# Corrosion of Breached Aluminide Fuel under Potential Repository Conditions

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2001 International High Level Radioactive Waste Management Conference
April 29-May 3, 2001
Las Vegas, NV

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# Corrosion of Breached Aluminide Fuel under Potential Repository Conditions

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## Introduction

Permanent disposal of spent nuclear fuel is proposed in a repository located in the volcanic tuff beds near Yucca Mountain, Nevada, and it is the responsibility of the National Spent Nuclear Fuel Program (NSNFP) to provide the Yucca Mountain Project (YMP) with information related to the release of fission products from the DOE-owned SNF resulting from SNF corrosion. Hydrologically unsaturated spent fuel tests ("drip" tests) are designed to simulate and monitor the release of radionuclides from the spent fuel under potential exposure conditions in the repository. Of the priority fuels being tested under the NSNFP, the aluminum-based fuels are included because of their high relative volume and uranium enrichment. The Al fuel structure is composed of fissile and aluminum powders pressed and annealed between Al plates to form thin metallic plates. The most widely used fissile powder was the intermetallic compound aluminide $UAl_x$ (where x=2,3,4). As part of this testing program, preliminary corrosion tests using unirradiated $UAl_x$ were initiated to address experimental design, sampling , and analysis issues prior to conducting tests with spent fuels.. However, during this program the decision was made by U.S. DOE to convert the aluminum-based fuels to safer enrichment levels by using the melt-dilute process at Savannah River. Nonetheless, the product ingot of the melt-dilute process resembles low enriched $UAl_x$ fuel and corrosion of the fuel is expected to be similar. This paper summarizes the preliminary testing results for the first year of the program and compares them to other corrosion testing results on aluminum fuels as well as other DOE fuel types.

## Work Description

This work was performed under the guidance of a QA Level 1 program. Groundwater from the J-13 well at the Yucca Mountain Site was reacted at 90°C for 21 days with crushed core samples of Topopah Spring tuff, simulating potential water chemistry at the proposed repository. J-13 well water

prepared in this manner is referred to as EJ-13 and is characterized by higher silicon and sodium content than J-13 water. The fuel meat is composed of low enriched $UAl_x$ (70.2% by mass U) in aluminum with surrounding AG3NE aluminum alloy cladding. A square coupon approximately 5-mm in length and 2.5-mm thick was cut from the middle of the fuel plate, one side of the fuel face was polished through the cladding to expose the fuel meat. At test start or restart, the fuel was placed in the top chamber of a three-chamber fuel holder, meat side up, and subsequently placed in a stainless steel test vessel. Five mL of EJ-13 was added to the base of the vessel and the vessel was sealed. The vessels were placed in a 90°C oven and 0.75 mL of EJ-13 water was injected on the fuel twice each week using an external injection port. Air was injected to ensure an oxygenated environment. Two tests (#1 and #2) were run concurrently. Specimen #1 was sampled after 33, 67, 118, and 183 days whereas specimen #2 was sampled after 16 and 55 days. Sampling was performed at room temperature and included inductively coupled plasma-mass spectrometric analysis of the liquid for important elements, colloid analysis by dynamic light scattering and transmission electron microscopy, and scanning electron microscopy of the fuel surface. Also, the entire volume of liquid was removed from the test vessel and the vessel was stripped of sorbed species using 1% $HNO_3$. Tests were restarted in the same vessel.

**Results**

Throughout the test the fuels remained in good mechanical condition. Macroscopically, the fuel surfaces appeared tarnished by the first sampling date but at no time did spallation of material from the fuel surface occur. The release of uranium from the fuel is presented in Figure 1. The figure includes the cumulative values from dissolved uranium in solution and uranium species or colloids sorbed onto the vessel walls of the fuel holder. The release rate of uranium from test #1 was 0.2-1.3 mg $U/m^2/d$ (avg 0.8 ± 0.5 mg/$m^2$/d) in contrast to 2.8 mg $U/m^2/d$ after 16 days from test #2. This discrepancy can probably be attributed to differing microscopic surface characteristics and will be discussed in the microscopy section. These release rates are comparable to those estimated for irradiated $UAl_x$ under flowthrough conditions[1] and from irradiated $UO_2$ commercial fuels under drip test conditions.[2]
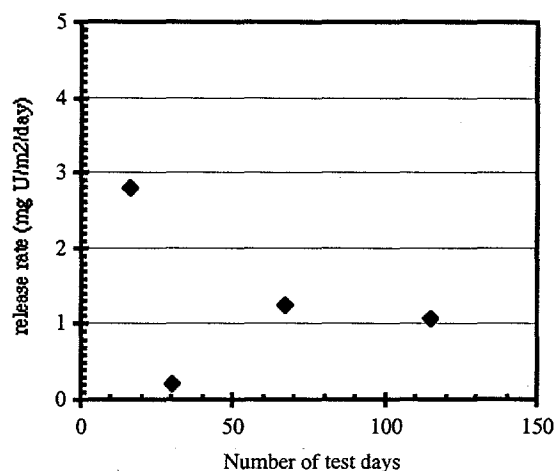
Figure 1. Uranium released from UAl$_x$ fuel between sampling periods (Test #1 after 31, 67, and 115 days and test #2 after 16 days testing).

Sorbed fractions (onto spent fuel holder and vessel walls) accounted for 82% of Al and 68% of U while 82% of Na and 63% Si was dissolved in solution. Given the near neutral pH of the solution, the propensity of uranyl and aluminum ions to hydrolyze, and the sorption properties of steel, it is not surprising that much of this material was sorbed to the vessel. However, the existence of charged U or Al-bearing colloids might also contribute to the sorbed fraction if these were found to exist. Dynamic light scattering analysis of the reacted EJ-13 revealed the presence of polydisperse colloid populations that have since remained stable for at least eight months in storage at room temperature. TEM analysis of the filtered colloids identified mainly agglomerated silicate materials but no uranium or aluminum-bearing colloids were found. Therefore, these tests suggest that primary colloids, that is, colloids formed by the direct spallation from the fuel surface, is not probable for the Al fuels under these test conditions and duration. However, the colloids present may serve as vehicles for the transport of fission products or actinides from irradiated fuels.

*Microscopy*

Dry oxidation of UAl$_x$ showed that uranium oxidizes to UO$_2$ and is removed from the UAl$_x$ matrix.[3] In studies on the corrosion of UAl$_x$ fuels in J-13[4] and water vapor,[5] a boehmite (Al$_2$O$_3$•H$_2$O) layer was formed on the surface and controled the release of the UAl$_x$ grains. It was proposed that the Al

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cathodically protected the UAl$_x$ from corrosion through a galvanic coupling. According to this model, as the boehmite layer grew, UAl$_x$ grains were uplifted and spalled into solution at which time they was free to dissolve. Longer-term vapor testing provided evidence of UAl$_x$ alteration prior to spalling.[6]

Microscopy performed under this program reveals that additional mechanisms are possible. The sample surfaces were covered with a thin, highly porous gel layer of Al oxide. The gel layer in the test #1 sample was thicker and also contained a thick bed of precipitates that covered about 30% of the fuel surface inhibiting the release rate of the underlying UAl$_x$ (as shown in Fig. 1). In both samples, UAl$_x$ alteration commenced almost immediately. Smooth, circular patches of uranyl oxyhydroxides were exposed through the gel layer and covered a significant fraction of the UAl$_x$ grains. These patches eventually crystallized to form small platelets, 1-2 $\mu$m on edge. The uranyl oxyhydroxides are known to form early as corrosion products of uraninite (UO$_2$).[7] Other cations are associated with the uranyl oxy-hydroxides and include Ca, Si, Al, and O. The platelet morphology is consistent with schoepite,[8] [(UO$_2$)$_8$O$_2$(OH)$_{12}$](H$_2$O)$_{12}$, and its presence on the fuel surface was observed at each sampling. Within the gel layer, dissolved uranium concentrated into nodules and, later, crystallized to form smaller platelets scattered within isolated regions of the fuel and having dimensions ~1 $\mu$m on edge.
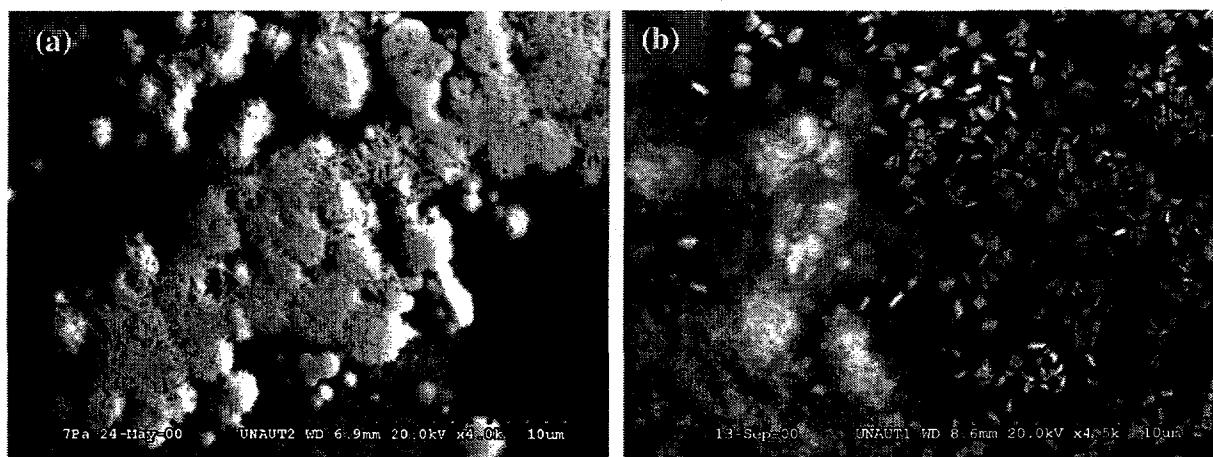


Figure 2. (a) Circular patches can be seen crystallizing into schoepite platelets after 16 days of testing. (b) In other areas within the Al-oxide gel, wispy U-rich growths eventually coalesce and crystallize to form smaller platelets seen as early as 55 days in test#2 and first observed after 115 days in test #1.

Other mineral structures of unknown composition were observed in the 115 and 183-day samplings of test #1. Highly fractured/altered $UAl_x$ grains gave rise to thin, elongated structures with triple terminations. Other elongated crystals (with flat terminations) were observed within and above the gel layer.

Transmission electron microscopy was performed on scrapings from test #2 after 16 days. Using electron diffraction and x-ray spectroscopy, faint patterns from dehydrated schoepite and becquerelite crystals were identified.

**Discussion and Conclusions**

The fuel corrosion and uranium release rates observed in this preliminary testing program indicate that longer test periods are necessary to predict long-term behavior of the fuel under potential repository conditions. Except for tarnishing, the $UAl_x$ fuel surface was little changed after one-half year of testing. Uranium release at this point in the program is comparable to irradiated $UO_2$ fuels, which have undergone testing for over 3 years at ANL. Of importance, no U- and Al-bearing colloids were found in the $UAl_x$ tests after 31 days of testing but colloids were generated, stable, and may serve as pseudocolloids for released fission products or actinides. We have shown that a thin Al-oxide gel layer is formed on the surface and serves as the reaction medium for uranyl oxyhydroxide formation. Studies of natural analogs[7] and observations from spent $UO_2$ fuel corrosion experiments[7] suggest initial crystallization of schoepite or becquerelite, which was confirmed by TEM; elongated crystals could not be positively identified. Although one might be tempted to model the corrosion of the oxidized uranium from $UAl_x$ fuels similar to $UO_2$ fuels, the presence of abundant aluminum does not rule out the possible formation of uranium-aluminum oxyhydroxides in the long-term and its effect on actinide and fission product disposition. Future work includes testing of irradiated melt-dilute fuels, comparing primary alteration phases with this work, and assessing fission product and actinide disposition.

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