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Title:

NEPTUNIUM REDOX BEHAVIOR AND SOLUBILITY
IN J-13 CONDITIONS

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Submitted to:

YUCCA MOUNTAIN SITE CHARACTERIZATION
PROJECT

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**TABLE A - Description/completion criteria location summary for U. S. Department of Energy
Report on Solubility Experiments. Deliverable No.: SP34FAM4. Due
Date: June 06, 1997.**

CRITERIA	TEXT LOCATION
<u>TECHNICAL REQUIREMENTS</u>	
This deliverable will be a letter report submitted to the M&O SPO office, and will be considered complete upon the acceptance of the product by the SPO technical lead for geochemistry.	
This report will document the technical results of trying to reduce Np(V) solutions to Np(IV) solutions using solutions with known Eh's from known ratios of common redox species Fe(II)/(III) and Mn(II)/(IV).	p. 7-12
The effects of high temperature (300°C) on a Np(V) solution will also be reported, as will the Np solubility from undersaturation and Ksp of a well characterized Np ₂ O ₅ sample.	pp. 27
Acquired data will be identified. This deliverable supports the level 3 reports:	
a) Summary report of geochemistry/transport lab tests,	
b) UZ site transport model,	
c) SZ site transport model.	

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SP34FAM4: Letter Report

Neptunium Redox Behavior and Solubility in J-13 Conditions

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INTRODUCTION:

Modeling work using the standard EQ3/6 database based on Lemire's data (Lemire, 1984) indicates Np(IV) solids should form in Yucca Mountain waters (Janecky et al, 1994; Janecky et al, 1995). However, the lack of observation of Np(IV) solids in solubility studies (Nitsche et al, 1992; Efurd et al, 1996) and the existence of other neptunium data (Rai and Ryan, 1985; Rai et al., 1987) requires the GEMBOCHS Np database to be challenged. It is entirely possible that the Np(V) solids formed in the solubility experiments may be metastable, requiring only time and/or a catalyst to transform to the Np(IV) solid. The most important effect of oxidation state on the Np solubility is that the Np(IV) solids (e.g. NpO_2) are orders of magnitude less soluble than the Np(V) currently considered in PA calculations. The objectives of this on-going study is to assess whether these low-solubility phases will control Np solubility under the proposed repository conditions. Reduction of Np(V) (e.g. Np_2O_5) to Np(IV) (e.g. NpO_2) in the solid state would occur in the solution phase in contact with the equilibrium (or steady state) solids. Therefore, in order to confirm that such a redox reaction may occur, solution phase studies must be performed to better understand the Np(IV/V) couple. The methods described in this report include exposure of Np(V) to solutions of known E_h as a function of pH and temperature. Furthermore, analytic results from on-going solubility experiments from undersaturation, using Np solids formed in previous oversaturation experiments, are reported.

In the first set of these solution experiments, the influence of known ratios of natural redox couples such as Fe(II)/Fe(III) and Mn(II)/Mn(IV) were tested in J-13 like water. In addition to experimenting with known redox conditions, these experiments will give preliminary evidence for the effects of mineral assemblages available at YM and which will act as a source (possibly along with rod containers) of these solution species. These experiments were carried out at pHs and temperatures (25 and 85°C) that essentially bracket

the conditions expected at YM. The temperature dependence part might determine if there is merely a kinetic barrier preventing the formation of Np(IV).

Finally, a scoping experiment testing the solubility of neptunium from undersaturation was performed in J-13 water. This neptunium solid came from the oversaturation experiments and had been found to consist mostly of Np_2O_5 and to be at least metastable in oversaturated solubility experiments in J-13 water. This scoping experiment results with the analytical neptunium solubility from J-13 solutions at pH 6, 7, and 8.5 and $T = 25$ and 90°C at the due date of the report and compares these values to those from the oversaturated experiment performed at LANL previously. This comparison would corroborate the attainment of equilibrium and would provide bracketed, and more defensible solubility ranges for YM.

This letter report documents the on-going technical results of attempting to reduce Np(V) solutions to Np(IV) using solutions with known E_h 's from known ratios of common redox species Fe(II)/Fe(III) and Mn(II)/Mn(IV). The experiments encompass relevant pH's and temperatures (25 and 80°C). In the second part, analytical neptunium concentrations are reported from scoping solubility experiments from undersaturation in J-13 water.

PART I. SOLUTION REDOX BEHAVIOR OF NP(V)

I.1 Introduction

As noted above, the identity of the thermodynamically stable solubility-limiting solid for neptunium in YMP-relevant conditions is a matter of contention. If a Np(IV) solid could be shown to form, the Project could take credit for at least 2 orders of magnitude lower Np solubility than present empirical results show, and Np sorption would also be considerably enhanced. Such a transformation would have to occur in the solution phase in contact with the solid, and it would have to involve the reorganization of the multiply bonded dioxo moiety (yl) that exists for the (V) state but not for the (IV) state. To encourage such a transformation, we investigated the capability of common redox reagents such as Mn(II) and Fe(II) to reduce Np(V). Figures 1 and 2 show schematics of the E_h -pH behavior for these species (Stumm and Morgan, 1981) with the Np(IV/V) redox couple (Hobart, 1990) overlaid. These diagrams are only schematics; while the Fe and Mn

Figure 1. Eh vs. pH diagram for manganese/manganese minerals in contact with air and for the Np(IV/V) couple.

Figure 2. Eh vs. pH diagram for iron/iron minerals in contact with air and for the Np(IV/V) couple.

diagrams are quite accurate and based on the thermodynamics (Stumm and Morgan, 1981), the Np(IV/V) E_h -pH diagram is not accurately known. From these diagrams, it is clear that iron(II) is more reducing than manganese(II), and that Np(V) can conceivably co-exist with Mn(II) throughout the relevant pH range. We have therefore concentrated on the Fe(II) studies. Furthermore, Fe(II) is more strongly reducing toward Np(V) at higher pH's. It is also important to emphasize that these diagrams are for room temperature, and the uncertainty only increases with increased temperature relevant to the near-field of any high-level nuclear waste repository.

I.2. Experimental

The basis for monitoring these experiments is the electronic absorption spectrum for NpO_2^+ and $\text{NpO}_2\text{CO}_3^-$, two of the three predominant Np(V) species in J-13 conditions for $20 < T < 90^\circ\text{C}$ (the third being NpO_2OH , Tait et al, 1995). Especially useful are the sharp, strong peaks in the near infrared (NIR) regions of the spectrum at 980 and 998 nm respectively (Nitsche et al, 1990; Neck et al., 1994). In contrast, Np(IV) species have very low solubility and extremely dark solids. Additionally, while Fe(II) absorbs very little in the visible to NIR region of the spectrum, Fe(III) has a strong absorption tail that extends from the ultraviolet region to the visible region, so oxidation of iron can be noticed immediately. Furthermore, Fe(III) hydrolysis complexes are much less soluble than Fe(II) complexes, so noticeable flocculation and precipitation of iron(III) oxy-hydroxides accompanies iron oxidation. Electronic absorption spectra were taken with a Perkin-Elmer Lambda 19 spectrophotometer in the absorbance mode at a scan speed of 60 nm/min, 2 nm slits (Vis region), NIR sensitivity = 2 ($\Rightarrow$ ~2 nm slits in the NIR region), 1 cm quartz cuvettes, and H_2O vs. H_2O background spectra.

The neptunium(V) stock solutions were purified and prepared as reported previously (Tait et al., 1995). Specifically, neptunium(V) was precipitated out of a stock solution using NaOH and washed with H_2O several times. The precipitate was then redissolved in 1M HCl and reduced to Np(III) on a mercury cathode electrode, resulting in a dark blue-purple colored solution of Np(III). This solution was sparged with air to give a green Np(IV) solution in 1M HCl. Two methods were used to load the Np(IV) onto an anion exchange resin column (Lewatit MP-500-FK, 40 to 70 mesh resin).

Method A. An equal volume of 16M HNO_3 was added to the Np(IV) solution to form the gray-colored nitrate complex of Np(IV) in 8M HNO_3 . This was loaded onto an

anion exchange resin column (Lewatit) which was pretreated with 8M HNO₃. The loaded column was washed several times with 8M HNO₃ and the Np(IV) was eluted with 0.5M HNO₃. The gray color of the Np(IV) nitrate complex dissipated and a green solution was collected. However, using this method, approximately 50% of the Np(IV) was oxidized to Np(V) by the HNO₃ and washed through the column. The washes containing the Np(V) were collected and recycled with other solutions for future column purification.

Method B. The appropriate amount of concentrated HCl was added to the Np(IV) solution to make a greenish-brown colored solution of Np(IV) in 9M HCl. This was loaded onto an anion exchange column (Lewatit) which had been pretreated by washing with 9M HCl. After several washings with 9M HCl the Np(IV) was eluted with 0.5M HCl. The brown color of the Np(IV) chloride complex dissipated and a green solution was collected. Only the middle portion of the band was collected, initial eluate and tailings are recycled into the next batch for column purification. This is the preferred method of purification method because oxidation of Np(IV) to Np(V) was decreased with the use of 9M HCl and approximately 70% of the Np(IV) was collected.

The purified Np(IV) stock solution was oxidized to Np(VI) using fuming perchloric acid. The Np(VI) solution was diluted with water to adjust the Np(VI) concentration to approximately 0.1M. Reduction to Np(V) was completed using a conventional 3-electrode electrochemical system (Hobart et al. 1982). The working electrode was a Pt-screen, the counter electrode a Pt-wire, and the reference electrode a saturated calomel. The electrodes were separated from the experimental solution with a Vycor frit. A potential of +0.56 V / SCE was applied. The resultant neptunium(V) solution was analyzed by spectrophotometry to ensure no other peaks from other neptunium oxidation states were found, and the concentration of the pure Np(V) stock solution was then determined using the 980 nm absorption peak, $\epsilon = 390 \text{ M}^{-1} \text{ cm}^{-1}$.

The pH was measured with a Ross Combination pH Electrode (Orion Research Inc., Boston, MA) using an Orion Model EA940 Expandable Ion meter (Orion Research Inc., Boston, MA.). The pH electrode was calibrated before each set of pH measurements using Fisher Certified 7.00 and 10.00 buffers, which were re-checked after the pH measurement. The temperature was controlled with an 1130 VWR heated water circulator, stable to $\pm 1^\circ \text{C}$.

I.3. Results and Discussion

As noted in the Introduction, Fe(II) should be less reducing toward Np(V) at acidic and neutral pHs than at basic conditions. To test this, the original experiment was carried out at pH = 7.1. The spectrum of 200 μ M Np(V) in 3 mM NaHCO₃ before addition of FeCl₂ is shown in Figure I.1.a, which is dominated by the 980 nm peak of NpO₂⁺. The "peak" at 1153 nm (and to a much lesser extent at 961 nm) is actually residual H₂O overtone absorption not exactly cancelled out by the two cells in the double beam spectrometer: sometimes it appears as a peak and other times it appears as a dip, depending on the positioning of the sample cell. The discontinuity at 865 nm is due to a filter change in the spectrometer as it changes from NIR operation to visible range operation. Upon addition of a stoichiometric amount of Fe(II) under an inert (Ar) atmosphere, the spectrum is unchanged (Fig. I.1.b). Periodic monitoring of the sealed cell (ground glass joint, double parafilm layers) continued to show no reduction to day 56 (Figure I.1.c), at which point we decided to heat the sample to see if the redox conditions at higher temperatures and/or better ability to surmount a kinetic activation barrier would allow for the reduction of NpO₂⁺.

The quartz cuvette containing the NpO₂⁺/FeCl₂ solution was clamped into the water bath of a VWR 1130 heated water circulator, with the circulating pump on low for mild water flow at the cell to ensure temperature transfer. The temperature control was set to 85°C, and the temperature of the bath ramped-up to this temperature over the course of 20 minutes. The temperature was held at 85°C for 15 more minutes, at which point the control was set back to 20°C. After 15 minutes with the heater off, the temperature of the bath had only dropped to 77°C, at which point the sample was removed and absorption spectra were taken. Figure I.2 shows the progression of the spectra as the sample cooled back to room temperature. In all of these spectra, the Np(V) peak is still evident, and the final spectrum is still unchanged from the original spectrum. The apparent new peaks at 1153 and 961 nm at increased temperature occurs only because the O-H overtone of H₂O is even more unbalanced than at room temperature and does not indicate any change in the neptunium. Therefore we conclude that at acidic and neutral pHs there is no evidence for the reduction of Np(V) by Fe(II) in J-13 like conditions to 85°C in an experimentally reasonable length of time.

Figure I.1 Absorption spectrum of 200 mM NpO_2^+ at pH=7.1 before and after addition of FeCl_2 .

The results were quite different at more basic pH (9.40) and in presence of more Fe(II). At this pH in J-13 like water, the Np(V) spectrum is dominated by the 989 nm peak of $\text{NpO}_2\text{CO}_3^-$ (Fig. I.3a). Addition of 2 mM FeCl_2 powder under anaerobic conditions (N_2 flush for 20 minutes before addition with a N_2 stream over the solution during the addition) resulted in the fast oxidation of Fe(II) to Fe(III), as evidenced by an orange-brown color developing in the solution. The sample was sealed in a 1 cm quartz cuvette (ground glass joint, 2 layers of parafilm as before) and the spectrum was immediately taken (Fig. I.3b). While the spectrum was taken, flocculation and precipitation of Fe(III) in the rest of the solution was observed, so when the spectrum I.3b was finished, another spectrum was taken (Fig. I.3c). It is to note that the oxidation of Fe(II) resulted in a change of pH in the remaining solution, which was re-measured at 7.51, consistent with hydrolysis occurring for the Fe(III) species leading to the precipitation of an oxy-hydroxide rust. Finally, another spectrum was taken 2 hours after I.3c (Fig. I.3d), and this spectrum is directly compared to the starting spectrum in Figure I.3d combined. Almost all of the Np(V) has been removed from solution by the addition of excess FeCl_2 . The question of whether the iron(II) was oxidized by the Np(V) or residual oxygen in solution will always occur in a positive result like this. However, if residual oxygen were responsible, the disappearance of the Np(V) must be explained. Sorption of NpO_2^+ or $\text{NpO}_2\text{CO}_3^-$ to the precipitating rust would be weak and should not quickly remove the neptunium. Coprecipitation with the iron rust might occur, but with time the Np(V) should re-enter solution. Such a re-solubilization was not observed in a spectrum taken 5 days after the experiment.

The investigations performed showed no reduction of Np(V) in J-13 up to 85°C. However, the increase of the Np(V) concentration in solution due to an increase in pH and Fe(II) concentration suggests the reduction of Np(V) to Np(IV). Further experiments have to be performed to prove that the decrease in Np(V) concentration is not related to a coprecipitation or sorption on the amorphous iron oxy-hydroxides and is in fact caused by the formation of Np(IV) and the expected precipitation of NpO_2 . A temperature increase to 85°C did not result in the formation of Np(IV). This result confirms the results from recent solubility studies performed from both under- and oversaturation where Np(V) oxide, Np_2O_5 , was found as the predominant solid phase. Experiments are in progress to study the redox stability of Np(V) in the temperature up to 300°C. The results from these high-temperature studies will be reported in the next milestone.

Figure I.2. Effect of heating Np(V)/Fe(II) solution of 85°C.

Figure I.3. Effect of Fe(II) addition at pH 9.4 on the redox stability of Np(V) .

Figure I.4. Overlaid spectra I.3.a and I.3.d.

PART II. SOLUBILITY EXPERIMENTS FROM UNDERSATURATION

II.1 PREFACE

This report is one in a series of reports documenting experimental solubility and speciation studies of radionuclides in groundwaters from the Yucca Mountain region. The objectives and experimental concepts were discussed in detail in the first report of the series (Milestone 3010), entitled "Measured Solubilities and Speciations of Neptunium, Plutonium, and Americium in a Typical Groundwater from the Yucca Mountain Region." (Nitsche et al., 1992) Portions of the objectives and experimental concepts from Milestone 3010 are included in this letter report to make it a stand-alone document.

II.2 ABSTRACT

Solubility and speciation data are important in understanding aqueous radionuclide transport through the geosphere. They define the source term for transport and retardation processes. Solubility and speciation data are useful in verifying the validity of geochemical codes that are part of predictive transport models. Ideally, solubility experiments should

approach solution equilibrium from both oversaturation and undersaturation. Milestone 3411 entitled "Measured Solubilities and Speciation of Neptunium and Plutonium in J-13 Groundwater" (Efurd, et al., 1996) reported the results for solubility experiments from oversaturation of neptunium and plutonium in J-13 groundwater at three different temperatures (25°, 60° and 90° C) and pH values (6.0, 7.0 and 8.5). Unlike previous solubility experiments, the pH was not controlled throughout the experiment, and hence the ionic strength of the solutions more closely resembles that of J-13 water. The characterized solids from the 25°C and 90° C experiments reported in Milestone 3411 were reintroduced into fresh solutions of J-13 groundwater to approach the steady state from undersaturation. The pH was not controlled throughout these undersaturation experiments, and hence the ionic strength of the solutions more closely resembles that of J-13 water. The results of the undersaturation experiments are summarized in this letter report. The neptunium solubility decreased with increasing pH. The solubilities of ^{237}Np ranged from a high of $(8.40 \pm 0.87) \times 10^{-4}$ at pH 6.0 and 90° C to a low of $(3.85 \pm 1.40) \times 10^{-6}$ at pH 8.5 and 90°C. The neptunium solubilities obtained in these undersaturation solubility experiments were consistent with those obtained in the oversaturation experiments reported in Milestone 3411.

II.3. EXECUTIVE SUMMARY

We studied the solubilities of neptunium in J-13 groundwater from the Yucca Mountain region, Nevada, from undersaturation at two temperatures and three hydrogen ion concentrations. The actinide solubilities were determined from undersaturation at 25°C and 90°C and initial pH at 6.0, 7.0 and 8.5. Table I summarizes the results. Sample evaporation was minimized in order to maintain the ionic strength of the solutions as close to that of J-13 water as practical for the duration of the experiments. The pH of each solution was initially adjusted at the initiation of the solubility experiments by bubbling carbon dioxide through the J-13 water. No pH adjustments were performed during the time the undersaturation solubility experiments were conducted. In general, the neptunium solubilities decreased with increasing pH. The neptunium solubilities obtained in these undersaturation solubility experiments were consistent with those obtained in the oversaturation experiments reported in Milestone 3411.

Table I. Summary of results for solubility experiments on neptunium in J-13 groundwater at pH 6.0, 7.0 and 8.5 at 25 °C and 90 °C

Steady state concentration (M)

	25 °C	90 °C
pH 6.0	$(6.5 \pm 1.1) \times 10^{-4}$	$(9.1 \pm 1.8) \times 10^{-4}$
pH 7.0	$(3.1 \pm 0.2) \times 10^{-5}$	$(8.6 \pm 2.3) \times 10^{-6}$
pH 8.5	$(1.5 \pm 0.6) \times 10^{-5}$	$(5.8 \pm 2.5) \times 10^{-6}$

II.4. PURPOSE AND OBJECTIVE

Yucca Mountain, Nevada, has been identified for site characterization as the location for a potential repository of high-level nuclear waste. A worst case scenario, intrusion of water into the repository, must be considered for risk assessment. Water moving through the emplacement area towards the accessible environment can transport radionuclides in two ways: either as dissolved species in the water or as particulate material 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 project (US DOE, 1988). The purpose of this study is to supply data for calculating radionuclide transport along potential transport pathways from the repository to the accessible environment.

In selecting these experiments, we have considered the generic U.S. Nuclear Regulatory Commission (NRC) technical position entitled "Determination of Radionuclide Solubility in Groundwater for Assessment of High-Level Waste Isolation" (Brooks and Cerrado, 1984). 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. To predict behavior at higher temperatures expected in the near field of a potential repository, 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.

Radionuclide concentrations in water passing through the emplacement area can be limited by two mechanisms: low dissolution rates of the solid waste form or solubility of individual radionuclides. If solid waste dissolution rates are low enough, it may not be necessary to depend on the solubility 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 provide an upper bound on radionuclide concentrations in solution and provide a basis for "extrapolation to long term behavior." The rate of groundwater flow through the waste is expected to be sufficiently slow to permit saturation of 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 for solution transport (Dozol and Hageman, 1993).

As radionuclides are transported along flow paths to the accessible environment, changing conditions of the water can alter their solubility. Decreases in solubility can decrease radionuclide concentrations. A knowledge of radionuclide solubilities under the conditions of 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 is 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 (Ogard and Kerrisk, 1984). Water from Well J-13 is a reference water for the unsaturated zone near the proposed emplacement area. The water 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 (Dozol and Hageman, 1993; Lemire, 1984; Pacquette and Lemire, 1981). These experiments therefore provide conservative results.

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) (Ogard and Kerrisk, 1984). The solubility experiments that use Well J-13 water were conducted at temperatures of 25 and 90 °C. This span covers the range from pre-emplacement temperatures to the maximum temperature at which solubility would be important.

II.5. CONCEPT OF SOLUBILITY STUDIES

Solubility establishes an upper limit for the dissolved components in the source term for radionuclide migration from a potential repository. Studies of the solubility of radionuclides in groundwater 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.

The solubility experiments described here will focus on a detailed knowledge of (1) the nature and chemical composition of the solubility-controlling solid and (2) the concentration of the components in solution. Determination of speciation of the radionuclide in the solution phase is the goal of other studies in the Solubility Task. Meaningful thermodynamic parameters can be determined when solubility studies satisfy three criteria: (1) attainment of steady state conditions, (2) determination of accurate solution concentrations, and (3) identification of the solid phase.

II.5.1. 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 steady state 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 time frame in solubility experiments and it must be demonstrated that steady state is reached. This can be accomplished by experimentally determining the solution concentration as a function of time. When the concentration stays constant for several months, it is assumed that steady state 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" (Brooks and Corrado, 1984). 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 solubility, but metastable solids having higher solubility than the thermodynamically defined solids. The term "steady-state" implies this 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 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. The results for the oversaturation experiments were reported in Milestone 3411. In this study we are reporting results for the undersaturation experiments.

II.5.2. Phase Separation

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

The solutions used to measure the neptunium concentrations were prepared by ultrafiltration. Each filter was preconditioned by passing a volume of the appropriate radionuclide solution through it and then discarding the filtrate.

II.5. 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 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 (Vorhees, 1985; Rard, 1989).

II.6 EXPERIMENTAL DETAILS

We studied the solubility of neptunium from undersaturation at 25° C and 90°C and pH values of 6, 7, and 8.5. The solubilities were studied from undersaturation by injecting a small amount of the neptunium solids formed during the oversaturation experiments into 25 mL aliquots of groundwater obtained from Well J-13.

II.6.1. Production of Neptunium Solids Used in Undersaturation Studies

Neptunium stock solution were prepared by dissolving ultra-pure neptunium metal in perchloric acid. The neptunium stock solution was prepared by placing 1.36 g of electrorefined neptunium metal in a 125 mL narrow mouth Teflon FEP bottle and adding 20 mL of ultra pure perchloric acid (Seastar Chemicals Inc, Sidney, BC Canada). The sample was heated in the bottle on a hot plate until the volume was reduced to approximately 1 mL. The sample was cooled to room temperature and the bottle was purged with argon until the excess perchloric acid was evaporated from the bottle. The sample was diluted with de-ionized water and adjusted to 1M with respect to perchloric acid. The solution was digested in an approximately 60° C water bath overnight. The neptunium solution was filtered through a 0.2 µm nylon syringe filter unit (Gelman Sciences, Ann Arbor, MI) into a 30 mL narrow mouth Teflon FEP bottle. This material was used to conduct the oversaturation solubility experiments. The precipitates formed in the 25 and 90° C oversaturation experiments were separated from the mother liquid by centrifugation. The solids were dried under the corresponding CO₂/Ar atmosphere used in the solubility experiment. These solids were then reintroduced into fresh J-13 water to conduct undersaturation experiments.

II.6.2. Characterization of Neptunium Solids

The steady-state Np solids formed in the oversaturation experiments were greenish brown in color. The solids were analyzed by X-ray diffractometry, diffuse reflectance spectroscopy, and Raman vibrational spectroscopy. A few milligrams of each neptunium precipitate were placed on a Teflon holder, covered with Kapton foil and secured with an O-ring to prevent contamination. The spinning sample was irradiated with Cu-K α 1 radiation generated by the X-ray powder diffractometer INEL CPS-120 (INEL Inc.). To calibrate the instrument the powder pattern of silicon, the NBS Standard Reference Material No. 640, CAS No. 7440-21-3, was collected before and after the sample analysis.

Only a few sharp Bragg reflections were observed and no difference in the d spacings could be observed with varying temperature or CO₂ partial pressure. However, due to the increased temperature the powder pattern of the neptunium solids produced at 90° C showed sharper peaks. Fig 1 shows the X-ray powder diffraction pattern of the neptunium solids formed at 90° C at pH = 6 (cell 2) and pH = 7 (cell 4) are shown. Both of these neptunium solids formed in the J-13 groundwater show the same powder diffraction pattern indicating the formation of solid phases with the same structural features.

Figure 1: X-ray diffraction powder pattern for the Np solids precipitated at 25 and 90 °C in J-13 groundwater.

Table II shows the X-ray powder diffraction pattern of the neptunium solids formed at 90 °C at pH = 6 (cell 2) and pH = 8.5 (cell 4) and in comparison with published data of Np_2O_5 and Np_3O_8 . The obtained powder patterns match the reported data of both Np_2O_5 and Np_3O_8 . Because of the low peak intensity, a definitive differentiation between the two oxides is not possible, but the formation of the more highly oxidized neptunium in Np_3O_8 is not likely. In addition to the Bragg reflections of the neptunium oxide, few peaks have been observed that could not be matched with any other neptunium solids reported in the literature. It appears that Np_2O_5 in different stages of crystallinity was the solubility limiting solid in the oversaturation solubility study.

Table II: Bragg reflections of the Np precipitates formed in J-13 Waters at 90° C in comparison with Np_3O_8 and Np_2O_5

Np_3O_8 d (Å)	Np_2O_5 d (Å)	Cell 2, 90 °C d (Å)	Cell 4, 90 °C d (Å)
		7.390	7.399
4.14		4.170	4.175
		3.712	3.720
3.45	3.470	3.469	3.469
3.27	3.300	3.279	3.289
		3.179	
		2.864	
	2.678		2.674
2.66	2.666	2.669	
2.58	2.586	2.583	2.589
		2.484	2.482
		2.452	2.454
		2.209	
2.09	2.092	2.093	2.094
2.04	2.043	2.038	2.043
1.93	1.934	1.929	1.931
1.83	1.841		1.839
	1.831	1.835	
1.79	1.796	1.795	1.780
	1.790	1.790	1.792
1.76	1.766	1.765	1.766
1.75	1.757		
1.73	1.736	1.736	1.737
1.65	1.646		
1.60	1.607	1.605	1.604

II.6.3. J-13 Water Used for Undersaturation Studies

The analysis of the J-13 water composition is listed in Table III (Ogard and Kerrisk, 1984).

Table III. Well J-13 Water Composition.

Species	Concentration mM
Ca	0.29
Mg	0.072
Na	1.96
K	0.136
Li	0.009
Fe	0.0008
Mn	0.00002
Al	0.0010
SiO ₂	1.07
F ⁻	0.11
Cl ⁻	0.18
SO ₄ ²⁻	0.19
NO ₃ ⁻	0.16
Alkalinity	2.3 mequiv/L
Total carbonate	2.28
pH	7.0
Eh	700 mV

The J-13 groundwater from barrel (spc 00504079.F27) was filtered through 0.05 μm polycarbonate membrane filters (Nuclepore Corp., Pleasanton, CA). The water's natural carbon dioxide partial pressure (pCO_2) could not be preserved during storage and filtration. The natural state was induced by re-equilibrating the water with CO_2 gas. The well water's total dissolved carbonate ($2.8 \times 10^{-3} \text{ M}$) was preserved at each individual pH by equilibrating the solution with mixtures of CO_2 in argon. The amount of CO_2 at a given pH and temperature was calculated from Henry's constant and the dissociation constants of carbonic acid from literature data (Phillips et al., 1985). 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.

Table IV. Concentrations (in percent) of Carbon Dioxide Gas in Argon Used to Maintain a Total Dissolved Carbonate Concentration of 2.8×10^{-3} M in J-13 Groundwater at Different pH and Temperatures.

	25 °C	90 °C
pH 6.0	6.06 ± 0.02	18.58 ± 0.02
pH 7.0	1.57 ± 0.02	4.05 ± 0.02
pH 8.5	0.060 ± 0.001	0.140 ± 0.001

II.6.4. Pressure Control System

External CO₂ control of the experimental solutions requires the exclusion of atmospheric CO₂. We used controlled-atmosphere glove boxes (Plas Labs, Lansing MI, Model 818-GBB). The test solutions were kept in 135 mL cells that were made of Polyether Etherketone (PEEK) (Polymer Corporation Bulletin, 1984). Each cell had a sealed port at the top that could be removed to withdraw samples and measure pH. Each cell was equipped with 1/8" diameter Teflon line for addition of the appropriate carbon dioxide-argon mixture required to maintain the well waters at their normal carbonate concentrations when their pH values are adjusted to conditions differing from their natural state. The cells were pressurized relative to the atmosphere within the glove boxes. The system was designed to ensure that no significant evaporative loss of the solutions occurred at elevated temperatures. The glove boxes contained an argon atmosphere.

II.6.5. Control System for pH

The pH and carbonate concentration of each cell was established at the initiation of the solubility experiments. No pH adjustments were made during the duration of the experiments. The pH values were measured each time solution was withdrawn to determine solubilities. The pH was measured with Ross Combination pH Electrodes (Orion Research Inc., Boston, MA) using an Orion Model 611 pH/Millivolt Meter (Orion Research Inc., Boston, MA.). The pH electrode was calibrated before each set of pH measurements using the detailed procedure documented in LANL-YMP-DP 35, R3.

II.6.6. Temperature Regulation

The temperature regulation system consists of an aluminum block having 9 cylinders drilled into the aluminum block to accommodate the PEEK cells. The interior of the aluminum block has channels approximately 1 cm wide by 7 cm tall spaced approximately 10 cm apart. Silicone fluid (Dow Corning Corporation, Midland, MI, 550 High Temperature Silicone Fluid) heated by a heating circulator (VWR Scientific, VWRbrand Model 1137) is circulated through the channels in the aluminum block. The aluminum block is insulated on top and sides with approximately 1 cm of extruded polystyrene (U C Industries, Parsippany, NJ) and on the bottom with approximately 0.3 cm of natural cork. The aluminum block was mounted on an orbital shaker (Lab-Line Inc., Melrose Park, IL), and all solutions were shaken continuously at approximately 100 rpm. Temperatures were controlled to within less than 1°C.

II.6.7. 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 and plutonium solutions. The filters contain a YM-type membrane with a calculated pore size of 4.1 nm (Cleveland, 1984). For the separations, the centrifuge (High-speed centrifuge, Speedfuge SFG10K, Savant Instruments Inc.) was heated to the appropriate temperature by passing silicone fluid (Dow Corning Corporation, Midland, MI, 550 High Temperature Silicone Fluid) heated by a heating circulator (VWR Scientific, VWRbrand Model 1137) through copper

coils mounted inside the centrifuge. The centrifuge's walls were insulated with approximately 1 cm of extruded poly styrene (U C Industries, Parsippany, NJ).

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. We used one filter per solution and filtered consecutive 500 μL 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 experiments indicated that 2000 μL preconditioning volumes were ultraconservative. The active sites on the filters were saturated with the first 1000 μL of solution for all temperatures and pH's.

II.6.8. Analysis

After separation of the solution and solid phases, the two components were analyzed separately. Concentration measurements of the supernatants were made by counting aliquots which were stippled onto stainless steel disks, evaporated to dryness under a heat lamp, flamed to dull red and counted on an alpha scintillation counter (Eberline Instrument Corporation, Santa Fe, NM, model SAC-4). The counting efficiency of the scintillation counter was determined by counting plutonium samples traceable to NIST.

II.6.9. 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. The first concentration measurements were performed 27-31 days after initiation of the solubility experiments. Each cell was sampled periodically during the course of the experiments. The number of solubility measurements was kept to a minimum because there was a finite risk associated with opening the cells. If a cell is not properly re-sealed the solution evaporates and the experiment is lost. The solubilities reported are the simple averages of the solubilities determined during the course of the experiments.

II.7. RESULTS AND DISCUSSION

II.7.1 Neptunium Solubility

Concentration profiles as a function of equilibration time and pH for the experiments are shown in Figures 2 and 3. The individual measurements are shown in Appendix A. In general, the neptunium solubility decreased with increasing pH and temperature. Comparison of these analytic results from undersaturation with the results reported previously from oversaturation (Efurd et al., 1996) shows remarkable consistency. It is important to note that the ionic strength in these experiments were much closer to J-13 waters than the original oversaturation experiments. In the original experiments we had to add 6 M NaOH to the J-13 waters to neutralize the HClO_4 that was in the neptunium stock solution. The Na^+ concentrations in the original oversaturation experiments were 2.3 to 4.1 times the original amount found in the J-13 waters. In the present experiments from undersaturation, the neptunium was added as a solid. Hence, there was no initial NaOH or HClO_4 that required the addition of the neptunium stock solution as in the oversaturation experiments. The initial pHs after equilibration with Argon-carbon dioxide were pretty close to the proper values. The initial setting of the pH and carbonate concentrations were relatively simple and did not require addition of very much NaOH and/or HClO_4 . Therefore, the Na^+ concentrations were only increased by 10%-53% over their original concentrations in J-13 waters, while the original oversaturation experiments doubled to quadrupled the Na^+ concentrations. The consistency of these measurements therefore corroborates the relevance to YM of the previous oversaturation experiments (Efurd et al, 1996), as did the identification of non-sodium solid phases in that study.

This study confirms the results of the Np solubility in J-13 determined from oversaturation. In fact, the conditions in this undersaturation experiment were closer to those of J-13 than in the previous investigation. Clearly, Np(V) oxides are favoured over Np(V) carbonate due to the low carbonate concentration in J-13. This leads to a significant lower solubility of Np(V) in J-13. The thermodynamic solubility product of Np_2O_5 will be determined in well-defined low concentrated electrolyte solution (0.1 m NaClO_4). The Np solubility in J-13 do not represent a thermodynamic K_{sp} of a Np solid phase since potential ligands available in the complexed groundwater may complex Np in solution. Thus both complexation reactions and solubility product of the solubility limiting solid phase are implemented in the apparent Np solubility in J-13. In order to model the Np solubility in J-13, experiments are ongoing to determine the thermodynamic solubility product of Np_2O_5 .

Figure 2. Solution concentration of ^{237}Np at 25°C as a function of time. pH 6 (closed diamonds), pH 7 (closed squares), pH 8.5 (closed triangles).

Figure 3. Solution concentration of ^{237}Np at 90 °C as a function of time. pH 6 (closed diamonds), pH 7 (closed squares), pH 8.5 (closed triangles).

Table V. Solution concentrations of ^{237}Np as a Function of pH and Temperature as Measured in Oversaturation and Undersaturation Experiments.

	pH 6	pH 7	pH 8.5
25 °C	$*(6.5 \pm 1.1) \times 10^{-4}$ $**[5.9 \pm 1.4] \times 10^{-4}$	$(3.1 \pm 0.2) \times 10^{-5}$ $[2.7 \pm 0.7] \times 10^{-5}$	$(1.5 \pm 0.6) \times 10^{-5}$ $[1.8 \pm 0.8] \times 10^{-5}$
90 °C	$(9.1 \pm 1.8) \times 10^{-3}$ $[8.4 \pm 0.8] \times 10^{-4}$	$(8.6 \pm 2.3) \times 10^{-6}$ $[1.5 \pm 0.8] \times 10^{-5}$	$(5.8 \pm 2.5) \times 10^{-6}$ $[3.9 \pm 1.4] \times 10^{-6}$

*Oversaturation values reported in parentheses were derived from Milestone 3411.

** Values reported in brackets were derived from this study.

Neptunium Solubility in J-13 Waters at 25°C

Figure 4. Results of Neptunium Solubility Experiments from Oversaturation and Undersaturation in J-13 water as a function of pH at 25°C

*Oversaturation values reported in parentheses were derived from Milestone 3411.

** Values reported in brackets were derived from this study.

Figure 5. Results of Neptunium Solubility Experiments from Oversaturation and Undersaturation in J-13 water as a function of pH at 90°C

*Oversaturation values reported in parentheses were derived from Milestone 3411.

** Values reported in brackets were derived from this study.

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APPENDIX A

RESULTS OF NEPTUNIUM SOLUBILITY FROM UNDERSATURATION EXPERIMENTS IN J-13 GROUNDWATER

Appendix A I. Results of neptunium solubility from undersaturation experiments in J-13 groundwater at 25° C

Sample I. D.	Days	pH	Concentration (M)
25° C Cell 2 #1	31	5.98	$(6.81 \pm 1.15) \times 10^{-4}$
25° C Cell 2 #2	63	5.95	$(6.53 \pm 0.98) \times 10^{-4}$
25° C Cell 2 #3	89	5.97	$(4.29 \pm 0.63) \times 10^{-4}$
Average Day 31 - 89			$(5.88 \pm 1.38) \times 10^{-4}$

Appendix A II. Results of neptunium solubility from undersaturation experiments in J-13 groundwater at 25° C.

Sample I. D.	Days	pH	Concentration (M)
25° C Cell 4 #1	31	6.99	$(3.38 \pm 0.93) \times 10^{-5}$
25° C Cell 4 #2	63	6.99	$(2.87 \pm 0.70) \times 10^{-5}$
25° C Cell 4 #3	89	6.96	$(1.97 \pm 0.72) \times 10^{-5}$

Average Day 31 - 89 $(2.74 \pm 0.71) \times 10^{-5}$

Appendix A III. Results of neptunium solubility from undersaturation experiments in J-13 groundwater at 25° C.

Sample I. D.	Days	pH	Concentration (M)
25° C Cell 6 #1	31	8.46	$(1.01 \pm 0.24) \times 10^{-5}$
25° C Cell 6 #2	64	8.43	$(1.54 \pm 0.32) \times 10^{-5}$
25° C Cell 6 #3	89	8.45	$(2.71 \pm 0.91) \times 10^{-5}$

Average Day 31 - 89

$(1.75 \pm 0.87) \times 10^{-5}$

Appendix A IV. Results of neptunium solubility from undersaturation experiments in J-13 groundwater at 90 ° C.

Sample I. D.	Days	pH	Concentration (M)
90 ° C Cell 2 #1	27	5.97	$(8.99 \pm 1.15) \times 10^{-4}$
90 ° C Cell 2 #2	60	5.96	$(9.15 \pm 1.83) \times 10^{-4}$
90 ° C Cell 2 #3	91	5.96	$(7.25 \pm 1.17) \times 10^{-4}$
90 ° C Cell 2 #4	111	5.95	$(8.19 \pm 1.10) \times 10^{-4}$

Average Day 27 - 111

$(8.40 \pm 0.87) \times 10^{-4}$

Appendix A V. Results of neptunium solubility from undersaturation experiments in J-13 groundwater at 90° C.

Sample I. D.	Days	pH	Concentration (M)
90° C Cell 4 #1	27	6.98	$(1.02 \pm 0.18) \times 10^{-5}$
90° C Cell 4 #2	60	6.96	$(9.35 \pm 1.99) \times 10^{-6}$
90° C Cell 4 #3	91	6.92	$(2.55 \pm 0.27) \times 10^{-5}$
90° C Cell 4 #4	111	6.97	$(1.37 \pm 0.31) \times 10^{-5}$

Average Day 27 - 111 $(1.47 \pm 0.75) \times 10^{-5}$

Appendix A VI. Results of neptunium solubility from undersaturation experiments in J-13 groundwater at 90° C.

Sample I. D.	Days	pH	Concentration (M)
90° C Cell 6 #1	27	8.49	$(3.21 \pm 0.57) \times 10^{-6}$
90° C Cell 6 #2	60	8.57	$(5.94 \pm 2.12) \times 10^{-6}$
90° C Cell 6 #3	91	8.57	$(3.19 \pm 0.79) \times 10^{-6}$
90° C Cell 6 #4	111	8.52	$(3.04 \pm 0.98) \times 10^{-6}$

Average Day 27 - 111

$(3.85 \pm 1.40) \times 10^{-6}$

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