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Solubility and Speciation Studies for Nuclear Repository Performance Assessment

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SOLUBILITY AND SPECIATION STUDIES FOR NUCLEAR REPOSITORY PERFORMANCE ASSESSMENT

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ABSTRACT

Solubility and speciation data are important in understanding aqueous radionuclide transport through the geosphere. They define the source term for transport retardation processes such as sorption and colloid formation. Solubility and speciation data are useful in verifying the validity of geochemical codes that are part of predictive transport models. Radionuclide solubility studies in groundwaters from a repository region will provide limits on radionuclide concentrations in these waters. Meaningful thermodynamically defined solubility studies must satisfy four criteria: (1) solution equilibrium conditions, (2) effective and complete phase separation, (3) a well-defined solid phase, and (4) knowledge of the speciation/oxidation state of the soluble species at equilibrium. Results from solubility and speciation experiments of $^{237}\text{NpO}_2^+$, $^{239}\text{Pu}^{4+}$, and $^{241}\text{Am}^{3+}/\text{Nd}^{3+}$ in J-13 groundwater (from the Yucca Mountain region, Nevada, which is being investigated as a potential high-level nuclear waste disposal site) at three different temperatures (25°, 60°, and 90°C) and pH values (6, 7, and 8.5) are presented.

ESSENTIAL PHENOMENA CONTROLLING AQUEOUS RADIONUCLIDE TRANSPORT THROUGH THE GEOSPHERE

Gaseous and aqueous transport are two principal mechanisms of radionuclide transport from a potential nuclear waste repository to the environment. Aqueous radionuclide migration through the geosphere is controlled by several chemical and physico-chemical phenomena, including the dissolution rate of the waste package, formation of secondary solids, radionuclide complexation in the solution phase, and sorption processes on the geomeia. These processes are interconnected and depend strongly on each other.

Solubility describes the concentration of radionuclides in the aqueous phase. It is controlled by the formation of solubility controlling secondary solids that are in equilibrium with soluble species. The soluble species in turn can form solution complexes by reacting with ligands that are present in the groundwater. Complex formation is dependent on the oxidation state and charge of the radionuclide in the solution phase, as well as the nature and the amount of potentially complexing ligands present in the groundwater. The electrical charges of the solution complexes can vary widely. Detailed knowledge of the species and associated charges are very important for understanding their sorption on the geomeia. Differently charged species adsorb differently. Understanding of sorption processes is also very beneficial in understanding colloidal transport. Colloid transport can be seen as a special form of aqueous transport in which colloidal polynuclear radionuclides and radionuclides that attach themselves to suspended solid material can be transported.

APPLICATIONS OF SOLUBILITY AND SPECIATION DATA

Solubility studies of radionuclides yield good estimates of upper most radionuclide concentrations in groundwaters from the region of potential waste repositories. Such measurements will provide upper concentration limits because the secondary steady-state solids formed can still change from a higher to a lower free energy, which would result in lower

solution concentrations. These changes may be very slow and may require very long or even infinite experimental times, which we do not have.

Model Verification, Data Base Validation, and Risk Assessment

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.

To predict behavior at higher temperatures, data bases used for modeling calculations must contain data on thermodynamic functions at elevated temperatures. To date, many of these data are unavailable and are therefore estimated by extrapolation from lower temperature data. Agreement between modeling calculations and experimental results would also validate such estimates, whereas significant discrepancies would identify the need for data base improvement. Improvements can be made by filling the gaps with generic experimental data.

In addition, experimental solubility data also provide the source terms or the starting concentrations for experimental sorption studies. To be valid, sorption studies should be conducted at or above the solubility limit because only soluble species can be transported and participate in the sorption process.

SOLUBILITY MEASUREMENTS FOR THE YUCCA MOUNTAIN PROJECT

Concept

The concept of solubility and speciation measurements has been discussed and illustrated [1]. Meaningful thermodynamically defined solubility studies should satisfy four criteria: (1) equilibrium conditions, (2) accurate solution concentrations, (3) a well-defined solid phase, and (4) knowledge of the speciation/oxidation state of the soluble species at equilibrium. This study was conducted according to these criteria

Experimental Approach

The solubilities of $^{237}\text{NpO}_2^+$, $^{239}\text{Pu}^{4+}$, and $^{241}\text{Am}^{3+}/\text{Nd}^{3+}$ were determined in J-13 groundwater from the Yucca Mountain region. To bracket a variety of possible pH and temperature conditions, solubility and speciation data were obtained for each radionuclide solution at three different pH values (pH 6, 7, and 8.5) and at three temperatures (25°, 60°, and 90°C). Further experimental details are described elsewhere [1, 2].

Neptunium

Results of the neptunium solubility experiments are shown in Figure 1. The steady-state solids in each experiment were sodium neptunium carbonate hydrates with different water content. The solid formed at 90°C and pH 7 was a mixture of sodium neptunium carbonate hydrate and neptunium pentoxide. The solubility decreased at each temperature with increasing pH; this is due to the increasing concentration of CO_3^{2-} with increasing pH, resulting in lower solubilities through the formation of more insoluble sodium neptunium carbonate hydrates. The supernatant solutions were analyzed by absorption spectrophotometry to determine the oxidation state and speciation. The solutions showed increased carbonate complexation with increasing pH for the 25° and 60°C series. The amount of carbonate complexing increased with increasing temperature for the pH 8.5 solutions. It decreased with increasing temperature for the pH 7 solutions. Very little carbonate complexation occurred for both pH 5.9 solutions. In the 90°C experiments only the pH 8.4 solution contained carbonate complexes.

Plutonium

Results of the tetravalent plutonium solubility study are shown in Figure 2. The solubility-controlling solids were mixtures containing mainly polymeric plutonium(IV) and smaller portions of plutonium carbonates. This explains the drastic decrease in plutonium solubility with increasing temperature. The plutonium(IV) polymer peptizes with increasing temperature and becomes more stable; over extremely long times it may possibly convert to PuO_2 . This also explains why the solubilities did not vary significantly with different pH at each temperature. The solubility of Pu(IV) polymer remains rather unaffected by pH changes. Hydrous plutonium dioxide or plutonium(IV) polymer, however, is thermodynamically ill-defined, and the solubility product constant used in thermodynamic data bases may not be applicable to other polymeric plutonium(IV) precipitates. Such precipitates may differ in their amorphous composition, which may result in calculated solubilities that are significantly higher or lower than the ones determined in experiments.

The plutonium supernatant solutions at steady state were analyzed for their oxidation state distributions. The speciation studies are made difficult by the low solubility of plutonium. The solutions' concentration levels lie below the sensitivity range of methods such as absorption spectrophotometry, which would allow the direct measurement of the species present. Therefore, we developed a method to determine the oxidation states indirectly. The method involves a combination of solvent extractions and coprecipitation. It was tested on solutions of known plutonium oxidation state mixtures with both high-level and trace-level concentrations [2]. Results of this study for 25°, 60°, and 90°C are given in Table I.

All solutions, except the 90°C solution at pH 7, contained predominantly Pu(V) and Pu(VI), whereas Pu(III), Pu(IV), and Pu(IV) polymer are present only in small or insignificant quantities. These observed valence distributions cannot be explained by disproportionation equilibria and complex stabilization [3]. It is possible that oxidation products formed by α -radiolysis of the water 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 without any colloidal or polymeric plutonium being present. This treatment separates all Pu(IV) polymer larger than 4.1-nm from the solution. Therefore, we refer to Pu(IV) polymer in the context of this determination only to the fraction that is smaller than 4.1 nm.

At pH 7 and 90°C, Pu(V) is measured to be equal to the sum of Pu(III) and Pu(IV) polymer. We explain this measured decrease of Pu(V) and the increase of Pu(III + poly.) by leakage of the 4.1-nm Amicon filter used for phase separation. Such leakage would introduce more polymer and change the relative oxidation state distribution. This explanation is supported by comparison of the assay taken as a reference standard for the extraction at pH 7 and 90°C, with a parallel sampling for the solubility determination; the extraction sample contained 2.36 times more plutonium. Unfortunately, we could not repeat this experiment, because not enough supernatant was left for the test. From the other distribution results, we see no reason to doubt that this solution, too, contained probably mostly Pu(V) and Pu(VI).

Americium

Results of the americium solubility experiments are shown in Figure 3. No clear trend of the solubility was found with increasing temperature and increasing pH. Much higher solubilities were found for 60°C compared to 25°C and 90°C. All solids were AmOHCO_3 , with orthorhombic structure for all temperatures at pH 7 and 8.5 and for 60°C at pH 6, and with hexagonal structure for 25°C and 90°C at pH 6. Orthorhombic AmOHCO_3 appears to have a much higher solubility at pH 6 and 60°C than the hexagonal form at the same pH and 25°C or 90°C. As could be expected for the experimental conditions, we found no higher americium oxidation states in the supernatant solutions. The trivalent americium did not change its oxidation state.

CONCLUSIONS AND RECOMMENDATIONS

This study, though limited in scope, shows that data for steady-state solids of some radionuclides are missing in the data base (e.g., $\text{NaNpO}_2\text{CO}_3 \cdot 2.5 \text{H}_2\text{O}$, hexagonal AmOHCO_3 , a range of amorphous plutonium(IV) hydrous oxide solubility products instead of one single value). Very limited data are available for higher temperatures.

Generally, solubility and complexation studies at higher temperatures, up to 150°C , are recommended in order to improve predictive modeling capabilities for scenarios that represent temperatures in the near field.

It is also of great interest to know how alpha self-irradiation effects the solubility of secondary solids. Is the solubility of short-lived ^{238}Pu significantly higher than that of ^{242}Pu with a 4483 times longer half-life?

Furthermore, model and data base validation should be extended through intermediate scale experiments and field tests. Kinetic limitations and heterogeneity of the geomeedia should be incorporated in chemical/transport models. Solubility studies and subsequent comparison with results from modeling calculation should be extended to other important nuclear waste radionuclides, such as nickel, zirconium, cadmium, radium, and thorium.

In summary, we showed in this paper that experimental solubility and speciation studies are useful and very important in understanding radionuclide transport through the geosphere.

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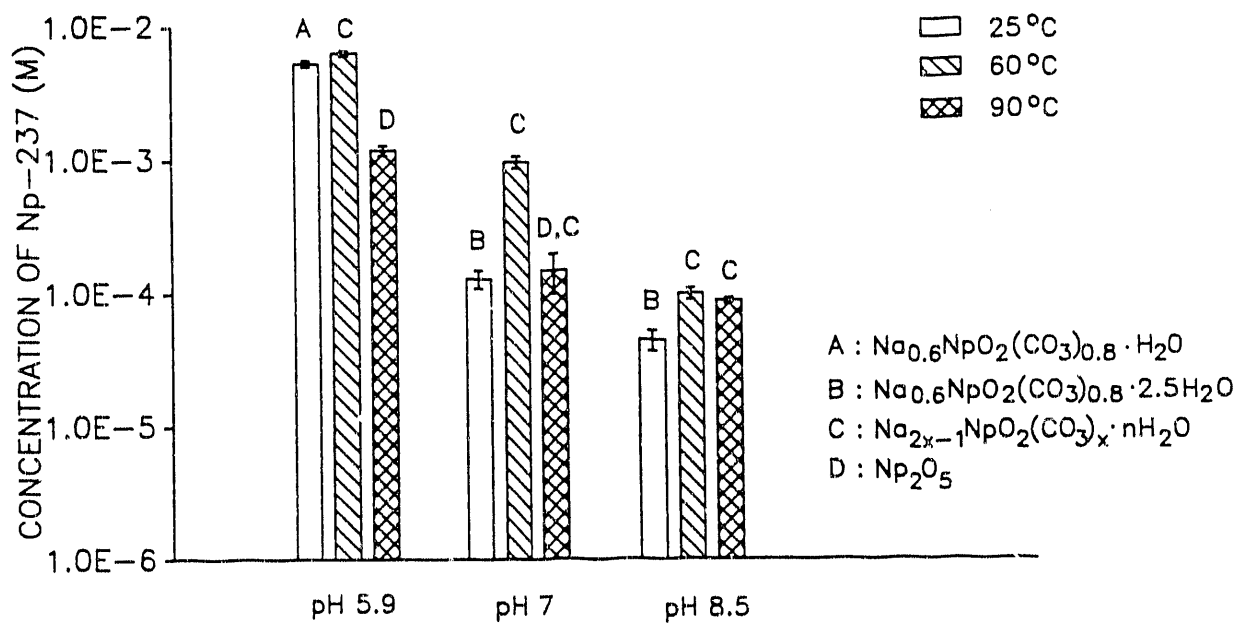
1. H. Nitsche, *Radiochim. Acta* 52/53, 3-8 (1991).
2. H. Nitsche, S.C. Lee, R.C. Gatti, *J. Radioanal. Nucl. Chem.*, 124 (1), 171-185 (1988).
3. G. L. Silver, *Radiochem. Radioanal. Lett.* 9, 5-6, 315-320 (1972).

APPENDIX

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

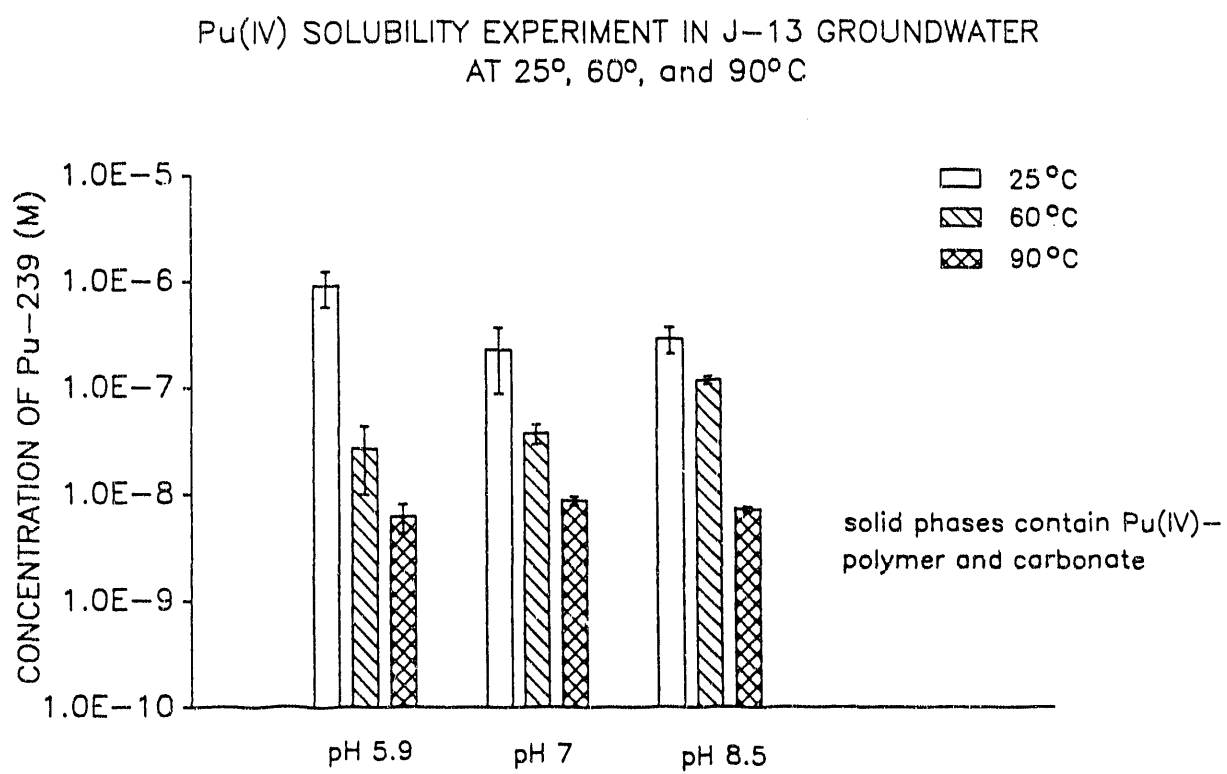
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TWS-LBL-05-88-02, pp. 3-251;
TWS-LBL-01-89-01, pp. 99-293;
TWS-LBL-01-89-02, pp. 3-251;
TWS-LBL-07-89-01, pp. 5-75;
TWS-LBL-02-90-03, pp. 31-75;
TWS-LBL-02-90-04, pp. 63-188;

Np(V) SOLUBILITY EXPERIMENT IN J-13 GROUNDWATER
AT 25°, 60°, and 90°C



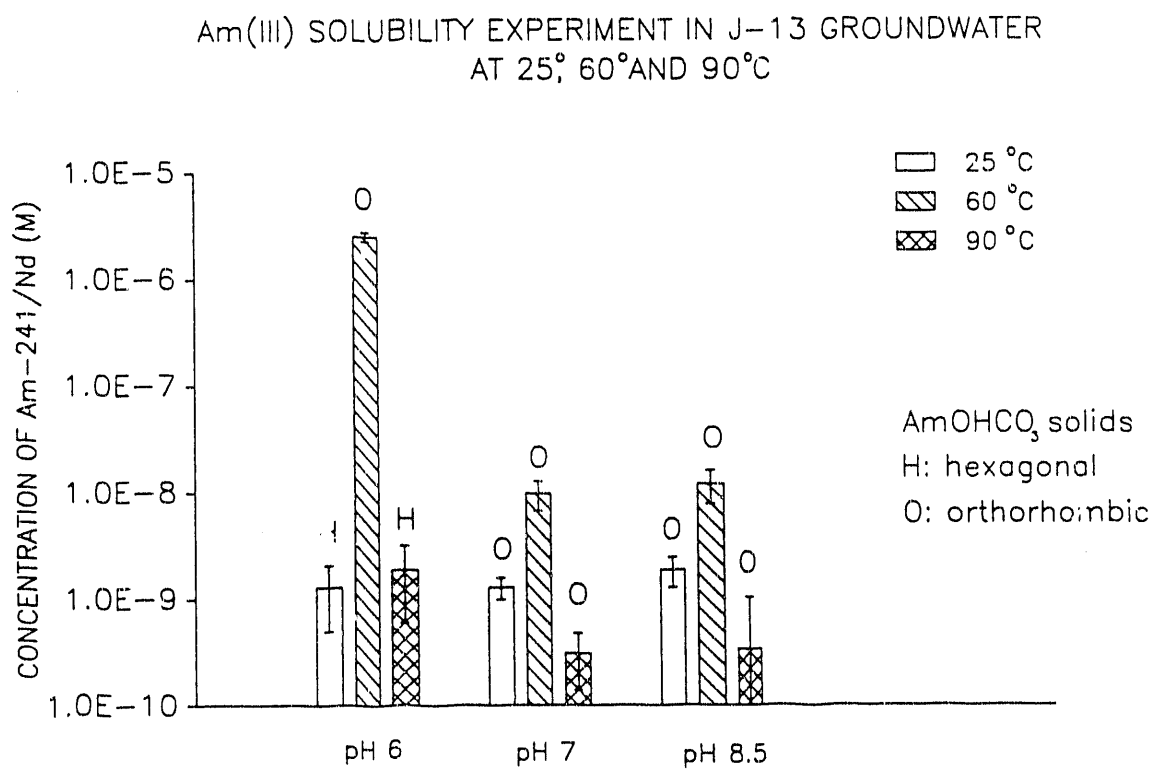
XBL 8911-395

Figure 1. Results of Neptunium(V) Solubility Experiments in J-13 Groundwater as a Function of pH and Temperature.



XBL 8911-3926

Figure 2. Results of Plutonium(IV) Solubility Experiments in J-13 Groundwater as a Function of pH and Temperature.



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Figure 3. Results of Americium(III) Solubility Experiments in J-13 Groundwater as a Function of pH and Temperature.

Table I. Distribution of plutonium oxidation states in J-13 groundwater solutions at steady state and various pH values and temperatures of 25°, 60° and 90°C.

| pH | Oxidation States (%) | | | | | | | | | | | |
|------------------|----------------------|--------|--------|--------|--------|--------|--------|--------|-------|-----------------|--------|--------|
| | Pu(IV) | | | Pu(V) | | | Pu(VI) | | | Pu(III + poly.) | | |
| | 25°C | 60°C | 90°C | 25°C | 60°C | 90°C | 25°C | 60°C | 90°C | 25°C | 60°C | 90°C |
| 5.9 ^a | 5 ± 1 | 2 ± 1 | 6 ± 5 | 68 ± 7 | 17 ± 5 | 79 ± 7 | 29 ± 3 | 72 ± 5 | 7 ± 5 | 3 ± 1 | 10 ± 2 | 9 ± 5 |
| 7.0 ^b | 6 ± 1 | 2 ± 1 | 13 ± 1 | 73 ± 7 | 44 ± 9 | 48 ± 3 | 18 ± 2 | 52 ± 4 | 3 ± 3 | 5 ± 1 | 3 ± 1 | 45 ± 2 |
| 8.5 ^c | 6 ± 1 | 13 ± 1 | 10 ± 2 | 63 ± 6 | 58 ± 2 | 85 ± 4 | 27 ± 3 | 24 ± 1 | 3 ± 3 | 3 ± 1 | 5 ± 4 | 11 ± 2 |

poly. = Pu(IV) polymer

^a 25°C: 5.9 ± 0.1; 60°C: 5.9 ± 0.1; 90°C: 5.9 ± 0.3;

^b 25°C: 7.0 ± 0.1; 60°C: 7.0 ± 0.1; 90°C: 7.2 ± 0.2;

^c 25°C: 8.4 ± 0.1; 60°C: 8.5 ± 0.1; 90°C: 8.5 ± 0.1.

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