Office of
Science and Technology and International

Source Term Targeted Thrust
FY 2004 Projects

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PREFACE

This booklet contains project descriptions of work performed by the Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM), Office of Science and Technology and International's (OST&I) Source Term Targeted Thrust during Fiscal Year (FY) 2004. 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 2004 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 Thermodynamics at Elevated Temperatures - Collecting High-Temperature Actinide Thermodynamic Data
OCRWM S&T Program Thrust	Source Term
Project Performers	Pacific Northwest National Laboratory, Lawrence Berkeley National Laboratory
Principal Investigators	Judah Friese, Linfeng Rao
FY 2004 Funding	$430,000

Abstract **BACKGROUND**: Thermodynamic data used to predict the chemical speciation of contaminants in the environment relies on data measured at 20°C or 25°C. In the waste package and disturbed zone of the repository where elevated temperatures will exist, the calculated speciation can be dramatically different than that at 20-25ºC. For instance, one, two or even three orders of magnitude difference in the extrapolated and actual stability constants has been observed. Typical mathematical extrapolation techniques, such as the van't-Hoff or Helgeson-Kirkham-Flowers equations, do not accurately predict the chemical system at higher temperatures due to the assumption that the enthalpy of the reaction ($\Delta_r H_{m,T}$) is independent of temperature. This assumption is typically valid over a small temperature range. On the other hand, water that may contact spent nuclear fuel may have temperatures up to 96°C.

As shown in Table 1, the thermodynamic constants for uranyl acetate complexes are different at higher temperatures. This effect is important for input into models. Jiang et al. concluded that the van't-Hoff extrapolation of 20-25ºC data has limitations especially for the treatment of higher order complexes due to the strength of complexation, and more experimental measurements are needed to more accurately apply thermodynamic models to elevated temperature systems[1]. The temperature dependence of stability constants must be accounted for in order to better predict the chemical species, confirm assumptions, and reduce the uncertainty in calculations used in TSPA.

Table 1. Thermodynamic data for uranyl acetate (Ac) complexes at 25 and 70ºC

Complex	T °C	Log $\beta_{m,T}$	$\Delta_r H_{m,T}$ kJ/mol	$\Delta_r S_{m,T}$ J/mol K
$[UO_2Ac]^+$	25	2.60	8.9	79.6
	70	3.15	12.7	97.3
$[UO_2Ac_2]^o$ (aq)	25	4.44	23	162
	70	5.34	33	198
$[UO_2Ac_3]^-$	25	6.94	16.6	188.5
	70	7.82	24.0	219.6

OBJECTIVES: Actinide elements released from spent nuclear fuel (SNF) in the proposed Yucca Mountain repository are expected to be in contact with condensed water and/or pore water. The contents of condensed and pore water contain ligands that will complex the actinide elements and affect their environmental mobility. The thermodynamic data at elevated temperatures for these ligands have

[1] Jiang et al., J. Chem. Soc., Dalton Trans., 2002, 1832-1838.

received little experimental study. For example, a review of the NIST stability constant database [2]reveals that there are no data for UO_2^{2+}, NpO_2^{+}, Pu^{4+}, PuO_2^{+}, PuO_2^{2+} and Am^{3+} complexation with carbonate at elevated temperatures, however, a recent literature review indicates limited temperature data for the carbonate complexes[3,4,5]. These reviews give limited thermodynamic data for other important ligands (sulfate, chloride, fluoride, etc.) at elevated temperatures, and a goal of this work is to expand thermodynamic information on the actinides.

APPROACH: The approach is to experimentally determine the thermodynamic properties for radionuclide aqueous species with complexants present in Yucca Mountain groundwater. The relevant radionuclides of interest include U, Np, Pu, and Am. The potentially important complexants in groundwater solutions include CO_3^{2-}, SO_4^{2-}, Cl^-, F^-, phosphate, silicate, small organic acids, and humic acids. Thermodynamic values will be measured at elevated temperatures and compared to extrapolated values using current mathematical techniques. Thermodynamic values will be measured using calorimetric, spectrophotometric, solvent extraction and potentiometric techniques. Calorimetric methods involve measuring the "heat" of the reaction, and yield the stability constants as well as ΔH, ΔS, and ΔG of the observed reaction. Spectrophotometry can directly measure the speciation of the system as well as determine the oxidation state of the elements.

Spectrophotometic methods will be necessary for studying Pu because of the multiple oxidation states that can be present in solution. Potentiometric and solvent extraction are indirect methods of determining the stability constants and data interpretation must rely on assumptions about the species present in solution. However, these approaches tend to be very cost effective. These four methods are complementary and yield thermodynamic properties and speciation information needed for modeling the species present at elevated temperatures. Computational methods will also be explored to analyze trends to develop predictive models for thermodynamic data at elevated temperatures. The science behind actinide complexation reactions in general is uncertain, and this proposed approach will add to our knowledge of the thermodynamic properties and add temperature data to a thermodynamic database for the actinides. A combination of these methods will yield a good understanding of the formation of radionuclide complexes at elevated temperatures and their impact on the release of radionuclides from a proposed repository.

BENEFITS TO OCRWM: This work will acquire actinide solution chemistry data at elevated temperatures. The current database of thermodynamic information relies on mathematical extrapolations to provide the data necessary for all calculations not at 25º C.

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[2] NIST Standard Reference Database 46, 1997, *Critically Selected Stability Constants of Metal Complexes: Version 4.0.* NIST Standard Reference Data, Gaithersburg, MD, Grethe et al. 1992; Lemire et al. 2001; Silva et al. 1995.
[3] Wanner, H., Forest, I., *Chemical Thermodynamics Vol. 1, Chemical Thermodynamics of Uranium,* OECD Nuclear Energy Agency, Elsevier, Amsterdam, The Netherlands.
[4] Silva, R.J., *chemical Thermodynamics Vol. 2, Chemical Thermodynamics of Americium,* OECD Nuclear Energy Agency, Elsevier, Amsterdam, The Netherlands.
[5] Lemire, R.J., *Chemical Thermodynamics Vol. 2, Chemical thermodynamics of Neptunium and Plutonium,* OECD Nuclear Energy Agency, Elsevier, Amsterdam, The Netherlands.

Project Title	Chemical and Coordination Structure of Radionuclides in Spent Nuclear Fuel and Its Alteration Products: Understanding Release Pathways
OCRWM S&T Program Thrust	Source Term
Project Performers	Argonne National Laboratory, Argonne, IL
Principal Investigators	Jeffrey A. Fortner, Robert J. Finch, A. Jeremy Kropf
FY 2004 Funding	$300,000

Abstract **BACKGROUND:** Understanding the complex chemistry of trace fission products and transuranium actinides in spent nuclear fuel (SNF) and related materials will complement independent thermodynamic and solution chemistry experiments. The project will focus on the solid-state chemistry and release of the multivalent radionuclides Tc, Np, and Pu from SNF because of their significance to the proposed repository and to containment/stabilization issues. In particular, the applied research addresses two significant challenges for developing an advanced model for spent fuel behavior:

1) understanding the chemical state of radionuclides in as-received spent nuclear fuel, and
2) developing mechanistic kinetic models for radionuclide release from fuel to the repository environment.

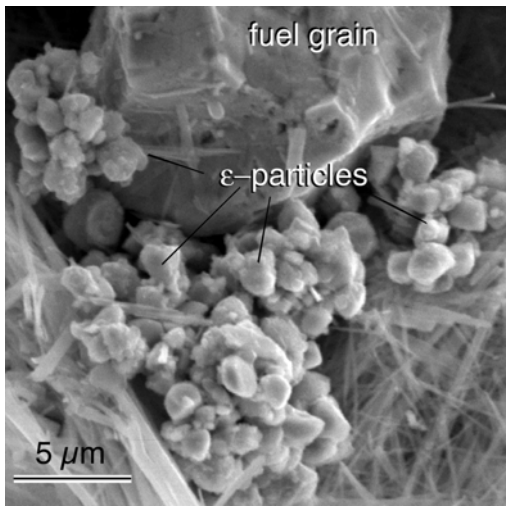
Addressing these two topics is relevant not only to the present repository models but to determining their applicability to very-high burnup fuels and wastes from advanced fuel cycles.

OBJECTIVES: This project will explore how solid state chemistry affects the release kinetics of radioactive fission products, (Tc), and activation products (Np, Pu) from SNF. The objective is to provide definitive information about the crystal chemistry and partitioning of these key radionuclides into grain boundaries, the fuel/cladding gap, and the UO_2 matrix and to determine the impact of these phenomena on release behavior during SNF corrosion. Possible sequestration of these radionuclides in more stable minor phases (e.g., exsolved, metallic "epsilon" particles) and secondary alteration phases will be addressed. The project will study both as-discharged SNF and SNF that has been partially corroded by exposure to hydrothermal conditions that represent those expected in the repository.

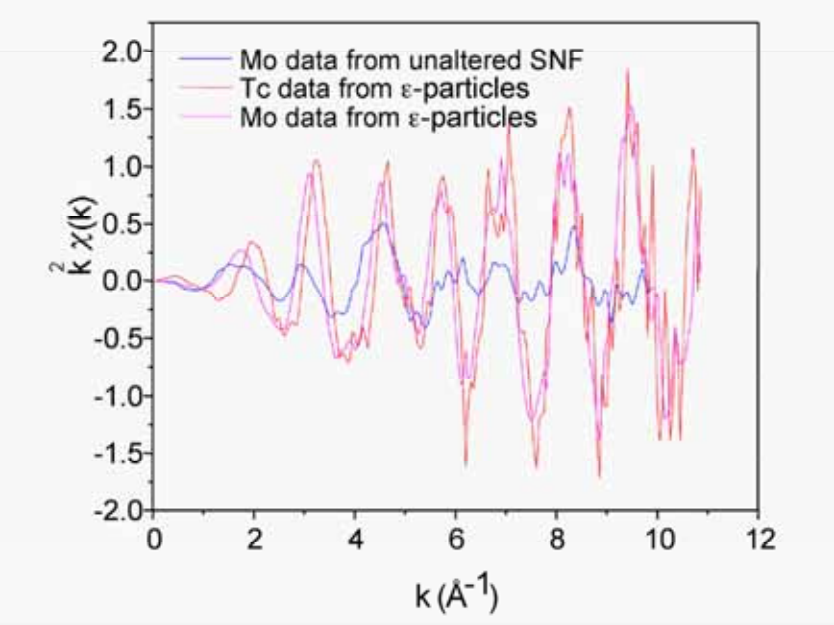
APPROACH: This project will use synchrotron x-ray spectroscopy to explore oxidation states and near-neighbor coordination environments by x-ray absorption near edge spectroscopy (XANES) and by extended x-ray absorption fine structure (EXAFS) methods, respectively. The measurements will be made on the insertion device beamline of the Materials Research Collaborative Access Team (MRCAT) at Argonne's Advanced Photon Source (APS) synchrotron. Also utilized will be Argonne's long-standing expertise in the area of coupled synchrotron/ electrochemical measurements to perform *in situ* studies under controlled conditions of radiolysis, electrochemical potential, and pH. The electrochemical

studies will focus on the corrosion of the epsilon-phase metal, but other relevant materials may be studied by this method as resources and time allow. A novel "bent-Laue analyzer" detection scheme developed or refined by our collaboration at MRCAT will be implemented.

Synchrotron XANES/EXAFS studies of SNF and its corrosion alteration products is uniquely suited to understanding the solid state chemical disposition of the trace elements Tc, Np, and Pu, with consequent confidence building in current or proposed alternative models. Argonne has on-hand several high burnup fuels (PWR and BWR, approaching 70,000 GW d/Mt), including a fuel with gadolinium added as a burnable poison. Some relatively high burnup fuels, along with more moderate burnup fuels, have been corrosion tested and provide potential information on SNF evolution under possible hydrothermal alteration conditions. Such materials have, to date, been under-represented in corrosion and characterization studies. Understanding this high burnup fuel is important for consideration of SNF generated by modern and next-generation nuclear reactors.



Scanning electron micrograph of corroded SNF showing metallic, Mo- and Tc-rich particles concentrated on the surface of a corroded UO_2 fuel grain. In the foreground are acicular uranium (VI) silicates that formed during the corrosion process.



EXAFS from a region of corroded SNF rich in Tc and Mo indicate that the signals originate from the same metallic phase, consistent with segregated ε-particles. By contrast, the Mo EXAFS signal from a typical region in uncorroded SNF indicates a mixture of metal and oxide. The more labile Mo-oxide may be preferentially removed from the SNF during corrosion, leaving behind the metallic phase.

BENEFITS TO OCRWM: By providing definitive molecular-level information about the chemical environment of Tc, Np, and Pu in SNF and its corrosion products, an enhanced understanding of the chemical state of radionuclides in SNF, and data for advanced models of radionuclide release from fuel to the repository environment will be provided. Also addressed is the possible sequestration of these radionuclides in more stable minority phases (e.g., epsilon particles) and secondary alteration phases. By strengthening the science underlying models developed to predict the long-term performance of SNF in the proposed repository, the need for extensive testing of high burnup, advanced concept, and alternative fuel types that will be produced by future reactor operations will be mitigated.

Project Title	Corrosion of Spent Nuclear Fuel: The Long-Term Assessment
OCRWM S&T Program Thrust	Source Term
Project Performers	University of Michigan
Principal Investigators	Rod Ewing
FY 2004 Funding	$200,000

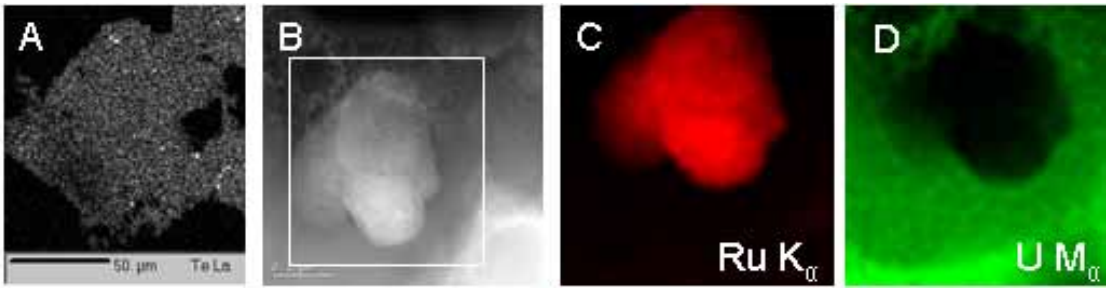
Abstract **BACKGROUND:** Spent nuclear fuel (SNF) is essentially UO_2 with approximately 4-5 atomic percent actinides and fission product elements. A number of these elements have long half-lives (^{239}Pu: 24,500 years; ^{237}Np: 2 million years; ^{129}I: 16 million years; ^{79}Se: 1.1 millions years; ^{99}Tc: 200,000 years); hence, the long-term behavior of the UO_2 is important in the evaluation of the safety and risk of a proposed repository for SNF. One of the unique and scientifically most difficult aspects of the successful disposal of SNF is the extrapolation of short-term laboratory data (hours to years) to the long time periods (10^3 to 10^5 years) as required by the performance objectives set in regulations. The direct verification of these extrapolations or interpolations is not possible, but methods can be developed to demonstrate compliance with government regulations and to satisfy the public that there is a reasonable basis for accepting the long-term extrapolations of SNF behavior. In recent years "natural analogues" for both the repository environment (e.g., the Oklo natural reactors) and nuclear waste form behavior (e.g., corrosion and alteration of uraninite, UO_{2+x}) have been cited as a means of achieving confirmation of long-term extrapolations. In particular, considerable effort has already been made to establish that uraninite, UO_{2+x}, with its impurities, is a good structural and chemical analogue for the analysis of the long-term behavior of the UO_2 in SNF. This work is based on the study of uraninite and the naturally occurring alteration products of UO_{2+x} under oxidizing and reducing conditions.

This project will provide the data and information for the models that enhance the performance assessment of a proposed repository for SNF. Studies of natural samples of great age and appropriate geochemical environments offer the possibility of reducing uncertainties in these corrosion models. This project focuses on near-field phenomena, i.e., waste form degradation. This is important because the enhanced understanding of relevant phenomena in the near-field reduces uncertainties in the total system performance assessment.

OBJECTIVES: This project is a broad-based effort, including natural analogue studies, to understand the long-term behavior of SNF and its alteration products in a geologic repository. SNF corrosion is being examined on the basis of the interactions of molecular water with UO_2 surfaces. The radiation effects of alteration phase evolution are being probed. New techniques, exploiting high resolution transmission electron microscopy, are being developed to characterize, on the nano-scale, low concentrations of radionuclides in the fuel matrix and alteration phases. These techniques and detailed mineralogical, chemical and isotopic analyses are being applied to samples from the Oklo and Okelobondo natural fission reactors to provide additional data on the migration of radionuclides.

APPROACH: The research program includes:

- surface science and computational studies of the interactions of molecular water with UO_2
- nano-scale characterization of low-concentrations (1-10 ppm) of trace elements and radionuclides in UO_2 U^{6+} alteration phases, and related colloids
- investigation of the fate of radionuclides at the Oklo natural fission reactors as a function of geochemical and hydrological conditions
- an evaluation of radiation effects on the stability and composition of secondary U^{6+} phases.



A) electron microprobe X-ray map of ε-particle (bright areas are Te) in UO_2 matrix. B) STEM-HAADF image of several Ru-rich nanoparticles (boxed) in uraninite matrix, C) elemental map of Ru (Kα) particles ~100 nm in diameter from the boxed region in Fig 8B, D) elemental map of showing deficiency of U (Mα) in region of Ru-particles.

New techniques (e.g., high-angle annular dark-field imaging, HAADF), exploiting high-resolution transmission electron microscopy combined with electron and ion-beam irradiation, are being developed to characterize, on the nano-scale, low concentrations of radionuclides in the fuel matrix and alteration phases. These techniques and detailed mineralogical, chemical and isotopic analyses are being applied to samples from the Oklo and Okelobondo natural fission reactors to provide data to support models of release and migration of radionuclides under reducing and oxidizing conditions.

BENEFITS TO OCRWM: This project will provide data on the corrosion processes and resulting alteration products of the UO_2 of spent nuclear fuel under oxidizing conditions including:

- Identification of principal phases and their proportions as a function of geochemical conditions and reaction progress
- Analysis of uranium phases for their trace element content, to determine the fate of impurity elements that are released during matrix dissolution of UO_2
- An evaluation of the long-term stability of uranium phases under oxidizing conditions
- Estimation of the thermodynamic stability of uranium phases based on natural occurrences
- The response and stability of U(VI) alteration phases to radiation damage.

These data can be used to enhance geochemical codes used to estimate or extrapolate:

- Reaction progress (the types and sequence of phases formed during spent fuel corrosion)
- Thermodynamic stabilities or uranium phases, the kinetics of the UO_2 corrosion process, and the nucleation and growth of alteration phases
- Fission-product and actinide contents of secondary uranium phase assemblages resulting from alteration under oxidizing or reducing conditions.

The data and their use as a test of the geochemical codes used in performance assessment will be of particular value because a study of natural systems captures the large-scale complexity and extended time periods that are relevant to the performance assessment of a proposed repository for SNF. Of particular importance, will be the study of the Oklo natural fission reactors because they provide well constrained geochemical conditions.

Project Title	Dissolution Rates in Humid Air and Low Water Conditions
OCRWM S&T Program Thrust	Source Term
Project Performers	Pacific Northwest National Laboratory
Principal Investigators	Brady Hanson, Edgar Buck, Bruce McNamara, Adam Poloski, Chuck Soderquist
FY 2004 Funding	$725,000

Abstract: **BACKGROUND:** Previous studies on spent nuclear fuel (SNF) and unirradiated UO_2 have focused on quantifying the effect of changes in water chemistry on fuel dissolution and subsequent radionuclide release. These same studies have used single-pass flowthrough testing to determine the forward rate of matrix dissolution; that is, the rate found with flows sufficiently high such that solubility concerns and back reactions are not encountered. This results in highly conservative radionuclide release rates from SNF under the relatively low water flux conditions expected at Yucca Mountain.

Previous work has shown that the oxidation of SNF is affected by its burnup, or roughly the amount of fission products and actinides soluble in the UO_2 matrix. Fuels with higher burnup or larger quantities of these non-uranium impurities have been shown to be more resistant to oxidation beyond UO_2 because of the change in the fuel chemistry (i.e., chemical potential), much the same way that stainless steels are more resistant to corrosion than carbon steels because of the small quantities of impurities (Cr, Ni, etc.) present. These chemical properties should act to slow the dissolution rate of SNF when exposed to moisture in the event of a waste package breach in the proposed repository, both by effectively reducing the surface area exposed to any leachant and by inhibiting or delaying the oxygen transport necessary for oxidative dissolution to occur. Figure 1 shows an example of the less soluble elements such as Pu and Zr building up on the surface of corroded SNF.

Similarly, under low water flux conditions, including humid air corrosion, alteration products will form on the surface of the spent fuel. These alteration products should serve as a barrier to radionuclide release by delaying water and oxygen contact with the unreacted matrix beneath them and because of the hydrophobic nature of many of these secondary phases (see Figure 2). Finally, SNF today has a much higher radiation field associated with it than it will 300-500 years from now when much of the β and γ fields will have decreased due to decay of ^{90}Sr and ^{137}Cs. The reduction of radiolytic oxidants produced by these fields should result in a decrease in matrix dissolution rates, even under an oxidizing environment and significant changes in radionuclide chemistry.

OBJECTIVES: The main objective of this project is to determine the effects of fuel chemistry changes on the dissolution of the SNF matrix and subsequent release of radionuclides under conditions relevant to the proposed Yucca Mountain repository. The main subtask objectives are:

- Determine the oxidation and dissolution rate of unirradiated, doped-UO_2 fuels as a function of dopant type and concentration, temperature, dissolved oxygen and carbonate concentrations, pH, and water flux. Subsequent tests will examine the

effects due to groundwater and brine constituents (e.g., Na, Fe, Ca, Si, Ni, etc.)

- Determine the dissolution rate of UO_2 and RADFUEL as a function of radiolytic field (α vs. β vs. γ). This includes an examination of the effects of vapor or humid air conditions compared to saturated conditions and to examine changes in the chemistry of key radionuclides (Pu, Tc, and Np) in different radiation environments

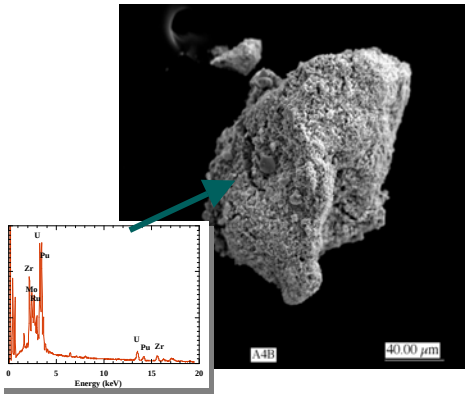


Figure 1. SEM/EDS examination of corroded spent fuel showing a concentration of less soluble elements at the fuel surface.

Figure 2. Example of hydrophobic nature of schoepite on the surface of UO_2 (left) compared to unaltered UO_2 (right). Water appears to be repelled by the schoepite.

- Quantify the ability of alteration phases to reduce matrix dissolution resulting from both the diffusion barrier and hydrophobic nature of these phases
- Determine the water thickness and water chemistry (pH, Eh, etc.) on the surface of fuel and cladding as a function of fuel temperature and ambient temperature and relative humidity.

APPROACH: These objectives will be accomplished by testing doped-UO_2 and RADFUEL under a variety of conditions, including single-pass flowthrough, static, and humid air corrosion tests. Each test will examine differences associated with changes in fuel surface area to water volume (i.e., pellet vs. fragment vs. powder) to allow for a water flux dependence and surface area term to be determined. RADFUEL is a simulated high burnup fuel where the proper constituents, including radioactive isotopes, are added to UO_2 and pressed and sintered into pellets to simulate fuel at varying ages (e.g., 500, 1000, 10,000 year decay). Advanced surface science techniques including XRD, AFM, EELS, EFTEM, XPS, SIMS, and Auger spectroscopy will be used to characterize the morphology, precipitated secondary phases, radionuclide behavior, and electrical surface properties of the samples.

BENEFITS TO OCRWM: This project will provide a large database to be used in modeling efforts to determine the dissolution rate of the SNF matrix under a variety of conditions, but specifically the low water flux scenarios anticipated at Yucca Mountain. It is anticipated that these data will allow an enhanced dissolution and release model to be developed. Current hypotheses are that this improved model will

be less conservative than the present models and will allow the waste form to serve as a primary barrier to radionuclide release under repository relevant conditions.

Project Title	Impact of Uranyl Alteration Phases of Spent Fuel on Mobility of Np and Pu
OCRWM S&T Program Thrust	Source Term
Project Performers	Notre Dame University
Principal Investigators	Peter Burns
FY 2004 Funding	$250,000

Abstract **BACKGROUND**: Previous studies have demonstrated that uranyl phases formed during the alteration of spent nuclear fuel (SNF) can incorporate various radionuclides, thereby having a potentially profound impact upon their mobility and on repository performance. Studies of natural analogues have clearly established that these uranyl phases may persist for hundreds of thousands of years. Applied research for this project is exploring the uptake and retention of Np by uranyl alteration phases as a function of crystal structure, pH, temperature, time and counter-ions present in solution. The stabilities, structures and chemistries of uranyl peroxides and the extent to which these phases may incorporate Np under repository relevant conditions are being investigated, and thermodynamic properties of relevant uranyl phases are being measured.

OBJECTIVES: The alteration phases of SNF will impact the mobility of some radionuclides, but detailed understanding of the mechanisms is needed in order to provide estimates of radionuclide releases, as required for performance-assessment models. Radionuclides identified as important for the long-term performance of a proposed geological repository for nuclear waste include Np, Pu, U, Am, Se, I, and Tc. Under the conditions where UO_2 SNF is actively altering to uranyl phases (moist, oxidizing conditions), the oxidation states of concern for these elements include Np(IV, V), Pu (IV, V), Am(III), Se(IV), and Tc(VIII). It has been argued, on the basis of crystal chemistry, that Np(IV, V), Pu (IV, V), Am(III) and Se(IV) may be incorporated into uranyl phases, whereas incorporation seems unlikely in the case of Tc(VII). Recently, researchers provided experimental evidence for the retention of Np^{5+} by powders of uranophane and Na-compreignacite, to levels of approximately 400-500 ppm. In 2004 other researchers reported XAS spectra that confirmed that Np associated with Na-compreignacite is pentavalent.

APPROACH: This project will focus on experimental verification of incorporation mechanisms of Np^{5+}, Pu^{4+}, Am^{3+}, Se^{4+} and I^{5+} into uranyl phases that are likely to form in Yucca Mountain (Table 1). These oxidation states are thought to be the most likely, and are of considerable concern owing to their high solubility in groundwater (except Pu^{4+}, which is more likely to be transported by colloids). Applied research into incorporation of radionuclides into uranyl phases will:

- Determine the extent of Np, Pu, Am, Se and I (with appropriate oxidation states) incorporation possible in the phases listed in Table 1
- Examine the impact of temperature, pH, the presence of counter ions, and time on radionuclide incorporation into the phases listed in Table 1
- Examine, from an experimental perspective, the crystal chemical factors that impact radionuclide incorporation into the uranyl phases listed in Table 1

- Provide other S&T researchers with well-characterized specimens of uranyl phases containing radionuclides of interest.

Each of the uranyl phases of interest will be synthesized in the presence of trace levels (100-500 ppm) of the radionuclide in question (or non-radioactive isotopes in the cases of Se and I). Synthesis will be conducted over a range of conditions relevant to the repository (i.e., temperatures from 50 to 150ºC, pH from 3 to 8), in the presence of various counter ions that may provide appropriate charge-balance mechanisms to enhance incorporation, and over a range of time to account for grain size factors. As such, it will be possible to delineate the impact of various geochemical conditions on radionuclide incorporation. Considerable effort will be invested in perfecting synthesis techniques to attain high yields and purities. Synthesized uranyl phases will be characterized by powder X-ray diffraction and ICP-MS, and selected samples will be studied using XAS to verify oxidation states of the incorporated radionuclides, as well as to provide information on incorporation mechanisms.

Table 1. Uranyl phases for incorporation experiments

Uranophane	$Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$
Boltwoodite	$(K,Na)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$
Na-compreignacite	$Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$
Becquerelite	$Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$
Metaschoepite	$UO_3.2H_2O$
Dehydrated schoepite	$UO_3(H_2O)_{0.8\text{-}1.0}$
Soddyite	$(UO_2)_2(SiO_4)(H_2O)_2$
Studtite	$[(UO_2)(O_2)(H_2O)_2](H_2O)_2$
Metastudtite	$[(UO_2)(O_2)(H_2O)_2]$

In some cases (i.e., compreignacite and becquerelite), it will be possible to synthesize large crystals (i.e., 100-500 micrometers), and microprobe techniques will be used to verify incorporation of radionuclides. For example, in the case of the actinides, laser ablation ICP-MS will be used to obtain radionuclide concentrations in single crystals, with spatial resolution to about 20 micrometers. Samples of such materials will be provided to other researchers for additional studies.

Following delineation of the extent of incorporation of radionuclides into uranyl phases, additional experiments will be executed to examine the fate of the radionuclides during alteration of the earlier-formed uranyl phases. For example, in Yucca Mountain uranyl oxide hydrates are expected to form early during alteration of SNF, and uranyl silicates are expected to gradually replace these phases with continued alteration.

Thermochemistry of the uranyl phases - Demonstration of radionuclide incorporation into uranyl phases will not impact performance assessment unless the thermochemistry and solubility of the incorporating phases are also well constrained. Using well-characterized synthetic specimens of high purity, the

heats of formation and solubilities of each of the phases of interest will be measured. Atomic force microscopy will be used to examine the dissolution kinetics of selected phases under a variety of aqueous conditions.

Uranyl peroxides - Radiolysis of water associated with nuclear waste will generate potentially significant quantities of peroxide, which may combine with uranium (and other actinides) to form uranyl peroxides. The extent to which such phases will form in Yucca Mountain is unclear, but under some geochemical conditions uranyl peroxides are more stable than many of the uranyl oxide hydrates. In general, the phase chemistry of uranyl peroxides is poorly understood. Under sufficient peroxide and uranyl concentrations and low pH, studtite or metastudtite readily form. However, under neutral to somewhat alkaline pH, other as yet unknown uranyl peroxides may crystallize. Research will be conducted into the uranyl peroxide system, with aqueous solutions containing a range of cations typical of groundwater at Yucca Mountain. Phases will be characterized using single-crystal X-ray diffraction, and full structural analysis will be completed where feasible.

Uranyl phases, such as uranyl oxide hydrates and uranyl silicates that form in Yucca Mountain in the vicinity of nuclear waste may later come in contact with solutions containing substantial peroxide. It is possible that such phases will alter to uranyl peroxides relatively rapidly under some conditions. Well-characterized powders of uranyl phases (Table 1) will be treated with peroxide-bearing solutions, at room temperature, to evaluate the extent to which alteration occurs, as well as the kinetics of the reactions.

BENEFITS TO OCRWM: This project will provide fundamental data concerning the release of Np and Pu from the near-field environment within the repository. Current performance assessment models assume that Np and Pu will be released from spent nuclear fuel upon corrosion and alteration of the waste form. However, incorporation of Np and Pu into the uranyl phases that form locally in the repository as SNF is altered is likely to occur, and potentially will greatly reduce the release rates of these radionuclides. This project will establish the extent of incorporation of Np and Pu possible in uranyl phases that form when SNF is altered, as well as the factors that impact such incorporation. The results will support a more realistic model for radionuclide release rates from altering nuclear waste.

Project Title	Implications of Deliquescence and Decay Heat on Source Term Degradation
OCRWM S&T Program Thrust	Source Term
Project Performers	Argonne National Laboratory
Principal Investigators	James L. Jerden Jr.**,** Margaret M. Goldberg, James C. Cunnane
FY 2004 Funding	$480,000

Abstract **BACKGROUND:** A key process that is not explicitly addressed within the current chemical models for the proposed Yucca Mountain Repository is the deliquescence of hygroscopic phases present within the spent fuel pins. Deliquescence is the process by which a hygroscopic mineral draws water from the surrounding atmosphere to form an aqueous solution. This process may play a key role in spent fuel degradation and radionuclide release.

Typical commercial spent nuclear fuel (SNF) contains thousands of mg/kg cesium and barium and hundreds of mg/kg strontium and iodine. These elements are known to form hygroscopic phases and to contribute to water vapor pressure lowering of aqueous solutions. Cesium in particular is known to form a number of potentially deliquescent phases that have been observed or are predicted to be present in concentrated fission product deposits within spent fuel.

If water accumulates on the SNF surface (by deliquescence, adsorption, and dripping water), fission products such as cesium, barium, strontium, and iodine will be supplied to the aqueous film as the fuel dissolves. These fission products are expected to lower the activity of water in the aqueous film and will cause the brine to absorb water from the atmosphere as dissolution of the fuel continues. Spent fuel dissolution in a thin aqueous film (such as may form from deliquescence and water adsorption) could cause a flux of water at the SNF surface due to water activity lowering in the aqueous film. This process could maintain a corrosive aqueous brine on the fuel surface despite the fact that the fuel is the hottest material in the breached waste package. There is, however, evidence suggesting that this deliquescence process may be self-limiting in the sense that U(VI) minerals that form as the fuel corrodes may sequester deliquescent components. This hypothesis is supported by preliminary experimental results[6].

OBJECTIVES: The three major objectives of this project are:

- Develop a predictive understanding of the on-set of deliquescence on spent fuel by quantifying the deliquescence thresholds (as a function of temperature) of hygroscopic primary phases in the fuel or fuel/cladding gap (e.g., CsI, Cs_2Te, Cs-uranates, Cs_2MoO_4). Integrating results from these tests with water adsorption studies will help define the conditions under which aqueous solutions first contact the SNF as well as how much solution will be present and how its volume will change over time
- Develop a predictive understanding of how the aqueous films that may form

[6] *Implications of Deliquescence and Decay Heat on the Source Term, ANL: J.L. Jerden, M.M. Goldberg, and J.C. Cunnane*

from deliquescence and water adsorption evolve chemically (i.e., evolution of water activity) as the fuel corrodes at relevant temperatures and relative humidities

- Determine the paragenesis, mineral chemistry and deliquescence behavior of alteration phases that form as SNF corrodes in aqueous films that may form from deliquescence, and in brines that may form as seepage waters drip onto failed fuel pins.

APPROACH: The deliquescence of fission product salts will be studied using an isopiestic approach which involves the reaction of a dry powder of the hygroscopic mineral of interest with air of a known relative humidity at a controlled temperature. The relative humidity of the air is controlled using an aqueous salt solution such as NaCl, KCl or $CaCl_2$. When the deliquescence threshold of the sample is exceeded, the amount of water that accumulates due to deliquescence is measured volumetrically and gravimetrically. This isopiestic approach will also allow us to measure the activity of water in the brines that form from deliquescence.

This project will also involve the development of improved techniques for studying deliquescence and its potential role in SNF corrosion. The focus of this task will be on setting up two complementary types of instruments:

1) a temperature and relative humidity controlled gravimetric system consisting of a microbalance in a controlled atmosphere furnace, and
2) an infrared spectroscopic system that could be used to monitor the formation and evolution of aqueous films on hygroscopic mineral surfaces as a function of relative humidity and temperature.

The corrosion of SNF in the types of solutions that could form from deliquescence and seepage waters will be studied by reacting SNF surrogates (e.g., Ba, Sr doped uranium oxides) with potentially important deliquescent minerals and brines of appropriate compositions at controlled relative humidities and temperatures. The mineral chemistry and deliquescence behavior of alteration phases produced during these tests will be characterized. A focus of these experiments will be to test the hypothesis that the deliquescence process may be limited by the incorporation of deliquescent components in uranyl alteration phases.

BENEFITS TO OCRWM: The processes leading to the formation and evolution of aqueous films on failed fuel pins are uncertain. Current models (e.g. In-Package-Chemistry, Dissolved Concentrations) deal with these issues by making conservative assumptions. These experiments will provide the technical basis for modeling the formation and evolution of aqueous films on SNF and will determine how these processes influence spent fuel corrosion behavior and radionuclide release.

Project Title	In-Package Sequestration of Radionuclides at Yucca Mountain
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Abstract