 25°C where the solubility was lower in UE-25p #1. The precipitates in both groundwaters had a dark green appearance, and they 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 plutonium oxidation state distribution was determined by a combination of solvent extractions and coprecipitation.<sup>6</sup> The plutonium exists in both groundwaters predominantly as Pu(V) and Pu(VI), although it was initially added to the solutions as Pu(IV).

**Table IV. Results for  $\text{Pu}^{4+}$  solubility experiments in J-13 and UE-25p #1 groundwaters at 25° and 60° C**

pH	Concentration (M)			
	J-13		UE-25p #1	
	25° C	60° C	25° C	60° C
6	$(1.1 \pm 0.4) \times 10^{-6}$	$(2.7 \pm 1.1) \times 10^{-8}$	$(8.3 \pm 0.4) \times 10^{-7}$	$(8.9 \pm 1.4) \times 10^{-8}$
7	$(2.3 \pm 1.4) \times 10^{-7}$	$(3.7 \pm 0.9) \times 10^{-8}$	$(4.5 \pm 0.4) \times 10^{-7}$	$(9.1 \pm 1.2) \times 10^{-8}$
8.5	$(2.9 \pm 0.8) \times 10^{-7}$	$(1.2 \pm 0.1) \times 10^{-7}$	$(1.0 \pm 0.1) \times 10^{-6}$	$(9.3 \pm 6.0) \times 10^{-7}$

## Americium

Steady-state solubility concentrations are listed in Table V. The americium solubility difference between the two waters is significant. At 25 C°, the solubility in UE-25p #1 water was about two to three orders of magnitude higher than in J-13

water. This trend was reversed for the 60 C° experiments, and not quite as pronounced for the pH 7 solutions. The solids in both waters are crystalline americium hydroxycarbonates, AmOHCO<sub>3</sub>. We established that the trivalent americium did not change its oxidation state during the experiment.

**Table V. Results for Nd<sup>3+</sup>/<sup>241</sup>Am<sup>3+</sup> solubility experiments in J-13 and UE-25p #1 groundwaters at 25° and 60° C**

pH	Concentration (M)			
	J-13		UE-25p #1	
	25° C	60° C	25° C	60° C
6	$(1.8 \pm 0.6) \times 10^{-9}$	$(2.5 \pm 0.7) \times 10^{-6}$	$(3.1 \pm 1.1) \times 10^{-7}$	$(2.7 \pm 0.4) \times 10^{-9}$
7	$(1.2 \pm 0.3) \times 10^{-9}$	$(9.9 \pm 9.2) \times 10^{-9}$	$(3.2 \pm 1.6) \times 10^{-7}$	$(7.1 \pm 0.5) \times 10^{-10}$
8.5	$(2.4 \pm 1.9) \times 10^{-9}$	$(1.2 \pm 1.3) \times 10^{-8}$	$(3.1 \pm 0.8) \times 10^{-6}$	$(7.8 \pm 4.3) \times 10^{-9}$

## 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 UE-25p #1 than in J-13 water. We believe these solubility effects result from the different carbonate content of the water. Plutonium solubilities did not significantly change with changing water composition. We are currently measuring the solubilities of these radionuclides in a non-complexing sodium perchlorate electrolyte with ionic strengths and carbonate contents similar to J-13 and UE-25p #1 well waters. These experiments will help to establish if the solubility changes are only due to the different carbonate contents of the waters or if the other chemical groundwater components also influence the solubility significantly. We are also assembling a thermodynamic data set, including solubility product and complex equilibrium constants, that will allow us to compare our experimental results

with modeling calculations. Agreement between the experimental results and the modeling calculations will validate the data base and the chemical module of the transport model.

## ACKNOWLEDGMENTS

This work was prepared by Yucca Mountain Site Characterization Project (YMP) participants as part of the U.S. Civilian Radioactive Waste Management Program. The Yucca Mountain Site Characterization Project (YMP) is managed by the U.S. Department of Energy, Yucca Mountain Project. This work was performed at the Lawrence Berkeley Laboratory (LBL) for the Los Alamos National Laboratory (LANL). The Lawrence Berkeley Laboratory is operated by the University of California for the U.S. Department of Energy under Contract DE-AC-03-76SF00098. The Yucca Mountain Project Automated Technical Data Tracking Number is LA000000000033.001.

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