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*Solubility and Speciation Results from  
Oversaturation Experiments on Neptunium,  
Plutonium, and Americium in a Neutral  
Electrolyte with a Total Carbonate Similar to  
Water from Yucca Mountain Region  
Well UE-25p #1*

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*Solubility and Speciation Results from Oversaturation  
Experiments on Neptunium, Plutonium, and Americium in a  
Neutral Electrolyte with a Total Carbonate Similar to Water  
from Yucca Mountain Region Well UE-25p #1*

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**SOLUBILITY AND SPECIATION RESULTS FROM OVERSATURATION  
EXPERIMENTS ON NEPTUNIUM, PLUTONIUM, AND AMERICIUM  
IN A NEUTRAL ELECTROLYTE  
WITH A TOTAL CARBONATE SIMILAR TO  
WATER FROM YUCCA MOUNTAIN REGION WELL UE-25P #1**

by

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**ABSTRACT**

Solubility and speciation 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 a part of predictive transport models. Theoretically, solubility experiments will approach solution equilibrium from both oversaturation and undersaturation. In these experiments we have approached the solubility equilibrium from oversaturation. Results are given for solubility and speciation experiments from oversaturation of  $^{237}\text{NpO}_2$ ,  $^{239}\text{Pu}^{4+}$ , and  $^{241}\text{Am}^{3+}/\text{Nd}^{3+}$  in a neutral electrolyte (0.18 M  $\text{NaClO}_4$ ) containing a total carbonate concentration similar to UE-25p #1 groundwater (from the Yucca Mountain region, Nevada, which is being investigated as a potential high-level nuclear waste disposal site) at 25°C and three pH values (6, 7, and 8.5). In these experiments, the solubility-controlling steady-state solids were identified and the speciation and/or oxidation states present in the supernatant solutions were determined. The neptunium solubility decreased with increasing pH in the neutral electrolyte. The soluble neptunium remained in the pentavalent state with varying degrees of carbonate complexation at each pH value. Plutonium concentrations in the neutral electrolyte were all within an order of magnitude of each other, with the pH 8.5 solution concentration being slightly higher than those of the pH 6 and pH 7 solutions. Oxidation state analyses of the plutonium supernatants indicated oxidation from the +4 state to the +5 and +6 states. For the americium/neodymium solutions, solubility decreased significantly with increasing pH. Oxidation state analyses of the pH 6 and 7 americium/neodymium supernatants were performed and the possibility of radiolytic oxidation is discussed.



## **PREFACE**

This is the fourth in a series of reports documenting experimental solubility and speciation studies of radionuclides in groundwaters from or relevant to the Yucca Mountain region. The objectives and experimental concepts were discussed in detail in the first report of this series (Milestone 3010), titled "Measured Solubilities and Speciations of Neptunium, Plutonium, and Americium in a Typical Groundwater from the Yucca Mountain Region".<sup>1</sup> Sections 2, 3, and 4 of this report are, except for minor changes, identical to the respective sections of the first report. They are, however included here to make this report a stand-alone document.





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## 1. EXECUTIVE SUMMARY

We studied the solubilities of neptunium, plutonium, and americium in a modified 0.18 M  $\text{NaClO}_4$  solution from oversaturation at 25°C and pH's 6, 7, and 8.5. Tables I, II, and III summarize the results for neptunium, plutonium, and americium, respectively. The nuclides were added to the neutral electrolyte from oversaturation at the beginning of each experiment as  $^{237}\text{NpO}_2^+$ ,  $^{239}\text{Pu}^{4+}$ , and  $\text{Nd}^{3+}$  with tracer  $^{241}\text{Am}^{3+}$  added to facilitate nuclear counting. Because we maintained constant pH values of 6, 7, and 8.5 during the course of the experiments by adjusting with acid and base, the final solutions were closer to 0.18 M in total ionic strength with the constituents being sodium and perchlorate. At the conclusion of these oversaturation experiments, the resulting solids were removed and characterized.

The neptunium solubility decreased with increasing pH in these experiments. The steady-state concentrations ranged from  $4 \times 10^{-3}$  M at pH 6 to  $1 \times 10^{-5}$  M at pH 8.5. The soluble neptunium did not change oxidation state at steady-state. The pentavalent neptunium was increasingly complexed by carbonate with increasing pH. The steady-state solids were crystalline monosodium neptunium carbonates with varying degrees of hydration.

The steady-state plutonium concentrations showed no trend with pH. The plutonium concentrations in the pH 6 and 7 solutions were virtually identical. The steady-state plutonium concentration in the pH 8.5 solution was slightly higher; however, all plutonium concentrations were within an order of magnitude of each other. The solubility in the three cells ranged from  $5 \times 10^{-8}$  M to  $4 \times 10^{-7}$  M. The dominant oxidation state in the plutonium supernatants were Pu(V) and Pu(VI), with increasing amounts of Pu(VI) with increasing pH. The species responsible for this oxidation are unknown. The solubility-controlling solids from the pH 6 and 7 solutions were crystalline but remain unidentified. The solid produced in the pH 8.5 solution is amorphous Pu(IV) polymer.

For the americium/neodymium solutions, the solubility decreased significantly with increasing pH. The steady-state americium/neodymium concentrations ranged from  $6 \times 10^{-6}$  M at pH 6 to  $3 \times 10^{-10}$  M at pH 8.5. The solids produced in the americium/neodymium solubility experiments in 0.18 M  $\text{NaClO}_4$  at pH 6 and 8.5 were amorphous mixtures of orthorhombic  $\text{NdOHCO}_3$  and  $\text{Nd}_2(\text{CO}_3)_3 \cdot 2 \text{H}_2\text{O}$ .

Table I. Summary of results for solubility experiments of neptunium in 0.18 M NaClO<sub>4</sub> from oversaturation at pH 6, 7, and 8.5 and 25°C.

	Steady State Concentration (M)	Oxidation State in Supernatant Solution (%)
pH 6	$(3.78 \pm 0.10) \times 10^{-3}$	V: 100% 3 % carbonate complex
pH 7	$(1.92 \pm 0.21) \times 10^{-4}$	V: 100% 24 % carbonate complex
pH 8.5	$(1.47 \pm 0.19) \times 10^{-5}$	V: 100% 77 % carbonate complex

	Eh (mV) vs. NHE	Solid Phase
pH 6	$(455 \pm 15)$	NaNpO <sub>2</sub> CO <sub>3</sub> · nH <sub>2</sub> O
pH 7	$(431 \pm 15)$	NaNpO <sub>2</sub> CO <sub>3</sub> · nH <sub>2</sub> O
pH 8.5	$(324 \pm 15)$	NaNpO <sub>2</sub> CO <sub>3</sub> · nH <sub>2</sub> O



Table II. Summary of results for solubility experiments of plutonium in 0.18 M NaClO<sub>4</sub> from oversaturation at pH 6, 7, and 8.5 and 25°C.

	Steady State Concentration (M)	Oxidation State in Supernatant Solution (%)
pH 6	$(4.84 \pm 0.49) \times 10^{-8}$	III + Poly : $(2.6 \pm 0.3) \%$ IV : $(6.5 \pm 0.7) \%$ V : $(70.1 \pm 8.4) \%$ VI : $(20.8 \pm 2.3) \%$
pH 7	$(5.30 \pm 1.04) \times 10^{-8}$	III + Poly : $(1.3 \pm 0.3) \%$ IV : $(14.3 \pm 1.2) \%$ V : $(42.1 \pm 8.9) \%$ VI : $(42.3 \pm 4.2) \%$
pH 8.5	$(3.91 \pm 0.76) \times 10^{-7}$	III + Poly : $(4.4 \pm 1.0) \%$ IV : $(8.9 \pm 0.6) \%$ V : $(32.7 \pm 6.6) \%$ VI : $(54.0 \pm 4.6) \%$

	Eh (mV) vs. NHE	Solid Phase
pH 6	$(230 \pm 15)$	Crystalline (unidentified)
pH 7	$(175 \pm 15)$	Crystalline (unidentified)
pH 8.5	$(121 \pm 15)$	Amorphous Pu(IV) polymer

Table III. Summary of results for solubility experiments of americium/neodymium in 0.18 M NaClO<sub>4</sub> from oversaturation at pH 6, 7, and 8.5 and 25°C.

	Steady State Concentration (M)	Oxidation State in Supernatant Solution (%)
pH 6	$(6.00 \pm 4.23) \times 10^{-6}$	III : $(90.8 \pm 3.6) \%$ V : $(9.2 \pm 0.5) \%$
pH 7	$(3.04 \pm 1.44) \times 10^{-7}$	III + Poly : $(80.5 \pm 3.1) \%$ V : $(19.4 \pm 0.8) \%$
pH 8.5	$(2.99 \pm 1.68) \times 10^{-10}$	Not Available

	Eh (mV) vs. NHE	Solid Phase
pH 6	$(298 \pm 15)$	$(\text{Am})_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ and orthorhombic AmOHCO <sub>3</sub>
pH 7	$(217 \pm 15)$	$(\text{Am})_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ and orthorhombic AmOHCO <sub>3</sub>
pH 8.5	$(253 \pm 15)$	$(\text{Am})_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ and orthorhombic AmOHCO <sub>3</sub>

## 2. PURPOSE AND OBJECTIVE

Yucca Mountain, Nevada, was identified for site characterization as the location for a potential repository of high-level nuclear waste. As a worst case scenario, intrusion of water into the potential repository must be considered for risk assessment. Water moving through the emplacement area towards the accessible environment can transport radionuclides in two ways: either as dissolved species in the water or as particulate material by the water. The Yucca Mountain Site Characterization Plan (SCP) requires "Studies to Provide the Information Required on Radionuclide Retardation by Precipitation Processes along Flow Paths to the Accessible Environment" before licensing and construction of the potential repository.<sup>2</sup> The purpose of this study is to supply data for calculating radionuclide transport along potential transport pathways from the potential repository to the accessible environment. Data derived from solubility studies are important for validating geochemical codes that are part of predictive radionuclide transport models. Such codes should be capable of predicting the results of solubility experiments, where the measured solubility is the sum of the equivalent concentrations of all of the species in equilibrium with a specified solid. 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 basic 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 below the solubility limit because only soluble species can be transported and participate in the sorption process.

In selecting these experiments, we have considered the generic U.S. Nuclear Regulatory Commission (NRC) technical position titled "Determination of Radionuclide Solubility in Groundwater for Assessment of High-Level Waste Isolation."<sup>3</sup> This technical position served as guidance for our experiments to determine radionuclide solubility. It requires that if radionuclide solubility is used as a factor in limiting radionuclide release, experiments must be designed to determine solubility under site-specific conditions.

Radionuclide concentrations in water passing through the emplacement area can be limited by two mechanisms: low dissolution rates of the solid waste form or solubilities of individual radionuclides. If solid waste dissolution rates are low enough, it may not be necessary to depend on solubilities to limit radionuclide concentrations. However, the solid waste forms have not yet been determined, and therefore the dissolution rates of the solid waste are unknown. Determination of radionuclide solubility limits provides an upper bound on radionuclide concentrations in solution and provides a basis for "extrapolation to long-term behavior." The rate of groundwater flow through the potential repository is expected to be

sufficiently slow to permit saturation of the water with radionuclides. Dissolution limited by saturation will provide maximum concentration limits. Therefore, an assessment of radionuclide release rates using a saturation-limited dissolution model represents the most conservative approach possible.

As radionuclides are transported along flow paths to the accessible environment, changing conditions of the water (pH, Eh, and concentrations of complexing species) can alter solubilities. Decreases in solubility can decrease radionuclide concentrations. A knowledge of radionuclide solubilities under the conditions along possible flow paths is necessary to assess this scenario. Solubility studies are very time-consuming because long times are often needed to reach equilibrium. Because we cannot investigate every possible solubility scenario, we selected pH and temperature values to bracket the expected range of conditions by choosing parameters that represent lower and upper limits.

Neptunium, plutonium, and americium are expected to be sparingly soluble with solubility-limited dissolution. Water samples with compositions that bracket the range of waters expected in the vicinity of Yucca Mountain were chosen for solubility measurements.<sup>4</sup> These samples come from two sources. Water from Well J-13 is a reference water for the unsaturated zone near the proposed emplacement area. Well UE-25p #1 taps the carbonate aquifer that underlies the emplacement horizon. This water has an ionic strength and total carbonate content higher by approximately one order of magnitude than that of Well J-13 water. UE-25p #1 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. In order to assess the role of carbonate in the natural ground waters, it is also necessary to conduct solubility experiments in a neutral electrolyte of similar ionic strength and carbonate concentration. Furthermore, solubility measurements in dilute sodium perchlorate electrolyte will provide data for a relatively simple system where only hydrolysis and carbonate complexation occur, and only carbonate, hydroxycarbonate, and/or hydroxide precipitates may form. We, therefore, chose to conduct these experiments in 0.1 M NaClO<sub>4</sub> with a carbonate concentration similar to that of UE-25p #1 groundwater. These experiments will provide conservative solubility results for a simple electrolyte system. In this study we are reporting on the results in 0.18 M NaClO<sub>4</sub> solutions from oversaturation.

The maximum temperature of the host rock in which liquid water is present is expected to be limited by the boiling point of water at Yucca Mountain (95°C). The solubility experiments that use Well J-13 water were conducted at temperatures between 25° and 90°C. This span covers the range from pre-emplacement temperatures to the maximum temperature at which solubility would be important. For Well UE-25p #1 water, solubility experiments were limited to a maximum temperature of 60°C. Maximum temperatures in the saturated zone under the emplacement area and those along the flow paths away from the emplacement area are expected to be less than 60°C.<sup>5</sup> The current solubility experiments in sodium perchlorate were done at 25°C, but higher temperatures may be investigated in future experiments.

### 3. CONCEPT OF SOLUBILITY STUDIES

Solubility establishes an upper limit for the dissolved components in the source term for radionuclide migration from a repository. Studies of the solubility of radionuclides in groundwaters from a repository horizon will provide limits on their potential concentrations in those waters. Such limits are important for (1) validating an essential part of the radionuclide transport calculations and (2) providing guidance in choosing the maximum starting concentrations for radionuclide sorption experiments. Compared with multi-parameter transport models, laboratory solubility experiments are controlled by fewer variables. If geochemical codes such as EQ3/6 are to be included in the transport model, the model should be capable of predicting the results of solubility experiments.

Complete solubility experiments should provide detailed knowledge of (1) the nature and chemical composition of the solubility-controlling solid, (2) the concentration of the components in solution, and (3) the identity and electrical charge of the species in the solution phase.

Meaningful thermodynamically defined solubility studies must satisfy four criteria: (1) attainment of equilibrium conditions; (2) determination of accurate solution concentrations; (3) attainment and identification of a well-defined solid phase; and (4) knowledge of the speciation/oxidation state of the soluble species at equilibrium.

#### 3.1. Oversaturation and Undersaturation

Ideally, solubility experiments should approach solution equilibrium from both oversaturation and undersaturation. The approach from oversaturation consists of adding an excess amount of the element in soluble form to the aqueous solution and then monitoring the precipitation of insoluble material until equilibrium is reached. The solid formed must then be isolated and characterized. The approach from undersaturation consists of dissolving the same well-defined solid in an aqueous solution until equilibrium is reached. In both cases, the solution concentration is measured as a function of time until equilibrium is reached.

Kinetic processes will control the equilibration speed in solubility experiments. Some solutions equilibrate rapidly, others more slowly. It must be demonstrated that equilibrium is reached. This can be accomplished by experimentally determining (for both oversaturation and undersaturation experiments) the solution concentration as a function of time. When the concentration stays constant for several weeks to several months, it is assumed that equilibrium has been established. Because this assumption is based on judgment, the term "steady-state" instead of "equilibrium" is more precise. The U.S. Nuclear Regulatory Commission (U.S. NRC) defines "steady-state," as "the conditions where measurable changes in concentrations are not occurring over practical experimental times."<sup>3</sup> At steady state, thermodynamic forces may still change the solution composition: solids may become less soluble as they change from a higher to a lower free energy. The change may be controlled by kinetics and may therefore be very slow and may not show in the experiment even after several years. These infinitesimal changes may require infinite experimental times. The steady-state solids formed in the experiments may therefore not represent the

thermodynamically most stable solids with the lowest possible solubilities, but metastable solids having higher solubilities than the thermodynamically defined solids. The term "steady-state" implies this metastable condition.

Despite this constraint, time-limited laboratory solubility experiments can supply valuable information. They provide good estimates on the upper limit of radionuclide concentrations in solution because the experimentally determined steady-state concentrations are higher than the equilibrium concentrations.

A reliable method of proving that an equilibrium has been reached is to approach steady state from both oversaturation and undersaturation. When these two experimental approaches independently produce equal solution concentrations, the data are considered reliable. For unknown solubility systems, one should first perform experiments approaching steady-state concentration from oversaturation and then characterize the solids. This has the advantage of not specifying the solid that controls solubility but of allowing the system under investigation to determine the solid that will precipitate. These solids can then be used in confirmation experiments that approach steady state from undersaturation. In this study we are reporting results for only oversaturation experiments.

### **3.2. Phase Separation**

The second criterion for meaningful solubility experiments is the determination of accurate solution concentrations. This requires that phase separations must be as complete as possible. The separation of the solid from the solution often represents a significant practical problem in measuring solubility. Apparently higher or lower solubilities, compared with the steady-state values, can result from incomplete phase separation or from sorption of solute during and after the separation. Incomplete phase separations (leaving some of the solid with the solution phase) lead to higher radionuclide solubilities. Lower solubilities are measured if constituents of the steady-state solution have been sorbed on filters during a filtration and on container walls after the separation.

Experimentally, the solids and solutions are separated on the basis of differences in size (via filtration) or density (via sedimentation or centrifugation). Filtration is the more commonly applied technique because it physically partitions the solute and solids. Ultrafiltration (i.e., filtration using membranes with pore sizes  $\leq 0.1 \mu\text{m}$ ) can effectively remove solids and colloidal particles from aqueous solutions. A potential problem with ultrafiltration is adsorption of soluble species on filtration membranes. Effective filters for solubility studies must pass soluble species quantitatively; that is, either the filter should have no active sorption sites at all, or any such sites should be irreversibly blocked. Filters are adequate if they have a small enough pore size to retain the solids and colloids and if they also show no sorption, or only minimal sorption, during multiple filtrations. Because adsorption of soluble radionuclide species on filters can be dependent on the solution's pH and on the solution species, it is mandatory to verify that possible sorption sites are indeed blocked. Usually the sorptive sites on a filter and filter housing are blocked by preconditioning of these materials. The filter is preconditioned by filtering a volume of the respective radionuclide solution through it and

then discarding the filtrate. The volume required for preconditioning is determined experimentally. Details for this procedure are given in Section 4.5, Phase Separation.

### 3.3. Solid Phase

Solubility depends strongly on the state of the solid phase. Thermodynamically meaningful results require the existence of a well-defined solid phase, which ideally consists of crystalline material. The solids formed from the oversaturation in solubility tests must be clearly identified by physical or chemical characterization methods. Radionuclide solids formed in laboratory experiments and in nature are often thermodynamically ill-defined amorphous precipitates. Most amorphous solids, however, will become more crystalline with time. Freshly precipitated microcrystalline solids can also convert in time to a macrocrystalline material. Improved bonding at the lattice surface results in decreasing surface area. Thus the crystalline solid of higher free energy changes to one of lower free energy (Ostwald ripening, Ostwald step rule) and becomes less soluble.<sup>6-9</sup>

### 3.4. Determination of Oxidation States and Speciation

Information on oxidation states and speciation of the radionuclides in steady-state solubility solutions is important for transport models simulating migration and sorption along the flow path to the accessible environment. The charge and speciation of radionuclides will control their sorption and transportation in the geologic host. Speciation measurements identify complexes that may form between radionuclides and complexing ions present in the groundwater near the potential repository. Radionuclides, like all nuclides, can have a single or several different oxidation states in solution. They can be present as simple ions or as complexes. When the ions react with one or several other solution components, they can form soluble complexes.

Oxidation states and speciation in solution are commonly determined by (1) absorption spectrophotometry, (2) ion exchange chromatography, (3) solvent extraction, (4) coprecipitation, (5) potentiometry and (6) electrochemistry. Of these methods, only absorption spectrophotometry can provide information on speciation, while the others identify only the oxidation state in solution.

Absorption spectrophotometry for neptunium, plutonium, and americium in dilute sodium perchlorate has a detection limit of about  $10^{-5}$  M. This relatively high concentration level limits the application of spectrophotometry for speciation determination in solutions from radionuclide solubility studies because the solubilities can be several orders of magnitude below  $10^{-6}$  M. Laser-Induced Photoacoustic Spectroscopy (LIPAS) provides much greater sensitivity, approaching  $10^{-8}$  to  $10^{-9}$  M.<sup>10-15</sup>

The methods listed above as 2 through 6 determine only the oxidation state in solution because they cannot determine species. They detect the oxidation state of ions indirectly. This process is different from absorption spectrophotometry, which detects oxidation states and sometimes the solution species directly. The indirect methods, however, detect very small concentrations (down to  $10^{-10}$  M), which is useful for radionuclide solubility studies. Solvent

extraction and coprecipitation are often used successfully to determine the oxidation states of ions in very dilute solutions.<sup>16</sup> Ion exchange chromatography is less reliable for this purpose because the exchange resin often reduces the solution ions, which gives incorrect results for the oxidation state distribution. Electrochemical detection reduces or oxidizes the solution ions and measures the potentials of the reduction and oxidation reactions, respectively. The potential then is used to identify the individual ion. Electrochemistry needs fast kinetics and reversible thermodynamics for the reduction or oxidation step. These experiments greatly limit the use/usefulness of the method because many radionuclide ion redox reactions are irreversible and slow (e.g., the reactions of  $\text{NpO}_2^+/\text{Np}^{4+}$ ,  $\text{PuO}_2^+/\text{Pu}^{4+}$ )<sup>17</sup>.

The neptunium solution species were determined by spectrophotometry because the solution concentrations were greater than  $10^{-5}$  M. The oxidation states of plutonium and americium species in solution were determined by a solvent extraction technique, which is described in principle by Nitsche et al.<sup>16</sup> and in detail in Section 5.2.2.

#### 4. EXPERIMENTAL DETAILS

We studied the solubilities of neptunium, plutonium, and americium from oversaturation in 0.18 M  $\text{NaClO}_4$  at 25°C and pH values of 6, 7, and 8.5. Measurements were made in an inert-atmosphere *glovebox* to avoid contamination of solutions by atmospheric  $\text{CO}_2$ . The solubilities were studied from oversaturation by injecting a small amount of actinide stock solution into 80 mL of 0.1 M  $\text{NaClO}_4$  equilibrated with a  $\text{CO}_2$  / Ar gas mixture to achieve a carbonate concentration similar to that of UE-25 p#1 groundwater. Details of this procedure are described in Section 4.3. Pressure Control System and 4.4. Solutions. The sodium perchlorate solution was prepared in an inert-atmosphere *glovebox* by dissolution of anhydrous  $\text{NaClO}_4$  (GFS Chemicals, ACS Reagent Grade, Lot #: P3) in distilled deionized water.

##### 4.1. Controlled-Atmosphere Glovebox

Due to the radiation hazard of the actinide elements under investigation, all experimental work was performed in *gloveboxes*. External  $\text{CO}_2$  control of the experimental solutions requires the exclusion of atmospheric  $\text{CO}_2$ . To satisfy both conditions, we used a controlled-atmosphere *glovebox*.

##### 4.2. Control System for pH and Temperature

Because the solubilities are highly sensitive to pH and temperature changes, close control of these parameters is necessary. Daily pH adjustments were performed and recorded manually. The temperature of 25°C was controlled to within less than 1°C.



### 4.3. Pressure Control System

We designed and manufactured a pressure regulation system to maintain a carbonate concentration equivalent to UE-25p #1 groundwater in the sodium perchlorate solutions when the pH values are adjusted to conditions differing from the natural state of UE-25p #1. The system also ensured that no significant evaporative loss of the solutions occurred.

### 4.4. Solutions

The actinide stock solutions were prepared by using established methods.<sup>18,237</sup> Np(V) stock solutions were prepared by dissolving its oxide in HCl. <sup>239</sup>Pu(IV) stock was prepared from plutonium metal. Stable neodymium(III) was used as an analog for americium(III).<sup>1</sup> It was prepared by dissolving Nd<sub>2</sub>O<sub>3</sub> in HClO<sub>4</sub>. The solution was then spiked with purified <sup>241</sup>Am(III) tracer to enable the use of nuclear counting for the determination of the neodymium solution concentrations. Further details for these <sup>241</sup>Am/Nd mixtures are given in Section 5.3. The actinide solutions were purified from possible metal contaminants by ion exchange chromatography. For neptunium and plutonium, anion exchange was used, while cation exchange was employed for americium<sup>19</sup>. The solutions were converted to a non-complexing perchlorate system. The neptunium and plutonium stock solutions were in the +6 oxidation state after their conversion to perchloric acid (2 to 3 M) and were reduced electrolytically to NpO<sub>2</sub><sup>+</sup> and Pu<sup>3+</sup>, respectively. Pu<sup>4+</sup> was prepared by electrolytic oxidation of pure Pu<sup>3+</sup> immediately before the start of the plutonium solubility experiments in order to minimize the disproportionation of Pu<sup>4+</sup>.<sup>18,20,21</sup> Valence purity of the stock solutions was established by absorption spectrophotometry.<sup>22,23</sup> Oxidation states other than Pu(IV) were not detected. With our absorption spectrophotometer (Guided Wave Model 260, El Dorado Hills, CA), the limits of detection for Pu(III), Pu(V), and Pu(VI) are approximately 10<sup>-4</sup>, 3 x 10<sup>-4</sup>, and 10<sup>-5</sup> M, respectively.

The actinide stock solutions, and all other solutions utilized in this experiment, were filtered through 0.22 μm polyvinylidene difluoride syringe filter units (Millipore Corp., Bedford, MA). Filtration was used to remove suspended particulate material, e.g., dust or silica, that could absorb the actinide ions to form pseudocolloids. For the oversaturation experiments, before adding between 1 and 4 mL of the actinide stock solutions was added to approximately 80 mL of the 0.1 M NaClO<sub>4</sub>, a small amount of CO<sub>2</sub>-free sodium hydroxide solution was added in order to keep the pH values at or above the desired solution pH. Letting the pH drop below the target value would necessitate addition of concentrated base to the system while the actinide ion is already present in the solution. Addition of strong base can result in unpredictable microprecipitation and formation of microcolloids.

The neptunium oversaturation experiments were started by adding small volumes of 5 M sodium hydroxide (CO<sub>2</sub>-free) to the dilute sodium perchlorate solutions. This was done in order to neutralize the perchloric acid that would be introduced with the stock solution. We added the acidic stock followed by 1 M HClO<sub>4</sub>, 1 M NaOH, or both if necessary, to attain the desired pH for the experiment. At pH 6, the added acid and base led to additional concentrations of Na<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> of 4.75 and 1 mM, respectively, resulting in an insignificant increase in the initial concentration of Na<sup>+</sup> and ionic strength of the sodium perchlorate

solution. At pH 7 and 8.5 similar additions were also made, neither of which significantly altered the ionic strength of the sodium perchlorate.

For the plutonium experiments, we also added 5 M NaOH to the sodium perchlorate solution before we introduced the acidic plutonium stock solution. The plutonium stock solution was  $5 \times 10^{-3}$  M in total plutonium and 1 M in  $\text{HClO}_4$ . For all three solutions, adjustments led to additional concentrations of  $\text{Na}^+$  and  $\text{ClO}_4^-$  of no greater than 1 and 4.9 mM, respectively. These additions did not significantly effect the initial  $\text{Na}^+$  and ionic strength of the sodium perchlorate solutions.

For the neodymium/ameridium experiments, we added small amounts of 5 M NaOH before we introduced the acidic Am/Nd stock solution. The Am/Nd stock solution was  $1.7 \times 10^{-2}$  M in total Am/Nd and 1 M in  $\text{HClO}_4$ . The initial acid and base adjustments to the three Am/Nd sodium resulted in additional concentrations of  $\text{Na}^+$  and  $\text{ClO}_4^-$  of no greater than 1 mM. This did not significantly alter the initial  $\text{Na}^+$  content and ionic strength of the sodium perchlorate solutions.

In summary, initial additions of sodium hydroxide and perchloric acid to the neptunium, plutonium and ameridium/neodymium solutions did not significantly alter the  $\text{Na}^+$  content or the ionic strength of the solutions. At the beginning of each of the experiments, the solutions were 0.1 M in  $\text{NaClO}_4$ .

The UE-25p #1 groundwater has total dissolved carbonate equal to  $1.531 \times 10^{-2}$  M. This concentration was induced in the sodium perchlorate solutions at each individual pH by equilibrating them with mixtures of  $\text{CO}_2$  in argon.<sup>4</sup> The amount of  $\text{CO}_2$  at a given pH and temperature was calculated from Henry's constant and the dissociation constants of carbonic acid from literature data.<sup>24</sup> If the value at the given temperature was not available, the number was derived by interpolation of adjacent values. Activity coefficients were adjusted for ionic strength using the Davies equation. The concentrations of the equilibration gas mixtures are given in Table IV together with the dissociation constants used to determine them.

The test solutions were kept in 90 mL cells that were made of polyether etherketone (PEEK).<sup>25</sup> All cells had sealed ports at the top that accommodate the emplacement of a pH electrode, an opening to draw samples, and a 1/16" port for the addition of the  $\text{CO}_2$ -argon gas mixture to the experimental cell via a Teflon gas line.

Table IV. Concentrations (in percent) of carbon dioxide gas in argon to maintain a total dissolved carbonate concentration of  $1.531 \times 10^{-2}$  M in 0.1 M NaClO<sub>4</sub> at different pH's together with the values for Henry's constant and the dissociation constants for carbonic acid used to determine the pCO<sub>2</sub> values.

	25°C		25°C
pH 6	26.08	pK <sub>H</sub>	1.47
pH 7	5.424	pK <sub>1</sub>	6.14
pH 8.5	0.1869	pK <sub>2</sub>	9.90

The temperature was controlled by placing the test cells in a heated aluminum block of LBNL design. The electric heater was mounted on an orbital shaker (Lab-Line Inc., Melrose Park, IL), and all solutions were shaken continuously at approximately 100 rpm. The solutions' pH values were monitored, adjusted (when necessary) and recorded manually. Combination pH electrodes from Broadley-James Corp., Model E-1393EC1-A03BC, were used to monitor the solutions pH values.

The combination pH electrodes from Broadley-James Corp. were used in the experiments because of their expectedly better long-term pH stability. These electrodes, however, went out of calibration quite often with deviations of up to 0.2 units. These deviations were the result of the electrode's going out of calibration, and not a result of the instability of the experimental equilibria. To avoid unnecessary pH adjustment in the experiments, we calibrated the electrodes often and only adjusted the solution's pH by hand after the calibration. The deterioration of the electrode is mainly due to the dissolution of the Ag/AgCl layer of the reference electrode wire and also of the wire used in the pH sensing compartment itself.

The effect on the composition of the 0.1 M NaClO<sub>4</sub> solution due to the addition of acid and/or base during the experiment is a rather complicated one. At the start of the oversaturation experiments, the ionic strengths of the solutions were unchanged with the introduction of the actinide stock solutions and the sodium hydroxide needed to neutralize the perchloric acid in the stock solutions. Therefore, the initial ionic strengths were 0.1 M. However, during the course of the solubility experiments, 1 M perchloric acid and/or sodium hydroxide were used to maintain the desired pH of the solubility experiments. Also during that time, we assayed the solutions for concentration and speciation determinations. The volumes of acid and base added to the experiments ranged from 2 to 5 mL; whereas, to perform all of the concentration and speciation determinations throughout the experiment, we removed ~30 to 50 mL of solution. In the worst case, the net effect on 80 mL of an initially 0.1 M solution of removing 50 mL for assays and then adding 5 mL of 1.0 M acid and/or base solutions to adjust the pH would result in increasing the ionic strength to approximately 0.22 M. This is/has a net effect of increasing the ionic strength by a factor of ~2. Therefore, the final ionic strength of these solutions may be closer to 0.2 M. The addition of acid and base, however, ran concurrently with the removal of solution volumes for assays, so it is rather difficult to establish exactly the true ionic strength of these solutions at the conclusion of the

experiments. Of course, for the solutions to which we added very little acid and/or base, the final ionic strengths will be close to their initial ionic strengths.

The addition of 1 M solutions of acid and base during the course of the experiments increased the ionic strength by no more than a factor of 2 in any of the solutions. With an approximate analysis based on final volumes, we can only say that the final ionic strengths in all of the solubility experiments were probably closer to  $0.18 \text{ M} \pm 50\%$ . This increase in the ionic strength of 0.1 M  $\text{NaClO}_4$  solutions shows the difficulties in trying to maintain constant solution conditions in long term solubility experiments such as these.

#### 4.5. Phase Separation

Achievement of steady-state conditions for the solubility measurements was monitored by sampling aliquots of the solution phases and analyzing for the respective radioisotope as a function of time. We used Centricon-30 centrifugal filters (Amicon Corp., Danvers, MA) for separating the phases of the neptunium, plutonium, and americium solutions. For the separations, the centrifuge (High-speed centrifuge, Model HSC-1000, Savant Instruments Inc.) was maintained at  $25^\circ\text{C}$  with a circulating water bath. The filters contain a Yucca Mountain-type membrane with a calculated pore size of  $4.1 \text{ nm}^{26}$ . To ascertain that we achieved complete phase separation and minimal adsorption on the filters during the preparation of the solution assays, we conducted a series of filtration tests.

For each solution, these tests were done when significant changes in the radionuclide concentration were observed during the equilibration period. We used one filter per solution and filtered consecutive 500  $\mu\text{L}$  to 1000  $\mu\text{L}$  portions of solution through it. Each filtrate was acidified to minimize sorption in the filtrate-collection container and an assay was taken. The concentration was plotted as a function of total volume passed through the filter. This was repeated until the assays showed a constant concentration. The volume necessary to saturate the filter was the cumulative amount of volumes used until the assay concentration remained constant. The presaturation volume was radionuclide and pH-dependent.

We determined and used the following preconditioning volumes: 500  $\mu\text{L}$  for all of the neptunium and plutonium solutions; and 500  $\mu\text{L}$ , 1000  $\mu\text{L}$  and 2500  $\mu\text{L}$  for the americium pH 6, 7, and 8.5 solutions, respectively. As is evident by the preconditioning volumes, adsorption of americium/neodymium to the filters is significant at elevated pH.

#### 4.6. Analysis

After separation of the solution and the solid phases, the two components were analyzed separately. Concentration measurements of the supernatants were made by counting liquid aliquots with a germanium low-energy counting system (LBNL design). For  $^{237}\text{Np}$  and  $^{241}\text{Am}$ , the 29.38 keV and 59.54 keV  $\gamma$ -ray lines were used, respectively.  $^{239}\text{Pu}$  was analyzed by utilizing the U L x-rays coming from the  $\alpha$ -decay of the plutonium. Possible contributions to the L x-rays from the decays of other radionuclides, also present in small amounts, were corrected by subtraction.<sup>27</sup> In selected cases, liquid scintillation counting was also used for plutonium concentration determinations (LKB Instruments, Inc., Wallac Oy, Model 1219

RackBeta). We used the "Pulse Shape Analysis" feature of the 1219 RackBeta to discriminate all  $\beta$ -emitting solution contaminants from the plutonium  $\alpha$ -radiation. Repeated sample counting and the observation of a constant count rate in the  $\alpha$ -window ensured no  $\beta$ -contribution to the  $\alpha$ -count.

#### 4.7. Criteria for Steady-State Concentrations

Constant concentrations over time with minimal deviation during that time span are the criteria for determining the average steady-state concentration from the individual concentration measurements. For experiments in which the aqueous concentration continually increases (or decreases), the final concentration measurement taken from the experiment will be reported as the final steady-state concentration. This concentration may not be the actual steady-state concentration, and for these cases all that can be stated is that the steady-state concentration is probably greater than (or less than) or equal to the value reported.

#### 4.8. Eh Measurements

We are aware of the various problems associated with Eh measurements in groundwater systems. Lindberg and Runnells<sup>28</sup> point out that in the apparent absence of an internal redox equilibrium, as it is the case for many groundwater systems, Eh measurements may not accurately predict the equilibrium chemistry of the system. Because our experimental systems contained a very limited number of components and may be well poised, we measured the Eh at the end of each solubility experiment. In each case, we obtained stable readings, usually within several hours of measurement. Despite the limitations of Eh readings in our systems, we conducted these measurements in order to supply future chemical modeling efforts (of neptunium, plutonium, and americium solubilities in 0.18 M NaClO<sub>4</sub> solutions) with an approximate value indicating the general oxic nature of the system. Without modeling, however, the Eh measurements are only of limited value, because they may represent a combination of many different redox reactions for each individual solubility solution despite the limited number of components.

We measured the Eh with a platinum electrode versus a Ag/AgCl/sat. NaCl reference. We cleaned the platinum electrode with 6 M HNO<sub>3</sub> before and after each measurement. The electrode setup was checked with "Zobell Solution" before and after each measurement.<sup>29,30</sup>

#### 4.9. Identification of Solids

The solid compounds were analyzed by x-ray powder diffraction measurements. A few micrograms of each actinide precipitate were placed in a 0.33 mm diameter quartz capillary tube, and the tube was sealed with an oxy-butane microtorch. The tube was mounted in an 11.46 cm diameter Debye-Scherrer camera and then irradiated with x-rays from a Norelco III x-ray generator (Phillips Electronics, Inc.). Copper K $\alpha$  radiation filtered through nickel was used.

## 5. RESULTS AND DISCUSSION

### 5.1. Neptunium. 5.1.1. Solubility

Results of the neptunium solubility studies are shown in Figure 1. The neptunium was initially introduced as  $\text{NpO}_2^+$  into the 0.1 M  $\text{NaClO}_4$ . The steady-state concentrations and the solutions' Eh values are given in Table V. The pH 6 solubility experiment had the highest redox potential and the pH 8.5 solubility experiment had the lowest potential. Concentration profiles as a function of equilibration time and pH for the experiments are shown in Figure 2. The individual measurements are listed in Appendix A. Results from neptunium filtration experiments are shown in Figure 3. The filtration experiments are described in section 4.5. We found no volume effect for the neptunium in these experiments. We therefore used 500  $\mu\text{L}$  of solution as presaturation volume for routine separations. In summary, the neptunium solubility decreased with increasing pH.

**Neptunium(V) Solubility Experiments  
in 0.18 M NaClO<sub>4</sub> Solutions at 25° C**

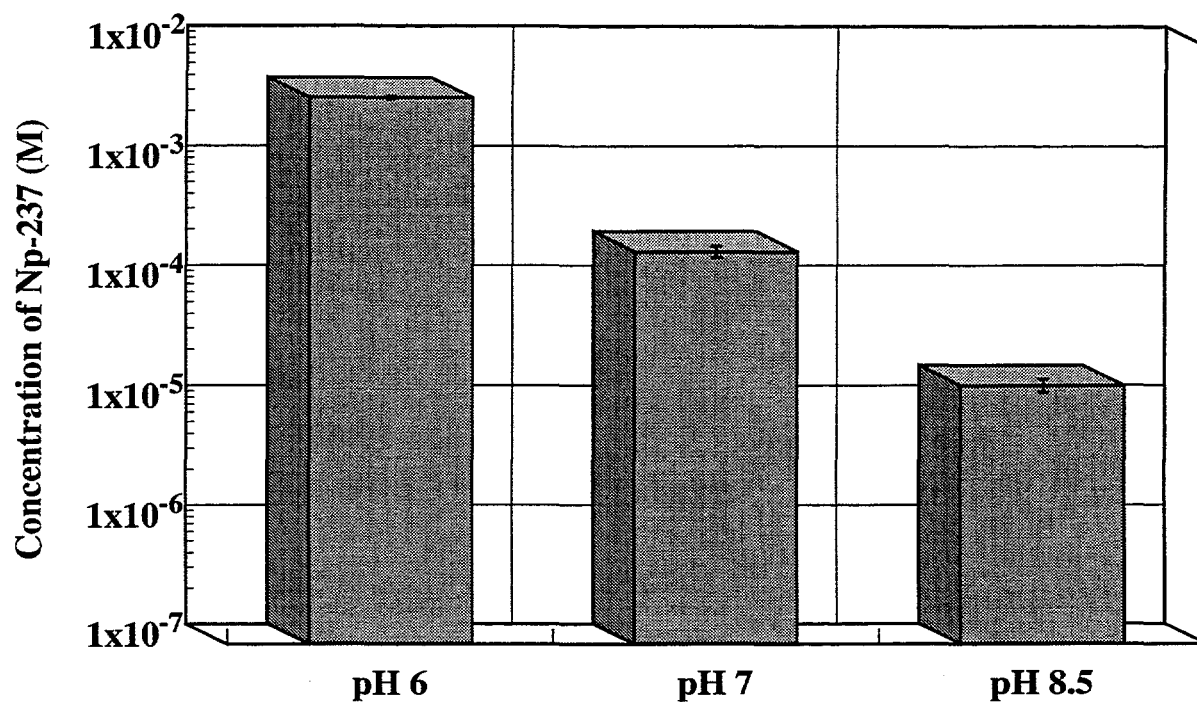


Figure 1. Results of the neptunium solubility experiments from oversaturation in 0.18 M NaClO<sub>4</sub> solutions as a function of pH.

Table V. Comparison of steady-state solution concentrations and Eh for neptunium oversaturation experiments in 0.18 M NaClO<sub>4</sub> at 25°C.

Neptunium(V)		
pH	Concentration	Eh (mV vs. NHE)
6	$(3.78 \pm 0.10) \times 10^{-3}$	$455 \pm 15$
7	$(1.92 \pm 0.21) \times 10^{-4}$	$431 \pm 15$
8.5	$(1.47 \pm 0.19) \times 10^{-5}$	$324 \pm 15$

# **Approach to Equilibrium of Neptunium(V) in 0.18 M NaClO<sub>4</sub> Solutions at 25° C**

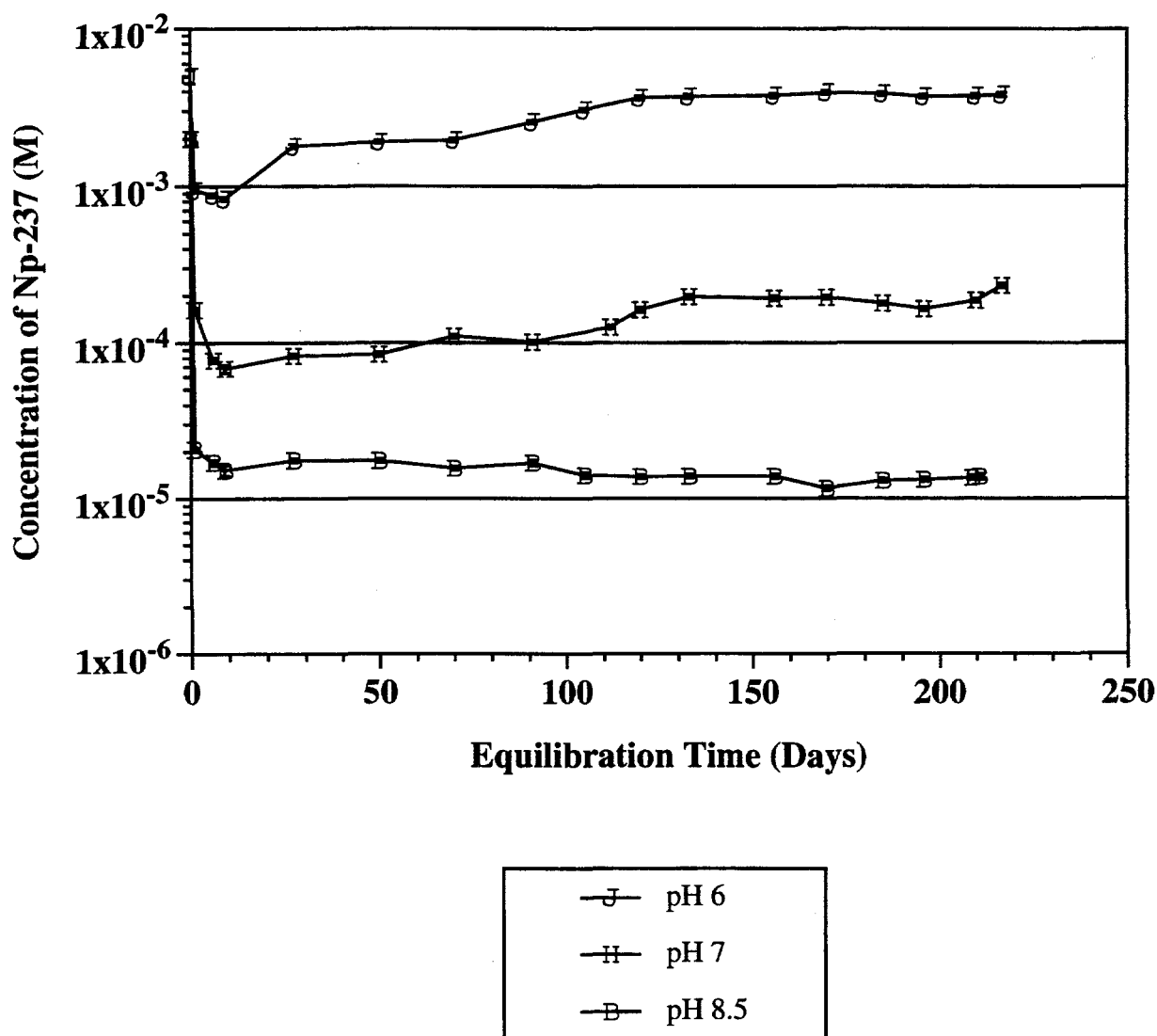


Figure 2. Solution concentrations of <sup>237</sup>Np in contact with precipitate obtained from supersaturation of 0.18 M NaClO<sub>4</sub> at 25°C as a function of time. pH 6.0 ± 0.1 (closed circles), pH 7.0 ± 0.1 (closed triangles), and pH 8.5 ± 0.1 (closed squares). The neptunium was added initially (day 0) as NpO<sub>2</sub><sup>+</sup>; initial concentrations were 5.0 × 10<sup>-3</sup> M (pH 6), 2.0 × 10<sup>-3</sup> M (pH 7), and 2.0 × 10<sup>-3</sup> M (pH 8.5).



Neptunium Filtration Experiments at pH 6, 7, and 8.5  
in 0.18 M NaClO<sub>4</sub> Solutions at 25° C

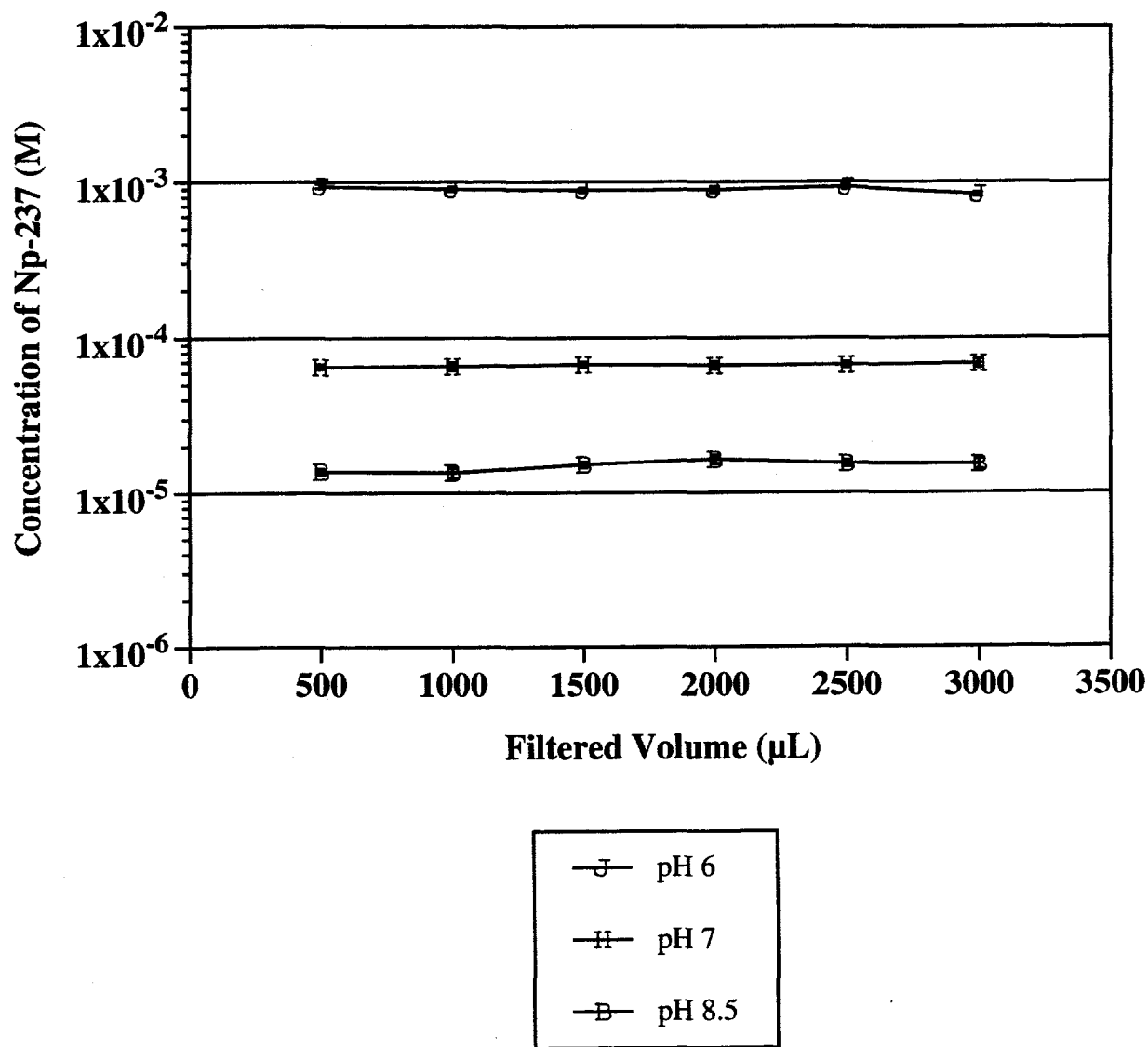


Figure 3. Results of neptunium filtration experiments at 25°C and pH 6, 7, and 8.5 conducted 9 days after the start of the experiments.

### 5.1.2. Speciation

The supernatant solutions from the neptunium solubility experiments were analyzed by absorption spectrophotometry to determine the oxidation state and speciation. The spectra for the pH 6, 7, and 8.5 experiments are shown in Figures 4, 5, and 6, respectively. Depending on the pH, the spectra show either the  $\text{NpO}_2^+$  main absorption band at 980.6 nm and/or an additional band at 991 nm that increases with pH due to the increasing carbonate complexation. The band at 980.6 nm is characteristic of uncomplexed  $\text{NpO}_2^+$ . The band at 991 nm was established by Nitsche et al.<sup>31</sup> It is typical for neptunyl(V) carbonate complexation.

To show that the band at 991 nm was indeed due to neptunyl(V) complexation by carbonate, we acidified the solutions to liberate the carbonate as carbon dioxide. Each of the solutions was acidified to pH ~0 with  $\text{HClO}_4$  and observed for gas formation. All solutions, with the exception of the pH 6, gave off detectable amounts of  $\text{CO}_2$  gas. The spectra of the acidified cell was then immediately taken. The absorption band at 991 nm disappeared, and only the band at 980.6 nm from uncomplexed neptunium(V) remained. Through this procedure, we established that all solutions contained neptunyl(V) carbonate complex(es). We determined the relative amounts of free neptunium and complexed neptunium (present as carbonate complex) from the difference between the total amount of neptunium in solution (determined by  $\gamma$ -spectroscopy) and the free  $\text{NpO}_2^+$  determined from the 980.6 nm absorption band. The results of our neptunium speciation study are summarized in Table VI.

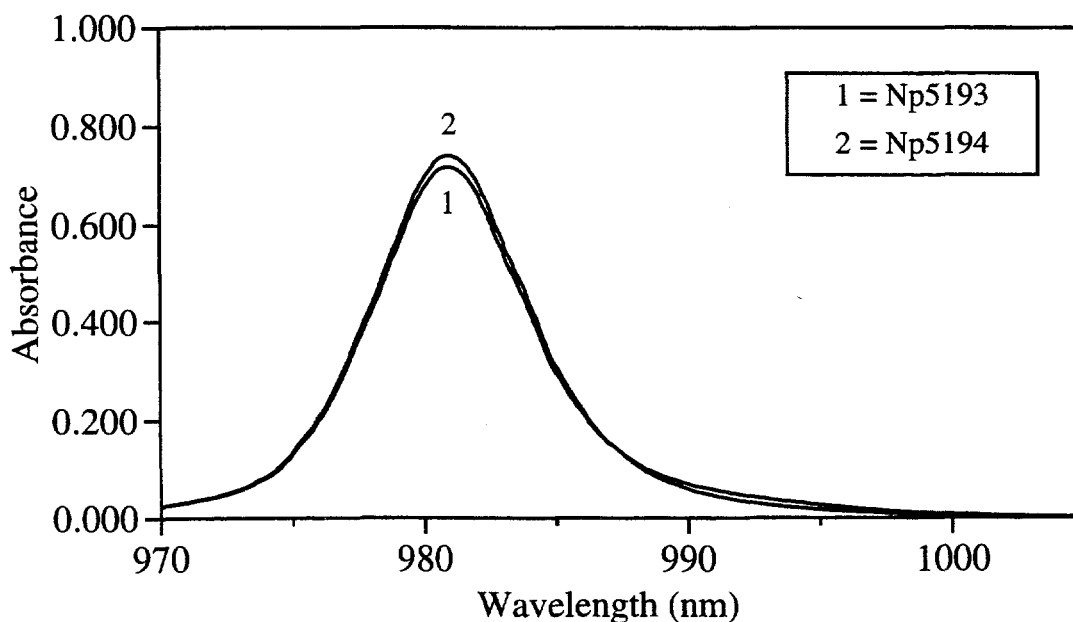


Figure 4. Near-IR absorption spectra of Np supernatant solutions at steady state formed in 0.18 M  $\text{NaClO}_4$  solutions from oversaturation at 25°C and pH 6: (1) at the experimental pH and (2) after acidification with  $\text{HClO}_4$  to pH 0.

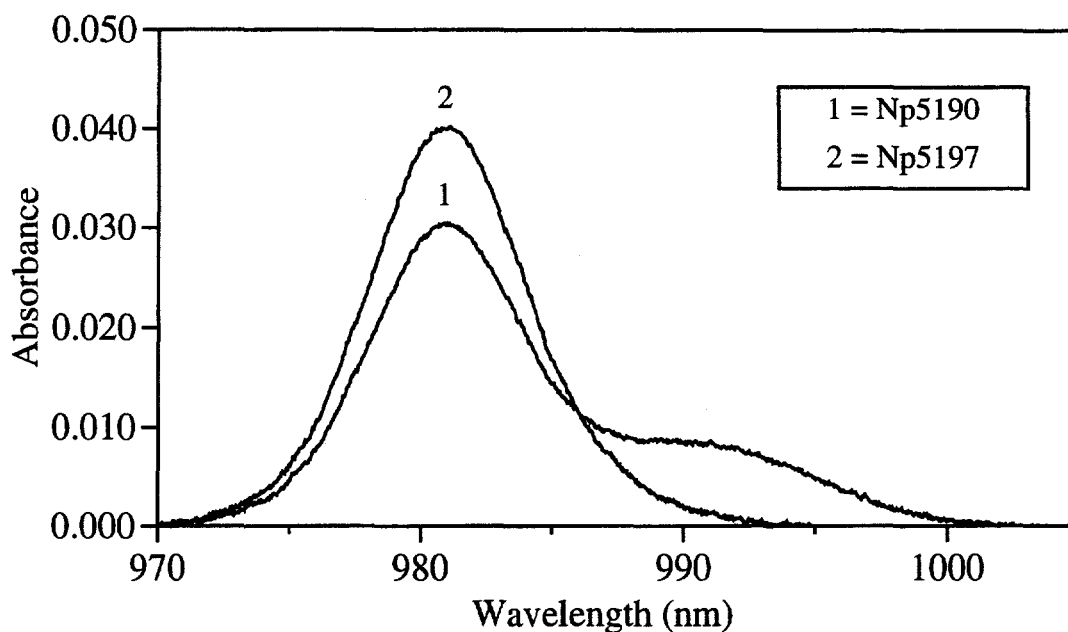


Figure 5. Near-IR absorption spectra of Np supernatant solutions at steady state formed in 0.18 M  $\text{NaClO}_4$  solutions from oversaturation at 25°C and pH 7: (1) at the experimental pH and (2) after acidification with  $\text{HClO}_4$  to pH 0.

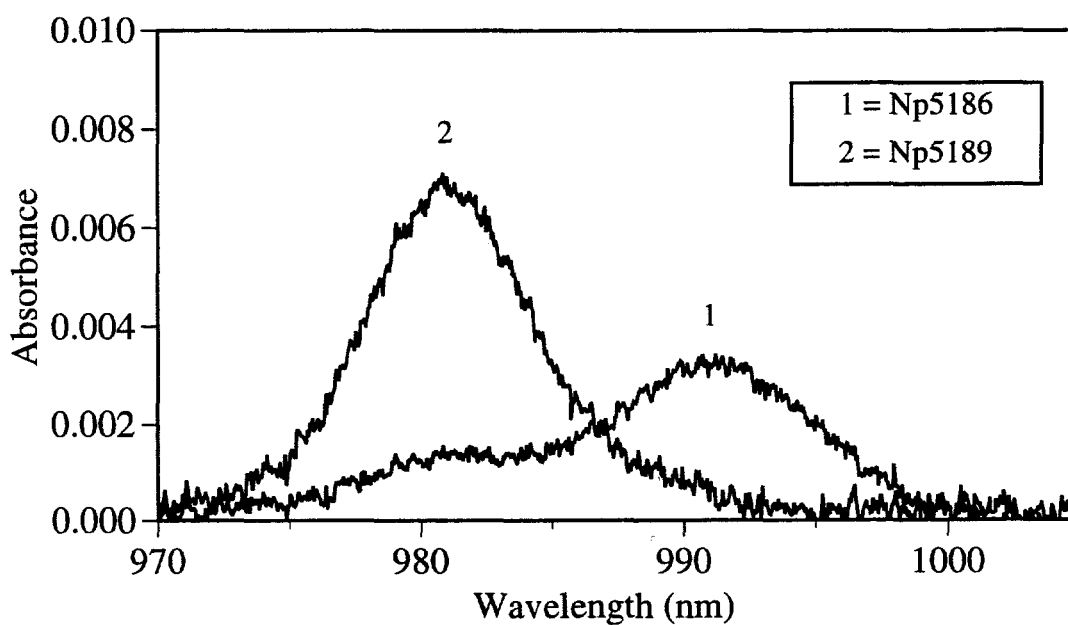


Figure 6. Near-IR absorption spectra of Np supernatant solutions at steady state formed in 0.18 M  $\text{NaClO}_4$  solutions from oversaturation at 25°C and pH 8.5: (1) at the experimental pH; (2) after acidification with  $\text{HClO}_4$  to pH 0.

Table VI. Comparison of extent of carbonate complexation for steady state solutions of neptunium in 0.18 M NaClO<sub>4</sub> solutions from oversaturation at 25°C.

Neptunium Carbonate Complexation (%)		
pH	NpO <sub>2</sub> <sup>+</sup>	NpO <sub>2</sub> (CO <sub>3</sub> ) <sup>-</sup>
6	97	3
7	76	24
8.5	23	77

We used a non-linear, least-squares peak fitting routine (Spectra Calc, Galactic Industries Corporation, Salem, NH) to deconvolute the three absorption spectra that showed carbonate complexation in order to determine the complex stoichiometry. The results for the spectrum from the pH 7.0 solution, shown in Figure 7, indicate that the spectrum is composed of only two peaks: one at 980.6 nm for the uncomplexed NpO<sub>2</sub><sup>+</sup> and a second one at 991 nm for the NpO<sub>2</sub>CO<sub>3</sub><sup>-</sup> complex. Higher complexes, such as the NpO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>3-</sup> complex, did not fit the spectrum. This was the case for all of the complexed spectra.

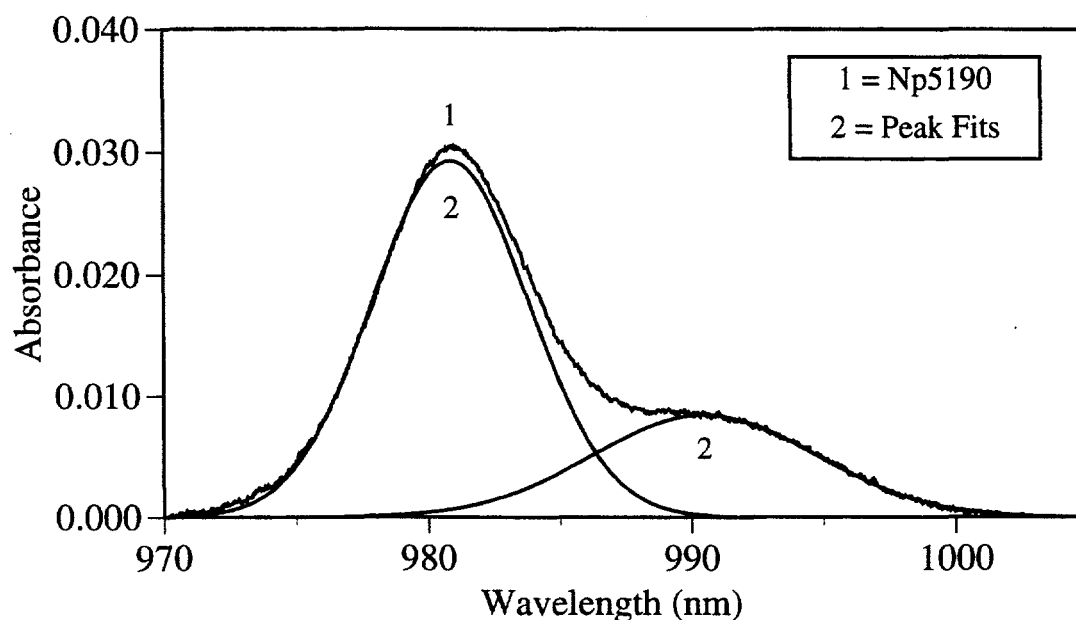


Figure 7. Deconvolution of the spectrum from the neptunium experiment at pH 7 and 25°C showing the two deconvoluted peaks at 980.6 and 991 nm.

### 5.1.3. Identification of Solids

The precipitates formed in the neptunium solutions were collected by centrifugation, washed with a small amount of CO<sub>2</sub>-free water, and dried with a jet of argon. All precipitates were white crystalline solids. X-ray powder diffraction patterns taken from precipitates produced distinct lines; d-spacings and relative intensities are listed in Table VII.

All of the solids obtained from the three neptunium oversaturation experiments matched very well. Nearly all of the lines in the pH 7 and pH 8.5 experiments are identical. The pH 6 solid had no lines in the region from 1.74 Å to 1.13 Å, where the pH 7 and 8.5 solids showed weak and trace lines. These missing lines are probably the result of the pH 6 solid's shorter exposure time. However, the strong and medium intensity lines of the pH 6 pattern matched well with those of the pH 7 and pH 8.5 solids.

The solids obtained were compared to neptunium solids found in the literature.<sup>32-35</sup> The d-spacings and intensities of the solids showed the best match with the NaNpO<sub>2</sub>CO<sub>3</sub>•nH<sub>2</sub>O series (where n = 3.5, 3, 2, 1, and 0) reported by Volkov et al.<sup>32</sup> In particular, the dihydrate solid of NaNpO<sub>2</sub>CO<sub>3</sub> fit very well. Eleven out of 16 lines from the pH 6 solid matched the NaNpO<sub>2</sub>CO<sub>3</sub>•2H<sub>2</sub>O pattern to within ± 0.03 Å. The pH 7 solid matched every d-spacing in the NaNpO<sub>2</sub>CO<sub>3</sub>•2H<sub>2</sub>O pattern to within ± 0.02 Å. The powder pattern obtained from the pH 7 solid had many more lines than found in the NaNpO<sub>2</sub>CO<sub>3</sub>•nH<sub>2</sub>O solid. This is most likely due to the long exposure times for the pH 7 solid giving rise to many weak and trace lines that would otherwise go undetected. The pH 8.5 solid also matched every line in the NaNpO<sub>2</sub>CO<sub>3</sub>•2H<sub>2</sub>O pattern with many additional lines from 1.96 to 1.13 Å. Again, these extra lines are probably an effect of the long exposure times for this solid. A comparison of the powder pattern of NaNpO<sub>2</sub>CO<sub>3</sub>•2H<sub>2</sub>O with the powder patterns obtained from the experimental solids is given in Table VII. In summary, the solids attained in all experiments are mono sodium neptunyl carbonate hydrates.

Table VII. X-ray powder diffraction patterns of neptunium solid phases from oversaturation in 0.18 M NaClO<sub>4</sub> at 25°C and pH 6, 7, and 8.5. compared the pattern of NaNpO<sub>2</sub>CO<sub>3</sub>•2H<sub>2</sub>O.<sup>32</sup>

pH 6.0		pH 7.0		pH 8.5		NaNpO <sub>2</sub> CO <sub>3</sub> •2H <sub>2</sub> O	
<u>d(Å)</u>	<u>Ia</u>	<u>d(Å)</u>	<u>Ia</u>	<u>d(Å)</u>	<u>Ia</u>	<u>d(Å)</u>	<u>Ia</u>
9.77	m						
8.43	m	8.47	w-	8.37	m+		
6.86	m	6.86	s+	6.85	s	6.90	s+
4.91	m-	4.89	s	4.89	m+	4.89	s
4.68	w	4.72	t	4.63	w		
4.26	w	4.27	s	4.24	m	4.27	m-
3.99	w-	3.99	s	3.98	m	3.99	m+
		3.89	t	3.85	t		
3.65	w	3.63	s	3.63	m	3.63	m+
3.44	w-	3.44	s	3.44	m	3.44	m-
				3.32	t		
3.23	w	3.21	s	3.22	m+	3.22	s
2.92	w-	2.93	s	2.91	m+	2.91	s
		2.81	w	2.81	w	2.82	w-
		2.72	w				
2.65	t			2.68	w	2.68	w-
				2.63	t		
		2.45	w+	2.44	w	2.45	w-
				2.42	t		
		2.36	m	2.35	m-	2.36	m-
2.32	t	2.31	m	2.30	m-	2.30	m-
		2.16	t	2.16	t		
		2.13	m	2.13	w+	2.12	m+
		2.08	w	2.08	w	2.08	w-
		2.03	s	2.03	m	2.03	s
2.00	s	2.00	m+	1.99	m+		
		1.98	m-				
1.94	t	1.96	m-	1.96	w		
		1.89	m-	1.88	w+		
		1.87	m-				
		1.81	m-	1.81	w+		
1.74	w	1.73	w+	1.73	w		
		1.70	w+	1.71	w		
		1.68	w-	1.68	t		
		1.63	t	1.63	t		
				1.62	t		
		1.61	t	1.61	t		
		1.59	t	1.59	t		
		1.57	w+		w+		
		1.53	w	1.53	w+		
		1.49	w	1.49	w+		
		1.48	t	1.48	t		
		1.41	t	1.41	t		
		1.40	t	1.40	w-		
				1.37	t		
		1.34	t	1.35	w+		
		1.32	t	1.32	w-		
		1.30	t	1.31	w		
		1.28	t	1.28	w+		
		1.24	t	1.24	t		
		1.22	t	1.22	w-		
		1.18	t	1.18	w-		
		1.17	t	1.16	w		
				1.15	t		
				1.13	t		

(a) Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak, t = trace.

### 5.2. Plutonium. 5.2.1. Solubility

Results of the plutonium solubility studies are shown in Figure 8. The plutonium was initially introduced as  $\text{Pu}^{4+}$  into the 0.1 M  $\text{NaClO}_4$ . The steady-state concentrations and the solutions' Eh values are given in Table VIII. Concentration profiles as a function of time and pH are shown in Figure 9. The individual measurements are listed in Appendix B. Results from plutonium filtration experiments are shown in Figure 10. Methods used for the filtration experiments are described in Section 4.5. We could not find any volume effect for the plutonium, so we used 500  $\mu\text{L}$  of solution as presaturation volume for routine separations.

In summary, plutonium steady state concentrations from the oversaturation experiments at pH 6 and 7 are equal. The pH 8.5 experiment led to steady state concentrations one order of magnitude higher than those of the pH 6 and pH 7 experiments.

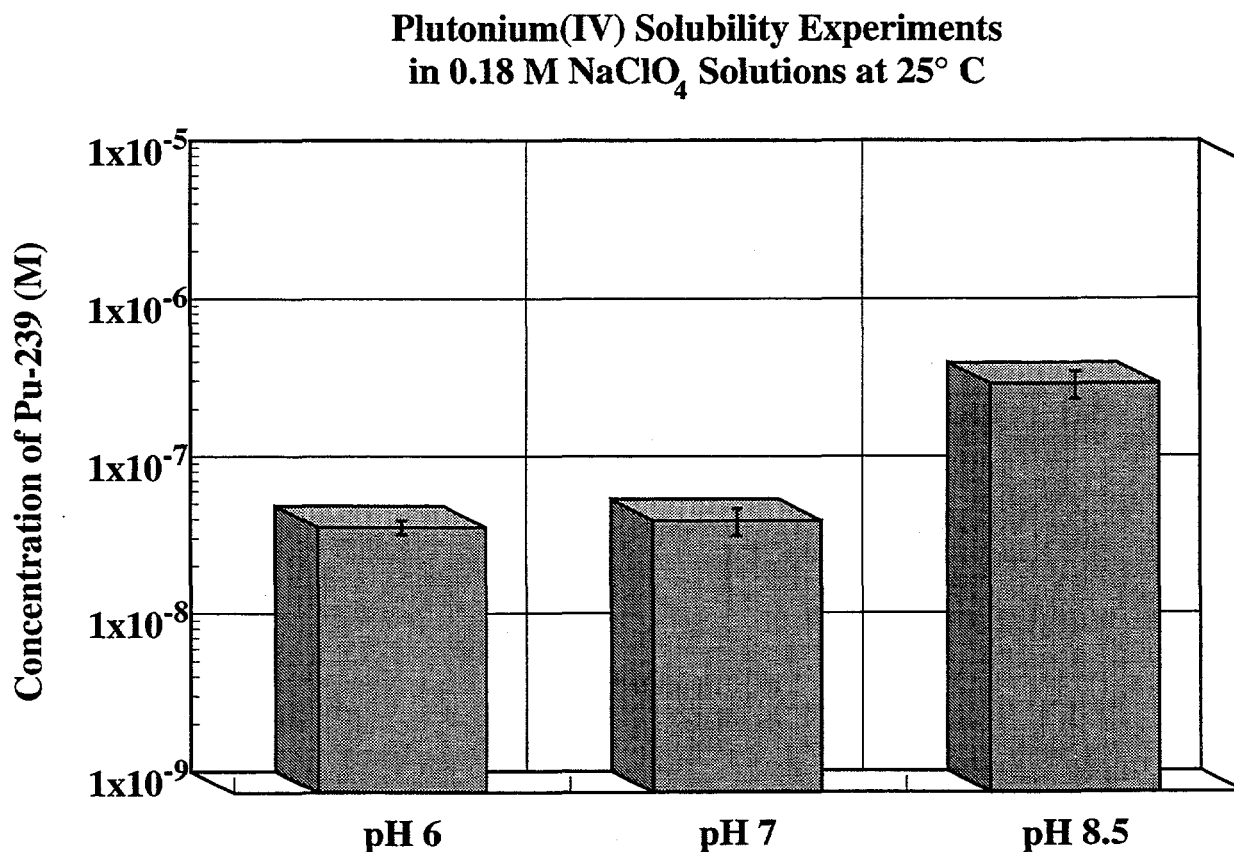


Figure 8. Results of the plutonium solubility experiments from oversaturation in 0.18 M  $\text{NaClO}_4$  solutions at 25°C as a function of pH.

Table VIII. Comparison of steady-state solution concentrations and Eh for plutonium oversaturation experiments in 0.18 M NaClO<sub>4</sub> solutions at 25°C.

Plutonium(IV)		
pH	Concentration	Eh (mV vs. NHE)
6	$(4.84 \pm 0.49) \times 10^{-8}$	$230 \pm 15$
7	$(5.30 \pm 1.04) \times 10^{-8}$	$175 \pm 15$
8.5	$(3.91 \pm 0.76) \times 10^{-7}$	$121 \pm 15$



**Approach to Equilibrium of Plutonium(IV) in  
0.18 M NaClO<sub>4</sub> Solutions at 25° C**

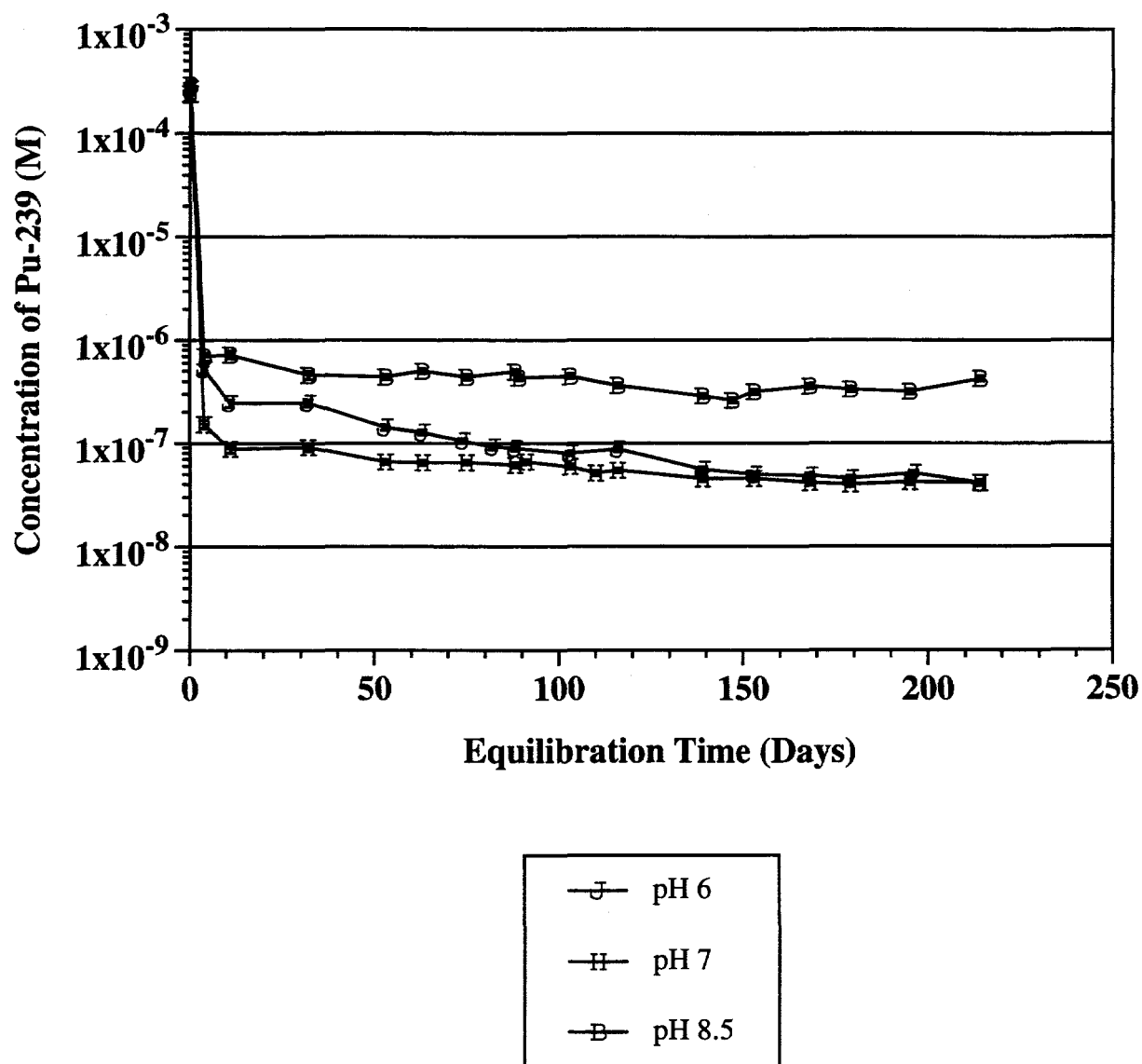


Figure 9. Solution concentrations of  $^{239}\text{Pu}$  in contact with precipitate obtained from supersaturation of 0.18 M NaClO<sub>4</sub> at 25°C as a function of time. pH  $6.0 \pm 0.1$  (closed circles), pH  $7.0 \pm 0.1$  (closed triangles), and pH  $8.5 \pm 0.1$  (closed squares). The plutonium was added initially (day 0) as Pu<sup>4+</sup>; initial concentrations were  $2.6 \times 10^{-4}$  M (pH 6),  $2.4 \times 10^{-4}$  M (pH 7), and  $2.9 \times 10^{-4}$  M (pH 8.5).

**Plutonium Filtration Experiments at pH 6, 7, and 8.5  
in 0.18 M NaClO<sub>4</sub> Solutions at 25° C**

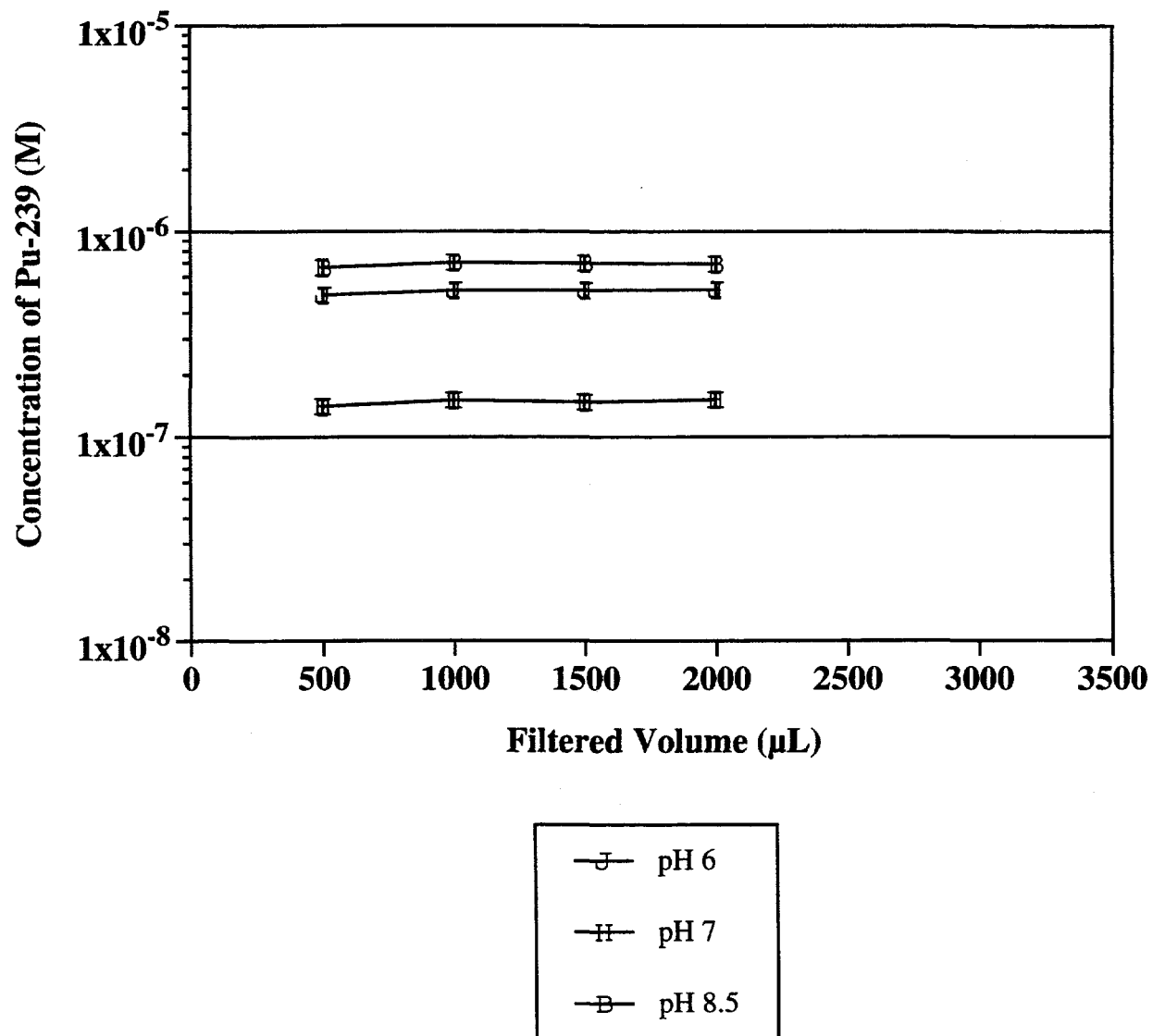


Figure 10. Results of plutonium filtration experiments at 25°C and pH 6, 7, and 8.5 conducted 4 days after the start of the experiments.

### 5.2.2. Speciation

The plutonium supernatant solutions at steady-state were analyzed for their oxidation state distributions. Speciation studies are made difficult by the low solubility of plutonium in 0.18 M NaClO<sub>4</sub> solutions. 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 plutonium oxidation states indirectly. The method involves a combination of solvent extractions that allows us to determine the relative amounts of plutonium oxidation states in solution. Table IX lists the methods used to determine the distribution of plutonium oxidation states in the experiments at 25°C.

Table IX. Methods used for determining plutonium oxidation states in solution.

Method	Oxidation State Distribution	
	Organic Phase	Aqueous Phase
1. 0.025 M PMBP Extraction at pH = 0	(+4)	(+3,+5,+6, p) <sup>a</sup>
2. 0.025 M PMBP Extraction at pH = 0 with Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	(+3,+4)	(+5,+6, p) <sup>a</sup>
3. 0.5 M HDEHP Extraction at pH = 0	(+4,+6)	(+3,+5, p) <sup>a</sup>
4. 0.5 M HDEHP Extraction at pH = 0 with Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	(+3,+4,+5,+6)	(p) <sup>a</sup>

(a) (p) = Pu(IV) polymer

For the experiments, we used 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (PMBP) as the extractant for Pu(IV). At pH 0, PMBP extracts Pu(IV) from aqueous solutions without significant decomposition by oxidants, such as dichromate. We used relatively small concentrations of extractant, therefore aiding in the nuclear counting of the fractions. Using PMBP and dichromate, we extract Pu(III) and Pu(IV) together by oxidation of Pu(III) to Pu(IV). At pH 0, di-(2-ethylhexyl)-orthophosphoric acid (HDEHP) extracts Pu(IV) and Pu(VI). Upon introducing dichromate to the aqueous phase before extraction, Pu(III) is oxidized to Pu(IV) and Pu(V) is oxidized to Pu(VI). HDEHP with dichromate extracts Pu(III), Pu(IV), Pu(V), and Pu(VI) by oxidation of Pu(III) to Pu(IV) and of Pu(V) to Pu(VI). The oxidation of Pu(III) to Pu(IV) is instantaneous when dichromate is introduced to the aqueous solution. After several hours, disproportionation and/or the oxidation of Pu(IV) to Pu(V) by dichromate may occur; however, the kinetics of these undesirable reactions are very slow and do not affect the extractions because they are completed in less than thirty minutes. This method was tested on plutonium solutions containing millimolar carbonate

concentrations. The oxidation state distribution was measured at the same time by Laser Induced Photoacoustic Spectroscopy (LIPAS) and by our extraction method.<sup>36</sup> The results from the two methods were found to be consistent.

In order to minimize the changing of plutonium oxidation states in solution, each of the extractions was carried out independently on a new solution sample. By taking differences in the relative amounts obtained in the four separations, the percent of each oxidation state can then be determined. Results of these studies are given in Table X, and are displayed in Figure 11.

All solutions contained predominantly Pu(V) and Pu(VI). With increasing pH, the relative amount of Pu(V) decreased and the relative amount of Pu(VI) increased. A small amount of Pu(IV) was present in all three cells, with the highest amount in the pH 7 cell. Pu(III) and Pu(IV) polymer were present in insignificant amounts in all experiments.

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. Therefore, we refer to the Pu(IV) polymer, in the context of this determination, as the fraction that is smaller than 4.1 nm. This colloidal or polymeric plutonium does not participate in the ionic solution equilibrium, and its removal will not immediately affect the oxidation state distribution in the solution.<sup>37</sup>

The observed valence distributions cannot be explained by disproportionation equilibria and complex stabilization. It is possible that oxidation products formed by  $\alpha$ -radiolysis of the 0.18 M NaClO<sub>4</sub> solutions may cause the predominance of high oxidation states. Another possible explanation for the predominance of high oxidation states at steady state may lie in the plutonium stock solution itself. Because of the limits of detection associated with our spectrophotometer, the solubility experiments may have contained initial concentrations of Pu(III), Pu(V), and Pu(VI) as high as  $2 \times 10^{-6}$ ,  $6 \times 10^{-6}$ , and  $2 \times 10^{-7}$  M, respectively. These concentrations could result based on the maximum concentrations that would have been undetected in the  $10^{-2}$  M Pu(IV) stock solution. Assuming complete precipitation of the lower oxidation states, one could conclude that the potential initial concentrations of Pu(V) and Pu(VI) may represent the steady-state oxidation state distributions and the total aqueous plutonium concentrations.

It is interesting to note that the increase in the [Pu(VI)]/[Pu(V)] ratio with increasing pH takes place even with a decreasing trend in the Eh. This can be explained by radiolysis effects in the solution. The total plutonium concentration increases with increasing pH. As the concentration increases, the radiolysis of the solution increases, and more radiolytic species are formed, which can then oxidize the plutonium to the VI state. It is most likely that the Eh of the solution is controlled by radiolytic species redox couples and not by the rather low concentration of plutonium couples. This explains why the cell with the lowest Eh has the highest relative amount of Pu(VI) in solution. Again, this sheds light on the problems associated with Eh measurements in systems where radiolysis is present, and further reinforces

that the Eh measurements yield only approximate values indicating the general redox nature of the system.

Table X. Plutonium oxidation state determinations in 0.18 M NaClO<sub>4</sub> at pH 6, 7, and 8.5 and at 25°C .

pH	Oxidation States (%)			
	Pu(IV)-polymer + Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
6.0	(3 ± 1)	(7 ± 1)	(70 ± 8)	(21 ± 2)
7.0	(1 ± 1)	(14 ± 1)	(42 ± 9)	(42 ± 4)
8.5	(4 ± 1)	(9 ± 1)	(33 ± 7)	(54 ± 5)

**Plutonium Oxidation State Distributions in 0.18 M NaClO<sub>4</sub> Solutions from Oversaturation at 25° C as a Function of pH**

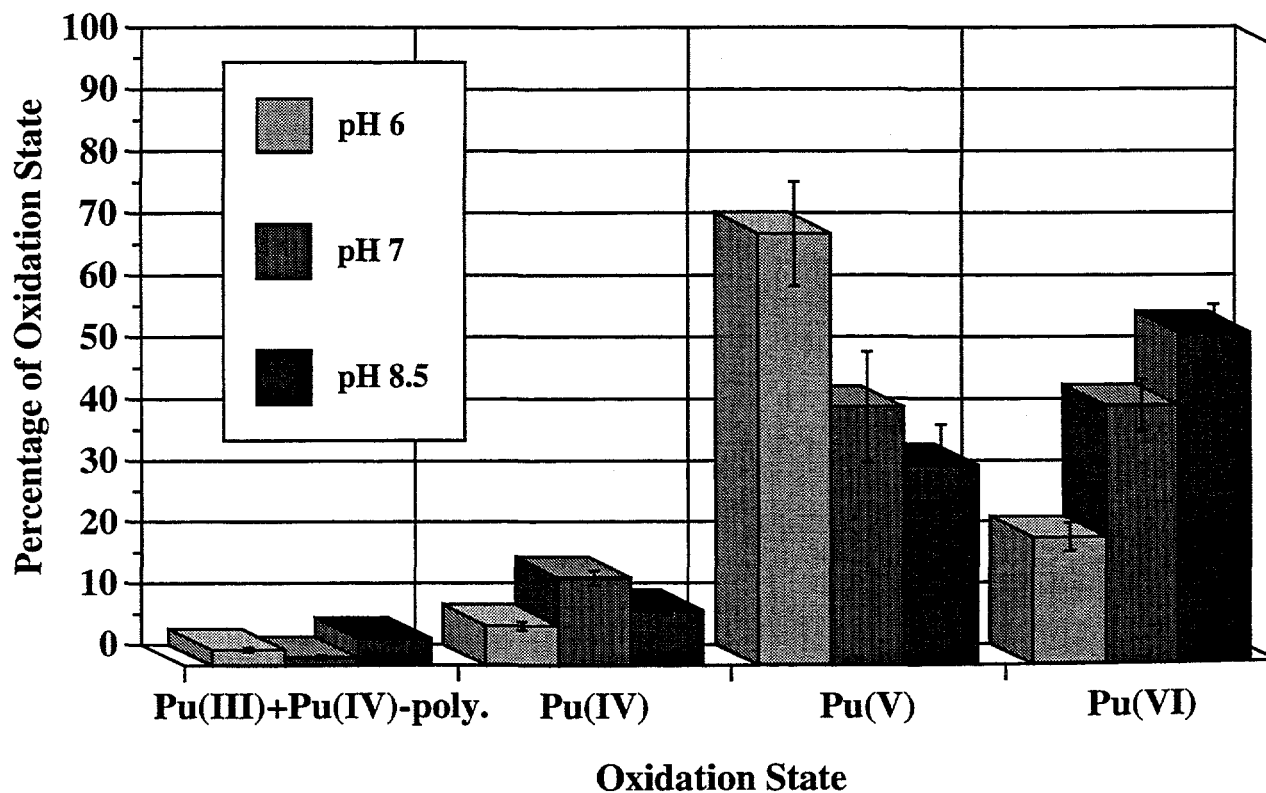


Figure 11. Plutonium oxidation state distributions of the supernatant at steady state for Pu<sup>4+</sup> solubility experiments from oversaturation in 0.18 M NaClO<sub>4</sub> solutions at pH 6, 7, and 8.5 and 25°C The solutions were filtered through 4.1 nm filters.

### 5.2.3. Identification of Solids

The plutonium precipitates from the solutions were collected by centrifugation, washed with a small amount of CO<sub>2</sub> free water, and dried with a jet of argon. The precipitates from the pH 6 and 7 cells were dark green and the precipitate from the pH 8.5 cell was a light brown-slightly greenish color. D-spacings and relative intensities of the x-ray powder diffraction patterns from the precipitates are listed in Table XI.

The solids removed from the pH 6 and pH 7 cells gave 18 and 17 lines, respectively. The pH 8.5 solid gave five rather diffuse lines in its diffraction pattern. All three solids were compared to patterns of crystalline PuO<sub>2</sub>,<sup>38</sup> PuO<sub>3</sub>•0.8H<sub>2</sub>O,<sup>39</sup> KPuO<sub>2</sub>CO<sub>3</sub>,<sup>40</sup> NH<sub>4</sub>PuO<sub>2</sub>CO<sub>3</sub>,<sup>40</sup> and PuO<sub>2</sub>CO<sub>3</sub>.<sup>41</sup> No match was found among any of these patterns, so all we can conclude is that the solids from the pH 6 and pH 7 cells are crystalline but not yet identified. The pH 8.5 solid gave rise to a few rather diffuse lines. This is indicative of a low degree of crystallinity which is typical for Pu(IV) polymer. The slightly greenish color also suggests at least a partial component of Pu(IV) polymer.

Table XI. X-ray powder diffraction patterns of plutonium solid phases from oversaturation in 0.18 M NaClO<sub>4</sub> solutions at 25°C and pH 6, 7, and 8.5.

pH 6		pH 7		pH 8.5	
d(Å)	I <sup>a</sup>	d(Å)	I <sup>a</sup>	d(Å)	I <sup>a</sup>
5.16	m	5.17	w		
3.96	m	3.94	s		
3.64	s	3.64	w+		
3.60	w	3.52	s		
3.43	s	3.43	w+		
2.96	w	2.96	m		
2.84	w	2.84	t		
2.77	w	2.77	t		
2.67	w-	2.64	t	2.64	t
2.44	t				
2.40	t	2.40	m-		
		2.28	t	2.29	t
2.20	w	2.21	t		
1.99	s	1.99	s	1.99	s
1.96	t			1.95	w-
1.92	t	1.91	t		
1.82	w				
1.74	m	1.73	m+	1.73	w+
1.69	t	1.69	t		
		1.56	t		

(a) Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak, t = trace.

### 5.3. Americium

We used non-radioactive neodymium in place of americium to minimize radiation-induced degradation of the solubility cell. Neodymium is chemically similar to americium.<sup>42</sup> It has an ionic radius of 0.983 Å that is very close to that of 0.975 Å for trivalent americium.<sup>43</sup> The neodymium was spiked with a small amount of <sup>241</sup>Am to facilitate sample counting using the 59.54-keV photo-peak. The use of the neodymium spiked with <sup>241</sup>Am tracer reduced the alpha-radiation to a fraction of the radiation that would have been present if we had used pure <sup>243</sup>Am instead. The mole ratio  $(([\text{Am}] + [\text{Nd}])/[\text{Am}])$  used in these solubility experiments was 113.7:1

We confirmed in an earlier study that neodymium is a good stand-in element for americium.<sup>1</sup> The differences between the solubilities of Nd/<sup>241</sup>Am and pure <sup>243</sup>Am were insignificant at each of the studied pH values.

#### 5.3.1. Solubility

Results of the solubility studies are shown in Figure 12. The steady-state concentrations and the solutions' Eh values are given in Table XII. Concentration profiles as a function of equilibration time and pH for the experiments are shown in Figure 13. Individual measurements are listed in Appendix C. Results for americium/neodymium filtration experiments are shown in Figure 14. The filtration experiments are described in Section 4.5. Filtration experiments on day one of the experiments at pH 6, 7, and 8.5 required 500, 1000, and 2500 µL, respectively, as preconditioning volumes. When the concentrations dropped to 10<sup>-8</sup> to 10<sup>-10</sup> M in the pH 8.5 cell, around day 65, we repeated the filtration experiments and confirmed that indeed 2500 µL was a sufficient preconditioning volume to use over the time of the entire solubility experiment. The large drop in americium/neodymium solubility in the pH 6 cell, starting at day 250, remains unexplained. We reassayed the cell several times after the drop in solubility to confirm that this was a real effect and not an error in our assays. We checked our prefiltration assay volumes to ensure that we were saturating the filter. No additional adsorption on the filter membrane could be found. Nonetheless, we increased our prefiltration volume to 2500 µL to ensure proper saturation. We assayed the cell several times over two weeks to monitor the drop in concentration, but we were forced to decrease the number of assays taken due to the low solution volume remaining in the cell. By day 312, the solubility of the Am/Nd had returned to the level seen previously. We took two more assays to verify the concentration, but were forced to stop taking assays due to low solution volume. The last two assays confirmed that the solubility had returned to the 10<sup>-5</sup> M level.

In summary, the solubility of americium/neodymium from oversaturation in 0.18 M NaClO<sub>4</sub> solutions at 25°C decreased with increasing pH.

**Americium/Neodymium(III) Solubility Experiments  
in 0.18 M NaClO<sub>4</sub> Solutions at 25° C**

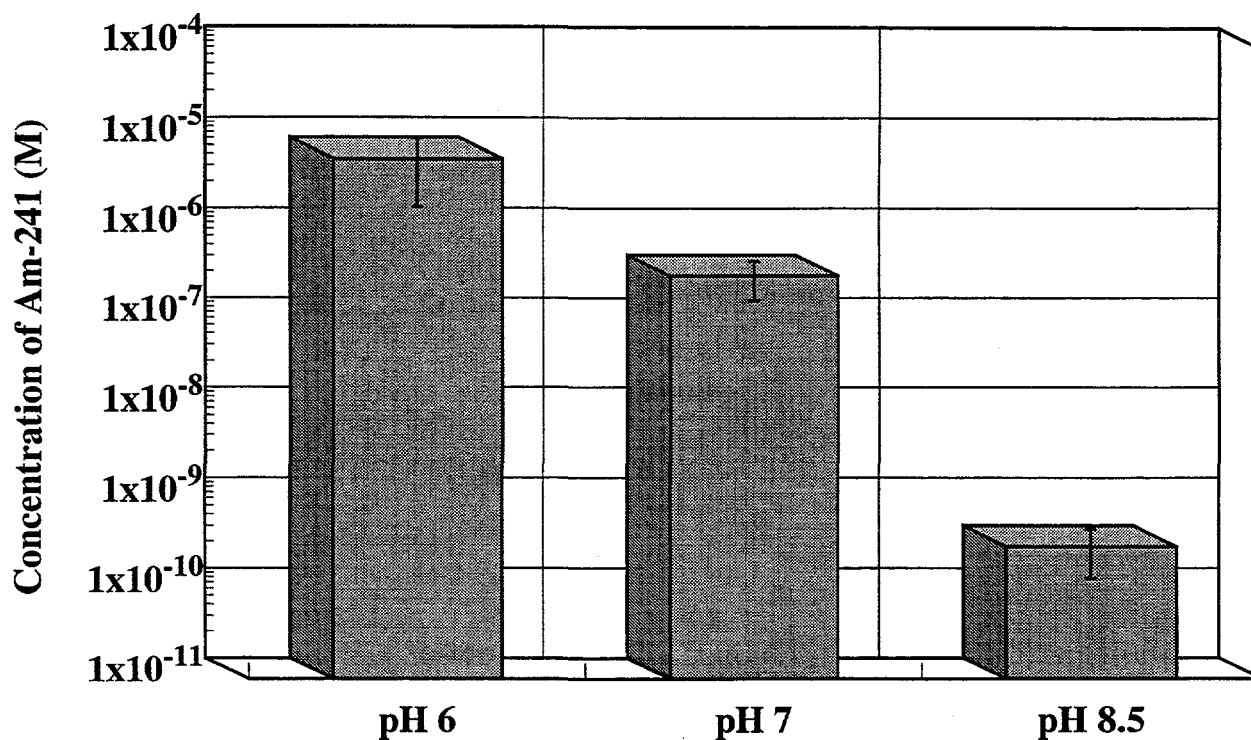


Figure 12. Results for  $^{241}\text{Am}^{3+}/\text{Nd}^{3+}$  solubility experiments from oversaturation in 0.18 M NaClO<sub>4</sub> at 25°C as a function of pH.

Table XII. Comparison of steady-state solution concentrations and Eh for americium/ neodymium oversaturation experiments in 0.18 M NaClO<sub>4</sub> solutions at 25°C.

Americium(III)		
pH	Concentration	Eh (mV vs. NHE)
6	$(6.00 \pm 4.23) \times 10^{-6}$	$298 \pm 15$
7	$(3.04 \pm 1.44) \times 10^{-7}$	$217 \pm 15$
8.5	$(2.99 \pm 1.68) \times 10^{-10}$	$253 \pm 15$



**Approach to Equilibrium of Americium/Neodymium(III) in  
0.18 M NaClO<sub>4</sub> Solutions at 25° C**

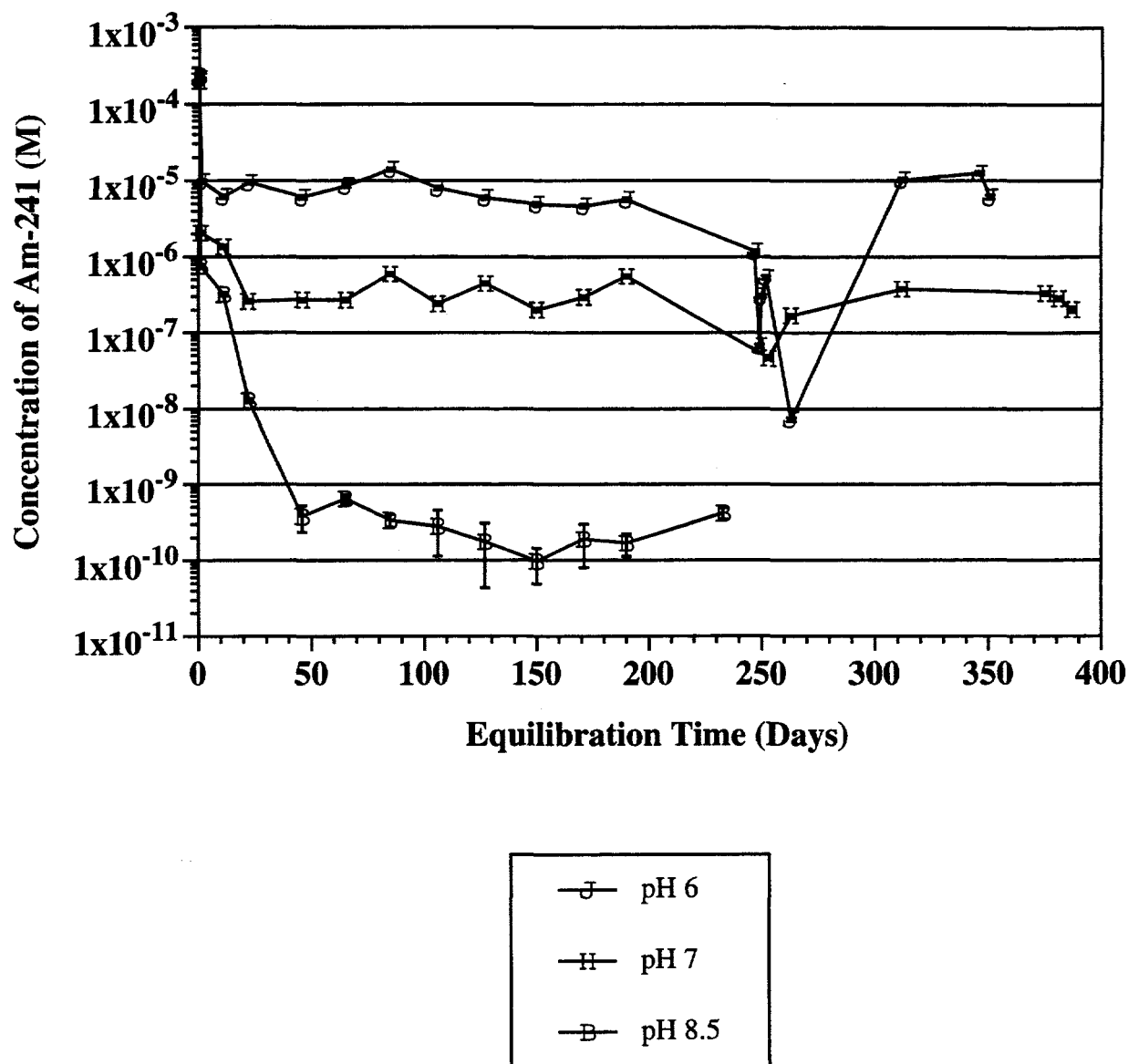


Figure 13. Solution concentrations of  $^{241}\text{Am}/\text{Nd}$  in contact with precipitate obtained from supersaturation of 0.18 M NaClO<sub>4</sub> solutions at 25°C as a function of time. pH  $6.0 \pm 0.1$  (closed circles), pH  $7.0 \pm 0.1$  (closed triangles), and pH  $8.5 \pm 0.1$  (closed squares). The americium/neodymium was added initially (day 0) as  $^{241}\text{Am}^{3+}/\text{Nd}^{3+}$ ; initial ( $^{241}\text{Am}^{3+} + \text{Nd}^{3+}$ ) concentrations were  $2.2 \times 10^{-4}$  M (pH 6),  $2.0 \times 10^{-4}$  M (pH 7), and  $2.4 \times 10^{-4}$  M (pH 8.5).

**Americium/Neodymium(III) Filtration Experiments at pH 6, 7, and 8.5  
in 0.18 M NaClO<sub>4</sub> Solutions at 25° C**

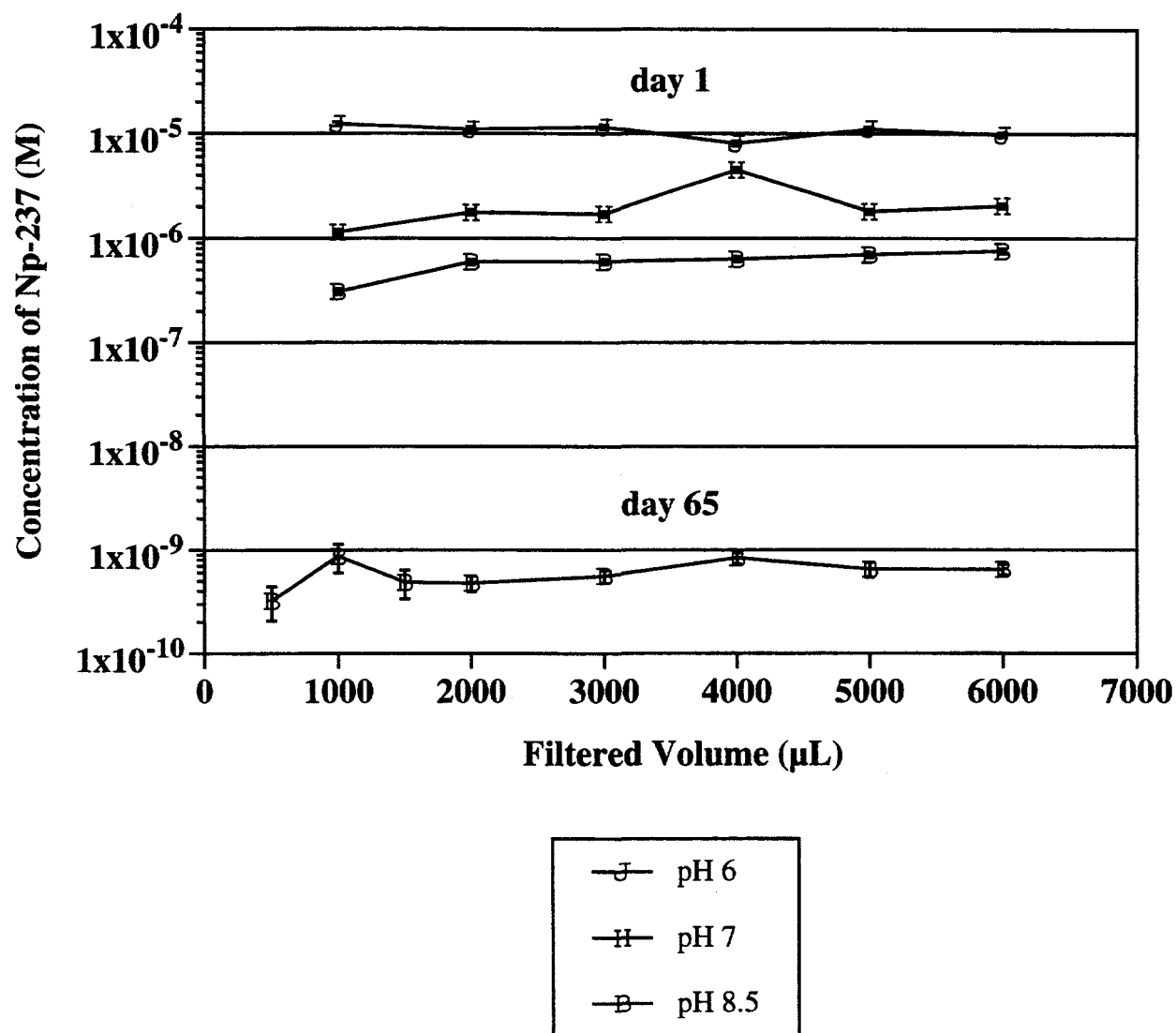


Figure 14. Results of americium/neodymium filtration experiments at 25°C and pH 6, 7, and 8.5 conducted 1 day and 65 days after the start of the experiments.

### 5.3.2. Speciation

Speciation measurements could not be carried out because of the low solution concentrations. The trivalent neodymium is expected, under these experimental conditions, not to change its oxidation state. We determined whether the  $^{241}\text{Am}$  tracer undergoes a change in oxidation state. We used extractions with 0.5 M thenoyltrifluoroacetone (TTA) or 0.025 M 1-phenyl-3-methyl-4-benzoyl-pyrazolin-5-one (PMBP) at pH 0 and coprecipitations with  $\text{LaF}_3$  for this test. TTA or PMBP extracts the oxidation state IV and leaves the oxidation states III, V, and VI in the aqueous solution. The lanthanum fluoride (with holding oxidant) coprecipitates the oxidation states III and IV, and leaves the V and VI in the supernatant. Both the pH 6 and pH 7 cells showed the americium to be predominantly in the trivalent state. However, we also observed a significant percentage of  $\text{Am(V)/Nd}$  in these solutions; approximately 9% and 19%, for the pH 6 and 7 cells respectively. This was an unexpected result, but was confirmed by performing the oxidation state determinations several times. This leads to a problem with the determination of the solution concentrations because our tracer of  $^{241}\text{Am}$  was always presumed to be in the +3 oxidation state. However, at maximum, this would lead to a 20% error in the measurements. We were not able to analyze the pH 8.5 cell due to its low solution concentrations. In light of the unexpected oxidation of the americium to the pentavalent state as determined by results of the oxidation state measurements, we need to reevaluate the use of  $\text{Nd}^{3+}$  as an analog for this type of study. Further investigation into the apparent oxidation of the  $\text{Am(III)}$  in 0.1 M  $\text{NaClO}_4$  is also desirable.

### 5.3.3. Identification of Solids

The neodymium/americium-241 precipitates were collected by centrifugation, washed with a small amount of  $\text{CO}_2$ -free water, dried with a jet of argon, and analyzed by x-ray powder diffraction. All solids were white and appeared to be crystalline. The d-spacings and relative intensities of all of the solids are listed in Table XIII. All of the solids appear to be very similar to one another. Table XIV lists the x-ray powder diffraction patterns of the solids from the pH 6, 7 and 8.5 solubility experiments at  $25^\circ\text{C}$  together with the reference patterns of  $\text{Nd}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ <sup>42</sup> and orthorhombic  $\text{NdOHCO}_3$ .<sup>44</sup> It has been shown in the literature that americium hydroxycarbonates are isostructural to the analogous neodymium hydroxycarbonates.<sup>42,44,45</sup> The solids obtained from the pH 6 and 8.5 experiments appear to be a mixture of orthorhombic  $\text{NdOHCO}_3$  and  $\text{Nd}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ . However, the powder patterns obtained from the experimental solids show fewer, more diffuse lines than those of normal solids. This leads us to conclude that the solids have an amorphous character also. The pH 7 solid pattern matches the literature pattern of  $\text{Nd}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$  very well. Nearly all of the lines from the experimental solid match up, with only a few of the weaker lines missing. In light of the fact that both  $\text{NdOHCO}_3$  and  $\text{Nd}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$  were formed in the pH 6 and pH 8.5 experiments, it is likely that the pH 7 solid was a mixture of these two components, but the characteristic lines from  $\text{NdOHCO}_3$  were too faint to be readily identified.

In summary, the americium/neodymium oversaturation solubility experiments in 0.18 M  $\text{NaClO}_4$  yielded mixtures of  $\text{Nd}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$  and  $\text{NdOHCO}_3$  solids with relatively low crystallinity.

Table XIII. X-ray powder diffraction patterns of Nd<sup>241</sup>Am solid phases in 0.18 M NaClO<sub>4</sub> solutions from oversaturation at 25°C and pH 6, 7, and 8.5.

pH 6		pH 7		pH 8.5	
<u>d(Å)</u>	<u>I<sup>a</sup></u>	<u>d(Å)</u>	<u>I<sup>a</sup></u>	<u>d(Å)</u>	<u>I<sup>a</sup></u>
		7.81	m+		
		5.77	s-		
		4.70	s-		
		3.98	s		
		3.66	m		
		3.53	s-		
		3.10	w		
		3.04	m		
2.96	t	2.95	m-		
		2.84	t		
		2.77	t	2.78	w-
2.64	t	2.60	m-	2.64	w-
		2.41	w		
		2.36	t		
2.31	t	2.27	w	2.29	w-
		2.18	t		
		2.17	t		
		2.10	t		
		2.04	w		
1.99	s-	2.00	w	1.99	s
		1.91	w	1.95	w-
		1.89	w		
		1.84	t		
		1.79	t		
1.74	w			1.74	w+

(a) Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak, t = trace.

Table XIV. X-ray powder diffraction patterns of Nd/<sup>241</sup>Am solid phases in 0.18 M NaClO<sub>4</sub> from oversaturation at 25°C and pH 6, 7, and 8.5 compared with reference patterns of: 1.) Nd<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>•2H<sub>2</sub>O; 2.) orthorhombic NdOHCO<sub>3</sub>.<sup>42,44</sup>

pH 6		pH 7		pH 8.5		Ref. #1		Ref. #2(b)	
d(Å)	I <sup>a</sup>	d(Å)	I <sup>a</sup>	d(Å)	I <sup>a</sup>	d(Å)	I <sup>a</sup>	d(Å)	I <sup>a</sup>
		7.81	m+			7.56	m		
		5.77	s-			5.68	s		
		4.70	s-			4.67	s	5.50	m-
								4.28	m
		3.98	s			3.93	s	4.24	vs
						3.83	w		
		3.66	m			3.62	m	3.68	t
		3.53	s-					3.65	m
		3.10	w			3.09	s	3.32	m
2.96	t	3.04	m			3.02	s		
		2.95	m-			2.98	w	2.94	t
								2.91	m
		2.84	t			2.87	w		
2.64	t	2.77	t	2.78	w-	2.75	w	2.75	m
				2.64	w-			2.63	m
		2.60	m-			2.58	s		
		2.41	w					2.48	s
		2.36	t					2.40	t
2.31	t			2.29	w-			2.32	w
		2.27	w			2.25	w	2.31	m-
		2.18	t			2.17	w	2.14	w
		2.17	t					2.12	s
		2.10	t					2.10	t
1.99	s-	2.04	w			2.02	m	2.03	w
		2.00	w	1.99	s	1.98	w	1.96	w
		1.91	w	1.95	w-			1.93	w
		1.89	w			1.87	m	1.88	t
		1.84	t			1.83	m	1.83	s
1.74	w	1.79	t	1.74	w+	1.78	m	1.81	w
						1.74	w	1.72	w
								1.69	w
								1.68	t
								1.66	t
								1.62	w
								1.60	w
								1.58	t
						1.56	m	1.57	w
								1.54	m
								1.52	w
								1.50	t
								1.47	w
								1.46	w
								1.44	t
								1.42	t
								1.37	t
								1.31	w

(a) Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak, t = trace.

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## **APPENDIX A**

### **RESULTS OF NEPTUNIUM SOLUBILITY EXPERIMENTS IN 0.18 M NaClO<sub>4</sub>**



**Appendix IA. Results of Neptunium solubility experiments  
in 0.18 M NaClO<sub>4</sub> at 25° C and pH 6.0**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	6.00	$(5.00 \pm 0.50) \times 10^{-3}$
1-1A1S2	1	6.09	$(9.41 \pm 0.28) \times 10^{-4}$
1-2A1S2	6	6.08	$(8.79 \pm 0.27) \times 10^{-4}$
1-3A1S2	9	6.08	$(8.30 \pm 0.23) \times 10^{-4}$
1-4A1S2	27	6.08	$(1.79 \pm 0.06) \times 10^{-3}$
1-5A1S2	50	5.99	$(1.92 \pm 0.05) \times 10^{-3}$
1-6A1S2	70	6.06	$(1.97 \pm 0.06) \times 10^{-3}$
1-7A1S2	91	6.12	$(2.57 \pm 0.07) \times 10^{-3}$
1-8A1S2	105	6.22	$(3.06 \pm 0.08) \times 10^{-3}$
1-9A1S2	120	5.95	$(3.63 \pm 0.11) \times 10^{-3}$
1-10A1S2	133	5.92	$(3.70 \pm 0.11) \times 10^{-3}$
1-11A1S2	156	5.90	$(3.77 \pm 0.11) \times 10^{-3}$
1-12A1S2	170	5.89	$(3.95 \pm 0.12) \times 10^{-3}$
1-13A1S2	185	5.96	$(3.87 \pm 0.11) \times 10^{-3}$
1-14A1S2	196	6.00	$(3.72 \pm 0.10) \times 10^{-3}$
1-15A1S2	210	6.02	$(3.75 \pm 0.12) \times 10^{-3}$
1-16A1S2	217	6.03	$(3.82 \pm 0.12) \times 10^{-3}$

average 1-9A1S2 through 1-16A1S2

$(3.78 \pm 0.10) \times 10^{-3}$

**Appendix IIA. Results of Neptunium solubility experiments  
in 0.18 M NaClO<sub>4</sub> at 25° C and pH 7.0**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	7.00	$(2.00 \pm 0.20) \times 10^{-3}$
2-1A1S2	1	6.83	$(1.62 \pm 0.05) \times 10^{-5}$
2-2A1S2	6	6.90	$(7.72 \pm 0.32) \times 10^{-5}$
2-3A1S2	9	6.90	$(6.79 \pm 0.42) \times 10^{-5}$
2-4A1S2	27	6.95	$(8.25 \pm 0.26) \times 10^{-5}$
2-5A1S2	50	6.96	$(8.43 \pm 0.28) \times 10^{-5}$
2-6A1S2	70	6.96	$(1.10 \pm 0.03) \times 10^{-4}$
2-7A1S2	91	7.02	$(1.01 \pm 0.03) \times 10^{-4}$
2-9A1S2	112	7.03	$(1.26 \pm 0.04) \times 10^{-4}$
2-10A1S2	120	7.03	$(1.62 \pm 0.06) \times 10^{-4}$
2-11A1S2	133	6.96	$(1.96 \pm 0.06) \times 10^{-4}$
2-12A1S2	156	6.94	$(1.92 \pm 0.07) \times 10^{-4}$
2-13A1S2	170	6.90	$(1.95 \pm 0.06) \times 10^{-4}$
2-14A1S2	185	6.93	$(1.78 \pm 0.05) \times 10^{-4}$
2-15A1S2	196	6.99	$(1.64 \pm 0.05) \times 10^{-4}$
2-16A1S2	210	7.03	$(1.86 \pm 0.06) \times 10^{-4}$
2-17A1S2	217	6.94	$(2.31 \pm 0.07) \times 10^{-4}$

average 2-11A1S2 through 2-17A1S2

$(1.92 \pm 0.21) \times 10^{-4}$

**Appendix IIIA. Results of Neptunium solubility experiments  
in 0.18 M NaClO<sub>4</sub> at 25° C and pH 8.5**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	8.50	$(2.00 \pm 0.20) \times 10^{-3}$
3-1A1S2	1	8.27	$(2.07 \pm 0.06) \times 10^{-5}$
3-2A1S2	6	8.42	$(1.71 \pm 0.08) \times 10^{-5}$
3-12A1S2	9	8.49	$(1.52 \pm 0.12) \times 10^{-5}$
3-4A1S2	27	8.57	$(1.77 \pm 0.05) \times 10^{-5}$
3-5A1S2	50	8.27	$(1.76 \pm 0.06) \times 10^{-5}$
3-6A1S2	70	8.29	$(1.57 \pm 0.05) \times 10^{-5}$
3-7A1S2	91	8.30	$(1.70 \pm 0.07) \times 10^{-5}$
3-8A1S2	105	8.52	$(1.41 \pm 0.06) \times 10^{-5}$
3-9A1S2	120	8.46	$(1.38 \pm 0.04) \times 10^{-5}$
3-10A1S2	133	8.62	$(1.39 \pm 0.04) \times 10^{-5}$
3-11A1S2	156	8.47	$(1.39 \pm 0.05) \times 10^{-5}$
3-12A1S2	170	8.28	$(1.16 \pm 0.04) \times 10^{-5}$
3-13A1S2	185	8.35	$(1.30 \pm 0.04) \times 10^{-5}$
3-14A1S2	196	8.41	$(1.32 \pm 0.04) \times 10^{-5}$
3-15A1S2	209	8.38	$(1.36 \pm 0.05) \times 10^{-5}$
3-16A1S2	211	8.41	$(1.38 \pm 0.06) \times 10^{-5}$
average 3-2A1S2 through 3-16A1S2			$(1.47 \pm 0.19) \times 10^{-5}$





## **APPENDIX B**

### **RESULTS OF PLUTONIUM SOLUBILITY EXPERIMENTS IN 0.18 M NaClO<sub>4</sub>**



**Appendix IB. Results of Plutonium solubility experiments  
in 0.18 M NaClO<sub>4</sub> at 25° C and pH 6.0**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	6.00	$(2.60 \pm 0.30) \times 10^{-4}$
4-1A1S2	4	6.02	$(5.19 \pm 0.45) \times 10^{-7}$
4-2A1S2	11	6.14	$(2.43 \pm 0.21) \times 10^{-7}$
4-3A1S2	32	5.94	$(2.45 \pm 0.20) \times 10^{-7}$
4-4A1S2	53	6.01	$(1.41 \pm 0.09) \times 10^{-7}$
4-5A1S2	63	5.94	$(1.27 \pm 0.08) \times 10^{-7}$
4-6A1S2	74	5.95	$(1.05 \pm 0.06) \times 10^{-7}$
4-7A1S2	82	5.98	$(9.19 \pm 0.54) \times 10^{-8}$
4-8A1S2	88	6.00	$(8.89 \pm 0.50) \times 10^{-8}$
4-9A1S2	103	6.07	$(7.95 \pm 0.44) \times 10^{-8}$
4-10A1S2	116	6.09	$(8.71 \pm 0.46) \times 10^{-8}$
4-11A1S2	139	6.02	$(5.54 \pm 0.33) \times 10^{-8}$
4-12A1S2	153	6.09	$(4.95 \pm 0.30) \times 10^{-8}$
4-13A1S2	168	5.90	$(4.83 \pm 0.29) \times 10^{-8}$
4-14A1S2	179	5.98	$(4.52 \pm 0.27) \times 10^{-8}$
4-15A1S2	196	5.91	$(5.08 \pm 0.30) \times 10^{-8}$
4-16A1S2	214	5.93	$(4.09 \pm 0.25) \times 10^{-8}$

average 4-11A1S2 through 4-16A1S2

$(4.84 \pm 0.49) \times 10^{-8}$

**Appendix IIB. Results of Plutonium solubility experiments  
in 0.18 M NaClO<sub>4</sub> at 25° C and pH 7.0**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	7.00	$(2.40 \pm 0.20) \times 10^{-4}$
5-1A4S2	4	6.98	$(1.52 \pm 0.13) \times 10^{-7}$
5-2A1S2	11	7.10	$(8.77 \pm 0.76) \times 10^{-8}$
5-3A1S2	32	6.99	$(9.12 \pm 0.79) \times 10^{-8}$
5-4A1S2	53	7.01	$(6.54 \pm 0.42) \times 10^{-8}$
5-5A1S2	63	7.07	$(6.47 \pm 0.43) \times 10^{-8}$
5-6A1S2	75	6.99	$(6.48 \pm 0.36) \times 10^{-8}$
5-7A1S2	88	7.04	$(6.13 \pm 0.34) \times 10^{-8}$
5-8A1S2	91	7.01	$(6.60 \pm 0.37) \times 10^{-8}$
5-9A1S2	103	6.97	$(5.91 \pm 0.32) \times 10^{-8}$
5-10A1S2	110	---	$(5.11 \pm 0.28) \times 10^{-8}$
5-11A1S2	116	7.06	$(5.43 \pm 0.29) \times 10^{-8}$
5-12A1S2	139	7.00	$(4.51 \pm 0.27) \times 10^{-8}$
5-13A1S2	153	7.07	$(4.54 \pm 0.27) \times 10^{-8}$
5-14A1S2	168	6.95	$(4.13 \pm 0.25) \times 10^{-8}$
5-15A1S2	179	7.02	$(3.98 \pm 0.24) \times 10^{-8}$
5-16A1S2	195	6.95	$(4.19 \pm 0.25) \times 10^{-8}$
5-17A1S2	214	7.09	$(4.11 \pm 0.25) \times 10^{-8}$

average 5-4A1S2 through 5-17A1S2

$(5.30 \pm 1.04) \times 10^{-8}$

**Appendix IIIB. Results of Plutonium solubility experiments  
in 0.18 M NaClO<sub>4</sub> at 25° C and pH 8.5**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	8.50	$(2.90 \pm 0.30) \times 10^{-4}$
6-1A1S2	4	7.75	$(6.91 \pm 0.59) \times 10^{-7}$
6-2A1S2	11	8.51	$(7.23 \pm 0.62) \times 10^{-7}$
6-3A1S2	32	8.35	$(4.58 \pm 0.39) \times 10^{-7}$
6-4A1S2	53	8.27	$(4.37 \pm 0.24) \times 10^{-7}$
6-5A1S2	63	8.39	$(5.00 \pm 0.27) \times 10^{-7}$
6-6A1S2	75	8.30	$(4.37 \pm 0.24) \times 10^{-7}$
6-7A1S2	88	8.45	$(4.92 \pm 0.27) \times 10^{-7}$
6-8A1S2	89	8.47	$(4.31 \pm 0.24) \times 10^{-7}$
6-9A1S2	103	8.37	$(4.47 \pm 0.23) \times 10^{-7}$
6-10A1S2	116	8.54	$(3.64 \pm 0.19) \times 10^{-7}$
6-11A1S2	139	8.47	$(2.87 \pm 0.17) \times 10^{-7}$
6-12A1S2	147	8.45	$(2.60 \pm 0.15) \times 10^{-7}$
6-13A1S2	153	8.49	$(3.15 \pm 0.19) \times 10^{-7}$
6-14A1S2	168	8.32	$(3.59 \pm 0.21) \times 10^{-7}$
6-15A1S2	179	8.26	$(3.33 \pm 0.20) \times 10^{-7}$
6-16A1S2	195	8.38	$(3.17 \pm 0.19) \times 10^{-7}$
6-17A1S2	214	8.50	$(4.22 \pm 0.24) \times 10^{-7}$

average 6-3A1S2 through 6-17A1S2

$(3.91 \pm 0.76) \times 10^{-7}$



## **APPENDIX C**

### **RESULTS OF AMERICIUM/NEODYMIUM SOLUBILITY EXPERIMENTS IN 0.18 M NaClO<sub>4</sub>**





**Appendix IC. Results of Americium/Neodymium solubility experiments in 0.18 M  
NaClO<sub>4</sub> at 25° C and pH 6.0**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	6.00	$(2.20 \pm 0.22) \times 10^{-4}$
7-1A6S2	1	6.00	$(9.75 \pm 0.51) \times 10^{-6}$
7-2A1S2	11	6.41	$(6.19 \pm 0.32) \times 10^{-6}$
7-3A1S2	22	6.20	$(9.40 \pm 0.48) \times 10^{-6}$
7-4A1S2	46	6.06	$(6.06 \pm 0.31) \times 10^{-6}$
7-5A1S2	65	6.05	$(8.49 \pm 0.46) \times 10^{-6}$
7-6A1S2	85	5.95	$(1.41 \pm 0.07) \times 10^{-5}$
7-7A1S2	106	6.08	$(7.93 \pm 0.40) \times 10^{-6}$
7-8A1S2	127	5.93	$(5.98 \pm 0.31) \times 10^{-6}$
7-9A1S2	150	5.97	$(4.91 \pm 0.26) \times 10^{-6}$
7-10A1S2	171	5.99	$(4.65 \pm 0.24) \times 10^{-6}$
7-11A1S2	190	5.97	$(5.63 \pm 0.29) \times 10^{-6}$
7-12A1S2	247	5.99	$(1.17 \pm 0.06) \times 10^{-6}$
7-13A1S2	249	5.95	$(6.64 \pm 0.38) \times 10^{-8}$
7-14A1S2	250	5.95	$(3.04 \pm 0.15) \times 10^{-7}$
7-15A1S2	252	5.94	$(5.37 \pm 0.31) \times 10^{-7}$
7-16A1S2	263	5.87	$(7.21 \pm 0.43) \times 10^{-9}$
7-17A1S2	312	6.02	$(1.02 \pm 0.06) \times 10^{-5}$
7-18A1S2	346	5.98	$(1.26 \pm 0.07) \times 10^{-5}$
7-19A1S2	351	5.96	$(6.09 \pm 0.35) \times 10^{-6}$

average 7-1A6S2 through 7-19A1S2

$(6.00 \pm 4.23) \times 10^{-6}$

**Appendix IIC. Results of Americium/Neodymium solubility experiments in 0.18 M  
NaClO<sub>4</sub> at 25° C and pH 7.0**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	7.00	$(2.00 \pm 0.22) \times 10^{-4}$
8-1A6S2	1	6.93	$(2.05 \pm 0.11) \times 10^{-6}$
8-2A1S2	11	7.16	$(1.35 \pm 0.07) \times 10^{-6}$
8-3A1S2	22	7.20	$(2.59 \pm 0.14) \times 10^{-7}$
8-4A1S2	46	7.01	$(2.73 \pm 0.14) \times 10^{-7}$
8-5A1S2	65	7.03	$(2.71 \pm 0.15) \times 10^{-7}$
8-6A1S2	85	6.94	$(5.96 \pm 0.30) \times 10^{-7}$
8-7A1S2	106	7.02	$(2.42 \pm 0.12) \times 10^{-7}$
8-8A1S2	127	7.07	$(4.47 \pm 0.23) \times 10^{-7}$
8-9A1S2	150	6.98	$(2.02 \pm 0.11) \times 10^{-7}$
8-10A1S2	171	6.99	$(2.95 \pm 0.15) \times 10^{-7}$
8-11A1S2	190	6.95	$(5.58 \pm 0.29) \times 10^{-7}$
8-12A1S2	253	6.95	$(4.64 \pm 0.30) \times 10^{-8}$
8-13A1S2	263	6.93	$(1.70 \pm 0.09) \times 10^{-7}$
8-14A1S2	312	7.02	$(3.78 \pm 0.16) \times 10^{-7}$
8-15A1S2	375	6.95	$(3.36 \pm 0.18) \times 10^{-7}$
8-16A1S2	381	7.04	$(2.86 \pm 0.17) \times 10^{-7}$
8-17A1S2	387	7.02	$(2.05 \pm 0.17) \times 10^{-7}$
average 8-3A1S2 through 8-17A1S2			$(3.04 \pm 1.44) \times 10^{-7}$

**Appendix IIIC. Results of Americium/Neodymium solubility experiments in 0.18 M  
NaClO<sub>4</sub> at 25° C and pH 8.5**

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	8.50	$(2.36 \pm 0.22) \times 10^{-4}$
9-1A6S2	1	8.43	$(7.57 \pm 0.45) \times 10^{-7}$
9-2A1S2	11	8.32	$(3.21 \pm 0.18) \times 10^{-7}$
9-3A1S2	22	8.41	$(1.28 \pm 0.07) \times 10^{-8}$
9-4A1S2	46	8.30	$(3.80 \pm 0.41) \times 10^{-10}$
9-5A8S2	65	8.64	$(6.45 \pm 0.80) \times 10^{-10}$
9-6A1S2	85	8.32	$(3.39 \pm 0.63) \times 10^{-10}$
9-7A1S2	106	8.38	$(2.83 \pm 1.70) \times 10^{-10}$
9-8A1S2	127	8.36	$(1.77 \pm 1.33) \times 10^{-10}$
9-9A1S2	150	8.48	$(9.64 \pm 4.72) \times 10^{-11}$
9-10A1S2	171	8.40	$(1.91 \pm 1.11) \times 10^{-10}$
9-11A1S2	190	8.42	$(1.69 \pm 0.56) \times 10^{-10}$
9-12A1S2	233	8.38	$(4.15 \pm 0.71) \times 10^{-10}$

average 9-4A1S2 through 9-12A1S2

$(2.99 \pm 1.68) \times 10^{-10}$

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

TWS-LBL-01-93-02, pp. 81-302

TWS-LBL-01-93-03, pp. 39- 67 (open)

TWS-LBL-01-93-04, pp. 1- 241 (open)

TWS-LBL-12-93-02, pp. 1- 151 (open)