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**CORROSION TESTING OF SPENT NUCLEAR FUEL PERFORMED AT  
ARGONNE NATIONAL LABORATORY FOR REPOSITORY ACCEPTANCE**

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# **CORROSION TESTING OF SPENT NUCLEAR FUEL PERFORMED AT ARGONNE NATIONAL LABORATORY FOR REPOSITORY ACCEPTANCE**

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## **Abstract**

Corrosion tests of DOE-owned spent nuclear fuel are performed at Argonne National Laboratory to support the license application for the Yucca Mountain Repository. The tests are designed to determine corrosion rates and degradation products formed when fuel is reacted at elevated temperature in different aqueous environments, including vapor, dripping water, submersion, and liquid film contact. Corrosion rates are determined from the quantity of radionuclides released from wetted fuel and from the weight loss of the test fuel specimen as a function of time. Degradation products include secondary mineral phases and dissolved, adsorbed, and colloidal species. Solid phase examinations determine fuel/mineral interface relationships, characterize radionuclide incorporation into secondary phases, and determine corrosion mechanisms at grain interfaces within the fuel. Leachate solution analyses quantify released radionuclides and determine the size and charge distribution of colloids. This paper presents selected results from corrosion tests on metallic fuels.

## Introduction

The U.S. Department of Energy (DOE) currently owns approximately 2500 metric tons of spent nuclear fuel (SNF) that it plans to permanently store, along with commercial spent fuel and high-level waste (HLW), in an underground repository at Yucca Mountain, Nevada. The DOE-SNF is comprised of more than 200 types of spent fuel, with the largest fraction, approximately 80% on the basis of the metric tons of heavy metal (MTHM), being metallic fuel (1). Smaller fractions of the inventory consist of oxides, carbides, hydrides, and other miscellaneous fuels.

Acceptance of these fuels into the repository requires that DOE provide sufficient evidence that the filled repository will pose no greater human health risk for a period of 10,000 years than the unmined uranium from which the fuel was produced. Extensive technical requirements and criteria for acceptance of the repository, waste forms, and containers are provided in several documents (2,3,4). To provide experimental data addressing these criteria, the National Spent Fuel Program coordinates testing programs at selected national laboratories. The spent fuel characterization and corrosion-testing program at Argonne National Laboratory (Argonne) addresses the following fuel acceptance criteria that pertain to the chemical and physical behavior of DOE-owned spent fuels (5).

- *Particulate Content:* SNF must be in a solid form or any particulates must be consolidated and/or sealed in a high-integrity container (2). A maximum of 1.4 kg total existing and projected reactive particulates are permitted per canister, and a maximum of 1.6 kg total existing and projected non-reactive respirable particulates are permitted per PWR single-element-sized canister (3).
- *Pyrophoric, Combustible, Explosive Nature:* Materials that ignite spontaneously in air at or below temperatures of 400°C, at pressures of 1-5 atm, and at or above a relative humidity of 5% are prohibited from the repository unless it can be shown that they will not adversely affect the repository (3).
- *Gas Generation:* After closure, the canistered waste form shall not contain or generate free gas other than air, residuals of air, inert cover, and radiogenic gases with an immediate internal gas pressure  $\leq 150$  kPa (22 psia) at 25°C (2). Gas generation from SNF is only allowed to the extent that it will not degrade repository function (5).
- *Material Compatibility:* Waste package contents must be compatible with each other and with the canister material such that there will be no adverse effect on container integrity from material interactions (2).
- *Isotope Content and Leachability:* Radioactive releases to the accessible environment are regulated for 10,000 years (4).

Several methods are considered acceptable to demonstrate compliance of DOE-SNF with the regulatory criteria. The recommendation from the National Spent Fuel Program (5) to sites with DOE-owned spent fuel is to use the following methods to satisfy data needs, and in the interest of economy, to apply the methods in the preference order listed:

1. Provide sufficient published data to satisfy the criteria.
2. Demonstrate acceptability by comparison of DOE-SNF with an acceptable commercial SNF that may be either a similar fuel or a bounding fuel type.
3. Calculate required information using NRC-approved codes and software.

4. Provide sufficient test data to satisfy the criteria, or if the fuel is not acceptable, physically treat or condition the fuel to render it acceptable.

Because of the high cost and (often) long test periods required for corrosion testing of radioactive spent fuel, an experimental testing regime is undertaken only when the required data cannot be provided by less costly methods. Consequently, the experiments performed at Argonne are designed to maximize generation of useful information and minimize testing time. In practice, this means that experiments are designed with bounding conditions (rather than conditions that may be more typical of the repository or fuel), that only selected fuel types are tested, and that a limited number of different tests are performed.

Currently, Argonne is performing corrosion testing of commercial (uranium dioxide) spent fuels, high-level waste, and three types of DOE-owned spent fuels: Zircaloy-clad metallic uranium, aluminum-based fuels, and mixed oxide (U,Pu O<sub>2</sub>) fuels. Tests on a fourth type of DOE-SNF, a graphite fuel, are planned to commence in the near future. This manuscript draws examples from several fuels but focuses on work with metallic uranium fuel from the Hanford N Reactor.

### **DOE-SNF Testing Program at Argonne National Laboratory**

The fuel characterization and corrosion-testing program at Argonne is designed to provide data required for determining fuel acceptability in the repository. The primary data needs driving the program are the isotope content and leachability of the fuel. Secondary research questions are (1) the quantity, size distribution, and chemical nature of particulates formed during fuel corrosion; (2) the pyrophoricity of the corrosion products; (3) the quantity and identity of gas generated (especially H<sub>2</sub>); and (4) the material compatibility of co-disposed (i.e., SNF and HLW glass) waste forms with each other and with canister materials.

To address these data needs, we perform characterization analyses to establish the initial (un corroded) nature of the spent fuel, then corrode the fuel with groundwater at elevated temperature, and finally determine the release rate, physical form, and chemical form of radionuclides released from the fuel. The initial characterization analyses include metallographic and isotopic analysis of the fuel and correlation of elemental distributions with observed physical features (e.g., cracks, fuel/clad interface, grain boundaries). Characterization of the physical form of the reaction products includes quantitation of the solid/particulate, dissolved, colloidal, adsorbed, and gas fractions produced. Characterization of the chemical form includes determination of the elemental and isotopic distribution of species, mineral phase identification, and in some cases, determination of valence state. These characterization and testing activities are explained in more detail below.

#### **Initial Fuel Characterization**

To characterize the initial state of the fuel, multiple segments are prepared for analysis. Some segments are dissolved in acids, and the total elemental and isotopic content is determined by inductively coupled plasma mass spectrometry. Other segments are prepared for solid state metallography and electron microprobe analysis.

The following is an example of initial fuel characterization performed on spent metallic uranium fuel, specifically, N Reactor fuel element SFEC5,4378. This Zircaloy-clad fuel element was irradiated in the Hanford N Reactor and then stored for approximately 10 years under water in the Hanford K West basin. The element exhibited a cladding breach starting at one end of the element and terminating approximately 1 inch away. The first 2 inches of this

element (section S1A) were sectioned and metallographically characterized at Pacific Northwest National Laboratory (6), and the next 1-inch segment (S1AB), which did not exhibit any cladding breach, was sectioned for study at Argonne. Visual and metallographic examination of these samples revealed two important physical features: cracks and uranium hydride inclusions. Water and hydrogen can penetrate a significant distance into the fuel if the cracks form a network. The consequence of such penetration is rapid anoxic reaction of  $H_2O$  with metallic U, forming  $H_2$  gas and highly pyrophoric  $UH_3$  particulates. Thus, investigation of the cracks and uranium hydride inclusions is especially important in addressing data needs regarding pyrophoricity, gas generation, and particulate formation. In the following summary, comments about segment S1A are from Marschman et al. (6), and those regarding segment S1AB are from work performed at Argonne (7).

Although the cladding breach did not extend beyond the lowest 1 inch of the damaged fuel element (segment S1A), cracks were observed at all heights and in all regions of segments S1A and S1AB. That is, cracks were observed in the fuel along the fuel/clad interface (extending from the fuel into the clad) and in the interior of the fuel (away from the cladding). In the breached segment, S1A, a crack network was observed only in the region of the breach, while in some regions of the unbreached segment, S1AB, the cracks appeared to form a network roughly parallel to the fuel/clad interface (see Figure 1).

Uranium hydride inclusions were observed in both fuel segments, but they were much more extensive in the breached segment, S1A. The only network of uranium hydride observed was along the crack network in S1A in the region of the breach. However, away from the breach region and throughout the undamaged segment, S1AB, uranium hydride inclusions were generally observed as discrete, isolated phases scattered through the fuel matrix with no apparent concentration gradient (see Figure 1).

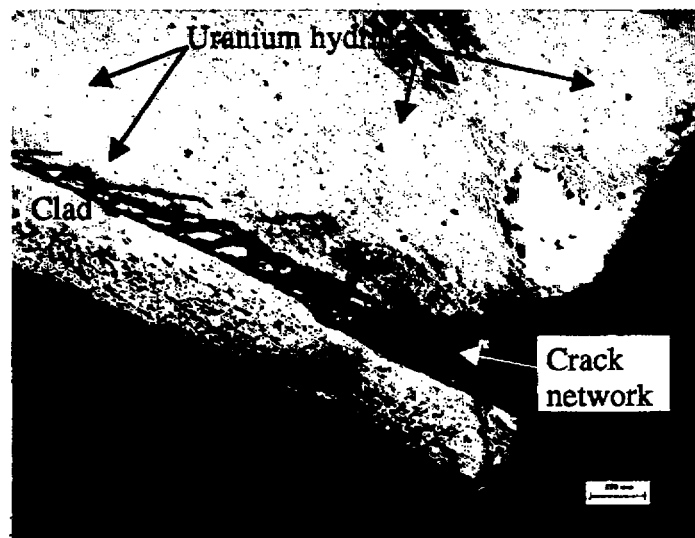


Figure 1. Scanning electron micrograph of etched N Reactor fuel segment, S1AB, showing network of cracks at the fuel-clad interface, uranium hydride inclusions as white "halos," and uranium carbide inclusions as angular, light-colored phases. Scale bar is 0.250 mm.

From this characterization analysis, it is expected that the presence of and relationship among cracks in the fuel will be important in the overall fuel corrosion and especially in the formation of  $H_2$  gas and  $UH_3$ . In addition, the highly heterogeneous nature of the fuel with respect to distribution of chemical phases suggests that the fuel will not release radionuclides congruently or at a single rate. For these reasons, interpretations of corrosion data on N Reactor fuel samples must reflect the physical and chemical heterogeneity and complexity of the specimens.

### Unsaturated Corrosion Tests

The unsaturated corrosion tests conducted on metallic fuels at Argonne are tests in which a fuel coupon is periodically wetted by injection of groundwater, which then drains away from the fuel into the base of the test vessel. In this configuration, the fuel is never submerged in water, but because the tests are conducted at  $90^\circ C$  in a sealed vessel, an atmosphere of saturated water vapor develops. Thus, the coupon is always wet but never submerged.

The objective of the test is to determine the reactivity of spent fuel under oxidizing, unsaturated conditions potentially representative of repository conditions at some time in the future. Specifically, some of the most important experimental goals are to determine the

- Release rate of fission products and radionuclides from the fuel into solution,
- Chemical and physical form of the released radionuclides, and
- Type and sequence of solid alteration products formed.

The design of the unsaturated tests consists of a fuel coupon placed in the top chamber of a three-part, vertically stacking fuel holder that is suspended inside a stainless steel test vessel. Each chamber has an inert metal sieve at its base, allowing injected water to contact the fuel, drain through the three chambers, and collect as leachate in the bottom of the test vessel.

Leachate solutions are characterized (pH, cations, anions, elemental composition, radionuclide speciation) periodically and at test termination. Gas generated during the test duration is also monitored and analyzed. At test termination and at selected sampling periods, the solid corrosion products are characterized (x-ray powder diffraction analysis, electron microprobe, metallography, transmission electron microscopy, and scanning electron microscopy). This approach is illustrated by the following selected results from tests of two fuels.

In unsaturated tests conducted on unirradiated N Reactor and aluminum-clad  $UAl_x$  fuels, the tests resulted in rapid degradation of the fuel and formation of solid alteration phases. In both fuels, uranium oxidation products, including uraninite ( $UO_2$ ) and schoepite ( $UO_3 \cdot xH_2O$ ), were observed. Figure 2 shows the fuel holder chambers containing the metallic uranium coupon with loosely adhered and spalled oxides after 48 days in test. Fine particles in the bottom chamber clogged the  $10\text{-}\mu m$  holes and retained injected groundwater. The oxides were identified by SEM (see Figure 3) and x-ray powder diffraction analysis as primarily  $UO_2$  with minor amounts of higher oxides of uranium. Gas analysis of the atmosphere in the sealed vessel revealed that  $H_2$  gas is produced immediately (within the first day of testing), and that it comprises up to 2% of the vessel atmosphere within 4 days.

Corrosion of  $UAl_x$  fuel is more complex. Like the metallic uranium, the  $UAl_x$  is observed to start reacting and forming uranium oxides almost immediately. However, by test day 16, a layer of boehmite ( $Al_2O_3 \cdot H_2O$ ) nearly covers the fuel surface. Uranium-rich mineral aggregates are seen as clusters of spheroids and thin plates (Figures 4 and 5) that appear to grow on top of  $UAl_x$  phases in isolated regions that are not completely covered by aluminum oxide.



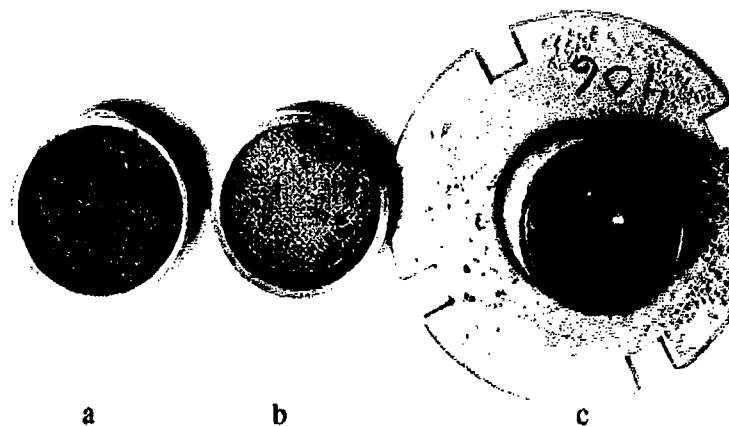


Figure 2: N Reactor fuel after 48 days in unsaturated test. a) fuel coupon covered by oxide corrosion products in top chamber; b) spalled oxides in middle chamber; and c) retained water and particulates in bottom chamber.



Figure 3. SEM image of spalled uranium oxides from N Reactor fuel test after 48 days. Particles appear to be platelets and agglomerates of sub-micron micro-crystallites.

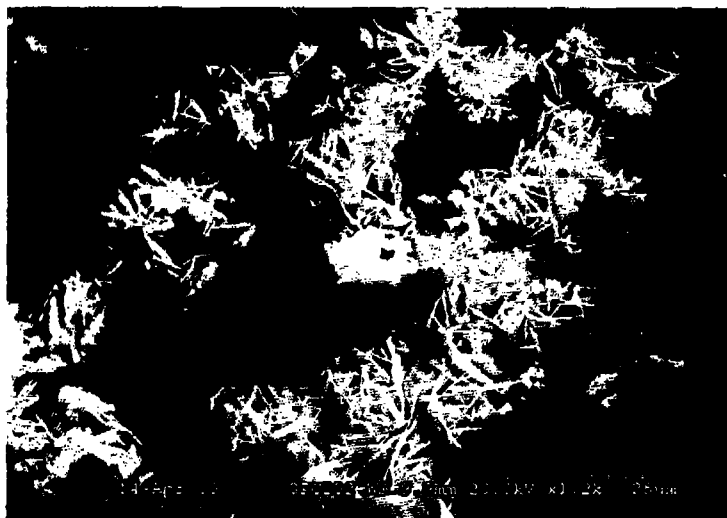


Figure 4. SEM image of unirradiated Al-UAl<sub>x</sub> after 16 days in unsaturated test. Dark blocks are aluminum oxides; white plates and clusters are uranium oxides.

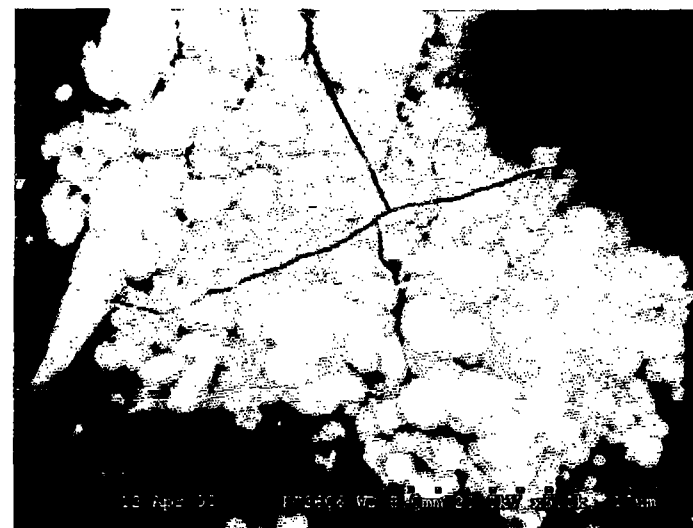


Figure 5: Spheroidal agglomerates of uranium-rich minerals on UAl<sub>x</sub> fuel surface after 16 days in unsaturated test.

## Colloid Tests

Both spent nuclear fuels and high-level-waste glasses have been shown to generate colloids when allowed to react with groundwater. Sparingly soluble radionuclides released from the waste forms can associate with the colloids at concentrations that substantially exceed the aqueous solubility of the radionuclide. If appropriate hydrological conditions exist, the radionuclide-associated colloids can travel long distances in the subsurface environment. Recent studies at the Nevada Test Site have shown that plutonium associated with colloids composed of clays, zeolites, and cristobalite was transported 1.3 km from its origin in 30 years (8). Thus, understanding colloid formation and stabilization processes is essential for predicting radionuclide concentrations at Yucca Mountain.

For the purpose of the tests performed at Argonne, colloids are defined as particles that are highly dispersed in aqueous media with at least one dimension between 1 and 1000 nm. The purpose of the tests is to characterize colloids formed during corrosion tests on spent nuclear fuel and unirradiated fuel analogues. Specific objectives include characterization of the colloids with respect to chemical, mineral, and radionuclide composition; size distribution; and charge distribution.

Colloids generated from unsaturated tests on spent  $\text{UO}_2$  and mixed oxide fuels and from unirradiated metallic uranium and  $\text{Al-UAl}_x$  fuels have been studied to date. All of these fuels have been found to generate colloids, but the metallic uranium fuels generate relatively large quantities of colloids rapidly and, therefore, are the focus of the following discussion.

Dynamic light scattering was used to determine the particle size distribution of colloids present in leachates from unsaturated N Reactor fuel tests sampled on test days 12, 48, and 77. In all samples, a bimodal distribution of particle sizes was found, with approximately equal concentrations of particles with mean sizes of approximately 4 nm and 160 nm. Analysis by TEM and SEM confirmed the particle sizes and showed that the particles are actually composed of individual micro-crystallites of approximately 4 to 10 nm that are aggregated into units with irregular shapes and overall dimensions of approximately 100 to 200 nm. Mineral phase characterization, performed by XRD analysis, identified the colloids as  $\text{UO}_2$  and also provided a diffracting unit dimension of approximately 10 nm, consistent with the size of individual  $\text{UO}_2$  particles. More details of these investigations are provided by Mertz et al. (9). Although these results were obtained from unirradiated fuel analogues rather than from spent fuel, they are considered highly significant to the repository application because they demonstrate that small, highly stable colloids are generated in large quantities directly from metallic uranium fuel. Ongoing unsaturated tests will determine if radionuclides from spent N Reactor fuel associate with the colloids or with other corrosion product phases.

In addition to analyzing colloids generated under unsaturated conditions, we are currently studying generation of colloids under static, saturated conditions and hydrodynamic shear conditions. The results from these tests are expected to provide necessary information about colloid formation mechanisms in spent fuel corrosion that can be used in predicting colloid concentrations in the repository.

## Discussion and Summary

The DOE spent fuel corrosion testing program at Argonne National Laboratory is designed to satisfy data needs of the National Spent Fuel Program for repository storage of DOE-owned spent fuels. Five fuel acceptance criteria form the basis for the research activities: particulate content, pyrophoricity, gas generation, material compatibility, and isotope content/leachability. The tests performed at Argonne address these acceptance criteria by (1) determining the initial isotopic content of the fuel and its distribution of mineral phases and physical features, and (2) determining the chemical and physical characteristics of the products of aqueous corrosion.

Examples provided from studies on metallic fuels showed that even for a material as relatively simple as metallic uranium, the spent fuel specimens are physically and chemically heterogeneous. The distribution of important chemical phases (e.g., uranium hydride and uranium carbide) and the presence of both isolated and networked cracks throughout the fuel suggest that the fuel will not release radionuclides congruently or at a single rate.

Unsaturated tests are designed to determine radionuclide release rates, generation of gases, paragenesis of solid alteration phases, and formation of colloids and particulates under test conditions in which the fuel is wet in an oxygenated environment, but is not submerged. For example, unsaturated tests on unirradiated metallic uranium fuel have shown that the fuel degrades very rapidly when wetted at 90° C, that it generates large quantities of particulates composed primarily of  $UO_2$  and higher oxides of uranium, that it generates  $H_2$  gas as water reacts with the uranium, and that significant quantities of stable colloids are formed. Unsaturated tests performed on aluminum-clad  $UAl_x$  fuels are ongoing, but results to date indicate that this fuel also corrodes rapidly under these test conditions. Oxides of uranium are observed to form rapidly, but the fuel surface becomes nearly coated with crystals of boehmite within 16 days. Uranium oxidation continues in discrete patches where the boehmite layer is cracked or absent. Preliminary analysis of leachates from these samples indicated that colloids are present but at lower concentrations than observed in the metallic uranium tests.

Colloid characterization research has determined the size distribution and mineral identity of colloids in leachates from unsaturated tests. Examples from the unsaturated tests on unirradiated metallic uranium fuel showed that a bimodal distribution of colloid sizes is generated and that the colloids are stable in groundwater. The colloidal particles were shown to be composed of individual micro-crystallites of  $UO_2$  approximately 4 to 10 nm in size and aggregated clusters of these micro-crystallites with dimensions approximately 100 to 200 nm. These results demonstrate that colloids can form and remain stable under unsaturated conditions, but the formation mechanisms, radionuclide association, and stability regime are not known. For that reason, additional tests are being performed at Argonne to enable modeling of colloid generation and stability fields under conditions that might exist in the repository.

The tests conducted to date have shown qualitatively or semi-quantitatively that particles, colloids, hydrogen gas, and potentially pyrophoric minerals are generated by groundwater corrosion of unirradiated analogues of DOE-owned metallic fuels. Quantitative tests with spent metallic fuels are currently underway. Results will be provided to satisfy the data needs of the National Spent Fuel Program for permanent storage of DOE-owned spent fuels.

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