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**Source Term Targeted Thrust
FY 2005 New Start Projects**



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PREFACE

This booklet contains project descriptions of work to be performed by the Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM), Office of Science and Technology and International (OST&I), Source Term Targeted Thrust as part of Fiscal Year 2005 new starts. The Source Term Targeted Thrust is part of OST&I's Science and Technology Program which supports the OCRWM mission to manage and dispose of high-level radioactive waste and spent nuclear fuel in a manner that protects health, safety, and the environment; enhances national and energy security; and merits public confidence. In general, the projects described will continue beyond FY 2005 assuming that the technical work remains relevant to the proposed Yucca Mountain Repository and sufficient funding is made available to the Science and Technology Program.

Project Title Actinide Adsorption to U(VI) Silicates
OCRWM S&T Program Thrust Source Term
Project Performers Washington State University, Idaho National Laboratory
Principal Investigators Sue Clark, Laurence Hull
FY 2005 Funding \$200,000

Abstract **BACKGROUND:** While a significant amount of work has been devoted to developing thermodynamic data describing the sorption of radionuclides to iron oxides and other geomedia, little data exist to describe the interaction of key radionuclides found in high-level radioactive waste with the uranium surfaces expected in corroded spent nuclear fuel (SNF) waste packages. Recent work indicates that actinide adsorption to the U(VI) solids expected in the engineered barrier system may play a key role in the reduction of dissolved concentrations of radionuclides such as Np(V). However, little is known about the mechanism(s) of adsorption, nor are the thermodynamic data available to represent the phenomenon in predictive modeling codes. Unfortunately, this situation makes it difficult to consider actinide adsorption to the U(VI) silicates in either geochemical or performance assessment (PA) predictions.

The primary goal in the Source Term Targeted Thrust area is to “study processes that control radionuclide release from the waste form”. Knowledge of adsorption of actinides to U(VI) silicate solids and parameterization in geochemical models will be an important step towards this goal.

OBJECTIVES: The goal of this work is to develop a thermodynamic description of the adsorption of key actinide cations to relevant U(VI) silicates. The thermodynamic description will be represented as a surface complexation reaction. The objectives of the work are:

1. *Study the surface charge associated with well-characterized U(VI) silicate solids* using pH titration under chemical conditions representing the waste package after corrosion. We will also consider the problem of heterogeneity in surface structure and surface dynamics by considering site occupancy as opposed to site affinity.
2. *Develop thermodynamic data to describe the adsorption of actinide cations to well-characterized U(VI) silicate solids.* Adsorption experiments will be conducted under conditions designed to address the complexity of the engineered barrier system chemistry. Both adsorption and desorption will be measured to quantify bulk hysteresis that may reduce actinide lability from the surface.
3. *Verify surface charge behavior and adsorption processes/mechanisms with appropriate spectroscopic tools.* We will develop a molecular description of the U(VI) silicate surfaces and actinide sequestration at these surfaces.
4. *Use experimental results to parameterize a geochemical model describing actinide sorption to U(VI) silicate solids.* Surface charge data will be used to

derive protonation constants for adsorption sites on uranyl minerals. Experimental adsorption edge data will be used to derive intrinsic adsorption coefficients for actinide species to specific surface adsorption sites on uranyl minerals. This surface complexation approach will use the diffuse double layer model that can be incorporated into geochemical codes such as EQ3/6.

APPROACH: This project will develop thermodynamic data to describe the adsorption of isotopes of U, ^{239}Pu , ^{237}Np , and ^{241}Am to U(VI) silicate solids. We will focus on the U(VI) silicates because they are expected to predominate on a geologic time scale after SNF corrodes. The data will be derived from experiment, and will result in the development of a geochemical model that can predict the degree of adsorption of these radionuclides with changes in waste package chemistry. We will also consider molecular-level processes that lead to hysteresis in sorption, which can further reduce dissolved concentrations of radionuclides.

Task 1: Measuring the surface charge of the U(VI) silicates

One of the most important parameters for understanding the sorption of contaminants to surfaces is the electrostatic charge of that surface as a function of pH and ionic strength. Task 1 must be completed for each U(VI) silicate solid before thermodynamic data describing actinide adsorption to these surfaces can be developed. We expect that we will be able to determine surface charge for uranophane in the first 9 months of the project, and we will continue to determine surface charge for boltwoodite and sklodowsite for the next 9 months (1.5 years total time).

Task 2: Developing thermodynamic data on adsorption reactions of key radionuclides

Once we have determined surface charge parameters for the U(VI) solids, we will then study the adsorption of actinides to these solids under a range of pH and in solutions relevant to the engineered barrier system. The radionuclides that we will focus on will be isotopes of U, ^{239}Pu , ^{237}Np , and ^{241}Am . Late in the first year of this project, we expect to complete surface charge experiments with uranophane (Task 1). We will begin our actinide adsorption work by studying Np interactions with uranophane, since Np represents a potentially significant contributor to dose in a Yucca Mountain repository. We will continue our adsorption studies with uranophane with the other isotopes listed above. Upon completion of the surface charge measurements for boltwoodite and sklodowskite (Task 1), we will begin adsorption measurements with Np, followed by the other actinides. Since this task represents a significant level of effort in the proposed work, we expect it to continue through the final quarter of the project. We expect to have initial adsorption data for Np with uranophane completed by the second quarter of the second year, and this information can then be used in our modeling efforts described in Task 4. As we complete additional adsorption experiments, we expect to hand off the information to Task 4.

Task 3: Verify speciation, surface structure, and adsorption

processes/mechanisms with appropriate spectroscopic tools.

As described above, we believe it will be unwise to rely simply on bulk level observations and geochemical modeling to describe the adsorption of actinide cations to U(VI) silicate surfaces. Modeling efforts may require consideration of more than one type of adsorption site (e.g., surface vs. edge, or SiOH vs. UOH). Often these differences in interactions between the cation and the surface can be observed directly with spectroscopic tools. Such direct observation improves confidence in assumptions made during geochemical modeling (Task 4). Spectroscopic studies also provide direct evidence for hysteresis and the potential advantage in reduction of actinide dissolved concentrations, if these processes can be adequately represented. Potential problems that may arise in Task 2 are: (1) the alteration of the solid phase during the adsorption measurements, and (2) changes in solution speciation. Explanations for these problems come from spectroscopic evidence. Consequently, we must use molecular-level observations at various key points in Tasks 1 and 2 to identify such problems and account for them. We expect this task to begin in the first year of our work, and continue to the end of the project.

Task 4: Use experimental results to parameterize a geochemical model describing radionuclide sorption to U(VI) silicates.

Adsorption to U(VI) silicates will be conceptualized using the surface complexation model. This approach considers adsorption to result from direct interaction between the radionuclide and a specific surface site. The existence of surface charge can alter the extent of reaction via the electrostatic field at the mineral surface. Modeling sorption with the surface complexation model requires knowledge of: (1) the variation in surface charge with pH and concentration of adsorbed ions, (2) the number of available surface sites, and (3) the equilibrium constant for the formation of the intrinsic chemical interaction between the surface site and the solute / contaminant / radionuclide of interest. This information is incorporated in the geochemical model as: (a) surface protonation constants for surface adsorption sites, (b) a site density per gram of mineral, and (c) intrinsic equilibrium constants for the adsorption of a radionuclide to a surface site. All this is performed within the context of a conceptual model of the electrical double layer at the mineral surface.

Project Title Migration of the Release of I-129 from Spent Nuclear Fuel via Uptake by Uranyl Alteration Phases
OCRWM S&T Program Thrust Source Term
Project Performers Auburn University and Manchester University
Principal Investigators Thomas Albrecht-Schmitt, Iain May
FY 2005 Funding \$128,000

Abstract **BACKGROUND:** ^{129}I is a long-lived ($t_{1/2} = 1.7 \times 10^7$ years) β -emitting fission product present in spent nuclear fuel. In groundwater, such as that from the J-13 well near Yucca Mountain, it is expected to exist as both iodate, IO_3^- , and iodide. The objective of this program is to study the potential incorporation of $^{129}\text{IO}_3^-$ into uranyl alteration phases that will likely form as the result of the interaction of spent nuclear fuel with groundwater at the repository. We propose that the trigonal pyramidal iodate anion can substitute in trace amounts in the place of tetrahedral $[\text{SiO}_3(\text{OH})]^{3-}$ and PO_4^{3-} , as well as for trigonal planar CO_3^{2-} . We anticipate that the formation of uranyl alteration phases will indeed act as a mechanism for the retardation of the release of ^{129}I . The data that we generate may ultimately be used to modify current models for the release of ^{129}I into the environment from spent nuclear fuel.

OBJECTIVES: The Source Term Thrust seeks to promote collaboration with international investigators to probe relevant technical topics: in-package sequestration, alteration phases or matrix dissolution, and/or projects that will advance our understanding of the release of key radionuclides. In an effort to meet this challenge, this project is a collaborative effort between the actinide chemistry program at Auburn University in the USA, headed by Dr. Thomas Albrecht-Schmitt, and Dr. Iain May at the Centre for Radiochemistry Research at the University of Manchester in England. This program will investigate the potential mitigation of the release of ^{129}I into groundwater at Yucca Mountain by uranyl alteration phases that may form as the result of the oxidation of spent nuclear fuel (SNF). This program also has links to work in the area of Uranyl Alteration Phase Impacts on Radionuclide Release because it will also address the mechanisms of radionuclide incorporation into U(VI)-phases and structural studies of U(VI)-phases and relevant radionuclide crystal chemistry.

APPROACH: Most of the exploratory syntheses in recent uranyl chemistry have either been performed under ambient conditions or under hydrothermal conditions near 200 °C. Conditions relevant to the repository are expected to be near 70 – 90 °C. We will approach the incorporation of ^{237}Np and ^{129}I in two different ways. First, experiments will be performed whereby uranyl silicates, phosphates, and carbonates are crystallized in the presence of ^{237}Np and ^{129}I . Second, we will allow previously crystallized uranyl alteration phases to equilibrate with solutions containing trace amounts of NpO_2^+ and IO_3^- . Bulk product composition will be determined using powder X-ray diffraction. The uptake of radionuclides will be

measured using a scintillation counter, ICP-MS, and ICP-AES. In the case of uranyl carbonates such as rutherfordine, $\text{UO}_2(\text{CO}_3)$, charge balance requirements may allow for the simultaneous incorporation of both $^{129}\text{IO}_3^-$ and $^{237}\text{NpO}_2^+$. Experiments to test for this concomitant uptake will also be performed.

Project Title An In-Situ Spectroelectrochemical Study of Np Redox, Dissolution, and Precipitation Behavior at the Corroding CSNF/Alteration Phase Interface

OCRWM S&T Program Thrust Source Term

Project Performers Argonne National Laboratory, Northern Illinois University

Principal Investigators Artem Guelis, Jeremy Kropf, Christopher Johnson, Jeffrey Fortner, Petr Vanysek

FY 2005 Funding \$258,000

Abstract **BACKGROUND:** In considering processes that impact the release of ^{237}Np from corroding spent nuclear fuel it is important to understand how conditions at the corroding fuel surface will influence the availability of aqueous Np(V) species for incorporation into uranyl alteration phases as they precipitate onto the corroding fuel and undergo subsequent paragenesis. Available data for the standard reduction potentials for $\text{NpO}_2^+/\text{Np}^{4+}$ and $(\text{UO}_2)^{2+}/\text{U}^{4+}$ couples indicate that Np(IV) may not be effectively oxidized to Np(V) at the corrosion potentials of uranium dioxide spent nuclear fuel in air-saturated aqueous solutions. Also, the fuel's UO_2 matrix may facilitate reductive precipitation of any aqueous Np(V) species that are formed. A better scientific understanding of the fuel's matrix effects on the oxidative dissolution and reductive precipitation of Np is needed to clarify the Np release behavior at the corroding fuel surface (i.e. to clarify Np release behavior at the start of its reaction path). This is important because it will influence assessment of the availability of aqueous Np(V) species for incorporation into uranyl alteration phases while the fuel is corroding and uranyl alteration phases are precipitating onto the corroding fuel surfaces and while these initially-formed phases undergo subsequent paragenesis.

OBJECTIVES: The objective of this project is to examine the oxidative dissolution of Np(IV) and the reductive precipitation of aqueous Np(V) species at $\text{U}_{(1-x)}\text{Np}_x\text{O}_2$ [$0 \leq x \leq 10^{-1}$] and other surfaces. This will be done under applied oxidation potential conditions relevant to the range of corrosion potentials expected for the surface of corroding spent UO_2 fuels in air-saturated solutions (i.e. at applied potentials near the fuel's corrosion potential).

The specific goals are to:

- Design electrochemical cells suitable for performing the Np oxidative dissolution and reductive precipitation measurements *in situ* at ANL's Advanced Photon Source (APS), Materials Research – Collaborative Access Team (MR-CAT) beamline hutch.
- Study the thermodynamic properties of Np and U in a solution phase under the relevant conditions using an electrochemical setup with a standard three-electrode cell
- Use a Bent Laue analyzer as needed to select trace Np fluorescence in the presence of U for conducting XANES and EXAFS analyses of solution species and precipitated solids. The possible effects of the X-ray beam on promoting reduction of Np(V) solids will be examined by doing time-resolved spectroscopy to identify changes that occur with irradiation time.

- Identify the applied potential ranges for congruent and incongruent release of Np(V) and U(VI) from $U_{(1-x)}Np_xO_2$ surfaces.
- Determine the applied potential range for reductive precipitation of Np(V) onto $U_{(1-x)}Np_xO_2$ [$0 \leq x < \sim 0.1$] and inert (e.g. carbon or pyrolytic graphite) electrode surfaces

APPROACH: The proposed method involves monitoring the oxidative dissolution of both U and Np from $U_{(1-x)}Np_xO_2$ [$0 \leq x < \sim 10^{-1}$] working electrodes under a range of controlled potential and water chemistry (pH and carbonate concentration) conditions. It also includes examination of the reductive precipitation of aqueous Np(V) onto $U_{(1-x)}Np_xO_2$ [$0 \leq x < \sim 0.1$] and inert (e.g. carbon or pyrolytic graphite) working electrode surfaces under a range of controlled potential conditions.

The planned work scope is divided into the following tasks:

Task 1 – Development of Electrochemical Cell

This task will involve development of an electrochemical cell design including appropriate configurations for the working, auxiliary, and reference electrodes. We plan to adapt an electrochemical cell design that has been used successfully at ANL for electrochemical control and *in-situ* X-ray absorption investigation of aqueous Np speciation for this study. Key differences will be development of a design that allows use of $U_{(1-x)}Np_xO_2$ [$0 \leq x < 0.1$], and other working electrodes.

Task 2 – Testing of Cell and Electrode Performance

This task will involve setup and testing of the electrochemical cell and associated hardware in a fume hood. This setup will be used for shakedown testing and characterization of the cell performance with various working electrodes and electrolytes prior to installation and use at the MR-CAT beam line. The stability of the electrodes, both chemical and morphological, will be investigated before the actual electrochemical work commences. Characterization of the cell or the cell model with model (non radioactive) working electrodes in an electrochemical lab at NIU and subsequently at ANL with $U_xNp_{(1-x)}O_2$ electrodes will be done to make sure there are no surprises (e.g., effects stemming from the cell geometry, for example).

Task 3 – Electrochemical Study

This task will involve potentiometric investigations in a standard three-electrode cell with the associated software to study the electrochemical behavior of uranium and neptunium in the solution under relevant conditions using an inert working electrode (e.g. Pt rod). Controlled-potential techniques such as linear sweep voltametry and cyclic voltametry will be applied to asset the thermodynamic properties of these actinides in the aqueous media.

Task 4 - *In-Situ* Spectroelectrochemical Studies

This task will involve installation of the cells at the MR-CAT beam line in a configuration suitable for identifying dissolved U and Np species under a range of working electrode potentiostatic conditions. The work will involve *in situ* monitoring of the oxidative dissolution of both U and Np from $U_{(1-x)}Np_xO_2$ [$0 \leq x < \sim 0.1$] working

electrodes under a range of controlled potential and water chemistry (pH and carbonate concentration) conditions. It will also include examination of the reductive precipitation of aqueous Np(V) onto $U_{(1-x)}Np_xO_2$ [$0 \leq x < \sim 0.1$] and inert (e.g., carbon or pyrolytic graphite) working electrode surfaces under a range of controlled potential conditions while monitoring the dissolved Np(V) concentration. For these tests, the *in situ* control and monitoring of the Np oxidation state will use the methods already established for Np aqueous species.

Task 5 – XAS Characterization of Electrode Surfaces

This task will involve characterization of the oxidation states and structural environments of Np in the working electrode surfaces before and after each potentiostatic experiment. By careful preparation of the electrode surface, we will be able to use glancing incidence angle X-ray absorption spectroscopy to study the surface before the electrode is used in spectroelectrochemical studies. This geometry is well suited to the Bent Laue analyzer as it provides a line source of X-rays. It will be possible to probe the Np incorporated into the deposited electrode surface layer down to a concentration of approximately 10^{-3} atoms Np/atom U. After the electrode has been used in the spectroelectrochemical cell, glancing incidence angle spectroscopy will allow us to profile the altered surface and possibly the substrate as well using the same technique. Since these will not be polished mirror surfaces, the surface sensitivity will come from geometric effects rather than the total external reflection of X-rays from the substrate.

Project Title Natural Sequestration of Radionuclides in Volcanic Tuff and Secondary Phases

OCRWM S&T Program Thrust Source Term

Project Performers Pacific Northwest National Laboratory, Rice University

Principal Investigators Jonathan Icenhower, Edgar Buck, Kevin Rosso, Andres Luttge, Dawn Wellman, Eric Pierce

FY 2005 Funding \$80,000

Abstract: BACKGROUND: Safety evaluations of Yucca Mountain (YM) as a potential repository for disposal of commercial spent nuclear fuel (CSNF) have been fashioned from arguments based on experimental data. Uncertainties in some key data sets curtail efforts to realistically model radioactive element release. The resulting level of uncertainty has required the use of conservative models of radionuclide mobility in the subsurface. Our multi-disciplinary investigation will utilize a complementary approach consisting of testing, direct imaging, analysis, and modeling techniques available at Pacific Northwest National Laboratory (PNNL) and at Rice University. The objective is to rigorously test the ageing process of the CSNF analog, UO₂, under conditions expected for the repository. Retention mechanisms that affect the entire suite of radioactive elements as they migrate from UO₂ through the near-field volcanic tuff will be determined in detail. If it can be shown that important radioactive elements are less mobile than presently assumed, and that aqueous corrosion of CSNF (presently assumed to be at the forward rate of reaction) is far slower than current models indicate, more realistic source-term and attenuation values could be utilized in repository performance assessments.

OBJECTIVES: The principal objective is to quantitatively determine the mobility of radionuclides released during corrosion of CSNF to the near-field volcanic tuffs. This goal will be realized using a combination of complementary experimental, analytical, and modeling methods. Corrosion experiments on UO₂ will be conducted using PNNL's patented pressurized undersaturated flow (PUF) column in which conditions of controlled redox, CO₂, temperature, fluid flow rate, and water saturation state (partial to full) can be maintained. The column will be set up with layers of crushed or mechanically fractured analogs that represent the repository materials including waste packages, CSNF, the crushed tuff invert, and the near-field volcanic tuff. Fluid chemistry, initially comparable to well water from the YM region, will change progressively as it interacts with the various materials and as secondary mineral assemblages evolve over time. Secondary mineral formation on the surface of UO₂ grains and within fractured volcanic tuff will be analyzed using white light vertical scanning interferometry (VSI) and transmission electron microscopy (TEM) equipment to determine progressive changes in mineralogy and to identify potential sinks for radionuclide retention. Changes in secondary mineralogy, which provide data for establishing source-term and retention parameters, will be modeled. These data will underpin a more realistic model of radionuclide migration and retention.

APPROACH:

Pressurized Unsaturated Flow (PUF) Experiments

To obtain the needed quantitative data, we will use a set of experiments and equipment available at PNNL, namely the patented PUF apparatus designed and built at PNNL for accelerated weathering of waste forms planned for disposal in vadose zone environments. Our plan is to synthesize an input solution consisting of deionized water and water equilibrated with crushed tuff. The solution will, therefore, contain dissolved constituents that replicate YM well water, including Na^+ , K^+ , Ca^{2+} , Mg^{2+} , $\text{SiO}_2(\text{aq})$, HCO_3^- , Cl^- , $(\text{SO}_4)^{2-}$, and $(\text{PO}_4)^{3-}$. In addition, solutions will be doped with trace elements of interest (Mo , ^{241}Am , ^{237}Np , Re as a chemical analog of ^{99}Tc , and nonradioactive Se , Cl , and I for ^{79}Se , ^{36}Cl , and ^{129}I , respectively) together with a non-reactive tracer such as ^3H or B . We will also dope the incoming solution with H_2O_2 to simulate formation of radiolysis products. Doping the solution with radionuclides of interest, rather than using actual CSNF, is desirable because using highly-radioactive CSNF would require massive redesign efforts to shield the PUF system from radiation damage effects. In addition, extensive dissolution of CSNF would be required to bring the elements of interest up to steady-state values; this will not be necessary using the doping technique.

The configuration of solids in the column will include a sequence of layers along the solution flow path. The layers, from top to bottom, include metallic grains (simulating the waste package), a layer of UO_2 powder (representing CSNF), followed by a layer of crushed cement (to simulate the crushed tuff invert on which the waste packages rest), and finally a layer of crushed or fractured volcanic tuff. The input solution will cause the UO_2 to oxidize and form corrosion products. As the solution travels through the cement and tuff layers, uranium will be adsorbed on the surfaces of the grains. However, adsorption sites are limited and once persistent U-phases evolve, the conditions of downstream equilibrium will be met and the concentration of uranium in the effluent will reflect equilibrium with the uranium-bearing phase. If other radionuclides, such as ^{237}Np , form solid solutions with uranium-bearing phases, the downstream equilibrium condition will be met for that element of interest as well. This can be tested by changing the velocity of the influent solution; if equilibrium conditions prevail, the concentration of the element of interest (in the example, ^{237}Np) should not change. Although we will confirm retention of radionuclide elements in uranium host phases using a suite of analytical tools (see below), the data garnered by the PUF test will give us a preliminary indication of radionuclide retention. We expect that precipitation of uranium phases will first occur as oxy-hydroxides and then transform into silicate phases, following the paragenetic evolution of secondary uranium mineralogy observed in experiment and in the field. Thus, precipitation of uranyl silicates, such as soddyite $[(\text{UO}_2)_2\text{SiO}_4(\text{H}_2\text{O})_2]$, boltwoodite $[\text{K}(\text{UO}_2)(\text{SiO}_3\text{OH})(\text{H}_2\text{O})1.5]$, and uranophane $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2(\text{H}_2\text{O})_5]$ will occur eventually, both on the UO_2 surface and along the flow path in the volcanic tuff.

Quantitative Analysis of Corrosion Products

Detailed examination and identification of secondary phases will be performed after test termination. An epoxy resin will be added and allowed to harden so that the PUF

column can be sliced at different intervals along its length. Uranium-bearing minerals can be identified easily by color, and representative materials will be selected. The porous Ti plate at the base of the column will be removed and carefully examined to identify and segregate colloidal particles not entrained by the porous media. Extremely thin slices of materials of interest will be made using Ultramicrotome techniques and TEM, SEM, and X-ray diffraction (XRD), and selective area electron diffraction (SAED) analyses will be carried out to identify the mineral phases. In addition, EELS will be used to quantify the amount of actinide elements present in host uranium phases. Oxidation state information can also be extracted from the fine structure and M4/M5 ratios of actinides using a cold stage to prevent electron beam reduction, and this type of data will help to establish direct evidence for incorporation. TEM-EELS may be the most promising method for obtained evidence of actinide and U co-precipitation because it is possible to obtain both structural and chemical information from the same nano-sized location in a sample. X-ray absorption methods cannot provide this type of information, and no other technique has sufficient spatial resolution.

Further analysis of the reacted UO_2 surface will be accomplished using VSI methods. VSI can precisely quantify both the absolute topography of a mineral surface and critical changes in topographical features due to ongoing dissolution, corrosion, or growth processes. VSI scans produce precise measurements of surface-normal height changes that can be converted directly into intrinsic dissolution or growth rates of the entire solid surface.

Computer Modeling

We plan to apply a combined *ab initio*/kinetic Monte Carlo approach to quantitatively evaluate energy barriers in the dissolution of UO_2 , and to assess their statistical significance over long simulation periods. The *ab initio* calculations will be used to compute barrier shapes and heights for key dissolution steps, such as elementary oxidation or bond dissociation reactions, and these will be used to parameterize kinetic Monte Carlo simulations. Regarding the *ab initio* calculations, we will employ density functional theory (DFT) and *ab initio* molecular dynamics calculations (by the Car-Parrinello method) to compute structures, energies, and to identify and quantify any important energetic barriers. Because many of the important reactions take place on the UO_2 solid surface, we will use the plane-wave pseudo-potential approach on periodic slab models of the surface. This will provide energy-minimized and transition state structures and energies for parameterization of the kinetic Monte Carlo simulations of UO_2 dissolution. Computer simulations will complement the experimental work by helping to identify conditions of key importance for further experimental investigation. For example, an important objective of the experimental work is the application of direct observational techniques to identify and quantify the formation of secondary phases at the dissolving UO_2 surface. In this part of the study, we will focus in particular on simulating the kinetics of coupled dissolution-precipitation reactions involving primary and secondary phases.

Project Title Surface Charge and Radionuclide Adsorption Characteristics of U (IV/VI) Oxides at 25-150°C under Repository Chemical Environments

OCRWM S&T Program Thrust Source Term

Project Performers Oak Ridge National Laboratory, University of Tennessee, Illinois State Water Survey

Principal Investigators David Wesolowski, Donald Palmer, Laetitia Delmau, Lawrence Anovitz, Michael Machesky

FY 2005 Funding \$200,000

Abstract **BACKGROUND:** Using potentiometric pH titration methods and facilities uniquely-developed in the laboratories at ORNL, we will determine in NaCl and/or NaCF₃SO₃ brines from 25 to 100°C at 1 atmosphere, and from 100 to at least 150°C at vapor saturation pressure: a.) the pH and temperature dependence of the proton-induced surface charge density of depleted UO₂ (uraninite) and a representative oxidized alteration phase (UO₂)₈O₂(OH)₁₂(H₂O)₁₂ (schoepite); b.) the pH of zero net surface charge (pH_{pzc}) of these phases; and c.) new solubility data on these phases using direct sampling and *in situ* pH-monitoring. For-these phases, we will then conduct proton-release and direct sampling studies of the sorption of multivalent analog cations and anions for charge types and ionic radii representative of primary source term radionuclides. This information will be used to develop surface site complexation models to describe ion adsorption under near-field repository conditions, which will be tested for their relevance to radionuclide adsorption by comparing them with the results of batch adsorption studies of trace quantities of the actual radionuclides of interest (^{238,235,234,233}U, ²³⁷Np, ²³⁹Pu, ²⁴¹Am, ¹²⁹I, ⁹⁹Tc, ⁷⁹Se, ³⁶Cl) on these model oxide phases at selected temperatures and chemical environments in ORNL's radiochemical facilities. Batch adsorption studies will also be conducted on actual spent fuel samples in order to gauge the relevance of our proposed studies of pure oxide phases.

OBJECTIVES: This research will be a fundamental step toward the ultimate incorporation of experimentally-calibrated and thermodynamically-rigorous radionuclide sorption models into models that address the primary source term. The new solubility data that we will obtain are intended to demonstrate the utility of *in situ* pH monitoring as a powerful tool in demonstrating the attainment of equilibrium and of highly accurate and reversed solubilities of important minerals under near-field conditions, which can then be used to extract speciation. This project will also focus on collaborative interactions with existing and future members of the Source Term Targeted Thrust research group, in order to maximize the benefits of complementary capabilities.

APPROACH:

Introduction: The source term in radioactive waste repository performance assessment involves prediction of: a.) the timing of first release of radioisotopes from the primary containment; b.) the fluxes or concentrations of individual

radionuclides in liquid water (with the exception of certain species such as I and Cl, which can also be transported in vapor) as a function of time after first release; c.) the overall duration of radionuclide release; d.) the evolution of local environmental parameters (temperature, redox state, chemical composition of air and water present, etc.) during the release period; and e.) the chemical forms of the released radionuclides.

Proposed Research: Under reducing conditions, such as will prevail in our hydrogen electrode pH-titration and sampling cells, UO_2 is highly insoluble over wide ranges of pH, temperature and ionic strength, and thus, proton-release and ion-sorption titrations can be conducted rapidly. The first phase of experiments will be the determination of the proton-induced surface charging and point of zero charge of UO_2 in 0.01 to 0.1m NaCl solutions at 25, 50, 100, and 150°C. During the course of surface charging studies of UO_2 , we will conduct an additional set of sampling experiments to determine the solubility of this phase. If chloride complexation proves significant, we can repeat these experiments in NaTriflate (NaCF_3SO_3) solutions.

The next phase of titration studies will be proton release and direct solution sampling studies of multivalent ion sorption on UO_2 powders in the hydrogen electrode cell, involving those surrogate ions that are stable under reducing conditions (discussed below). These experiments will also be conducted in 0.01 and 0.1m NaCl solutions at 25, 50, 100, and 150°C.

Schoepite and other oxidized U(VI) minerals are not stable under reducing environments, but ORNL has demonstrated that identical surface charging results for rutile ($\alpha\text{-TiO}_2$) were obtained using a glass-electrode autotitrator system from 10-50°C as were obtained using our hydrogen electrode cells. This system can be operated at temperatures up to 75°C, and ORNL initial studies of schoepite surface charge, ion adsorption and solubility will be conducted in this system (Mettler DL70). This system can also be used for sorption studies of redox-sensitive analog ions on U(IV,VI) oxide surfaces. As described for UO_2 , we will conduct separate sampling experiments in NaCl and/or NaTr solutions to determine the solubility of this phase.

For higher temperature studies of schoepite surface charge development, and for all sorption studies of the redox-sensitive analog elements (discussed below), we have several options. With support from other DOE programs, ORNL is currently developing an Ir/IrO₂ pH-sensing electrode that preliminary tests indicate will give rapid and Nernstian response in the 50-150°C range, requiring no calibration (thermodynamic response) when used in the concentration-cell configuration. This sensor can be used in air-saturated solutions and is highly inert, chemically. Alternatively, high-temperature glass electrode systems have been used in several laboratories for long-term mineral solubility studies to 200°C, and we can adapt this approach for higher-temperature studies of the redox-sensitive systems.

Batch adsorption studies will be conducted in our radiochemical laboratories with the oxide phases discussed above. Three series of experiments will be conducted: a.) with the surrogate ions and non-radioactive species discussed above at significant concentrations (10^{-3} to 10^{-4} molal) in contact with the proposed oxide phases, in order to serve as a direct link with our titration/sampling studies described above; b.) with the same surrogates and non-radioactive species at trace levels ($\sim 10^{-6}$ molal) ; and c.) with the actual radionuclides of interest ($^{238,235,234,233}\text{U}$, ^{237}Np , ^{239}Pu , ^{241}Am , ^{129}I , ^{99}Tc , ^{79}Se , ^{36}Cl) at trace levels. These experiments will be conducted as batch adsorption experiments, by equilibrating several milliliters of the solution of interest with about 0.1 grams of the powdered oxide at selected temperatures and ionic strengths, and with the pH fixed by sufficient free HCl or NaOH, or by noncomplexing Tris and Bis-Tris buffers at intermediate pH's. Polypropylene/polyethylene disposable syringes will be used at temperatures up to about 70°C , with solution samples removed at temperature through disposable submicron syringe filters. For higher-temperature studies, to at least 150°C , we will employ specially-designed ca. 20 mL titanium vessels consisting of an elongated cylinders that are threaded together in the middle. A platinum frit is housed in the middle of the vessel, where the vessel is sealed by Teflon gaskets. The solid powder and the solution of interest are placed in one half of the cylinder, the frit is emplaced, and finally the top half of the cell is screwed on. The cylinder is then placed in an air oven and allowed to equilibrate. The cylinder is then inverted, leaving the solid phase perched on the frit while the solution is separated at temperature into the bottom section. In addition to the model oxide phases, a limited series of batch adsorption studies of the radionuclides of interest on actual spent fuel samples will be conducted as well. Solutions containing ppb-levels of the radionuclide species will be analyzed by a variety of techniques including decay counting and a dedicated ICP-MS system in our radiochemical laboratories. All the results of these experiments will be modeled as described above.

Project Title Direct Determination of the Thermodynamic Properties of Uranyl Minerals Important for the Performance of the Geological Repository at Yucca Mountain

OCRWM S&T Program Thrust Source Term

Project Performers University of Notre Dame, University of California at Davis

Principal Investigators Jeremy Fein, Peter Burns, Alexandra Navrotsky

FY 2005 Funding \$205,000

Abstract **BACKGROUND:** Uranyl mineral phases will be the primary alteration products of spent nuclear fuel in repository settings such as Yucca Mountain. It is probable that uranyl minerals forming due to the alteration of spent fuel will incorporate radionuclides such as Np and Pu, and this process may have a profound impact upon repository performance. However, currently, there is insufficient understanding of the thermochemical parameters of uranyl minerals to assess the mobility of the pertinent radionuclides. This project will determine the solubility and thermodynamic properties of a range of environmentally-important uranyl mineral phases, and will quantify the effect of Np-substitution on these parameters. We will conduct solubility and calorimetry experiments in order to provide rigorous constraints on the Gibbs free energies of formation, enthalpies of formation, and standard entropies for these solids. Solubilities of representative members of the uranyl oxide hydrates and uranyl silicates will be measured both for the end-member phases as well as for selected phases containing a range of substituted Np within the crystal structure. The solubility experiments will be conducted as functions of pH and ionic strength, and will yield Gibbs free energies of formation of the phases of interest. Solubility measurements conducted as a function of Np content of the uranyl minerals will enable us to extract solid phase activity coefficient parameters to use in thermodynamic models that quantify the effect of the Np on uranyl mineral stabilities and solubilities. The calorimetric data will enable determination of the enthalpies of formation for these phases, so together the standard entropies can be determined as well. The resulting internally-consistent thermodynamic dataset will enable determination of the effect of Np-substitution on the solubilities and thermodynamic stabilities of environmentally-important uranyl phases relevant to a repository setting.

OBJECTIVES: The objective of this study is to determine the thermodynamic properties for a broad range of environmentally-important uranyl mineral phases using solubility and calorimetric measurements, producing an internally-consistent dataset that is useful in modeling spent nuclear fuel alteration and U mobility behavior in near-surface environments.

APPROACH: In the proposed research program, we will synthesize and measure the solubility of a wide range of uranyl mineral phases, including representative phases from the uranyl oxide hydrates and uranyl silicates. In order to improve the accuracy and precision of the thermodynamic interpretation of the data, solubility

measurements will be conducted primarily under the low pH conditions at which $(\text{UO}_2)^{2+}$ is the dominant aqueous uranyl species. Solubility experiments will be conducted as a function of pH and temperature over the temperature range 25 – 100 °C. Experiments will be reversed to rigorously demonstrate the attainment of equilibrium, and experiments for some uranyl mineral phases will also be conducted with varying concentrations of mineral impurities to ascertain the effects of solid solution on thermodynamic stabilities and solubilities. Calorimetric measurements will be made using pure end-member uranyl phases, as well as using uranyl phases with varying degrees of trace element incorporation. The experimental results will yield an internally-consistent set of thermodynamic properties for a wide range of environmentally-important uranyl mineral phases.

Thermodynamic Approach. The proposed experimental solubility and calorimetric measurements will be valuable as a direct indication of the concentration of uranium and other elements in solution in equilibrium with environmentally-important uranyl mineral phases. In addition, the solubility experiments will enable determination of the Gibbs free energies of formation for the mineral phases as well. Solution calorimetry in a molten oxide solvent is a well established technique to determine the enthalpy of formation of a complex oxide from its binary components. Taken together, solubility measurements in conjunction with calorimetric measurements of formation enthalpies can be used to derive other thermodynamic properties of the uranyl mineral phases, in particular standard entropies of formation and the temperature dependences of the solubility products for the mineral phases.

While the direct determination of uranyl mineral solubilities are of use, the extraction of standard state Gibbs free energies of formation for the uranyl mineral phases is perhaps of greater importance in modeling stabilities and solubilities of uranyl minerals under potential repository conditions. The calculated Gibbs free energy values for the uranyl minerals can be used to determine relative stabilities of uranyl mineral phases under a wide range of fluid composition conditions of environmental and geologic interest. The Gibbs free energy values for the uranyl minerals can also be used to calculate equilibrium constant values for any reaction involving the studied uranyl mineral phases, enabling estimation of the solubility of any mineral assemblage at a range of conditions of interest. Because it is impossible to measure uranium concentrations in equilibrium with all uranyl phases of environmental interest under all conditions of interest in the laboratory, it is crucial to be able to estimate uranyl mineral solubilities in order to assess the mobility of uranium in systems not directly studied in the laboratory. The thermodynamic properties that we determine in the proposed research program will enable these extrapolation techniques.

Project Title	A Model for Radionuclide Release from Spent Commercial Nuclear Fuel
OCRWM S&T Program Thrust	Source Term
Project Performers	Lawrence Berkeley National Laboratory
Principal Investigators	Carl Steefel, John Apps, Nic Spycher, Eric Sonnenthal
FY 2005 Funding	\$100,000

Abstract **BACKGROUND:** Current practice in the treatment of radionuclide release is highly conservative. The rate of degradation of the spent fuel is assumed to depend on the concentrations of gases like O₂, but their concentrations are fixed rather than dynamic, resulting in a conservative estimate of radionuclide release. Similarly, seepage water into the waste form in the current approach can range from about 0.1 to 15 liters/year, but accounting for the reduction in fluid mass as a result of evaporation would reduce this seepage flux into the waste form by three to four orders of magnitude. The change in chemistry as a result of evaporation is accounted for in current modeling approaches, but the effect is the prediction of very high fluxes of evaporated brine when the evaporated brine chemistry is combined with unadjusted seepage fluxes. Formally considering evaporation as affecting both water mass and chemistry simultaneously results in a more realistic and less conservative estimate of brine seepage into the waste form. Condensation of water vapor is considered, but the current approach does not include the physics that would make it unlikely for condensation on the hot waste to occur. Solubility limits are considered for the important radionuclides like Np and Am assuming these limits are set by the solubility of the least stable (most soluble) phase that could form. This approach could be made less conservative by accounting for the thermodynamics and kinetics of secondary uranyl phase formation and the incorporation of radionuclides into the structure of these phases, as is to be evaluated here. Because of the conservatism of the current models, a step-by-step reappraisal is called for. The problem can be made tractable only through initial simplification and the identification of sub-systems for independent investigation before attempting a generalized waste package release model. Accordingly, the initial effort will focus on one critical aspect of the system: the direct corrosion of the Commercial Spent Nuclear Fuel (CSNF) by seepage and condensate water in a system with a range of prescribed fluxes. This smaller scale, but chemically detailed, model will consider how seepage and condensate water moving along a crack will dissolve the spent fuel and precipitate a sequence of kinetically and thermodynamically controlled secondary phases. Based on the results emerging from the combination of modeling proposed here and experimental studies conducted elsewhere in the Source Term Thrust and other parts of the Science and Technology Program, a model encompassing the entire waste package, drift, and near-field environments will be developed in Year 3 of the project based on upscaling of the results.

To develop a more realistic and eventually general model for CSNF degradation, several geochemical processes must first be understood theoretically, following which suitable algorithms can be developed. The most important of these include:

- the nucleation and kinetic controls on the growth and sequence of metastable uranium phases from supersaturated solutions, taking into account the impact of differing interfacial free energies and seepage water compositions;
- solid solution models that replicate substitution of minor actinide components in secondary uranyl and uranyl phases;

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- the response of the system to radiolysis of the aqueous phase by ambient radiation, control of oxidation state, and non-attainment of homogeneous equilibrium within the aqueous phase;

- the thermodynamic properties of uranyl phases;
- the aqueous speciation of actinide radionuclides and the components expected in

Project Title Np-Incorporation into the U⁶⁺-Alteration Phases of Spent Nuclear Fuel and Np-Sorption onto Oxide Phases
OCRWM S&T Program Thrust Source Term
Project Performers University of Michigan
Principal Investigators Udo Becker
FY 2005 Funding \$110,000

Abstract **BACKGROUND:** In order to elucidate the fate of Np during the corrosion of spent nuclear fuel under oxidizing conditions, this project is composed of three related subprojects involving quantum mechanical calculations and *in situ* observations of adsorption experiments.

Quantum mechanical and empirical force-field calculations of Np incorporation into different U⁶⁺ alteration phases: These calculations will clarify the mechanism of (coupled) substitution of Np into U⁶⁺ containing minerals. In addition, the project will evaluate the thermodynamics of (Np(V), U(VI)) oxide and hydroxide solid solutions. This information is important in order to evaluate how much Np can be incorporated into U⁶⁺ alteration phases and determine the long-term stability of these solid solutions.

Quantum mechanical calculations allow for the determination of the lattice energy, structure, and electronic configuration of substitution sites in U⁶⁺ alteration phases. Together with the hydration energies for dissolved species that will be calculated, differences in solubility products between different host minerals and incorporation scenarios can be determined. Calibrated with experimental and field-determined values for long-term stability of pure uranium alteration phases, this information will help to assess the dissolution rate as a function of Np concentration, environmental parameters (e.g., temperature), and host minerals. This sub-project will focus on Np in U⁶⁺ alteration phases (schoepite in different stages of hydration, metastudtite, uranophane, compreignacite), as well as other minerals that can potentially host large cations, such as jarosites and clays. In addition, Pu and Tc will be evaluated as adsorbents. This comparison will further the understanding of the specificity of the energetics and structure changes of Np incorporation into U⁶⁺ alteration phases.

Quantum mechanical calculations on the thermodynamics of Np adsorption on Fe-oxide phases: Iron phases and iron oxide are the major products of corrosion of containers containing spent nuclear fuel. Therefore, the stability of Np adsorbates on these oxide phases and the mechanisms of stabilization as a function of redox processes is instrumental to determine corroded phases as a potential “trap” for Np. These calculations will help to understand the thermodynamics of Np adsorption, the potential to form Np-oxy-hydroxide clusters on oxides, and potential incorporation mechanisms into oxide minerals.

In situ scanning probe microscopy observations of Np adsorption on oxide phases at different redox potentials: In our laboratory, we have the opportunity to test the mechanism of adsorption as a function of electrochemical potential at the atomic scale. *In situ* observations of Np adsorption to Fe oxide surfaces will be performed as a function of the redox potential and the solution chemistry. These experiments allow testing of the findings from the quantum mechanical calculations. In addition, the strongest adsorption sites can be identified and site-dependent adsorption/desorption kinetics determined.

In summary, the calculations that we propose in combination with atomic scale observations are the ideal tool to determine reaction mechanisms and energies, and allow for the separation of processes that are governed by different environmental parameters.

OBJECTIVES:

1. Np Incorporation

Under oxidizing conditions in the presence of water, or even moisture, the UO_2 in spent nuclear fuel (SNF) is not stable. Because of the oxidizing conditions, U^{4+} will oxidize to U^{6+} , forming the higher uranium oxides (i.e., U_3O_7 or UO_3) under dry conditions, or the uranyl molecule, $(\text{UO}_2)^{2+}$, in solution, which readily reacts with a wide variety of inorganic and organic anions that form complexes that increase the concentration of uranium in solution. Thus, in oxic, near-surface environments, uranium is mobile, forming precipitates of uranyl phases that generally have high solubilities. The reaction kinetics of these alteration reactions and the formation of secondary uranyl phases are rapid. These secondary U^{6+} -phases also commonly form on natural UO_2 under oxidizing conditions. Thus, over the long term, one expects substantial alteration of the UO_2 to these U^{6+} -secondary phases.

These secondary U^{6+} -phases may, depending on their structure, incorporate some of the radionuclides released during the corrosion of the UO_2 in SNF. One of the most important possibilities is that transuranic elements may be incorporated into the U^{6+} -phases and hence limit their mobility in the geosphere. Due to their long half-lives, the most important transuranic radionuclides are ^{237}Np (2.1 million years) and ^{239}Pu (24,100 years) because they have made substantial contributions to total doses in past performance assessments of Yucca Mountain.

Future studies will converge to a better understanding of the Np-incorporation in the different U^{6+} -phases; however, there are substantial analytical challenges to be overcome in confirming Np-incorporation at such low concentrations, less than a fraction of a weight percent. Also, the demonstration of incorporation in a specific experiment does not explain why and under what conditions one may expect radionuclide incorporation to occur. A thorough understanding of the incorporation mechanisms requires an understanding of the energetics of the possible substitution mechanisms in the different U^{6+} -structure types.

2. Np ADSORPTION ONTO IRON OXIDE SURFACES

Sorption of neptunium onto iron oxide surfaces is a viable removal mechanism that will inhibit the release of Np into the near and far field of a repository. Iron oxide minerals are of the most important potential Np adsorbers, as they are commonly found within close proximity to high-level waste material, which are planned for storage in iron-based canisters. Over the past decade, Np has become of greater concern because of its high mobility and long half-life (2.1×10^6 years). Several experimental studies have made attempts to determine the sorption kinetics of Np onto Fe-oxide surfaces. The parameters considered in the determination of the fate of neptunium in the repository setting include pH, crystal type of adsorber, and CO_2 concentration. The state of Np, whether Np or NpO_2^+ , upon sorption, as well as the oxidation state, Np(IV) or Np(V), can control the adsorption energy, kinetics, and mechanism.

Little modeling of the Np(V) sorption and reduction mechanisms has been compiled. No molecular modeling at the quantum mechanical level has been performed but there is a small number of studies using surface complexation theory to quantify adsorption equilibria. The data calculated were directly compared to experimental data in attempts to explain Np sorption behavior. The effect of pH on the sorption characteristics was also modeled and compared to experimental data. Interpretation of the data from the SCM indicates that Np is often sorbed from solution as the neptunyl cation.

The importance of information concerning actinide fate, especially neptunium, is overwhelming. While past research on neptunium sorption onto iron oxide surfaces is adequate, more definitive quantitative data are still required for a better understanding of the fate of neptunium in a repository.

APPROACH:

1. Np Incorporation

There are literally hundreds of U^{6+} -structure types. In this study, we have selected phases that are expected to occur as alteration products during the oxidative corrosion of UO_2 or that represent structure types that allow us to investigate different schemes of coupled substitution. The structure types selected for study include:

schoepite $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}(\text{H}_2\text{O})_{12}$

metaschoepite $\text{UO}_3 \cdot 2\text{H}_2\text{O}$

dehydrated schoepite $\text{UO}_3(\text{H}_2\text{O})_{0.8-1.0}$

studtite $[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$

metastudtite $[(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2]$

uranophane $\text{Ca}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_5$

compreignacite $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$

Na-compreignacite $\text{Na}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_7$

Quantum mechanical calculations will be performed using *CASTEP* (Cambridge

Sequential Total Energy Package, plane-waves as basis functions), VASP (Vienna Ab initio Simulation Package, plane-waves), *CRYSTAL03* (Gaussian functions), and NWCHEM (PNNL, both types of basis sets). These software packages use density functional theory (DFT), Hartree-Fock theory (HF), or hybrids thereof to provide a good atomic-level description of minerals. They give information about total energies, forces and stresses on an atomic system, as well as calculating optimum geometries, band structures, optical spectra and other electronic properties.

Due to the computational expense of these programs (they scale with N^3 where N is the number of valence electrons explicitly calculated), the number of atoms in the unit cell that can be calculated is limited to about 60-80. This means that for larger unit cells, and some of the minerals to be investigated have larger unit cells, we will require program packages that scale linearly with the number of atoms, predominantly *SIESTA* (Spanish Initiative for Electronic Simulations with Thousands of Atoms). Once we have obtained consistent values for incorporation and adsorption energies, empirical potentials can be derived to mimic the substitution/adsorption behavior precisely. Empirical potentials will allow us to move to larger systems and to perform molecular dynamics simulations to model the behavior of adsorption and incorporation at elevated temperatures and in hydrous systems. For potential development, we will use the GULP code. For applications of empirical force fields to large systems, molecular dynamics and hydration processes, GULP and Cerius2 codes will be applied.

In order to calculate substitution at more dilute Np concentrations and to model substitution at elevated temperatures, it will be necessary to apply empirical force field calculations. However, the reliability of these calculations depends on the accuracy of the empirical potentials employed. Therefore, it is crucial to test the empirical force fields that we have developed for other uranium phases and that we will develop for Np oxide phases, and for the actual minerals used in this project. If necessary, force fields can be fine-tuned to mimic substitution energies and structural properties of Np substitution.

A special case of incorporation is the insertion of Np(V) into the interlayer of sheet-like uranium phases such as uranophane and compreignacite. A number of different sites have to be tested as candidates for such adsorption processes such as sites at the corners and edges of the sheets, inter-layer sites, and sites within the bulk structure of the sheets. If interlayer adsorption is a viable process, it needs to be clarified how charge compensation takes place and if additional water is needed to compensate for a possible widening of the interlayer (year 2).

2. Np ADSORPTION ONTO IRON OXIDE SURFACES

Most surface complexation models (e.g., SCM) are based on the fitting of experimental data, or, when these are not available, on approximating binding constants on the acidity of surface sites. Even though this procedure gives valuable information of a particular sample, little information is revealed on the

adsorption mechanism(s), especially the role of the surface to catalyze redox reactions. In addition, the adsorption thermodynamics and kinetics as a function of specific surface sites (terraces, steps, kinks, defect sites/vacancies) cannot be clarified.

Therefore, we propose to perform systematic studies of Np(IV,V) and neptunyl adsorption on a number of different surface sites on different Fe oxides (ferrihydrite, goethite, hematite, magnetite) and clay minerals for comparison. We will perform similar studies on Pu and Tc to understand the role of the redox chemistry of the adsorbing material and to compare metal cations that have different charges and coordination chemistry (year 1). However, in this project, we will focus on Np for reasons of clarity.

Our quantum mechanical and empirical force-field calculations will give us the framework on which reactions are thermodynamically possible and which are not. Therefore, adsorption experiments can be optimized to test the mechanisms of adsorption, especially where redox processes are involved. In principle, there are two options to control the redox conditions of an adsorption experiment: (i) to fix the composition of the reaction fluid, in particular the oxygen content or the concentration of other redox-active reagents and (ii) to control the redox potential electrochemically. Both options are available in the UMich laboratory. Thus, we will perform a series of adsorption experiments *in situ* and *ex situ* and examine the adsorbates using AFM, in particular for insulators, and STM for semiconductors when higher resolution is required to resolve the adsorption mechanism (the electrochemical kit for STM is requested within this proposal). Both experimental techniques can be performed in an electrochemical cell such that the reaction conditions for adsorption reaction can be controlled for: pH, temperature, redox potential and/or redox chemistry, adsorbate concentration, and composition of background electrolytes. Observing reactions at the atomic scale allows the distinction of adsorption to different surface sites. This is important because for typical concentration levels of Np in the vicinity of repositories, adsorption to sites for which strong adsorption is known to occur, e.g., kinks and vacancies in the oxides, may be sufficient. In standard wet-chemical batch experiments, adsorbate concentrations are often significantly higher (concentrations in thin films in the environment can still be high, though the overall amount of Np would still be limited) and only an average, overall adsorption site can be probed.

In addition, our approach will allow for much better separation of environmental parameters, which is important for long-term assessment of adsorption equilibria. Subsequent to our modeling and adsorption experiments, a thermodynamic and kinetic complexation model needs to be developed as a function of crystal surface parameters (type of mineral, surface exposed, surface and defect site distribution), concentration of Np in solution, and environmental parameters (pH, Eh, T, and fluid composition, year 2).

Since both of our approaches, molecular simulations and adsorption studies using

scanning probe microscopy (SPM) techniques, probe adsorption at the microscopic level, they need to be tested for agreement with existing SCM models when reaction conditions are applied to our model. Surface diffusion and, due to proximity effects, enhanced surface diffusion will lead to extended adsorbates on the surface. These (in this case Np-oxy-hydroxide) nanostructures can again undergo surface diffusion until they find the energetic minimum site on, e.g., an iron oxide surface. We will calculate the stability and surface diffusion of these potential intermediate products and will be able to directly observe them in our *in situ* SPM studies. This will help us to elucidate the mechanism of adsorption and possible incorporation of Np-oxy-hydroxide clusters into Fe oxide phases.