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Determination of the Solubilities and Complexation of Waste
Radionuclides Pertinent to Geologic Disposal at the Nevada Tuff Site

Topical Report

Solubilities and Speciation of Actinide Ions in Near-Neutral Solution

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Abstract

The solubilities and oxidation state distribution of neptunium, plutonium, and americium were determined in a groundwater (J-13) of the proposed nuclear waste repository site at Yucca Mountain and in aqueous perchlorate solutions of similar pH. In the non-complexing perchlorate solution, hydroxide formation and hydrolysis are the sole controlling factors of actinide solubility. In the groundwater, additional anions can influence the actinide solubility by the formation of new solids and/or the formation of new solution complexes.

In these studies steady state solution concentrations were determined in separate batch experiments starting with Pu$^{4+}$, PuO$_2^+$, PuO$_2^{2+}$, NpO$_2^+$, NpO$_2^{2+}$, and Am$^{3+}$ under supersaturated conditions at 25°C and a pH of 7.0. The oxidation state distributions at steady state were investigated by spectrophotometry or by an extraction-coprecipitation method. The precipitates were characterized by X-ray powder diffraction measurements.

Comparison of the results showed that some groundwater ions exert an important influence on the Pu and Am solubility, and that hydroxide formation is not the principal factor controlling solubility. The solubility for Np showed no significant difference in either solution. Regardless of the initial oxidation state, the oxidation state present in solution at steady state was a) +5 for Np and b) +5 and +6 for Pu. The results have potential significance for geochemical modeling studies performed to characterize the nuclear waste disposal site.
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1.0 INTRODUCTION

The permanent disposal of nuclear waste in repositories excavated in deep geologic formations appears to be technically feasible. 1

The Nevada Nuclear Waste Storage Investigation (NNWSI) Project, managed by the Department of Energy Nevada Operations Office is investigating a site called Yucca Mountain, a tuff formation located on the Nevada Test Site, as a potential disposal site. If selected, waste packages would be emplaced in a repository in Yucca Mountain whose overall performance would have to meet regulations of the Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA). 2,3 At this time, it has not been decided what types of waste form will be emplaced in the repository. The two principal types are spent fuel in the form of cladded fuel elements and high level waste embedded in a glass matrix from reprocessed spent fuel.

In the event of canister corrosion and waste form failure, migration of contaminated groundwater is considered to be the principal mechanism for radionuclide transport from the underground storage site to the accessible environment. The radioelements can potentially react with various chemical components of the groundwater and host geological medium. Formation of solution species and solubility controlling solid phases can define the maximum concentrations and migration characteristics of radionuclides. The nature of the compounds and solution species formed will depend on the oxidation state of the radioelement, the nature and concentrations of the precipitating ions and complexing ligands, the temperature, the pH and the redox properties of the groundwater, and the surrounding geomedia.
To meet the regulations and requirements of the EPA and the NRC for site characterization, predictions on the nature of insoluble compounds and the speciation of solution complexes that will form as a result of the chemical reactions between the actinides and the groundwater ions may be necessary. Generally, predictions can be made by two different scientific approaches.

The first one utilizes geochemical models with input based purely on thermodynamic solution data. An extensive and accurate data base is needed on solubility data, formation constants and speciation of complexes for every important individual reaction that may occur between the radionuclides and the groundwater components. Unfortunately, many of the required input data are either not available or are burdened by rather large experimental errors. Since the usefulness of a geochemical model depends strongly on the entirety and quality of its data base, more and better thermodynamic data are needed to improve the reliability of its predictions.

The second approach uses a somewhat more empirical solution to the problem. Solubilities of individual waste elements are determined in laboratory experiments using actual groundwater from a prospective disposal site. After reaching steady state conditions, the solid and aqueous phases are separated and analyzed individually. The solid is characterized and solution speciation is studied. The specific repository site can be assessed rather realistically from these experimental results. Furthermore, the data can validate results from geochemical modeling studies using the same scenario. Therefore, the data may serve as a quality test of a given model and its data base.
Several actinides with long half-life, emplaced in an underground repository, can represent a hazard to the biosphere even after several thousand years. The EPA has developed a standard for concentrations of radioactivity in the environment of a high-level radioactive waste disposal site. Using EPA standards, several studies have been made to rank the waste elements according to their potential hazard based on their toxicity, half-life, and potential migration ability. Neptunium, plutonium, and americium are among the elements representing a significant long-term hazard.

Many inorganic components present in groundwaters have an important influence on the formation of insoluble precipitates and solution complexes with the waste radioelements. Groundwater ions of significance which react with the actinides are hydroxide, carbonate, fluoride, phosphate, and silicate. Hydroxide exists in all groundwaters, and it is therefore expected to play an important role in controlling the speciation and the solubilities of the key actinides.

The objective of this study is to determine the solubilities and speciation of neptunium, plutonium, and americium in a groundwater of the proposed repository at Yucca Mountain and in aqueous perchlorate solution of similar pH. In non-complexing perchlorate solution, hydroxide formation and hydrolysis are the sole controlling factors of actinide solubility. However in groundwater, the additional anions can influence the actinide solubility by either the formation of new solids or the formation of new solution complexes or by both.

A comparison of the results in these solutions can show whether the groundwater anions are an important influence on the actinide solubility or if hydroxide formation is the principal solubility-controlling...
factor. Furthermore, the results in perchlorate solution can validate existing literature data on the solubilities of actinide hydroxides.
2.0  EXPERIMENTAL SECTION

2.1  Radionuclides

All nuclides used in these experiments were obtained through the U.S. Department of Energy's Heavy Element Production Program at Oak Ridge National Laboratory. Throughout these experiments several radioanalytical methods were used for nuclide identification and concentration determination. They are:

- alpha energy analysis with a gold-silicon surface barrier detector (Oak Ridge Technical Enterprise Co.) coupled to a low noise preamplifier, main amplifier and biased amplifier of LBL design and to a multichannel analyzer (Tracor Northern Inc., Model TN1705);

- low energy gamma ray analysis with a planar intrinsic germanium detector coupled to an amplifier (both LBL design) and to a multichannel analyzer (Tracor Northern Inc., Model TN1710);

- gross alpha counting with an argon-methane gas proportional counter of LBL design;

- alpha or beta counting with a microprocessor-controlled liquid scintillation counter (Packard Instrument Co., Model 460C). A modification of the instrument allowed monitoring the liquid scintillation spectrum. A preblend scintillating cocktail was used (Research Products International Corp., complete counting cocktail 3a70B) for sample preparation.
2.1.1. Neptunium

A purified $^{237}\text{NpO}_2^+$ stock solution was prepared from neptunium dioxide. The $\text{NpO}_2$ was dissolved in 8 M $\text{HNO}_3$ containing a trace of NaF to facilitate the dissolution. A precipitation as the hydroxide with NaOH followed. After washing, the precipitate was dissolved in 0.1 M $\text{HNO}_3$ and the Np reduced to the +3 state by contacting the solution with zinc-amalgam. Purging of the resulting solution with air for a few minutes converted all the Np to the +4 oxidation state. The Np was then purified in the tetravalent state by anion-exchange chromatography. The anion-exchange column was prepared with 100-200 mesh Biorad AG 1 x 8 resin. Loading and washing was with 8 M $\text{HNO}_3$ and elution was with 0.3 M $\text{HNO}_3$. The eluates were fumed twice with concentrated $\text{HClO}_4$ to near dryness. The residue was then redissolved in 10 ml of 0.1 M $\text{HClO}_4$. Alpha counting and microtitration with EDTA were used for standardization of the stock solution. The standardized solution was $1.17 \pm 0.03 \times 10^{-1}$ M. A 100 µg sample was analyzed by spark emission spectroscopy for metal contaminants. The results of the analysis are given in Table 1.

2.1.2. Plutonium

Since the Pu solubility was expected to limit solution concentrations to $10^{-8}$ M at the experimental pH of 7, the specific alpha activity of our $^{242}\text{Pu}$-stock solution was increased by spiking with $^{238}\text{Pu}$. This facilitated concentration measurements at low levels by liquid scintillation counting. $^{242}\text{Pu}$ and $^{238}\text{Pu}$ stock solutions were prepared individually from oxide powders. The oxides were dissolved in 6 M HCl and converted to the perchlorate by fuming twice to near dryness.
with concentrated HClO₄. After taking up the residues in perchloric acid, the ⁹²⁴Pu solution was spiked with a small amount of ²³⁸Pu solution. The mixture was fumed again with concentrated HClO₄ and the residue was redissolved in 1 M HClO₄. The concentration of this stock solution was determined to be 3.3 x 10⁻¹ M from the results of gross alpha counting of dried aliquots with a gas proportional counter and from liquid aliquots with a scintillation counter. Alpha- and gamma-pulse height analysis indicated the following composition by alpha activity and weight, respectively: ²³⁸Pu - 99.38% and 4.61%, ²⁴²Pu - 0.46% and 95.39%, and ²⁴¹Am - 0.14% and 0.003%. The specific activity of this mixture was 1.79 x 10⁶ dpm/µg. A 30 µg sample was submitted for spectrochemical analysis. The results of this analysis are listed in Table 1.

2.1.3 Americium

Since the Am was in solution from a previous experiment, it was cleansed of soluble salts and silica by two NaOH precipitation-dissolution cycles. The resulting tan colored Am(OH)₃ was then dissolved in 0.05 M HCl. Alpha pulse height analysis showed the sample to be 86.65% ²⁴³Am, 1.91% ²⁴¹Am, and 11.44% ²⁴⁴Cm by activity. The Am was separated from the Cm and other cations by cation-exchange chromatography using Biorad AG 50 x 12 resin (- 400 mesh). The resin was converted to the NH₄⁺-form by washing with 1 M NH₄-α-hydroxyisobutyrate (NH₄-BUT) (pH = 4.05) and conditioned with 0.4 M NH₄-BUT (pH = 4.05). Approximately 4 mg of Am was loaded onto the column in 0.05 M HCl and the elution made with 0.4 M NH₄-BUT (pH = 4.05). The composition of the Am fraction from the column was found to be 97.53%
and 99.87% $^{243}$Am, 2.15% and 0.13% $^{241}$Am, and 0.32% and 0.0008% $^{244}$Cm by alpha activity and weight, respectively.

A final purification and separation from the NH$_4$-BUT was accomplished by cation-exchange chromatography on Biorad AG 50 x 8 resin. The column was loaded with the 0.05 M, washed with 2 M HCl, and the Am eluted with 6 M HCl.

Spark emission spectroscopic analysis was performed on a 30 µg sample. The results of the analysis are given in Table 1.

2.2 Solutions

All solutions, except the groundwater, were prepared with deionized-distilled CO$_2$-free water under an inert gas atmosphere. The water was taken from the distillation apparatus while it was still hot and was stored in an inert-gas glove box to eliminate CO$_2$ uptake. Prior to their use, the water and all other solutions were filtered through a 0.05 µm polycarbonate membrane filter (Nuclepore Corp.). Filtering was used to remove suspended particulate material, e.g. dust or silica, that could absorb the actinide ions to form pseudo colloids. A partial CO$_2$-pressure of 0.014 atmospheres was maintained at all times above the surface of the J-13 groundwater solutions to avoid the loss of CO$_2$ during the experiment. Reagent grade NaClO$_4$ (G.F. Smith Chemical Company) was recrystallized twice from H$_2$O before it was used to make the 0.1 M NaClO$_4$ non-complexing supporting electrolyte solution.

Groundwater was taken from the proposed site for a geologic nuclear waste repository at Yucca Mountain, Nevada. It was pumped from Well J-13. The Nevada Nuclear Waste Storage Investigation (NNWSI) program
has chosen this water as a reference groundwater for various studies. The analysis of the water composition is listed in Table 2.

2.3 Procedures and Equipment

2.3.1 Solubility Measurements

2.3.1.1 Background

There are two principal methods to determine the solubility of a compound in solution: (1) undersaturation and (2) supersaturation.

In the case of undersaturation a prepared, well-defined solid phase is placed in contact with an aqueous solution and the dissolution of the solid is studied.

Supersaturated conditions require addition of an excess amount of the compound in soluble form to the aqueous solution and then the precipitation of the insoluble material is monitored.

For meaningful results it is necessary to have:

(1) reached steady state conditions between solution and solid phase from both super- and undersaturation;
(2) effectively separated solution and solid phase;
(3) a well-defined solid phase.

The solution concentration is measured as a function of time until steady state conditions are reached. A steady state is achieved when the solution concentration remains constant over several weeks, and it is then assumed that equilibrium conditions have been established.

The separation of the solid phase from the solution phase is considered adequate when the solution concentration obtained from the filtrates through two different sized filters are equal within experimental error.
Well-defined solids are generally crystalline material which are characterized by X-ray diffraction measurement or if this does not clearly identify the compound, chemical analysis is required.

2.3.1.2 Experimental Details

The solubility measurements were made in an inert-atmosphere box (Vacuum Atmospheres Co., Model HE-43-2) to avoid contamination of solutions by CO₂ and O₂. Substantial drifts in pH can occur in periods as short as 24 hours in poorly buffered solutions. Since the solubility measurements at pH 7 were of this type, an automated pH control was necessary. A laboratory computer (Laboratory Data Control, Milton Roy Company, Model CCM) control system was used to sense any one of six microcombination pH electrodes (Beckman Instr. Inc., Model 39522) via a pH-electrode switch (Orion Research, Inc., Model 605, modified for remote control) and a pH meter (Radiometer America, Inc. Model pHm 84). If the pH of the selected solution was not within the preselected range, five microliters of dilute HClO₄ or NaOH were dispensed on computer command to the appropriate solution through a computer-selectable, six-position solvent delivery valve (Eldex Laboratories, Inc., Model SV-1062) by a digital diluter (Hamilton Company, Model 100000). All solutions were continuously monitored and pH corrections were made as required. The diluter, associated electronics, and acids and bases are contained in an argon atmosphere box (Labconco Corp.) adjacent to the inert box to avoid radioactive contamination. The CO₂-content of the box atmosphere was determined periodically with a gas chromatograph (Gow-Mac Instruments Company, Model 69-750p).
To avoid clogging of the pH electrode's electrolyte bridge from formation of insoluble KClO$_4$, the KCl/AgCl bridge electrolyte was replaced with a concentrated NaCl solution, which was saturated with AgCl. The pH electrodes were calibrated with buffers at least twice every week to correct for possible electrode drift.

Solubility measurements were made in 100 ml polypropylene cells with sealed ports at the top to allow permanent emplacement of a pH electrode, addition of 0.05 M HClO$_4$ or 0.05 M NaOH for pH correction, and sampling. The HClO$_4$ was made from doubly distilled concentrated stock (G.F. Smith Chemical Company); NaOH pellets "low in carbonate" (J.T. Baker Chemical Co.) were used for preparation of the NaOH solution. Solutions were prepared as described previously. Samples were shaken at 80 rpm with an automatic shaker (Lab-Line, Inc., Model Junior Orbit).

Due to time restrictions for this project, we decided to measure solubilities from the supersaturation direction. Approaching solubility measurements in this way allows an upper limit to be determined for the material of interest. Aliquots of NpO$_2$$^{2+}$, NpO$_2$$^{4+}$, Pu$_4$$^{4+}$, PuO$_2$$^+$, PuO$_2$$^{2+}$, and Am$^{3+}$ stock solutions were placed in separate polypropylene cells with 50 ml of the aqueous phase at 25 ± 1°C. The initial solution concentrations were for NpO$_2$$^{2+}$ 4.3 x 10$^{-3}$ M and 2.2 x 10$^{-3}$ M, for NpO$_2$$^{4+}$ 8.6 x 10$^{-4}$ M and 2.3 x 10$^{-3}$ M, for Am$^{3+}$ 3.3 x 10$^{-4}$ M and 2.0 x 10$^{-4}$ M, for Pu$_4$$^{4+}$ 4.1 x 10$^{-4}$ M and 5.5 x 10$^{-4}$ M, for PuO$_2$$^{4+}$ 4.1 x 10$^{-4}$ M and 5.3 x 10$^{-4}$ M, and for PuO$_2$$^{2+}$ 3.9 x 10$^{-4}$ M and 1.1 x 10$^{-3}$ M for 0.1 M NaClO$_4$ and J-13 groundwater, respectively. The pH of the supporting electrolyte (0.1 M NaClO$_4$ or J-13 groundwater) was kept slightly basic, in order to compensate for the amount of acid which was introduced by adding the
actinide stock solution. Special care was taken not to allow the pH-value to drop below 7, which would have necessitated addition of base to adjust the pH back to 7. Addition of base can result in unpredictable microprecipitation and formation of polymers.

The various oxidation states of Pu and Np in the stock solutions were adjusted by controlled-potential coulometry. The coulometric cell was a three electrode set-up. A platinum wire counter electrode, an Ag/AgCl/3 M NaCl reference electrode (AgCl) and a platinum gauze working electrode were used. The counter and reference electrodes were separated from the analyte solution by Vycor fritted salt bridges which contained 1 M HClO₄. Solution purging or blanketing with argon was accomplished through a port in the cell top. Solution stirring was achieved with a magnetic spinbar and an electric stirrer.

The neptunium in the stock solution was in the +6 oxidation state after its initial preparation. It was reduced to NpO₂⁺ at 645 mV (AgCl).

The plutonium stock was completely PuO₂²⁺ after the fuming procedure. PuO₂⁺ was prepared by reducing one part of the PuO₂²⁺ at a pH of 3.5 at 400 mV (AgCl). The reduction from the plutonium-dioxo-cations to Pu⁴⁺ cannot be performed directly. Due to the irreversibility of the reaction PuO₂⁺ to Pu⁴⁺, a large overpotential must be applied. This leads to the formation of Pu³⁺. Therefore, all PuO₂⁺ was reduced at -100 mV (AgCl) to Pu³⁺, and then oxidized at 1100 mV (AgCl) to Pu⁴⁺.

Purity control for each valence state was established by absorption spectrophotometry utilizing a recording spectrometer (Varian Instruments Division, Cary Products, Model 17). A minicomputer (Digital Equipment Corp., Model MINC-11-B, LSI-11/2) was interfaced to the spectrometer and allowed digital data collection and manipulation, e.g., background
subtraction and data smoothing. For molar absorptivities with values below 100 M\(^{-1}\) cm\(^{-1}\) cells of 100 mm pathlength were utilized; for solution ions with higher molar absorptivities a 10 mm cuvette gave sufficient response at given concentration levels. For all measurements, solutions corresponding to the analytical solution without radionuclides were used as reference. The spectra were taken in the range from 350-1250 nm. Spectra obtained for each individual oxidation state were identical with published data, with the exception of the Pu(IV) spectrum.\(^{19-21}\) The location of the absorption maxima in our spectrum agreed well with Cohen's Pu(IV) spectrum, but we did not observe any "background sloping" towards higher absorbance values in the frequency range below 460 nm.

Achievement of steady state conditions for the solubility measurements was monitored by sampling aliquots of the solution phases and analyzing for the respective radioisotope. The efficiency of the separation of solid and solution phase is strongly dependent on the method of separation. We have studied the effect of various separation methods for Pu\(^{4+}\).

Approximately 1 mg of \(^{242}\)Pu was added to 10 ml of a slightly basic aqueous solution; the pH was adjusted to a value of 7 by addition of diluted HClO\(_4\). After 6 days, the pH was checked again and the solution centrifuged at 7,000 g for 15 minutes. Then the remaining supernatant underwent the following separate treatments:

1. filtration through a 0.22 μm filter disc (Millipore Corp.);
2. centrifugation in an Eppendorf microcentrifuge (Brinkman Instruments Corp., Model 5412) at 10,000 g for 15 minutes; calculated sizing ~0.1 μm;
3. filtration through a 0.015 μm polycarbonate membrane (Nuclepore Corp.);
4. filtration through a 0.010 μm polycarbonate membrane (Nuclepore Corp., new product);
5. centrifugal filtration with Centricon Microconcentrator (Amicon Corp.), MW cutoff 30,000. According to the manufacturer the membrane used in these units is the YMT-type; the pore size is calculated to 0.0041 μm by Kim and Bernkopf.22

For this experiment and for all other ultra filtrations, possible absorption of soluble material on the filters was minimized by first filtering an aliquot of the sample and discarding the filtrate before filtering a second sample for analysis. Always one drop of 9 M HCl was added to the filtrate collecting vial to prevent possible absorption of radioactive material on the container walls, which would lead to erroneous results for the concentration determination of the solution phase. Analysis was done by liquid scintillation and α-gross counting. Use of treatments (1)-(3) resulted in a linear count rate dependence on pore size. Treatment (4) was unsuccessful; no liquid could be pressed through the membrane. Filtration through the Centricon Microconcentrator (treatment (5)) decreased the count rate by only a factor of 2 compared to treatment (3). Although the polycarbonate membrane with 15 nm pore size gives nearly the same results as the YMT membrane with 4.1 nm pore size, we decided to use the YMT membrane filters in order to assure effective separation if unexpected small particle sizes would be encountered during the actual experiments. The
effectiveness of these filters has also been proven for aqueous solutions of neptunium and americium. 22, 23

After separation of solution and solid phase the two components were analyzed separately. Concentration measurements of the supernatants were made for
- $^{243}$Am and $^{237}$Np by counting the 74.67 keV or the 29.34 keV $\gamma$-ray line with the germanium low-energy $\gamma$-counting system, respectively;
- $^{242,238}$Pu by $\alpha$-liquid scintillation assay.

The solid compounds were analyzed by X-ray powder diffraction measurements. A few micrograms of each actinide precipitates were placed in a 0.33 mm diameter quartz capillary tube, and the tube was sealed with a oxy-butane microtorch. The tube was mounted into an 11.4 cm diameter Debye-Scherrer camera and then irradiated with X-rays from a Norelco III X-ray generator (both Philips Electronics Inc.). Copper $K_{\alpha}$ radiation filtered through Ni was used.

2.3.2 Plutonium Polymer

Since the presence of Pu polymer was expected in the supernatants of the Pu solutions, we wanted to familiarize ourselves with its solution properties.

The Pu(IV) polymer was prepared in an inert-gas atmosphere from $^{242,4+}$Pu stock by hydroxide precipitation and redissolution of the precipitate in a small amount of 6 M HCl. Dilution with distilled, $CO_2$-free water gave a solution with $1.4 \times 10^{-3}$ M total Pu concentration and a pH of 1.3. After standing for seven days at room temperature an
absorption spectra of the solution was obtained. The analysis showed 61% of the Pu was converted to Pu(IV) polymer. The remaining ionic Pu in solution was found to be approximately 21% Pu\(^{3+}\), 16% PuO\(_2^+\) and 2% PuO\(_2^{2+}\). The concentration of Pu\(^{4+}\) was below detection limit (< 1%). A part of this solution underwent a cation-exchange column separation on DOWEX AG-50 resin (100-200 mesh) in order to obtain pure Pu(IV) polymer. The absorption spectra of the polymer are given in Figs. 1 and 2. The spectra agreed well with published data, although the molar absorptivity value of 11-12 M\(^{-1}\)cm\(^{-1}\) for the 613 nm line appears to be somewhat lower.\(^{27}\)

The Pu polymer mixture before the ion exchange and the pure Pu(IV) polymer solution were analyzed by absorption spectrophotometry as a function of time. After 7, 21 and 27 days no change was noticeable in oxidation state distribution for both solutions within the uncertainty limit of approximately 5%. Furthermore, the particle size range of the colloidal polymer was determined by use of different solid-liquid separation methods. Precipitation by centrifugation at 15000 rpm for 15 minutes (12,000 x g, particles < 100 nm remain in solution) and with a Centricon Microconcentrator (particles < 4.1 nm remain in solution) showed that 66% of the polymer particles were smaller than 100 nm, and less than 0.5% were below the size of 4.1 nm.

2.3.3 Oxidation State Determination

After separation of the solid and solution phases, the supernatants were analyzed to determine the oxidation state distribution of solution species. For the NpO\(_2^+\), NpO\(_2^{2+}\) and Am\(^{3+}\) solutions we used spectrophotometry. The rather low concentrations of our Pu-supernatant
solutions required a different method for the determination of oxidation state distribution of solution species. The most commonly used method utilizes a combination of coprecipitation with rare earth fluorides and both thenoyl-trifluoro-acetone (TTA) and methyl-isobutyl-ketone (hexone) extractions. A TTA extraction step at pH 4 was added to the scheme for further discrimination between the oxidation state +3 and +4 which coextract into TTA at pH 4. Table 3 surveys the methods used and their selectivity for specific oxidation states.

The efficiency of separation for the methods used to determine the plutonium oxidation state distribution was tested individually on a Pu$^{4+}$ solution and on Pu$^{3+}$/Pu$^{4+}$, and Pu$^{4+}$/PuO$_2$$^{2+}$ mixtures of known concentration at the 10$^{-4}$ M level in air. Oxidation state distribution was verified by absorption spectroscopy.

TTA was recrystallized twice from cyclohexane. It was dissolved in xylene to make a 0.5 M solution. The extractant was presaturated with acid prior to its use. TTA-extractions at pH 0 always yielded 98 ± 2% Pu$^{4+}$. TTA-extractions at pH 4 were performed in acetate buffered solution. The recovery was 96 ± 4% for the sum of Pu$^{3+}$ and Pu$^{4+}$.

The methyl-isobutyl-ketone used for hexone extractions was doubly distilled and acid presaturated prior to its use; Ca(NO$_3$)$_2$ was used as salting agent.

Due to the fact that the phase boundaries between hexone and the aqueous solution are not very distinct, since they are formed by two colorless solutions, the extractions were sometimes burdened by a relatively large error. On the average 90 ± 20% Pu$^{4+}$ and PuO$_2$$^{2+}$ could be found in the organic phase. However, since the $^{242}$Pu test solution contained a small amount of $^{241}$Pu, the daughter nuclide $^{241}$Am$^{3+}$ was used
as an internal tracer to correct the yields. Since the trivalent $^{241}\text{Am}$ should remain completely in the aqueous phase its presence in the organic phase served as indicator for the effectiveness of the separation and appropriate yield corrections for Pu$^{4+}$/PuO$_2$$^{2+}$ mixture were made.

LaF$_3$-precipitates were performed with Na$_2$Cr$_2$O$_7$ as oxidizing agent. The La-carrier concentration was 20 mg/ml and HF was used as the precipitation reagent. It was pretreated with a trace of Na$_2$Cr$_2$O$_7$ to eliminate the presence of possible reductants. 92 ± 3% Pu$^{4+}$ and Pu$^{3+}$/Pu$^{4+}$ mixture, respectively, were found in the precipitate; it was redissolved in 1 M HCl for counting. The recovery for PuO$_2$$^{2+}$ in the supernatant was also 92 ± 3%. Our study showed that Pu oxidation state measurements are more reliable and reproducible if fewer extraction steps are involved. For example, a TTA-extraction on the Pu$^{3+}$/Pu$^{4+}$ mixture of pH 0 to recover Pu$^{4+}$, followed by an additional TTA-extraction for Pu$^{3+}$ on the same solution at pH 4 gave an erroneous value for the Pu$^{3+}$. However the determination as the difference of the results from two extractions performed on separate solutions agreed well with the Pu$^{3+}$ value determined by spectrophotometry.

Finally, Pu$^{3+}$, Pu$^{4+}$, Pu(IV) polymer, and PuO$_2$$^{2+}$ mixtures were analyzed by the above described methods at the $10^{-4}$ M and $10^{-7}$ M levels in an Ar-atmosphere glove box. First, the concentration of a Pu$^{3+}$/Pu$^{4+}$/PuO$_2$$^{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 $1.844 \times 10^{-4}$ M (solution 1). And third, this solution was diluted with 1 M HCl to give a total Pu concentration of $9.67 \times 10^{-8}$ M (solution 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. Results are given in Table 4.

The recovery for \( \text{Pu}^{4+} \) by TTA extraction at pH 0 agreed well for solution 1 and solution 2 with the result obtained by absorption spectroscopy on solution 1. The results for the TTA-extraction at pH 4 appear to be too high for the sum of \( \text{Pu}^{3+} \) and \( \text{Pu}^{4+} \). It is very difficult to discriminate between the absorption bands for \( \text{Pu}^{3+} \) and \( \text{PuO}_2^{2+} \) in the presence of large amount of \( \text{Pu}^{4+} \) and Pu(IV) polymer. Therefore the amount of \( \text{Pu}^{3+} \) and \( \text{PuO}_2^{2+} \) in solution 1 was determined by taking the difference between the total amount of Pu from nuclear counting and the sum of \( \text{Pu}^{4+} \), Pu(IV) polymer, and \( \text{PuO}_2^{2+} \) from the absorption spectra; the value was \( 15 \pm 12\% \). The sum of this value and the amount of \( \text{Pu}^{4+} \) from the spectral data is \( 62 \pm 13\% \) for \( \text{Pu}^{4+} \), \( \text{Pu}^{3+} \), and \( \text{PuO}_2^{2+} \). This value even at the upper limit is substantially smaller than the result from the TTA-extraction at pH 4. It is known that Pu(IV) polymer shows a tendency to adhere to container walls in neutral and slightly acidic solutions. However, vigorous agitation of the solution can lead to partial resuspension.\(^{28}\) This phenomenon seems to play an important role in the TTA-extractions at pH 4. Apparently Pu(IV) polymer absorbed on the walls is partially resuspended during the extraction process which then leads to high values for the organic phase. One must conclude that in the presence of large amounts of polymer, TTA-extractions at pH 4 are unsatisfactory. However, the experiment on Pu(IV) polymer described earlier in this paper showed that solutions filtered through 4.1 nm centrifugal filters contained only small amounts of polymer. Because we
utilized these filters in our solubility experiments, we expected the concentration of Pu(IV) polymer to be negligibly small compared to the overall Pu concentration. Therefore, we could expect that TTA-extraction at pH 4 performed on the solution phases of the solubility experiment would lead to accurate results as they did on test runs with no polymer present.

The hexone extractions of solutions 1 and 2 resulted in good values for the recovery of Pu$^{4+}$ and PuO$_2$$^{2+}$ in the organic phase. Subtracting the amount of Pu$^{4+}$ obtained from the TTA-extraction at pH 0 from this value produced a value for PuO$_2$$^{2+}$ recovery, which was in excellent agreement with the direct findings by spectroscopy.

The lanthanum fluoride precipitates contained Pu$^{3+}$, Pu$^{4+}$, and Pu(IV) polymer. Subtracting the value for Pu$^{4+}$ (TTA, pH 0) from this number, a value for the sum of Pu$^{3+}$ and polymer was obtained. Though no reliable value for Pu$^{3+}$ was available from the TTA-extraction at pH 4, this amount can only be compared to the amount of polymer determined by spectroscopy. The difference indicates the presence of a rather small amount of Pu$^{3+}$ and lies within the uncertainty limits of the Pu(IV) polymer value from the spectra. The PuO$_2^+$ and PuO$_2$$^{2+}$ remain in the supernatant solution and, by subtracting the calculated PuO$_2$$^{2+}$ value, one gains also a rather small number for PuO$_2^+$, which again was indicated by the spectroscopic analysis of solution 1.

The extraction-coprecipitation experiments have demonstrated their usefulness to study plutonium speciation in the absence of Pu polymer. Although some results may have relatively large errors associated with them, this method will nevertheless provide a reasonably complete
understanding of Pu speciation in solutions of unknown oxidation state distribution at trace levels.
3.0 RESULTS AND DISCUSSION

A summary of the results is given in Appendix A.

3.1 Americium

Results of solubility measurements at pH 7.0 ± 0.1 at 25 ± 1°C as a function of equilibration time are shown in Figure 3. Steady state values were calculated from the last 5 data points for 0.1 M NaClO₄ solution and from the last 4 concentrations for J-13 groundwater.

X-ray powder diffraction studies of the tan colored solid formed in 0.1 M NaClO₄ indicated only two very weak diffraction lines from which we conclude that the material was mostly amorphous.

Examination of the 0.1 M NaClO₄ solution by spectrophotometry showed that all of the Am remained in the +3 oxidation state (Fig. 4). The characteristic absorption band at 503 nm was not displaced or broadened and appeared similar to observations in acidic solutions. However, the molar absorptivity value $\varepsilon = 290 \text{ M}^{-1} \text{ cm}^{-1}$ was substantially lower compared to $\varepsilon = 378 \text{ M}^{-1} \text{ cm}^{-1}$ in 0.1 M HClO₄. This might indicate formation of hydrolytic species, although the band at 812 nm, which is very sensitive to changes due to complex formation, also remained unchanged.

The solubility value of $10^{-3.52 \pm 0.02} \text{ M} ((3.0 \pm 0.1) \times 10^{-4} \text{ M})$ agrees with the value of approximately $10^{-3.5} \text{ M}$ gained by extrapolation at pH 7 from the solubility-pH graph for amorphous $^{243}$Am(OH)₃ published by Rai et al. Silva's value, also derived from the solubility-pH plot, is about $10^{-4.5} \text{ M}$ for crystalline $^{243}$Am(OH)₃ in 0.1 M NaClO₄ solution. The lower solubility for crystalline Am(OH)₃ can be attributed to the increase in energy required during the dissolution...
process to break up the crystal lattice. From the agreement of our value with the data of these investigators we deduce that the solid present in our solution is amorphous \( \text{Am(OH)}_3 \). Values given by Kim et al. for \( ^{241}\text{Am(OH)}_3 \cdot n\text{H}_2\text{O} \) and \( ^{241}\text{AmO}_2 \) in 0.1 M NaClO\(_4\) at pH 7 are approximately \( 10^{-6.5} \) M and \( 10^{-9} \) M, respectively.\(^{22}\) The significantly lower results were determined independently for supersaturated and undersaturated conditions on amorphous material.

The solubility of \( \text{Am}^{3+} \) in J-13 groundwater was \( 10^{-5.96} \pm 0.08 \) M (\( (1.1 \pm 0.2) \times 10^{-6} \) M), substantially lower than in non-complexing NaClO\(_4\) solution. The d-spacings and relative intensities derived from an X-ray powder diffraction pattern of the grayish tan colored solid are given in Table 5. The pattern appears to resemble d-spacings and intensities present in X-ray powder diffraction measurements of both \( \text{NdOHCO}_3 \)-type \(^3\) and \( \text{Nd}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O} \).\(^{33}\) Since neodymium is a good analog element for americium, and it is known that AmOHCO\(_3\) has a pattern similar to \( \text{NdOHCO}_3 \),\(^{33}\) one can conclude that the americium precipitate formed in J-13 groundwater may contain a mixture of AmOHCO\(_3\) and \( \text{Am}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O} \).

3.2 Neptunium

The results of solubility measurements at pH 7.0 ± 0.1 and 25 ± 1°C as a function of equilibration time are given in Figure 5.

In 0.1 M NaClO\(_4\), steady state values for the solution with \( \text{NpO}_2^+ \) initially added were calculated to be \( 10^{-3.36} \pm 0.01 \) M (\( (4.4 \pm 0.1) \times 10^{-4} \) M) using all data points. For the solution containing initially \( \text{NpO}_2^+ \) the value of \( 10^{-3.46} \pm 0.02 \) M (\( (3.5 \pm 0.1) \times 10^{-4} \) M) was derived from the last three measurements.
The X-ray powder diffraction pattern taken from the brown precipitate formed in the solution with NpO$_2^{2+}$ is listed in Table 6. Though the solid is crystalline, no comparable X-ray data was found in the literature to identify the precipitate. The NpO$_2^+$ solution produced a brownish-yellow colored precipitate from which no pattern was obtained by X-ray diffraction; therefore, it can be considered as being amorphous.

Oxidation state distribution analysis of both supernate solutions was performed by absorption spectrophotometry. The spectra for the solution containing initially NpO$_2^+$ is shown in Figure 6 and for the solution with initially NpO$_2^{2+}$ in Figure 7. The Np in the initially pentavalent Np-solution remained in the +5 oxidation state, while that in the hexavalent Np-solution underwent complete conversion to NpO$_2^+$.

The literature provides an upper limit for the solubility products of both NpO$_2$OH and NpO$_2$(OH)$_2$. The values are: log $K_s < -9.2$ for NpO$_2$OH and log $K_s < -21.4$ for NpO$_2$(OH)$_2$, respectively. At our experimental pH of 7, the calculated solubility for NpO$_2^+$ in equilibrium with NpO$_2$OH would be smaller than $6.3 \times 10^{-3}$ M. This number agrees rather well with the experimentally determined solubility of $4.4 \times 10^{-3}$ M. Since our precipitate was amorphous, and it is well known that the preparation of crystalline NpO$_2$OH requires particular experimental efforts, i.e. heating under reflux, we conclude that the solid phase formed was amorphous NpO$_2$OH. It is difficult to decide on the possible nature of the precipitate formed in the solution initially containing NpO$_2^{2+}$. Since the experimental solubility number of $3.5 \times 10^{-4}$ M differs substantially from the literature value of $4 \times 10^{-8}$ M for
$\text{NpO}_2^{2+}/\text{NpO}_2(\text{OH})_2$ and the soluble neptunium was converted completely to $\text{NpO}_2^{+}$, one could speculate that the solid phase was not $\text{NpO}_2(\text{OH})_2$, but contained large amounts of $\text{NpO}_2\text{OH}$. This would suggest that solubility measurements conducted over even a longer time period than done in this study would lead eventually to identical solution concentrations and solid phases. Though the initial neptunium oxidation state in solution was +6 or +5, only the reaction $\text{NpO}_2\text{OH} = \text{NpO}_2^{+} + \text{OH}^{-}$ seemed to control the equilibrium conditions for both solutions.

In J-13 groundwater, steady state values were calculated as $10^{-2.85 \pm 0.19} \text{M} \ (1.6 \pm 0.6) \times 10^{-3} \text{M}$ from the last three data points for the solution with initially $\text{NpO}_2^{+}$. For the J-13 groundwater initially containing $\text{NpO}_2^{2+}$, the steady state concentration was calculated to be $10^{-3.14 \pm 0.04} \text{M} \ (7.2 \pm 0.7) \times 10^{-4} \text{M}$ from the last 5 points.

The whitish precipitate formed in the latter solution was analyzed by X-ray powder diffraction; the pattern is listed in Table 7. The solid is crystalline, but no data was found in the literature to identify this precipitate. The color of the bright lime green precipitate formed in the groundwater to which $\text{NpO}_2^{+}$ was added had a strong resemblance with the color of a "grasshopper cocktail". Its pattern is also listed in Table 7 together with literature values for $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$. Although the line intensities of our solid are different than the ones reported for $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$, we suggest that the solid formed may be $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$, possibly $\text{CaNaNpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ or $\text{MgNaNpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$. This conclusion is supported by the very pronounced color of the solid which is described as blue-green in the literature. This result is in conflict with literature data which
indicates that the monocarbonate, a grayish white colored compound should form at the given carbonate concentration in J-13 groundwater.\(^{39}\)

The absorption spectra for the NpO\(_2\)\(^{2+}\)-groundwater solution at steady state are shown in Figures 8a and 8b. All soluble neptunium remained in the +5 oxidation state. Using \(\varepsilon = 395 \text{ M}^{-1}\text{cm}^{-1}\) for the band at 980 nm, the solution concentration of \(1.3 \times 10^{-3} \text{ M}\) was derived, which agrees well with the value of \((1.6 \pm 0.6) \times 10^{-3} \text{ M}\) obtained by nuclear counting. Figures 9a and 9b depict the absorption spectra at steady state taken on the initially NpO\(_2\)\(^{2+}\)-groundwater solution. No absorption bands for NpO\(_2\)\(^{2+}\) were found for this solution and similar to the NaClO\(_4\) solution, the spectrum indicated the sole presence of NpO\(_2\)\(^{+}\). Again, as in the non-complexing solution, the neptunium was reduced from the oxidation state +6 to +5 in J-13 groundwater. However, the characteristic NpO\(_2\)\(^{+}\) band at 980 nm was broadened and consisted of two peaks with maxima at 980 nm and 990 nm as shown in Figure 9b. Sevost'yanova and Khalturin have observed the same combination of absorption bands in a spectrophotometric study on the hydrolytic behavior of neptunium(V), and they assigned the peak at 990 nm to hydrolyzed Np(V).\(^{40}\) The first hydrolysis constant is quoted in the literature as \(\log Q = -8.85\).\(^{37}\) From this number one can calculate that the amount of NpO\(_2\)\(^{+}\) in our solution is less than 2% of the total amount of soluble NpO\(_2\)\(^{+}\). It seems unlikely that this small amount would produce a signal of the magnitude as observed in the spectrum. We have determined in a previous investigation on the carbonate complexation of NpO\(_2\)\(^{+}\) that the 990 nm peak is due to carbonate complexation and not to hydrolysis.\(^{41}\) From this fact the spectrum indicates that approximately 68% of the NpO\(_2\)\(^{+}\) is complexes by carbonate. The question remains open as
to why one Np<sup>2+</sup>-supernate solution underwent carbonate complexation whereas the other one did not.

3.3 Plutonium

The results of solubility measurements at pH 7.0 ± 0.1 and 25 ± 1°C as a function of equilibration time are shown in Figure 10.

In the 0.1 M NaClO<sub>4</sub> solutions the solubility concentrations at steady state were calculated as listed below for Pu given in the initial oxidation state:

1. +4, 10<sup>-7.68 ± 0.22</sup> M ((3 ± 2) x 10<sup>-8</sup> M) using all data points;
2. +5, 10<sup>-8.66 ± 0.17</sup> M ((2 ± 1) x 10<sup>-9</sup> M) using all data points;
3. +6, 10<sup>-7.01 ± 0.18</sup> M ((1.0 ± 0.5) x 10<sup>-7</sup> M) using all data points.

All three solutions formed a light green precipitate which was subjected to X-ray analysis. The solids of the Pu<sup>4+</sup> and the PuO<sub>2</sub><sup>2+</sup> solution were amorphous since they did not produce a powder pattern. The solid phase of the PuO<sub>2</sub><sup>+</sup> solution yielded a pattern which could not be identified since there is very little literature reference data available; the d-spacings and relative intensities are listed in Table 8.

The supernatants were analyzed by the coprecipitation/extraction method described in section 2.3.2 to determine the oxidation state distribution of solution species. The results of this analysis are listed in Table 9. The speciation can be summarized as follows:
(a) initially \( \text{Pu}^{4+} \):
\[
\begin{align*}
\text{Pu}^{3+} + \text{Pu}^{4+} + \text{Pu(IV) polymer} & = 3 \pm 2 \% \\
\text{PuO}_2^+ + \text{PuO}_2^{2+} & = 95 \pm 4 \% \\
\text{PuO}_2^+ & = 68 \pm 9 \%
\end{align*}
\]

(b) initially \( \text{PuO}_2^+ \):
\[
\begin{align*}
\text{Pu}^{3+} + \text{Pu}^{4+} + \text{Pu(IV) polymer} & = 5 \pm 4 \% \\
\text{PuO}_2^+ + \text{PuO}_2^{2+} & = 95 \pm 4 \% \\
\text{PuO}_2^+ & = 70 \pm 17 \%
\end{align*}
\]

(c) initially \( \text{PuO}_2^{2+} \):
\[
\begin{align*}
\text{Pu}^{3+} + \text{Pu}^{4+} + \text{Pu(IV) polymer} & = 3 \pm 2 \% \\
\text{PuO}_2^+ + \text{PuO}_2^{2+} & = 97 \pm 2 \% \\
\text{PuO}_2^+ & = 82 \pm 16 \%
\end{align*}
\]

Although the plutonium was present in different oxidation states in each solution, \( \text{PuO}_2^+ \) is the dominant species at steady state in the solution phase. At this time we do not fully understand the reactions that cause this change. This interesting effect should be the subject of further investigation.

The spread in solubility for the plutonium solution appears at first rather puzzling, since the final solution compositions are similar. One possible reason for the solubility spread may be found in the nature of the precipitating solids. If these ions precipitated as \( \text{PuO}_2\text{OH} \) and \( \text{PuO}_2(\text{OH})_2 \), respectively, their solubility values would be about the same order of magnitude as the values for the analogous Np-hydroxides.
Presumably the solids in all three Pu-solutions are Pu(IV)-hydroxides or hydrous oxides. This is supported by a) identically green physical appearance of the precipitates and b) by the low solubility values for the initially PuO$_2^+$ and PuO$_2^{2+}$ solutions. The literature shows the solubility at pH 7 for crystalline Pu(IV) oxide of 10$^{-8}$ M and for amorphous hydrous Pu(IV) oxide of 10$^{-6.5}$ M. The solubility seems to depend not only on whether the material is amorphous or crystalline, but also on the properties of the amorphous state, i.e. the transition from amorphous Pu(OH)$_4$ to amorphous PuO$_2$·H$_2$O which would gradually display differences in solubility.

The results of the solubility experiments in J-13 groundwater at pH 7 and 25°C are also shown in Figure 10. The solubility concentrations at steady oxidation state were calculated as listed below for Pu in the given initial oxidation state:

1. $^{+4}, 10^{-5.78 \pm 0.03}$ M $(1.6 \pm 0.2) \times 10^{-6}$ M from the last 6 data points;
2. $^{+5}, 10^{-5.08 \pm 0.10}$ M $(8 \pm 3) \times 10^{-6}$ M from the last 3 data points;
3. $^{+6}, 10^{-4.47 \pm 0.17}$ M $(3 \pm 2) \times 10^{-5}$ M from the last 3 data points.

The precipitates were:

1. dark brown-green colored and amorphous for the Pu$^{4+}$-solution;
2. dark mustard colored and crystalline for the PuO$_2^+$-solution;
3. chalky yellow colored and crystalline for the PuO$_2^{2+}$-solution.

Table 10 lists the X-ray diffraction data on the latter two solids. Both patterns could not be identified since no comparable data was found in the literature.
Apparently the solubility spread for the three plutonium solutions is related to the different composition of the solid phases.

Table 11 gives the results of the speciation experiment. They can be summarized as follows:

(a) initially \( Pu^{4+} \)

\[
\begin{align*}
Pu^{3+} + Pu^{4+} + Pu(IV) \text{ polymer} &= 2 \pm 3 \% \\
PuO_{2}^{+} + PuO_{2}^{2+} &= 98 \pm 3 \% \\
PuO_{2}^{+} &= 40 \pm 5 \%
\end{align*}
\]

(b) initially \( PuO_{2}^{+} \)

\[
\begin{align*}
Pu^{3+} + Pu^{4+} + Pu(IV) \text{ polymer} &= 0 \pm 2 \% \\
PuO_{2}^{+} + PuO_{2}^{2+} &= 100 \pm 2 \% \\
PuO_{2}^{+} &= 68 \pm 6 \%
\end{align*}
\]

(c) initially \( PuO_{2}^{2+} \)

\[
\begin{align*}
Pu^{3+} + Pu^{4+} + Pu(IV) \text{ polymer} &= 2 \pm 2 \% \\
PuO_{2}^{+} + PuO_{2}^{2+} &= 98 \pm 2 \% \\
PuO_{2}^{+} &= 67 \pm 6 \%
\end{align*}
\]

Similar to the conditions in perchlorate solutions, the major species present in groundwater are \( PuO_{2}^{+} \) and \( PuO_{2}^{2+} \). With the exception of the \( Pu^{4+} \) solution, where both species are distributed evenly, the \( PuO_{2}^{+}:PuO_{2}^{2+} \) ratio is approximately 2:1.

Recently Cleveland et al. studied plutonium speciation in J-13 groundwater.\(^{42}\) Either low-oxidation state (\( Pu^{3+} + Pu^{4+} \)) or high-oxidation state plutonium (\( PuO_{2}^{+} + PuO_{2}^{2+} \)) was added to the groundwater at 25°C. After 30 days of equilibration time the solution speciation was determined by \( PrF_{3} \) carrier precipitation and TTA extraction. For the
low-oxidation state solution the analysis indicated 45% Pu$^{3+}$, 18% Pu$^{4+}$, and 43% PuO$_2^+$ + PuO$_2^{2+}$ in the soluble phase. Our study showed that regardless of the initial oxidation state the only significant solution species present at steady state are PuO$_2^+$ and PuO$_2^{2+}$.

Geochemical modeling studies in J-13 groundwater have employed a Pu solubility of $1.8 \times 10^{-8}$ M in equilibrium with Pu(OH)$_4$ solid.$^{34}$ This number agrees with our experimental results for the solution which had Pu$^{4+}$ as the initial oxidation state added. However the runs in which PuO$_2^+$ or PuO$_2^{2+}$ was the starting species showed a solubility increase of roughly one order of magnitude. One possible reason for the difference in solubility may be found in the different solid phases.

Each solid in our experiments was different from each other and may not have consisted solely of Pu(OH)$_4$ as was assumed in the model. However, the solution speciation calculated from the model is in excellent agreement with our experimental results.$^{43}$ Kerrisk calculated the distribution to be 71% PuO$_2^+$, 26% PuO$_2^{2+}$ present as fluoride and carbonate complexes, and 3% Pu$^{4+}$ present as Pu(OH)$_5^-$. 
4.0 CONCLUSIONS

The goal of this study was to determine the solubility of Np, Pu and Am in J-13 groundwater from the prospective repository site at Yucca Mountain in Nevada and in 0.1 M NaClO₄ solution.

A comparison of the results for these two solutions should show if certain ions present in groundwater have an important influence on the actinide solubility, or if hydroxide formation is the principal solubility-controlling factor. From our experimental results we obtain the following conclusions:

1. The solubility of Np⁰²⁺ and Np⁰²⁺, respectively, was slightly enhanced in the groundwater compared to the non-complexing solution. Additional complexation by groundwater anions increased the solubility by only a factor of 2-3.

2. Regardless of the initial oxidation state (+5, or +6) in both solutions the soluble neptunium at steady state was always Np⁰⁺.

3. A neptunium solubility limit of 3 x 10⁻³ M in J-13 groundwater used for geochemical modeling represents a conservative and safe assumption. The experimentally determined number is actually slightly smaller.

4. The solubility of Am⁢³⁺ decreased by about two orders of magnitude as the solution was changed from perchlorate to the groundwater. Solubility was decreased by the formation of the more insoluble carbonate compounds of Am.

5. The Am⁢³⁺ did not undergo any change in oxidation state.

6. The geochemical data base uses a solubility of 1 x 10⁻⁸ M for Am in J-13 water. Our experimental value is larger by more
than two orders of magnitude. A solubility limiting value of at least $1.3 \times 10^{-6}$ M should be considered for modeling purposes.

7. The solubility of $\text{Pu}^{4+}$, $\text{PuO}^+$ and $\text{PuO}_2^{2+}$, respectively, was significantly enhanced in the groundwater compared to the perchlorate solution.

8. Regardless of the initial oxidation state (+4, +5, or +6) in both solutions, the soluble plutonium at steady state was converted nearly totally to $\text{PuO}_2^+$ and $\text{PuO}_2^{2+}$. The $\text{PuO}_2^+ : \text{PuO}_2^{2+}$ ratio was always 2:1 with the exception of initially $\text{Pu}^{4+}$ in J-13 water where equal amounts of both species were present at steady state.

9. The model data base uses a solubility limit for Pu of $1.8 \times 10^{-6}$ M. An upper limit of $5 \times 10^{-5}$ M was determined from this experiment in J-13 groundwater.

Due to the limited time during which the investigations for this report were performed, many problems had to remain unaddressed. A variety of questions have arisen during this work which should be addressed:

1. Does the radiation field from the actinide decay in both solution and solid affect the solubility? Is it possible to reach equilibrium conditions under conditions where continuous solvent radiolysis may trigger a series of redox reactions?

2. What reactions are taking place in the Pu system where, depending on the initial oxidation state, either oxidation
(Pu$^{4+}$ to PuO$_2^+$) or reduction (PuO$_{2}^{2+}$ to PuO$_2^+$) occurs in the same solvent?

3. Why is the initial NpO$_2^{2+}$ solution reduced to NpO$_2^+$? What is the reducing agent?

4. The remaining uncharacterized solids formed in our solutions need identification. One possible way to achieve this would be the synthesis of compounds of similar chemical composition that the uncharacterized solids are expected to have, and then by comparing their powder patterns identifying them. This, of course, is rather an iterative than a straight-forward procedure and is not applicable for amorphous materials.

Despite the above listed limitations, we conclude that important insights into the solubility and speciation of radioactive waste elements at a prospective disposal site can be obtained in laboratory experiments using the actual groundwater from the repository. The adequacy of an existing thermodynamic data base used for geochemical modeling can be validated by these results and a more realistic assessment of a specific repository site is feasible. Particular emphasis must be given to the correct speciation of soluble waste radionuclides in groundwater since it will have a major effect on the migration and release rates in the host rock. However within the region of one repository site the groundwater may differ in its chemical composition and redox properties, and this might affect the solubility and speciation.

It seems most important to have information available on all possible different scenarios to which the waste package might be subjected. All this information should be included in the data base
which is used to predict the migration of radionuclides from a nuclear waste disposal site.
5.0 ACKNOWLEDGEMENTS

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Appendix A. Analytical Results of Solutions in Equilibrium with their Solid Phase (Supersaturated Starting Conditions) in 0.1 M NaClO₄ and J-13 Groundwater at pH = 7.0 ± 0.1, 25 ± 1°C.

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<thead>
<tr>
<th>Initial No.</th>
<th>Species</th>
<th>Solubility (M)</th>
<th>Final Oxidation State of Soluble Species</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NaClO₄</td>
<td>J-13</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>NpO₂⁺</td>
<td>(4.4±0.1) x 10⁻⁴</td>
<td>(1.6±0.6) x 10⁻³</td>
<td>+V = 100%</td>
</tr>
<tr>
<td>2.</td>
<td>NpO₂²⁺</td>
<td>(3.5±0.1) x 10⁻⁴</td>
<td>(7.2±0.7) x 10⁻⁴</td>
<td>+V = 100%</td>
</tr>
<tr>
<td>3.</td>
<td>Am³⁺</td>
<td>(3.0±0.1) x 10⁻⁴</td>
<td>(1.1±0.2) x 10⁻⁶</td>
<td>+III = 100%</td>
</tr>
<tr>
<td>4.</td>
<td>Pu⁴⁺</td>
<td>(3±2) x 10⁻⁸</td>
<td>(1.6±0.2) x 10⁻⁶</td>
<td>III+IV+p = 3±2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V+VI = 95±4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V = 68±9%</td>
</tr>
<tr>
<td>5.</td>
<td>Pu₂⁺</td>
<td>(2±1) x 10⁻⁹</td>
<td>(8±3) x 10⁻⁶</td>
<td>III+IV+p = 5±4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V+VI = 95±4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V = 70±17%</td>
</tr>
<tr>
<td>6.</td>
<td>Pu₂⁺²⁺</td>
<td>(1.0±0.5) x 10⁻⁷</td>
<td>(3±2) x 10⁻⁵</td>
<td>III+IV⁺p = 3±2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V⁺⁺ = 97±2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V = 82±16%</td>
</tr>
</tbody>
</table>

p = Pu(IV)polymer.
Table 1. Spectrochemical Analyses of Np, Pu, and Am Stock Solutions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Np</th>
<th>Pu</th>
<th>Am</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>&lt;0.5</td>
<td>&lt;0.03</td>
<td>0.1</td>
</tr>
<tr>
<td>Am</td>
<td>-</td>
<td>&lt;0.5</td>
<td>100</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt;0.05</td>
<td>&lt;0.16</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt;0.1</td>
<td>0.03</td>
<td>0.2</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>-</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Dy</td>
<td>-</td>
<td>&lt;0.03</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>La</td>
<td>-</td>
<td>&lt;0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Mg</td>
<td>0.03</td>
<td>&lt;0.03</td>
<td>0.2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Na</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.01</td>
<td>&lt;0.15</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>&lt;1</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>U</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.1</td>
<td>&lt;0.3</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Zr</td>
<td>-</td>
<td>&lt;0.03</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>

Numbers represent weight percent.
Table 2. Well J-13 Water Composition.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (mM)</th>
<th>mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.29</td>
<td>12</td>
</tr>
<tr>
<td>Mg</td>
<td>0.072</td>
<td>1.7</td>
</tr>
<tr>
<td>Na</td>
<td>1.96</td>
<td>3.8</td>
</tr>
<tr>
<td>K</td>
<td>0.136</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.00002</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.0010</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>F⁻</td>
<td>0.11</td>
<td>641</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.18</td>
<td>17</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Alkalinity</td>
<td>2.34 mequiv/l</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Eh</td>
<td>700 mV</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Methods to Study Plutonium Solution Speciation.

<table>
<thead>
<tr>
<th>Method</th>
<th>Oxidation State Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Organic Phase</td>
</tr>
<tr>
<td>TTA-extraction at pH 0</td>
<td>IV</td>
</tr>
<tr>
<td>TTA-extraction at pH 4</td>
<td>III and IV</td>
</tr>
<tr>
<td>Hexone-extraction</td>
<td>IV and VI</td>
</tr>
<tr>
<td>LaF$_3$-precipitation method with holding-oxidant</td>
<td>III, IV, polymer in precipitate</td>
</tr>
</tbody>
</table>
Table 4. Results in Percent of Oxidation State Distribution Determination on $^{242}\text{Pu}$-Oxidation State Mixtures at 25 ± 1°C, Ar-Atmosphere. The superscripts a, b, c refer to various solution fractions. The nomenclature b-a means solution b minus solution a, etc.

<table>
<thead>
<tr>
<th>Method</th>
<th>TTA, pH 0</th>
<th>TTA, pH 4</th>
<th>Hexone</th>
<th>LaF$_3$</th>
<th>Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>IV$^a$</td>
<td>49±3</td>
<td>56±6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III,IV,VI,p</td>
<td>51±3</td>
<td>44±6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III,IV$^b$</td>
<td></td>
<td>(88±3)</td>
<td>(81±3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V,VI,p</td>
<td></td>
<td>(12±3)</td>
<td>(19±3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III$^b$-a</td>
<td></td>
<td>(39±4)</td>
<td>(25±7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV,VI$^c$</td>
<td></td>
<td></td>
<td>56±4</td>
<td>66±4</td>
<td>56±4</td>
</tr>
<tr>
<td>III,V,p</td>
<td></td>
<td></td>
<td>44±6</td>
<td>34±6</td>
<td></td>
</tr>
<tr>
<td>VI,c-a</td>
<td></td>
<td>7±5</td>
<td>10±7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V,VI$^d$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III,IV,p$^e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V$^d$-c-a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III,p$^e$-a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III,V</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

III,IV,VI = Pu oxidation states.
p = Pu(IV)polymer
Table 5. Comparison of X-ray Powder Diffraction Pattern of Am Solid Phase in J-13 Groundwater with Patterns Reported in the Literature.

<table>
<thead>
<tr>
<th>Am Solid Phase</th>
<th>NdOHCO$_3$</th>
<th>$\text{Nd}_2\text{(CO}_3\text{)}_3\cdot2\text{H}_2\text{O}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>d(A) $^a$ I$^b$</td>
<td>d(A) I$^a$</td>
<td>d(A) I$^a$</td>
<td></td>
</tr>
<tr>
<td>3.03 s</td>
<td>7.56 m</td>
<td>5.68 s</td>
<td></td>
</tr>
<tr>
<td>4.28 100</td>
<td>4.67 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.24 15</td>
<td>3.93 s</td>
<td>3.83 w</td>
<td></td>
</tr>
<tr>
<td>3.68 35</td>
<td>3.09 s</td>
<td>3.02 s</td>
<td></td>
</tr>
<tr>
<td>3.65 25</td>
<td>2.98 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.32 35</td>
<td>2.94 25</td>
<td>2.91 50</td>
<td></td>
</tr>
<tr>
<td>2.87 w</td>
<td>2.63 30</td>
<td>2.75 w</td>
<td></td>
</tr>
<tr>
<td>2.49 w</td>
<td>2.48 25</td>
<td>2.58 s</td>
<td></td>
</tr>
<tr>
<td>2.40 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.32 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.31 18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.27 w</td>
<td>2.25 w</td>
<td>2.17 w</td>
<td></td>
</tr>
<tr>
<td>2.09 w</td>
<td>2.05 40</td>
<td>2.08 w</td>
<td></td>
</tr>
<tr>
<td>2.03 13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.98 40</td>
<td>2.02 m</td>
<td>1.98 w</td>
<td></td>
</tr>
<tr>
<td>1.93 25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.91 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.87 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.83 19</td>
<td>1.87 m</td>
<td>1.83 m</td>
<td></td>
</tr>
<tr>
<td>1.80 10</td>
<td>1.78 m</td>
<td>1.74 w</td>
<td></td>
</tr>
<tr>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.60 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.43 m</td>
<td>1.56 m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Relative intensities visually estimated. s=strong, m=medium, w=weak.

$^b$Relative intensities by diffractometer in percent.
Table 6. X-ray Powder Diffraction Pattern of Np Solid Phase Formed by Addition of NpO$_2^{2+}$ to 0.1 M NaClO$_4$.

<table>
<thead>
<tr>
<th>d(A)</th>
<th>I$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.62</td>
<td>w</td>
</tr>
<tr>
<td>8.63</td>
<td>w</td>
</tr>
<tr>
<td>5.93</td>
<td>s</td>
</tr>
<tr>
<td>4.88</td>
<td>w</td>
</tr>
<tr>
<td>3.53</td>
<td>m</td>
</tr>
<tr>
<td>3.33</td>
<td>m</td>
</tr>
<tr>
<td>2.92</td>
<td>w</td>
</tr>
<tr>
<td>2.57</td>
<td>w</td>
</tr>
<tr>
<td>2.02</td>
<td>w</td>
</tr>
</tbody>
</table>

$^a$Relative intensities visually estimated. s=strong, m=medium, w=weak.

<table>
<thead>
<tr>
<th>Np Solid Phase (NpO(_2^2^+))</th>
<th>Np Solid Phase (NpO(_2^+))</th>
<th>Na(_3^)NpO(_2^+(CO_3)_2) (\times) H(_2^)O(_3^)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(A)</td>
<td>I(^a)</td>
<td>d(A)</td>
</tr>
<tr>
<td>7.58 m</td>
<td></td>
<td>6.07 21</td>
</tr>
<tr>
<td>4.79 s</td>
<td>5.08 w</td>
<td></td>
</tr>
<tr>
<td>4.34 s</td>
<td>4.40 m</td>
<td>4.39 100</td>
</tr>
<tr>
<td>4.07 w</td>
<td>4.23 m</td>
<td>4.29 5</td>
</tr>
<tr>
<td>3.75 w</td>
<td>3.81 m</td>
<td>4.34 s</td>
</tr>
<tr>
<td>3.11</td>
<td></td>
<td>3.32 m</td>
</tr>
<tr>
<td>2.86 s</td>
<td></td>
<td>2.80 6</td>
</tr>
<tr>
<td>2.62 m</td>
<td>2.54 s</td>
<td>2.53 50</td>
</tr>
<tr>
<td>2.17 w</td>
<td>2.27 w</td>
<td>2.27 38</td>
</tr>
<tr>
<td>2.09 w</td>
<td>2.02 w</td>
<td>2.09 38</td>
</tr>
<tr>
<td>1.99 s</td>
<td>1.97 5</td>
<td>1.94 7</td>
</tr>
<tr>
<td>1.92 w</td>
<td>1.90 7</td>
<td></td>
</tr>
<tr>
<td>1.73 m</td>
<td>1.79 w</td>
<td></td>
</tr>
<tr>
<td>1.61 w</td>
<td>1.65 w</td>
<td></td>
</tr>
<tr>
<td>1.27 w</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Relative intensities visually estimated. s=strong, m=medium, w=weak.

\(^b\)Relative intensities by diffractometer in percent.
Table 8. X-ray Powder Diffraction Pattern of Pu Solid Phase in 0.1 M NaClO₄ Solution. The Initial Pu-Oxidation State at Addition was +5.

<table>
<thead>
<tr>
<th>Pu Solid Phase</th>
<th>d(A)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.26</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>1.95</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td>w</td>
</tr>
<tr>
<td></td>
<td>1.18</td>
<td>w</td>
</tr>
</tbody>
</table>

\(^{a}\)Relative intensities visually estimated. s=strong, m=medium, w=weak.
Table 9. Results in Percent of Oxidation State Distribution Determination on $^{238-242}$Pu/0.1 M NaClO$_4$ Solution at 25 ± 1°C After Reaching Steady State Conditions.

<table>
<thead>
<tr>
<th>Method</th>
<th>TTA, pH 0</th>
<th>TTA, pH 4</th>
<th>Hexone</th>
<th>LaF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation States</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pu$^{4+}$</td>
<td>IV</td>
<td>III, V, VI, p</td>
<td>III, IV</td>
<td>V, VI</td>
</tr>
<tr>
<td>PuO$_2$</td>
<td>1±2</td>
<td>99±2</td>
<td>2±1</td>
<td>98±1</td>
</tr>
<tr>
<td>PuO$_2$$^{2+}$</td>
<td>2±2</td>
<td>98±2</td>
<td>2±1</td>
<td>98±1</td>
</tr>
<tr>
<td>PuO$_2$$^{3+}$</td>
<td>1±2</td>
<td>99±2</td>
<td>1±1</td>
<td>99±1</td>
</tr>
</tbody>
</table>

$^{a}$Oxidation state at addition. p = Pu(IV) polymer.

<table>
<thead>
<tr>
<th>Pu Solid Phase&lt;sup&gt;a&lt;/sup&gt;</th>
<th></th>
<th>Pu Solid Phase&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(A)</td>
<td>I&lt;sup&gt;c&lt;/sup&gt;</td>
<td>d(A)</td>
</tr>
<tr>
<td>2.92</td>
<td>s</td>
<td>2.81</td>
</tr>
<tr>
<td>2.85</td>
<td>s</td>
<td>2.68</td>
</tr>
<tr>
<td>2.79</td>
<td>s</td>
<td>2.08</td>
</tr>
<tr>
<td>2.47</td>
<td>m</td>
<td>2.02</td>
</tr>
<tr>
<td>2.09</td>
<td>s</td>
<td>1.99</td>
</tr>
<tr>
<td>2.06</td>
<td>s</td>
<td>1.75</td>
</tr>
<tr>
<td>1.81</td>
<td>m</td>
<td>1.65</td>
</tr>
<tr>
<td>1.75</td>
<td>m</td>
<td>1.49</td>
</tr>
<tr>
<td>1.65</td>
<td>w</td>
<td>1.45</td>
</tr>
<tr>
<td>1.28</td>
<td>w</td>
<td></td>
</tr>
</tbody>
</table>

Initial oxidation state at addition was (a) +5, (b) +6.

<sup>c</sup>Relative intensities visually estimated. s=strong, m=medium, w=weak.
Table 11. Results in Percent of Oxidation State Distribution Determination on $^{238-242}$Pu/J-13 Groundwater Solutions at 25 ± 1°C After Reaching Steady State Conditions.

<table>
<thead>
<tr>
<th>Method Oxidation States</th>
<th>TTA, pH 0</th>
<th>TTA, pH 4</th>
<th>Hexone</th>
<th>LaF$_3$</th>
<th>III,IV,p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu$_{4+}$</td>
<td>IV</td>
<td>III,IV</td>
<td>IV,VI</td>
<td>V,VI</td>
<td>III,IV,p</td>
</tr>
<tr>
<td>PuO$_2$</td>
<td>0±3</td>
<td>100±3</td>
<td>0±4</td>
<td>100±4</td>
<td>58±4</td>
</tr>
<tr>
<td>PuO$_{2+}$</td>
<td>0±3</td>
<td>100±3</td>
<td>2±5</td>
<td>98±5</td>
<td>32±5</td>
</tr>
</tbody>
</table>

$^a$ Oxidation state at addition.
p=Pu(IV)polymer.
Figure 1. Absorption spectra of Pu(IV) polymer, $1.02 \times 10^{-3} \text{ M}$, pathlength 10 mm, reference solution 0.05 M HCl.
Figure 2. Absorption spectra of Pu(IV) polymer, pathlength 10mm, reference solution 0.05 M HCl.
Figure 3. Solution concentrations of $^{243}$Am in contact with precipitate obtained from supersaturation at pH 7.0 ± 0.1 and 25 ± 1°C as a function of time. Open symbols are for 0.1 M NaClO$_4$ solution; filled symbols are for J-13 groundwater. The $^{243}$Am was at initial addition $^{243}$Am$^{3+}$. 
Figure 3
Figure 4. Absorption spectrum of $^{243}$Am in 0.1 M NaClO$_4$ after reaching steady state solubility conditions at pH 7.0 ± 0.1 and 25 ± 1°C. $A = 0.087$, $\varepsilon = 290$ M$^{-1}$cm$^{-1}$, $[\text{Am}^{3+}] = 3.0 \times 10^{-4}$ M, pathlength 10 mm.
Figure 4
Solution concentrations of $^{237}\text{Np}$ in contact with precipitate obtained from supersaturation at pH 7.0 ± 0.1 and 25 ± 1°C as a function of time. Open symbols are for 0.1 M NaClO$_4$ solution; filled symbols are for J-13 groundwater. Initial oxidation state at addition is depicted by squares for $^{237}\text{NpO}_2^+$ and by triangles for $^{237}\text{NpO}_2^{2+}$. 
Figure 5
Figure 6. Absorption spectrum of $^{237}$Np in 0.1 M NaClO$_4$ after reaching steady state solubility conditions at pH 7.0 ± 0.1 and 25 ± 1°C. Initial oxidation state at addition was NpO$_2^+$. $A = 0.1774$, $\varepsilon = 395$ M$^{-1}$cm$^{-1}$, $[\text{NpO}_2^+] = 4.5 \times 10^{-4}$ M, pathlength 10 mm.
Figure 7. Absorption spectrum of $^{237}\text{Np}$ in 0.1 M NaClO$_4$ after reaching steady state solubility conditions at pH 7.0 ± 0.1 and 25 ± 1°C. Initial oxidation state at addition was $\text{NpO}_2^{2+}$. $A = 0.1374$, $\varepsilon = 395$ M$^{-1}$ cm$^{-1}$, $[\text{NpO}_2^+] = 3.5 \times 10^{-4}$ M, pathlength 10 mm.
Figures 8a and 8b. Absorption spectrum of $^{237}$Np in J-13 groundwater after reaching steady state solubility conditions at pH 7.0 ± 0.1 and 25 ± 1°C. Initial oxidation state at addition was NpO$_2^+$. $A_{980\text{ nm}} = 0.503$, $\varepsilon = 395\text{ M}^{-1}\text{cm}^{-1}$, $[\text{NpO}_2^+] = 1.27 \times 10^{-3}\text{ M}$, pathlength 10 mm.
Figures 9a and 9b. Absorption spectrum of $^{237}$Np in J-13 groundwater after reaching steady state solubility conditions at pH 7.0 ± 0.1 and 25 ± 1°C. Initial oxidation state at addition was NpO$_2^+$. $A_{980 \text{ nm}} = 0.0895$, $\varepsilon = 395 \text{ M}^{-1} \text{ cm}^{-1}$, $[\text{NpO}_2^+] = 2.27 \times 10^{-4} \text{ M}$, pathlength 10 mm.
Figure 10. Solution concentrations of $^{238-242}$Pu in contact with precipitate obtained from supersaturation at pH 7.0 ± 0.1 and 25 ± 1°C as a function of equilibration time. Open symbols are for 0.1 M NaClO$_4$ solution; filled symbols are for J-13 groundwater. The Pu oxidation state at initial addition is depicted by diamonds for Pu$^{4+}$, by squares for PuO$_2^{+}$ and by triangles for PuO$_2^{2+}$. 
Figure 10
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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