Chemical Speciation of Neptunium in Spent Fuel

DE-FG03-99SF21903

1st Annual Report 15 August 1999 to 15 August 2000

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Annual Report

Chemical Speciation of Neptunium in Spent Fuel DE-FG03-99SF21903

1st Annual Report

Reporting Period

15 August 1999 to 15 August 2000

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Project Overview

This project will examine the chemical speciation of neptunium in spent nuclear fuel. The R&D fields covered by the project include **waste host materials** and **actinide chemistry**. Examination of neptunium is chosen since it was identified as a radionuclide of concern by the NERI workshop. Additionally, information on the chemical form of neptunium in spent fuel is lacking. The identification of the neptunium species in spent fuel would allow a greater scientific based understanding of its long-term fate and behavior in waste forms.

Research to establish the application and development of X-ray synchrotron radiation (XSR) techniques to determine the structure of aqueous, adsorbed, and solid actinide species of importance to nuclear considerations is being conducted at Argonne. These studies extend current efforts within the Chemical Technology Division at Argonne National Laboratory to investigate actinide speciation with more conventional spectroscopic and solids characterization (e.g. SEM, TEM, and XRD) methods. Our project will utilize all these techniques for determining neptunium speciation in spent fuel.

We intend to determine the chemical species and oxidation state of neptunium in spent fuel and alteration phases. Different types of spent fuel will be examined. Once characterized, the chemical behavior of the identified neptunium species will be evaluated if it is not present in the literature. Special attention will be given to the behavior of the neptunium species under typical repository near-field conditions (elevated temperature, high pH, varying Eh). This will permit a timely inclusion of project results into near-field geochemical models. Additionally, project

results and methodologies have applications to neptunium in the environment, or treatment of neptunium containing waste.

Another important aspect of this project is the close cooperation between a university and a national laboratory. The PI has a transuranic laboratory at MIT where students can perform spectroscopic and radiochemical experiments. Through the ANL partner, students can have additional experience performing research in a DOE setting. This will provide a unique and constructive opportunity for developing quality graduate students with experience and expertise in handling actinides. Our ability to produce experienced actinide scientists is currently restricted by the dearth of radiochemistry and nuclear research at universities. Regardless of all else, future researchers must be trained and educated if the United States is to maintain a leadership role in nuclear technology. This project provides such an opportunity.

Summary

This is the first annual report for the project. The first year covers the following topics.

Task 1. Speciation of Neptunium in Spent Fuel and Alteration Products

Development of equipment for XANES/EXAFS with spent fuel

Analyze Np solid phases

Information of Np alteration phases

Task 2. Chemical Behavior of Np Solids in Spent Fuel

Behavior of Np species with ligands

Data for modeling

A description of progress made for each task is below.

Progress in Task 1. Speciation of Neptunium in Spent Fuel and Alteration Products

Development of equipment for XANES/EXAFS with spent fuel

Progress in this area is described in Appendix 4. The application of synchrotron-based methods, X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS), to the identification and characterization of environmentally relevant solids is well established. This work will be done at the Chemical Technology Division Material Research Collaborative Access Team (MR-CAT) beamline at the Advanced Photon Source located at Argonne.

The application of synchrotron methods to establish the oxidation states of actinides in precipitated, altered, and unaltered neptunium phases has also been demonstrated. We are proceeding with the characterization of carefully prepared neptunium standards to build a library

of spectra that will help establish the nature of the unknowns. Preparations for synchrotron studies of neptunium-bearing solids were also completed. A beamline run is scheduled for late August 2000.

Analyze Np solid phases and Information of Np alteration phases

Progress in these areas involved two separate efforts describe in Appendix 4. The subsurface chemistry of neptunium when organics are present and the effects of microbiological activity on neptunium speciation and phase alteration were examined.

The reactivity of Np(VI) with citrate was investigated as a model system to understand the role of complexation and redox conditions in defining the oxidation state distribution under subsurface conditions. We established that citrate reduces Np(VI) to Np(V) within days under all conditions investigated. The disappearance of Np(VI) was first-order under all conditions investigated but the pseudo first order rate constant was not proportional to the concentration of citrate due to changes in the reaction mechanism. Complexation affected the apparent rate of reaction in ways that are still under investigation. The reactivity was predominantly defined by the carboxylates present, with a small but significant contribution from the tertiary alcohol. The much higher reactivity observed, however, with cytochrome C (which is a biologically derived reducing agent present in the subsurface) shows that we still cannot account for redox effects in biologically active systems.

Research was also initiated to establish the effects of microbiological activity on the speciation of neptunium. Emphasis is on a *Shewanella* strain that is an anaerobic metal-reducing bacterium common to many subsurface aquifers. The methodology for growing and studying this isolate was established. Interaction experiments with neptunium are planned for the early part of the second year in the project.

Progress Task 2. Chemical Behavior of Np Solids in Spent Fuel

Behavior of Np species with ligands

The sorption of Np(V) onto clay and mineral solid phases is described in Appendix 2. These experiments studied the sorption and precipitation of Np(V) on goethite, montmorillonite, and tuff. The first experiment was done in 0.1 M NaClO₄, at room temperature, and in a nitrogen glove box. The second experiment was done in 0.1M NaClO₄, at room temperature, and under an air atmosphere. The third experiment was done in J-13 groundwater, at room temperature, and under an air atmosphere. Supernate concentrations were measured and the solid phase was analyzed at the Advanced Photon Source at ANL.

Our current results show sorption of Np(V) to goethite, montmorillonite, and tuff. The proton exchange capacity was found to be 0.228 ± 0.018 meq OH/g for FeOOH and 0.770 ± 0.016 meq OH/g for montmorillonite. This data will be used to model Np(V) sorption..

From our sorption study the concentration of neptunium in solution decreases significantly at pH greater than 10, because of precipitation of neptunium(V) hydroxide. However, a much greater decrease occurred in the samples containing goethite and montmorillonite at lower pH. Thus, it appears that sorption occurred in the mineral phases and is based on interaction of free neptunyl. The Np concentration in the goethite supernate decreased more than the montmorillonite supernate. EXAFS analysis revealed that goethite was complexing with hydroxide as suspected. However, the montmorillonite was complexing with carbonates, suggesting a carbonate phase in the natural montmorillonite sample.

In further studies under inert atmosphere the supernate concentrations in the goethite samples dropped to approximately 60% of the original Np concentration at low pH, and decreased to very low concentrations by pH 7.5. The Np concentrations in the tuff samples were slightly higher than those in the goethite samples at low pH. This trend continued until approximately pH 9.5, which is the pH where hydrolysis is predicted to begin. At this point, Np concentration decreased dramatically until pH 11. After pH 11, Np concentration increased again. This suggests a pH dependent precipitation of Np within the tuff system or a pH dependent sorption effect. Previous studies elsewhere found sorption within the pH range of 6.5 to 8.5, but also found that some tuff samples exhibited negligible sorption. Further studies are necessary to better understand the change in supernate concentration as a function of pH.

Data for modeling

Modeling of Np speciation is described in Appendix 2. Modeling of Np under Yucca Mountain conditions from pH 5 to pH 12, Eh from 0 V to 1.5 V and temperature from 25 °C to 100 °C was performed with CHESS 2.4. seven different main Np species were observed in the calculations. In conditions below 0.5 V the tetravalent NpO_2 is formed. Three pentavalent Np species, NpO_2^+ , $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2\text{OH}_{(\text{aq})}$ are dominant in the potential ranging from 0.5 V to 1.15 V. Three hexavalent Np species: $\text{NpO}_2(\text{CO}_3)_3^{4-}$, $\text{NpO}_2(\text{CO}_3)_2^{2-}$, NpO_2OH^+ , are in the oxidizing conditions above 1.15 V. Other species with fluoride, sulfate and phosphate are calculated to exist but at very low concentrations. The database lack mixed ligand species or possible Np mineral type phases that may be found in spent fuel. In addition, the predicted behavior of NpO_2 indicates future efforts need to examine the dissolution kinetics.

Other progress

Appendix 1 describes our electrodeposition system for alpha spectroscopy. Electrodeposition has been shown to be the most effective method of actinide sample preparation for alpha spectroscopy. An electrodeposition apparatus was made in order to meet the laboratory alpha spectroscopy sample preparation needs associated with the Np speciation project.

The cooperation and interchange between ANL and MIT was strengthened by a visit to MIT by Dr. Don Reed. The visit occurred in March 2000. Dr. Reed visited our laboratory, held

discussions with students, and presented a lecture in 22.76, nuclear chemical engineering. Christi Sherman from MIT spent June-August 2000 performing laboratory research at ANL in the laboratory of Dr. Don Reed. We expect to expand our cooperative exchange efforts with our XAFS studies at the ANL APS.

Appendixes

Appendix 1: Electroplating System for Production of Samples for Alpha Spectroscopy

Appendix 2: The Effect of pH on Neptunium(V) Sorption on Goethite, Montmorillonite, and Tuff under Air and Inert Atmospheres in 0.1 M NaClO₄ and J-13 Groundwater

Appendix 3: Modeling Neptunium Speciation in Yucca Mountain Environment

Appendix 4: Speciation of Neptunium in Spent Fuel (ANL report)

Appendix 1

Electroplating System for Production of Samples for Alpha Spectroscopy

J. Plaue, K.R. Czerwinski, Nuclear Engineering Department, Massachusetts Institute of
Technology

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Appendix 1

Electroplating System for Production of Samples for Alpha Spectroscopy

J. Plaue, K.R. Czerwinski, Nuclear Engineering Department, Massachusetts Institute of Technology

Description of Electroplating Apparatus

Electrodeposition has been shown to be the most effective method of actinide sample preparation for alpha spectroscopy. An electrodeposition apparatus was made in order to meet the laboratory alpha spectroscopy sample preparation needs associated with the Np speciation project. The device consists of three main parts.

The tray portion (Figure 1) has five separate plating stations allowing for the simultaneous plating of five samples. Each station consists of a contact electrode and a platinum wire dip electrode, which are individually controlled with toggle switches for safety. For added containment, the tray used is a high-density polyethylene deep well-type sample tray.

Figure 1: Electrodeposition Tray

Each plating station requires a plating vial (Figure 2). The vials used are 5 mL and are manufactured from Teflon-coated, high performance plastic. A small hole was drilled in the base of each vial in order to facilitate access for filling the vial and the dip electrode. Electrodeposition occurs on a 19mm nickel planchet that sits in the cap of the vial. The planchets are thoroughly rinsed in acetone prior to use. A Teflon-coated silicon o-ring is used to create a seal between the vial cap, which is sold with an access hole, the planchet, and base of the vial. The hole in the cap allows for contact to the base contact electrode.

The power source (Figure 3) is an Accupower 4000 programmable power supply. The supply can operate under constant conditions with a maximum of 4000V, 500mA, or 400W. Power is supplied in parallel to each of the five plating stations.

Figure 2: Sample Vial

Figure 3: Power Supply

Construction of Electrodeposition Apparatus

The tray portion of the setup can easily be constructed from typical supplies. The tray used was Rubbermaid #3510. The contact electrode consists of small machine screws, which are fastened to holes drilled through the tray. For the dip electrode, a 0.5mm diameter piece of platinum wire was soldered to an ordinary wire lead from the switch. Varying lengths of wire were used in order to accommodate different volumes of plating fluid. Each electrode is wired to an ordinary toggle switch, which in turn are wired together in parallel to a female banana plug connection. Common banana-plug jumpers are used for the connection between the tray and the power source. This allows for easy reversal of polarity to accommodate electrodeposition of both anionic and cationic species.

The electrodeposition sample vials are made from a few simple modifications to 5mL Chemware Teflon vials by Norton Performance Plastics. As mentioned previously, a 0.3 cm hole was drilled in the base of the vial to accommodate the dip electrode. The only other modification was to core a hole in the Teflon-coated septa that come with the vials. The size of the hole will dictate the area of the metal deposit.

Operation of Apparatus

Normal electrodeposition operation is simple. Attachment 1 presents the laboratory standard operating procedure for use of the electrodeposition apparatus. Essentially, an ethanol-based sample solution is made from mixing 100% ethanol with a small amount of the actinide-containing solution. Then, an aliquot of this solution is placed into the sample vials and the power source is turned on for specified amount of time. Experiments will be performed to isolate the best operating conditions (voltage, current, plating fluid, plating time) for each isotope to produce a consistent yield. Figure 4 shows an alpha spectrum of ^{237}Np produced from a run of the electrodeposition equipment.

Figure 4: Np-237 Alpha Spectrum

Attachment 1: Laboratory Standard Procedure for Electrodeposition of Alpha Samples

Electrodeposition System Procedures

Purpose: To plate a sample for alpha spectroscopy

1. Using a sharp metal object (screwdriver) scratch your sample ID on to one side of an acetone washed nickel planchet.

Note: marker will come off during the process

2. Assemble a plating cell according to the diagram. Inside the cap, place the planchet with ID faced to the plastic. Next, place a Teflon-coated silicon O-ring with the Teflon (white shiny side) facing the inside of the vial. Finally screw the vial together making sure to keep the planchet centered (it will tend to wiggle).

3. Prepare an ethanol solution of your activity. Low concentration acid solutions can be mixed directly with the EtOH. Keep in mind, concentrated acids WILL react with the EtOH. No more than 100 μ L of concentrated acid should be added to 10 mL of EtOH.

4. Load the vial with 4mL of your EtOH solution. The recommended loading procedure is to use the 5mL pipettor. After drawing the sample up, use a 100 μ L tip in series with the 5mL tip to direct the sample into the small hole on the bottom of the vial.

5. Set up the plating station. For safety, put it the hood. This is a high voltage piece of equipment, so be careful

→make sure all of the switches are in the off position

→place the vial(s) on a plating station and insert Pt dip-electrode (use the small alligator clips or tape to secure the wire)

→put the cells switches to the ON position (up)

→turn on the power supply. Enter in desired plating conditions and time

→observe the sample for the first time. *Note:* some samples will evaporate below the electrode. If this happens, refill with additional pure EtOH

6. After you have been plating for the proper length of time:

→ turn off the power to each station

→watch the voltmeter and allow the system time to drain voltage

→ remove the probe and then the vial

7. Empty the remaining solution into the liquid radwaste container. It works best if you turn the vial rightside up and then loosen the cap (the fluid will drain through the hole). Remove the O-ring and planchet with tweezers.

8. Cleaning of the vial parts is very crucial for other users. Please rinse thoroughly using the 0.1M EDTA solution, then DI water, before placing in the acid bath.

Appendix 2

The Effect of pH on Neptunium(V) Sorption on Goethite, Montmorillonite, and Tuff under Air and Inert Atmospheres in 0.1M NaClO₄ and J-13 Groundwater

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Appendix 2

**The Effect of pH on Neptunium(V) Sorption on Goethite,
Montmorillonite, and Tuff under Air and Inert Atmospheres
in 0.1M NaClO₄ and J-13 Groundwater**

C. Sherman, K.L. Noyes, K.R. Czerwinski, Nuclear Engineering Department, Massachusetts Institute of Technology

1.0 Summary

Sorption is an important characteristic which determines the migration and retardation of neptunium in the geosphere. These studies investigated these characteristics of Neptunium(V) (Np(V)) and the data will be used to model neptunium's behavior in the environment. These experiments studied the sorption and precipitation of Np(V) on goethite, montmorillonite, and tuff. The first experiment was done in 0.1 M NaClO₄, at room temperature, and in a nitrogen glove box. The second experiment was done in 0.1M NaClO₄, at room temperature, and under an air atmosphere. The third experiment was done in J-13 groundwater, at room temperature, and under an air atmosphere. Supernate concentrations were measured and the solid phase was analyzed at the Advanced Photon Source at ANL.

2.0 Purpose and Objective

Yucca Mountain, NV has been identified by the department of Energy (DOE) for site characterization as a potential high level nuclear waste repository for the United States [1]. Risk assessment of Yucca Mountain includes worst case scenarios [2], such as water intrusion into the repository, and the subsequent removal of radionuclides as either particulate or dissolved species [3].

The isotope ²³⁷Np is long-lived with a half-life of 2.14x10⁶ years [4]. Although its initial percentage concentration in nuclear fuel is low (0.03%) it is a daughter of ²⁴¹Am decay. Thus, after about 100,000 years ²³⁷Np will be large contributor to the radiation inventory of nuclear waste repositories [5]. Understanding the behavior of neptunium in the event of a worst case scenario is an important task in site characterization. Sorption is a key characteristic of Np, which affects its migration and retardation in the geosphere. Better understanding of sorption will improve models of the behavior of Np in the environment.

3.0 Concept of Sorption Studies and Background Information

The solubility, speciation, and sorption of radionuclides are major components which determine the actinide's movement through the environment. Solubility establishes an upper concentration limit of the dissolved radionuclide in migration. Oxidation states and speciation of

the radionuclide determine the complexes that will form which will affect sorption and transportation by way of colloids. Sorption can either increase migration of the radionuclide or it can hinder it.

3.1 Solubility

Solubility is the concentration of the soluble form of an element in an aqueous solution at equilibrium. It is a function of temperature and components in the system [2]. Kinetic processes control the rate at which equilibrium is reached, meaning that the rate at which solution reaches equilibrium varies based on the solution. Once a concentration has reached a constant level for several weeks or months, it is assumed that equilibrium has been reached. However, in reality slower thermodynamic processes may still be at work, converting the solid phases to less soluble phases with lower free energies [3]. Tighter bonding occurs, resulting in decreased surface area [6]. This process may take years and thus may not be seen in laboratory experiments. Thus, stability seen in experiments is designated by the U.S. Nuclear Regulatory Commission as a “steady state,” “the conditions where measurable changes in concentrations are not occurring over practical experimental times.” [7].

3.2 Oxidation States and Speciation

The oxidation state and speciation of a radionuclide determines its sorption and movement through the geosphere. The speciation of a radionuclide determines which potential ions radionuclides may complex with and which of these processes will dominate under certain conditions [3].

3.2.1 Neptunium Oxidation State

The oxidation state of a nuclide is a measure of the number of electrons gained or lost with respect to its reference state [3]. Aqueous neptunium is found in five oxidation states Np(III), Np(IV), Np(V), Np(VI), and Np(VII) [8]. Three of neptunium’s oxidation states, Np(IV), Np(V), and Np(VI), can exist in natural systems [4]. Of these states, NpO_2^+ is the most common in oxygen-rich natural waters [8] and the most mobile. However, Np(IV) is expected to dominate in reducing conditions [9]. Np(VI) is not expected to be present because of quick reduction from Np(VI) to Np(V) [4]. However, it is possible that in an environment such as a waste repository, where the concentrations of actinyl ions is high, radiolysis could provide redox agents that form uranyl(VI) complexes with heavier actinyl ions [8].

The oxidation state of an element determines its affinity for a mineral phase. This affinity can either lead to retardation through sorption [6] or transportation by colloid formation [10]. This knowledge can be used to develop better models to understand neptunium’s interactions and behavior in the environment. The oxidation state of an element can be measured using spectroscopy [6].

3.2.2 Neptunium Speciation

The speciation of neptunium refers to its complexation with other constituents. Like oxidation states, speciation is an important factor in radionuclide behavior, because it governs neptunium’s ability to interact with mineral phases and other components of groundwater. This

knowledge also contributes to building better models and greater understanding of the behavior of neptunium in the environment. The speciation of elements in solution can be measured using spectrophotometry [6].

3.2.3 The Carbonate System

Carbonate is present in most natural waters and many carbonate-containing materials [8] and its complexation with elements affects their solubilities [11]. Dissolution of CO_2 in water results in H_2CO_3 and HCO_3^- . In an open system, the concentration of carbonate in water equilibrates as a function of the partial pressure of CO_2 in the atmosphere. In a closed system, the exchange with the environment is much slower.

Carbonate solutions are complicated because hydroxide ions are also present, meaning that there are always at least three competing ligands in the system: OH^- , HCO_3^- , and CO_3^{2-} , and their relative concentrations are interdependent [8].

3.2.4 Literature on Neptunium and Carbonate Complexes

At high ionic strengths carbonate stabilizes Np(VI) , keeping it in a dominant oxidation state [12]. J-13 groundwater, however, is at low ionic strength, only in the millimolar range. The dominant ligands are CO_3^{2-} and OH^- [2].

Similarly, carbonate complexation of Np(V) also dominates over hydrolysis in a brine system. At high carbonate concentrations, under brine conditions, the thermodynamically stable Np(V) carbonate solid is $\text{Na}_3\text{NpO}_2(\text{CO}_3)_{0.8} \cdot n\text{H}_2\text{O}$ [7].

Studies on J-13 groundwater found varied results. Nitsche, et al found that $\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8} \cdot 2.5\text{H}_2\text{O}$ was the solid phase [1] while Eford, et al found $\text{Np}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ as the solid [2]. As suspected, the average concentrations between the two studies also differed. These values are shown in table 3.1. Nitsche et al also compared results from J-13 groundwater with UE-25p#1 groundwater, which has a carbonate concentration five times greater than J-13 [13]. They found that the solubility effects were a result of carbonate concentrations [1]. In both studies, steady state appeared to be reached after 150 days [2, 3].

Table 3.1 Comparison of literature values for averaged concentration of ^{237}Np (mol/L) at 25°C after steady state as measured from oversaturation and undersaturation.

Method	pH 6	pH 7	pH 8.5	Reference
Oversaturation	$(6.5 \pm 1.1) \times 10^{-4}$	$(3.1 \pm 0.2) \times 10^{-5}$	$(1.5 \pm 0.6) \times 10^{-5}$	[1]
Undersaturation	$(6.5 \pm 1.0) \times 10^{-4}$	$(2.9 \pm 0.7) \times 10^{-5}$	$(1.5 \pm 0.3) \times 10^{-5}$	[1]
Oversaturation	$(5.32 \pm 0.28) \times 10^{-3}$	$(1.27 \pm 0.18) \times 10^{-4}$	$(4.4 \pm 0.7) \times 10^{-3}$	[2, 3]

3.2.5 Yucca Mountain Groundwater

Well J-13 takes water from the unsaturated zone near the proposed repository site in Fortymile Wash [10]. The water from this well is expected to be representative of natural water with the highest concentrations of dissolved species in the Yucca Mountain area [1]. Its

composition is shown in table 3.2 [13]. Water from the J-13 well has fairly low ionic strength, and its primary ligands are hydroxide and carbonate [2]. The water is oxidizing [1]. Typically, oxidizing conditions give rise to higher solubilities than would occur under reducing conditions [3].

Table 3.2 J-13 Groundwater Composition [13]

Component	mmol/L
Na ⁺	1.96
K ⁺	0.14
Ca ²⁺	0.29
Mg ²⁺	0.07
SiO ₂	1.07
Carbonate (total)	2.81
Cl ⁻	0.18
SO ₄ ²⁻	0.19
F ⁻	0.11
pH	7.0
Eh	700 mV
TDS	130.4 mg/L

3.3 Physical Processes in Sorption Studies

Interactions between particles in solution can produce many results including precipitation, colloid formation, and sorption.

3.3.1 Precipitation

Precipitation is the act of an insoluble particle settling out of solution. Thus, precipitation is a function of solubility, which in turn is a function of such factors as temperature, pH, and ionic strength. Significant precipitation of Np at 0.1M ionic strength will begin to occur due to hydrolysis at pH >9.5 [14].

3.3.2 Colloid Formation

Colloids are small particles composed of either single large particles or clusters of smaller molecules which range in size from 0.001 to 0.1μm. For example, neptunium can attach to small particles of a mineral phase. This can result in more rapid migration through the groundwater [10].

3.3.3 Sorption

Sorption is a reaction on a surface where one substance is attached to another. The goal of this study is to compare the capacity of the mineral phases for Np sorption and the condition under which sorption will occur.

3.4 Phase Separation

Accurate supernate concentrations are important in sorption studies. Insoluble material that is in the supernate produces higher concentrations. Centrifuging the samples can be used to separate the phases, by concentrating the solid phase on the bottom of the vial and the solution phase on the top.

Colloid formation can also result in increased supernate concentrations, because the tiny particles may still be able to stay in the supernate even after centrifuging. To avoid this problem, larger mineral phase particles greater than 1 μ m can be used in the experiment.

3.5 Mineral Phases

3.5.1 Tuff

Yucca Mountain is composed primarily of tuff, a volcanic rock formed from hot ash which was compressed over time. Previous studies on Yucca Mountain tuff has shown low but consistent sorption suggesting that there is a limited number of sorption sites for neptunium. One theory is that neptunium sorbs to the trace amounts of ferric oxides present in the rocks. However, the sites are not always present in tuff samples. Some zeolitic, vitric, and devitrified tuff samples exhibit negligible affinity for neptunium within the pH range from pH 6.5-8.5, while others with similar mineral compositions have much higher sorption. This suggests that sorption is controlled by a minor primary or secondary phase which varies in abundance. One theory is that neptunium sorbs to the trace amounts of ferric oxides or iron containing minerals present in the tuff. The ferric oxides are present in trace amounts in most tuff samples from Yucca Mountain. Tuff samples containing calcite also exhibit higher neptunium sorption [10].

3.5.2 Goethite

Weathering of iron-containing rocks, under aerobic conditions, can form secondary iron oxide minerals, which are found in surface and groundwater systems. These iron oxides precipitates, especially Fe-hydroxides are good scavengers of trace elements in natural waters [15]. Goethite is the most common sorbent in soils and its structure is stable over a large pH range [16]. Eckhardt et al showed that neptunium's affinity for iron oxide was very high within the range of 6.2-6.9 [10], and Nakayama et al looked at the range pH 4-11 and found that goethite had strong sorption above pH 6 [17]. An EXAFS study by Combes et al found that the neptunium removed from solution by goethite was a result of sorption, not precipitation or coprecipitation [18]. Neptunium's high affinity for ferric oxides and oxyhydroxides, and minerals that contain ferrous iron is probably because the Fe²⁺ in the compounds or on the surface of these minerals reduces Np(V) to Np(IV) [10]. Solids composed of Np(IV) are generally less soluble than Np(V) solids, and Np(IV) has a high tendency to form aqueous complexes [5].

3.5.3 Montmorillonite

Montmorillonite is a common clay mineral found in soils [19] which is also found coating fracture walls in Yucca Mountain tuff [10]. It is the dioctahedral form of smectite, a clay which is unique because of its swelling ability, adsorption of ions, and plasticity. These properties are the result of its highly negative surface charge which attracts cations such as Na⁺ and K⁺. These

cations can be exchanged for other cations depending upon the competing ions affinity for smectite [19]. In general, Np does not seem to have a high affinity for clays and zeolites, possibly because of the large size of the neptunyl ion and the small charge-to-radius ratio [10]. Studies done on montmorillonite found that neptunium sorption reached its maximum at pH 8-8.5 when experiments were conducted in an atmosphere with CO₂. However, carbonate complexation occurs at pH > 8 hindering sorption [20].

3.6 Pilot Study Results

The results of our pilot study are shown in Fig 3.6. The total concentration of Np is 50 μ M with 0.015 g of solid phase. The predicted concentration of NpO₂⁺ in solution was calculated based on values from Neck et al. [21]. As shown in the figure, concentration of neptunium in solution decreases significantly at pH greater than 10, because of precipitation of neptunium(V) hydroxide (NpO₂OH). The decrease in the solution Np concentration in samples without solid phase is due to the formation of hydroxide precipitates. However, a much greater decrease occurred in the samples containing goethite and montmorillonite at lower pH. Thus, it appears that sorption occurred in the mineral phases and is based on interaction of free neptunyl. The Np concentration in the goethite supernate decreased more than the montmorillonite supernate.

EXAFS analysis revealed that goethite was complexing with hydroxide as suspected. However, the montmorillonite was complexing with carbonates, suggesting a carbonate phase in the natural montmorillonite sample.

Table 3.6 Np solution phase concentration from data presented in Figure 3.6.

pH	no solid phase	montmorillonite	goethite
7.15	5.11E-05		
8.11	5.03E-05		
8.37	5.36E-05		
9.46	4.70E-05		
11.48	7.16E-06		
6.39		4.58E-05	
7.74		4.58E-05	
8.44		3.76E-05	
8.93		2.04E-05	
9.45		2.23E-05	
11.45		2.07E-05	
5.71			3.14E-05
8.00			2.26E-06
8.13			5.82E-06
8.73			6.89E-07
9.60			2.24E-07
11.52			1.37E-07

Figure 3.6 Np supernatant concentration at various pH with goethite and montmorillonite

4.0 Sorption Experiment Details

Sorption of Np(V) to goethite, montmorillonite, and tuff was studied with the range of pH 2 - 12 under three separate conditions. The first experiment was done in 0.1 M NaClO₄ under an inert atmosphere. The second was done in 0.1M NaClO₄ in an air atmosphere. The third was done in J-13 groundwater in an air atmosphere.

4.1 Sorption Under Inert Atmosphere

This experiment was conducted in a glove box under a nitrogen atmosphere at room temperature. Ten tubes within the pH range of 2-12 were prepared for each material using 16 mg of the mineral phase, 4 mL of 50 μ M Np(V) solution in 0.1M NaClO₄, and enough 0.1M HCl or 0.1M NaOH to obtain the desired pH. Ten tubes within this pH range were also prepared without mineral phase. Samples were shaken or sat for at least 110 hours.

Scintillation assays were taken of the supernate to estimate the Np concentration left in solution. EXAFS samples were prepared of the solid phase in the glovebox and sealed in polystyrene to maintain anoxic conditions. EXAFS analysis was conducted to determine complexation and precipitates formed.

4.1.1 Controlled-Atmosphere Glovebox

In order to avoid carbonate complexation, this experiment was performed in an inert atmosphere glovebox that excluded atmospheric CO₂. The glovebox also served to contain the radioactive material used in this experiment.

4.1.2 Sources and Preparation of Mineral Phases

The goethite used in this experiment was obtained from Alfa AESAR. The montmorillonite was obtained from Aldrich. The tuff is a natural material from Topopah Springs. This is devitrified tuff, which is mainly composed of alkali feldspar. It also usually contains tridymite [10]. The goethite, montmorillonite, and tuff were sieved using different mesh ranges to obtain particles within the size range 45-75 μm for goethite and montmorillonite, and 75-250 μm for tuff. The material was dried on a hot plate at approximately 95°C.

4.1.3 Characterization of Mineral Phases

Small amounts of contaminants can greatly affect the results of a sorption study. In order to properly characterize the material in the mineral phase, X-ray diffraction of all mineral phases will be performed. BET analysis will also be performed to determine the surface area of each mineral phase. Proton Exchange Capacity was determined as described in section 5.

4.1.4 Solution Preparation

Np(V) and Np(VI) stock solutions were made from neptunium stock solutions. To make Np(VI), the neptunium stock solution was dried in hydrochloric acid, dried in 8 M HNO_3 , and fumed in perchloric acid and 8 M HNO_3 . Finally, it was added to nanopure water to the desired concentration. Np(V) was made from Np(VI) by reduction with H_2O_2 , precipitation with carbonate, carbonate wash, and finally the addition of nanopure water. Verification of the oxidation states was established by UV-visible spectrometry. Concentration was determined by scintillation.

4.1.5 Avoidance of Carbonate Complexation

The pilot study showed carbonate complexation in montmorillonite samples even though the experiment was conducted under an Ar atmosphere. To avoid this problem prior to addition of solution, 0.01M HClO_4 will be added to montmorillonite to outgas CO_2 from the mineral phase. Ten of these samples of decarbonated montmorillonite were prepared, as well as ten samples where no acid was added to compare the results. EXAFS analysis was performed on both sample groups to determine if carbonate complexation occurred.

4.1.6 Neptunium Hydrolysis

The solubility of Np(V) decreases with increasing pH. At experimental concentrations, significant hydrolysis should occur at $\text{pH} > 9.5$ [14]. Thus, change in supernate concentration will occur partly because of hydrolysis. To distinguish between hydrolysis and sorption precipitation, control samples will be prepared identically, but without mineral phase. These results and a model of expected Np speciation shown in Figure 3.1 will be compared for the mineral phase results. In addition, EXAFS analysis was performed to aid in distinguishing the results.

4.2 Sorption Under Air Atmosphere

This experiment was conducted under an air atmosphere at room temperature. Eight tubes within the pH range of the 5-12 were prepared for each material (goethite, montmorillonite, and tuff) using 16 mg of the mineral phase, 4 mL of 50 μM Np(V) solution in 0.1M NaClO_4 , and enough 0.1M HCl or 0.1M NaOH to obtain the desired pH. An additional eight tubes were

prepared for each material using J-13 groundwater instead of 0.1M NaClO₄. Eight tubes within this pH range were also prepared without mineral phase for each medium. Samples were shaken for at least 105 hours.

Like the sorption experiment conducted under an inert atmosphere, scintillation assays were taken of the supernate to estimate the Np concentration left in solution.

Mineral phase origin and preparation is described in section 4.1.2. Solution preparation for the Np(V) solutions is described in section 4.1.4. The effect of neptunium hydrolysis is described in section 4.1.6.

5.0 Titration of Goethite and Montmorillonite (45-75 μ m) to Determine Proton Exchange Capacity (PEC)

Proton Exchange Capacity (PEC) is a measure of the number of proton exchanging sites available for interaction. Determination of this number is important for input in models of neptunium behavior.

5.1 Procedure

The goethite used in this experiment was made according to Sun et al. [22]. The goethite was sieved using different mesh ranges to obtain particles within the size range 45-75 μ m. The material was dried at 93.2° C. X-ray diffraction of goethite using a copper anode at 45 kV and 35 mA showed that goethite was the major phase with some contribution from hematite and maghemite. X-ray defraction of montmorillonite at the same settings showed that the montmorillonite also contained some quartz.

The proton exchange capacity of the size selected goethite (45-75 μ m) was examined by a pH titration with 0.1M NaOH. The titration was performed with a Metrohm GP Titrino system. In order to make sure that all the sites were protonated, an additional 20 mL of 0.1M HClO₄ was added to the solid goethite. The solution was agitated overnight. After that, it was centrifuged, to remove excess liquid, and frozen for approximately 24 hours. Following the freezing, the solution was freeze-dried for approximately 24 hours and stored in an oven at approximately 40° Celsius. The electrode was calibrated with a three-point method using pH 4,7, and 10 buffer. In a titration vessel, the dried goethite was added to 0.1M NaClO₄. During the experimental trials, approximately 0.025g dried FeOOH and 17 mL 0.1M NaClO₄ were used. The vessel was sealed and argon was bubbled into the system for one-hour prior to the addition of 0.1M NaOH to allow time for the system to equilibrate. A 0.005 mL increment of 0.1M NaOH was added every 20 minutes. The total volume of 0.1M NaOH added was 0.49 mL.

The same experiment was conducted to determine the PEC of montmorillonite using approximately 20 mL 0.1M NaClO₄ and 0.025 g montmorillonite.

5.2 Results and Discussion

The proton exchange capacity (PEC) is determined by evaluating the moles of OH added for the solution to reach the titration endpoint (the maximum of the first derivative of the first titration curve). The experiment was repeated three times with slightly varying amounts of the FeOOH and 0.1M NaClO₄. The average PEC was 0.228 meq OH/g FeOOH with a standard

deviation of 0.018. This value is consistent with the value used by Warwick et al. [23] of 0.2 meq OH/g FeOOH. The average PEC of montmorillonite was 0.770 meq OH/g montmorillonite with a standard deviation of 0.016.

5.3 Future Work

The PEC of Yucca Mountain tuff will also be determined. These values will be used to model the behavior of neptunium in the environment to better understand its sorption to mineral phases and its transport through groundwater.

6.0 Np Solution Phase Concentration Results for Goethite and Tuff Samples

6.1 Results for Goethite Samples

The results of the scintillation measurements of the supernate in the goethite samples are shown in Figure 6.1, and compared to the predicted hydrolysis curve explained in section 4.1.6. The supernate concentrations in the goethite samples dropped to approximately 60% of the original Np concentration at low pH, and decreased to very low concentrations by pH 7.5. Hydrolysis was expected to begin around pH 9.5 and is shown through the calculation of Np in the absence of sorption using literature data. This suggests that sorption occurred in this pH range of pH 7.5-9.5, and possibly at higher pH as well.

Table 6.1 Np solubility data from Figure 6.1

pH	Goethite	Tuff
2.09	2.73E-05	
2.45	3.03E-05	
6.63	1.86E-05	
7.41	6.70E-07	
9.34	1.70E-07	
10.08	2.72E-07	
10.32	1.13E-22	
11.02	8.52E-08	
11.52	3.27E-07	
2.21		3.25E-05
2.44		3.31E-05
5.84		3.28E-05
6.09		3.34E-05
6.49		3.19E-05
8.88		2.95E-05
10.23		1.54E-06
10.96		1.41E-06
11.22		3.16E-06
11.66		6.51E-06

Figure 6.1 Np concentration under inert atmosphere with 0.016 g solid phase in 4 mL solution with 50 μ M total Np

6.2 Results for Tuff Samples

As shown in figure 6.1, Np concentrations in the tuff samples were slightly higher than those in the goethite samples at low pH. This trend continued until approximately pH 9.5, which is the pH where hydrolysis is predicted to begin. At this point, Np concentration decreased dramatically until pH 11. After pH 11, Np concentration increased again. This suggests a pH dependent precipitation of Np within the tuff system or a pH dependent sorption effect. Previous studies found sorption within the pH range of 6.5 to 8.5, but also found that some tuff samples exhibited negligible sorption [10]. Sorption on the tuff samples from this experiment appears to be negligible. Further studies are necessary to better understand the change in supernate concentration as a function of pH.

6.3 Future Work

Scintillation results from the montmorillonite, decarbonated montmorillonite, and control samples performed under an inert atmosphere will be analyzed and compared to the tuff and goethite sample results. Scintillation results from the 0.1M NaClO₄ and J-13 groundwater experiments performed in an air atmosphere will also be analyzed and compared to each other and the results from the inert atmosphere experiment.

7.0 EXAFS Analysis of the Solid Phase

7.1 Limits of Detection with the Higher Energy Beam (18 keV)

Seven solid phase samples were analyzed at 18 keV at the Advanced Photon Source at ANL. To detect neptunium in the solid phase, approximately 50% of the neptunium which was originally in solution had to be present in the solid phase sample. In the goethite samples, 80-100% of the neptunium was present in the solid phase, allowing good detection. However, the montmorillonite, decarbonated montmorillonite, and tuff samples did not contain as high a percentage, and the neptunium could not be detected at the higher energy. Some samples will be reanalyzed using a lower energy beam.

7.2 Results of EXAFS Analysis of the Goethite Solid Phase

Previous studies have suggested that with interaction between Np(V) and goethite, reduction to Np(IV) occurs allowing sorption [10]. EXAFS analysis also showed this result. In the lower pH samples, Np(IV) reduction occurred. However, because of the overlap in the Np(IV) and Np(V) edges, it is difficult to discern the relative percentage of each species in the case of mixed oxidation states. In higher pH samples, precipitation of Np(V) complexes seemed to dominate over reduction to Np(IV).

7.3 Results of EXAFS Analysis of the Tuff, Montmorillonite, and Decarbonated Montmorillonite Solid Phases

Previous experiments with tuff have shown that tuff exhibits low sorption of neptunium [10]. This was also observed in the EXAFS analysis. Scintillation samples taken after centrifuging the solution phase revealed that high percentages of the neptunium had dropped out of solution. However, EXAFS analysis of the solid phase at 18 keV did not detect significant amounts of neptunium in the solid phase. This suggests that the remaining neptunium was originally suspended in the solution prior to centrifuging the sample. Similar results were found in the analysis of both the decarbonated montmorillonite and montmorillonite samples.

7.4 Future Work

Tuff and montmorillonite samples will be reanalyzed using a lower energy beam to explore the hypothesis that the neptunium remained suspended in the solution. In addition, the experiment may be repeated with the intent of determining the complexes formed by neptunium in these samples.

8.0 References

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Appendix 3

Modeling Neptunium Speciation in Yucca Mountain Environment

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Appendix 3

Modeling Neptunium Speciation in Yucca Mountain Environment

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Abstract

Speciation of Np was modeled in J-13 groundwater conditions using the hydro-geochemical equilibrium code CHESS from pH 5 to pH 12 in a temperature range of 25 °C to 100 °C. The potential was varied between 0 and 1.5 V. The main inorganic ligands taken into account were carbonate hydroxide and phosphate. Pentavalent Np and, in a lower degree Np(IV) complexes dominate the speciation. The temperature and the pH favor the formation of carbonate and, in high pH conditions, hydroxides.

Introduction

Neptunium is an important radioactive component of nuclear wastes disposed of in high-level waste repositories. Its behavior in groundwater is critical to the issue of Np transport in the geosphere. This behavior strongly depends on the chemical environment in the repositories. Neptunium has several oxidation states (IV, V and VI), which could exist in these different natural systems. According to the literature the predominant oxidation state of ²³⁷Np from nuclear fuel wastes in solution, would be the pentavalent state [1]. Moreover, tetravalent Np is expected to dominate in reducing environments. In certain conditions of temperature and potential, the hexavalent state is indicated to form according to the modeling. In a repository many components are known to play an important role in Np and other actinides speciation through adsorption, complexation, dissolution and precipitation reactions. Inorganic ligands present in nearly all natural water at various degree, and organic ligands can react with Np and consequently affect its speciation and behavior through the formation of numerous compounds. Among all of these materials, carbonate is of interest because of its large amount and its high reactivity with actinides. Phosphate may also be expected from the package, even if it is in very small quantity and is examined due to its high complexation strength.

The consequences of a water intrusion into the repository on the speciation of Np was investigated using the geochemical model CHESS version 2.4 [2]. The Geochemist's Workbench version 2.0 [3] has also been considered with Act2 for Redox-pH diagrams.

J-13 water composition [4] at pH 7 and Eh = 700 mV. Constituent concentration in mmol/L

Constituent	mmol/L
Na ⁺	1.96
K ⁺	0.136
Li ⁺	0.009
Ca ²⁺	0.29
Mg ²⁺	0.075
Mn ²⁺	0.00002
Fe ³⁺	0.0008
Al ³⁺	0.001
F ⁻	0.11
Cl ⁻	0.18
NO ₃ ⁻	0.16
SO ₄ ²⁻	0.19
Total carbonate	2.81

The composition of J-13 groundwater is given above. The measured redox potential has been reported slightly lower, 430 ± 50 mV [5]. The ionic strength is about 3.7 mM. During the modeling the ionic strength remained between 3.8 and 8.0 mM. The quantities of Np(V) (NpO₂⁺) and of phosphate considered were respectively 10^{-6} mM and 2.81×10^{-2} mM (1% of total carbonate).

The first set of conditions for the calculations are given below. First, as the potential was varied from 0 to 1.5 V. The temperature was fixed between 25 °C and 100 °C. The pH was varied from pH 5 to pH 12. In this set of pH, a gap between 8.25 and 10.75 is evident. It results from a problem of convergence in the root-finding routine for working with nonlinear multidimensional system. At 50 °C, this problem occurred for between pH 7.9 and pH 10.75; The second set of conditions varied the temperature at the pH was held constant. The third set of runs consists in having the temperature vary continuously from 25 to 100 °C and examine the influence of the pH. These two last sets are both run for two potentials: 430mV and 700mV [4,5].

As a conclusion, this study allows to highlight seven different main Np species. In conditions below 0.5 V the tetravalent NpO₂ is formed. Three pentavalent Np species, NpO₂⁺, NpO₂CO₃⁻, NpO₂OH_(aq) are dominant in the potential ranging from 0.5 V to 1.15 V. Three hexavalent Np species: NpO₂(CO₃)₃⁴⁻, NpO₂(CO₃)₂²⁻, NpO₂OH⁺, are in the oxidizing conditions above 1.15 V. Some other species with fluoride, sulfate and phosphate are calculated to exist but at very low concentrations.

Influence of pH on the speciation of Np for a potential ranging from 0 to 1.5 V

Introduction

The potential is increased from 0 V to 1.5 V. Four temperatures are considered 25 °C, 50 °C, 75 °C, 100 °C. To study the influence of pH on the speciation of Np, the pH is varied from pH 5 to pH 12. The pH of J-13 water, pH 7, has been set as the reference. Because of the large amount of carbonate attention is made between pH 7 and pH 8. Between pH 8.25 and pH 10.75, no modeling is available due to divergence of the calculations, but an extrapolation of the data can be easily made.

Results

Three domains are highlighted according to the oxidization state of the Np, IV V and VI, respectively corresponding to region I (RI), region II (RII) and region III (RIII). The limits between them strongly depend on temperature, as expected by the Nernst equation, as the following graph shows.

Figure 1: Variation of the potential separating R1/R2 and R2/R3 with pH
Lx means lowest limit at x degree Celsius; and Hx means highest limit at x degree Celsius.

As the pH increases, the potentials demarcating the regions decreases meaning that for the potential range of interest 430 and 700 mV ($\pm 20\%$). The oxidation state changed respectively from IV to V and V to VI. Moreover, each time the domain of consideration is at the border and a slight evolution of the conditions in the medium may vary the oxidation state of the species. As the temperature increases, the domain of stability of the pentavalent species increases. To conclude, a certain rise of both pH and temperature favor the Np(V) species for the potentials of interest. The species of interest will now be detailed for the different temperatures.

Np speciation under J-13 conditions at pH 7 with an Eh range of 0.0 V- 1.5 V

The following graphic presents the main species of each oxidation state at 25 °C for pH J-13 water at pH 7. The lone tetravalent species remaining predominant for a potential lower than 555 mV is NpO_2 . Three pentavalent species occurred between 555 and 1065 mV. The NpO_2^+ ion is the predominant Np(V) species with a relative amount of 95%, while $\text{NpO}_2\text{CO}_3^-$ and NpO_2OH represent respectively about 4 and 1 %. In the hexavalent oxidization state predominate the following carbonated species: $\text{NpO}_2(\text{CO}_3)_3^{4-}$ (>77%) and $\text{NpO}_2(\text{CO}_3)_2^{2-}$ (about 15%). The neptunyl hydroxide cation, NpO_2OH^+ , is the third species present for high potentials. Moreover, as the potential keeps on increasing, the neptunyl tri-carbonate remains the lone species in the medium.

Speciation of Neptunium at 25 °C & pH=7

Figure 2: Speciation of Np at 25 °C and pH 7

Note: the main species have been taken into account in this graph. However, other species (sulfate, fluoride and so) are also present in the medium, but in lower quantity.

Np speciation under J-13 conditions at pH < 7 with an Eh range of 0.0 V- 1.5 V

If the pH decreases, the number of tetravalent and pentavalent species decreases. At pH 5, the main and lone tetravalent specie is the Np pentaphosphate. The neptunyl begins to dominate at pH 6. Thus a quantity of phosphate equal to 1% of the quantity of carbonate doesn't have any influence on the medium for a potential below 555 mV; The situation is identical for the pentavalent oxidation state since NpO_2^+ represents about 100% of the Np species; The hexavalent region of stability is a little more complex since five species can be noticed. The aqueous neptunyl phosphate dominates the speciation while neptunyl hydroxide and neptunyl fluoride cations represents respectively 20 % and 10 % of the relative species. When the pH increases, the phosphate compounds disappears, replaced by the carbonated species described previously.

Np speciation under J-13 conditions at pH > 7 with an Eh range of 0.0 V- 1.5 V

For basic pH, NpO_2 is still the lone tetravalent specie in the medium. More interesting are the changes occurring for the Np(V) species. The three species previously described are still dominant, but their ratios are modified as the pH increases. As the pH increases, the overall concentration of NpO_2^+ diminishes. At the same time, the amounts of carbonate and hydroxide Np increase. The monocarbonate specie is greater than the hydroxide specie amount initially, but as the pH increases, this proportion tends to reverse for higher pH. Moreover, while the proportion of hydroxide compound keeps on rising with pH, the amount of carbonated Np starts decreasing above pH 11. The evolution of the medium for higher potentials is in favor of the neptunyl tetracarbonate, which predominated the speciation for pH > 8.25. The dominant species are the same for the higher temperatures.

Study of the relative quantity of each main specie

Tetravalent species

NpO_2 is almost the only tetravalent specie performed in the medium; indeed, for $\text{pH} < 6$, pentaphosphate Np(IV) may have a significant role at low temperatures. As soon as temperature increases, this phosphate specie disappears.

Speciation of Neptunium at 25 C & $\text{pH}=5$

Figure 3: Role of phosphate at low pH and low temperature

Pentavalent species

Changes in pH significantly effect the formation of pentavalent compounds. An increase in pH, especially above pH 9.5 reduces the formation of NpO_2^{+} : Above pH 9.5 the carbonate and hydroxide species begin to dominate

Figure 4: Influence of pH on the formation of NpO₂⁺

Figure 5: Influence of pH on the formation of NpO₂(CO₃)⁻

Figure 6: Influence of pH on the formation of NpO₂OH_(aq)

Figure 7: Influence of pH on the formation of NpO₂(CO₃)₃⁴⁻

Hexavalent species

Among the hexavalent species of interest, NpO₂HPO₄⁻ is predominant up to pH 7, while for basic pH the neptunyl di- and tri- carbonate lead the speciation. Contrary to NpO₂(CO₃)₃⁴⁻, whose formation is driven by the basicity, the formation of NpO₂(CO₃)₂²⁻ is enhanced by a decrease of the acidity of the medium, but the trend reverses above neutrality.

$\text{NpO}_2(\text{CO}_3)_2^{2-}$ formation at 75 °C in accordance with pH and potential

Figure 8: Influence of pH on the formation of $\text{NpO}_2(\text{CO}_3)_2^{2-}$

Conclusion for study of the relative quantity of each main specie

The presence of phosphate in low quantity has no influence on the speciation of Np. Three region of predominance are drawn depending on the potential. monocarbonate and then hydroxide dominate the speciation for intermediate potentials. This is the domain where Np(V) predominates. Carbonate species with higher valences dominate as potential is more oxidizing.

Influence of temperature at fixed pH on the speciation of Np for a potential ranging from 0 to 1.5 V

Introduction

The potential is increased from 0 V to 1.5 V. A wide range of pH is considered from pH 5 to pH 12. To study the influence of temperature on the speciation of Np, the pH was varied from 25 °C to 100 °C. The calculations at pH 7 are still taken as the reference. The effects of the temperature on the predominant species shown in the previous paragraph are investigated.

Results

Np(IV) compounds

As the temperature increases, the Eh where the tetravalent species begin to oxidized decreases. For Np speciation in nuclear waste, this influence may be important since any tetravalent species present will experience a temperature gradient.

Np(V) compounds

The behavior of pentavalent compounds is more complicate. The temperature effects have to be considered along with the pH effects. As a consequence the competition between the different species is varied. The ion NpO_2^+ occurred mainly at low temperatures. For instance, its relative quantity drops from 95% at 25 °C to 10% at 100 °C at pH 7, as show below. The same behavior is noticed for all the pH that has been considered.

NpO₂ formation at pH=7 in accordance with temperature and potential

Figure 9: Influence of temperature on the formation of NpO₂

Figure 10: Influence of the temperature on the formation of NpO₂⁺ at pH 7

i

The competition between the carbonate and the hydroxide groups is strongly affected by the temperature. Relative quantities of both NpO₂CO₃⁻ and NpO₂OH_(aq) increase with temperature. When the pH is high enough the trend is reversed. This occurs at pH 8 for NpO₂CO₃⁻ and higher for NpO₂OH_(aq);

Figure 11: Influence of the temperature on the formation of $\text{NpO}_2\text{CO}_3^-$

Figure 12: Formation of $\text{NpO}_2\text{CO}_3^-$ and NpO_2^+ at 25 °C and 100 °C

Figure 13: Formation of $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2\text{OH}(\text{aq})$ between 25 °C and 100 C

Temperature effects the competition between NpO_2^+ and $\text{NpO}_2\text{CO}_3^-$ in an acidic or a soft basic medium. For $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2\text{OH}(\text{aq})$, a more basic medium is required to effect the relative amount of species. The temperature enhances the complexation of neptunyl with carbonate. The relative quantity of $\text{NpO}_2\text{OH}(\text{aq})$ remains steady and thus, doesn't seem to affect the competition between NpO_2^+ and the complex $\text{NpO}_2\text{CO}_3^-$: An increase of the temperature is favorable to the formation of $\text{NpO}_2\text{CO}_3^-$, while it makes the relative quantity of $\text{NpO}_2\text{OH}(\text{aq})$ fall significantly.

Np(VI) compounds

The two compounds of interest are $\text{NpO}_2(\text{CO}_3)_2^{2-}$ and $\text{NpO}_2(\text{CO}_3)_3^{4-}$: The temperature favors the first specie.

Conclusions on the influence of temperature at fixed pH on the speciation of Np for a given potential

If the temperature of the medium increases, the formation of neptunyl mono- and di-carbonate will be enhanced and it will reduce the formation of complexes with hydroxide group if the pH remains low.

Formations of $\text{NpO}_2(\text{CO}_3)_2^{2-}$ and $\text{NpO}_2(\text{CO}_3)_3^{4-}$ at pH=7 in accordance with temperature and potential

Figure 14: Influence of the temperature on the formation of $\text{NpO}_2(\text{CO}_3)_2^{2-}$ and $\text{NpO}_2(\text{CO}_3)_3^{4-}$

Conclusion and further models

The potential is fixed at 430 mV and then at 700 mV. The temperature is increased from 25 °C to 100 °C. The speciation of Np is investigated between pH 5 and pH 12. This study agrees with previous calculations [4,5].

At these potentials, only Np(IV) and Np(V) species are observed. The temperature and the pH are significantly favorable to the formation of $\text{NpO}_2\text{CO}_3^-$ compared with the formation of both NpO_2^+ and $\text{NpO}_2\text{OH}_{(\text{aq})}$. As the temperature and pH increase, the relative quantity of the monocarbonate complex increases. However, at high pH, either the hydroxide aqueous specie (at 430 mV) or the di- and tetra- carbonate complexes (at 700mV) become predominant. Among those three compounds, only $\text{NpO}_2(\text{CO}_3)_2^{2-}$ follows the same trend as the temperature. The phosphate doesn't affect the speciation of Np unless the pH becomes very acidic. Sulfate, chloride and fluoride have no impact under the conditions modeled.

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Appendix 4

Speciation of Neptunium in Spent Fuel Nuclear Energy Research Initiative (NERI) Annual Report August 1999 – July 2000

Donald T. Reed, Chemical Technology Division, Argonne National Laboratory
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Technology

Anne Hermes, Department of Civil Engineering, Northwestern University

NERI Project: Speciation of Np in Spent Nuclear Fuel
1st Annual Report 15 August 1999-15 August 2000
Appendix 4

Speciation of Neptunium in Spent Fuel
Nuclear Energy Research Initiative (NERI)
Annual Report
August 1999 – July 2000

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Executive Summary

Speciation of Neptunium in Spent Fuel

Progress is reported for the first year (August 1999 to July 2000) of an Argonne project to investigate the speciation of neptunium in spent fuel. This project is jointly funded with researchers at MIT but also involved collaborations with students at Northwestern University and Ohio State University.

Three research areas are being pursued: 1) the subsurface chemistry of neptunium when organics are present, 2) the effects of microbiological activity on neptunium speciation and phase alteration, and 3) synchrotron-based characterization studies of neptunium solids. This work is integrated with the speciation studies and modeling efforts at MIT. A long-term goal of this project is to establish the speciation of Np in spent fuel, the fate of this element in the subsurface (i.e. formation of alteration phases), and the subsequent effects on speciation once the neptunium is dissolved in groundwater (e.g., organic reactions and biological effects).

Progress in the past year was made in all areas, but mostly in neptunium subsurface chemistry. The reactivity of Np(VI) with citrate was investigated as a model system to understand the role of complexation and redox conditions in defining the oxidation state distribution under subsurface conditions. We established that citrate reduces Np(VI) to Np(V) within days under all conditions investigated. The disappearance of Np(VI) was first-order under all conditions investigated but the pseudo first order rate constant was not proportional to the concentration of citrate due to changes in the reaction mechanism. Complexation affected the apparent rate of reaction in ways that are still under investigation. The reactivity was predominantly defined by the carboxylates present, with a small but significant contribution from the tertiary alcohol. The much higher reactivity observed, however, with cytochrome C (which is a biologically derived reducing agent present in the subsurface) shows that we still cannot account for redox effects in biologically active systems.

Research was also initiated to establish the effects of microbiological activity on the speciation of neptunium. Emphasis is on a *Shewanella* strain that is an anaerobic metal-reducing bacterium common to many subsurface aquifers. The methodology for growing and studying this isolate was established. Interaction experiments with neptunium are planned for the early part of the second year in the project.

Preparations for synchrotron studies of neptunium-bearing solids were also completed. A beamline run is scheduled for late August 2000.

Speciation of Neptunium in Spent Fuel

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Speciation of Neptunium in Spent Fuel Annual Report, August 99 to July 2000

1.0 Project Overview and Key Accomplishments

This report summarizes the progress made at Argonne National Laboratory (ANL) during the August 1999 to July 2000 period in the Nuclear Energy Research Initiative (NERI) project entitled "Neptunium Speciation in Spent Fuel." This reporting period corresponds to the first year of a joint collaboration between Donald Reed (ANL) and Professor Ken Czerwinski at the Massachusetts Institute of Technology (MIT).

1.1 Project Overview

The overall goal of this project is to develop a basic understanding of the chemistry of neptunium as it pertains to the long-term behavior of spent fuel in the subsurface. This includes the characterization of neptunium phases in spent fuel, the degradation and alteration of these phases under subsurface conditions, and the subsequent groundwater chemistry of dissolved neptunium species. An understanding of the subsurface chemistry of this important multivalent actinide is needed to establish its potential for migration after final disposal in a repository. A viable approach for the final disposal of nuclear waste is an essential part of the nuclear fuel cycle and is currently under investigation by a variety of projects supported by the Department of Energy.

This project has a strong university-national laboratory focus. This research approach directly supports a key agenda in the NERI initiative to promote and facilitate interactions between university and national laboratory researchers in actinide research important to the nuclear fuel cycle. Along with the collaboration with MIT researchers, which is directly supported by NERI, there are also contributions to this project through a long-standing collaboration between Argonne and Professor Bruce Rittmann at Northwestern University, as well as ongoing interactions with Professor Russell Pitzer at Ohio State University.

During this reporting period, the project goals at Argonne were as follows:

- 1) Train student researchers to handle and work with radioactive materials to perform actinide research.
- 2) Perform studies to establish the subsurface chemistry of neptunium, a key factor in defining subsurface migration. Special emphasis is placed on organic and microbiological interactions.
- 3) Develop synchrotron-based techniques to establish neptunium speciation in solids and waste forms.

1.2 Summary of Key Accomplishments

During the first year of this project, progress was made in all three project goals. Highlights for each overall goal are summarized below:

- 1) Interactions with academia – training of students in the field of radiochemistry
 - A seminar entitled “Actinide Microbiological Interactions in the Subsurface” was presented by D. Reed at MIT in January of this year.
 - Christine Sherman, MIT nuclear engineering graduate student working under the direction of Ken Czerwinski, has been working at ANL since June. During this time she has completed both hands-on and formal course work in radioactive material handling, and has been performing Np(V) sorption studies at Argonne under the direction of D. Reed.
 - Anne Hermes and Warinthorn Songkasiri, Northwestern graduate students in the department of civil engineering, worked at ANL throughout the year. They have completed radioactive materials training coursework and are pursuing Np(V) interaction studies with metal-reducing subsurface bacteria under the direction of D. Reed.
 - A joint paper on the spectroscopy of Np(V) was written with Professor Russell Pitzer in the chemistry department at Ohio State University.
- 2) Subsurface chemistry of neptunium
 - The visible-near-infrared (vis-nir) spectrum of Np(V) in perchlorate media was measured with emphasis on the lesser-known absorption bands. These data were provided to researchers at Ohio State University to challenge their theoretical efforts to calculate Np(V) electronic spectra.
 - A detailed study of the reaction between Np(VI) and citric acid was initiated and is 80% complete. This model system study leads to insight on the important role that organics, and hence microbes, play in the subsurface redox chemistry of multivalent actinides.
 - A study to look at the subsurface redox chemistry of neptunium in the presence of sulfate reducing bacteria was completed. This study was in progress prior to the start of the NERI funding and has led to a paper entitled “Reduction and Precipitation of Neptunium(V) by Sulfate-Reducing Bacteria,” accepted for publication in *Radiochimica Acta*.
 - An atomic force microscope, Molecular Imaging model 10-100, was ordered. This will be used to better characterize Np samples in both the subsurface chemistry and synchrotron-based studies.

3) Synchrotron-based analysis of neptunium solids

- Synchrotron studies on neptunium solids were initiated. Safety-related aspects of performing synchrotron studies on radioactive materials were completed. A beamline run is scheduled for late August 2000.

Presentations and Publications

Presentations:

- "Actinide Microbiological Interactions in the Subsurface," seminar presented by D. Reed at MIT in January 2000.
- "Oxidation/Reduction of Multivalent Actinides in the Subsurface," invited paper presented by D. Reed at Plutonium Futures 2000 Conference, Santa Fe, NM, July 2000.

Publications:

- "Reduction and Precipitation of Neptunium(V) by Sulfate-Reducing Bacteria," James E. Banaszak, Bruce E. Rittmann, and Donald T. Reed. Supported in part by NERI, accepted for publication in *Radiochimica Acta*.
- "Intensities in the Spectra of Actinyl Ions," S. Matsika, R. M. Pitzer, and D. T. Reed. Submitted to J. Phys. Chem for publication.

1.3 Overview of the ANL/NERI Budget

A summary of the dollars spent at Argonne for the NERI project, as a function of time, is shown in Figure 1. Total budget was \$275.3 K. There is no carry-over anticipated at the end of the reporting period.

Figure 1. Summary of planned expenditure and actual expenditure spent during FY 2000 for the ANL part of the NERI project.

2.0 Background: Neptunium Speciation and Subsurface Chemistry

2.1 Neptunium in Spent Fuel

Neptunium is an important actinide constituent of spent fuel that is formed by reaction of neutrons with ^{238}U and ^{235}U in nuclear reactors. Its long half-life, combined with the high mobility of the Np(V) oxidation state in the environment, makes it an important, if not the key, concern for the long-term disposal of spent nuclear fuel. The redox properties of neptunium are important because only its higher oxidation states are mobile in the subsurface.

Argonne has been studying spent fuel behavior in an unsaturated (e.g. water vapor, air) environment over the past four years [1-4]. In these studies the dissolution of spent fuel constituents into the aqueous medium is being investigated. The extent and degree of surface reaction are being established by solids characterization techniques involving the use of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The key results and observations from these studies are:

- Uranium dioxide, in an unsaturated environment, is oxidized, leading to the formation of alteration phases on the spent fuel surface. Both chemical and radiolytic processes contribute to the oxidation reactions observed.
- Important alteration phases of uranium have already been identified. These are uranyl oxide hydrates, sodium boltwoodite (uranium-silicate) phases, and dehydrated schoepite.
- Spent fuel composition, specifically, the fission product and actinide content, has a significant, but not well defined, effect on the phase distribution in these samples.
- Neptunium was identified as a constituent of a uranium alteration phase, although the mechanism for this is not understood.

The observations made in these experiments raise a number of key issues with regard to neptunium speciation. Most importantly, the mechanism by which neptunium becomes incorporated into the uranyl alteration phase is not well understood. How this occurs, and its extent in a repository setting, are important considerations in the overall assessment of neptunium release into the surrounding environment. For example, if oxidation is a necessary step, then high potential for dissolution as a mobile form exists. Conversely, if incorporation without oxidation is the mechanism, then mobility is unlikely since Np(IV) is relatively immobile in the environment.

A second issue is the speciation of neptunium in spent fuel prior to reaction/alteration. This has not been determined because of the complexity of the spent fuel matrix and the inherent difficulty of obtaining oxidation state information by non-destructive analyses. The characterization of the neptunium oxidation state in reacted spent fuel using synchrotron-based methods is a long-term goal of this project.

2.2 Neptunium as a Subsurface Contaminant

Relatively little is known about the basic chemistry and geochemistry of neptunium in the near neutral to high pH regime that is of most interest to its environmental geochemistry. Neptunium(V) (i.e., NpO_2^+), which is believed to be the most stable oxidation state under many environmental conditions, is relatively non-complexing and hence mobile in the subsurface. This expected very-high mobility is what identifies neptunium as a significant potential problem for a nuclear high-level waste repository.

In the subsurface the most important factors that define radionuclide speciation are inorganic complexation, organic complexation, oxidation-reduction reactions (including biotic transformations), and colloidal/polymeric properties. The relative importance of each of these depends on the composition of the groundwater, important environmental parameters for that groundwater (e.g., pH, redox), the presence of other inorganic/organic contaminants (most importantly organic complexants), and microbiological processes.

Inorganic Complexation

In natural systems, the following inorganic ligands are potentially important complexants of radionuclides in solution: $\text{CO}_3^{2-}/\text{HCO}_3^-$, OH^- , Cl^- , $\text{SO}_4^{2-}/\text{S}^{2-}$, F^- , and phosphate. The relative importance of these complexants depends on the pH, radionuclide oxidation state, and concentration of the complexant. General reviews of the inorganic complexation of radionuclides have been written by Ahrlund et al. [5] and Jones and Choppin [6]. These are a compilation of existing data obtained for acidic systems. Specific reviews on the carbonate-actinide [7, 8] and hydroxide-actinide [9] complexes also have been written. A number of papers written in connection with the high-level nuclear waste programs describe the effects of groundwaters on actinide solubilities. The most important of these are the paper of Nitsche and Edelstein [10], who report the effect of tuff groundwater on radionuclide solubility (the repository in tuff is the only remaining candidate site in the U.S. for high-level nuclear waste disposal), and the report by Allard [11], who summarized radionuclide solubility under conditions typical of the granitic sites under consideration in Sweden. Both of these documents contain qualitative, rather than quantitative, information on the effects of complexation on actinide speciation.

The role and importance of redox reactions in determining radionuclide mobility have been strongly emphasized in waste management programs [12]. Redox control in geochemical systems usually is interpreted according to the iron mineralogy and aqueous chemistry of the site [13, 14] as well as biotic transformations [15,16]. Since most radionuclides have significantly lower solubilities in the lower oxidation states (i.e., under reducing conditions), their reduction in the near-field has a significant effect on their mobility. The geochemistry of radionuclide systems (in particular, the effect of complexation on this chemistry) has not been well studied in groundwater systems.

Organic and Microbiological Effects

In the subsurface, understanding the role of organics and microbes in defining neptunium speciation is key to understanding its subsurface mobility. Whereas Np(V) is the predicted oxidation state when inorganic speciation predominates, Np(IV) is the likely oxidation state when microbiological activity and organic species are present. This is very significant since Np(IV) has significantly lower solubility and mobility.

The potential effect of microbiological activity on the redox chemistry of actinides is illustrated in Figure 2. Here the redox potential generated by the various classes of subsurface bacteria is compared to the half potential of redox couples important in the environmental chemistry of the multivalent actinides. For neptunium, +4 is the predicted oxidation state for anaerobic microbiological systems (e.g., sulfate reducing bacteria, methanogens, and metal reducers).

Figure 2. Expected dominant oxidation states of the actinides as a function of standard reduction potential in pH 7 water at equilibrium with atmospheric CO_2 . The expected redox potentials associated with common microbial electron acceptor couples are shown schematically at the top of the figure [19].

Also important is that there is a transition from aerobic to anaerobic (i.e., oxygen deficient) systems as actinide migration progresses from the point of contamination to the far field. As oxygen depletion occurs, anaerobic systems, which are more strongly reducing, will predominate and exert a strong influence on the nature of the mobile

actinide species. So the role and importance of these systems increase when far-field migration is the most important.

That microbiological activity has a strong influence over the redox chemistry of neptunium has been demonstrated in our laboratory [17, 18]. In lake bottom sediments, methanogenic activity resulted in the reduction of neptunium to Np(IV) species, leading to its precipitation and immobilization. In this relatively complicated system (Np in clay sediments), we were able to perform X-ray absorption near-edge spectroscopy (XANES) of the Np present and compare this spectrum against neptunium solid standards to establish that the Np in the sediments was a Np(IV) phase. This study is a good example of the application of synchrotron techniques to the identification of unknown actinide species in environmentally relevant samples.

The mechanism by which microbiological activity affects the redox chemistry of Np is not well understood but is moderated or directly involves reaction with bio-derived organics. Additionally, many complexing agents used to reprocess nuclear fuels are often present and can act as reducing or oxidizing agents in the subsurface. The role of organics, the functional group dependence of the reactivity noted, and its connection to biological process are a key focus of the work at Argonne in this project.

3.0 Research Progress

3.1 Subsurface Chemistry of Neptunium

3.1.1 *Neptunium(V) Spectrum*

The absorption spectra of neptunium species in aqueous media have long been recognized for their value as “fingerprint” spectra to identify the various oxidation states of dissolved neptunium [21-25]. The absorption spectra of these species are complex and typically consist of bands corresponding to un-allowed electronic transitions. They, however, tend to follow the Beer-Lambert law, so they are widely used to establish oxidation-state-specific concentrations. Our purpose in re-determining this spectrum was to provide high-resolution spectra for the weaker lower-absorbance bands that are the focus of the theoretical studies on neptunium electronic spectra being conducted at Ohio State University by Professor R. Pitzer.

Neptunium-237 (82% purity by alpha activity, and > 99% purity by mass) was oxidized to NpO_2^{2+} by fuming in perchloric acid (Aldrich reagent grade). This was reduced to NpO_2^+ by adding hydrogen peroxide and precipitated as a $\text{NaNpO}_2\text{CO}_3$ solid by titration with 0.1 M sodium carbonate solution. The white carbonate solid was re-dissolved in 0.1 M perchloric acid. The pH, measured with a Ross combination electrode, was 1.69 ± 0.01 with an ionic strength of 0.1. A neptunium concentration of 1.55 ± 0.02 mM was measured by a Packard instrument 2 B alpha scintillation counter combined with alpha spectrometry and by inductively coupled plasma-mass spectrometry (ICP-MS) using NIST-traceable standards.

Spectra for Np(V) were taken at 21 ± 0.5 °C on a Varian CARY 5 spectrometer using a bandpass of 0.3 nm in the near infrared region (850 to 1300 nm) and 1.2 nm at shorter wavelengths (350 to 850 nm). Reproducibility of the spectrum was established by re-taking the spectrum five times at 2 hour intervals, showing that these spectra were indistinguishable. The resolution of the wavelengths reported is within 0.1 nm, with an overall uncertainty of 0.3 nm in the peak positions. The optical density (OD) measurements are within 0.5%.

A listing of the various bands identified in the Np(V) spectrum, along with the measured extinction coefficient, is given in Table 1. The measured extinction coefficient for the 980.2 nm band, typically used for Np(V) analysis, was 398 ± 4 M⁻¹cm⁻¹. The total and expanded Np(V) spectra are shown in Figure 3.

Assessment of Literature Values for Neptunium(V) Extinction Coefficients

The absorption spectrum of the neptunyl cation is dominated by the spin-forbidden f-f electron transition at 980.2 nm. This band and the lesser intense absorption band at 616.5 nm, follow Beer-Lambert behavior [23] and are often used analytically to establish the concentration of neptunyl species in solution. Because these two bands are also affected by complexation, they are frequently used to study the complexation behavior of neptunyl.

The extinction coefficients generally used for the 980.2 and 616.5 nm bands are 395 ± 12 M⁻¹cm⁻¹ and 22 ± 1 M⁻¹cm⁻¹, respectively [21-23]. These are the values

tabulated in the general texts [21, 22] but are based on the values determined by Hagan and Cleveland [23] in 2 M perchloric acid. Earlier reports [24] that these bands may not follow Beer-Lambert behavior, hence the significantly lower extinction coefficients reported, were shown to be due to the use of too large of a bandpass [23, 25, 26] in taking the absorption spectrum. When the proper band pass is used, and there is no change in speciation with concentration, all the absorption bands of Np(V) follow Beer-Lambert behavior.

The reported uncertainty in the extinction coefficient for the 980.2 nm peak [23] is $\pm 3\%$ leading to a value of $395 \pm 12 \text{ M}^{-1}\text{cm}^{-1}$. This compares favorably to the value of $387 \pm 20 \text{ M}^{-1}\text{cm}^{-1}$ reported by Sullivan [27]. It is also within the uncertainty of the value of $398 \pm 4 \text{ M}^{-1}\text{cm}^{-1}$ reported in Table 1. In summary, we have confirmed the results reported by Hagan and Cleveland, made a more accurate determination of the wavelength and extinction coefficient, and reported wavelength and extinction coefficient data for the lesser known absorption bands.

Table 1. Peak Location for Np(V) absorption bands, measured OD, and calculated extinction coefficients

Peak Location (nm)	Measured OD	Extinction Coefficient ($\text{M}^{-1}\text{cm}^{-1}$)
1116.9 *	0.0098	6.3 ± 0.1
1097.0	0.0385	24.8 ± 0.2
1022.8	0.0142	9.2 ± 0.1
980.2	0.6172	398 ± 4
913.1	0.005	3.2 ± 0.1
769.5	0.006	3.9 ± 0.1
686.9	0.0082	5.3 ± 0.1
616.5	0.0338	21.8 ± 0.2
476.1	0.0115	7.4 ± 0.1
430.2	0.0116	7.5 ± 0.1
* There are no absorption bands between 1150 and 1350 nm.

Figure 3. Absorption Spectrum of 1.55 mM Np(V) in 0.1 M perchloric acid. The expanded plot (bottom) shows the fine structure of the low-extinction coefficient bands, and the unexpanded plot (top) shows the 980.2 nm band generally used for analysis of Np(V).

3.1.2 Reduction of Np(VI) by Citrate

The reactivity of Np(VI) towards citrate was investigated as a model system to establish the relationship between complexation and redox activity. Citrate is an important anthropogenic and naturally occurring subsurface contaminant that is linked to the complexation behavior of natural organics (e.g., fulvic and humic acids) and biological activity.

Neptunium(VI) is known to be unstable in high pH groundwater systems and is reduced to Np(V), which is the most stable form of Np in the subsurface [10,11]. The favorable spectroscopy of Np(V) and Np(VI), the inherent stability of the Np(V) species, and the low tendency of Np(V) toward hydrolysis make these species an ideal oxidation state couple for this type of investigation.

In the presence of a reducing agent, the following overall reaction is expected:

If the concentration of the reducing agent $\gg [\text{Np(VI)}]$, then a pseudo first order condition exists and the disappearance of the Np(VI) is first order with an effective rate constant of $k [\text{reducing agent}]$ where k is the rate constant for the appropriate simple reaction.

When the reducing agent is also a complexant, the complexation leads to changes in the relative rates of reaction and changes in the overall stability of the various oxidation states of the multivalent actinide.

For citric acid (H_3Cit), which is tri-protic, the following reaction pathway is expected at low pH ($\text{pH} \leq 1$), where essentially no complexation or acid dissociation is taking place:

At low to moderate pH ($\text{pH} = 1$ to ~ 3), the H_3Cit dissociates to form significant amounts of H_2Cit^- and HCit^{2-} (pK_a of 3.14 and 4.77, respectively), but the Np(VI) remains primarily as an aquo species since very little Np(VI) hydrolysis has taken place. These citrate species can complex with the Np(VI) and Np(V) to effect the overall rate of reaction and associated mechanism [28]. The reported formation constant for Np(V), the $[\text{NpO}_2\text{-HCit}]^-$ complex, is $490 \pm 125 \text{ M}^{-1}$ which means that typically over 90% of the Np(V) is complexed when HCit^{2-} is the predominant form of citric acid in solution. There is however no data on the corresponding Np(VI) complexes, which by analogy with U(VI) is likely to form much stronger complexes with citrate.

To account for the overall reactivity of Np(VI), one needs to take into account the various complexes that are formed. The more important of these are:

At higher pH (pH > 4), Np(VI) hydrolysis competes with citrate complexation, possibly forming mixed ligand complexes and citric acid undergoes further dissociation to form Cit^{3-} (pKa = 6.40). So reactivity is a function of the sum of the reaction of several species with the citrate in solution. The following hydrolytic species become important:

These species can form mixed ligand complexes. If citrate (Cit^{3-}) is the complexant, then the following complexes are probable:

as well as multiple-ligand complexes with the citrate species. The overall rate of reaction, when the concentration of citrate is in excess, is then given by the following expression:

$$-d[\text{Np(VI)}]/dt = \sum k_{\text{Np-Cit}} [\text{Np(VI)}] \quad (6)$$

where $k_{\text{Np-Cit}}$ are pseudo first order rate constants that correspond to the reaction of the various Np(VI)-citrate complexes with citrate to form specific Np(V)-citrate complexes and degradation products. The brackets indicate concentration of a particular species.

Reactions/complexes given in 1-5 show that the overall mechanism should be strongly dependent on pH and citrate concentration, since there are significant changes in speciation. The apparent rate of reduction is the sum of the rate of reduction for each of the complexes present in solution with any of the acid forms of citrate.

Experimental Approach

The Np-237 (82% purity by alpha activity, >99% purity by mass) was oxidized to Np(VI) by fuming in perchloric acid. The oxidation state purity was verified by taking an absorption spectrum using the CARY5 spectrometer. The pH was adjusted by the addition of either sodium hydroxide or perchloric acid. Neptunium concentration was monitored by absorption spectrometry (1221 nm band of Np(VI) and the 980 nm band of

Np(V)) to track oxidation state. A 1 cm quartz gas-tight cuvette was used for all spectroscopic determinations. Alpha scintillation counting was used to measure overall concentrations. All experiments were performed at room temperature ($21 \pm 2^\circ\text{C}$) and in the dark to prevent photolytic effects. See Table 2 for further experimental details.

Three organics were used to establish reactivity of Np(VI):

Citrate: $(\text{COOHCH}_2)_3\text{C-OH}$

Tri-carballylic acid: $(\text{COOHCH}_2)_3\text{C-H}$

3-Et-3-pentanol: $(\text{CH}_3\text{CH}_2)_3\text{C-OH}$

Citric acid is a tri-carboxylic acid with a tertiary alcohol on the central carbon. Tri-carballylic acid is identical in structure to citric acid except that the alcohol group has been replaced with hydrogen. The pentanol is also analogous to citric acid except that methyl groups have replaced the carboxylate groups. This series of reactants was used to establish the relative contribution of the carboxylates and tertiary alcohol to the observed reactivity. Additionally, the reduction of Np(VI) by cytochrome C, which is a reductase identified as a metal reducing agent in sulfate reducing bacteria (SRBs), was also investigated to put the observed reactivity of the organics in perspective.

Table 2. Experimental Conditions and Half-life of Np(VI) as a Function of Organic Species, pH, and Concentration.

Organic	pH	Concentration (M)	Half-life	Np(IV) ?
None	0.9	0.0093	>> 2 months	No
	1.9	0.00076	> 2 months	No
Citrate	1.4 ± 0.1	0.115	8 hours	No
		0.250	16 hours	No
		0.460	30 hours	No
		0.935	30 hours	No
	1.6 ± 0.2	0.002 – 0.7	8 hours	Yes
	4 ± 0.1	0.12 – 0.9	32 minutes	Yes
Tri-carballylic Acid	2.4	0.2	12 hours	No
	3.8	0.2	4 hours	No
	5.8	0.2	4 hours	No
Pentanol	4	0.2	> 10 days	No
Cytochrome C (Reductase)	2	0.002	< 1 minute	No

Autoradiolysis of Np(VI)

Neptunium, as NpO_2^{2+} in the +6 oxidation state, is not stable in water in the absence of oxidizing agents. The rate of reduction is affected by radiolysis due to the

alpha decay of the neptunium [22]. Experiments were performed at two concentration and pH values to establish the time window for the reduction of NpO_2^{2+} when reducing agents (e.g., organics) are present in solution.

Figure 4 shows the results obtained for NpO_2^{2+} in 0.1 M perchlorate at pH = 0.9 for the 7.6 mM solution and pH = 1.9 for the 0.62 mM solution. The important experimental observation is that the reduction, under these conditions, is relatively slow. After 2046 hours (~85 days), only 4.5% of the NpO_2^{2+} has been reduced to NpO_2^+ at the higher concentration studied. At the lower neptunium concentration, ~ 10% is reduced over the first 1000 hours (~42 days), but a faster rate is observed at longer times. For the Np(VI) reaction with organics, which were typically two days or shorter, the contribution of autoradiolysis can be ignored.

If the only cause of reduction is radiolysis, then the effective yield of the Np(V) species is $\gg 20$ molec/100 eV. This value is not realistic (it is too high), which signifies that reaction with water (or trace impurities in the water), not radiolysis, is responsible for most of the reduction observed. At the higher concentration (7.6 mM), where radiolysis is more prevalent, reduction is slowed rather than accelerated, suggesting that radiolysis may lead to increased oxidation not reduction.

Figure 4. Reduction of NpO_2^{2+} as a function of time in ~ 0.1 M perchlorate at pH = 0.9 and 1.9 for high and low concentration neptunium samples.

Reduction of Np(VI) by Citrate

In the presence of citric acid, Np(VI) was rapidly reduced to Np(V), and in two cases noted in Table 2, some Np(IV) was formed. A typical concentration profile is shown in Figure 5. The overall spectrum showing the Np(V) and Np(VI) bands is given in Figure 6. These concentration data, at a fixed pH and citrate concentration were pseudo first-order, that is, the plot of $\ln [\text{Np(VI)}]$ as a function of time is linear. A typical first-order plot is shown in Figure 7.

The observed half-lives for Np(VI) are tabulated in Table 2. These values are uncorrected for the effects of citrate concentration (this is still in progress). They show a strong dependence of the rate of reaction on pH but not as strongly on concentration. For a given concentration of citrate, the half-life decreases from 12 h to 8 h to 32 min as the pH is increased from 1.4 to 4.0.

The effect of citrate concentration is not straightforward. For the low pH series, a linear dependence is observed when the apparent rate constant is plotted against citrate concentration. This is the expected result for the reaction of Np(VI) + citrate at low pH. At higher pH, however, increased concentration of citrate does not lead to corresponding increases in the rate of reaction. These tendencies are evidence that the changes in speciation with citrate concentration and pH do not lead to a straightforward interpretation of the reactivity. Determining the different contributions of the various species is the focus of ongoing efforts.

Figure 5. Concentration of Np(VI) as a function of time in the presence of 0.115 M citrate and in the absence of uv-vis light (pH = 4, 21 ± 2 °C).

Figure 6. Absorption spectrum of Np(V) and Np(VI) citrate complexes in the presence of 0.25 M citric acid at pH = 4 and 21 ± 2 °C. The Np(V)-citrate complex ($\lambda_{\text{max}} = 984.7$ nm) is being formed as the Np(VI)-citrate complex ($\lambda_{\text{max}} = 1228.6$ nm) is being reduced.

Figure 7. Pseudo first order decay of Np(VI) as a function of time for 0.115 M citrate and pH = 4.

Reduction of Np(VI) by Tri-carballylic Acid

The reaction of tri-carballylic acid with Np(VI) was studied as a function of pH at a concentration of 0.2 M. The pH values were 2.4, 3.8, and 5.8. In all cases the reaction proceeded rapidly (4-h and 12-h half-lives) but was slower than the corresponding reaction with citrate. There was no evidence of the further reduction of Np(V) to Np(IV) in any of the systems studied. The formation of Np(V) as a function of time is shown in Figure 8.

Reduction of Np(VI) by Pentanol

Pentanol reduces Np(VI) very slowly relative to citrate and tri-carballylic acid. The reaction progress as a function of time for 0.2 M pentanol at pH 4 is shown in Figure 9. After approximately 40 days, only 4.5% of the Np(VI) initially present was reduced to Np(V). This shows that the tertiary alcohol, by itself (i.e., in the absence of complexation by carboxylates), is not very redox active.

Figure 8. Formation of Np(V) is indicated by the increase in the absorption at 980.2 nm, as a function of time due to reduction of Np(VI) by tri-carballylic acid. Each scan represents a different time in the reaction progress.

Reduction of Np(VI) by Cytochrome C

Cytochrome C is an important reductase that is present in anaerobic systems such as SRBs. This reductase has already been implicated as the reducing agent for the reduction of U(VI) to U(IV). This is an iron-based biomolecule that has a deep red coloration in the visible but is near infrared transparent (see Figure 10). The reduction of Np(VI) in this medium was instantaneous and led to the formation of Np(V) that was

stable over a period of four days (see Figure 11). No evidence of further reduction to form Np(IV) was observed.

Figure 9. Reaction of Np(VI) with 0.2 M pentanol at pH 4. Reaction progress is slow and comparable to that observed for “autoradiolysis.”

Figure 10. Spectrum of cytochrome C in high purity water.

Figure 11. Spectrum of neptunium in cytochrome C solution after 4 days. Spectrum indicates that only Np(V) is present, with no evidence for Np(VI) or Np(IV).

3.2 Microbiological Effects: Effect of Iron Reducing Bacterium, *Shewanella alga* BrY, on Np(V) Species

Microbiological-actinide interaction studies are being done to investigate the fate of neptunium in the subsurface for biologically active systems. This work is the focus of the collaboration between Argonne and Northwestern University and is a continuation of past efforts in this area [17-19]. Our emphasis in the NERI project is on the anaerobic systems that are likely to be important in the long-term migration of neptunium in the subsurface. This work is just now getting underway.

Microbially catalyzed metal reduction by microorganisms is expected to remove actinides from aqueous streams, as the microbe catalyzes the reduction of an organism from a soluble to an insoluble oxidation state. The emphasis is on Np(V), which is the most stable oxidation state of the actinide in aerobic natural conditions [29]. In most systems studied, the end result is the reduction of Np(V) to Np(IV), leading to the precipitation of Np from solution.

A pure culture of the Fe(III)-reducing bacterium, *Shewanella alga* BrY, is being used to assess its capability in reducing Np(V) to Np(IV). This microbe is being used because it has previously been shown to reduce several metals, including iron and manganese, but most importantly U(VI) to U(IV) [30]. We are currently reproducing the anaerobic experiments under non-growth conditions to confirm Fe(III) and U(VI) reduction by BrY as described in Truex, et al.[30]. We will soon be adding Np(V) to the

medium to determine BrY's ability to use Np(V) as a terminal electron acceptor in dissimilatory reduction. Cells are being cultured under aerobic conditions in Tryptic Soy Broth (TSB) on a rotary shaker at 35°C. They are then washed in an anoxic NaHCO₃ solution. All experiments are being performed using strict anaerobic conditions. Total actinide concentrations will be determined by a combination of alpha scintillation counting and ICP-MS. Absorption spectrometry using a Varian CARY-5 will be used to establish the specific structure and distribution of various actinide species present in the microbial systems being studied. To measure BrY concentrations, cells are directly counted using the Petroff-Hausser counting method and chambers [31].

We will use the CCBATCH model to interpret experimental results associated with the actinide speciation in the given experimental medium. We will include sub-models of precipitation/dissolution and primary-substrate control of dechlorination kinetics. We have created an input file for the experimental medium previously discussed and are interpreting the results by considering several degradable forms of organics.

3.3 Synchrotron Studies of Neptunium Compounds

The application of synchrotron-based methods, X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS), to the identification and characterization of environmentally relevant solids is well established. This work will be done at the Chemical Technology Division Material Research Collaborative Access Team (MR-CAT) beamline at the Advanced Photon Source located at Argonne.

The application of synchrotron methods to establish the oxidation states of actinides in precipitated, altered, and unaltered neptunium phases has also been demonstrated [17, 19]. We are proceeding with the characterization of carefully prepared neptunium standards to build a library of spectra that will help establish the nature of the unknowns. The first beamline run for this project is scheduled for late August of this year.

4.0 Future Research Direction

In our first year of the project a good start was made on understanding the neptunium chemistry described in the proposal. Studies to investigate key subsurface processes were initiated. Significant involvement between MIT and ANL occurred, laying a good foundation for long-term collaborations and student-national laboratory interactions.

For the upcoming year, the following research goals were identified:

- Complete the Np(VI) + citrate study to determine the synergistic effects of complexation and redox on the oxidation state stability and distribution of neptunium.

- Perform synchrotron studies on neptunium solids and related subsurface neptunium studies.
- Initiate anaerobic microbiological studies to establish the fate of neptunyl species in the subsurface.
- Continue the strong academic interaction and student involvement in the research performed at Argonne.

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