Progress Report

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

1st Progress Report

Reporting Period

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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

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to maintain a leadership role in nuclear technology. This project provides such an opportunity.

Financial

MIT:

Total budget for year: \$148373

Actual expenditure to date: \$35500

Expected expenditure to date: \$49450

ANL

Total budget for year: \$222000

Actual expenditure to date: \$63900

Expected expenditure to date: \$91900

Summary

This is the first progress 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

The MIT team performed work in Task 2. The sorption of Np to mineral phases was examined as a function of pH. The data will be used for geochemical modeling.

The ANL team organized the acquisition of equipment under Task 1. In Task 2, experiments were performed on the reactivity of Np with sulfide.

Appendix 1 MIT contribution
23 September 1999-31 January 2000

During the past months, experiments have been done within Task 2 to better understand the behavior neptunium with ligands, specifically goethite and montmorillonite. Goethite is the most common sorbent in soils, and its structure is stable over a large pH range [1], and montmorillonite is a clay mineral. Previous studies on Yucca Mountain tuff have 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. Eckhardt et al showed that neptunium's affinity for iron oxide was very high within the range of 6.2-6.9 [2], and Nakayama et al looked at the range pH 4-11 and found that goethite had strong sorption above pH 6 [3]. 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 [4]. Studies done on montmorillonite found that neptunium sorption reached its maximum at pH 8-8.5 weight experiments were conducted in an atmosphere with CO₂. However, carbonate complexation occurs at pH > 8 hindering sorption [5].

This study further examined the Np(V) sorption properties of goethite and the montmorillonite at various pH in the range pH 6-12 under an argon atmosphere. Np was purified by reducing Np(V) to Np(IV) using KI, and running the Np(IV) through a column to remove impurities such as Fe and Pa. Afterwards, the Np(IV) was converted to Np(V) using heat. A 1×10^{-4} M Np(V) solution was made in 1M HCl.

The goethite and montmorillonite were sieved using different mesh ranges to obtain particles within the size range 45-75 μ . The material was dried at 93.2 degrees 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 diffraction of montmorillonite at the same settings showed that the montmorillonite also contained some quartz.

The remainder of the experiment was conducted in a glove box under an argon atmosphere at room temperature. Six tubes of pH 5,7,8,9,10, and 12 were prepared for both goethite and montmorillonite using 15 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. Samples were shaken for 90 hours, and the pH in some samples was readjusted after 24 hours. The pH of some samples changed during this time period as result of the buffering capacity of the mineral phase. Scintillation assays were taken of the supernate to estimate the Np concentration left in solution.

Figure 1 shows the scintillation assays results of Np concentration from our experiment in the supernate as a function of pH. The predicted concentration of neptunium in solution was calculated based on values from Neck et al. [6]. 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 predicted decrease is similar to our control data. 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. The Np concentration in the goethite supernate decreased more than the montmorillonite supernate.

Further experiments are being conducted to determine the proton exchange capacity of the goethite to better model the behavior of goethite with neptunium.

References

1. Peak, Aaron, Ford, Robert G., Sparks, Donald L.: An in situ ATR-FTR Investigation of Sulfate Bonding Mechanisms on Goethite, *Journal of Colloid and Interface Science*, 218,289-299, (1999).
2. Eckhardt, Roger C.: Summary and Synthesis Report on Radionuclide Retardation for the Yucca Amount Site Characterization Project, Yucca Mountain Site Characterization Program Milestone 3784M, (October 1997).
3. Nakayama, S., Sakamoto, Y.: Sorption of Neptunium on Naturally Occurring Iron-containing Minerals, *Radiochimica Acta*, 52-53(part 1), 153-157, (1991).
1. Peak, Aaron, Ford, Robert G., Sparks, Donald L.: An in situ ATR-FTR Investigation of Sulfate Bonding Mechanisms on Goethite, *Journal of Colloid and Interface Science*, 218,289-299, (1999).
4. Combes, J. M., et al.: EXAFS Spectroscopic Study of Neptunium(V) Sorption at the α -iron hydroxide oxide (α -FeOOH)/Water Interface, *Environmental Science Technology* 26(2), 376-382 (1992).
5. Turner, D. R., Pabalan, R. T., Bertetti, F. P.: Neptunium(V) Sorption on Montmorillonite: An Experimental and Surface Complexation Modeling Study, *Clays Clay Miner* 46(3), 256-269 (1998).
6. Neck, V., Kim, J. I., Kanellakopulos, B.: Solubility and Hydrolysis Behavior of Neptunium(V), *Radiochimica Acta* 56(1), 25-30 (1992).

Chemical Speciation of Neptunium in Spent Fuel
Argonne National Laboratory
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Progress Report
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Project Scope and Objective

The primary goal of the Chemical Speciation of Neptunium in Spent Fuel project is to establish and understand the chemistry of Neptunium under conditions relevant to the Yucca Mountain High Level Waste Project. This includes the distribution of Neptunium in spent fuel, its reaction products under repository-relevant conditions and its likely speciation when spent fuel dissolves. More specifically the scope of this project includes the following research areas:

- oxidation state and phase of neptunium in simulated, actual and reacted spent fuel
- redox chemistry of neptunium once dissolved in low-ionic strength media at moderate to high pH (pH = 5-10).
- speciation of spent fuel in the subsurface to establish the effects of chemical and biological activity on its likely mobility

Our research emphasis in year 1 at Argonne National Laboratory is in the following areas:

- 1) Redox chemistry of Neptunium (V) and Neptunium (VI) at near-neutral pH with sulfide/sulfate and citric acid
- 2) Synthesis/analysis of neptunium solid standards to establish a suitable library for the interpretation of XANES and EXAFS data
- 3) Bio-reduction studies of Np(V) in anaerobic and aerobic systems

Summary of Progress During the Reporting Period

Most of the time spent in the first five months of the project was on preparations in the laboratory to do the research. Some preliminary studies were, however, also completed.

The reactivity of Np(V) towards sulfide is being investigated in the pH range of 5-10. Initial results show that the overall reactivity of sulfide towards Np(V) was very low. What is most interesting about these results are the speciation data that suggest the formation of a Np(V) complex with an oxygen-containing sulfur species other than sulfate when sulfide is oxidized at low pH. Work is ongoing to establish the nature of this complex and extend the redox studies to include the reactivity of Np(VI) with sulfide.

Synchrotron studies on Np solids are planned for March 2000. The goal of these experiments is to develop a base library of XANES/EXAFS spectra to more completely define the structure, edge position, and edge shape for Np solids to establish the background of information needed to understand speciation in spent fuel samples. These experiments will be done at the Material Research Society Collaborative Access Team beamline at the Argonne Advance Photon Source using procedures we have developed in past studies. Syntheses of Np solids are underway. XANES/EXAFS spectra of these solids, once characterized, will be taken.

The microbiological interaction studies, are ongoing and focus on interactions of anaerobic bacteria with Np(V). We have just completed a study showing that Np(V) is biologically reduced due to microbial activity of *D. Vulgaris* (a sulfate-reducing bacteria). These studies are being continued to establish the mechanism of reduction and extended to investigate other anaerobic systems and *pseudomonas fluorescens*.

Lastly, we are proceeding with the purchase of an Atomic Force Microscope with the capital equipment received through this project. A Molecular Imaging system was identified that is suitable for the in-situ studies of aqueous systems. This will be used to look at phase formation/structure at the nano-scale level for the various experiments in this project.

Publications

J. E. Banaszak, D. T. Reed and B. E. Rittmann, "Reduction and Precipitation of Neptunium(V) by Sulfate-Reducing Bacteria" accepted for publication in *Radiochimica Acta*, 2000

D. T. Reed, A. J. Kropf, S. B. Aase, S. Zygmunt, and L. Curtiss, "Oxidation State and Structure of Actinides in Environmental Samples Using Synchrotron-Based Techniques" in preparation.