
NUCLEAR ENERGY RESEARCH INITIATIVE

6. Waste Management

This program area includes 5 NERI research projects awarded in FY 1999. It addresses the long-term R&D goal related to fuel cycle research, which considers the impact of fuel cycle options on waste generation, waste form, and waste storage and disposal.

Projects currently funded include R&D that addresses nuclear waste with regard to technological improvements

in the back-end fuel cycle process. Novel approaches are proposed to reduce the physical volume of spent nuclear fuel and to recycle or reuse spent nuclear fuel without reprocessing in a manner that maintains the highest degree of proliferation-resistance. Additional R&D is being performed in the use of concrete for nuclear waste containment.

NUCLEAR ENERGY RESEARCH INITIATIVE

Directory of Waste Management Project Summaries

| | |
|----------------------------------------------------------------------------------------------------------------------------------|------|
| 99-126 Monitoring the Durability Performance of Concrete in Nuclear Waste Containment | .203 |
| 99-127 Chemical Speciation of Neptunium in Spent Fuel | .207 |
| 99-200 Experimental Investigation of Burn-up Credit for Safe Transport, Storage, and Disposal of Spent Nuclear Fuel | .211 |
| 99-217 Deterministic Prediction of Corrosion Damage in High Level Nuclear Waste | .215 |
| 99-219 A Single Material Approach to Reducing Nuclear Waste Volume | .219 |

NUCLEAR ENERGY RESEARCH INITIATIVE

Monitoring the Durability Performance of Concrete in Nuclear Waste Containment

Primary Investigator: Franz-Josef Ulm,
Massachusetts Institute of Technology

Project Number: 99-126

Collaborators: Commissariat a l'Energie Atomique
(French Atomic Energy Commission)

Project Start Date: August 1999

Project End Date: August 2002

Research Objectives

Concrete is commonly employed in radioactive waste disposal as an effective construction material for containment barriers, liners, and encasement of containers. The objective of this research is to develop the scientific knowledge and the appropriate engineering tools required to evaluate and quantify the durability performance of concrete containment of nuclear waste subjected to the negative chemical-degradation scenario of calcium leaching. Monitoring the durability performance here means the quantitative assessment, in time and space, of the integrity of the container during the entire storage period, and requires the consideration of the multiple couplings between diffusion-dissolution of calcium and deformation and cracking.

With regard to the time-scale, a durable design for waste containers needs to take into account some reference scenario of chemical degradation, in particular the unfavorable one of calcium leaching by pure water. This design scenario refers to the risk of water intrusion in the storage system. For the reference scenario at hand, it is generally assumed that concrete is subject to leaching by a permanently renewed deionized water acting as a solvent. The calcium ion concentration in the interstitial pore solution leads to dissolution of the calcium bound in the skeleton of Portlandite Crystals, $\text{Ca}(\text{OH})_2$, and calcium-silica-hydrates (C-S-H), with sharp dissolution fronts. This calcium leaching leads to a degradation of the mechanical properties of concrete (material strength, Young's modulus). Cracks increase the diffusivity of the calcium ions through the structure, and can lead to an acceleration of the chemical degradation, and hence to accelerated aging of the structure. This process can lead to a closed loop of accelerated structural degradation.

Research Progress

The important scientific findings that will translate into industrial benefits in the field of concrete durability in nuclear waste storage are as follows:

- (1) The chemical process of calcium leaching involving kinetics and mineral composition was studied, including the use of alternative leaching agents. State-of-the-art material tests were employed. Based on the scientific analysis of the calcium leaching process, an accelerated material leaching test was conceived and put into practice, allowing for a 300-fold accelerated calcium-leaching process (see Figure 1). This makes it possible to test different kinds of cementitious materials with regard to their leaching characteristics before they are used in industrial applications. Changes in mineral composition due to calcium leaching are now predictable and can be incorporated into industrial planning and design tools. For instance, the thickness of containment structures can be adopted with regard to the demineralization design scenario.

The developed test is now being used in several laboratories internationally for the assessment of the long-term mechanical stability of construction materials.

- (2) The role of cracks on demineralization of porous materials was the object of an extensive study. Using dimensional analysis, similar properties that govern calcium leaching and degradation of concrete were thoroughly identified. In particular, studying the similar properties of the governing equations of 'real' calcium leaching in concrete, it was shown that a pure diffusive mass transport through a crack or fracture will not significantly affect the overall degradation kinetics of a

concrete structure. However, it was also shown that advective transport may accelerate the degradation process.

The in-depth analysis of influential parameters concerning cracks in cementitious materials and their consequences on leaching have immediate industrial application. For example, it is now possible to analyze the suitability of a given cementitious material or structure for industrial applications at any moment during its life span. This can improve the decision-making process compared to a decision based solely on the crack size, as is common practice in parts of industry today.

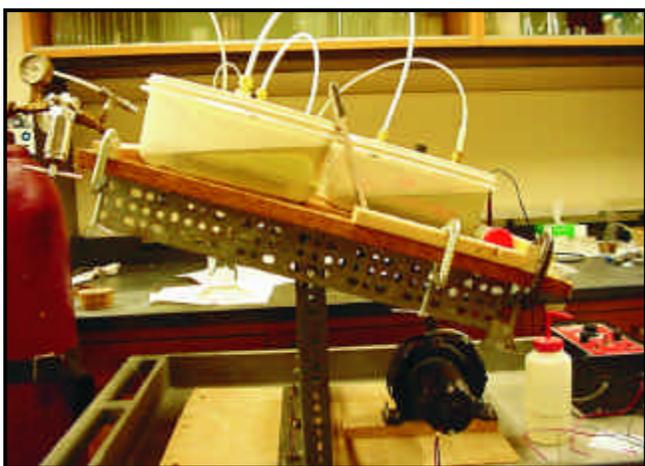


Figure 1. The MIT-NERI accelerated leaching test device uses containers filled with an optimized ammonium-nitrate solution mounted on an oscillating table.

(3) The consequences of calcium leaching on the mechanical behavior of cement paste were identified in mechanical tests, invoking three-dimensional stress states. For the first time, the governing mechanical parameters were identified in 3-D at multiple scales ranging from the nanometer level (see Figure 2) to the centimeter-level of concrete materials. These included the following:

- By means of instrumented nanoindentation, the effect of calcium leaching on stiffness and strength of C-S-H was quantified. It was found that calcium leaching has an important mechanical impact on the so-called outer products of the C-S-H, while the inner products are less affected. This result was a breakthrough in the field of material sciences of cementitious materials (see Figure 3), since for the first time, it was shown conclusively that

calcium leaching on the smallest scale accessible to mechanical testing affects only part of the matter. This explains, in part, why calcium-leached, cement-based materials, even when severely leached, still have a residual stiffness and strength.

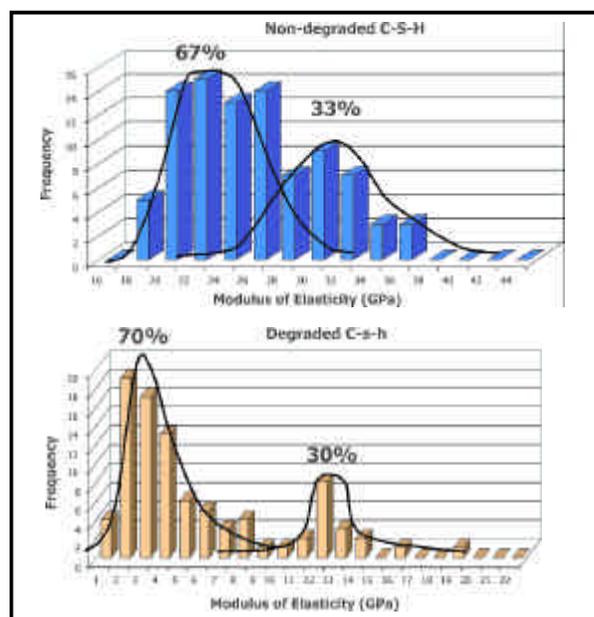
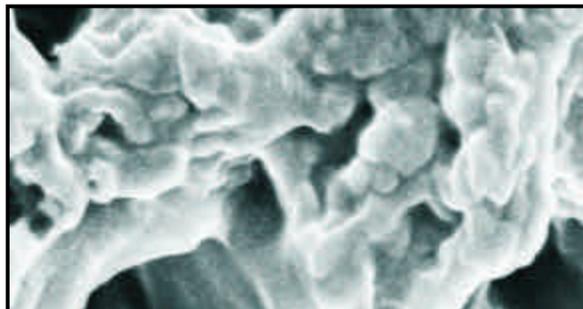


Figure 2. (top) The SEM-picture is of an artificially aged mortar (asymptotic state), equivalent to 300 to 1,000 years of natural material subjected to "natural" leaching or weathering.

Figure 3: (bottom) The graphs present results from 200 nanoindentation tests on non-degraded and degraded C-S-H. The results show that calcium leaching does not affect the volume proportions of the two types of C-S-H, and that the low-density C-S-H (outer products) are heavily affected by calcium leaching, in contrast to the high-density C-S-H.

- By means of macroscopic triaxial compressive tests and direct tensile tests the assessment was completed of the strength and stiffness of asymptotically leached, cement-based materials (cement paste and mortar). This extensive series of tests provided conclusive evidence of the residual-strength domain of calcium-leached materials, which has a relatively low standard deviation, and which therefore can be taken into account in the design of concrete for nuclear

waste disposal structures (containment and/or containers).

- While the experimental database was developed for cement paste and mortars, a novel micromechanical model was developed that allows one to upgrade both the stiffness and the strength properties of calcium-leached materials, from the lowest level of cement-based materials to concrete. This novel approach, which was developed for both highly confined stress states and low confinement states, has been validated with the experimental values obtained by nanoindentation and macroscopic material testing. Based on this validation, investigators are confident that the database can now be used for concrete as construction material for containment structures.
 - Based on yield design, a safe lower bound solution was developed for the residual design strength of calcium-leached materials, with application in the nuclear waste storage domain. This is a new design concept, and one that should be considered as an economical solution in concrete containment structures for the storage of radioactivity over extended time periods.
- (4) The results of mechanical testing are a key element for the mechanical modeling of calcium leaching. This modeling is needed to support industrial monitoring and decision-making regarding safe storage systems. Further aspects of this finding are as follows:
- It is common practice today to assume that because calcium-leached materials are stiff and reduced in strength, they should not be considered mechanically active for the design and operation of concrete employed in nuclear waste storage systems. This will increase the cost of using concrete in nuclear waste storage systems. The experimental and theoretical results of these studies provide clear evidence that asymptotically leached materials have a sustainable residual strength and a stiffness that can be factored into the design and operation of concrete subjected to aging over extended periods of time. This new design concept, once applied, will help to substantially reduce the costs for storage solutions, particularly over longer storage times.
- The multiscale experimental and theoretical approach provides the foundation for optimizing concrete solutions for nuclear waste storage design, starting at the smallest intrinsic level of the material. In particular, given the nanoindentation results, it appears that a concrete with a higher inner-product concentration is much more sustainable, in terms of long-term mechanical performance, than the standard materials employed today.
 - The most critical issue in the development of materials and structures for sustainable and economic nuclear waste storage is the predictability of physical states the material may undergo over 300 to 1,000 or more years. The approach developed here, in which time/age is replaced by chemical equilibrium states associated with mechanical performance provides a new basis for the industrial development of such solutions.
- (5) The research carried out in the course of this project is now close to delivering a blue-print of the elementary aging components of cement-based materials. These elementary aging components control the mechanical performance of the materials over extended periods of time, although they do not change from one cement-based material to another. Instead, they are intrinsic to the matter, which makes it possible to upscale the micro-behavior assessed by, for example, nanoindentation, to the macroscopic scale, where concrete is employed in nuclear storage systems. This blue-print of the chemomechanical behavior of cement-based materials is the backbone of the micro-chemo-mechanics theory of calcium leaching the researchers have developed for cementitious materials, which ultimately provides the missing link between physical chemistry and mechanics. Further aspects of these novel developments are as follows:
- The engineering implementation of this multi-scale model in a finite-element program makes it possible today to predict and anticipate with a high level of confidence the physical state of concrete materials and structures subjected to calcium leaching over extended periods of time that correspond to the lifetime of nuclear waste storage systems. This finite-element implementation was validated through

comparison with experimental structural data, which shows the capacity of the material model to improve the understanding of experimental results at the scales of structures subjected to leaching.

- The model and its implementation form a powerful durability design tool that can be used for the design of new structures and the lifetime analysis of existing nuclear waste storage structures. In particular, by using multi-scale, model-based simulations, it was possible to show that a new generation of ultra-high-performance cementitious materials (UHPC that is currently entering the market offers superior durability performance for nuclear waste storage systems. The sources of the improved leaching resistance of UHPC could be identified and quantified: The

absence of Portlandite and the lower porosity significantly slow down the leaching process and reduce the extent of deterioration of the material properties.

- (6) The research carried out in the course of this project provides the basis for the development of a new generation of "intelligent" storage systems. In these systems, continuous monitoring of the physical state of the materials and structures, blended with advanced modeling tools developed in this project, will allow the industrial development of the next generation of sustainable and economic nuclear waste storage systems.

Planned Activities

The NERI project has been completed.

NUCLEAR ENERGY RESEARCH INITIATIVE

Neptunium Speciation in Spent Nuclear Fuel

Primary Investigator: Ken Czerwinski,
Massachusetts Institute of Technology

Project Number: 99-127

Collaborators: Argonne National Laboratory (ANL),
Chemical Technology Division

Project Start Date: August 1999

Project End Date: August 2002

Research Objectives

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

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

The chemical species and oxidation state of neptunium will be determined in spent fuel and alteration phases. Different types of spent fuel will be examined. Once characterized, the chemical behavior of the identified neptunium species will be evaluated if this information is not present in the literature. Special attention will be given to the behavior of the neptunium species under typical repository, near-field conditions (elevated temperature, high pH, varying Eh). This will permit a timely inclusion of project results into near-field geochemical models. Additionally, project results and methodologies have applications to neptunium in the environment, or treatment of neptunium-containing waste.

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

Research Progress

Progress on the various tasks of the project will be discussed in turn.

Development of XANES/EXAFS Experiments: The ANL team organized equipment for developing X-Ray Absorption Near Edge Structure (XANES)/Extended X-Ray Absorption Fine Structure (EXAFS) experiments. The equipment was utilized in the subsequent XANES/EXAFS experiments with Np.

Analysis of Np Solids: ANL prepared and analyzed NpO₂. High isotopic purity of Np-237 was used in the preparation of the oxide. The neptunium was reduced to Np⁴⁺ by taking to dryness in concentrated hydrobromic acid, and the occurrence of complete reduction was verified by absorption spectrometry. The neptunium oxide samples were analyzed by XANES/EXAFS at the MR-CAT¹ beamline to provide reference spectra for future reaction/alteration.

¹ Materials research collaborative access team at the Illinois Institute of Technology.

Phase matching and shifts in the radial distribution of the oxygen in this system will be used to identify and establish the changes in the oxide due to reaction with the air-steam environment.

The ANL team has also preformed theoretical calculations for evaluating XANES/EXAFS spectra. Theoretical calculations on dissolved neptunium species were initiated. The overall goal of this work is to calculate the structures of aqueous neptunium species.

Analysis of Np and Alteration Products: MIT calculated the production of ^{237}Np from ^{236}U . It is intended to produce $^{236}\text{UO}_2$ for irradiation in the MIT Reactor. This will produce ^{237}Np in the same manner as nuclear fuel. The speciation of Np in the UO_2 matrix will be examined by XAFS at ANL. Initial calculations show enough Np can be produced with a two-day irradiation to provide suitable XAFS samples. A sample of $^{236}\text{UO}_2$ was created from a ^{236}U -nitrate solution by precipitation reaction. The precipitate was dried, calcined, and finally sintered under a reducing atmosphere to produce the oxide. X-ray diffraction spectroscopy was performed on a $^{238}\text{UO}_2$ standard prepared identically to the ^{236}U sample to verify that UO_2 was created.

The ANL team examined air-steam reaction on neptunium oxides. The safety review was completed and approved and all vessels needed for the experiments are in hand. The matrix for these experiments was developed, Np(IV)O_2 and $\text{Np(V)}_2\text{O}_5$. The changes in structure and oxidation state in these two solids will be established as a function of temperature (25°C and 150°C), oxygen (air and nitrogen gas) and the presence of water vapor (dry and 100 percent RH). In all cases the changes in structure will be investigated using synchrotron-based techniques (primarily XANES) along with continued characterization of oxide standards.

Examination of Np Chemical Speciation: The sorption of Np to mineral phases was examined as a function of pH, solution, and mineral phase. Goethite, montmorillonite, and tuff were the mineral phases examined. The pH was varied from 5 to 12. Both Ar and air atmospheres were used to analyze the impact of carbonate. The solutions examined were 0.1M NaClO_4 and J-13 groundwater. In all case there was sorption of Np to goethite. This sorption was most pronounced under Ar. In the presence of carbonate, in both the air and J-13 conditions, there was less Np sorption to goethite. This indicates the formation of carbonate species, which decrease Np sorption to the goethite. For tuff and montmorillonite, sorption occurred near pH 10 due to Np precipitation. An increase in Np

solution concentration was observed above this pH. However, the concentration of Np in solution for all the solids above pH 10 was less than the control solution without solid phases. This indicates the solid phases retain Np at higher pH.

The kinetics of the sorption of pentavalent Neptunium onto Tuff, Montmorillonite, and Goethite mineral phases were investigated in a glovebox under an inert atmosphere by MIT. Two series of samples were run respectively at pH 7 and 9. The ionic strength was set at 0.1M with NaClO_4 and the pH was adjusted with 0.1M HClO_4 and 0.1M NaOH . Supernatant concentrations were measured by alpha liquid scintillation counting. BET surface analysis provided the specific surface area of Goethite, Tuff, and Montmorillonite, respectively, as $248.06 \pm 0.87 \text{ m}^2/\text{g}$, $163.43 \pm 4.63 \text{ m}^2/\text{g}$, and $193.88 \pm 4.50 \text{ m}^2/\text{g}$. Titration experiments provided the Proton Exchange Capacity to be $0.2275 \pm 0.0184 \text{ meq}_{\text{OH}}/\text{gG}$, $0.1645 \pm 0.0281 \text{ meq}_{\text{OH}}/\text{gT}$, and $0.2722 \pm 0.0675 \text{ meq}_{\text{OH}}/\text{gM}$, respectively for Goethite, Tuff, and Montmorillonite. It was found that the sorption of Neptunium on Montmorillonite was faster than on Goethite, and itself faster than on Tuff. One-term exponential regression fits the kinetics of Montmorillonite while a two-term exponential regression fits those of Goethite and Tuff, assuming that in the last case the surface sorption is fast and occurs within the first 5 hours. Then, a combination of surface sorption and diffusion occurs slower until reaching saturation. In the case of Montmorillonite, a linear regression between the concentration of Neptunium at saturation and the initial concentration of Neptunium has been found to be

$$[Np]_{\text{sat}} = 0.0825 * [Np]_{\text{ini}} + 5 * 10^{-07}; R^2 = 0.9998$$

The calculated distribution coefficients given in $\text{Log}(K_d)$ are $3.490 \pm 0.210 \text{ mL/g}$ for Goethite, $3.4509 \pm 0.304 \text{ mL/g}$ for Tuff, and $3.477 \pm 0.116 \text{ mL/g}$ for Montmorillonite. A linear regression shows the relation between PEC and $\text{Log}(K_d)$ to be

$$\text{Log}(K_d) = -0.2974 * \text{PEC} + 3.5578; R^2 = 0.9999$$

The logarithm of complexation constants were evaluated as 6.27, 6.71, and 6.94, respectively, for goethite, tuff, and montmorillonite. Correlations with SSA and PEC were established. The data will be incorporated into geochemical codes.

The ANL team examined the complexation of Np(VI) to organics. It was found that Neptunium (VI), as

NpO_2^{2+} , was not stable in the presence of either lactate or acetohydroxamic acid. Slow reduction was observed with lactic acid, presumably due to reaction with the secondary hydroxyl group. For acetohydroxamic acid, reduction to NpO_2^+ was instantaneous under all conditions investigated. This fast reduction is typically observed for many amines. Once reduced, Np(V) , as NpO_2^+ , was stable in the presence of both lactic acid and acetohydroxamic acid for periods of weeks. There was no evidence of even trace reduction to form Np(IV) species when lactate was present. Some very slow reduction was noted for acetohydroxamic acid. For this reason, only upper limits for the rate constants were determined. The ANL team also examined the interaction of Np with bacteria.

Performance of Modeling: MIT performed focused speciation calculations on the behavior of Np at Yucca Mountain using the hydro-geochemical equilibrium code CHESS. The influence of the pH on the speciation of Np is studied at different temperatures for a fixed potential. The

pH is varied from 4 to 12, the successive temperatures are 25°C, 50°C, 75°C, and 100°C, and the potential is 700mV. The main inorganic ligands taken into account were carbonate and hydroxide. Np(V) and, to a lower degree, Np(IV) complexes dominate the speciation. The temperature and the pH favor the formation of $\text{NpO}_2\text{CO}_3^-$ and NpO_2^+ below pH 10 and $\text{NpO}_2\text{OH(aq)}$ and $\text{NpO}_2(\text{CO}_3)_3^{4-}$ above pH 10.

Final activities focused on the XAFS analysis of the Np-containing phase. The ANL team collected spectroscopic data on Np-bearing secondary phases and Np in spent nuclear fuel. The MIT team evaluated the data and determined the Np oxidation state in the material. Additionally, under Task 2, the MIT team incorporated project data into the geochemical code CHESS and performed speciation calculations of Np in the repository near-field.

Planned Activities

The NERI project has been completed.

NUCLEAR ENERGY RESEARCH INITIATIVE

Experimental Investigation of Burn-up Credit for Safe Transport, Storage, and Disposal of Spent Nuclear Fuel

Primary Investigator: Gary A. Harms, Sandia National Laboratories

Project Number: 99-200

Project Start Date: August 1999

Project End Date: September 2002

Research Objectives

The Nuclear Energy Research Initiative has funded a critical experiment focused on burn-up credit issues at Sandia National Laboratories. The experiment, when complete, will provide benchmark data that can be used to test the methods and data used in the criticality safety analyses of shipping, storage, and disposal of spent nuclear fuel.

Burn-up credit is the process of accounting for the decrease in the reactivity of spent nuclear fuel produced by the changes in the fuel actinide concentrations and the buildup of fission product absorbers caused by the burning of the fuel. To apply burn-up credit safely, the methods used in its application must be validated: the fuel isotopic composition in the burned state must be accurately predicted, and the neutron multiplication of spent fuel configurations also must be accurately predicted. This project addresses the second part of the validation issue.

A critical assembly with low-enriched UO_2 fuel has been built at Sandia. The assembly concept is shown in Figure 1. The figure shows a cut-away view of the assembly core along with a photograph of the assembly. It consists of a water-moderated array of driver fuel elements surrounding a smaller number of experimental fuel elements. Test materials can be inserted between the fuel pellets in the experimental elements to allow accurate measurements of the reactivity worth of important fission products. The assembly also includes three fuel-followed control/safety elements and a fueled source element. Critical experiments can be performed in the unperturbed assembly and with a test material, a fission product simulant, present in the assembly. The benchmark data from the experiment is the difference in the critical array size between the two configurations. The results of criticality safety analysis methods can be compared with the benchmark results to test the analysis methods.

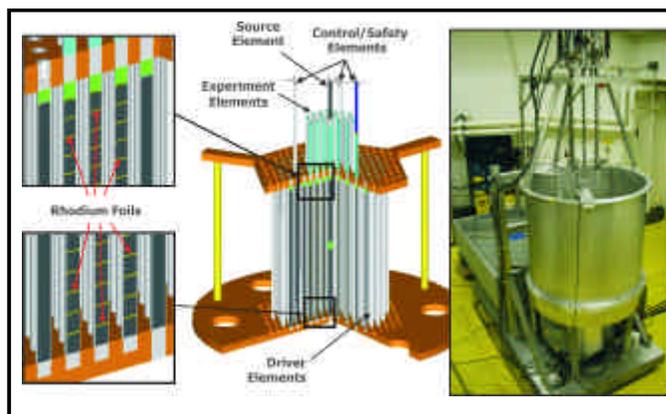


Figure 1. A cut-away view of the Burnup Credit critical assembly is illustrated. The photograph shows the critical assembly tank and associated hardware.

The critical experiment is structured as a three-year project. Five broad tasks were outlined in the project proposal:

- Task 1 - Obtain the necessary National Environmental Policy Act (NEPA) approvals.
- Task 2 - Prepare safety basis documentation for the experiment and obtain approvals.
- Task 3 - Design and procure the experimental hardware.
- Task 4 - Perform the benchmark experiments.
- Task 5 - Decommission and decontaminate the experiment.

Research Progress

The NEPA approvals for the experiment were obtained in the first year of the project. Sandia filed an Environmental Checklist/Action Description Memorandum with the Department of Energy requesting that the experiment be categorically excluded from further NEPA documentation. The exclusion was granted.

The critical experiments were performed in the reactor room of the Sandia Pulsed Reactor Facility (SPRF) in Sandia's Technical Area V. Early in the project, the determination was made that an addendum to the SPRF Safety Analysis Report (SAR) would be required to establish the safety basis for the critical experiments. The SAR addendum was completed. A document was written that described the Technical Safety Requirements derived from the SAR addendum for the operation of critical assemblies. Both documents were submitted to the Sandia Internal Review and Appraisal System (SIRAS) for safety review. The SIRAS review was completed in April 2001. The SAR addendum and the TSR were then submitted for DOE approval, which was received in December 2001. A three-part readiness assessment was then initiated, which culminated in a review of the facility and the experiment by a DOE team in late February 2002. Issues identified by the DOE readiness assessment team were resolved and approval was obtained to operate the critical assembly.

The design of the critical assembly hardware was completed and procurement of the non-fuel hardware was initiated in the second year of the project. The assembly hardware was received and assembled. Two grid plate sets were obtained, each with different fuel element spacing, to give different neutron spectra in the assembly. The critical assembly is controlled with an instrumentation and control system from an earlier critical experiment that was modified for this project. The driver fuel elements, which were fabricated in 1996 as part of another critical experiment, were transferred from Los Alamos National Laboratory to Sandia. The experimental fuel elements, the control/safety elements, and the source elements utilize the same uranium dioxide fuel stock as that used in the driver fuel fabrication. These fuel elements utilize cladding assemblies fabricated by a commercial nuclear fuel vendor and loaded with fuel pellets at Sandia.

The critical experiments conducted as part of this project were designed to investigate the reactivity effect of rhodium on the assembly. Circular rhodium foils with the same diameter as the fuel pellets were obtained in three thicknesses. The foils are placed between the fuel pellets in the experimental fuel elements. First, the critical array size with only driver fuel was determined. Then the central fuel elements were removed and replaced with experimental fuel elements that had been "poisoned" with rhodium, and the critical array size measured. The benchmark data from the experiment is the difference between the critical array size with the poison and the

critical array size without the poison. Experiments with three different foil thicknesses give data for different levels of self-shielding in the foils.

All ten of the critical experiments planned as part of the project have been performed. Five experiments were done with each of the two grid plates: one with driver fuel only; one with experiment elements containing no poison foils; and one with each of the three sets of experiment elements loaded with rhodium foils. During each of the experiments, the critical assembly was loaded in a sequence of steps starting with a low multiplication configuration and proceeding to progressively higher multiplication. Each step provides an updated estimate (by extrapolation) of the number of rods required to achieve a critical configuration. The data from these steps is plotted as $1/M$ (inverse multiplication) to display the current estimate and guide the determination of the number of rods to load in the next step. Measurements are compared with the results from an extensive series of MCNP calculations to confirm the expected trends. The inverse multiplication graph and a photograph of the critical configuration of the initial BUCCX core, one with only driver fuel, are shown in Figure 2.

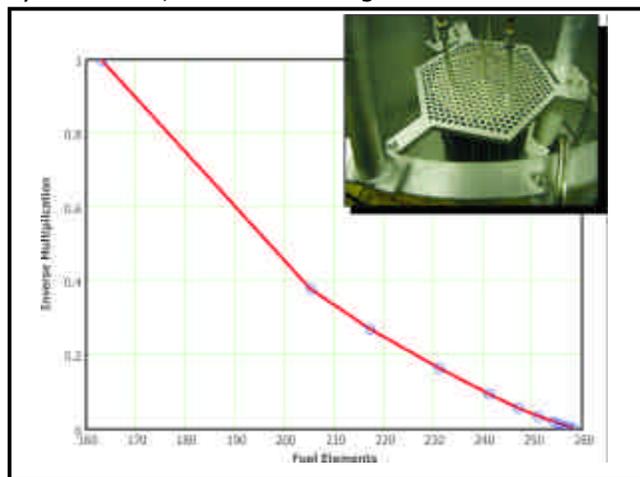


Figure 2. The graph illustrates the inverse multiplication ($1/M$) plot for the first Burnup Credit critical assembly. The final fuel rod configuration for this core is shown in the photographic insert.

Planned Activities

The following items will complete the project:

- The final report will document the results of the critical measurements and provide a detailed comparison to the previous analytic results. The critical experiments performed in this project will provide data on rhodium, one of a number of fission products important to full burn-up credit.

Funding will be sought for further experiments using other fission product materials to provide further data in support of efforts to obtain approval for full burn-up credit.

- The experiment will be decontaminated and decommissioned. Since a large fraction of the experimental hardware will be used in another NERI-funded critical experiment, NERI Project 01-124, most of the decontamination and decommissioning activities will be deferred to the completion of subsequent critical experiments.

NUCLEAR ENERGY RESEARCH INITIATIVE

Deterministic Prediction of Localized Corrosion Damage to Alloy C-22 High Level Nuclear Waste Canisters

Primary Investigator: Palitha Jayaweera, SRI International

Project Number: 99-217

Project Start Date: August 1999

Project End Date: October 2002

Research Objectives

This research involves developing deterministic models and associated computer codes for predicting the evolution of corrosion damage to high level nuclear waste (HLNW) containers. The principal challenge is to ensure isolation of the waste from the biosphere for periods up to 10,000 years under conditions that can only now be estimated. The lack of relevant databases for the corrosion of candidate alloys means that we cannot rely on empirical methods to provide the design, materials selection, and reliability assessment information. Instead, only strategies based on the employment of deterministic models can be used, because the natural laws (laws of conservation) that are the foundation of these models constrain the solutions to physical reality and are invariant with time.

Existing deterministic models of general and localized corrosion allow us to predict the accumulation of corrosion damage in many systems. However, these models must be customized for predicting damage in HLNW canisters in a tuff repository. Thus, the influence of radiolysis on the corrosion potential and hence on the corrosion rate, for example, must be included in the models. Particular attention must be given to repassivation phenomena, because they eventually determine the extent of damage. Attempts to quantitatively describe localized corrosion damage without proper consideration of repassivation phenomena greatly underestimate the service lives of containers. It is also important to customize the models to the conditions to which the containers are expected to be exposed over their design lives.

The principal objectives of this project follow:

- Develop deterministic models and associated computer codes for predicting the evolution of corrosion damage (i.e., "integrate" damage) to HLNW containers in the Yucca Mountain repository. Corrosion processes that will be considered include

general corrosion (oxidation), pitting corrosion, crevice corrosion, and stress corrosion cracking.

- Develop deterministic methods for extrapolating corrosion rate data obtained under "accelerated" laboratory conditions, to the field.
- Use the models to predict the fates of containers after exposure in the repository under various conditions (e.g., humid air, contact with dripping water, repository inundation).

Research Progress

Damage Function Analysis (DFA), which is based upon the Point Defect Model (PDM) for passivity breakdown, upon deterministic models for cavity growth, and upon the concept of delayed repassivation, has been used to predict damage functions for pitting corrosion in simulated repository environments for times up to 10,000 years. The differential equations for calculating the damage function (DF) have been derived. By analytical or numerical solution of these equations, it is possible to calculate DF under arbitrary conditions if the rate of nucleation and propagation, and the probability of survival of corrosion events are known. The maximum depth of penetration is predicted to be of the order of 1.9 cm, which is of the same order as the design wall thickness of the canister. However, the maximum penetration depth is a sensitive function of the rate constant for the delayed repassivation of active pits, with the maximum depth decreasing as the rate constant increases. No data is currently available for the delayed repassivation rate constant, but methods have been devised in the present program for measuring this important parameter.

A general mathematical model and corresponding computer code have been developed for calculating potential and concentrations distributions in active

corrosion cavities. Mass transfer by diffusion and migration, anodic and cathodic processes at the cavity tip and on the sides of the cavity, and hydrolysis and saturation solubility reactions were included in the model. The model also takes into account the potential drop in the external environment (outside the cavity). Based on the general model, a simple, but nevertheless analytical model for calculating potential and concentration distributions, along with cavity propagation rates, has been developed for metals with very low passive corrosion current densities, e.g., Hastelloy C-22. The importance of this development is that it permits simplification of the mathematics, and allows one to predict the potential and concentration distributions without knowing various parameters, such as the equilibrium constants for homogeneous chemical reactions and the kinetic parameters of electrochemical reactions that do not significantly change the concentrations of the principal ionic species in the cavity. The fact that reliable analytical expressions can be obtained for the rate of pit or crevice propagation is very important, because accurate numerical simulation of corrosion damage for a long period (up to 10,000 years) may require a prohibitively large amount of computer time. The conditions that allow the investigator to consider the pit propagation rate as a constant have also been obtained.

Detailed radiochemical simulations of the effects of ionizing γ and neutron radiation on the properties and chemical composition of electrolyte solutions under repository conditions indicate that the impact on pH and corrosion potential should be minimal. However, the long exposure times in actual repository systems preclude excluding radiolytic effects completely. Resolution of this issue will require accurate experimental data for the influence of pH and potential on the kinetics of oxygen reduction on Alloy C-22.

It has been shown in this program that, in principle, the possibility that corrosion initiates and propagates on HLNW containers in the Yucca Mountain repository at short times (hundreds of years) when the temperature is significantly above the boiling temperature of water cannot be ignored. This is because the surfaces are covered by highly hydrophilic oxides, hydroxides, and oxyhydroxides that will hydrate to the form of corresponding hydroxides and/or retain water, thereby acting as proton conductors and hence as electrolytes.

Alloy C-22 is found to undergo pitting attack in very aggressive, low-pH, high-chloride, high-temperature environments, with the breakdown potential being near

the transpassive dissolution potential. However, because of the distributed nature of the breakdown potential, pits are expected to nucleate at potentials that are significantly more negative than the mean, so that pitting is expected under considerably less aggressive conditions, provided the observation time is sufficiently long. The pits, as observed in short-term experiments, are open and of low aspect ratio (depth/diameter) as shown in Figure 1.



Figure 1. The photomicrograph shows pitting and grain boundary corrosion in Alloy C-22 after exposure to saturated NaCl solution at 80°C under 997 mV (vs. Standard Hydrogen Electrode, SHE) applied potential for 10-days (photograph area 75 x 40 μm).

Experimental data is being measured for a variety of model parameters, including the kinetic parameters (exchange current densities and Tafel constants) for the reduction of oxygen and the evolution of hydrogen, and for the oxidation of the substrate, on Alloy C-22 in sodium chloride solution as a function of temperature and pH. The greatest challenge has been to achieve quasi steady-state conditions, to conform to the constraints of the models. Achieving steady-state conditions is particularly difficult with respect to the anodic oxidation current, because of the extraordinarily long time that the transients last. Nevertheless, a reasonably complete set of parameter values is being assembled, which will be of value not only in the present work, but also in studies being carried out elsewhere on the most challenging problem of HLNW disposal.

Planned Activities

Measurements of key model parameters will be continued during the remainder of the project period. The principal emphasis will be on the measurement of damage functions for Alloy C-22 in well-defined environments under well-defined electrochemical conditions as a function of observation time. The damage functions will allow estimates to be made of a delayed repassivation constant for Alloy C-22 in prototypical repository environments and

hence will allow values to be obtained for this most important parameter, as identified by the theoretical work carried out in this program. The value of delayed repassivation constant is very important for predicting the evolution of corrosion damage, because if this value is sufficiently high the probability of survival of a pit over a long observation time is negligible. Considerable effort is also being given to the development the Mixed Potential Model for predicting corrosion potential and general

corrosion rate for Alloy C-22. Emphasis in this task is being placed on the measurements of passive anodic current density as function of potential, temperature, and pH (reliable experimental data for cathodic processes on Alloy C-22 has been already obtained in this program). The general computer code for predicting the simultaneous accumulation of general and localized corrosion damage to HLNW canisters will be completed shortly.

NUCLEAR ENERGY RESEARCH INITIATIVE

A Single Material Approach to Reducing Nuclear Waste Volume

Primary Investigator: James V. Beitz, Argonne National Laboratory

Project Number: 99-219

Collaborators: Nuclear Environment Technology Institute (Daejeon, Republic of Korea)

Project Start Date: October 1999

Project End Date: September 2002

Research Objective

This project is concerned with developing an innovative single-material, minimum-volume approach for the selective sorption of metal ion radionuclides from aqueous waste solutions and creating a final nuclear waste form that is suitable for long-term storage or geological burial. The project is based on a chemically functionalized porous silica, termed Diphosil. Diphosil was created as an ion exchange medium that selectively and nearly irreversibly sorbs highly charged metal ions, such as actinides, from appreciably acidic aqueous solutions. The chelating power of Diphosil is due to diphosphonic acid groups that are anchored to its silica surface via organic spacer groups. Approximately 90 percent of the weight of dry Diphosil is silica (SiO₂).

Underlying this project is the hypothesis that heating metal ion-loaded Diphosil in air will oxidize its organic content to water vapor and carbon dioxide and its phosphonic acid groups to phosphoric acid that would react with the sorbed metal ions to produce metal phosphates. Based on literature reports of the properties of porous silica, it was further hypothesized that additional heating would either volatilize any excess phosphoric acid or cause it to react with the silica to form silicon phosphates. At still higher temperatures, pore collapse should occur, thereby microencapsulating and chemically fixing the sorbed metal ions in phosphate-rich metal phases in vitreous silica. Vitreous silica is one of the most radiation-resistant glasses known.

Research Progress

Project activities to date have confirmed the hypotheses as to the events that might occur when metal ion-loaded Diphosil is heated in air. The process of converting porous silica to fully dense silica is referred to as thermal densification in the literature because it occurs

at temperatures far below the melting point of bulk silica and consequently does not involve a phase change such as melting. The term thermal densification has been adopted to refer to the entire set of processes that occur when metal-ion-loaded Diphosil is heated in air to the point of pore collapse and beyond. The project has investigated the following topics of importance to a single-material approach to reducing nuclear waste volume.

Solution Composition Effect on Metal Ion Sorption:

This work has investigated the influence of solution composition variables on sorption of heavy metal ions into a chemically functionalized porous silica (Diphosil). Diphosil has been shown to extract metal ions from aqueous solutions that contain significant concentrations of ethylenediaminetetracetic acid (EDTA) at near-neutral pH. Aqueous solutions of EDTA are frequently used in decontaminating surfaces because of its powerful chelating action for many metal ions. Using laser-induced fluorescence methods, evidence was obtained that Diphosil sorbs trivalent metal ions from concentrated phosphoric acid that contains a small concentration of nitric acid. This mixed-acid media corresponds to the expected composition of the spent working medium of a nitric-phosphoric acid oxidation process for treating organic waste with significant plutonium contamination.

Maximum Metal Ion Loading: To determine the maximum heavy metal ion loading using Diphosil, optical spectroscopy was used to measure metal ion concentration during the sorption process. For example, the maximum uptake of trivalent neodymium ions (Nd³⁺) into Diphosil from dilute nitric acid was determined by monitoring a characteristic near-infrared optical adsorption band of Nd³⁺ and was found to be 2 percent of the dry weight of the Diphosil used.

Densification Optimization: On-line, real-time infrared analysis has been carried out of the gases evolved during

thermal densification of Diphosil in purified air as a function of heating rate and metal ion loading (see Figure 1). Optimal thermal densification conditions have been identified by varying heating and gas flow rates. The resulting material contains the selectively sorbed heavy metal ions in fully encapsulated nanophases that are embedded in nearly colorless, nonporous vitreous silica that is highly resistant to radiation damage. Small-angle neutron scattering studies using silica contrast matching, at the Intense Pulsed Neutron Source at Argonne National Laboratory, provided clear evidence for the nanophase character of metal ion-loaded Diphosil that had undergone thermal densification. Furthermore, the nanophases produced were found to be inaccessible to water and their size dependent on the type of metal ion.

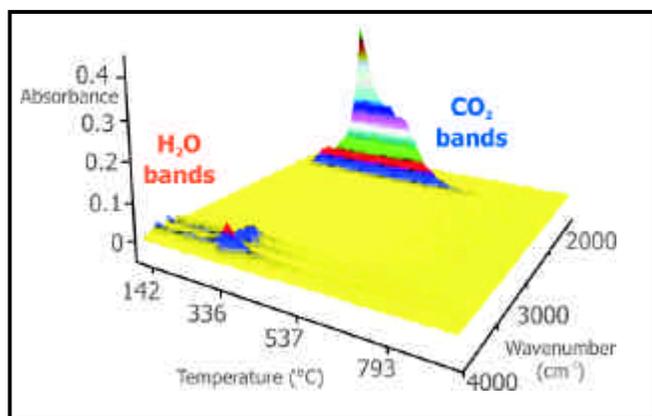


Figure 1. FT-IR absorption spectra of gases evolved as fully uranyl (UO_2^{2+}) loaded Diphosil was heated at $2^\circ\text{C}/\text{minute}$ in flowing dry, purified air. At this heating rate, the organic content of Diphosil is converted to water vapor and carbon dioxide while its phosphonic acid groups oxidize to phosphoric acid that reacts with UO_2^{2+} and the surrounding silica.

Nonradiative decay: Studies on luminescence decay rates of 3d electron states of a transition metal ion, 4f electron states of trivalent lanthanide ions, 5f electron states of trivalent actinide ions, and charge transfer states of actinyl ions provided rapid means of assessing the proximity of such ions to each other in metal ion-loaded Diphosil prior to and following thermal densification processing. Facile ion-ion energy transfer dominated nonradiative decay processes and resulted in highly nonexponential luminescence decays for each of these cases when Diphosil was loaded with a single type of metal ion, such as Eu^{3+} . Studies in which a luminescing metal ion, such as Eu^{3+} , and a spectroscopically silent metal ion, such as La^{3+} , were simultaneously incorporated into Diphosil, provided a means of controlling ion-ion energy transfer rates and thereby proving that the observed nonexponential decays arose primarily from ion-ion energy

transfer. Nonradiative decay studies also provided evidence of complete dehydration of metal ions in thermally densified, heavy metal ion-loaded Diphosil.

Leach rate and radiation damage: Radiation damage studies were carried out on Diphosil into which had been sorbed primarily trivalent lanthanum ions along with lesser amounts of the radioisotopes Cm-245, Bk-249, and Es-253. This material then underwent thermal densification at $1,100^\circ\text{C}$. Damage resulting from alpha decay of Es-253 (20.5 day half life) to Bk-249 was tracked using time- and wavelength-resolved, laser-induced fluorescence on 5f electron states of Cm^{3+} , Bk^{3+} , and Es^{3+} ions. These studies showed that decay daughter Bk ions were ejected from the heavy metal phosphate nanophases that contained the parent Es ions and were stopped primarily in the vitreous silica in which those nanophases had been embedded by thermal densification. Calculations of ion stopping distances using TRIM 2000, an ion implantation computer code, support the conclusions we reached from our laser-induced fluorescence studies.

Criticality control: Thermally densified Diphosil contains primarily silicon, oxygen, and phosphorus atoms. As such, it provides some moderation of fission neutrons but will not readily capture thermal neutrons. Anomalous small-angle, X-ray scattering (ASAXS) has been used at the Basic Energy Sciences Synchrotron Radiation Center at the Advanced Photon Source at Argonne National Laboratory to investigate an innovative method for incorporation of gadolinium (Gd) of natural isotopic abundance into Diphosil with no loss of fissile isotope loading. Gadolinium is a nearly ideal criticality control agent for our purposes due to its large thermal neutron absorption cross section. ASAXS provides a means of identifying phases that contain resonant metal ions (Gd in this case) and the size of such phases down to the nanometer scale. ASAXS studies confirmed the expected increase in size of the nanophases that result from thermal densification of Diphosil into which Gd^{3+} ions had been incorporated using our method following full loading of Diphosil with terbium ions bound to diphosphonic acid groups.

Emerging Waste Stream Application: Diphosil possesses the unusual ability to selectively and strongly sorb high valent metal ions, such as actinides, from aqueous solutions. Assessment of the range of aqueous waste solutions that are amenable to processing via Diphosil is being pursued. In particular, spent chloride salts have been identified, such as are generated during electrometallurgical or pyroprocessing of spent nuclear reactor fuel, as an emerging waste stream application for

a single material approach to reducing nuclear waste volume. The working medium in present electrometallurgical processing and in many pyroprocesses is a chloride salt or a mixture of chloride salts. Eventually such salts become spent and then must be disposed of although they contain some fission products and actinides.

In the case of such spent process salts, the present high-level reference waste form is glass-bonded sodalite. Unfortunately, glass-bonded sodalite retains the chloride content of the spent salt, which raises concerns about chloride-induced stress corrosion cracking when such a waste form is in contact with stainless steel over prolonged periods of time such as would be the case at the Yucca Mountain geologic repository.

The present work has shown that Diphosil provides sufficient chelating power to remove trivalent lanthanide

ions (surrogates for actinide ions such as trivalent americium) from concentrated salt solutions that can be formed by dissolving spent process salts in dilute hydrochloric acid. Rinsing the metal ion-loaded Diphosil with water removed chloride ions and subsequent thermal densification processing chemically fixed and nanoencapsulated the sorbed lanthanide ions in vitreous silica. This project's single material approach to reducing nuclear waste volume is also a promising method for creation of a minimum volume, chloride-free, high-level waste form in the treatment of spent electrometallurgical and pyroprocessing salts.

Planned Activities

The NERI project has been completed.