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for Activity WP 1221

Unsaturated Drip Condition Testing of Spent Fuel and Unsaturated Dissolution Tests of Glass

by P. A. Finn, D. J. Wronkiewicz, R. J. Finch, J. C. Hoh, C. Mertz, J. W. Emery, E. C. Buck, J. Fortner, S. F. Wolf, L. A. Neimark, and J. K. Bates

Chemical Technology Division **Chemical Technology** Division



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ARGONNE NATIONAL LABORATORY 9700 South Cass Avenue Argonne, Illinois 60439

YUCCA MOUNTAIN PROJECT — ARGONNE NATIONAL LABORATORY, ANNUAL PROGRESS REPORT, FY 1997

for

Activity WP 1221

UNSATURATED DRIP CONDITION TESTING OF SPENT FUEL and UNSATURATED DISSOLUTION TESTS OF GLASS

by

P. A. Finn, D. J. Wronkiewicz, R. J. Finch, J. C. Hoh, C. Mertz J. W. Emery, E. C. Buck, J. Fortner, S. F. Wolf, L. A. Neimark, and J. K. Bates

Chemical Technology Division

June 1998

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NOMENCLATURE

analytical transmission electron microscopy
Alpha-Gamma Hot Cell Facility (at ANL)
Argonne National Laboratory
autoradiography
Approved Test Material
boiling water reactor
charge coupled device
computer modeling program
dynamic light scattering
U.S. Department of Energy
Defense Waste Processing Facility
electron diffraction
energy dispersive spectroscopy
electron energy loss spectroscopy
electrophoretic light scattering
U.S. Department of Energy's Office of Environmental Restoration and Waste
Management
fiscal year
General Electric Nuclear Energy
high-level waste
Lawrence Livermore National Laboratory
low-level waste
U.S. Department of Energy's Management and Operating Contractor
Materials Characterization Center
Pacific Northwest National Laboratory
product consistency test
Powder Diffraction File
photomultiplier tube
ratio of mass of radionuclide collected to mass of radionuclide calculated
relative humidity
surface area
scanning electron microscopy
Special Nuclear Material Division (at ANL)
Statement of Work
Savannah River Laboratory
transmission electron microscopy
inductively coupled-plasma mass spectroscopy
volume
vapor hydration test
waste package assemblage
West Valley Demonstration Project
X-ray diffraction
Yucca Mountain Project

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ABSTRACT

This document reports on the work done by the Nuclear Waste Management Section of the Chemical Technology Division of Argonne National Laboratory in the period of October 1996 through September 1997. Studies have been performed to evaluate the behavior of nuclear waste glass and spent fuel samples under the unsaturated conditions (low-volume water contact) that are likely to exist in the Yucca Mountain environment being considered as a potential site for a high-level waste repository. Tests with actinide-doped waste glasses, in progress for over 11 years, indicate that the transuranic element release is dominated by colloids that continuously form and spall from the glass surface. The nature of the colloids that form in the glass and spent fuel testing programs is being investigated by dynamic light scattering to determine the size distribution, by autoradiography to determine the chemistry, and by zeta potential to measure the electrical properties of the colloids.

Tests with UO₂ have been ongoing for 12 years. They show that the oxidation of UO₂ occurs rapidly, and the resulting paragenetic sequence of secondary phases forming on the sample surface is similar to that observed for uranium found in natural oxidizing environments. The reaction of spent fuel samples in conditions similar to those used with UO, have been in progress for over six years, and the results suggest that spent fuel forms many of the same alteration products as UO₂. With spent fuel, the bulk of the reaction occurs via a through-grain reaction process, although grain boundary attack is sufficient to have reacted all of the grain boundary regions in the samples. New test methods are under development to evaluate the behavior of spent fuel samples with intact cladding: the rate at which alteration and radionuclide release occurs when water penetrates fuel sections and whether the reaction causes the cladding to split. Alteration phases have been formed on fine grains of UO₂ in contact with small volumes of water within a several month period when the radiolysis product H_2O_2 is added to the groundwater solution. The test setup has been mocked up for operation with spent fuel in the hot-cell.

EXECUTIVE SUMMARY

Work is ongoing at Argonne National Laboratory -East in support of the Yucca Mountain Project (YMP). This work consists of studies that evaluate the behavior of commercial spent nuclear fuel samples and defense high-level waste (HLW) glass under conditions likely to occur in the potential repository at Yucca Mountain. This report consists of a general overview of drip tests that have been in progress for over five years, with the data tabulated through 3.7 years. Additionally, there are detailed discussions of analyses that have been done on the samples taken from the drip tests. Two new sets of tests that have been developed for use with spent fuel samples are discussed. These are batch tests and drip and vapor tests with clad fuel. Also, drip and vapor hydration tests (VHTs) performed with HLW glass are described.

The drip tests on spent fuel are being done with Approved Test Materials (ATMs) 103 and 106. Considerable information has been presented regarding these tests, and in this report, selected aspects of the data are discussed. Our conclusions for the high-drip-rate tests are as follows.

- 1. The ⁹⁹Tc interval release fractions provide a lower limit for the spent fuel reaction in the high-drip-rate tests. In the ATM-103 fuel, 3 wt% of the total inventory of ⁹⁹Tc is released in 3.7 years.
- 2. Oxidation of the ε -phase suggests that the oxidizing potential at the fuel surface may be as high as 0.6 V. The oxidant may be H₂O₂, a product of alpha radiolysis of water.
- 3. The constancy of the ⁹⁹Tc release fractions over 3.1 years of reaction indicates that a surface reaction is the rate-controlling mechanism for fuel reaction under unsaturated conditions and that the oxidant is possibly H_2O_2 , a product of alpha radiolysis of water.
- 4. Two reaction pathways have been identified from scanning electron microscopy (SEM) examination of through-grain dissolution, seen at the fragment scale, with subsequent formation of uranyl alteration products and dissolution along grain boundaries. The latter pathway results in friability of a spent fuel fragment.
- 5. The major alteration product identified by X-ray diffraction (XRD) and SEM is Naboltwoodite, Na[$(UO_2)(SiO_3OH)$]·H₂O, which is formed from sodium and silicon in the water leachant.
- 6. Elements other than uranium, including Ru, Mo, Cs, and Ba, are incorporated into the U^{6+} alteration products examined so far.
- 7. Plutonium appears to be concentrated in the spent fuel. It is not found in the leachate nor the alteration products.

The high-drip-rate tests appear to have sufficient liquid to transport dissolved material from the spent fuel to the test vessel. For the low-drip-rate tests, water was sufficient for fuel reaction, but due to water evaporation because of decay heat, the amount of water was reduced too much for radionuclide transport.

Combined optical, SEM, XRD, and energy-dispersive spectroscopy (EDS) examinations of samples taken from tests being performed on the two ATM fuel samples provided detailed information regarding the reaction progress. These examinations indicate that the rate at which groundwater contacts the fuel samples may be the most important single factor determining which alteration phases form as spent UO₂ fuel corrodes in a humid oxidizing environment. Results of the three tests (high-drip-rate, low-drip-rate, and vapor) show several similarities, including corroded grain boundaries, dissolution of fuel grains, and precipitation of U⁶⁺ phases. The vapor tests display the simplest assemblage of alteration products: only U and the radionuclides in the fuel dissolve into the thin film of water in contact with the fuel surfaces. The most abundant phase identified in the vapor tests is probably dehydrated schoepite, $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$ ($0 \le x \le 0.15$).

The drip tests display more chemically complex alteration phases due to interaction of the fuel with EJ-13 water (rather than only water vapor). The most abundant elements in EJ-13 water are Na and Si, and not surprisingly, the most abundant alteration products in the drip tests are Na and Si-bearing U⁶⁺ phases. Other U⁶⁺ phases are also present, including metaschoepite and β -uranophane, indicating the importance of additional minor phases and elements to the overall corrosion process.

An important observation at this stage is that the time-dependent evolution of the alterationphase assemblage appears to be strongly dependent on the rate at which the EJ-13 water contacts the spent fuel. Fuel samples exposed to the higher drip rates (nominally 10-times higher than the low-drip rates) display a comparatively simple phase assemblage, consisting of two uranophanegroup silicates, β -uranophane and Na-boltwoodite. In contrast, the sample from the low-drip-rate test displays a more complex alteration-phase assemblage, with four or five phases identified. We believe that the simpler phase assemblage in the high-drip-rate tests reflects higher reaction rates for the spent fuel in these tests. Also, samples were not taken from the first sampling periods, and it is possible that the first phases in the paragenetic sequence actually formed but were simply not detected.

Another important observation concerns the identification of uranyl oxy-hydroxides in the VHTs. The precipitation of dehydrated schoepite and metaschoepite in these tests indicates that the film of water that forms on the fuel surface is sufficiently corrosive to dissolve the fuel and form a thin corrosion rind of alteration products. Such a water film is likely present in the drip tests as well, during those intervals when EJ-13 water is not being dripped onto the fuel. It seems likely that the corrosion processes important in the vapor tests are also important in the drip tests. Dehydrated schoepite and/or metaschoepite may continue to form in the drip tests between water injections. If these phases are present when contacted by EJ-13 water, they may be at least as susceptible to dissolution and/or replacement as the unoxidized fuel. The degree to which this phenomenon may be important is unknown.

The mechanism by which the fuel reacted during these tests is important, although we have only limited information available at this time. Most striking is that the fuel in the high-drip-rate test on sample ATM-103 has dissolved along a uniform front that has penetrated from the outer surface into the spent fuel fragments. This "through-grain" dissolution has proceeded without regard to existing grain boundaries. The replacement of the fuel by Na-boltwoodite at the fuel surface may also be self-accelerating. Through-grain dissolution appears to be an important mechanism by which the fuel is reacting in the high-drip-rate tests. Of course, the dissolution of the fuel along grain boundaries is also important in the high-drip-rate tests. This dissolution is especially evident from the extent to which the grain boundaries in one fragment of ATM-103 had been opened, resulting in a friable fragment that decomposed during sample handling.

These data are still preliminary. We must examine additional grains and fragments of reacted fuel to understand more fully the corrosion and alteration processes, including grainboundary penetration by water, changes in the reactive surface area, and the distribution of radionuclides between the alteration phases and the EJ-13 water.

The drip tests currently being performed on UO_2 and spent UO_2 fuel have demonstrated that these tests are effective methods for examining the alteration of UO_2 and spent fuel in an unsaturated environment, such as may be expected in the proposed repository at Yucca Mountain. Previous drip-test results demonstrated that UO_2 and spent fuel both react with a thin film of water to form a suite of U^{6+} alteration phases. With current experimental designs, the suite of U^{6+} phases takes two to five years to fully develop. A new type of test termed a "petri-dish" test is intended to accelerate alteration reactions observed in drip tests, so that relevant observations might be made in six months or less, allowing more rapid evaluation of alteration phases. In addition, the composition of the film of water in contact with UO₂ or fuel is not well-known for the drip tests. In the current drip-test methodology, a solution of known composition (EJ-13) is injected into a test vessel, where the water reacts with UO₂ or fuel. This solution eventually drips down through the UO₂ or fuel and accumulates at the bottom of the reaction vessel, where it is periodically sampled. The analysis gives an indication of chemical changes that the solution undergoes between injection and sampling; however, detailed knowledge of the composition of the thin film of water that is actually reacting with the UO₂ or fuel remains elusive. By providing just enough water to maintain a constant film on a small quantity of fuel in a batch test, we plan to monitor the compositional evolution of the water as it reacts to form U⁶⁺ alteration phases. Note, however, that in drip tests, cations consumed during reaction are replenished, while in the petri-dish tests, the cations are not replenished.

A set of batch tests performed at a high ratio of the UO_2 surface area (S) to the volume of leachant (V) were run as trial experiments for setting up similar tests on spent UO_2 fuel. At this stage, test components and procedures have been examined, with the goal of understanding what factors are most important for the tests on spent fuel. No systematic study of all the experimental conditions has been made yet. Nevertheless, the information gained from these few experiments on UO_2 provides insight into the corrosion of UO_2 at high S/V ratios. We have also gained additional understanding of the potential importance of H_2O_2 (and by implication, radiolytic products) in enhancing fuel dissolution and possibly changing the mechanisms by which fuel corrodes, including the alteration phases that may precipitate. The ease of implementation and relatively rapid results makes these batch tests useful for increasing our understanding of fuel corrosion in an unsaturated environment. These tests are response tests and, thus, provide specific data related to the test conditions. Some information may not be readily available from these tests (e.g., sorption of elements by the screens and vessel walls). However, with proper planning and sample analysis, a great deal can be learned from these experiments.

While the ongoing drip tests simulate the reaction that takes place between a breached fuel rod and dripping water or saturated water vapor, it is likely that the initial contact between water and spent nuclear fuel will be occur when cladding is nearly intact, with only minor perforations existing for water ingress. Under this limited liquid water or water vapor contact, the extent, nature, and rate of spent fuel reaction is of interest. In particular, if the cladding stays mainly intact, even during alteration of the fuel, the release of radionuclides may be reduced. Two sets of tests are being developed to address the reaction of spent nuclear fuel under conditions of intact cladding: (1) water dripping slowly through a defected rod and (2) water vapor reacting with fuel in a defected rod.

The objectives of these dripping-water tests are the same as those for the ongoing drip tests. In addition, the effect of fuel reaction on cladding integrity will be observed. It is possible that alteration products may not form due to stress within the spent fuel section or, if they do form, they may obstruct the throughflow of water. The tests with vapor will be done to determine whether reaction with vapor, which will occur prior to contact by liquid water, will cause failure of the cladding. These tests have been mocked-up and are ready to be started with spent fuel samples.

Ongoing tests with spent nuclear fuel are being performed with Approved Testing Materials (ATMs) that were procured and characterized by the Materials Characterization Center in support of the YMP. Through a review process that included the YMP, the M&O, Lawrence Livermore National Laboratory (LLNL), Pacific Northwest National Laboratory (PNNL), and Argonne, it was determined that additional ATMs are required to complete the suite of spent fuel types that may

be placed in the repository. This year it was determined to procure a high burnup spent fuel, characterize it, and distribute it for testing.

The fuel chosen is a high burnup (60-80 MWd/kU) boiling water reactor (BWR) fuel that satisfies the YMP need for testing the highest burnup BWR fuel currently available. Four of the segments procured contain UO_2 fuel with an original U-235 enrichment of 3.0 or 3.8 wt%. The current enrichments are estimated to be 0.05 and 0.15 wt%, respectively. The other two segments contain (U,Gd)O₂ fuel with original enrichments of 3.0 wt% U-235 and 2.0 wt% Gd; the current U-235 enrichment is estimated to be 0.12 wt%. The samples have been received at ANL and are undergoing characterization.

Drip tests designed to replicate the synergistic interactions between waste glass, repository groundwater, water vapor, and sensitized 304L stainless steel in the proposed Yucca Mountain Repository have been in progress for over 10 years with actinide-doped glasses. The N2 Test Series on Defense Waste Processing Facility (DWPF)-type glass has clearly demonstrated the importance of alteration phases in controlling actinide release from the corroding waste glass. These alteration phases may be spalled from the glass surface, releasing the actinides as solution-borne colloids and particulates. The N3 Tests on West Valley Demonstration Project (WVDP)-type glass has formed unusual actinide-containing phases, several of which have been identified. As in the N2 Tests, the N3 Tests initially retain actinides in alteration phases, later releasing them by layer spallation as glass corrosion progresses. This alteration/spallation process effectively results in near-congruent release of elements from the glass, regardless of their solubilities.

Prior to contact with liquid water, HLW glass will contact water vapor (vapor hydration), which will corrode the glass and alter its properties such that the glass initially contacted by dripping water likely will not be as-cast fresh glass. To predict the amount of vapor hydration that will occur under disposal conditions, it is necessary to establish the rate of reaction between water vapor and glass in a water-vapor-saturated air atmosphere as a function of glass composition and temperature. On the basis of on these measurements, it is possible to calculate an activation energy and rate constant for each glass and, from this information, to extrapolate the reaction of glass in saturated water vapor to different temperatures as required by repository performance assessment calculations. As part of this work, a procedure will be developed and documented that can be used to perform the VHT to provide quantitative rate information. As part of the VHT, the alteration phases that form on the surface of the glass will be identified. Although we recognize that radiation may affect the rate of vapor hydration of glass, the bulk of the tests will be performed using glasses containing no fission products. The glasses may contain U or Th. Some tests will be done using a sludge-based radioactive glass to confirm the results generated with the nonradioactive glass.

Development of colloid characterization techniques will provide essential information on colloids generated from waste-form reaction in tests that simulate the expected conditions for the repository. Dynamic light scattering (DLS) has been demonstrated as a technique to examine and monitor waste-form colloids. This task shows that DLS measurements can provide useful information on the particle size distribution and concentration of colloidal species that form during the corrosion of waste forms. Test solutions from ongoing glass and spent fuel tests have been examined by the DLS method. In situ DLS measurements have shown that waste-form colloids exist as stable species (for 10 days in two of the cases examined in this study). Dynamic light scattering is a technique that can minimize disadvantages in studying colloids due to poor statistical representation of the leachate colloids, and possible sample preparation artifacts with analytical electron microscopy, and interactions with filter membranes is sequential filtration techniques.

I. UNSATURATED TESTS WITH IRRADIATED SPENT FUEL

A. Introduction

A potential site for the U.S. high-level waste repository is in the volcanic tuff beds at Yucca Mountain, Nevada, a hydrologically unsaturated zone. To qualify this site for licensing, performance assessment calculations are needed to evaluate the impact of potential radionuclide releases. Information and data feed for a source term in these calculations is provided from laboratory information on the reaction behavior of spent fuel under unsaturated and oxidizing conditions. Testing under unsaturated, i.e., limited water, and oxidizing conditions are in progress to evaluate the long-term behavior of commercial spent nuclear oxide fuel at 90°C. In the tests, a thin film of water continuously contacts and reacts with the fuel. All tests are performed in a saturated water vapor environment to evaluate the reactivity of fuel under that condition. In some tests, water is dripped on the fuel to provide additional liquid for transport of reacted material. All tests are done at 90°C. The nominal drip rate is 0.75 mL every 3.5 days in the high-drip-rate test and 0.075 mL every 3.5 days in the low-drip-rate-test.

The purpose of the experiments is to determine the relationship between the rate of fuel alteration and the release rate of radionuclides under unsaturated conditions. Therefore, the extent of spent fuel alteration, e.g., dissolution, under unsaturated conditions is assessed, as is the effect of fuel alteration on radionuclide release. In all tests, a film of water, maintained by the saturated water vapor atmosphere environment, continuously contacts the fuel fragments and provides a potential pathway for material transport. In the high-drip-rate tests, excess water is available to enhance transport of reacted material. The low-drip-rate tests have less water available, thus reducing the amount of radionuclides transported. In the vapor tests, minimum water is available for transport, and the absence of added cations and anions limits the type of alteration products that may form.

B. <u>Objective</u>

The objective of this report is to provide an update on the behavior of commercial oxide spent fuel after 4.1 years of reaction under oxidizing and unsaturated conditions. We report several sets of results: (1) corrosion of ε -phase intermetallic particles composed of Ru-Mo-Tc-Rh-Pd as measured by leachate results and transmission electron microscopy (TEM) examination of the fuel, (2) radionuclide release into the leachate, and (3) reaction of the UO₂ matrix as noted from scanning electron microscopy (SEM) examination. The three sets of results provide a picture of extensive corrosion of the spent fuel. The four areas to be examined are (1) evidence from leachate and TEM data that supports reaction of the ε -phase particles and the use of ⁹⁹Tc as a marker for fuel reaction, (2) data on the release of radionuclides other than ⁹⁹Tc, (3) evidence from SEM data that provides information on the types of predominant reaction pathways, and (4) insight into the reaction kinetics based on the ⁹⁹Tc release behavior. The leachate data for the high-drip-rate tests cover the first 3.7 years of reaction. Scanning electron microscopy and TEM data are available for a few samples at the later test intervals. Detailed discussions of these latter data are found in other sections of this report, while this section provides a general overview.

C. Background and Experimental Approach

Samples of two pressurized-water-reactor fuels, ATM-103, [GUENTHER-1988a] and ATM-106 [GUENTHER-1988b], with burnups of 30 and 45 MW·d/kg U, respectively, are used in the tests. The grain sizes are 17-20 μ m and 6-16 μ m, respectively. The fuel samples, 7 - 8.5 g each, are fragments with masses in the range of 0.3-1.2 g. The average geometric surface area of the fragments is 2.1 x 10⁻⁴ m²/g. The measured percent distribution of ⁹⁹Tc [GRAY-1992] for both fuels in the gap, grain-boundary, and fuel matrix is <0.1, <0.1, and >99.8%, respectively. The reported distribution [THOMAS-1989] of ⁹⁹Tc in ϵ -phase particles in ATM-103 is as follows.

Most ε -phase particles are within the grains and their diameters vary as a function of radial position, being 20 nm diameter at the pellet edge and 50-100 nm diameter in the pellet mid- and center sections. Particles at (or along) grain boundaries are $\leq 1 \mu m$ diameter and are located in the mid- and center sections. For ATM-106 fuel [THOMAS-1992], the ε -phase particles within the grains are 20-100 nm diameter in the mid-section. Near the pellet center, 3-10 μm diameter particles were found along grain boundaries. These particles also contained gas bubbles and secondary precipitates.

The experimental configuration, the test procedures, and the composition of the leachant, EJ-13, have been described previously [FINN-1994]. Solution compositions were analyzed with inductively-coupled plasma mass spectroscopy (ICP-MS) in the single standard scan mode with an indium internal standard. For samples after 2.5 years of reaction, bismuth is used as the internal standard for actinides. This technique has a precision of $\pm 15\%$ for the isotopes in the middle mass range (80-160 atomic mass units), but for the actinides and the light elements, the precision may be $\pm 50\%$. The uncertainties in the ICP-MS data are a maximum of $\pm 50\%$, depending on radionuclide concentration. The assignment of a mass unit to a particular isotope is done by comparison with the isotopic distribution given in results from ORIGEN code calculations [GUENTHER-1988a]. The term "interval" for the leachate data refers to the time between sequential samplings of the leachate. The "interval release fraction" for a given radionuclide is defined as the ratio (R/T) where R is the mass of radionuclide collected in a given interval, i.e., the total mass in the leachate and the acid strip, and T is the mass of radionuclide calculated to be in the fuel [GUENTHER-1988a]. Since material incorporated into alteration products, adsorbed on the Zircaloy sample holder or adsorbed on the spent fuel, is not included in solution, the release rate of the radionuclide with the largest interval release fraction provides a minimum estimate of the spent fuel reaction rate. The interval release fractions are used to compare releases of different radionuclides for the same reaction interval and of the same radionuclide for different reaction intervals. A "cumulative release fraction" is the sum of the individual interval release fractions over total reaction time.

Sampling took place twice in the last year. The physical appearance of the spent fuel in each test was recorded on videotape by using a macro lens with 10-19X magnification. A fragment of fuel was removed from each test at the 4.1-year test interval for characterization using SEM and TEM. Tape was rolled over the removed fragment to collect alteration products and small pieces of fuel with alteration products attached. This process resulted in the removal of some of the porous alteration products.

The results to date of these characterizations are reported here and in other sections of this report. When appropriate, electron diffraction (ED) data are compared to X-ray diffraction (XRD) data to assist in identification of alteration phases found on the fuel.

D. <u>Results and Discussion</u>

We report results for (1) corrosion of ε -phase intermetallic particles composed of Ru-Mo-Tc-Rh-Pd as interpreted from leachate results and TEM examinations of reacted fuel, (2) radionuclide release into the leachate, and (3) reaction of the UO₂ matrix as noted from SEM and TEM examinations that provide information on reaction pathways.

1. Reaction of the ε -Phase and the Release of ⁹⁹Tc to the Leachate

This section examines the reaction of the ε -phase in high-drip-rate tests in the leachate for the first 3.1 years of reaction and in some TEM samples from high-drip-rate and vapor tests.

a. <u>Leachate Results</u>

Table 1 provides a summary of the release behavior of the five elements in the ε -phase (Tc, Mo, Ru, Rh, Pd) for tests with ATM-103 for successive reaction intervals. Similar information for the ATM-106 test is shown in Table 2. The information includes (1) the released mass (µg) for the isotope of each element with minimal interference from other elements; (2) the total released mass of each element calculated on the basis of the isotope measured and the element's isotopic distribution; (3) the calculated mass of elements from the ε -phases that reacted, based on the ⁹⁹Tc release and the distribution of each element in the ε -phase; and (4) the amount of each element that was not released, based on the difference between the material released (column 2) and that calculated to have reacted (column 3). The isotope ⁹⁹Tc was the dominant element released from ATM-103 and ATM-106 at each reaction interval. Ten per cent of the Mo and only trace amounts of Rh, Ru, Pd were detected in the leachate.

b. <u>TEM Results</u>

Microtomed samples of reacted fuel were examined to determine if ε -phase particles (Ru-Mo-Tc-Rh-Pd) were being oxidized as proposed [FINN-1997]. Table 3 shows the distribution of the five elements in unreacted fuel and the ratio Mo/(Ru+Pd), which can range from 0.9 to 1.5, depending on fission yield [GUENTHER-1988a] or the distribution found in unreacted fuel [GUENTHER-1988a]. To determine if the ε -phase particles had reacted in both the ATM-103 high-drip-rate and the vapor tests, the Mo/(Ru+Pd) mass ratio also was measured in reacted particles, as was the change in the relative masses of the five elements in the ε -phase particles.

Reaction of the ε -phase particles as fuel grains dissolve is evident in Fig. 1, in which individual ε -phase particles <10 nm diameter are shown. Three locations in the TEM sample were examined to find ε -phase particles from the high-drip-rate test that had not totally reacted. The regions are designated edge, dissolution pit, and Pu-rich region. The edge region refers to a location on a reacted fuel grain. The dissolution pit is an area in which only reacted ε phase particles are found. The Pu-rich region is one in which the Pu concentration is 20 times greater than that expected from the fuel burnup. In Fig. 2, the TEM/electron energy loss spectrum (EELS) spectrum at the U-M absorption edge shows the Pu increase in an area in which spent fuel has reacted. A similar buildup in Pu concentration for reacted fuel has been found in the ATM-103 vapor test. In all three regions in the fuel from the high-drip-rate test (see Table 3), the ε -phase particles have reacted in a similar fashion, i.e., the proportional Ru and Rh content is greater than that of the unreacted ε -phase, and the particles have a new composition in which the Mo/(Ru+Pd) mass ratio is 0.2-0.3. In both the edge region and the Pu-rich region, there is a significant decrease in the Tc and Mo concentrations, but an increase in the Pd concentration. Thus, ε -phase particles that are not totally reacted (i.e., disappeared from the fuel) are depleted in Tc and Mo.

In the ATM-103 vapor test after 4.1 years of reaction, several reacted ε phase particles were examined (see Table 3). All had a Mo/(Ru+Pd) mass ratio that was lower than that for the unreacted particle, i.e., 0.4-0.5 versus 0.9, and had also retained more Mo than had those in the high-drip-rate test, i.e., about 80% more based on the Mo/Ru mass ratio.

Reaction and dissolution of the ε -phase particles with later incorporation of Mo, Rh, Ru, Pd in alteration products is indicated by two additional pieces of data. First, Mo is found in $(Cs_{0.9}Ba_{0.55})[(UO_2)_5(MoO_2)O_4(OH)_6] \cdot 6H_2O$, a compound found attached to a reacted fuel grain [BUCK-1997]. Second, 1-2 wt% of Ru and Mo are incorporated into β -uranophane, a uranyl silicate, whereas only parts per million of Tc are found in β -uranophane (See Fig. 3).

	Measured ^a	Calculated	Calculated				
	Released	Released	Amount	Element			
	Element ^b	Element ^c	Reacted	Retained ^d			
Isotope	(µg)	(µg)	(µg)	(mass %)			
		0.3 Years Reaction					
⁹⁹ Tc	20	20	20	<u> </u>			
⁹⁷ Mo	0.9	4	50	93			
¹⁰¹ Ru	0.02	0.07	50	100			
¹⁰³ Rh	0.6	0.6	7	92			
¹⁰⁵ Pd	0.04	0.1	0.5	75			
		0.8 Years Reaction					
⁹⁹ Tc	10	10	10				
⁹⁷ Mo	0.05	2	30	94			
¹⁰¹ Ru	6E-5	2E-4	40	100			
¹⁰³ Rh	0.06	0.06	5	99			
¹⁰⁵ Pd	ND ^e	ND	0.3	100			
		1.6 Years Reaction	·····				
⁹⁹ Tc	40	40	40				
⁹⁷ Mo	8	30	100	77			
¹⁰¹ Ru	2E-3	7E-3	200	100			
¹⁰³ Rh	0.02	0.02	20	100			
¹⁰⁵ Pd	2E-3	9E-3	1	100			
2.1 Years Reaction							
⁹⁹ Tc	5	5	5				
⁹⁷ Mo	2	10	20	44			
¹⁰¹ Ru	8E-5	2E-4	20	100			
¹⁰³ Rh	7E-3	7E-3	3	100			
¹⁰⁵ Pd	8E-3	0.03	0.2	83			
2.5 Years Reaction							
⁹⁹ Tc	10	10	10				
⁹⁷ Mo	1	6	30	82			
¹⁰¹ Ru	6E-4	2E-3	30	100			
¹⁰³ Rh	0.02	0.02	5	100			
¹⁰⁵ Pd	5E-3	0.02	0.3	94			

Table 1. Disposition of Elements in ϵ -Phase for Selected Reactive Intervals — ATM-103 High-Drip-Rate Test

^aMeasured mass in leachate. Values were rounded to one significant figure.

^bThe isotopic distribution for each element and the mass of the measured isotope were used to determine the total mass released.

^cFor ATM-103, the wt% in the ε -phase are: Tc(11.8); Mo(39.9); Ru(42.3); Rh(5.6); Pd(0.4) [GUENTHER-1998a]. The released ⁹⁹Tc was the basis for the reacted amount of a given element. ^cThis is the minimum amount retained and is based on ⁹⁹Tc and its wt% in the ε -phase. ^eND = not detected.

	Measured*	Calculated	Calculated				
	Released	Released	Amount	Element			
	Element [®]	Element ^e	Reacted	Retained ^d			
Isotope	(μg)	(µg)	(µg)	(mass %)			
	0.3 Years Reactions						
⁹⁹ Tc	0.07	0.07	0.07				
⁹⁷ Mo	0.05	0.2	0.2	4			
	0.03	0.1	0.2	50			
¹⁰³ Rh	0.1	0.1	0.04	XS°			
¹⁰⁵ Pd	0.04	0.2	0.1	XS			
		0.8 Years Reaction					
⁹⁹ Tc	0.9	0.9	0.9				
⁹⁷ Mo	4	20	3	XS			
¹⁰¹ Ru	0.02	0.05	3	83			
¹⁰³ Rh	0.02	0.02	0.4	50			
¹⁰⁵ Pd	ND ^r	ND	2	100			
1.3 Years Reaction							
⁹⁹ Tc	0.4	0.4					
⁹⁷ Mo	0.08	0.3	1	70			
¹⁰¹ Ru	8E-3	0.03	1	97			
¹⁰³ Rh	0.03	0.03	0.2	85			
¹⁰⁵ Pd	0.03	0.1	0.8	87			
		1.6 Years Reaction					
⁹⁹ Tc	10	10	10	—			
⁹⁷ Mo	2	9	40	77			
¹⁰¹ Ru	6E-4	2E-3	30	100			
¹⁰³ Rh	4E-3	4E-3	5	100			
¹⁰⁵ Pd	ND	ND	20	100			
2.1 Years Reaction							
⁹⁹ Tc	30	30	30				
⁹⁷ Mo	0.07	3	105	97			
¹⁰¹ Ru	1E-3	3E-3	90	100			
¹⁰³ Rh	6E-3	6E-3	15	100			
¹⁰⁵ Pd	3E-3	0.01	60	100			
2.5 Years Reaction							
"Tc	30	30	30				
"'Mo	0.07	3	105	100			
^{IVI} Ru	1E-4	3E-4	90	100			
¹⁰³ Rh	0.01	0.01	15	100			
¹⁰⁵ Pd	5E-3	0.02	60	100			

Table 2. Disposition of Elements in ε-Phase for Selected Reactive Intervals - ATM-106 High-**Drip-Rate Test**

^aMeasured mass in leachate. Values were rounded to one significant figure. ^bThe isotopic distribution for each element and the mass of the isotope that was measured were used to determine the total mass released. ^CThe wt% for ATM-106 for the ε -phase were: Tc(10); Mo(35); Ru(30); Rh(5); Pd(20) [THOMAS-1992]. The released ⁹⁹Tc mass was the basis for the amount of a given element

that reacted.

⁶This is the minimum amount retained and is based on ⁹⁹Tc and its wt% in the ε -phase.

^eXS = excess measured.

 $^{f}ND = not detected.$

Unreacted Particles							
·		Fission	Grains [▶]				
Element		Yield ^a	Boundary		Grains ^b		
Mo	40		39.9		52		
Tc		10	11.8		8		
Ru		30	42.3		23		
Rh		5	5.6		6		
Pd		15	0.4	<u> 12 </u>			
Mo/(Ru+Pd)		0.9	0.9		1.5		
High-Drip-Rate Test after 3.7 Years of Reaction							
		Edge	Pit		Pu-Rich ^c		
Element		Region	Region		Region		
Mo	12 17		17	15			
Tc	5		10		4		
Ru		42	45 45		45		
Rh	8		8		10		
Pd		33	11		26		
Mo/(Ru+Pd)		0.2	0.3		0.2		
Vapor Test after 4.1 Years							
	Sample	Sample	Sample	Sample	Sample		
Element	#1	#Ż	#3	#4	#Ś		
	29			29	26		
Tc	9	12	11	17	15		
Ru	40	30	30	33	42		
Rh	<u> </u>						
<u>Pd</u>	22	28	28	22	17		
Mo/(Ru+Pd)	0.5	0.5	0.5	0.5	0.4		

Table 3. Composition of Reacted ε-Phase Particles in ATM-103 Tests (elements in wt%)

^aThis is the average distribution in the fuel. ^bGuenther-1988a ^cQuantification of the electron energy loss spectrum was done using a 100-eV window and the oscillator strength values calculated from a Dirac-Foch model.



Fig. 1. Image of Corroded Pit in Altered Fuel Grain with Reacted ϵ -Phase Particles at Fuel Surface



Fig. 2. ATM-103 High-Drip-Rate Test after 3.7 Years of Reaction: Concentration of Pu (Pu- M_5 peak) in Unreacted Fuel (minor peak) and in Reacted Fuel (large peak)



Fig. 3. Electron Energy Loss Spectrum of β -uranophane on the ATM-103 Fragment. (Uranophane has incorporated at least 1-2 wt% Ru [also seen in the energy dispersive spectrum], and Mo and 100 times less Tc [See insert]).

c. Oxidation Potential

The presence of soluble forms of ⁹⁹Tc and ⁹⁷Mo in the leachate (pH 7 at room temperature) indicates that the fuel matrix surrounding the ε -phase particles dissolves, exposing the particles to an oxidizing environment. For comparison, Kleykamp [KLEYKAMP-1985] notes that complete dissolution of ε -phase particles 0.15-1.5 µm in diameter requires eight hours for complete dissolution in boiling nitric acid.

In our "unsaturated" tests, water vapor at 90°C supplies a continuous thin film of water on each spent fuel surface, a film that may be <10 nm thick [HAGYMASSY-1969]. Allen noted that the primary yield of H_2O_2 from alpha radiolysis of water is 1.2 times that from gamma radiolysis of water [ALLEN-1961]. The unique nature of alpha radiolysis is that the H_2O_2 is produced in dense tracks within the first 30 μ m (the alpha particle range) of the fuel surface, thus ensuring that the relative concentration of the H_2O_2 is very high at the surface of the spent fuel.

We estimate how high an oxidation potential exists at the fuel surface in two ways. Shoesmith et al. [SHOESMITH-1985] note that for reaction of unirradiated UO₂ at pH 9.5 with an alpha source 30 μ m away, the redox potential is 0.11 V (versus a saturated calomel electrode), a value similar to that in an equivalent H₂O₂ solution or in a saturated O₂-containing solution. (The corresponding corrosion potential would be -0.14 V.)

Since we note dissolution of Ru, Mo, and Tc in the unsaturated tests, we estimate the corrosion potential in the unsaturated tests by considering the Eh required to form soluble ions of Tc, Mo, Ru, Rh, and Pd based on Eh/pH diagrams [BROOKINS-1988] for 10^{-8} M concentrations. For Mo and Tc at pH 7, a minimum Eh of 0 and 0.3 V, respectively, is needed to stabilize TcO₄⁻ and HMoO₄²⁻, whereas for PdO₂ and RuO₄⁻, a minimum Eh of 0.5 and 0.6 V, respectively, is needed. For Rh, a soluble form is noted only at pH 4 and an Eh of 0.65 V. Recognizing that these diagrams are applicable for 25°C, we applied them to the test conditions; thus, the oxidation potential at the fuel surface may be as high as 0.6 V since Ru dissolved and is incorporated into β -uranophane. Thus, ϵ -phase particles (<1-100 nm diameter) could react and release ⁹⁹Tc in each 0.5 year reaction interval, but larger particles (1 µm) might not completely react (see Fig. 1).

Since the ε -phase particles are homogeneously dispersed in the ATM-103 fuel matrix [GUENTHER-1988a] and both fuels have similar ⁹⁹Tc release behavior, we propose the use of ⁹⁹Tc release fraction as an indicator of the minimum extent of the reaction of the fuel matrix under unsaturated and oxidizing conditions. Support for this proposal can be found in comments of earlier workers. Forsyth and Werme [FORSYTH-1991] found that after 2.7 years of reaction under oxidizing conditions, ⁹⁹Tc was the only radionuclide whose release fraction had remained constant in batch tests with spent oxide fuels. They suggested that ⁹⁹Tc was oxidized and released as the matrix around the ε -phase particles reacted. Wilson [WILSON-1990] also suggested that Tc was oxidized prior to release in "semi-static" tests. Curtis and Gancarz [CURTIS-1983] proposed that oxidative dissolution of the uraninite at the Oklo natural reactor site in Gabon, Africa, was caused by water radiolysis in the reactor zones, which led to production of species that oxidized uraninite, dissolved the ε -phase, and permitted transport of soluble species from the reactor zone.

2. <u>Radionuclide Releases Compared to the ⁹⁹Tc Release</u>

The use of the ⁹⁹Tc release fraction as a marker for the minimum extent of the spent fuel reaction (minimum since there may be some Tc holdup in alteration products - see below) has been proposed [FINN-1997]. The ⁹⁹Tc interval release fraction has been relatively constant over 3.7 years of reaction for the high-drip-rate tests for ATM-103 fuel (Fig. 4) and from 1.3 to 3.7 years of reaction for ATM-106 fuel (Fig. 5). Also shown in Fig. 4 and Fig. 5 are the interval release fractions for ²³⁸U and ²³⁹Pu. The decrease in the U and Pu release fractions after 1.6 years of reaction is apparent in both figures.



Fig. 4. ATM-103 High-Drip-Rate Test: ⁹⁹Tc, ²³⁸U, and ²³⁹Pu Interval Release Fractions



Fig. 5. ATM-106 High-Drip-Rate Test: ⁹⁹Tc, ²³⁸U, and ²³⁹Pu Interval Release Fractions

Our estimate of the mass of fuel dissolved at the time is based on the Tc results. The estimate will be improved with additional analyses of the reacted samples. However, the small amount of Tc held in β -uranophane, combined with the close structural similarity of Naboltwoodite to β -uranophane, makes the following calculation a reasonable first approximation. Based on our Tc release data, three percent of the spent fuel has been dissolved as of 3.7 years. The fuel initially contained approximately 95% or greater UO₂, and since each test contains approximately 8 g of fuel approximately 0.23 grams of UO_2 was in the fuel that dissolved. As a first approximation, we assume that Na-boltwoodite incorporated all the dissolved UO, (99.9% actually) and that Na-boltwoodite is the only alteration product formed. Ideally, Na-boltwoodite contains 66.8 wt% UO₂, which implies the formation of approximately 0.34 g of Na-boltwoodite. We can assume further that the concentration of Tc found in β -uranophane is the same as in Naboltwoodite, i.e., a few ppm Tc (say, 2.5 ppm). This means alteration products (modeled as Naboltwoodite) contain approximately 8.5 x 10^{-7} g Tc. The concentration of Tc in the original fuel was approximately 10^{-5} Ci gram of UO₂, meaning that 2.3 x 10^{-6} Ci of Tc have been dissolved from the fuel. The specific activity of Tc is 1.69 x 10^{-2} Ci g⁻¹, so that a total 1.36 x 10^{-4} g of Tc was dissolved along with the 0.23 g of UO₂. This simple approach indicates that alteration products have retained approximately 0.6% of the Tc dissolved from the fuel. We have made some simplifying assumptions, implying a fairly high degree of uncertainty. Nevertheless, the actual amount is almost certainly within a fractor of 10.

In Table 4, the cumulative release fractions for ⁹⁹Tc, ²³⁸U, and ²³⁹Pu, as well as for ¹³⁷Cs and ⁹⁷Mo, are shown for several cumulative reaction times. Table 4 illustrates the following points. First, after 3.7 years of reaction, the cumulative ⁹⁹Tc release fractions for the two fuels are similar, 3% of the total inventory for ATM-103 and 2% for ATM-106. Second, for the ATM-103 fuel, the ⁹⁷Mo cumulative release fraction after 3.7 years of reaction is similar to the ⁹⁹Tc cumulative release fraction; however, for the ATM-106 fuel, the ⁹⁷Mo release fraction is only 10% of the ⁹⁹Tc release fraction. Thus, some of the ⁹⁷Mo appears to be held up in the ATM-106 test. However, at 4.1 years of reaction, the ⁹⁷Mo and ⁹⁹Tc release fractions for the two fuels are similar but are only 10-20% of the cumulative ⁹⁹Tc release fraction. It appears that most ¹³⁷Cs is held up. An alteration product that can incorporate both Cs and Mo is (Cs_{0.9}Ba_{0.55})[(UO₂)₅(MoO₂)O₄(OH)₆] · 6H₂O [BUCK-1997]. The formation of this alteration product could account for the hold up of ¹³⁷Cs and ⁹⁷Mo relative to ⁹⁹Tc, especially in the ATM-106 test prior to 4.1 years of reaction. Fourth, prior to the first 1.6 years of reaction, both fuels had a large ²³⁸U release fraction (Figs. 4 and 5), but thereafter, most (99.9%) of the reacted uranium remained on the fuel surface in alteration products. This point is based on the difference in release fractions between ⁹⁹Tc and U, the visual appearance of the fuel, and the weight gain measured. Fifth, prior to the first 1.6 years of reaction that was equivalent to 10-40% of the U release fraction. At longer reaction times, most of the Pu was held up. (See Figs. 4 and 5).

The reaction suggested by the leachate data for both fuels is one in which there is a continuous release of ⁹⁹Tc over four years of reaction, consisting of at least 0.3% of the total inventory in each six-month interval. The U release effectively ceases after about a year, but uranium is incorporated into alteration products that form on the surface of the fuel. Alteration phase formation increases after 1.6 years of reaction, but the ⁹⁹Tc release does not increase. The ⁹⁹Tc release fraction can be used to calculate the fraction and thus the mass of uranium that has reacted. This value can be compared to the amount of sodium and silicon removed from the dripped EJ-13 water. In addition, the mass gain for the reacted spent fuel can be compared to the expected increase in mass due to the formation of alteration products. These data are summarized in Table 5 for the two fuels after 3.1 years of reaction. (Units of moles are used for simplicity in comparing the different elements.)

Table 4. Camadative Release Fractions for the High Dhp Rate Fests							
ATM No.	⁹⁹ Tc	⁹⁷ Mo	¹³⁷ Cs	²³⁸ U	²³⁹ Pu		
		1.6 Years o	f Reaction				
ATM-103	2 1F-2 ^b	19F-3	1 8E-3	8 6F-5	9 8F-6		
ATM-105	1.6E-3	8.5E-4	3.0E-3	1.8E-4	1.4E-4		
		·		····			
2.5 Years of Reaction							
	·····						
ATM-103	2.4E-2	2.6E-3	2.0E-3	9.0E-5	9.9E-6		
ATM-106	9.6E-3	<u>1.0E-3</u>	3.4E-3	1.8E-4	1.4E-4		
3.1 Years of Reaction							
ATM-103	2 QF-2	1 4F-2	37E_3	0.2F-5	1.0E-5		
	2.7L-2 1.7E 2	1.40-2	3.7L-3	9.2L-J 1 0E A			
ATM-100	1.76-2	0.6E-3	4.0E-5	1.0C-4	1.46-4		
3.7 Vers of Perction							
ATM-103	3.0E-2	1.6E-2	4.7E-3	9.3E-5	1.0E-5		
ATM-106	2.0E-2	2.1E-3	5.0E-3	1.8E-4	1.4E-4		

Table 4. Cumulative Release Fractions^a for the High-Drip-Rate Tests

^aCumulative release fractions have been rounded to two significant figures.

^bExponential notation is used. The number following the E refers to the exponent of 10 by which to multiply the number before the E; e.g., 2.1E-2 means 2.1×10^{-2} .

Table 5. High-Drip-Rate Tests - Alteration Products after 3.1 Years of Reaction						
	Na-	Dehydrated			Calculated	Measured
	Boltwoodite ^a	Schoepite ^b	Excess ^c	Total	Weight ^d -UO ₂	Weight Gain ^e
Species	(mol)	(mol)	(mol)	(mol)	(g)	(g)
ATM-106					0.07	0.06
U	2.9E-4	6E-5	1E-4	4.5E-4		
Si	2.9E-4	<u> </u>		2.9E-4		
Na	2.9E-4	—	6E-4	8.9E-4		
ATM-103					0.07	0.05
U	2.7E-4	2E-4	2.9E-4	8E-4		
Si	2.7E-4	_	<u> </u>	2.7E-4		
Na	2.7E-4		5E-5	3.2E-4		

* Formula: Na[(UO₂)(SiO₃OH)] \cdot H₂O. This was the major alteration product based on XRD analysis; the silicon was assumed to be primarily in this product. The total moles of uranium are based on the ⁹⁹Tc release fraction.

^b Formula: $UO_3 \cdot 0.8 H_2O$. This was identified in the vapor test.

^c The moles listed are the difference between the measured and the total moles. The excess may result from uncertainty in the analyses of Na and U in solution and U unaccounted for during solids analysis.

^d Difference between sum of masses of alteration products and the original fuel's UO_2 .

^e Difference between original fuel weight and that after 3.1 years of reaction. The weight gain for the interval between 2.5 and 3.1 years was estimated as the average over the previous 2.5 years: 0.01 g/0.5 yr for ATM-106 and 0.007 g/0.5 yr for ATM-103. Weights when water was retained were not used.

The major alteration product in the high-drip-rate tests is Na-boltwoodite on the basis of SEM and XRD analyses. Some uranium is also incorporated into dehydrated schoepite on the basis of its identification in the vapor test [BUCK-1998]. Other alteration products present include the Cs-bearing uranyl molybdenum-oxy-hydroxide.

3. <u>Spent Fuel and Its Alteration Products</u>

As spent fuel reacts, there is the potential for incorporation of radionuclides from the reacted spent fuel into alteration products. This incorporation could reduce or delay the release of radionuclides from the waste package. For example, using TEM, Np was detected in dehydrated schoepite that formed in a vapor test. See later sections of this report for details.

Bright-yellow alteration products are first clearly observed on the fuel surface in the high-drip-rate tests after 2.5 years of reaction [FINN-1995]. Examination of the fuel fragments from these tests after 3.7 years of reaction indicate two layers of light-yellow alteration products. The outer layer is easily manipulated with a fine tungsten needle, but a thinner inner layer immediately adjacent to the fuel is denser and adheres tenaciously to the surface.

As a fuel fragment in the ATM-103 high-drip-rate test was examined after 3.7 years of reaction, it disintegrated into individual grains and clumps of grains. This suggests that reaction occurs along the grain boundaries throughout the fuel fragment. A piece of this friable fragment was polished and examined with SEM. Based on crystal morphology, chemical composition (energy dispersive spectroscopy [EDS]), and XRD, the most abundant (~80 vol%) alteration product is Na-boltwoodite, Na[(UO₂)(SiO₃OH)] \cdot H₂O. Additional minor phases are detected by TEM and XRD analyses, including β -uranophane, Ca[(UO₂)(SiO₃OH)₂] \cdot 5H₂O (~10-20 vol%). (From TEM/EELS analysis, both Mo and Ru are found at levels of 1-3 wt% in the β -uranophane.)

In Fig. 6, a cross section through one piece of the reacted ATM-103 fragment is shown. Gaps of $\leq 0.5 \,\mu\text{m}$ between the fuel grains are visible in the brightest region in the image. No alteration phases are detected between the grain boundaries, nor is Si evident in the grain boundaries from EDS. TEM examination of the edges of the fuel grains found no evidence for oxidation of UO₂ to UO_{2.25}, although evidence for additional reaction appears in some preliminary SEM micrographs.

Surrounding the fuel is an alteration layer (~20-40 μ m thick) consisting predominantly of Na-boltwoodite. This layer consists of two regions: a dense inner layer, 5-10 μ m thick, closest to the fuel surface, and a porous outer layer, 10-30 μ m thick. No difference in composition is evident between the two layers from EDS. Near the outer edge of the dense inner layer is an interface defined by a gap (dark band) that lies approximately 10 μ m above the fuel surface and 2-3 μ m below the outer edge of the dense layer. Below the gap, crystals of Na-boltwoodite have formed more or less perpendicular to the fuel surface, whereas above the gap, Na-boltwoodite forms a dense mat of crystals sub-parallel to the fuel surface. Above these flat-lying crystals is the porous outer layer. As the fuel dissolves, Na-boltwoodite replaces the fuel at the surface uniformly inward from the original outer surface in a fairly uniform fashion, thus forming the inner dense layer.



Fig. 6. (a) Cross Section through a Reacted Fragment of ATM-103 after 3.7 Years of Reaction. (Brightest area is fuel grains with grain boundary gaps. Medium contrast is Na-boltwoodite. Darkest contrast is epoxy.) (b) A Magnified View of the Right Side of the Cross Section Showing the Grain Boundary in the Fuel and the Two Layers of Na-boltwoodite. (c) A Magnified View of the Left Side of the Cross Section Showing a Thinner Reaction Layer of Na-boltwoodite.

A large volume of alteration products is forming on the surface of the spent fuel fragments. The presence of these alteration products does not appear to reduce the rate of spent fuel reaction in the high-drip-rate tests, as shown by the continued release of ⁹⁹Tc and the friable nature of the ATM-103 fuel fragment after 3.7 years of reaction. The disintegration of the ATM-103 fragment is similar to fuel behavior in oxidation tests done at 200°C [WASYWICH-1993] in the presence of water vapor. In those tests, schoepite formed along grain boundaries but did not impede further reaction progress throughout the grain-boundary network. Since our tests use a silicate-groundwater, yellow uranyl silicates form on the fuel surface. These products and their control over access of reactants to the fuel surface will be carefully examined in future evaluation of the test results.

4. <u>Reaction Pathways</u>

 $\geq - \forall g_{i},$

We have [FINN-1997] suggested that the dissolution of spent fuel is controlled by the oxidizing effect of the products of alpha radiolysis of the thin film (<10 nm [HAGYMASSY-1969]) of water at the fuel surface [SHOESMITH-1985]. The oxidants also facilitate oxidation and dissolution of the ε -phase particles. Since the ε -phase particles are homogeneously dispersed in the ATM-103 fuel matrix [GUENTHER-1988a], the rate of matrix dissolution should govern their rate of exposure to the oxidizing environment, and, consequently, the ⁹⁹Tc release fraction should reflect the minimum matrix dissolution rate.

In the ATM-103 high-drip-rate test, 3% of the ⁹⁹Tc inventory is released after 3.7 years of reaction. This release occurs in steady increments, which suggests either that the reaction pathways have been constant during this time or that the contribution from multiple reaction pathways has not varied over time. From mass balance considerations, i.e., the depletion of sodium and silicate from the EJ-13 leachant, the fraction of uranium that reacts to form Naboltwoodite is comparable to the fraction of ⁹⁹Tc released. The change in composition of partially reacted ε -phase particles is consistent with the leachate data, i.e., that the ε -phase particles are reacting as the spent fuel dissolves, leaving behind insoluble Rh and Pd.

The SEM data for the ATM-103 high-drip-rate sample provides insight into the possible reaction pathways that contribute to matrix dissolution. The two pathways seen in Fig. 6 are through-grain dissolution and grain-boundary dissolution. The configuration of the alteration products leads us to believe that the dense inner layer represents a region in which the spent fuel has been replaced by Na-boltwoodite. The gap, which is ~10 μ m above the fuel surface, is interpreted as corresponding to the position of the original surface of the unreacted fuel.

In Fig. 6c, the thickness of the dense layer is $\leq 5 \,\mu$ m at the extreme left corner, which may suggest that replacement is not isovolumetric. However, to obtain an estimate of the maximum amount of spent fuel that reacts by through-grain dissolution, one can use the average thickness of the reacted layer (10 μ m) and assume that replacement is 100% isovolumetric. The maximum amount of reacted fuel is then 2.3 wt% of the total mass of uranium in the test, assuming a geometric surface area of 2.1 x 10⁻⁴ m²/g and an ~8-g sample. However, because there is about a four-fold volume increase from cubic UO₂ (molar volume = 0.041 nm³) to monoclinic Na-boltwoodite (molar volume = 0.157 nm³), a maximum of 25% of the uranium in the replaced fuel layer is incorporated by the Na-boltwoodite within the dense inner layer. The remaining 75% of the uranium is transported out of this layer. Of this latter amount, perhaps up to half can be accounted for by the outer porous layer of Na-boltwoodite. The other half may be accounted for by (1) the portion of the alteration layer that is lost in preparing the SEM sample, (2) the nonuniform thickness of the alteration layer noted in visual examinations, (3) the amount of alteration phases remaining in the base of the Zircaloy fuel holder (noted but not measured), and (4) the uranium released to solution.

Dissolution also occurs along grain boundaries, as is evident from the friable nature of the fuel fragment and the gaps found between grains (Fig. 6). The minimum extent of the grainboundary reaction can be estimated by subtracting the maximum extent of through-grain reaction (2.3 wt%) from the cumulative ⁹⁹Tc release fraction (3 wt%); this minimum is 0.7 wt% of the total mass. Through-grain dissolution of the UO₂ fuel matrix seems to predominate over grain boundary dissolution, since the surface area of fuel reacted along grain boundaries is quite large compared to a uniform ~10-µm-thick surface replacement layer. Thus, as the grain boundaries open, the ⁹⁹Tc release fractions should increase if grain boundary dissolution predominates.

The formation of Na-boltwoodite at the fuel surface suggests that subsequent to matrix dissolution, uranium ions in solution coprecipitate with the sodium (Na⁺) and the silicon (H₄SiO₄) from the groundwater. An equation that accounts for the net oxidative dissolution of the

 $(2A_{i}^{*})^{*} = \{i,j\}$

 UO_2 fuel by an oxidizing source (represented by O_2), and the subsequent formation of Naboltwoodite is:

$$UO_2 + H_4 SiO_4 + Na^{\dagger} + 1/2 O_2 \implies Na[(UO_2)(SiO_3OH)] \cdot H_2O + H^{\dagger}$$
(1)

As Na- and Si-rich EJ-13 water is added to an unsaturated system with an oxidizing source, the net replacement reaction proceeds to the right provided H^+ is removed. The effects of other reactions are considered in Section IV.

5. Potential Mechanism in the Spent Fuel Reaction

Grambow et al. [GRAMBOW-1996] found that for unirradiated UO_2 the reaction rate depends only on the concentration of the oxidant and concludes that even under initially anoxic conditions, the spent fuel dissolution process is oxidative. Therefore, the local steady-state concentration of oxidants at the surface is of key importance for the extent of the fuel reaction and may provide an upper limit to the total amount of reaction.

In the unsaturated tests, there is a steady-state concentration of H_2O_2 , as well as other radiolysis products, in the thin film of water at the fuel surface. Reaction with the oxidants occurs at the surface and proceeds along grain boundaries as shown by the friable nature of the ATM-103 fragment. The alteration products do not form a protective layer that decreases fuel dissolution since the ⁹⁹Tc interval release fractions are constant over 3.1 years of reaction. Since ppm of ⁹⁹Tc are present in the alteration phases, the fuel reaction rate is slightly higher than that estimated from ⁹⁹Tc interval release fractions.

If one accepts ⁹⁹Tc release as a measure of fuel reaction rate, then it can be used to examine five suggested reaction processes [GRAMBOW-1990]. These are: (1) solubility-limited dissolution of alteration products, (2) transport of oxygen to the UO₂ surface, (3) growth of alteration products, (4) the rate of formation of oxidants by radiolysis, and (5) surface reaction.

For solubility-limited dissolution to control rate, radionuclide release rates have to decrease significantly as a function of time. This might control ²³⁸U release but not the reaction of the fuel, since the ⁹⁹Tc release fractions do not decrease as a function of time.

For oxygen transport to control the rate, a diffusion process has to be established. Diffusion does not appear to control the rate since the best fit of ⁹⁹Tc cumulative release was found to have a linear dependence on time (see Fig. 7).

For the growth of alteration products to control the rate, release should be constant or should increase as the surface area increases, i.e., as grain boundaries open. For both unsaturated tests, no increase was noted in the ⁹⁹Tc release rate as a function of time, although the surface area increased. Instead, the ⁹⁹Tc release fractions for ATM-103 are the same order of magnitude during 3.1 years of reaction. Thus, this mechanism does not appear to control the rate.

The rate of formation of oxidants by radiolysis also does not appear to control the fuel reaction rate since Grambow et al. noted [GRAMBOW-1996] that, even in a reducing environment, radiolysis supplied sufficient oxidants to oxidize spent fuel. However, if the rate of a surface reaction is faster than the rate of oxidant formation, the rate of oxidant formation could be rate controlling since it determines the oxidant concentration that is available for the surface reaction.



Fig. 7. Linear Time Dependence of ⁹⁹Tc Cumulative Release Fractions in the ATM-103 High-Drip-Rate Test (Equation is for linear least squares fit.)

Since the reaction rate defined by the ⁹⁹Tc interval release fractions remains constant with time, a surface reaction appears to be the rate-controlling mechanism. Support for control of the rate by a surface reaction is provided by Eriksen et al who observed in tests [ERIKSEN-1995] with spent fuel that nearly 100% of the oxidants from radiolysis are taken up by the fuel surface.

6. <u>Radionuclide Release in the ATM-106 Low-Drip-Rate Test after 10 Minute</u> <u>Immersion in EJ-13</u>

In Table 6, the cumulative release fractions for ⁹⁹Tc, ⁹⁷Mo, ¹³⁷Cs, ²³⁸U, and ²³⁹Pu for the ATM-106 low-drip-rate test after 2.5 years and 3.1 years of reaction are compared. At the longer time period, the fuel fragments were immersed in EJ-13 for 10 minutes to determine if reaction had occurred but that insufficient liquid had been present for transport of the released radionuclides. After immersion, the ⁹⁹Tc release fraction increased two orders of magnitude, yielding a total release of ~1%, which is comparable to the cumulative release of 3% in the high-drip-rate test after 3.7 years. Nearly all of the ⁹⁹Tc released after immersion (93%) was in the leachate, as was most of the ⁹⁷Mo release. From 90-100% of the ¹³⁷Cs, ²³⁸U, and ²³⁹Pu release in the 3.1 year interval is sorbed on the stainless steel. The sorption behavior on stainless steel is not surprising for the actinides but is not expected for cesium.
			Sampling
	Cumulative		Interval
Radionuclide	2.5 yr	3.1 yr	3.1 yr
⁹⁹ Tc	1.0E-4	9.4Ē-3	9.4E-3
⁹⁷ Mo	1.2E-4	1.1E-3	9.7E-4
¹³⁷ Cs	3.3E-6	4.9E-4	4.9E-4
²³⁸ U	1.8E-5	1.6E-4	1.4E-4
²³⁹ Pu	2.4E-5	2.0E-4	1.8E-4

Table 6. Release Fractions for the ATM-106 Low-Drip-Rate Test after 3.1 Years of Reaction and Immersion for Ten Minutes in EJ-13

The large fractional release after a short immersion in EJ-13 suggests that the fraction of fuel reacted is underrepresented by the ⁹⁹Tc release in the low-drip-rate tests because of minimal liquid for transport and because most of the reacted radionuclides are present on the fuel surface. If this hypothesis is true, then there is the potential for large radionuclide bursts if fracture flow occurs after a large portion of the spent fuel has reacted with low volumes of standing water or with water vapor for extended periods.

E. <u>Conclusions</u>

Our conclusions for the high-drip-rate tests are as follows. (1) The ⁹⁹Tc interval release fractions provide a lower limit for the spent fuel reaction. In the ATM-103 fuel, 3 wt% of the total inventory of ⁹⁹Tc is released in 3.7 years. (2) Oxidation of the ε -phase suggests that the oxidizing potential at the fuel surface may be as high as 0.6 V. The oxidant may be H₂O₂, a product of alpha radiolysis of water. (3) The constancy of the ⁹⁹Tc release fractions over 3.1 years of reaction indicates that a surface reaction is the rate-controlling mechanism for fuel reaction under unsaturated conditions and that the oxidant is possibly H₂O₂, a product of alpha radiolysis of water. (4) Two reaction pathways have been identified from SEM examination: a) through-grain dissolution with subsequent formation of uranyl alteration products and b) dissolution along grain boundaries. The latter results in the friability of a spent fuel fragment. (5) The major alteration product identified by XRD and SEM is Na-boltwoodite, Na[(UO₂)(SiO₃OH)]·H₂O, which is formed from sodium and silicon in the water leachant. (6) Elements other than uranium, including Ru, Mo, Cs, and Ba, are incorporated into (U⁶⁺) alteration products examined so far. (7) Pu appears to be concentrated on the spent fuel. It is not found in the leachate nor in the alteration products.

The high-drip-rate tests appeared to have sufficient liquid to transport dissolved material from the spent fuel to the test vessel. For the low-drip-rate tests, there is sufficient water for fuel reaction but, due to water evaporation from decay heat, water for radionuclide transport is reduced. Evaluation of the results from the vapor tests is ongoing.

F. Ongoing Studies

The unsaturated tests with ATM-103 and ATM-106 fuel samples are ongoing. Detailed analysis of the leachates will continue in the next year to determine if there is a diminution in the leach rate and a change in the concentration, form, and quantity of the radionuclides as determined from ICP-MS data. Identification of the alteration products on the spent fuel will continue using SEM, XRD, and TEM. The type and depth of reaction within a spent fuel fragment will be studied.

II. OPTICAL, SEM, AND XRD RESULTS FOR REACTED SPENT FUEL SAMPLES

This section describes results obtained during examination of reacted fuel by optical microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) analysis. We discuss the three types of tests, high-drip-rate, low-drip-rate, and vapor separately. We follow these sections with a summary of the results.

A. <u>Results for High-Drip-Rate Tests</u>

1. <u>ATM-103 Fuel - 3.7 Years Reaction</u>

The fragment removed from this test disaggregated upon manipulation during the initial sampling procedure, spreading particles of fuel grains and reaction products across the adhesive tape in the petri dish that contains the sample. Optical examination of the particles indicates fuel fragments range in size from approximately 10 to greater than 200 μ m. The fuel particles range from single grains to aggregates made up of several tens of grains; many of these have yellow material adhering to them. Clusters (<10 to 200 μ m) of light yellow acicular crystals are also abundant. In association with most of the yellow clusters is darker yellow material. Much of the dark yellow material is closely associated with adjacent fuel grains. This dark yellow material clings tenaciously to the fuel grains, where present.

We prepared several particles for SEM examination. Most are black fuel grains – essentially UO₂ (one cannot determine trace elements by SEM/EDS), most of which show some pitting, probably due to dissolution along the grain boundaries. The acicular crystals comprising the yellow clusters are an Na-U-silicate, shown from XRD analysis to be Na-boltwoodite, Na[(UO₂)(SiO₃OH)](H₂O). We did not identify other phases during our SEM analyses.

One of the particles had a core of black fuel grains surrounded by a rind of yellow alteration products (Fig. 8). Optically, this rind appears to contain two layers, a densely crystalline, dark yellow material next to the fuel grains and light yellow, finely crystalline material. We mounted this sample in epoxy for examination in SEM. Figure 8 shows a cross-section through this fragment. The SEM image shows the fuel (brightest region) in which the grain boundaries are readily visible. Gaps of approximately 0.5 μ m or less are visible between the fuel grains. We have not detected other alteration phases between the grain boundaries. Silicon is not evident from EDS analyses at the grain boundaries; however, strong absorption by the adjacent UO₂ matrix of the relatively low-energy Na-Ka and Si-Ka X-ray emissions emanating from alteration phases may preclude the detection of minor alteration phases within grain boundary regions.

Adjacent to the fuel is an alteration layer predominantly consisting of Naboltwoodite. The thickness of the layer varies but is approximately 20-40 μ m. This layer of Naboltwoodite consists of the two regions with diverse appearances: a dense layer, approximately 10 μ m thick, closest to the fuel surface, and a much less dense outer layer, 10-30 μ m thick. No difference in composition is evident between the two layers using EDS. Near the outer edge of the denser (inner) layer is an interface (Fig. 8b) defined by a gap (dark band). This gap lies approximately 10 μ m above the fuel surface and 2-3 μ m below the outer edge of the dense layer. Just below this interface, crystals of Na-boltwoodite have formed approximately perpendicular to the fuel surface, whereas, above this interface, Na-boltwoodite forms the dense mat of crystals sub-parallel to the fuel surface. Above these flat-lying crystals is the low-density outer layer. The inner region of the dense layer shows several curvilinear features that may be pre-existing grain boundaries, although artifacts produced during sample grinding and polishing are also evident. The different densities of the two layers manifest themselves as different colors under optical examination: the inner layer is dark yellow and the outer layer is pale yellow to white. The inner layer adheres quite tenaciously to the adjacent fuel grains, whereas the outer layer does not adhere strongly to the underlying denser layer. The consistency of the low-density outer layer might best be described as "fluffy."



(a)

(b)

Fig. 8. ATM-103 Sample: SEM Micrographs of Polished Sections through the Contact between Fuel Grains and Corrosion Rind (a) Particle Showing both Corrosion Layers and the Adjacent Fuel Grains and (b) Magnified View of Particle Shown in Part a Illustrating Details of the Dense Inner Layer of Na-boltwoodite (high-drip-rate, 3.7 years reaction).

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Table 7 contains the list of d-spacings and relative intensities (I values) obtained from scrapings from the surface of ATM-103 that had been reacted for 3.7 years. We measured these d-spacings from X-ray film following an eight-hour exposure (40 kV and 30 mA, Cu-Ka radiation, l = 0.154056 nm). The radiation from the sample is low and darkening of the X-ray film was slight. We identified 32 diffraction lines on the film, which are listed in bold type in Table 7. The X-ray powder patterns for natural β -uranophane, synthetic UO₂, and synthetic Na-boltwoodite are also listed in Table 7 for comparison to the experimental pattern. In addition, we show the dspacings calculated for a least squares refinement of the unit cell parameters based on the experimental powder pattern for ATM-103 (a 1.401, b 1.578, c 0.660 nm, b 90.50°). The calculated cell parameters compare well with the unit-cell parameters reported by Gorman and Nuffield for the Na-boltwoodite (a 1.4010, b 1.5550, c 0.664 nm, b 91.0° [GORMAN and NUFFIELD, 1955]). Deviations in cell parameters from those shown in Table II-1 may reflect differences in the formation temperatures and/or trace-element substitutions.

The experimental XRD pattern is consistent with a mixture of Na-boltwoodite (approximately 80-90 vol%) and β -uranophane (approximately 10 vol%). Minor UO₂ (< 5 vol%) is also evident in the pattern, which is consistent with the presence of the black grains observed within the yellow masses.

2. XRD Results for ATM-106 Fuel Sample from the Zircalov Retainer after 0.8 Years

We scraped the surface of the Zircaloy retainer from the base of the ATM-106 fuel test sample removing numerous particles for analysis by XRD. We mounted the resulting powdered material in a silica-glass capillary (0.2-mm inside diameter) without further grinding, then placed the capillary into a Debye-Scherrer X-ray camera (114-mm diameter).

Table 8 contains the list of d-spacings and relative intensities obtained from particles scraped from the Zircaloy retainer. We measured the d-spacings from X-ray film following a three-hour X-ray exposure (40 kV and 30 mA). The film was substantially darkened, presumably because of the high level of β and γ radiations caused by the large amount of Cs in the sample. We identified only ten diffraction lines on the film, and these are listed in bold-face type in Table 8. We also list five X-ray powder patterns from the Powder Diffraction File (PDF) for comparison.

The experimental XRD pattern for this sample is consistent with a mixture of predominantly two phases. One phase is probably a uranyl oxy-hydroxide, structurally related to billietite (PDF 29-208). The other phase is likely "dehydrated schoepite," $(UO_2)O_{0.25}(OH)_{1.5}$ [compositionally equivalent to $UO_3 \cdot 0.75H_2O$] (PDF 13-242). Table 8 also lists X-ray powder diffraction data for the minerals compreignacite and ianthinite (both structurally related to billietite) and for synthetic $UO_3 \cdot 0.8H_2O$ for purposes of comparison. These data support the interpretation of Buck et al. [BUCK-1997] that the Cs-Mo-U phase identified in this sample by analytical transmission electron microscopy (AEM) is structurally related to billietite, with a structural formula corresponding to $Cs_{0.9}Ba_{0.55}[(UO_2)_5(MOO_6)(OH)_6] \cdot nH_2O$ (n ~ 6).

The experimental pattern for our ATM-106 sample has one unidentified diffraction maximum, corresponding to 0.267 nm. The XRD data for billietite and compreignacite do not have this d-spacing, and the presence of a 0.267-nm diffraction maximum may indicate a third unidentified phase. However, this d-spacing may well correspond to the Cs-Mo-U phase. Although this d-spacing is not evident in the electron diffraction pattern obtained during AEM analysis, diffracted intensities can differ substantially between X-ray and electron diffraction.

·,	ATM-103	Na-b	oltwoodite ^b (1)	<u>β-u</u>	ranophane. 8-301	β-uranophane L-S cell fit		UO, 5-550
I	d (nm)	I	d (nm)	I	d (nm)	d (nm)	I	d (nm)
20	0.790			100	0.783	0.790		
100	0.680	46	0.678					
60	0.660			40	0.666	0.660		
		57	0.6464					
60	0.600			40	0.616	0.600		
5	0.540	34	0.539					
5	0.500			40	0.507	0.506		
50	0.480	59	0.473	40	0.485	0.482		
1	0.420	22	0.426					
1	0.410			30	0.411	0.411		
60	0.393			90	0.39	0.394		
5	0.374			10	0.375	0.380		
2	0.360	17	0.358					
30	0.347	72	0.347	60	0.351			
30	0.338	9	0.338	10	0.341	0.338		
		7	0.336	20	0.335			
1	0.319			50	0.319	0.320	100	0.316
15	0.309	36	0.3089	40	0.304			
		14	0.3058					
15	0.299			30	0.299	0.301		
80	0.294	100	0.2942					
		94	0.293	20	0.291			
				40	0.283			
1	0.272			30	0.278		48	0.274
1	0.259			50	0.259			
5	0.250	5	0.2517					
		4	0.2493					
		4	0.2246					
		6	0.2272					
		17	0.2219					
5	0.219	23	0.2179					
		17	0.2154					
1	0.1923						49	0.193
10	0.1875							
1	0.1855							
1	0.1825							
1	0.1725							
5	0.1673							
1	0.1645							
1	0.1580							
10	0.1500							
1	0.1225						_	

Tabl	e 7.	X-ray	Diffractio	on d-Spa	cings fo	r Sample	e from	ATM-103	3 Reacted	for 3.7 `	Years ^a

I > 15% for all Powder Diffraction File patterns

^aCu-Ka radiation (l = 0.154056 nm); $I_{(rel)} > 10\%$ for Powder Diffraction File PDF) patterns.

^bSource: Ref. Vochten-1997.

"Numbers are PDF designations.

^dLeast-squares fit to unit cell dimensions: *a* 1.401, *b* 1.578, *c* 0.660 nm, b 90.50° [refer to reported unit-cell dimensions from Gorman-1955: *a* 1.4010, *b* 1.5550, *c* 0.664 nm, b 91.0°; (GORMAN & NUFFIELD-1955)].

I	d (nm)	Billietite 29-208	Dehydrated schoepite 13-242	UO ₃ ·0.8H ₂ 10-309	Compreignacit 33-1049	Ianthinite 12-272
100	0.750	0.753			0.746	0.763
38	0.510		0.509	0.511		
9	0.380	0.376			0.371	0.381
		0.356			0.358	0.359
47	0.348	0.350	0.345	0.345-0.343		
					0.353	
4	0.340		0.339			0.335
					0.323	0.324
1	0.320	0.321-18			0.320	
						0.2950
9	0.2879		0.2890	0.2857		
1	0.2670					0.2690
					0.2579	0.2610
		0.2557	0.2540	0.2557	0.2564	0.2530
5	0.2500		0.2480	0.2487	0.2475	
						0.2390
		0.2295/67				0.2150
		0.2295/67		0.2138		0.2070
		0.2049/39	0.2023	0.2053	0.2032	0.2030
1	0.2000					
		0.1996	0.1993	0.1986		0.1992
T . 1	607 fam all					

Table 8. X-ray Diffraction d-Spacings in (nm) Measured for Specimen Scraped from Zircaloy Retainer from ATM-106 Reacted for 0.8 Years^a

I > 15% for all PDF patterns

The reported range in d-spacings is indicated by a -, while intensities for billietite ianthinite are indicated by /.

3. Analysis of Sample from ATM-106 Fuel after 3.7 Years Reaction

Optical examination shows that most of the particles removed from the alteration rind after 3.7 years of reaction consist of finely acicular (needle-shaped) crystals, approximately 1 μ m in diameter and up to approximately 50 μ m long. These crystals form pale-yellow clumps, 5-10 μ m across. Many of the clumps also contain black grains, as well as some darker yellow material associated with the black grains. In many respects, this sample closely resembles the sample taken from ATM-103 fuel that had been reacted for 3.7 years (see Section II.A.1), although no disaggregation of the fuel fragments occurred when we manipulated them during initial sample

preparation in the hot cell, as occurred for one fuel fragment from the ATM-103 fuel after 3.7 years reaction.

We examined two specimens by SEM: one mounted fraction and one polished cross section (Fig. 9a = fragment; Fig. 9b = cross section). The SEM examinations show that the yellow clumps are a tangled mat of acicular crystals, approximately 5-10 μ m long and less than 1 μ m in the direction perpendicular to elongation. EDS analyses indicate that these crystals are a Na-U-silicate, either Na-boltwoodite or possibly the Na-analogue of weeksite, $(K,Na)_2(UO_2)_2(Si_5O_{13})(H_2O)_3$. While weeksite is a possible phase because some of the X-ray emission spectra display higher Si:U ratios than observed for boltwoodite and uranophane (Si:U ratios of 1:1), the assignment as Na-boltwoodite is consistent with that made for ATM-103, and with the assignment made in the 4.1 yr ATM-106 sample. We did not perform XRD analysis of this sample because of a lack of material.

The polished section examined does not display an interface between the ATM-106 fuel and alteration layer, as shown (Fig. 8) in a similarly prepared section from ATM-103 (3.7 yr reaction). Whether this sample from ATM-106 has experienced grain-boundary-enhanced dissolution similar to that observed for ATM-103 within the same reaction interval cannot be determined yet; additional samples need to be analyzed. The very small amount of sample obtained from the ATM-106 fuel after a 3.7-year reaction interval precluded preparation of additional SEM polished sections. Thus, the reacted layers formed on ATM-106 fuel could not be compared directly with those on ATM-103 fuel at this time. Solution analyses and visual examinations of the reacted fragments indicated that the reaction progress of the ATM-106 fuel has lagged behind reaction of the ATM-103 fuel by approximately six months. Continued examination of samples from both ATM-106 and ATM-103 fuels obtained after further reaction intervals have occurred, will provide needed insight into sample-dependent differences. We will describe additional SEM examinations in subsequent reports.

4. Analysis of Sample from ATM-106 Fuel after 4.1 Years Reaction

Optical examination of the particles removed from a fragment of ATM-106 reacted fuel after 4.1 years of reaction indicate that the alteration products consist primarily of light-yellow, finely acicular crystals. These crystals form small aggregates(10-200 mm across), many of which contain small black inclusions that are probably fuel grains. We also extracted similarly sized aggregates of fuel grains from the reacted fuel fragment, although in a much lesser amount. Along with the light-yellow clumps, and often included within them, is darker yellow material without visible crystals when viewed at this scale.

We mounted several particles for SEM examination. To date, we have investigated only those particles mounted on aluminum stubs. Our EDS analyses and the morphologies of the crystals indicate that the most abundant phase in the clumps of yellow crystals is Na-boltwoodite. The X-ray emission spectrum of the more dense-appearing material is similar to that of the larger acicular boltwoodite crystals, suggesting a similar paragenesis as described for the ATM-103 samples that had been reacted for 3.7 years. We have examined a few fuel grains, and these display loosely aggregated, or discrete grains with pitted grain boundaries, suggesting grainboundary-enhanced dissolution of the fuel grains. We have not observed alteration phases within the gaps between fuel grains that were separated during SEM sample preparation.



(a)



(b)

Fig. 9. ATM-106 Sample: SEM Micrographs of Na-boltwoodite (a) Cluster of Acicular Crystals, (b) Polished Cross Section through Cluster Similar to that Shown in Part a (Scale Bars \cong 50 µm; high-drip-rate 3.7 years reaction, central stripe in (b) is an imaging artifact)

Table 9 lists the d-spacings and relative intensities obtained from the scrapings taken from this ATM-106 sample. We measured the d-spacings from X-ray film after a six-hour exposure (40 kV and 30 mA, Cu-Ka radiation, l = 0.154056 nm). The radiation due to the sample was moderate, darkening the X-ray film only slightly. We identified 18 diffraction lines on the film, and these are listed in bold type in Table 9 along with their relative intensities. We also list three X-ray powder patterns from the PDF for comparison: those of synthetic Na-boltwoodite, natural β -uranophane and synthetic soddyite.

The experimental XRD pattern (Table 9) is closely similar to that obtained from a sample from ATM-103 fuel that had been reacted for 3.7 years, so we have listed that pattern in Table 9 as well (compare with Table 7). The phase making up the bulk of this sample is Naboltwoodite (~80-90 vol%). The phase (or phases) composing the remainder of the sample is unknown at this time, and we are planning additional analyses to identify it (them). Numerous black grains are apparent within the yellow mass, indicating that UO_2 fuel is present; however, UO_2 is not evident in the powder diffraction pattern. Thus the fuel grains probably make up less than 1-2 vol% of the sample examined.

A notable difference between this sample and the sample from ATM 103 fuel reacted for 3.7 years is the absence of a diffraction peak corresponding to ~0.79 nm in the ATM-106 fuel sample. The 0.79 nm d-spacing is the most intense reflection in the powder pattern of b-uranophane [FRONDEL et al., 1956]. We attributed this diffraction peak to β -uranophane in the sample from ATM-103 reacted for 3.7 years (see Table 7). We are uncertain whether the absence of a 0.79 nm diffraction maximum in the ATM-106 fuel sample pattern indicates a lack of β -uranophane in this sample or whether some unknown cause reduced the intensity of this peak (for example, sample preferred orientation or a change in space-group symmetry indicating a polymorphic transformation). Given the very close similarity of the pattern from the ATM-106 fuel to that of the sample from ATM-103 reacted for 3.7 years, we believe that the mineral phase identification is also similar (despite the differences noted above). This similarity leads us to believe that any as-yet unidentified phases present in the ATM-106 fuel sample are likely also present in the sample from ATM-103 fuel reacted for 3.7 years. Examination of this sample and the data derived from it are preliminary and are continuing.

5. <u>Discussion of the High-Drip-Rate Tests</u>

Crystal morphologies, chemical compositions (as determined by EDS), and the XRD analyses indicate that the most abundant alteration product formed in the high-drip-rate experiments is Na-boltwoodite, Na[(UO₂)(SiO₃OH)](H₂O), with a lesser amount of β -uranophane, Ca[(UO₂)₂(SiO₃OH)₂](H₂O)₅. Additional phases present in amounts less than 5 vol% may also be present but have not been identified during SEM or XRD analyses. (Dehydrated schoepite and a Cs, Ba-U-Mo oxy-hydroxide were identified from the Zircaloy retainer after 0.8 years reaction (ATM-106), but these phases have not been identified in samples from later tests.) The β -uranophane apparently occurs primarily at the outermost surface of the alteration layers, whereas the bulk of the alteration layer is Na-boltwoodite. The apparent lack of alteration products formed along fuel-grain boundaries in the high-drip-rate tests may reflect depletion of dissolved Si in fluids penetrating the grain boundaries, possibly due to the precipitation of uranyl silicates on the outer surface.

				B-11ra	nonhane	a-ura	nonhane	ATM-	103 after
Ι	d (nm)	Na-bolt	woodite	8	-301	39	-1360	3.7	years
				100	0.783	100	0.79	20	0.790
100	0.686	46	0.678		•••••			100	0.680
47	0.669			40	0.666	7	0.664	60	0.660
		57	0.646					I	
57	0.602			40	0.616			60	0.600
		34	0.539			14	0.543	5	0.540
				40	0.507			5	0.500
43	0.482	59	0.473	40	0.485			50	0.480
			•						
		22	0.426					1	0.420
				30	0.411			1	0.410
40	0.395			90	0.39	90	0.3950	60	0.393
9	0.376			10	0.375			5	0.374
11	0.364	17	0.358			20	0.3600	2	0.360
49	0.347	72	0.347	60	0.351	4	0.3508	30	0.347
20	0.341	9	0.338	10	0.341			30	0.338
		7	0.336	20	0.335				
		2	0.325						
				50	0.319	10	0.3210	1	0.319
27	0.310	36	0.3089	40	0.304			15	0.309
		14	0.3058						
20	0.301			30	0.299	16	0.2993	15	0.299
73	0.294	100	0.2942					80	0.294
		94	0.293	20	0.291	11	0.2915		
8	0.281			40	0.283				
				30	0.278	11	0.2698	1	0.272
5	0.259			50	0.259	40	0.2633	1	0.259
						_			
		_				12	0.2560	_	
4	0.251	5	0.2517					5	0.250
		4	0.2493						
		4	0.2246						
		6	0.2227						
		17	0.2219			10	0.2207	_	
4	0.219	23	0.2179					5	0.219
		17	0.2154			12	0.2106		
3	0.209					15	0.2100	•	0 1000
_	A 4004					10	0 1000		0.1923
7	0.1883			- <u>-</u>		10	0.1890	10	0.18/5

 Table 9. X-ray Diffraction^a d-Spacings (in nm) for Sample from ATM-106 Fuel Reacted for 4.1 Years

^aCu-Ka radiation (l = 0.154056 nm); $I_{(rel)} > 10\%$ for all PDF patterns ^bSource: Ref. Vochten-1997 There appears to have been extensive dissolution along grain boundaries, as was especially evident from the friable nature of the fragment removed from ATM-103 fuel after 3.7 years reaction. Wide gaps between grains also support this conclusion (Fig. 8). Although the oxidation of UO₂ to UO_{2.25} may enhance the expansion of the gaps between grains, because of the smaller unit-cell size of UO_{2.25}, this sizes difference does not account fully for the observed widths of the gaps (~0.5 mm). Furthermore, no UO_{2.25} was identified during TEM examinations of fuel grains.

The replacement of the fuel by the alteration products has progressed uniformly inward from the original outer surface without regard to grain boundaries. This "through-grain" dissolution of the fuel grains is evident from the lack of embayment at grain-boundaries (Fig. 8). The through-grain dissolution of the UO_2 fuel matrix accounts for a significant amount of fuel that has dissolved in the high-drip-rate tests and is greater than the amount of fuel that has dissolved by means of grain boundary-enhanced dissolution (see discussion below and in Section I).

We can write the (simplified) reaction for the oxidative dissolution of the UO_2 fuel:

$$UO_2 + 2H^* + 1/2 O_2 \implies (UO_2)^{2*} + H_2O_2$$
 (2)

The precipitation of Na-boltwoodite is

$$(UO_2)^{2+} + H_4 SiO_4^{0} + Na^+ + H_2 O \implies Na[(UO_2)(SiO_3 OH)](H_2 O) + 3H^+.$$
 (3)

Thus the net reaction for the replacement of the UO2 fuel by Na-boltwoodite is

$$UO_2 + H_4SiO_4^0 + Na^+ + 1/2O_2 \implies Na[(UO_2)(SiO_3OH)](H_2O) + H^+.$$
 (4)

The reaction 4 (which is not an equilibrium expression) shows that the replacement reaction will continue as long as Na- and Si-rich EJ-13 water is added to the system and/or H⁺ is removed (due to flowing water and/or reaction with fuel via reaction 2), provided that a sufficient supply of oxidants is available. We suspect that an abundant supply of oxidants is probably available due to the effects of radiolysis and from free O₂ in the reaction vessel atmosphere.

We have written reactions 2 through 4 with all U being conserved in the solid phases, which is consistent with the low quantities of U released to solution in the high-drip-rate tests. At the low-drip-rate, we expect similar U retention by the alteration phases.

To date, the only cross section of reacted fuel analyzed that clearly shows the contact between fuel grains and the alteration products on the fuel surface is the sample from ATM-103 fuel that had been reacted for 3.7 years (Fig. 8). The interface between the dense layer of Na-boltwoodite and the overlying "fluffy" layer may represent the position of the surface of the original fuel fragment, or it may be an artifact of the original surface that has been "pushed out" by Na-boltwoodite, which precipitated as the fuel was dissolving. The matted flat-lying crystals of Na-boltwoodite that lie above this interface either precipitated at the original surface of the fuel or may have precipitated after the formation of the dense inner layer. The formation of the dense inner layer is somewhat enigmatic. Clearly, the fuel grains were dissolved and replaced by the dense layer of Na-boltwoodite. What remains uncertain is whether this replacement has been isovolumetric, without inflation of the dense inner layer during replacement, or whether the replacement of the fuel by Na-boltwoodite has resulted in a volume increase. Therefore, the thickness of the dense inner layer represents the *maximum* thickness of fuel that was dissolved and replaced by Na-boltwoodite. If there has been some inflation of the reacted layer as Na-

boltwoodite replaced the fuel, then the thickness of the dense inner layer is greater than the thickness of the fuel that was dissolved.

One can infer physical evidence for both types of replacement from the cross section shown in Fig. 8. Isovolumetric replacement of the fuel grains may leave evidence of the pre-existing grain boundaries ("relict" grain boundaries). Indeed, several curvilinear features of the dense inner layer are indicative of relict grain boundaries. On the other hand, the dense inner layer next to the "corner" of the fragment shown in Fig. 8 appears less thick than the thickness on either side of the corner. This texture suggests that some inflation of the alteration layer may have occurred during replacement (this effect appears exaggerated farther out in the low-density outer layer). However, this cross section also displays several artifacts due to sample preparation, such as "holes" in the alteration layer caused by plucking of material during grinding and/or ultrasonic cleaning, and scratches caused by grinding and polishing. These artifacts may mask, or mimic, some features in Fig. 8. Such artifacts are difficult to avoid because the hardness of the UO₂ fuel is greater than that of the adjacent alteration layers (and the embedding epoxy resin). Nevertheless, these artifacts complicate the interpretation of Fig. 8. Only careful preparation of additional cross-sectioned samples will clarify our interpretation. At this time, we believe there is evidence to suggest the interface represents the original fuel surface and that little expansion has occurred.

The unit-cell volume of UO₂ is approximately 0.164 nm³ (Z = 4), or 0.041 nm³ per U atom; the ideal density of UO₂ is 10.9 g·cm⁻³. The unit-cell volume of Na-boltwoodite is 0.6286 nm³ (Z = 4), or 0.157 nm³ per U atom; the ideal density of Na-boltwoodite is 4.5 g· cm⁻³. An approximate four-fold volume increase would be needed between cubic UO₂ and monoclinic Na-boltwoodite if Na-boltwoodite is to incorporate all the U from the UO₂. Only approximately 25% of the U in the replaced outer fuel layer can be incorporated into an equal volume of Na-boltwoodite (if this layer is 100% of theoretical density). The remaining 75% (or more) of the U must be transported out of the replaced volume. The dense inner layer of Na-boltwoodite is 10-15 mm thick, indicating that the thickness of fuel that has dissolved by "through-grain" dissolution is probably no less than approximately 3 µm and no more than 10-15 µm.

The volume density of the outer, less-dense layer is only approximately 10 or 20% of the ideal density from a combination of through-grain and grain boundary dissolution. The source of U that formed this outer layer is uncertain. If all the U derived from through-grain dissolution at the surface remained within the inner dense layer, then the U in the outer layer must be from dissolution along grain boundaries. If the Na-boltwoodite in the inner layer did not incorporate all of the U from the dissolved surface, then some U in the outer layer must have come from the dissolving surface. In the case of isovolumetric replacement of the surface, a maximum amount of U must be derived from through-grain dissolution.

From our SEM observations, we can calculate the approximate volume of fuel replaced by Na-boltwoodite. The estimated original geometric surface area was 2.1 $\times 10^{-4}$ m²/g, and the original mass of fuel was 8 g, giving an original total surface area of 0.00168 m². One may assume that the fragment of ATM-103 fuel shown in Fig. 8 is representative of the reacted fuel surface (that is, Na-boltwoodite replaced the outer 3-10 µm of the fuel surface). If this is true, the estimated volume of fuel that has reacted by through-grain dissolution is between 5.6 x 10⁻⁹ m³ and 1.7 x 10⁻⁸ m³. This range corresponds to the release of between 0.06 and 0.18 g of UO₂ ($D_{UO2} \approx 10.6 \text{ g/cm}^3$) or a fractional release of between 0.7 and 2.2% of all the U in the fuel after 3.7 years from the reacted layer only. To this number, the additional mass of U released due to dissolution along grain boundaries must be added. Based on Tc release, approximately 0.25 g of UO₂ has reacted, so the mass of U corresponding to the replacement volume represents between 25 and 80% of the total fuel reacted. Approximately 20-75% of the total U released from the fuel is due to dissolution along the grain boundaries. No U⁶⁺ alteration phases have been observed along reacted grain boundaries within the fuel fragments. This is an unexpected result considering that

concentrations of dissolved U may be expected to reach quite high levels in solutions between fuel grains that are dissolving. We have no explanation for this result at this time.

Only about 1% of the U estimated to have reacted is in solution (based on Tc release), which means that approximately 99% of the reacted U is in alteration products and on the vessel and retainer walls. The alteration rind (both layers) observed by SEM may contain, at most, about 50% of the total reacted U. We believe that the retainer must have adsorbed some U, which will be taken into account when the tests are terminated.

B. <u>Results for Low-Drip-Rate Tests</u>

1. <u>Analysis of Sample from ATM-103 Fuel after 4.1 Years Reaction</u>

Optical examination of the particles removed from a sample taken from ATM-103 fuel after 4.1 years reaction show abundant crystals that are various shades of yellow. The yellow crystals are commonly bladed or blocky, rarely equant and prismatic. In addition, there are numerous clumps of black grains and several reddish-orange particles. The black grains are approximately 10-100 μ m, and most of them are probably single fuel grains and aggregates of a few tens of fuel grains. The reddish particles are tabular, approximately 50 μ m by 100 μ m and 20-50 μ m thick.

SEM examination indicates that several U-containing alteration products are present (Fig. 10). These products include metaschoepite and/or dehydrated schoepite, soddyite, $(UO_2)_2(SiO_4)(H_2O)_2$, Na-boltwoodite, and an unidentified uranyl oxide hydrate (UOH) that may be the Na-analogue of compreignacite. This Na-UOH may have the structural formula $(Na,K)[(UO_2)_3O_2(OH)_3](H_2O)_4$ (based on analogy with compreignacite) To date, we have not performed XRD analyses on this sample. Phase identifications are therefore tentative, and the relative abundances of the alteration products are uncertain. However, metaschoepite and "Na-compreignacite" are abundant in the particles examined by SEM, and these two phases probably constitute the major alteration phases formed in this test after 4.1 years. In contrast, Na-boltwoodite appears to be rare; we observed only a few small crystals associated with a single particle in the sample examined by SEM.

The reddish-orange particles do not contain uranium (Fig. 11), and they appear chemically complex and inhomogenous. Qualitative chemical analyses by EDS indicate that the major elements in these particles include Na, Se, Si, S, Cl, and Cr. An outer layer of what looks like a finely crystalline coating covers most of the particles (Fig. 11). Beneath this outer layer the particles are relatively featureless, with low electron reflectance. Sodium is consistently a major constituent in all spot analyses by EDS, but the relative amounts of Se, Si, S, Cr, and Cl vary substantially across the sample, from minor constituents to abundances comparable to that of Na. We have not completed XRD or AEM analyses on these particles, so identification is uncertain.

2. Discussion of Low-Drip-Rate Tests

To date we have examined only samples from the low-drip-rate test on ATM-103 fuel. The alteration-phase assemblage observed from the sample ATM-103 reacted for 4.1 years consists of at least four different uranyl phases: two oxy-hydroxides and two uranyl silicates. This is a somewhat more complex assemblage of alteration products than was observed in the samples form ATM-103 fuel reacted at the high-drip-rate for comparable time (3.7-4.1 years). In the samples from high-drip-tests, we identified only one or two uranyl silicates as major alteration products. Although we have not identified a clear paragenetic sequence of alteration products, analogy with the UO₂ drip tests suggests that the uranyl oxy-hydroxides (metaschoepite and Nacompreignacite) probably formed before the uranyl silicates, soddyite, and, later, Na-boltwoodite.



Fig. 10. ATM-103 Sample: Fuel Grains (bottom) Covered by Mixed U_{6+} Alteration Phases, Mounted on C-Tape. Alteration phases in this sample include metaschoepite, an unidentified Na-uranyl oxy-hydroxide (blocky crystals at top) and soddyite (fine-grained crystals at right). Scale bar \cong 40 µm; low-drip-rate, 4.1 years reaction.



Fig. 11. ATM-103 Sample: Red-Orange Particle Mounted on C-Tape. Scale bar, top right $\approx 50 \ \mu m$; low-drip-rate, 4.1 years reaction.

An interesting difference between this test and the tests on unirradiated UO_2 is the apparent absence of becquerelite in the test on spent fuel; becquerelite is at least rare in the samples from this test. This observation may reflect minor differences in the compositions of the leachants used; however, chemical and other disparities between UO_2 and spent fuel (for example, composition, radiation field, etc.) may explain observed differences in the alteration-phase assemblages of UO_2 and spent UO_2 fuel. Also, sample inhomogeneities across the fuel surface may exist. We need to analyze more samples before we can compile a comprehensive list of alteration products formed in these tests at this time.

Notably, the uranyl alteration products identified in the low-drip-rate test are chemically and structurally similar to the uranyl alteration minerals that occur at Nopal I uranium deposit at Peña Blanca, Mexico. Researchers have studied Nopal I as a natural analogue for the long-term behavior of spent UO_2 fuel at the proposed repository at Yucca Mountain [PEARCY-1994]. Such mineralogical similarities between laboratory tests and a natural U-ore deposit demonstrate the relevance of these tests for understanding long-term, unsaturated corrosion of spent fuel in a repository setting.

The fact that several diverse types of alteration phases coexist within the corrosion rind on ATM-103 fuel after 4.1 years reaction implies that the reactions controlling phase formation are incomplete. The physical state of the corrosion rind at this time is simply an interim state of the reaction as the fuel alters to an assemblage of phases more stable under the current test conditions. A simplified view of the alteration reaction, with the formation of a single phase being used to illustrate the overall reaction, is not possible given the complexity observed in this test sample. We strongly suspect that the uranyl oxide hydrates (such as metaschoepite and Na-compreignacite) are kinetic products that are replaced by such uranyl silicates as Na-boltwoodite and uranophane. The most likely reason that the uranyl oxy-hydroxides have not been replaced after 4.1 years exposure is that there is less water and dissolved cations supplied to the samples in these tests compared to the tests performed at the high-drip-rate. Nevertheless, an overview of the reactions that may be important for the precipitation and possible replacement of the alteration phases identified in this test sample is informative.

Again, we begin with the simplified reaction for the oxidative dissolution of the UO_2 fuel:

$$UO_2 + 2H^+ + 1/2 O_2 \implies (UO_2)^{2+} + H_2O$$
. (5)

We identified four (or five) alteration phases (dehydrated schoepite is a tentative identification). Thus there are five precipitation reactions of interest. The precipitation of schoepite is

$$UO_{2}^{2+} + 3H_{2}O \implies UO_{3} \cdot 2H_{2}O + 2H^{+}.$$
 (6)

The precipitation of dehydrated schoepite is

$$UO_2^{2+} + 1.75H_2O \implies UO_3 \cdot 0.75H_2O + 2H^+.$$
 (7)

The following reaction represents the precipitation of Na-compreignacite:

$$3(UO_2)^{2+} + Na^+ + 9H_2O \implies Na[(UO_2)_3O_2(OH)_3](H_2O)_3 + 7H^+.$$
 (8)

The precipitation of soddyite is

$$2(UO_2)^{2*} + H_4 SiO_4^0 + 2H_2 O \implies [(UO_2)_2(SiO_4)](H_2O)_2 + 4H^*.$$
(9)

The precipitation of Na-boltwoodite is

$$(UO_2)^{2^+} + H_4 SiO_4^0 + Na^+ + H_2 O \implies Na[(UO_2)(SiO_3OH)](H_2O) + 3H^+.$$
 (10)

We believe that the replacement of the early formed uranyl oxide hydrates, metaschoepite, dehydrated schoepite, and Na-compreignacite, is probably important, based on the results of the UO_2 drip tests [WRONKIEWICZ et al.-1992; 1996]. For example, the replacement of metaschoepite by soddyite may be important

$$2UO_3 \cdot 2H_2O + H_4SiO_4^0 \Rightarrow [(UO_2)_2(SiO_4)](H_2O)_2 + 4H_2O$$
. (11)

The replacement of metaschoepite by "Na-compreignacite" may occur, although we did not observe evidence for this reaction:

$$3UO_3 \cdot 2H_2O + Na^+ \Rightarrow Na[(UO_2)_3O_2(OH)_3](H_2O)_3 + H_2O + H^+.$$
 (12)

Because both Si and Na are abundant in EJ-13 water, a reaction that is probably important is the replacement of "Na-compreignacite" by Na-boltwoodite:

$$Na[(UO_2)_3O_2(OH)_3](H_2O)_3 + 3H_4SiO_4^0 + 2Na^+ \Rightarrow 3Na[(UO_2)(SiO_3OH)](H_2O) + 5H_2O + 2H^+.$$
(13)

The replacement of soddyite by Na-boltwoodite may also be important:

$$[(UO_2)_2(SiO_4)](H_2O)_2 + H_4SiO_4^0 + 2Na^+ \Rightarrow 2Na[(UO_2)(SiO_3OH)](H_2O) + 2H^+.$$
(14)

All of these reactions are pH dependent. The precipitation and replacement of phases in the corrosion rind tend to decrease pH as these reactions remove Na from solution. A decrease in pH tends to enhance the dissolution of the spent fuel according to the reaction II-4. Other factors may moderate the pH; among the most important of these factors is carbonate equilibrium in the presence of atmospheric CO_2 :

$$HCO_3^- + H^+ = H_2CO_3$$
 $K_{s1} = 6.33 (25^{\circ}C)$. (15)

We have written the foregoing reactions with all U being conserved in the solid phases. This is consistent with the low quantities of U released to solution in the high-drip-rate tests. We expect similar U retention by the alteration phases in the low-drip-rate tests.

C. <u>Vapor-Hydration Tests</u>

1. Analysis of Sample from ATM-103 Fuel after 4.1 Years Reaction

We removed only a small amount of material from the reacted spent fuel during sampling of this vapor-hydration test of ATM-103 fuel after 4.1 years reaction. Two morphologies are apparent among the solids examined optically: (a) finely fibrous tan-colored crystals and (b) tabular to bladed yellow crystals. We were readily able to extract the yellow crystals from the tape adhesive, whereas the tan crystals were not so easily extracted. Both materials occur as scattered crystals, rather than as the tufts or clumps more common in the samples from the drip tests.

Scanning electron microscopy/energy dispersive spectroscopic (SEM/EDS) examination indicates that the tabular and blocky crystals are essentially pure U oxides. Most of these crystals are bladed to somewhat boat-shaped (Fig. 12), a morphology characteristic of dehydrated schoepite, $UO_3 \cdot 0.8H_2O$. However, the tabular morphologies of some crystals in this sample are characteristic of metaschoepite, $UO_3 \cdot 2H_2O$. Only pure H_2O reacts with the fuel (i.e., the condensed water vapor), and we expect U^{6+} oxy-hydroxides to be the most abundant alteration products formed in these tests. No transuranium- or fission-product-containing phases are apparent from SEM/EDS examinations of these samples. We did not conduct XRD analyses because of the extremely small amount of material obtained.



Fig. 12. ATM-103 Sample: Uranyl Oxy-Hydroxides from Surface of Sample, Mounted on C-Tape. Small crystals at left are probably dehydrated schoepite; central crystals may be metaschoepite; scale bar at bottom center $\cong 5 \ \mu m$; vapor test, 4.1 years reaction.

The fuel fragments display discrete fuel grains, and the surfaces of individual fuel grains are commonly pitted, which is indicative of dissolution along grain boundaries. Examination of a polished cross section shows an interface between the U^{6+} alteration phases and reacted fuel grains, but no clear reaction boundary is evident. Instead, the fuel grains show open grain boundaries – probably caused by grain-boundary-enhanced corrosion near the surface of the reacted fuel fragment – as well as clusters of fuel grains surrounded by the alteration products. Most of the alteration products occur along the outer margins of the fuel fragments.

2. <u>Analysis of Sample from ATM-106 Fuel after 4.1 Years Reaction</u>

We obtained only a small amount of material from the alteration rind during sampling of the vapor-hydration test of the ATM-106 fuel after 4.1 years reaction. The overall appearance of particles from this test resembles that of particles from vapor-reacted ATM-103 described above in Section II.C.1. The fuel grains form loosely aggregated clumps that fall apart

when manipulated. Scattered within the tape are numerous isolated crystals and small clusters of crystals. Two morphologies are apparent, differing slightly in hue: (a) finely fibrous light tanyellow crystals and (b) yellow, bladed to tabular crystals. Both morphologies are common, although the more equant yellow crystals are most abundant. We could not separate the fibrous crystals from the adhesive for examination by SEM/EDS. Under SEM examination, the fuel fragments display discrete fuel grains with pitted surfaces, indicating grain-boundary-enhanced dissolution. The yellow alteration products cling to the surfaces of the fuel grains, although not as tenaciously as observed for the drip-test samples. As noted for the sample from ATM-103 reacted in vapor, our SEM/EDS analyses indicate that the yellow crystals in this sample are essentially pure U oxides. Most are bladed or boat-shaped dehydrated schoepite, $(UO_2)O_{0.25+x}(OH)_{1.5-2x}$, although minor metaschoepite, $UO_3 \cdot 2H_2O$, may also be present (based on morphologies). We did not perform XRD analyses because of the small amount of material obtained.

3. Discussion of Vapor-Hydration Tests

The two samples of fuel examined from the vapor-hydration tests have similar appearance. Both show evidence for grain-boundary-enhanced dissolution. Pitted grain boundaries and loosely aggregated grains are common, and alteration products commonly surround the fuel grains nearest the surface. The extent of water penetration along the grain boundaries is uncertain at this time.

The alteration products identified include dehydrated schoepite and, possibly, metaschoepite. We detected no transuranic elements or fission-products as major constituents of any of the alteration products examined thus far with EDS (detection limit approximately 1-5 wt.%). See Section II-D for results of analyses of these samples using TEM.

The chemical reactions that occur in the water film on the fuel surfaces are important to understanding the evolution of the alteration products. Once again, we begin with the dissolution of the fuel. The (simplified) reaction for the oxidative dissolution of the UO_2 fuel is

$$UO_2 + 2H^+ + 1/2 O_2 \implies (UO_2)^{2+} + H_2O$$
. (16)

The precipitation of dehydrated schoepite is

$$UO_{2}^{2+} + 1.8H_{2}O \implies UO_{1} \cdot 0.8H_{2}O + 2H^{+}$$
. (17)

The replacement of the UO_2 fuel by dehydrated schoepite is

$$UO_2 + 1/2 O_2 + 0.8H_2O \Rightarrow UO_2 0.8H_2O$$
. (18)

There is no net effect on the pH from reaction (18) alone; however, we expect the pH to decrease somewhat due to hydrolysis of the uranyl ion:

$$UO_2^{2+} + yH_2O \implies UO_2(OH)_n^{(2-n)} + yH^+,$$
 (19)

and in the presence of bicarbonate, uranyl dicarbonate may be significant at near-neutral pH:

$$UO_2^{2^+} + 2HCO_3^- \Rightarrow UO_2(CO_3)_2^{2^-} + 2H^+$$
. (20)

At high concentrations of dissolved U (greater than approximately 10^{-6} M), polynuclear uranyl species become important:

$$xUO_2^{2+} + yH_2O \implies (UO_2)_x(OH)_y^{(2x-y)} + yH^+.$$
(21)

Atmospheric CO_2 will likely buffer the tendency towards lower pH values in the water film contacting the surface of the fuel. Furthermore, without additional cations available in solution, it is unlikely that pH values will decrease too sharply:

$$HCO_3^- + H^+ = H_2CO_3$$
 $K_{s_1} = 6.33 (25 \,^{\circ}C)$. (22)

We are uncertain at this time what roles that dissolved fission products and/or transuranic elements have on the pH. The concentration reached by such elements in the thin film of water that condenses on the surface of the fuel is probably small compared to total dissolved U, so the effect of dissolved U will dominate the chemistry of the water film. The abilities of the precipitated U^{6+} oxy-hydroxides, such as dehydrated schoepite, to incorporate additional elements may also influence the evolution of the water composition. Our early TEM results indicate that dehydrated schoepite and other U^{6+} oxy-hydroxides can incorporate some transuranic elements and fission products into their structures. Our simplifying assumption for the above equations, that the total U concentration effectively controls the chemistry of the film of water in the vapor-hydration tests, is probably valid.

D. <u>Summary</u>

Combined optical, SEM, EDS, and XRD examinations of samples taken from tests being performed on the two ATM fuels indicate that the rate at which groundwater contacts the fuel samples may be the most important single factor determining the alteration phases that form as spent UO₂ fuel corrodes in a humid oxidizing environment. Results from the three tests (high-drip-rate, low-drip-rate, and vapor) show several similarities, including corroded grain boundaries, dissolution of fuel grains, and precipitation of U⁶⁺-phases (Table 10). The vapor tests display the simplest assemblage of alteration products; only U and the radionuclides in the fuel dissolve into the thin film of water in contact with the fuel surfaces. The most abundant phase identified in the vapor tests is probably dehydrated schoepite, $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$ ($0 \le x \le 0.15$).

The drip tests display more chemically complex alteration phases, because of the interaction of the fuel with EJ-13 water (rather than water vapor only). The most abundant elements in EJ-13 water are Na and Si, and, not surprisingly, the most abundant alteration products in the drip tests are Na- and Si-bearing U⁶⁺ phases. Other U⁶⁺ phases are also present, including metaschoepite and β -uranophane, indicating the importance of additional minor phases and elements to the overall corrosion process.

An important observation at this stage is that the time-dependent evolution of the alterationphase assemblage appears to be strongly dependent on the rate at which the EJ-13 water contacts the spent fuel. Fuel samples exposed to the higher drip-rates (nominally 10 times higher than that of the low-drip-rate tests) display a comparatively simple phase assemblage, consisting of two uranophane-group silicates, β -uranophane and Na-boltwoodite (Table 10). In contrast, the sample from the low-drip-rate test displays a more complex alteration-phase assemblage, with four or five phases identified (Table 10). We believe that the simpler phase assemblage in the high-drip-rate tests reflects larger reaction rates for the spent fuel in these tests. Also, samples from the first sampling periods were not taken, and it is possible that the early phases formed but simply were not detected.

Phase	Formula	Test
Metaschoepite (?)	UO ₃ ·2H ₂ O (?) ^a	ATM-103 (LDR) ^b ATM-103 (vapor) ATM-106 (vapor)
Dehydrated schoepite	$(UO_2)O_{0.25-x}(OH)_{1.5+2x} \ (0 \le x \le 0.15)$	ATM-103 (LDR) (?) ATM-103 (vapor) ATM-106 (vapor)
Unidentified Na-UOH	$(Na,K)[(UO_2)_3O_2(OH)_3](H_2O)$ (?)	ATM-103 (LDR)
Soddyite	$(UO_2)_2 SiO_4(H_2O)_2$	ATM-103 (LDR)
β-uranophane	Ca(UO ₂) ₂ (SiO ₃ OH) ₂ (H ₂ O) ₅	ATM-103 (HDR) ^b
Na-boltwoodite	(Na,K)(UO ₂)(SiO ₃ OH)(H ₂ O)	ATM-103 (LDR) ATM-103 (HDR) ATM-106 (HDR)

Table 10. Alteration Phases Identified by SEM or XRD from ATM Test Samples

^a(?) indicates a tentative identification or an uncertain formula. ^bLDR = low-drip-rate test; HDR = high-drip-rate test.

Another important observation concerns the identification of uranyl oxy-hydroxides in the vapor-hydration tests. The precipitation of dehydrated schoepite and metaschoepite in these tests indicates that the film of water that forms on the fuel surface is sufficiently corrosive to dissolve the fuel and form a thin corrosion rind of alteration products. Such a water film is likely present in the drip tests as well during those intervals that EJ-13 water is not being dripped onto the fuel. It seems likely that the corrosion processes important in the vapor tests remain important in the drip tests. Dehydrated schoepite and/or metaschoepite may continue to form in the drip tests between water injections. If these phases are present when contacted by EJ-13 water, they may be at least as susceptible to dissolution and/or replacement as the unoxidized fuel. The degree to which this may be important is unknown at this time.

The mechanism by which the fuel has reacted during these tests is important, although we have only limited information available at this time. Most striking is that the fuel in the high-driprate test on the sample from ATM-103 has dissolved along a uniform front that has penetrated from the outer surface into the spent fuel fragments. This through-grain dissolution has proceeded without regard to existing grain boundaries. The replacement of the fuel by Na-boltwoodite at the fuel surface may also be self-accelerating. Through-grain dissolution appears to be an important mechanism by which the fuel is reacting in the high-drip-rate tests. Of course, the dissolution of the fuel along grain boundaries is also important in the high-drip-rate tests. This type of dissolution is especially evident from the extent to which the grain boundaries in one fragment of the ATM-103 sample had been opened, resulting in a friable fragment that decomposed during sample handling.

These data are still preliminary. We must examine additional grains and fragments of reacted fuel to understand more fully the corrosion and alteration processes, including grainboundary penetration by water, changes in the reactive surface area, and the distribution of radionuclides between the alteration phases and the EJ-13 water.



III. EXAMINATION OF SPENT NUCLEAR FUEL WITH ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY

A. Introduction and Background

Analytical transmission electron microscopy is a versatile technique for examining the microstructure of corroded spent fuel. Thomas et al. [THOMAS-1989, -1990, -1992] demonstrated through their numerous studies characterizing spent nuclear fuels, that AEM was ideal for developing an understanding the microstructure of the low burnup fuels, especially ATM-103, ATM-104, and ATM-106. The features of interest in these fuels were not visible by any other technique. We have found that to determine the nature of oxidative corrosion in these materials, AEM has proven again to be an invaluable technique. The AEM samples extremely small regions so the representativeness of the data obtained must always be examined. The sample preparation methods employed, comparison with SEM and optical microscopy, and the number of AEM samples examined has helped to improve the representativeness of the analysis. Three important issues are addressed in this section: (a) the retention of Np in a secondary phase, (b) dissolution of the ε -particles, and (c) the segregation of Pu. Each of these issues is controversial and may be impossible to defend solely with the AEM data. Therefore, the comparison with the solution data (Section I) is critical in determining the total mass balance in the system.

B. <u>Objectives</u>

The objective of this task is to obtain information on the nature of the corrosion process in spent fuel, including compositional and structural information on the secondary phases and altered fuel. The behavior of the fission and neutron capture products during the anticipated corrosion of spent nuclear fuel in an oxidizing environment is important for determining the long-term release rates of radionuclides. With AEM, it has been possible to provide some information on the possible fates of some radionuclides present in spent fuel. In this section of the report, we describe the methods used for investigating the nature of the ε -phases within the fuel grains and in the grain boundaries. This evidence of corroded ε -phases is needed to support the use of the normalized loss of Tc as a measure of spent fuel corrosion.

C. <u>Technical Approach</u>

Representative particles of the corroded fuel were embedded in an epoxy resin and cut into thin sections with an ultramicrotome. The resultant 30-50 nm electron-transparent cross sections of corroded fuel grains were transferred to carbon-coated copper grids and examined in a JEOL 2000 FXII analytical transmission electron microscope operated at 200 kV with a LaB₆ filament. The AEM is equipped with a Gatan 666 parallel electron energy-loss spectrometer, which has an energy resolution of about 1.6-1.8 eV. The actinide M-edges were obtained by operating the spectrometer in the second-difference mode [BUCK-1997A]. This technique removes the channelto-channel gain variation that occurs with parallel detectors. The method also acts as a frequency filter, enhancing such sharp features such as the "white-lines" on the absorption edges. Hence, peak shape will affect the ability to detect an element. A rounded or smooth edge, for instance, will be less visible than a sharp edge. Electron diffraction patterns were taken with a charged coupled device (CCD) camera, which permits very-low-intensity viewing and, therefore, is ideal for electron-beam-sensitive materials.

D. <u>Results and Discussion</u>

The results of AEM investigations with ATM-103 are discussed in three parts of this section. First, evidence for the incorporation of neptunium into an alteration product of spent fuel is presented. Second, we will describe the behavior of ε -particles in ATM-103 during vapor-phase

corrosion and under high-drip-rate conditions, which supports the use of Tc as a marker element for spent fuel corrosion. Third, we will show data indicating the enrichment of plutonium during the corrosion process.

1. Incorporation of Neptunium into Secondary Phases

Using a unique anion topology approach for comparing the structures of uranyl phases, Burns et al. [BURNS-1996] has predicted mechanisms by which transuranic species can be incorporated into the alteration products of corroded spent fuel. The U-O bond length (0.18 nm) in the linear species UO_2^{2+} is similar to that of Np-O in NpO₂⁺ (0.165-0.181 nm), and when coordinated by O²⁻, OH⁻, or H₂O, the equatorial Np-O bond distances are only about 0.01 nm longer than those found in similarly coordinated uranyl polyhedra. Thus, it is reasonable to expect isomorphic substitution of the neptonyl ion in uranyl ion sites [BURNS-1996]. However, because of valence bonding considerations, the axial oxygens on the linear neptonyl species may require additional valence contributions from interlayer cations or protons in the uranyl phase.

a. <u>Analysis of Dehydrated Schoepite from Vapor Tests with EELS</u>

Analysis of the dehydrated schoepite phase with EELS indicated the presence of Np (Fig. 13). Since we examined cross sections of the corroded fuel grains and alteration products, it is unlikely that the occurrence of Np is due to sorption on the dehydrated schoepite; however, we cannot totally exclude this mechanism for retention of Np in an alteration phase. Neptunium was observed with EELS in three samples of dehydrated schoepite that were taken from different regions of the corroded fuel pellets. The U:Np ratio was estimated to be between 1:0.003 and 1:0.006, based on five analyses. In the dehydrated schoepite ($UO_3 \cdot 0.8H_2O$) where Np was detected, this ratio corresponds to one Np atom for every 250 unit cells of $UO_3 \cdot 0.8H_2O$ or about 550 ppm (Table 11). The U:Np ratio in the ATM-103 fuel is 1:0.0005, taken from calculated values reported by Guenther et al. [GUENTHER-1988] for ATM-103 at 35 MWd/kgM after 15 years. The estimated U:Np ratio in the alteration phase indicates that a large proportion of the Np has entered into the phase. Due to the scarcity of water on the fuel surface in the vapor tests, only a small amount of water was able to flow into the steel collection vessel positioned at the bottom of the test apparatus. Under these conditions, it might be expected that the highly soluble elements will become concentrated enough in the thin film of water to precipitate secondary phases. The absence of Pu and Am in the dehydrated schoepite supports the contention that mainly Np and U were mobilized during the corrosion process and incorporated into a secondary phase.

Under more dynamic conditions, where flowing water was present, the retention of the Np in alteration phases may not occur. The next section presents similar EELS analysis of uranium-bearing alteration phases formed under relatively high flow conditions.

b. <u>Analysis of Uranium Silicate Alteration Phases from High-Drip-Rate Tests</u> with EELS

In the related high-drip-rate tests, analysis of the corrosion products failed to indicate the presence of Np at the same level observed in the vapor tests. However, dehydrated schoepite was not one of the phases detected. In Fig. 14a and b, the EDS and electron diffraction analysis suggested that the corrosion product from this test was related to β -uranophane (ideally Ca[(UO₂)(SiO₃OH)]₂·5H₂O). A trace amount of ruthenium is present in the phase, and it can also be seen in the energy-loss spectrum (see Fig. 14c). The form of the uranyl alteration phases is dependent on the composition of the fluid in contact with the fuel. In the high-drip-rate tests, the fuel is contacted by silica-saturated EJ-13; hence, uranyl silicates are the dominant alteration products.



Fig. 13. Electron Energy-Loss Spectrum of Dehydrated Schoepite Showing the Presence of Np in the Phase. The two intense uranium edges (M_5 at 3552 eV and U- M_4 at 3728 eV) dominate the spectrum; however, the Np- M_5 edge at 3666 eV is clearly visible. The intensity of the Np edges has been increased 20x for easier viewing. The Np- M_4 edge at 3850 eV does not appear to be visible above the background.)

Analyses	U	Np	U:Np Ratio*
1	397912	3462	0.009
2	364624	3715	0.01
3	533660	3312	0.006
4	135517	300	0.002
5	576382	3482	0.006
6	16950	50	0.003
7	50300	206	0.004
8	471401	4769	0.01
9	336676	2081	0.006
	Average in dehyrated s	choepite ~ 1000 ppm	0.006

Table 11. Analyses of Dehydrated Shoepite

*Assuming electron cross-sections between U and Np do not vary.



Fig. 14. (a) X-ray EDS of an Alteration Phase from a High-Drip-Rate Test Reacted for 44 Months; (b) Electron Diffraction Pattern Taken Along [010] from the Uranyl Silicate Phase is Shown. (A β -angle of about 93° was obtained from the analysis of the patterns.) (c) Electron Energy-Loss Spectrum of Uranyl Silicate Alteration Phase from the High-Drip-Rate Test Showing the U-N Edges and (d) Spectrum Showing the High Energy-Loss M-Edges of Uranium

Possibly some Np is in a uranyl silicate phase; if so, however, the levels are at or below the detection limits for the instrument. The estimated U:Np ratio is not more than 1:0.0005, which corresponds to <50 ppm Np in the phase; this level appears to be the detection limit. Substitutions of the type Np⁵⁺ \leftrightarrow U⁶⁺ may occur in all uranyl structures [BURNS-1997]; however, evidence from the majority of solution analyses from waste-form testing suggests that

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Np remains stable and complexes in solution under most common pH-Eh regimes. Nevertheless, within the thin film of water in contact with the spent nuclear fuel, significant alpha radiolysis will occur, leading to the possible formation of H_2O_2 . The altered Eh conditions may result in changes in the Np chemistry that may favor incorporation into the uranyl sheets. These sheets may be easily charge balanced through substitutions of the type $O^2 \leftrightarrow OH^2$. The most common oxidation state for Np in oxygen-rich waters is Np(V). In the vapor tests, because the pH of the contacting solution is unknown, describing the form of the Np would be speculative. However, calculations suggest that in a J-13 Yucca Mountain groundwater above pH 7.5, the dominant species is NpO₂(CO₃)², and below this pH 7.5 NpO₂⁺ would dominate[CLARK-1997]. The pH of the contacting solution in the high-drip-rate tests is known to be about 6 [FINN-1997], suggesting that NpO₂⁺ will be the most prominent species.

The incorporation of transuranics into the alteration products of oxide spent fuel corrosion has been predicted on the basis of crystal chemical considerations [BURNS-1996], although it has seldom been observed. The lack of observation may be due, in part, to the limitations of instrumental techniques and the difficulty in working with transuranic-bearing samples; however, knowledge of the specific conditions required for substitution of particular radionuclides into alteration phases may lead to development of engineered systems that may retard the migration of these radionuclides.

The observation of Np incorporation into dehydrated schoepite was only possible by examining thin sections of the reacted material with EELS. This technique has excellent detection capabilities and spatial resolution to locate regions where transuranics have been concentrated. Although the limits of detection for EELS are essentially functions of analysis time and beam intensity, when using the second-difference method, peak shape is also important. Future improvements in detection limits should be possible with the use of an energy-loss imaging filter that, when operated as a two-dimensional array spectrometer, is much more efficient than the parallel detector used in this study.

2. Evidence for the Dissolution of ε-Particles in Vapor and High-Drip-Rate Tests with ATM-103

As the ATM-106 fuel was not heated sufficiently to cause significant redistribution of fission products, the volatile fission products were unable to reach grain boundaries. However, temperatures in the fuel pellet centers (700-1200°C) were high enough to coarsen the "4d" ϵ -metal particles, fission gas bubbles, and pressurized fission-gas solids [GUENTHER-1988]. The fission products that form during burnup of oxide fuels may aggregate in one of three types of precipitates: gaseous, metallic, or oxide, depending on the burnup. Low burnup fuels, such as ATM-103, have not been found to contain ceramic oxide molybdates, zirconates, uranates, or cesium-bearing phases. However, high pressure Kr and Xe gas bubbles have been observed, along with ε -"ruthenium" phases that contain Mo, Tc, Ru, Rh, and Pd. Based on AEM and EDS analyses of the samples of spent nuclear fuel, most fission products in the low-release ATM-103 are thought to remain dispersed within the UO, matrix. Views to the contrary are based primarily on the evidence from short-term leach tests. These tests have shown preferential release of Cs, I, Sr, and Tc, which, it is argued, originate from the grain boundary regions. However, the detection limits for fission products within spent nuclear fuel analyzed with TEM-EDS are perhaps not sufficient to exclude the presence of fission products within the grain boundaries. Therefore, significant quantities of these elements could be present in the boundary regions, which if released first during corrosion testing, will exaggerate the estimated corrosion rate (it is assumed that the fission products are uniformly distributed throughout the UO₂ matrix).

The fission product, Tc, due to its high solubility and general tendency not to become incorporated into alteration phases, is being used as a "marker element" for calculating the

corrosion rate of spent nuclear fuel in the ongoing drip tests. Based on the preceding discussion, the Tc marker may be appropriate, at least for low burnup fuels. However, previous studies have suggested that the ε -phase is highly insoluble, and therefore the observed leached Tc must originate from grain boundary regions in the fuel.

Fission product segregation and precipitation in low-burnup, light-water-reactor fuels can only be effectively studied with AEM, as the features that are characteristic of these types of spent nuclear fuel can only be probed with a high spatial resolution instrument. As only limited transport of fission products occurred in the fuel, the features observed in one series of spent nuclear fuel grains are most likely representative of the entire material.

a. Corrosion of the ε -Phase

Particles of corroded spent fuel from the ATM-103 test were selected for further analysis with electron microscopy. Several interesting features were observed in this sample. Mo-Tc-Ru (ε -phase) phases were found within the spent fuel grain. The particles were extremely small, around 20 - 50 nm in diameter (Fig. 15). Some appeared weathered, but on the whole, they appeared uniform. The composition of many of the particles did not match that reported by Thomas et al. [THOMAS-1989; -1990, -1992] during AEM characterization of the ATM-103. Quantitative analysis by Thomas et al. of the 4d metals in the ε -particles agreed with the fission product ratio for these elements in ATM-103. This result supports the contention that all the 4d metals partition to the ε -phases. In this study of the corroded fuel, Tc and Mo appeared suppressed relative to Ru and Pd, suggesting that the phases may have experienced preferential leaching of Te and Mo.

We found two types of ε -ruthenium phase in the fuel, which again is consistent with the work of Thomas et al. (see Table 12); however, the Pd-rich phase may be described as α -Pd(Ru,Rh) phase based on tertiary plots by [KLEYKAMP-1985]. The εruthenium phase is the more acceptable 4d metal phase described by [THOMAS-1989]. Therefore, to describe the corrosion of the ε -phases, we have used the ratio of Mo/(Ru+Pd) to allow comparison of all particles observed. This ratio in uncorroded ATM-103 according to the ORIGEN2 code is one. Thomas et al. have also obtained this value in their analyses. In the particles found in the vapor test exposed to a corroding environment for 49 months, the Mo/(Ru+Pd) was found to be much lower for many of the analyzed particles. However, in comparison to the particles found in the ATM-103 high-drip-rate test, ɛ-ruthenium phases in the vapor tests retained more Mo (see Table 3). This indicates that the 4d-metal phases examined exhibited preferential removal of Mo during the corrosion tests. This partial corrosion of the εphases may provide some insight into the local oxidative conditions. The observed behavior is in agreement with the relative nobility of the 4d metals, but it goes against the egalitarian viewpoint of congruent alloy dissolution.

For comparison of quantification analysis results from Thomas and Charlot [THOMAS-1990] and from the ATM-103 high-drip-rate test fuel fragments are shown in Table 13. Thomas and Charlot [THOMAS-1990] were able to obtain very accurate EDS quantification of 4d metals in the ε -phases. We can quantify the ε -phases found in this vapor test, but for observing evidence of corrosion it may be better to use the spectra themselves. Table 12 also presents recent quantification of ε -phases with EELS and EDS. In the high-drip-rate sample, it was more difficult to prove evidence of corrosion of ε -ruthenium phases, as all appeared to be equally modified from the more typical composition. The Pu-rich region (Fig. 16) refers to a region in the ATM-103 fuel which had higher levels of Pu than most other portions of the fuel. This is discussed in more detail in the next section.

Evidence for the partial corrosion of the ε -phase supports the use of Tc as a marker element for spent fuel dissolution. However, there are still questions regarding the role of intra- and inter-granular ε -particles. Further analysis of thin sections of corroded fuel will be necessary to understand the possible differences.

3. <u>Plutonium Enrichment During the Corrosion of Spent Nuclear Fuel</u>

During the AEM examination of corroded ATM-103 fuel from both the vapor and high-drip-rate tests, regions were found that possessed anomalously high concentrations of plutonium (see Fig. 16). The enrichment levels in these regions far exceeded those reported in the uncorroded fuels [THOMAS-1989, -1992]. X-ray energy dispersive analysis indicated significant levels of Zr and Ru in this region. The origin of the Zr could be from either the cladding or the fuel. Although Zr is a fission product, the original fuel cladding was made of Zr and Zr is also the major component in the test apparatus as the retainer. It is possible that reaction might occur at the fuel's edge, where pellets are in contact with the Zr-bearing cladding. However, the levels of Pu in these regions are generally suppressed, due to the high burnup, and the regions exhibit high levels of fission products, such as rare earths. The EELS analysis indicated anomalously low concentrations of rare earths. Therefore, the enriched-Pu regions are most likely produced during oxidative corrosion. This may also suggest that Pu is not readily incorporated into uranyl phases. The possibility of $Pu^{6+} \leftrightarrow U^{6+}$ substitution or Pu^{4+} substitution into uranyl oxide hydrates and uranyl silicates has been speculated by Burns et al. [BURNS-1997]. In the high-drip tests, a possible pseudomorphic transformation of spent fuel (UO₂) to uranyl phases, might require isomorphic substitution of Pu for sites in the uranyl structures. To date, we have not found evidence for this occurrence; however, we do have supporting evidence for the accumulation of Pu into discrete areas in the corroded fuel. Regardless of their origin, the presence of enriched regions of Pu suggests that if these regions become friable, Pu-bearing colloids could be released.



Fig. 15. Transmission Electron Microscopy Image of ε -Ruthenium Particle within a Spent Fuel Grain

Element	Calculated ^a	Pd-Rich Partic	cles		
Mo	44	29	30	30	
Tc	11	9	12	11	
Ru	28	40	30	30	
Rh					
Pd	17	22	28	28	~100
Mo/(Ru+Pd)	0.98	0.47	0.51	0.52	
		Ru-Rich Parti	cles		
Мо		29	26	33	27
Tc		17	15	12	0
Ru		33	42	55	73
Rh ^c					
Pd		22	17		^b
Mo/(Ru+Pd)		0.53	0.44	0.60	0.36
	1				

Table 12. Composition of ϵ -Phase (elements in wt%) from the Results of the ATM-103 Vapor Hydration Tests

^aCalculated from Guenther et al. [GUENTHER-1989] for ATM-103 and normalized without Rh.

^bPd not analyzed in this case.

'Rh not analyzed in any sample.

Table 13. Composition of ε -Phase (elements in wt%) from the Results of the ATM-103 High-Drip-Rate Tests

		Unreacted	Edge	Pit	Pu-Rich
Element	Calculated ^a	Phase ^b	Region	Region	Region ^c
Mo	41.2	40	12.3	16.6	15.2
Tc	9.6	10	5.0	10.1	3.9
Ru	27.5	25	41.7	44.8	45.1
Rh	5.5	10	7.5	17.6	9.8
Pd	16.0	15	32.6	10.8	26.1
Mo/(Pd+Ru)	0.95	1.0	0.16	0.30	0.21
^a Calculated from (Guenther et al	GUENTHER-19	891 from ORI	GEN2 code for	30 MWd/kgM

ed from Guenther et al. [GUENTHER-1989] from ORIGEN2 code for 30 MWd/kgM at 15 years.

^bSemiquantitative EDS analysis by Thomas and Charlot [THOMAS-1990]. ^cQuantification of EELS was performed using a 100-eV window and the oscillator strength values calculated from a Dirac-Foch model by Ahn et al. [AHN-1989].



a

UO

100 nm

С





Fig. 16. Evidence of Pu-Rich Regions in a Vapor Test: (a) Transmission Electron Microscopy Image of Pu-Rich Regions within the Corroded ATM-103; (b) EDS of the Pu-Bearing Region Showing Enriched Levels of Ru and Zr; (c) Electron Energy-Loss Spectra from a High-Drip-Rate Test Comparing Enrichment of Pu in a Discrete Region against an Uncorroded Region of the Fuel.

E. <u>Future Studies</u>

We have demonstrated that the release of Np may be controlled by uranyl alteration phases formed during the corrosion of oxide spent nuclear fuel in an unsaturated environment. Although schoepite is only a transient phase in paragenesis of uraninite [WRONKIEWICZ-1997, FINCH-1992, PEARCY-1994], Finch et al. [FINCH-1989] have demonstrated that the schoepite at weathered uraninite deposit at Shinkolobwe has lasted over 250,000 years. Indeed, at the same site the uranyl carbonate, rutherfordine [UO₂(CO₃)], exhibited exceptional resistance to dissolution. This behavior may indicate that dehydrated schoepite may have the ability to retain neptunium for considerable periods.

The behavior of Pu during corrosion is extremely important, considering that even larger levels of Pu are being considered for placement in the proposed geologic repository. Accumulation of Pu as colloidal-sized aggregates imply for possible migration of Pu, whereas large accumulations of Pu may present criticality concerns. Further analysis of the nature of the Pu-rich regions is necessary to determine if the regions are amorphous sediments or well-defined structures.

IV. PETRI-DISH TESTS

A. Background

This section of the report describes several pilot tests that have been run to determine an experimental setup for batch tests on spent commercial fuel. These initial tests were not intended to be systematic experiments on the corrosion of UO_2 ; however, in addition to examining prospective test parameters, our results have provided some insights into UO_2 corrosion under the test conditions, and we describe our results here.

The "drip-tests" currently being performed on UO₂ and spent UO₂ fuel have demonstrated that these tests are effective methods of examining the alteration of UO₂ and spent fuel in an unsaturated environment, such as may be expected in the proposed repository at Yucca Mountain. Previous drip-test results demonstrated that UO₂ and spent fuel both react with a thin film of water to form a suite of U⁶⁺ alteration phases. Using current experimental designs, the suite of U⁶⁺ phases takes two to five years to fully develop. We have designed "petri-dish" batch tests that are intended to accelerate the alteration reactions observed in drip tests. We hope that relevant observations can be made in six months or less, allowing more rapid evaluation of test results.

In addition, the composition of the film of water in contact with UO₂ or fuel is not wellknown for the drip tests. In the current drip test method, a solution of known composition (EJ-13) is injected into a test vessel, where the water reacts with UO₂ or fuel. This solution eventually drips down through the UO₂ or fuel and accumulates at the bottom of the reaction vessel, from where it is periodically sampled for analysis. This analysis gives an indication of the chemical changes that the solution undergoes between injection and sampling; however, a more detailed knowledge of the composition of the thin film of water that is actually reacting with the UO₂ or fuel remains elusive. By providing just enough water to maintain a constant film of water on a small quantity of fuel in the batch test, we hope to more closely monitor the compositional evolution of water as it reacts to form U⁶⁺ alteration phases. Note, however, that in drip tests, cations consumed during reaction can be replenished, whereas, in the petri-dish tests, cations are not replenished.

B. Experimental Setup

As noted above, the tests on UO₂ described here are pilot tests. Results from each experiment were used to evaluate current test equipment and procedures, with changes being made where deemed necessary. Consequently, the experimental setup was modified during the course of the seven tests described here (Table 14) Modifications were, for the most part, minor, and included modifying the screen hanger design, adding H_2O_2 to the EJ-13 water in some tests, and changing screen material. Although each change had some impact on experimental results, a systematic study of the effects of each change was not attempted.

We did not want consumption of O_2 during the corrosion process to be a limiting factor. The 45-mL reaction vessel chosen for these tests is large enough to oxidize 0.2 g of UO₂ completely. The amount of water was limited by total surface area of UO₂; a relatively high rate of the sample surface area to solution volume S/V ratio was desired, as this is thought to be a critical factor controlling compositional changes to the thin film of water present in drip tests.

The initial equipment used for tests PDT-1 through PDT-6 consisted of a 45-mL, 304L stainless steel (SS) Parr reaction vessel (Fig. 17) with a hanger made of ~1.6-mm diameter (1/16-inch) 304L-SS to which a 316-SS, 325-mesh screen was spot welded (Fig. 17). Each reaction vessel was sealed with a Cu gasket and a Ni-plated brass compression fitting; the compression

fitting was tightened to 160 ft-lb at the beginning of each test. Tests were conducted in a convection oven kept at $90 \pm 1^{\circ}$ C.

Test ID	Screen Stainless Steel	Water	UO ₂ Prep.	UO ₂ Mass (g)	EJ-13 Mass (g)	S/V ^a (m ⁻¹)	Run (days)	(S/V) ^ª time (days·m ⁻¹)
PDT-1	316	EJ-13a	as sieved	0.1995	1.99	1200	42	50,400
PDT-3	316	EJ-13a	as sieved	0.2005	0.50	5000	28	140,000
PDT-4	316	EJ-13a (ox)	as sieved	0.2003	0.51	5000	35	175,000
PDT-5	316	EJ-13a	as sieved	0.1986	0.50	5000	114	570,000
PDT-6	316	EJ-13a (ox)	as sieved	0.2006	0.49	5000	70	350,000
PDT-7	304L	EJ-13b	EtOH rinsed	0.2004	0.50	5000	74	370,000
PDT-8	304L	EJ-13b (ox)	EtOH rinsed	1.9994	0.50	5000	70	350,000

 * S/V is ratio of solid surface area to solution volume; UO₂-particle surface areas calculated for spherical particles, 45 μ m in diameter.

Due to the corrosion of the 316-SS screens during the first six tests (the results are discussed in Section IV.C.2), a more corrosion-resistant screen material was used in the final two tests, PDT-7 and PDT-8. The new screen material chosen is a 304L-SS sintered and woven filter, manufactured by Pall (RigimeshTM). The new mesh was rated to remove 100% of particles greater than 45 µm in diameter and 98% of particles greater than 17 µm ("removal grade M").

The solid used in these tests was synthetic, unirradiated UO₂ with a natural isotopic abundance and an O:U ratio of 2.000 ± 0.002 (WRONKIEWICZ -1992). The UO₂, a pressed and sintered powder that had been formed into pellets (ANL special materials batch # 4-4-110), is the same material used in the unsaturated drip tests on UO₂ described by Wronkiewicz et al. [WRONKIEWICZ -1992, 1996]. X-ray diffraction analysis of the starting UO₂ powder demonstrated that storage had not oxidized the bulk of the UO₂.

Before use, pellets of UO₂ were crushed and ground by hand with an agate mortar and pestle. The resulting powder was sieved to between -200 and -325 mesh (particle sizes 75 - 45 μ m). The first five tests (PDT-1 through PDT-6) were performed with as-sieved UO₂ powder. For the final two tests, PDT-7 and PDT-8, sieved UO₂ powder was rinsed with ethanol (E+OH) to remove fines before use. Prepared UO₂ powders were analyzed by SEM to check grain size distributions. SEM micrographs of polished cross sections made from UO₂ from both preparations are shown in Fig. 18.





At the start of each test, we placed 0.20 g of UO₂ powder onto the stainless steel screen. The total O₂ in each 45-mL reaction vessel was sufficient to oxidize 8 x 10⁻⁴ moles of U⁴⁺ to U⁶⁺. The relevant reaction can be represented by reaction of the oxides: UO₂ + 1/2 O₂ \Rightarrow UO₃. One mole of air with 20 vol% O₂ occupies 22.4 L at 25°C and 1 atm. Thus, approximately 0.0004 mole of O₂ are in each vessel (the hanger and other test components are assumed to occupy approximately 1 mL). This amount of O₂ will oxidize 0.216 g of UO₂—hence our decision to use 0.2 g of UO₂ in these tests. Because of the small mass of UO₂ used, the total volume of water used was necessarily small.

SEM analyses of prepared UO₂ powder reveal a few solid impurities (Fig. 19). Qualitative chemical analyses of these impurities were performed by EDS during SEM examinations of polished sections. Material pictured in Fig. 19 is fine-grained and chemically inhomogeneous; it is probably a mixture of Fe-oxide(s) and an unidentified Fe-silicate. The number of known Fe-oxides and Fe-silicates that may occur as impurities in the UO₂ powder is extensive (Table 15), so more complete identification remains elusive at this time. Chemical impurities present in the initial UO₂ pellets at concentrations of greater than ~1 ppm include B, Si, Ca, Ni, Cu, Al, Cl, Th, and Fe [WRONKIEWICZ-1992]. Much of the Fe and Si are probably associated with Fe-silicate impurities, which are relatively common in the UO₂ starting material. EDS analyses of the Fe-silicate indicate Al, Ca, Mn, and U are also present. This material is very heterogeneous. The Fe-oxide has Al and minor Si.

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Fig. 18. SEM Micrographs of Polished Cross Sections through the UO₂ Starting Material:
(a) Unwashed; (b) Washed



Fig. 19. SEM Micrograph of a Polished Cross Section through the UO_2 Starting Material Showing an Unidentified Fe-Silicate Impurity

	Volui I office Oxides, I office Oxy Hydron	tides and I cirie Officates
Mineral or Compound	Formula	Comments
Bernalite	Fe(OH) ₁	"green rust," ← stottite grp.
Synthetic ferric hydroxide	Fe(OH) ₃	several preparations
Goethite	a-FeO(OH)	
Akaganeite	b-FeO(OH,Cl)	
Lepidocrocite	g-FeO(OH)	
Feroxyhite	d-FeO(OH)	
Ferrihydrite	FeO(OH)	poorly crystalline
Hematite	a-Fe ₂ O ₃	corundum group
Synthetic ferric oxide	b-Fe ₂ O ₃	
Maghemite	g-Fe ₂ O ₃	spinel group
Magnetite	Fe ₃ O ₄	spinel group
Greenalite-1T	$(Fe^{2+}, Fe^{3+})_{2,3}Si_2O_5(OH)_4$	kaolinite/serpentine grp.
Cronstedtite	$Fe_{2}^{2+}Fe_{3}^{3+}(SiFe_{3}^{3+})O_{5}(OH)_{4}$	kaolinite/serpentine grp.
Hisingerite	$Fe_{2}^{3+}Si_{2}O_{5}(OH)_{4}\cdot 2H_{2}O$	kaolinite/serpentine grp. (?)
Erlianite	$(Fe^{2^{+}},Mg)_{4}(Fe^{3^{+}},V^{5^{+}})_{2}Si_{6}O_{15}(O,OH)_{8}$	kaolinite/serpentine grp. (?)
Macaulayite	$(Fe^{3+},AI)_{24}Si_4O_{43}(OH)_2$	
Nontronite	$Na_{0.3}Fe^{3+}(Si,Al)_{4}O_{10}(OH)_{2} nH_{2}O$	smectite grp.
Synthetic Fe-silicate hydrate	$Fe_2Si_{90}O_{183}(H_2O)$	

Table 15. Listing of Several Ferric Oxides, Ferric Oxy-Hydroxides and Ferric Silicates

Other impurities identified during analyses of starting material or during analyses of reacted materials were much less abundant than Fe-oxides and Fe-silicates. These other impurities include particles of a metal alloy (Fig. 20) with Fe, Cr, Zr, Mo, Mn, Na, and Ni. A few small shards of silica glass (Fig. 21) were found in micrographs from some tests. Polycrystalline ThO₂, possibly with minor ThSiO₄ is rare, but it was found in test PDT-7. X-ray diffraction analyses of starting UO₂ powder indicate only UO₂ in the powder-diffraction pattern, so crystalline impurities make up less than 1% of the UO₂ powder analyzed by XRD.



Fig. 20. SEM Micrograph of a Polished Cross Section through Reacted Solids from PDT-3 Showing Metal-Alloy Impurity from PDT-3 (EDS)

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Fig. 21. SEM Micrograph of Glass Shard Found in Reacted Solids from PDT-3

The leachant used in these experiments was EJ-13 water. This water is from well "J-13" and has been heated at 90°C for 80 days in contact with powdered Yucca Mountain tuff (ground to -200 to +100 mesh). Two batches of EJ-13 were used in tests reported here. They are referred to as EJ-13a and EJ-13b and have the compositions listed in Table 16. In addition, three tests were conducted using EJ-13 water to which sufficient H_2O_2 was added to attain a concentration of approximately 0.1 M H_2O_2 (tests PDT-4, PDT-6, PDT-8). Addition of H_2O_2 was intended to allow examination of possible effects of radiolysis products on the rate of UO_2 dissolution and formation of alteration products. This concentration of H_2O_2 was chosen because it is within a concentration range for which kinetics of oxidative dissolution of UO_2 show a simple linear dependence on H_2O_2 concentration [dePABLO-1996].

While the same procedure was used to prepare both batches of EJ-13 water, there was some variability. Yucca Mountain tuff is a fine-grained volcanic rock (a rhyolite) containing minerals such as plagioclase, sanidine, and quartz, as well as volcanic glass. These components represent a solidified magma (a complex mixture of liquids, gases, and crystals) that was quenched at temperatures on the order of 800°C. "Equilibration" of water with a volcanic tuff is not possible at 90°C, because no water composition is in equilibrium with the components of a volcanic tuff at this temperature. Equilibration of groundwater would require complete alteration of the tuff components to an assemblage of minerals stable in the presence of water at 90°C, such as quartz, zeolites, and clays. The intention behind preparing EJ-13 water is to try to mimic the composition of a groundwater that may evolve in contact with tuff at elevated temperatures at a proposed repository at Yucca Mountain. Thus, of EJ-13 represents a kind of steady state for groundwater in contact with tuff at 90°C. Because the concentration of EJ-13 does not reflect true equilibrium, concentrations of EJ-13 prepared according to a specific procedure can be expected to vary somewhat, both because reaction of J-13 well water may not reach the same "steady state" in all preparations and because the composition of both J-13 and EJ-13 waters may vary over time, even after preparation. The variability of several analyses of EJ-13 water is illustrated in Fig. 22. Error bars shown in Fig. 22 indicate a variance of 30% in measured Na and Si concentrations. The value of 30% is used because this value is required in order to make analyses of identical batches overlap (i.e., to make them statistically identical). Such variability can affect the interpretation of data when the interpretation requires an accurate knowledge of the starting composition of the test solution. Thus, the EJ-13 water should be analyzed prior to initiating tests.

Element / Ion	EJ-13a	EJ-13b
Si	45.5	43.99
Na	53.6	58.19
Li	0.03	0.048
K	6.67	11.30
Ca	6.95	4.39
Mg	0.08	0.30
Fe	0	0.098
В	0.19	0.16
Al	0.68	1.02
U	0.001	0.001
F	2.4	3.4
Cl	7.5	21
NO ₃ -	10	14.9
NO ₂ .	0.12	0.71
SO4	20	27.9
HCO ₃	101.49	nd
pH	8.36	8.7

Table 16. Compositions of the Two Batches of EJ-13 Water Used in PDTs (concentrations in ppm except pH) (25°C)

Approximately 0.5 mL of EJ-13 was added to each reaction vessel. This volume of water was chosen to maximize the S/V ratio, while providing sufficient liquid to wet the UO_2 powder completely (and provide enough liquid for chemical analyses). The first test (PDT-1) used a slightly different hanger construction that required a greater solution volume to wet the sample. Therefore, PDT-1 has a much lower S/V ratio than other tests (Table 14).

C. <u>Analyses</u>

1. <u>Analytical Methodology</u>

At the completion of each test, the vessel was cooled in an ice bath and opened. The hanger was removed and set aside to air dry. Sufficient solution was taken for determining pH. If enough solution was available (usually more than ~300 μ L), 100 μ L was placed into an anion vial for anion analysis by ion chromatography. The remaining liquid was put into a 3-mL syringe and passed through a 0.45 μ m filter into a plastic (LPE) bottle where it was acidified to ~1% with high-purity nitric acid. The acidified, filtered solution was analyzed for cations by ICP-MS. The volume of water recovered at the end of each test varied, and anion analyses were not conducted for tests PDT-4 through PDT 8. Furthermore, due to loss of liquid to 0.45 μ m filters (approximately 0.025 mL), solution aliquots from PDT-4 and PDT-6 were not filtered, as so little liquid was recovered from these two tests (Table 17).



Fig 22. Reported Na and Si Concentrations in EJ-13 Waters Prepared by Reacting J-13 with Tuff at 90°C for 80 Days. Three preparations are shown, with analyses of each preparation indicated by the date of preparation. Error bars represent 30% sample variance. This is the variance necessary for different analyses from the same batch to be statistically identical. The analysis reported for EJ-13a in Table 16 is indicated by an asterisk.

	Table 17. Mass and Recover	y Rate of Solution Alic	quots at Test Termina	tion (al	l masses in gra	ms)
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Test ID	PDT-1C	PDT-3C	PDT-4C	PDT-5C	PDT-6C	PDT-7C	PDT-8C
Run loss [®]	0.08	0.09	0.04	0.14	0.19	0.13	0.24
Mass in vessel ^b	1.91	0.41	0.39	0.46	0.30	0.37	0.26
IC-PMS aliquot	1.40	0.195	0.125	0.183	0.175	0.189	0.046
pH & anion	0.15	~0.1	0.05	0.05	0.05	0.05	0.05
UO ₂ & screen ^d	~0.335	~0.09	~0.215	~0.202	~0.075	~0.106	~0.164
total mass lost ^e	~0.44	~0.205	~0.335	~0.267	~0.265	~0.261	~0.429
% recovery	78%	59%	34%	47%	46%	48%	19%

^aDifference between mass of vessel measured at test initiation and mass measured at test termination. This loss can be reduced by machining cut grooves into the vessel mating surface.

^b At test termination.

"Mass of solution aliquot analyzed (after filtration, if filtered).

^dMass retained as estimated by assuming 0.025 g left in the 0.45 µm filter (except PDT-4 & PDT-6).

^e Includes losses during run, loss to filter, and retention by UO₂ and screen.

Anion analysis was carried out for 0.1-mL aliquots taken from two tests (PDT-1 and PDT-3), although this analysis required too much solution; later test solutions have not been

analyzed for anions. Solutions for anion analysis were not filtered. The solution pH was measured after cooling the vessel to $\sim 20^{\circ}$ C by using a glass electrode and a Brinkman pH meter calibrated against approved NIST standard pH solutions.

After removing solid fragments of UO_2 and alteration products (if present) from each test vessel, they were dried in air while still on the screen. The dried powders were examined under an optical microscope. Particles were prepared for examination by SEM two ways: (1) several particles were selected during optical examination and mounted directly onto conductive carbon tape on an Al stub or (2) approximately one-half of the reacted powder (~ 0.1 g) was mounted in epoxy, which, when hardened, was ground and polished by hand using alumina polishing compound (0.3-µm final polish). All SEM samples were carbon-coated under vacuum. Analyses are performed with a TopCon SEM operated at an accelerating voltage of 15 kV and a beam current of 20 mA. Qualitative chemical analyses were performed by using EDS with a Lidrifted-Si solid-state detector and data-analysis software. Due to the small amount of reaction products generally present in these tests, the primary mode of phase identification was SEM/EDS. SEM provides information on phase morphologies and crystal habits, and EDS provides qualitative elemental analysis. When used in combination, these two methods usually permit positive identifications of most phases; however, anhedral or polycrystalline materials without distinct morphologies and chemically similar materials having similar habits cannot usually be distinguished without additional information.

Several U⁶⁺ phases known can be difficult to distinguish using SEM/EDS. These phases include, in particular, the U⁶⁺-oxyhydroxides, schoepite, $(UO_2)_8O_2(OH)_{12}(H_2O)_{12}$; metaschoepite, $UO_3 \cdot 2H_2O$; dehydrated schoepite, $(UO_2)O_{0.25-x}(OH)_{1.5+2x}$ (0 < x 0.15); and three synthetic hydroxide polymorphs of $UO_2(OH)_2$. Chemically, these phases appear virtually identical when examined by EDS. Morphologically, dehydrated schoepite tends to form small, thin, boatshaped crystals, as does α -UO₂(OH)₂. Schoepite and metaschoepite tend to form blockier crystals but display morphologies that are similar to each other. Dehydrated schoepite, schoepite, and metaschoepite are difficult to distinguish. Schoepite is not likely to form in the PDTs, however, because it is not stable at 90°C; it dehydrates to metaschoepite or dehydrated schoepite above ~ 40°C [FINCH et al.-1996]. Dehydration of hydrous minerals in the vacuum of the SEM (and during C-coating of samples) is also common, as is dehydration due to sample heating while under an electron beam.

Some other U⁶⁺ phases that can be difficult (or impossible) to distinguish by SEM/EDS include U-silicates. Boltwoodite, $K(UO_2)(SiO_3OH)(H_2O)$, and weeksite, $K_2(UO_2)_2(Si_5O_{16})(H_2O)_4$, are similar, as are their Na analogues, Na(UO₂)(SiO₃OH)(H₂O) and Na₂(UO₂)₂(Si₅O₁₆)(H₂O)₄. The two uranophane polymorphs (α and β), Ca(UO₂)₂(SiO₃OH)₂(H₂O)₄, cannot be distinguished with SEM/EDS, and haiweeite, Ca(UO₂)₂(Si₅O₁₆)(H₂O)₄, can be difficult to distinguish from the uranophane polymorphs. All these minerals share many structural elements and all have acicular habits. Weeksite, Na-weeksite, and haiweeite commonly form very small crystals, although this alone is rarely distinctive. Relatively high Si:U ratios in weeksite, Na-weeksite, and the uranophane polymorphs by EDS. Of course, the best way to distinguish these minerals is by diffraction methods, and diffraction is the only way to identify the uranophane polymorphs.

Finally, similarities in X-ray emission energies of $U-M_{\beta}$ and $U-M_{\lambda}$ lines to K-K_a and K-K_β lines make overlap of emission lines extreme. Potassium is exceedingly difficult to distinguish in the presence of uranium. Numerous K-bearing U⁶⁺ phases are known, and because of K in EJ-13 water, K-bearing phases might be expected to form. Only when K is present as a major constituent, however, can it be identified, but no semi-quantitative analysis of K is possible, even in that case.

The XRD powder diffraction is the most powerful technique for providing quantitative identification of materials present in sufficient quantities, usually ~1% or greater. TEM analysis can provide accurate phase identification, especially for very small crystals, provided that materials of interest can be isolated and adequately prepared. X-ray powder-diffraction data were collected from reacted solids from the PDT tests; however, we performed no TEM analyses on these samples.

In addition to phase identification, SEM provides information about replacement textures and phase paragenesis (sequence of phase formation). A paragenetic sequence can be inferred where late-stage minerals coat, replace, or surround earlier-formed phases.

2. <u>Results</u>

Solution compositions of leachates at test termination are reported in Tables 18 and 19. The mass of water recovered and recovery rate from each test are listed in Table 17. Solid U^{6+} alteration products identified are listed in Table 20.

Test ID	PDT-1C	PDT-3C	PDT-4C	PDT-5C	PDT-6C	PDT-7C	PDT-8C	
Filtration ^a	F	F	uF	F	uF	F	F	
Si	35.9	41.5	69.0	40.3	51.3	32.7	37.4	
Na	53.3	75.8	89.7	85.6	92.8	66.5	65.2	
K	7.91	< 21.3	< 22.1	< 84.3	< 21.5	< 86.3	< 104	
Li	0.385	< 5.33	< 5.52	< 6.33	< 5.37	< 6.48	< 7.83	
Ca	1.99	< 21.3	< 22.1	< 21.1	< 21.5	< 21.6	< 26.1	
Mg	0.208	1.34	3.16	4.00	1.94	0.543	1.40	
В	0.793	1.88	5.56	1.32	3.75	2.98	3.96	
Al	0.175	1.16	5.36	4.34	3.34	< 7.56	8.36	
U	0.812	36.9	3920	> 5.93	717	15.4	71.3	
F-	12	15	nd	nd	nd	nd	nd	
Cl-	12	23	nd	nd	nd	nd	nd	
NO ₃ -	42	184	nd	nd	nd	nd	nd	
NO ₂ -	1.6	< 5	nd	nd	nd	nd	nd	
SO4 ²⁻	57	105	nd	nd	nd	nd	nd	
pH	7.52	5.75	4.5	4.35	4.59	6.07	5.04	

Table 18. Concentrations of Components of EJ-13 Water and U at Test Termination (mg/L)

* Filtration of solution aliquots: F = filtered (0.45 µm); uF = unfiltered. nd = not determined

Test ID	PDT-1C	PDT-3C	PDT-4C	PDT-5C	PDT-6C	PDT-7C	PDT-8C
Cr	0.060	0.043	< 0.724	0.160	0.025	< 0.076	< 0.091
Mn	0.160	30. 3	14. 6	3.75	8.24	3.06	3.04
Fe	1.42	< 6.40	< 38.2	10.5	< 10.5	< 10.8	< 13.0
Ni	0.139	9.89	81.5	230	41.1	1.08	2.51
Мо	0.134	< 0.012	0.541	0.012	0.220	0.011	0.013

Table 19. Concentrations of Stainless Steel Components in Leachant at Test Termination (mg/L)

Table 20. Solid Alteration Products Identified or Suggested in PDTs^a

Solid Phase	Formula(s)	Test ID
dehydrated schoepite	$(UO_2)O_{0.25-x}(OH)_{0.15+2x}$ ($0 \le x \le 0.15$)	PDT-4, PDT-6, PDT-8 (?) ^b
metaschoepite	UO ₃ ·2H ₂ O	PDT-5
compreignacite (?)	K ₂ (UO ₂) ₆ O ₄ (OH) ₆ (H ₂ O) ₈	PDT-8
soddyite	$(UO_2)_2(SiO_4)(H_2O)_2$	PDT-6
uranophane (?)	$Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$	PDT-7
swamboite (?)	U ⁶⁺ (UO ₂) ₆ (SiO ₃ OH) ₆ (H ₂ O) ₃₀	PDT-7

*All phase identifications are tentative, and are based on SEM and EDS only.

^b"(?)" indicates a high degree of uncertainty in the phase indicated.

Results are presented separately for each test. Numbering of each test reflects the order in which each experiment was started; however, this does not necessarily reflect the order in which tests were completed. The discussion below is organized according to the order in which experiments were started. Some observations may therefore appear "out of order" in terms of reactions described. Results for those tests in which we used unmodified EJ-13 water (either from batch a or batch b) are presented first, followed by results for those tests in which EJ-13 water contained an added 0.1 M H_2O_2 ("EJ-13 ox"). H_2O_2 was added to three tests (PDT-4, PDT-6, and PDT-8) in order to enhance oxidative dissolution of UO_2 ; however, several other effects of adding the EJ-13 ox water to the starting test solution are apparent from the results. These effects include consistently lower pH values (Table 18), formation of dehydrated schoepite in only those tests with EJ-13 ox (Table 20), and a somewhat lower recovery rate of leachant at test termination (Table 17, Fig. 23).

Test PDT-1 was the first test conducted and served primarily as a preliminary test because we had little concrete information about potential reaction rates and what experimental conditions were necessary for a successful test run of minimal duration. Test PDT-1 had a much lower S/V ratio than other tests (Table 14). After terminating PDT-1, we decided to increase S/A in subsequent tests by decreasing the volume of water from approximately 2 g to approximately 0.5 g, resulting in a four-fold increase in the S/V (the mass of fuel is already near a maximum for the reaction vessel being used, and the grain sizes of UO₂ are as small as practicable). This decision required a slight redesign of the existing screen hanger, which was initially constructed with mesh screen welded to the top of a wire loop (Fig. 17). As discussed below, this change proved successful for enhancing dissolution of UO₂ and precipitation of alteration products. On the other hand, the smaller volume of water resulted in much less solution being available for chemical analyses at test termination (Table 17). However, it should be possible to do the major analysis with the amount of water recovered.



Fig. 23. Total Recovery Rate of Test Solutions

a. Experiments using EJ-13

<u>PDT-1 (42 days)</u> - The purpose of this test was to examine the proposed experimental parameters. The design for the screen hanger used in this test was slightly different from that used in all subsequent tests. A 316-SS, 325-mesh screen was spot-welded to the top of the wire loop at the base of the hanger (Fig. 17). We used UO₂ powder as sieved. This introduces some error in estimating S/V (the estimate is a minimum), but we were hoping to maximize the amount of UO₂ that would react. Initially, we added 0.8 g of EJ-13a water to the vessel bottom. We placed the hanger, with 0.1995 g of UO₂ powder, into the vessel and added EJ-13a water a drop at a time until the water reached the bottom of the mesh screen and wetted the UO₂. The total mass of water used in this test was 1.99 g (Table 14). The reaction vessel was kept at 90°C for 22 days, at which time we opened it and visually examined the contents. No obvious signs of reaction were apparent; i.e., no solid alteration products were visible (as discusses below, visual examination was not a suitable technique for judging the onset of alteration-phase formation). We resealed the vessel and returned it to the 90°C oven for another 20 days. After 42 days total reaction time, we terminated the test.

At test termination, water at the bottom of the vessel was clear, with several black grains apparent on the bottom. Enough solution remained in the reaction vessel after removing the hanger and UO₂ to permit analyses for both cations and anions. We extracted approximately 0.05 mL of solution to determine pH, and then took a 0.100-mL aliquot for anion analysis. We filtered the remaining solution through a 0.45- μ m filter using a 3-mL syringe. After filtration, we recovered 1.4 g of solution for cation analysis (Table 17).

Anion analysis (Table 18) indicates that concentrations of anions in the final solution are higher than in the starting solution, EJ-13a (Table 16). We have no explanation for this result at this time, except to note that the time between collecting solution at test termination and analyzing it by ion chromatography was three months; it is possible that some water evaporated during that interval.

The cation analysis (Table 18) indicates no significant change in major elements initially present in EJ-13a water. Of course, concentration of dissolved U increased due to dissolution of UO_2 . The solution concentration of U in this test is the lowest of the seven tests described here. The solution concentrations of 316-SS components (Cr, Mn, Fe, Ni, Mo) are low, although dissolved Fe is significantly higher in the test solution than in the EJ-13a water (Table 19). The solution pH in this test decreased from 8.2 to 7.5.

When we first opened this test vessel after 22 days, the UO_2 powder had spread out across the screen, forming a more or less uniform layer one or two particles thick. The powder was wet but was not covered with water. The powder appeared black. No discoloration of the stainless steel was apparent. The vessel was resealed, and mass loss during this interim examination was less than 0.03 g.

After an additional 20 days at 90°C, when we terminated the test, the appearance of the UO_2 powder on the screen was essentially unchanged from earlier observations. There were no obvious alteration products; the UO_2 powder was black and had spread evenly across the screen; UO_2 powder was uniformly wetted but not covered with standing water. After removing the screen hanger from the vessel, we noticed numerous black particles at the bottom of the vessel.

After drying the reacted powder on the screen, we examined the solids under an optical microscope. The powder was shiny black, and several reddish clumps were on the screen and within the UO₂ powder; several otherwise black grains showed some red reflectance in some orientations. There were no yellowish solids apparent, indicating a lack of U⁶⁺ alteration products.

The SEM examination of the reacted powder confirmed that no U_{6+} alteration products had precipitated. The UO₂ particles appeared similar to unreacted UO₂. Some dissolution along UO₂ grain boundaries was apparent (Fig. 24), but the extent of dissolution between grains is difficult to ascertain, because very minor grain-boundary gaps were also apparent in the starting material (Fig. 18). We found an unidentified Fe-silicate adhering to some grains of unreacted UO₂. An unknown Fe-silicate was also found in the reacted solids. Fig. 25 shows some Fe-silicate that appears to mimic the square grid of the mesh screen, indicating that this material may have precipitated during the test. EDS analyses indicate that the Fe-silicate is chemically heterogeneous and contains minor Al and Mn in addition to Fe and Si.



Fig. 24. PDT-1: SEM Micrograph of a Polished Cross Section through Reacted UO₂ (BSE image) Showing UO₂ Particle and Internal Grain Boundaries



Fig. 25. PDT-1: SEM Micrograph of a Polished Section through Reacted UO_2 (BSE image) Showing Heterogeneous Fe-Silicate that has Formed a Stringer which Appears to Mimic the Square Grid of the Mesh Screen. EDS of this material indicates minor Al and Mn.

An XRD pattern obtained from the reacted powder indicates that the powder is essentially UO_2 and had not oxidized to $UO_{2.25}$. Although the UO_2 particles were steel black at test termination, the powder appeared brick red after grinding it for XRD analysis. This color is consistent with a low O:M ratio in UO_2 ; i.e., O:M < 2.07 [FINCH -1991]. We could detect no minor phases in the diffraction pattern; the detection limit is only a few volume percent.

<u>PDT-3 (28 days)</u> - For the most part, this test was conducted identically to PDT-1 (Table 14) except the hanger design has been revised. For this test, a 316-SS, 325-mesh screen was spot-welded to the *bottom* of the hanger loop (Fig. 17). This configuration allowed us to use less EJ-13a water (0.5 g), which provided a higher S/V ratio without using additional UO₂. The S/V ratio estimated for this test is approximately 5000 m⁻¹, a factor of about four larger than estimated for PDT-1. When added to the vessel, the water did not uniformly wet the bottom of the vessel but remained as a "lens" that covered approximately one-third to one-half of the vessel bottom. We ran this test at 90°C for 28 days, about two-thirds as long as PDT-1; however, the S/V ratio was approximately four times higher. These conditions were still insufficient to precipitate any U⁶⁺-bearing alteration products. In fact, results from this test are similar to those from PDT-1.

At test termination, water at the bottom of the vessel was clear, with several black grains on the vessel bottom. Enough solution remained in the reaction vessel after removing the hanger and UO_2 to permit analyses for both cations and anions. We extracted approximately 50 µL of solution to determine pH and then took an approximate 75 µL aliquot for anion analysis (Table 18). We filtered the remaining solution through a 0.45-µm filter using a 3-mL syringe. After filtration, we recovered 0.195 g of solution for cation analysis. The total solution represents about 40% of the initial 0.5 g of water.

Anion analysis (Table 18) indicates that the concentrations of anions in the final solution is higher than in the EJ-13a starting solution (Table 16). We already noted in the preceding section (on PDT-1) that the time between collecting and analyzing the solution was three months; water evaporation may be a factor, although the lower volume of solution taken during test termination may also have had an effect. The solution was diluted before analysis of this solution aliquot.

Cation analysis (Table 18) indicates no significant change in major elements initially present in the EJ-13a water; however, measured concentrations of minor elements, Mg, B, and Al are approximately five times higher than in EJ-13a (Table 18; cf., Table 16). Estimated errors for ICP-MS analyses of light elements is approximately 15%, so the difference in the concentration of the minor elements is statistically small or insignificant. Dissolved U is almost two orders of magnitude greater than in PDT-1, a significant increase. Of the five 316-SS components (Cr, Mn, Fe, Ni, Mo), solution concentrations for only Mn and Ni are significantly higher than for PDT-1 (Table 19). Solution pH in this test decreased from 8.2 to 7.5.

At test termination the powder was spread more or less evenly across the screen. There were no obvious alteration products; the UO_2 powder was black. The powder was uniformly wetted but not covered with standing water. After removing the screen hanger from the vessel, numerous black particles were observed at the bottom of the vessel.

After drying the solids on the screen, we examined the reacted powder under an optical microscope. The powder was shiny black with numerous reddish clumps on the screen and within the UO_2 powder. The screen was slightly discolored, and several reddish particles of what looked like rust were apparent. We could see no yellowish solids.

We prepared the reacted powder for SEM examination. As for PDT-1, SEM examination demonstrated that the only U-bearing material present was UO_2 . The UO_2 particles appeared similar to unreacted UO_2 . There is some apparent dissolution along UO_2 grain boundaries, especially nearest the outer surfaces of particles (Fig. 26). Some particles display variable back-scattered electron contrast, a feature common in partly oxidized UO_2 , where brighter contrast material is usually $UO_{2.25}$. However, an XRD powder pattern obtained from the reacted powder indicated that the powder was predominantly UO_2 with little or no $UO_{2.25}$ apparent. Unit-cell parameters of the reacted powder have not been calculated at this time, however, and this is required before a more confident statement can be made. Nevertheless, upon grinding the reacted powder for XRD analysis, the powder was brick red, which is consistent with a low O:M ratio. No minor phases could be identified with confidence in the diffraction pattern, although some low-intensity diffraction peaks are evident above background.



Fig. 26. PDT-3: SEM Micrograph of a Polished Section through Reacted UO₂ Particles Showing Grain-Boundary-Enhanced Dissolution Near the Surface

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We found an unidentified Fe-silicate adhering to some grains of unreacted UO_2 . The more common Fe-bearing material, an oxide or oxy-hydroxide, occurs as both finegrained coatings on clusters of UO_2 grains (Fig. 27) and as discrete morphologies, commonly as hollow vase-shaped particles (Fig. 28). These latter particles were definitely formed during the test run.



Fig. 27. PDT-3: SEM Micrograph of the Fine-Grained Mixture of Ferric Oxy-Hydroxides and Fe-Silicate (?) on UO₂ Particles



Fig. 28. PDT-3: SEM Micrograph of Ferric Oxy-Hydroxide Precipitated on UO₂ Particles

<u>PDT-5 (114 days</u>) - This test was run for a total of 114 days at 90°C, the longest experimental run of the seven tests described here. The test was interrupted after 72 days, but due to a lack of apparent reaction progress, it was run for another 42 days. The experimental setup for this test is identical to that of PDT-3 (Table 14).

We made no visual observation of the solution during the interruption at 72 days, but at test termination, water at the bottom of the vessel was clear, with several black grains on the vessel bottom. No solution aliquot was taken for anion analyses. We extracted approximately 50 μ L of solution to determine pH, and filtered the remaining solution through a 0.45- μ m filter using a 3-mL syringe. After filtration, we recovered 0.183 g of solution for cation analysis, about 50% of the initial 0.5 g of EJ-13a water (Table 17).

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Cation analysis (Table 18) indicated no significant change in major elements initially present in EJ-13a water, although Na seemed to be somewhat high (Table 18). Measured concentrations of Mg and Al were elevated, about 20 times higher than in EJ-13a (Table 18; cf. Table 16). This difference is statistically significant. The concentration of dissolved U was high enough in solution to "swamp" the detector during ICP-MS, and there was not enough solution to conduct a second analysis. The reported U concentration is therefore a minimum (Table 18). Of the five 316-SS components (Cr, Mn, Fe, Ni, Mo), only Cr and Mo are unchanged relative to earlier tests, whereas Fe, Mn, and Ni are significantly higher (Table 19). The highest concentration is for Ni, which is, at its highest concentration among all the tests reported here. Solution pH in this test decreased from 8.2 to 4.35, which is the lowest value among all the tests (Table 18).

After 72 days, the reaction vessel was opened and the powder examined. The powder was spread evenly across the screen. No alteration products were obvious, and the UO_2 appeared black. The powder was uniformly wetted but not covered with standing water. There were no apparent U⁶⁺ alteration products (that is, no yellow material). The vessel was resealed and returned to the oven for another 42 days.

At test termination (114 days), the powder was spread more or less evenly across the screen; however, a few small clumps were visible. No alteration products were obvious, and the UO₂ appeared black. The powder was uniformly wetted but not covered with standing water. There were no apparent U^{6+} alteration products (no yellow material). The hanger wire was discolored to a light reddish brown over much of its surface.

After drying the reacted powder on the screen, we examined it under an optical microscope. Much of the powder had formed clusters of a few tens of particles. These clusters were held together by small translucent yellow crystals. These crystals were common, appearing throughout the powder, but they were most apparent in the clusters.

The screen and hanger appeared to have rusted. Numerous reddish precipitates were apparent on the screen and hanger. Abundant reddish particles were also apparent within the UO_2 powder, although they were approximately as abundant as found in the tests described below.

We prepared several clusters of UO₂ as well as some other particles for SEM examination. The translucent yellow crystals that held the clusters together are metaschoepite (identification based on crystal morphology and chemical composition from EDS analyses, Fig. 29). Except for metaschoepite crystals, the UO₂ surfaces appeared similar to unreacted UO₂. There were no obvious indications of more dissolution than occurred for tests in which no U⁶⁺ alteration phases had precipitated. Metaschoepite crystals are 10-50 μ m across and commonly form dense clusters between UO₂ particles. Many metaschoepite crystals in this test were coated by a fine-grained material (Fig. 30), but there was no apparent difference in the compositions of metaschoepite and the overlying material.

There was some apparent dissolution along UO_2 grain boundaries nearest the outer surfaces of the particles, but this dissolution did not extend more than a few grain diameters into the UO_2 particles (Fig. 31). The XRD powder pattern obtained from the reacted powder indicated that the powder is predominantly UO_2 with little or no $UO_{2.25}$, and the powder for XRD analysis was brick red after grinding. No minor phases could be identified with confidence in the diffraction pattern, although some low intensity diffraction peaks were evident above background. One peak near 12° 2q indicates metaschoepite. Only a few percent of the sample observed by SEM is composed of metaschoepite.

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Fig. 29. PDT-5: SEM Micrograph of Metaschoepite Crystals Precipitated among UO₂ Particles



Fig. 30. PDT-5: SEM Micrograph of Metaschoepite Crystals with Fine-Grained Coating. The large irregular masses are UO_2 particles.



Fig. 31. PDT-3: SEM Micrograph of Polished Section through Reacted UO_2 Showing Metaschoepite Crystals between UO_2 Particles. Note reacted grain boundaries.

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Additional particles in the reacted powder examined by SEM include Feoxides, a Cu fragment (probably from the Cu gasket used to seal the vessel), and an unidentified, polycrystalline particle containing Ti, Fe, U, and Si, with minor Al and V (Fig. 32). We found no Fe-silicate particles during SEM examination.



Fig. 32. PDT-5: SEM Micrograph of Unidentified Polycrystalline Particle

<u>PDT-7 (74 days)</u> - This test used EJ-13b water, a different batch of water than that used in the previously described tests. The composition of EJ-13b is given in Table 16. In addition, the UO_2 powder used in this experiment (and in PDT-8) was washed with ethanol to remove surface fines. Washing reduces the effective surface area of the powder and eliminates rapid dissolution of the smallest particles at the beginning of a test. Another change to the configuration of this test was that a new 304L-SS mesh was used. This screen is a woven steel made by Pall, called Rigimesh. We decided to use this material because it is considered more corrosion resistant than the 316-SS screens used so far. The complete test configuration is summarized in Table 14.

At test termination, water at the bottom of the vessel was clear, with several black grains on the vessel bottom. We extracted approximately $50 \,\mu$ L of solution to determine pH, No solution aliquot was taken for anion analysis. We filtered the remaining solution through a 0.45- μ m filter using a 3-mL syringe. After filtration, we recovered 0.189 g of solution for cation analysis. This represents less than 40% of the initial 0.5 g of EJ-13b water (Table 17).

Cation analysis (Table 18) indicated no significant change in major or minor elements initially present in EJ-1a, 3b, although B is somewhat higher than in EJ-13a (Table 18; cf., Table 16). The difference is probably not statistically insignificant. Dissolved U is comparable to that reported for PDT-3. Concentrations of the five 316-SS components (Cr, Mn, Fe, Ni, Mo) remained low, probably reflecting that a different material was used for the screen (Table 19). Solution pH in this test decreased from 8.2 to 6.07, which is a significantly greater change but is higher than in most other tests (Table 18).

At test termination (74 days), the powder was spread evenly across the screen, and no small clumps were visible. No alteration products were obvious, and the UO_2 appeared black. The powder was uniformly wetted but not covered with standing water. There were no apparent U⁶⁺ alteration products (no yellow material).

After drying the reacted powder on the screen, we examined it under an optical microscope. The powder appeared unreacted; it was uniformly black and only discrete grains were evident. There was little discoloration of the hanger wire or screen mesh, only a few reddish areas. No precipitates were obvious, although some of the UO_2 particles displayed a reddish reflectance. There were a few light green particles resembling lint in the reacted power.

We prepared some of the reacted UO₂ powder, as well as the light green particles, for SEM examination. Almost all of the UO₂ particles were free of precipitates; however, a few tiny needle-shaped crystals were evident along the edges and faces of a several UO₂ particles (Fig. 33). EDS indicates that these crystals are a uranium silicate, but they are so small (<1 μ m in diameter) that the EDS results are qualitative at best. These crystals resemble uranophane, Ca(UO₂)₂(SiO₃OH)₂(H₂O)₅, but Ca is not evident in the X-ray emission spectrum. Either Ca is difficult to detect from such small crystals, due to the strong signal from underlying UO₂, or the crystals may be swamboite, U⁶⁺(UO₂)₆(SiO₃OH)₆(H₂O)₃₀, which contains only U, Si, and O but has a morphology similar to uranophane.



Fig. 33. PDT-7: SEM Micrograph of UO₂ Particle with a Surface Covered by Small Acicular Crystals that May Be Uranophane

The XRD pattern obtained from the reacted powder indicates that the powder is predominantly UO_2 with little or no $UO_{2.25}$; the powder for XRD analysis was brick red after grinding. No minor phases could be identified with confidence in the diffraction pattern, although some low-intensity diffraction peaks were evident above background. One peak near 12° 2q indicates metaschoepite. Only a few percent of the sample observed by SEM is composed of metaschoepite.

One cluster with an Fe-oxide and Fe-silicate composition was found during SEM examination (Fig. 34). This cluster may be the impurity from the starting powder. The greenish particles show low electron reflectance, and appear amorphous (Fig. 35). Their compositions are variable, containing Ti, Fe, Si, Mg, Al, Ca, and minor Pb.

b. Experiments using EJ-13(ox)

<u>PDT-4 (35 days)</u> - Because no U⁶⁺ alteration products precipitated in tests PDT-1 and PDT-3 within the time period anticipated, we decided to add H_2O_2 to the EJ-13 water as an oxidizing agent. H_2O_2 has been shown to alter the corrosion kinetics of both UO₂ and spent



Fig. 34. PDT-7: SEM Micrograph of a Cluster of UO_2 Particles with Fe-Oxide (hollow) and Fe-Silicate (granular clump)



Fig. 35. PDT-7: SEM Micrograph of Unidentified Greenish Material. Note small crystals on their surfaces.

UO₂ fuel ([GRAMBOW et al.-1996]). A recent study by de Pablo et al. showed that, within the concentration range 10^{-3} to 10^{1} M H₂O₂, kinetics of UO₂ corrosion are linearly dependent on H₂O₂ concentration [dePABLO-1997]. We therefore added 10^{-1} M H₂O₂ to EJ-13a starting solution (0.0096 g of 10.5 M H₂O₂ solution to 1.05 g of EJ-13a). This amounts corresponds to a calculated concentration of 0.096 M H₂O₂, a value corroborated by titrating the solution. Otherwise, all other test components used in this test were the same as used for PDT-3 (Table 14).

At test termination, water at the bottom of the vessel was reddish brown and slightly turbid. No particles were apparent at the bottom of the vessel. We extracted approximately 50 μ L of solution to determine pH, but no aliquot was taken for anion analysis. Only 0.125 g of solution remained in the vessel, and it was not filtered in order to save as much solution as possible for ICP-MS analysis. The total solution recovered corresponds to approximately 34 % of the initial 0.51 g of EJ-13a (ox) water (Table 17).

Measured concentrations of Na and Si in this solution were approximately 50% higher than the Na and Si concentrations in the starting solution (Table 18); however, this is within 2σ of measured Na and Si concentrations in EJ-13a. Measured concentrations of Mg, B, and Al were one to two orders of magnitude higher EJ-13a (cf., Table 16), and these differences are statistically significant. The concentration of dissolved U was the highest of any of the solutions analyzed; the concentration was about 100 times higher than in test PDT-3, which was conducted under similar conditions. Of the five 316-SS components (Cr, Mn, Fe, Ni, Mo), only concentration of Mn and Ni were significantly higher than for previous tests. The concentration of Ni in this test solution is the highest of all other test solutions (Table 19). Solution pH decreased from 8.2 to 4.5, which was lower than occurred for PDT-3, but is still comparable to results for other tests that had been run for longer reaction times (Table 18).

At test termination (35 days), the powder had formed numerous clumps on the screen, apparently even when it was wet. The powder was uniformly wetted but not covered with standing water. There were no obvious alteration products, and the UO_2 appeared black.

After drying the reacted powder on the screen, we examined it under an optical microscope. The overall appearance of the UO_2 powder was black, although abundant reddish brown particles were scattered throughout. The UO_2 powder had formed clusters up to approximately 1 mm across. Many UO_2 particles seem to be bonded together by "rust" particles. A few particle surfaces were also coated by a thin layer of yellow material. The screen was discolored and appeared rusty, although less so than the screen in test PDT-3, which had reacted under similar conditions.

We prepared reacted powder for SEM examination. Almost every UO_2 particle examined was covered with a sparse layer of bladed-to-tabular crystals, approximately 1-µm thick and up to 10-µm across (Fig. 36). The habit of these "boat-shaped" crystals, combined with EDS analysis revealing only U and O, indicate dehydrated schoepite. A few UO_2 particles had a dense coating of dehydrated schoepite, 5 - 10 µm thick. Some UO_2 particles display evidence for substantial dissolution of their surfaces and along their grain boundaries (Fig. 37), but this is not uniform. Other particles show little evidence of dissolution, even those with dehydrated schoepite crystals on their surfaces (Fig. 38). In fact, there seems to be no correlation between the appearance of a UO_2 particle ("fresh" or corroded) and whether dehydrated schoepite has precipitated on its surface. Crystals of dehydrated schoepite show no evidence for incipient dissolution, such as surface pitting or embayment.



Fig. 36. PDT-4: SEM Micrograph of Dehydrated Schoepite Crystals on the Surface of UO_2 Particle (~300 μ m across)



Fig. 37. PDT-4: SEM Micrograph of Polished Section through Reacted UO_2 Showing Dissolution of UO_2 Particle and Replacement by Dehydrated Schoepite (Compare with Fig. 38.)



Fig. 38. PDT-4: SEM Micrograph of Polished Section through Reacted UO₂ Showing Particle Displaying Little Reaction Texture. Crystals on surface are dehydrated schoepite.

The XRD pattern obtained from the reacted powder indicates that the powder is predominantly UO_2 with no detectable $UO_{2.25}$. As for all the other samples, the powder for XRD analysis was brick red after grinding. No minor phases could be identified in the diffraction pattern. Only a few percent of the sample observed by XRD is composed of dehydrated schoepite; this is consistent with our SEM observations.

Two Fe-bearing solids were found: an Fe-oxide (goethite) that had clearly precipitated during the test run (Fig. 39), and an Fe-silicate (?) that may be inherited from the starting material. A limited number of small metal-alloy particles were found and are compositionally identical to those found in the starting material. The Fe-bearing solids did not seem to inhibit formation of dehydrated schoepite. No dehydrated schoepite was observed on the

1.0

1.11.14

surfaces of Fe-oxide, but the Fe-silicate commonly has small dehydrated schoepite crystals on their surfaces. The Fe-oxide had a few impurities detectable with EDS; minor amounts of Al and Cr were observed in a few spectra during spot EDS analyses.



Fig. 39. PDT-4: SEM Micrograph of Ferric Oxy-Hydroxide (goethite?) Precipitated on a UO₂ Particle

<u>PDT-6 (70 days)</u> - The configuration of this test was identical to that of PDT-3. This test was conducted with EJ-13a (ox) water and ran for 70 days, twice the duration of PDT-4. This test is the longest one that we ran using the 316-SS screen and oxygenated water. Table 14 lists the complete test configuration.

At test termination, water at the bottom of the vessel was clear, but no black particles were seen on the vessel bottom. We extracted approximately 50 μ L of solution to determine pH, but we took no aliquot for anion analysis. The remaining solution was not filtered because we recovered only 0.175 g of solution for cation analysis. This amount is about 35% of the initial 0.49 g of EJ-13 water (Table 17).

Cation analysis indicates no significant change in major elements initially present in EJ-13a water, except for Na, for which the measured concentration after testing was approximately twice that of EJ-13a (Table 18). Measured concentrations of Mg, B, and Al are approximately an order of magnitude greater than in EJ-13a (Table 18; cf. Table 16). This difference is statistically significant. Measured concentration of dissolved U is the second highest among the tests reported here but is less than one-fifth of the measured concentration of U in PDT-4 (Table 18). Of the five 316-SS components (Cr, Mn, Fe, Ni, Mo), Mn and Ni levels are comparable to concentrations of these two elements in PDT-4 (Table 19). Solution pH in this test decreased from 8.2 to 4.6, which is the lowest value among all these tests (Table 18).

At test termination (70 days), the powder had formed irregular "ridges" on the screen. The powder was uniformly wetted but not covered with standing water. There were no obvious yellow U^{6+} alteration products, and the UO₂ appeared black.

After drying the reacted powder on the screen, we examined it the under an optical microscope. The reacted solids appeared much like those in test PDT-4. There were minor amounts of "rust" and a few UO₂ particles with yellowish green coatings. Most UO₂ particles were black. The hanger wire and screen mesh were somewhat discolored. Reddish brown particles were common throughout the reacted powder.

Numerous UO₂ particles examined by SEM were covered with a dense layer of crystals of various sizes and habits (Fig. 40). The largest of these crystals were tabular and somewhat boat shaped, 1 μ m or less thick and 2-5 μ m across. EDS analysis showed only U and O, indicating these crystals were dehydrated schoepite. Very small pyramidal crystals (1 μ m or less) were also abundant and commonly coated the dehydrated schoepite (Fig. 41). EDS analyses of these crystals were variable, due to their small sizes, but consistently showed Si, U, and O. These pyramidal crystals are probably soddyite. Dehydrated schoepite and soddyite form on some UO₂ particles as a crystalline mat so dense that the underlying UO₂ surface is completely obstructed. These mats are also commonly composed of a gel-like material, which is predominantly U and O with variable amounts of Si and minor Fe and Cr in some regions.



Fig. 40. PDT-6: SEM Micrograph of UO₂ Particle Coated by Thick Layer of Mixed U⁶⁺ Alteration Phases. Blocky crystals are dehydrated schoepite; soddyite occurs as small crystals near the top of the image; lower left is primarily Fe-oxide. Note cracks in U⁶⁺ alteration layer suggesting formation from a gel.



Fig. 41. PDT-6: SEM Micrograph of Sub-Micron-Sized Soddyite Crystals Coating Dehydrated Schoepite Crystals

1. Oak

A few UO₂ particles displayed evidence for dissolution of their surfaces but rarely along grain boundaries. Grain-boundary-enhanced dissolution, where apparent, did not penetrate deeper than a one or two grain thickness (5-20 μ m). In fact, pristine UO₂ particles, with little or no evidence for dissolution, were most common. Even particles that had abundant U⁶⁺ alteration products on their surfaces commonly display surfaces that appear unreacted (Fig. 42). Whether a UO₂ particle appears "fresh" or corroded appears unrelated to whether any alteration products have precipitated on its surface. Alteration phases show little evidence for incipient dissolution, such as surface pitting or embayment; however, such evidence is difficult to ascertain given the very small crystal sizes.



Fig. 42. PDT-6: SEM Micrograph of Polished Section through Reacted UO₂ Showing a UO₂ Particle Covered by Dehydrated Schoepite

The XRD powder pattern obtained from the reacted powder indicated that the powder was predominantly UO_2 with no detectable $UO_{2.25}$. As for the previous samples, the reacted powder analyzed by XRD was brick red after grinding. No minor phases were identified in the diffraction pattern, although their presence was indicated by numerous low-intensity diffraction peaks. Only a few percent of the sample observed by XRD is composed of alteration products; this is consistent with our SEM observations.

As observed in some other tests, two Fe-bearing solids were found: an Fe-silicate (?), which is probably left from the starting material, and an Fe-oxide (goethite?), which clearly precipitated during the experiment (Fig. 43). The Fe-bearing solids did not inhibit formation of alteration products. In fact, dehydrated schoepite and soddyite were found on surfaces of Fe-silicates, commonly forming coatings a few micrometers thick. The configuration of these U⁶⁺-phase layers on at least one of the Fe-silicate particles is unusual in that the layer is in contact with only a small portion of the Fe-silicate surface (Fig. 44). The U⁶⁺ coatings on some UO₂ particles also contained minute crystals of Fe-oxides, often as thin coatings underlying U⁶⁺ phases. No U⁶⁺ phases were observed on surfaces of the largest Fe-oxide particles. These large Fe-oxide particles had few impurities detectable by EDS; minor amounts of Al and Cr were observed in a few spectra from spot EDS analyses.

<u>PDT-8 (70 days)</u> - Test PDT-8 used the same configuration as test PDT-7, except that EJ-13b (ox) water was used (Table 16), and the test ran for 70 days. The complete test configuration is summarized in Table IV-1. This test lost nearly one-half of the starting water mass

during the run (0.24 g), more than in any other test, and the solution recovery rate was the lowest among all these tests (Table 17).



Fig. 43. PDT-6: SEM Micrograph of Fe-Oxy-Hydroxide (goethite?) Precipitated on UO₂ Grains



Fig. 44. PDT-6: SEM Micrograph of Polished Section through Reacted UO_2 Showing Mixed Fe-Oxide and Fe-Silicate Impurity with a Coating of Dehydrated Schoepite (brightest contrast particles at right are UO^2). Note gaps between the precipitated layer and the underlying material.

At test termination, water at the bottom of the vessel was clear, with many black grains on the vessel bottom (more grains than seem other tests). We extracted approximately 50 μ L of solution to determine pH. No solution aliquot was taken for anion analysis. We filtered the remaining solution through a 0.45- μ m filter using a 3-mL syringe. After filtration, we recovered only 0.046 g of solution for cation analysis. This amounts represents less than 10% of the initial 0.5 g of EJ-13 (Table 17).

Cation analysis (Table 18) indicated no significant change in the major elements initially present in EJ-13b water; however, amounts of B, Mg, and in particular, Al were significantly higher than in EJ-13b (Table 18; cf., Table 16). This difference in Al is statistically significant. Concentration of dissolved U was lower than for tests PDT-4 and PDT-6. Of the five 316-SS components (Cr, Mn, Fe, Ni, Mo), only the Ni and Mn concentrations showed small but significant increases; however, these concentrations were still lower than in tests PDT-4 and PDT-6, which used a 316-SS screen (Table 19). Solution pH in this test decreased from 8.2 to 5.04, comparable to other tests using EJ-13(ox) water (Table 18).

At test termination (70 days), powder was spread evenly across the screen, although a few small clumps were visible. There were no obvious alteration products, and the UO_2 appeared black. The powder was uniformly wetted, without standing water. No U^{6+} alteration products were apparent (no yellow material).

After drying the reacted powder on the screen, we examined it under an optical microscope. The powder appeared black, except that it had a dusty coating of light-yellow material. Most particles were separate, but there were several clumps of a few tens of particles each. The hanger wire and screen mesh were somewhat discolored, but only two reddish brown spots were apparent on the screen. A few precipitates of Fe-oxides were seen as well, but none of these was successfully removed for SEM examination.

We prepared the reacted powder for SEM examination. Virtually all the UO₂ was covered by small bladed or plate-shaped crystals $(1 - 5 \mu m)$ (Fig. 45). We are still uncertain of the identity of these crystals, partly because of their small sizes. Analysis by EDS indicated only U and O; however, if minor K is present, its detection would be very difficult where U dominates the emission spectrum. Habits of these crystals are similar to those of dehydrated crystals on the surfaces of UO₂ particles in PDT-4 and PDT-6 tests (Figs. 36 and 40). However, many of the crystals from test PDT-8 appeared twinned (note re-entrant angles in Fig. 46), an uncommon feature of either metaschoepite or dehydrated schoepite. On the other hand, twinning is so common for natural crystals of compreignacite, K[(UO₂)₃O₂(OH)₃](H₂O)₄, that untwined crystals are extremely rare. Sodium was not evident by EDS testing of test PDT-8, and Na-free compreignacite is not expected to form in EJ-13 water (Table 16). A more definitive XRD analysis will probably require a larger volume of reacted material.



Fig. 45. PDT-8: SEM Micrograph of Surface of a Reacted UO_2 Particle Covered by Crystals that May Be Dehydrated Schoepite or Another Unidentified Uranyl Oxy-Hydroxide (possibly compreignacite). Crystals appear twinned.



Fig. 46. PDT-8: SEM Micrograph of Crystals on the Surface of a Reacted UO_2 Particle Covered by Crystals that May Be Dehydrated Schoepite or Another Unidentified Uranyl Oxy-Hydroxide (possibly compreignacite). Some of the acicular crystals may be uranophane. Small rounded precipitates are Fe-oxides.

The XRD powder pattern obtained from reacted powder indicated that the powder is predominantly UO_2 with little or no $UO_{2.25}$; the powder analyzed for XRD analysis was brick red after grinding. No minor phases were apparent in the diffraction pattern, nor were any diffraction peaks evident above background.

D. Discussion of UO, Dissolution and Alteration-Phase Formation

Dissolution of UO_2 in these tests releases U into solution. Some of this U remains in solution and some may adsorb onto reaction-vessel walls and stainless steel screen. When the concentration of dissolved U reaches a sufficient level, U can precipitate as U^{6+} solid alteration products. Relative to the total mass of U released from dissolving UO_2 , the mass of sorbed U may be substantial. However, it is the activity of dissolved U species that controls precipitation of solid alteration products. We are most interested in the concentration of dissolved U in those tests where solid alteration products precipitated. Uranium-bearing alteration products were identified in five of the seven tests described here.

Variation in dissolved U as a function of S/V times run time is shown for each test in Fig. 52. The two series of experiments are plotted separately. A general trend appears to be that the concentration of dissolved U increases rapidly and then decreases as reaction proceeds. This trend may be misleading, as the final datum point at right (for PDT-5) represents a minimum value (cf. Table 18). Figure 47 illustrates a notable difference between tests with EJ-13 and EJ-13(ox). Tests that used EJ-13(ox) have higher measured dissolved U concentrations than those tests that used unmodified EJ-13. The two tests for which test solutions were not filtered (PDT-4 and PDT-6) have the highest concentrations of U (marked uF in Fig. 47). The values for PDT-4 and -6 represent maximum concentrations of dissolved U in the corresponding solutions. Interestingly, the tests with EJ-13(ox) were also the only ones in which dehydrated schoepite was identified as an alteration product.



Fig. 47. Variation of U with Reaction Progress. The arrow points upwards from the minimum datum point.

Variation of solution pH for these tests is shown in Fig. 48. This parameter shows a general trend towards lower pH as reaction proceeds. Measured pH values for the tests run with EJ-13(ox) are consistently lower than for tests that used unmodified EJ-13. Aliquots for pH measurements were not filtered. The correlation between higher U concentrations in tests with EJ-13(ox) and lower pH of these solutions indicates that the measured U concentrations are real, although the exact magnitude is uncertain.

Variation of measured U concentrations as a function of pH is shown in Fig. 49. Except for the U value corresponding to PDT-5 at the left in the figure, the trend towards lower U concentrations with increasing pH is clear. Although measured U values for two unfiltered solutions (uF) represent maximum values, their true values may fall near a line extrapolated from the data points of the four filtered solutions (F). This correlation of dissolved U with pH is not entirely unexpected, but the degree to which it is evident is surprising, given the small sampling.

Variations of several EJ-13 cations is illustrated in Figs. 50 and 51. The two figures illustrate data for EJ-13 and EJ-13(ox), respectively. No clear trend is apparent from these data. Within measurement error, there are no significant changes in major components in either EJ-13 water used in the PDT experiments. Among minor components, only Mg, Al, and B show significant variability (values for Ca, K, and Li are maxima), and this is indicated for tests run with unmodified EJ-13.



Fig. 48. Variation of Solution pH with Reaction Progress



Fig. 49. Variation of U with pH. Filled symbols are for the two tests with 304L-SS screens. The symbol uF indicates that the solution was not filtered. The arrow indicates that this point represents a minimum.



Fig. 50. Variation of EJ-13 Components in Test Solutions as Reaction Proceeds. Dotted lines (Ca, K, Li) represent maximum values.



Fig. 51. Variation of EJ-13(ox) Components in Test Solutions as Reaction Proceeds. Dotted lines (Ca, K, Li) represent maximum values.

Figures 52 through 59 show changes in measured U with nine important elements in EJ-13. There is no correlation between dissolved U and any EJ-13 component except Al. This may seem surprising at first, but given the very small amounts of alteration products in these tests, it is expected. Soddyite is the only U⁶⁺ alteration phase identified with confidence that contains any of these nine EJ-13 components (that component is Si). Even given the tentative identification of uranyl silicates in PDT-7 and PDT-8 (Table 20), these silicate phases have precipitated in only very small amounts. Furthermore, uranyl oxy-hydroxides, metaschoepite, or dehydrated schoepite are by far the most abundant U⁶⁺ alteration products in these tests, and these products do not limit the amounts of dissolved cations other than U. The correlation with Al is positive and rather weak. Approximately 1 - 5 ppm of Al is present in the starting UO₂ powder [WRONKIEWICZ-1992], and Al may be present in some steel components. It is uncertain whether spot-welding the steel screens to the hangers introduces leachable Al.



Fig. 52. Variation of Dissolved U with Dissolved Si







Fig. 54. Variation of Dissolved U with Dissolved Ca. Single-sided error bars indicate maximum values.



Fig. 55. Variation of Dissolved U with Dissolved Mg



Fig. 56. Variation of Dissolved U with Dissolved K. Single-sided error bars indicate maximum values.

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Fig. 57. Variation of Dissolved U with Dissolved Li. Single-sided error bars indicate maximum values.



Fig. 58. Variation of Dissolved U with Dissolved Al



Fig. 59. Variation of Dissolved U with Dissolved B

E. <u>Thermodynamic and Kinetic Considerations</u>

Reactions most relevant to the chemical evolution of the solution are those that describe oxidation and dissolution of important reduced elements, Fe^0 in steel and U^{4+} in UO^2 , and precipitation of important dissolved elements, especially U, Si, Na, and Fe. The primary oxidant in these tests is $O_2(g)$, likely even for tests with added H_2O_2 (see below). A major concern when setting up these tests was consumption of O_2 caused by corrosion of the steel on the hanger. We felt that this could reduce fO_2 to levels below those necessary to oxidize and dissolve UO_2 in sufficient quantities to precipitate U^{6+} phases. Crystalline UO_2 remains virtually insoluble below $fO_2 \cong 10^{-40}$ atm (Fig. 60). Maintaining fO_2 above this level for the duration of each test is necessary for the success of these experiments. We observed solid U^{6+} alteration products in five of the tests, using a variety of test configurations, so the corrosion of steel does not seem to have had a detrimental effect on the desired outcomes within the time spans of these tests (< 115 days).

We do not believe that solution compositions in any PDT experiments reached steady-state before termination. However, the system tends toward equilibrium, and comparing alteration phases identified in these tests with those predicted from thermodynamic calculations may help us understand the chemical and kinetic state of the system at test termination. Unfortunately, we have thermodynamic data for few U⁶⁺ solid phases, and many existing data are of uncertain accuracy. Furthermore, most thermodynamic data on U⁶⁺ phases apply only to approximately 25°C, whereas we conducted these experiments at 90°C. Many phases identified in these and other corrosion experiments on UO₂ and spent UO₂ fuels conducted at elevated temperatures also occur in natural systems at or near ambient temperatures. This fact provides some confidence that thermodynamic



Fig. 60. Predicted Stability of U Species in EJ-13 Water as a Function of fO_2 and pH for $\{U\}_T = 10^{-5}$ M (25°C). Coffinite is predicted to replace the stability field of UO₂ in EJ-13 water. The coffinite stability field shown is approximately equal to (though slightly more extensive than) that of UO₂.

data for 25° C are *qualitatively* useful for modeling a U⁶⁺ phase assemblage at 90°C (at least for those phases with known thermodynamic data). There are important differences, however. Notably, schoepite is a common U⁶⁺ phase in natural systems, formed at ambient surface temperatures, but schoepite is not stable above ~ 40°C. Metaschoepite is the expected U⁶⁺ oxy-hydroxide in U-rich waters from approximately 50°C to 90° or 100°C [FINCH-1996], and metaschoepite decomposes to dehydrated schoepite near 100°C [HOEKSTRA-1973]. These phase transformations reflect the role of structurally bound water in schoepite-group minerals, and similar transformations may be important for other U⁶⁺ phases -- most of which also contain substantial amounts of structurally bound H₂O. Even if models using thermodynamic data applicable at 25°C successfully predict the *existence* of phases observed in experiments conducted at higher temperatures, these models may not predict *solubilities* accurately at the elevated temperatures. Murphy argues that many U⁶⁺ phases have retrograde solubilities, but sufficient data are still unavailable to confirm this [MURPHY-1997]. Nevertheless, given these problems, modeling the U⁶⁺ phase assemblage thermodynamically is helpful, even if in only a qualitative sense.

In this section, we focus on oxidation, dissolution, and reprecipitation of relevant Ubearing solids and the potential role of speciation of dissolved U. Probably the reaction of most interest in these tests is oxidative dissolution of solid UO_2 . In a dilute acidic solution, this reaction is

$$UO_2 + 2H^* + 1/2 O_2 \implies (UO_2)^{2*} + H_2O$$
. (23)

This reaction has a clear dependence on pH and $f O_2$. Dissolution of UO₂ is enhanced at low pH in the presence of O₂. Provided that pH does not become too high or the system become depleted in O₂, the above reaction proceeds to the right. In the presence of CO₂(g), pH dependence is complicated by the formation of dissolved uranyl-carbonate species, which can increase the solubility of UO₂ at higher pH. Dissolved uranyl carbonate species are not stable at low pH, but in the presence of bicarbonate, uranyl dicarbonate may be significant at near-neutral pH:

$$UO_2^{2+} + 2HCO_3^{-} \Rightarrow UO_2(CO_3)_2^{2-} + 2H^+$$
 (24)

Uranyl dicarbonate is not likely to be significant in our tests, where the pH is below approximately 5 (Table 18).

The hydrolysis of the uranyl ion is strongly pH dependent:

$$x(UO_2)^{2+} + yH_2O = (UO_2)_x(OH)_x^{(2x-y)} + yH^+$$
 (25)

And at high concentrations of dissolved U, polynuclear uranyl species may become important:

$$xUO_2^{2+} + yH_2O \implies (UO_2)_x(OH)_y^{(2x-y)} + yH^+ .$$
(26)

The fact that the pH of most of these tests are below 6, indicates that the UO_2^{2+} ion may be an important species in solution.

When modeled thermodynamically, however, UO_2F^+ is predicted as the most important dissolved U species in EJ-13 water over all reasonable ranges of U concentration (Fig. 61). The complexation of $(UO_2)^{2^+}$ by fluoride does not affect the pH directly:

$$\mathrm{UO}_{2}^{2+} + \mathrm{F}^{-} \Rightarrow \mathrm{UO}_{2}\mathrm{F}^{+}, \tag{27}$$

but it reduces the activity of the uranyl ion in solution. The predicted persistence of UO_2F^+ at low pH, even at very high dissolved U, is contrary to our observation of schoepite and dehydrated schoepite in several tests (PDT-4, -6, -5, and -8). Although we do not propose that these tests are near equilibrium, it seems unlikely that schoepite or dehydrated schoepite would precipitate if the current thermodynamic data for these phases at 25°C are appropriate at 90°C. We suggest that the stability constant for UO_2F^+ may be too large and/or that the solubilities of metaschoepite and dehydrated schoepite are lower at 90°C than at 25°C. These suggestions would be consistent with the proposal by Murphy that metaschoepite has retrograde solubility [MURPHY-1997].

The precipitation of U^{6+} alteration phases are strongly pH dependent. The reactions relevant to these tests include the precipitation of metaschoepite, dehydrated schoepite, soddyite, and possibly uranophane and compreignacite (Table 20).

The precipitation of metaschoepite is

$$UO_2^{2+} + 3H_2O \implies UO_3 \cdot 2H_2O + 2H^+$$
 (28)

The precipitation of dehydrated schoepite is

$$UO_{2}^{2+} + 1.75H_{2}O \implies UO_{3} \cdot 0.75H_{2}O + 2H^{+}$$
 (29)



Fig. 61. Predicted Stability of U Species in EJ-13 Water in Air $\log pO_2 = -0.7$ at 25°C. Test compositions are plotted [\blacksquare] and labeled according to PDT number.

The precipitation of soddyite is

$$2(UO_2)^{2+} + H_4 SiO_4^{0} + 2H_2 O \implies [(UO_2)_2(SiO_4)](H_2O)_2 + 4H^+ .$$
(30)

The precipitation of uranophane is

$$2(UO_2)^{2*} + 2H_4SiO_4^{0} + Ca^{2*} + 5H_2O \implies Ca[(UO_2)_2(SiO_3OH)_2](H_2O)_5 + 6H^{+} .$$
(31)

The precipitation of compreignacite is

$$6(UO_2)^{2*} + 2K^* + 18H_2O \implies K_2(UO_2)_6O_4(OH)_6(H_2O)_8 + 14H^* .$$
(32)

Among these phases, only uranophane and soddyite are predicted to form in EJ-13 water within the range of pH values observed (Fig. 61). If these two uranyl silicates are the thermodynamically stable phases expected, then the uranyl oxy-hydroxides metaschoepite and dehydrated schoepite are kinetic products. The precipitation of soddyite on dehydrated schoepite in PDT-6 is consistent with the conclusion that dehydrated schoepite is kinetically, but not thermodynamically, favored. What is interesting is that even the tests for which no U^{6+} alteration products were identified are well within the predicted stability field of uranophane, which suggests that uranophane is kinetically inhibited from precipitating. This conclusion is consistent with

inferences made from natural systems, where uranyl silicates are thought to precipitate only from supersaturated solution or by the replacement of more soluble minerals (e.g., schoepite) [FINCH -1992].

The uranyl silicates may require significantly supersaturated solutions to precipitate; however, this alone is insufficient. The concentration of U in PDT-3 is greater than that in PDT-7. No uranophane was identified in PDT-3, but PDT-7 has incipient crystals of what we believe is uranophane. The most important difference between the test configurations of PDT-3 and PDT-7 were the screens; we used a more corrosion-resistant screen in PDT-7. Other test parameters were the same (Table 14).

The U concentration indicated for PDT-5 is a minimum, and the datum point in Fig. 61 may plot closer to or within the soddyite field of stability. This does not change our previous conclusions regarding the relative stabilities of metaschoepite and UO_2F^+ ; however, this would suggest that metaschoepite is a kinetic product and would be replaced by soddyite given sufficient time. In fact, the thin coating of unidentified crystals in Fig. IV-14 may be incipient soddyite. We would be virtually unable to detect Si by EDS from such tiny crystals or a thin layer one or two micrometers thick.

Finally, we should comment on the role of Na in these experiments. No Na-bearing U^{6+} -alteration phases were identified in any test. This may seem surprising and is somewhat unexpected. Drip tests on spent UO₂ fuel have demonstrated the importance of Na-uranyl silicates to fuel corrosion. Even drip tests on unirradiated UO₂ have apparently precipitated Na-containing U phases, although no Na-dominant phases have been identified. However, the absence of Na-bearing phases in Fig. 61 suggests that they are not thermodynamically stable in EJ-13 water – at least at 25°C. Whether Na-bearing phases would precipitate in these tests after longer reaction times is uncertain and remains to be tested. But we suggest that the chemical evolution of EJ-13 water contacting spent UO₂ fuel may be significantly more complex than the changes occurring in experiments on unirradiated UO₂, and probably more complex than a simple geochemical model might predict.

F. Effect of H_2O_2

In order to examine whether additional oxidants might enhance UO₂ dissolution and alteration-phase formation in these tests, approximately 0.1 M H_2O_2 was added to EJ-13 water in three tests, PDT-4, -6, and -8. A 10.5 M solution of H_2O_2 was used. The mass of H_2O_2 solution was measured at the time of addition, and the molarity of the final EJ-13(ox) water was therefore known quite accurately. The concentration of H_2O_2 in EJ-13a (ox) was measured by gravimetric titration.

As stated above, we believe that the primary oxidant in these tests is O_2 . This is likely true even for tests with added H_2O_2 , as the concentration of H_2O_2 probably decreases rapidly due to decomposition of H_2O_2 in contact with steel. However, decomposition of H_2O_2 increases fO_2 in the vessel, according to the reaction,

$$H_2O_2 = H_2O + 1/2 O_2$$
. (33)

Thus, for every mole of H_2O_2 that decomposes, one-half mole of O_2 is produced. The 0.5 g of EJ-13(ox) with a concentration of 0.096 M H_2O_2 contributes 2.4 x 10⁻⁵ moles of O_2 to the reaction vessel upon decomposition of H_2O_2 . This decomposition increases the number of moles of O_2 in the reaction vessel by about 6%, from 4.0 x 10⁻⁴ to 4.24 x 10⁻⁴.
This change in the amount of O_2 may seem small, but the effects on the experiments are significant. The concentration of dissolved U increased more rapidly and remained at higher levels in the EJ-13(ox) tests compared to tests with unmodified EJ-13 (Fig. 47). The pH of the EJ-13(ox) solutions after reaction were also consistently lower (Fig. 48). Every test with EJ-13(ox) precipitated U⁶⁺ alteration products, and dehydrated schoepite precipitated only in those tests with EJ-13(ox) (the identification of dehydrated schoepite in PDT-8 is uncertain).

We do not fully understand the difference in the solid alteration products between the two test series. The structural relationship between schoepite and dehydrated schoepite is quite close [FINCH-1996], and they differ chemically only in their total water content. The transformation is represented by the following reaction:

$$UO_3 \cdot 2H_2O \Leftrightarrow UO_3 \cdot 0.9H_2O + 1.1H_2O(g) \quad K = pH_2O^{1.1}$$
 (34)

The transition depends on both temperature and partial pressure of H_2O . From thermodynamic data [O'HARE-1988], we know dehydrated schoepite is stable with respect to metaschoepite if pH₂O falls below 0.527 atm at 25°C. Metaschoepite alters to dehydrated schoepite in water near 100°C [HOEKSTRA-1973]. The temperature of our tests, 90°C, is close to the transition temperature at 100 % humidity (pH₂O = 1 atm), and the decomposition of H₂O₂ in the reaction vessel may be sufficient to decrease pH₂O sufficiently to stabilize dehydrated schoepite.

Another expected effect of H_2O_2 in these tests is to enhance the corrosion of the steel. This, however, is difficult to measure because of the very low amount of steel components in most test solutions. Only Ni was significantly higher in the EJ-13(ox) tests compared to the tests with unmodified EJ-13; Mn and Fe are higher in some tests. We suspect that an important effect of steel corrosion is a decrease in pH (see below), and enhanced steel corrosion may account for the lower pH of the EJ-13(ox) test solutions.

G. Steel Corrosion and Rust Formation

In addition to monitoring the corrosion of UO_2 and the chemical evolution of water under the test conditions, we also wanted to examine the suitability of the test components and some of the interactions between test components and UO_2 . This information will be used when setting up tests on spent UO_2 fuel. With these goals in mind, we analyzed chemical components present in the steel used in these tests. Early test configurations used a 316-SS screen, whereas, PDT-7 and PDT-8 used a woven mesh made from 304L-SS (Table 14).

Oxidative dissolution of steel releases components into solution that were not present in EJ-13 water in significant quantities. Figure IV-46 illustrates variations in steel components in tests with unmodified EJ-13 as reaction progresses. No clear trend is apparent. Nickel and Mn show the most variability. Both of these elements form soluble species in low pH, oxidizing waters. Figure 63 illustrates variations in steel components for tests with EJ-13(ox) water. In this case, data indicate that Rigimesh 304L-SS screen is more resistant to corrosion under the test conditions. The only element that does not show a decrease in this test is Fe; however, the dissolution of Fe-bearing impurities in the starting UO_2 may be one reason for this lack. Concentrations of all steel components are somewhat higher in some tests with EJ-13(ox) compared to tests with unmodified EJ-13 water (cf. Fig. 62); however, this is not consistent.

Observed variability in concentrations of steel components may be due to one or more several reasons. The starting UO_2 is a potentially important source for these elements. The UO_2 contains substantial amounts of Fe and Ni, and trace amounts of Cr and Mn, possibly within Fe-silicate and Fe-oxide impurities.



Fig 62. Concentrations of Stainless Steel Components from Tests with Unmodified EJ-13 Water as Reaction Proceeds



Fig. 63. Concentrations of Stainless Steel Components from Tests with EJ-13(ox) Water as Reaction Proceeds

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Figures 64 through 68 show the variation in U concentration with the elements present in the steel. It is interesting that all these plots show positive correlations between U concentration and concentration of steel constituents. Two obvious explanations can be put forth. First, the oxidative corrosion of UO_2 and steel proceed together. The system is far from equilibrium, and the dissolution of both UO_2 and steel are proceeding in all tests without any indication of abating. Second, many of the elements present in the steel are also present as impurities in the dissolving UO_2 powder. As UO_2 dissolves, it releases these impurities. Although the second hypothesis may be correct, we propose that the first explanation is the more important factor. The high degree of corrosion evident on the steel screens supports this.



Fig. 64. Variation of Dissolved U with Dissolved Fe



Fig. 65. Variation of Dissolved U with Dissolved Mn



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Fig. 66. Variation of Dissolved U with Dissolved Ni



Fig. 67. Variation of Dissolved U with Dissolved Cr. Single-sided error bars indicate maximum values.



Fig. 68. Variation of Dissolved U with Dissolved Mo. Single-sided error bars indicate maximum values.

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There are also several possible sinks for these elements. They may also be incorporated into the ferric oxy-hydroxides that precipitated in these tests. Some variability may be accounted for by tendencies of these elements to sorb to steel test components, as well as to UO_2 and solid alteration products.

We observed corrosion of stainless steel components in all tests, although the degree varies. The original 316-SS screen seemed to corrode more readily than 304L Rigimesh. Visible "rust" in the experiments with 304L-SS screens is noticeably less. However, even the two tests in which no U⁶⁺-bearing alteration products were observed (PDT-1 and PDT-3) displayed noticeable discoloration of the screens and precipitation of Fe-oxy-hydroxides. This observation is consistent with the relative reactivities of Fe²⁺ and U⁴⁺ under oxidizing conditions:

$$U^{4+} + 2H_2O \Rightarrow (UO_2)^{2+} + 4H^+ + 2e^- \qquad E^0 = -0.334 \text{ V}$$
(35)
Fe²⁺ = Fe³⁺ + e⁻ E⁰ = -0.770 \text{ V} (36)

Clearly oxidation of Fe^{2+} should precede the oxidation of U^{4+} in low pH solutions. The oxidation and dissolution of Fe^{0} in the steel is the rate-limiting reaction keeping the concentration of Fe^{2+} in solution relatively low. However, the solubilities of ferric oxy-hydroxides are quite low, and once oxidized from ferrous to ferric iron, Fe^{3+} tends to precipitate. The identification of Fe^{3+} oxy-hydroxides in these tests indicate that steel corrosion is an important factor controlling the chemistry of the water. The formation of Fe^{3+} oxy-hydroxides can be represented by the precipitation of ferrihydrite (cf. Table 15), a common early-formed phase:

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$$
 (37)

The potential effect of this reaction on solution pH is evident. We believe that this reaction is primarily responsible for the observed pH in our tests. Drip tests on both UO_2 and spent UO_2 fuel do not tend to have such low pH values; the pH values in those experiments tend to be near neutral [WRONKIEWICZ-1996; FINN-1997]. Nor do the drip tests experience the degree of steel corrosion apparent in these experiments. In addition, the two tests that used Rigimesh 304L-SS screens had significantly higher solution pH than comparable tests using 316-SS screens, suggesting that the decreased corrosion in the two experiments is correlated with higher solution pH (note that the relatively low pH of PDT-8 reflects EJ-13 ox; PDT-8 has the highest pH among the EJ-13 ox tests) (Table 18). We attribute the high degree of steel corrosion in these tests to the low volume of water and high surface area of the screen.

Coprecipitation of U with Fe oxides has been reported for both natural and experimental systems [PAYNE-1994, BRUNO-1995, MURAKAMI-1997]. We did not detect measurable quantities of U in Fe-oxide precipitates formed in these tests. Uranium is a common minor constituent of Fe-silicate impurities from the UO₂ starting material, but U is not likely to have been incorporated into these phases during test runs. Besides, UO₂ particles are clearly evident in these Fe-silicate impurities (Fig. 19).

H. <u>Summary and Conclusions</u>

These tests have been intended as trial experiments for setting up similar tests on spent UO_2 fuel. At this stage, test components and procedures have been examined, with the goal of understanding what factors are most important for the tests on spent fuel. No systematic study of all the experimental conditions has been made. Nevertheless, the information gained from these few experiments on UO_2 , provides insight into the corrosion of UO_2 at high S/V ratios. We have also gained some additional understanding of the potential importance of H_2O_2 (and by implication, radiolytic products) in enhancing fuel dissolution and possibly changing the mechanisms by which

fuel corrodes, including the alteration phases that may precipitate. Some of our results were unexpected and require further study.

These are short-term tests conducted far from equilibrium, and results for similar tests with spent fuel may differ. In particular, the observed time sequences of alteration phase formation may not be repeatable. Because the system is so far from equilibrium, small differences in starting conditions can lead to differences in experimental results. This can be overcome to some extent by conducting multiple replicate experiments or by doing time-sequenced experiments. It is fortunate that these tests are small scale and relatively straightforward to conduct because multiple, parallel tests are then possible. We suspect that tests on spent fuel will require some redundancy to reduce uncertainty in the results.

The only major changes to the test configurations over the course of these seven tests was altering the hanger design and switching to a 304L-SS screen. These changes increased the success of these experiments, as measured in terms of solid alteration-phase formation. However, both changes led to a decrease in the volume of solution that was recovered from each test. The very low solution volumes are a challenging part of this experimental design. When conducting these tests on spent fuel, we may be required to conduct parallel tests to obtain sufficient solution for the desired analyses.

Overall, these tests have proven successful in accelerating the reaction of UO_2 . Their ease of implementation and relatively rapid results makes them useful for increasing our understanding of fuel corrosion in an unsaturated environment. These tests are designed as response tests, and some information may not be available (e.g., sorption of elements by the screens and vessel walls). With proper planning, however, a great deal of information can be gained from these experiments.

V. DEVELOPMENT OF METHODS TO TEST CLAD FUEL

A. Introduction

While the ongoing drip tests simulate the reaction that takes place between a breached fuel rod and dripping or saturated water vapor, it is likely that the initial contact between water and spent nuclear fuel will occur when the cladding is nearly intact, with only minor perforations existing for water ingress. Under this more limited liquid water or water vapor contact, the extent, nature, and rate of spent fuel reaction is of interest. In particular, if the cladding stays mainly intact, even during alteration of the fuel, the release of radionuclides may be reduced. Two sets of tests are being developed to address the reaction of spent nuclear fuel under conditions of intact cladding: 1) water dripping slowly through a defect rod, and 2) water vapor reacting with fuel in a defected rod.

B. <u>Objectives</u>

The objectives of this dripping water test are the same as those for the ongoing drip tests, with the addition of observing the effect of fuel reaction on cladding integrity. It is possible that alteration products may not form due to stress within the spent fuel section, or if they do form, they may obstruct the throughflow of water. The tests with vapor will be performed to determine whether reaction with vapor, which will occur prior to contact by liquid water, will cause additional failure to the cladding.

C. Technical Approach

Task plans have been written for both sets of tests and approved by Lawrence Livermore National Laboratory (LLNL). Mock-up of the tests apparatus is in progress to provide assurance that the test will provide the required information when performed with spent fuel. No additional details of the approach are available at this time.

D. <u>Results</u>

The tests have not yet started so no results are available.

E. <u>Ongoing Work</u>

After the mock-up work has been completed, the hot-cell will be reconfigured to accommodate the new equipment required to perform the tests, and the tests will be initiated.



VI. PROCUREMENT OF A NEW APPROVED TESTING MATERIAL

A. <u>Introduction</u>

Ongoing tests with spent nuclear fuel are being performed with ATMs that were procured and characterized by the Materials Characterization Center (MCC) in support of the Yucca Mountain Project. Through a review process that included the Yucca Mountain Project, the M&O, LLNL, Pacific Northwest National Laboratory (PNNL), and Argonne, it was determined that additional ATMs were required to complete the suite of spent fuel types that may be placed in the repository. This year it was determined to procure a high burnup spent fuel, characterize it, and distribute it for testing.

B. <u>Objective</u>

The objective was to procure a high burnup spent fuel sample for testing purposes. The fuel will be characterized, a characterization report written, and be distributed for testing to ANL and PNNL.

C. <u>Technical Approach</u>

The approach used in the procurement and shipping of the fuel is outlined below.

1. <u>Procurement</u>

The YMP Commercial spent fuel is currently being tested to analyze waste form degradation and radionuclide release. The work is described in an LLNL Spent Fuel Scientific Investigation Plan. The material used in these tests is termed an ATM and is a well-characterized spent fuel sample with unique characteristics. The characteristics required of the different ATMs are determined by the YMP based on the expected operating history of spent fuels sent to the potential repository at Yucca Mountain. Following is a description of the steps taken to procure the latest ATM from General Electric Nuclear Energy (GENE).

First, LLNL contacted potential vendors of commercial spent fuel regarding the availability of spent fuel that met the requirements for a new ATM as defined in the publication "Rationale for Determining Spent Fuel Acquisitions for Repository Testing." The responses received from the vendors were reviewed by the laboratories involved in the waste form testing program — LLNL, ANL, and PNNL. A recommendation was then made to the YMP that the spent fuel offered by GENE met the criteria and would be a suitable choice for the new ATM. Upon receipt of a concurrence letter from the Yucca Mountain Site Characterization Office, Argonne proceeded with the procurement based on guidance provided in the FY 1997 Statement of Work (SOW).

Procurement information and supporting documentation were provided to the Procurement Section of the ANL Chemical Technology Division, which worked in conjunction with the ANL Special Nuclear Material (SNM) Division. The procurement followed Section III of the ANL Procurement Manual, and all shipping arrangements are done by SNM following Department of Transportation regulations. Documentation regarding the procurement will be completed upon receipt of the ATM.

The Procurement Section and the ANL YMP Program Manager worked out the details of the procurement to resolve some issues addressed by GENE. Further additions and clarifications were then made to the procurement SOW and sent to GENE. Agreement was reached on July 18, 1997, and receipt of the ATM occurred in October 1997.

2. <u>Shipping</u>

Six spent fuel rod segments, each about 30-35 in. long, from three different uranium oxide fuel rods irradiated in the Quad Cities-1 boiling water reactor (BWR) (operated by ComEd Co.), are being obtained for use in the YMP leaching studies. The high burnup on these rods, about 60 to 80 MWd/kU, satisfies the YMP need for testing the highest burnup BWR fuel currently available. Four of the segments contain UO_2 fuel with an original U-235 enrichment of 3.0 or 3.8 wt%. The current enrichments are estimated to be 0.05 and 0.15 wt%, respectively. The other two segments contain $(U,Gd)O_2$ fuel with original enrichments of 3.0 w/o U-235 and 2.0 wt% Gd; the current U-235 enrichment is estimated to be 0.12 wt%. Based on the fuel geometry and burnup, it is estimated that the six segments contain 3.54 g of U-235. The different fuel samples have been designated ATM-109a (3.8% enrichment), ATM-109b (3.0% enrichment), and ATM-109c (GD).

The fuel segments are being obtained from the General Electric Company's Vallecitos Nuclear Center in Pleasanton, California, and will be shipped from the GE hot cell to the ANL Alpha-Gamma Hot Cell Facility (AGHCF) site. There samples will be prepared for transfer to ANL's Chemical Technology Division and for shipment to the PNNL hot cell in Richland, WA.

After the tests are completed at these two sites, the sample remains will be disposed of as low-level waste (LLW). Any unused portions of the segments will be retained at ANL. No high-level waste (HLW) will be generated in this program.

The segments were shipped in DOE's "T-2 cask," a 13,000-lb cask that is under ANL's purview. Both ANL and GENE have had extensive experience in handling this cask over a number of years. Established procedures were followed for its use. The individual segments were contained in Type 304 stainless steel "protection tubes," welded closed on one end and with a threaded plug on the other. As required by the cask license, the six tubes were placed in a 2-R shipping container, which will be contained in the sealed "cask liner."

D. <u>Results</u>

The fuel was received by Argonne in October 1997. It is to be characterized and distributed in fiscal year (FY) 1998.

E. <u>Ongoing Work</u>

Characterization will begin in April, 1998. It is possible that another ATM will be procured.

VII. UNSATURATED DRIP TESTS WITH UO₂

A. Introduction

The reaction of UO_2 and spent nuclear fuel samples was examined in unsaturated drip tests that simulate potential conditions for the exposure of spent nuclear fuel in an unsaturated/oxidizing repository environment. The reaction of UO_2 occurs rapidly in these tests, resulting in the formation of a sequence of alteration phases that replicate the alteration patterns observed during the oxidative dissolution of uraninite in natural geologic systems. Overall reaction pathways for both UO_2 appear to be controlled by a combination of precipitation kinetics of alteration phases and evolving leachant composition.

B. <u>UO, Reactions</u>

The present set of experiments have shown that uranium release from the UO₂ samples was very rapid from one to two years of testing, followed by relatively low rates of release from two years, up to the present twelve years of reaction (Fig. 69). A detailed examination of the sample surface revealed (1) preferential corrosion along the grain boundaries between the original press-sintered granules comprising the samples, (2) development of a polygonal network of open channels along the intergrain boundaries, and (3) evidence for spallation of surface granules that had undergone severe grain boundary corrosion. Penetration of the dissolution front along the intergrain boundaries was highly irregular, typically occurring to a depth of two-to-three grains (~15 - 20 μ m) from the exposed external sample surface, but varying from regions with little visible grain boundary corrosion to regions where penetration occurred to depths of approximately 10 grains. The cause for preferential grain boundary corrosion is currently being investigated, but may be related to crystal stresses induced during the press-sintering process, electrochemical potential differences that exist along the boundary regions, and/or density changes of the UO_{2+x} occurring as a result of grain boundary oxidation.



Fig. 69. Cumulative Release of Uranium (mg) over Time for Tests 5 and 6. Each test contained three stacked pellets in a zicalloy sleeve. Test 5 terminated at 183 weeks; test 6 is ongoing.

Some of the uranium released to solution during the dissolution of the UO₂ samples had combined with such groundwater leachant components as Si, Na, K, Ca, and Mg to form a suite of alteration phases that precipitated on the test vessel components, sample surfaces, and within the corroded intergrain boundary regions. The top sample surfaces were characterized by the development of a paragenetic sequence of alteration phases where UO₂ \rightarrow uranyl oxide hydrates \rightarrow alkali and alkaline earth uranyl oxide hydrates \rightarrow uranyl silicates \rightarrow alkali and alkaline earth uranyl silicates + palygorskite clay. Uranyl oxide hydrates plus alkali and alkaline earth uranyl oxide hydrates were the only phases formed in the intergrain boundary regions, sides, and bottoms of the samples, reflecting the consumption of silicon from solution during the formation of the silicates and a lowering of the silicon concentrations as fluids migrate across the sample surface. The formation of a dense mat of alteration phases in the longer term tests enveloped the loosened UO, grains, resulting in a reduction in the rate of their spallation and a lowering of the uranium release rate after two years of testing. Despite the lowering in total release, uranium-bearing particulates continued to be released from the sample surfaces. A TEM examination of filtered residue from the test solutions revealed the presence of the elongated needles of Na-boltwoodite $[(Na,K)(H_3O)UO_2SiO_4 H_2O]$ and beta-uranophane $[Ca(UO_2)_2(SiO_3OH)_2 SH_2O]$, typically several microns in length, as well as the presence of subrounded, 100-200 nm diameter, particles of UO_{2+x}. The relatively large size of the silicate particles indicated that they were most likely generated as particulates that were subsequently spalled from the sample surface. The UO_{2+x} particles were of undetermined origin, either being generated as spalled particles like the silicates, or possibly precipitating directly from solution.

The quantity of uranium incorporated in the alteration phases was calculated by determining the volume of precipitated material on the sample surface, the proportion of each respective alteration phase present, the molar proportion of uranium contained in each phase, and by multiplying the calculated volume of each respective phase present by its respective density. Preliminary calculations for sample PMP8U-2, reacted for eight years, indicated that ~80 mg of uranium was incorporated into the alteration phases deposited on the sample or Zircaloy surfaces, an amount that far exceeds the 5 mg that was released from the Zircaloy sample assembly (as recovered in the acid strip component). An additional ~780 mg of uranium remained *in situ* as undissolved UO_{2+x} cores that had undergone some form of corrosion along their grain boundaries. The initial UO₂ pellet combined weights prior to testing were 29,166 mg (25,709 mg of uranium).

C. <u>Summary</u>

Reaction of the UO_2 pellets occurs along the boundaries between the original press-sintered UO_2 grains. Although dissolution rates for the samples were high, most of the dissolved uranium was reincorporated into alteration products that formed on the sample surfaces. A significant portion of the released uranium occurred as particulate matter. Both colloidal-sized uranyl silicates and UO_{2+x} particles were observed in the filtered residues from the tests. The observed alteration phase reaction paragenesis mimicked that of natural uraninite alteration under oxidizing conditions.

D. <u>Ongoing Work</u>

The reaction of UO_2 , while resulting in alteration products similar to those observed for ATM-103 and ATM-106, occurs in a radiation field (γ , β , α) much less than for spent fuel. Depending on the time of waste package failure and the exposure of spent fuel to water, the results of UO_2 reaction becomes of greater significance because of this decrease in radiation. Continuing work with the UO_2 tests will focus on striking comparisons that can be made between spent fuel and UO_2 reaction. To make the ongoing tests with UO_2 more similar to the tests with spent fuel, it is possible to increase the drip test ten fold. This change in test conditions would make more Si, Na, and Ca available for the formation of alteration phases and would allow us to simulate a higher flow condition that may occur during disposal.

Because of the flexibility available in changing conditions of the drip tests, while in progress, other changes in the test conditions are possible, and a comparison between the results of tests performed with UO_2 and spent fuel will be done. It is hoped that through this comparison, greater insight will be available for providing input to the repository license application.



VIII. UNSATURATED DISSOLUTION TESTS IN GLASS

A. <u>Introduction</u>

Drip tests designed to replicate the synergistic interactions between waste glass, repository groundwater, water vapor, and sensitized 304L stainless steel in the proposed Yucca Mountain Repository have been in progress with actinide-doped glasses. In these tests, slowly dripping, tuff-equilibrated groundwater reacts with a monolithic waste glass sample and sensitized 304L stainless steel in a water vapor saturated environment to determine synergistic interactions possible in a compromised pour canister under unsaturated conditions. The tests using actinide- and technetium-doped Savannah River Laboratory (SRL) 165 glass, termed the N2 Test Series, have been ongoing for over 11 years. Tests with a West Valley Demonstration Project former reference glass (ATM-10), also doped with Tc and actinides, have been in progress for nearly 10 years and are termed the N3 Test Series. The information provided in this report includes long-term data relevant to glass reaction under conditions anticipated for an unsaturated repository.

B. <u>Objective</u>

The N2 Unsaturated Glass Tests, performed on actinide- and technetium-doped SRL 165 glass, were begun in February 1986. These tests, which have now been in continuous operation for over 11 years, have been sampled periodically, with regular sampling at ~26-week intervals since December 1993. A report on results of the tests through one year, including analyses of solid material from the terminated (batch) tests, was issued in 1990 [BATES-1990], while partial solution data through about four years of testing were published later [BATES-1994a, b; FORTNER-1996]. While SRL 165 glass is no longer the reference glass to be used for the Defense Waste Processing Facility (DWPF), it does represent a glass within the production envelope, and the tests provide information that can be used for (1) model validation, (2) investigation of reaction mechanisms, (3) evaluation of synergistic effects, (4) the form of radionuclide release, and (5) glass reaction rates over long time periods under repository service conditions.

The N3 Unsaturated Tests, performed on WVDP actinide- and technetium-doped ATM-10 glass, were begun in July 1987. The ATM-10 glass is a former reference glass for the WVDP, and its composition differs only slightly from the present West Valley reference glass. Like the N2 tests, the N3 tests remain ongoing and have been sampled periodically, with regular ~26-week samplings being done since January 1994. Analysis of solid components of the N3 waste package assemblage were sponsored recently by DOE'S Office of Environmental Restoration and Waste Management (EM); these findings have been published elsewhere [BATES-1992; FORTNER-1995, 1997]. The combined solution and solids analyses for the N3 tests will provide a concerted description of the reaction behavior of the glass.

Measurements obtained from each test series include the rate of glass reaction and radionuclide release as a function of time, a description of the distribution of radionuclides in solution (i.e., dissolved in solution, associated with colloidal material, or sorbed onto metal components of the test), and monitoring of the interactions between the various components in the test. Ultimately, the results from these tests will be used to validate source terms of models used in waste-package performance-assessment codes.

C. <u>Technical Approach</u>

In the unsaturated tests, 0.075 mL (about 3 drops) of tuff-equilibrated groundwater from the J-13 well near Yucca Mountain (termed EJ-13 water) is dripped onto the simulated waste package in a sealed stainless steel test vessel every 3.5 days. Additional air is also injected into the test vessel with the water. The simulated waste package assemblage (WPA) used in the tests consists of a cylindrical monolith of waste glass, approximately 16 mm diameter and 20 mm high, contacted on the top and bottom by two perforated retainer plates made from sensitized 304L stainless steel, which are held in place by two wire posts, also made from 304L stainless steel. The entire test apparatus is enclosed in a 90°C oven except when samples are taken and observations made. Details of the unsaturated test procedure⁴ are given elsewhere [BATES-1990]. Each ongoing test series consists of three identically-prepared WPAs, each in its own test vessel, and a blank (empty test vessel). Water drips down the sides of the glass and accumulates at the bottom of the WPA. Eventually the water drips from the WPA to the bottom of the vessel. Ongoing parametric tests on nonradioactive SRL 165 frit glass will allow direct evaluation of surface area and inject rates on scaling, once the data are available. When the drip tests are sampled (currently at ~26-week intervals), the WPA is examined visually to qualitatively ascertain the degree of reaction, including evidence of alteration phase formation and possible spalling of the alteration phases and clay layer. After observation, the WPA is transferred to a fresh test vessel, the test solution removed for analysis, and the just-used vessel is acid-stripped to determine sorbed species.

The compositions of the glasses used in the N2 and N3 Tests are given in Table 21. These compositions include new data from a re-analysis of actinides in an archival portion of the doped SRL 165 glass used in the N2 Test series. The approximate composition of the groundwater (EJ-13) used in the tests is given in Table 22 for the most concentrated elements. These are typical values; the actual composition of the EJ-13 water used is monitored regularly and varies slightly with time. A compilation of EJ-13 composition measurements covering the past 11 years has been prepared and will be published as a separate report.

At each sampling, the waste package is visually examined for evidence of reaction progress, then transferred to a fresh test vessel pre-loaded with 0.5 mL EJ-13 water and returned to the 90°C oven. Solution from the just-completed test is submitted for elemental analysis (by ICP-MS), and high-resolution alpha spectroscopy (to determine transuranic composition). Analyses for anions, carbon, and pH are also conducted. If sufficient solution exists, either sequential filtering or ultracentrifuge filtration may be done. The filtered solution is submitted for high-resolution alpha spectroscopy to determine the distribution of transuranic species between particulates caught on the filter and truly dissolved species that pass through. Since the 1993 samplings, colloidal material was sometimes collected for examination by AEM, via a procedure described later in this report. The test vessel is then acid stripped to remove the remaining actinides. This acid strip solution is submitted for high-resolution alpha spectroscopy; since 1993, this solution has also been analyzed by ICP-MS.

D. <u>Results</u>

1. <u>Solution Cation Analyses</u>

In the discussion below, the solution collected in the test vessel that had contacted the waste package during the course of the test is designated the vessel rinse and the solution that results from soaking the vessel with acidified water is called the acid strip. As the glass reacts, material is released from the glass either truly dissolved in solution or as particulate material. The solution is also in contact with the pre-sensitized 304L stainless steel retainer during the reaction process, so the analysis of the solution collected in the bottom of the test vessel represents all the material that is transported from the glass and glass retainer. The solution is analyzed for its constituent parts as described above, but all the material analyzed in the test solution is considered to have been released from the glass/stainless steel assembly.

^{*} The unsaturated test procedure is governed by document NNWSI-05-011, Rev. 4, issued May 22, 1996.

A comparison of behavior among elements present in widely different concentrations in the glass is best made by examination of the *normalized releases*. The normalized release is $N_i = M / (\Delta t c_i A)$, where M_i is the measured mass of element *i* in the leachate solution, c_i is the fraction of element *i* in the source glass, Δt is the time interval between tests, and A is the surface area of the glass monolith (1.36 x 10⁻³ m²). However, the use of such a normalization process in the drip tests averages the three types of water contact that occur: humid air, dripping water, and standing water.

	N2 Tests	N3 Tests
Oxide	SRL 165 ^a	ATM-10 ^b
Al ₂ O ₃	4.08	6.65
AmO ₂	0.00091*	0.0064
B_2O_3	6.76	9.17
BaO	0.06	0.045
CaO	1.62	0.60
CeO ₂	<0.05	0.072
Cr ₂ O ₃	<0.01	0.253
CsO ₂	0.072	0.062
Fe ₂ O ₃	11.74	11.5
K ₂ O	0.19	3.34
La ₂ O ₃	<0.05	0.025
Li ₂ O	4.18	2.88
MgO	0.70	1.15
MnO ₂	2.79	1.29
Na ₂ O	10.85	10.5
Nd_2O_3	<0.05	0.168
NiO	0.85	0.296
NpO ₂	0.0283°	0.021
P_2O_5	0.29	2.34
PuO ₂	0.048°	0.0081
RhO ₂		0.012
RuO ₂		0.061
SO ₃		0.31
SiO ₂	52.86	45.8
SrO	0.11	0.025
Tc_2O_7	0.02	0.0031
ThO ₂		3.29
TiO ₂	0.14	0.858
UO ₂	1.25*	0.527
Y_2O_3		0.017
ZrO2	0.66	0.247

Table 21. Compositions, in Oxide Weight Percent, of Glasses Used in the N2 and N3 Tests

^aSource: BATES-1990, except as noted.

^bSource: MAUPIN-1988.

^cNew analysis by ICP-MS (April 1997) from archived N2 glass. These values supersede all previously published values.

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Element ^b	Concentration (mg/L)
Al	0.7
В	0.2
Ca	6.6
Fe	<0.1
К	7
Mg	0.15
Li	0.04
Na	53
Si	40
F⁻	3
Cl-	10
NO ₂ ⁻	<1
NO ₃ ⁻	11
SO ₄ ⁻	23
HCO ₃ ²⁻	100
Total carbon	25
Organic carbon	7

Table 22. Typical Composition of the EJ-13 Water^a Used in the N2 and N3 Tests

^bOther cations are < 0.1 mg/L.

a. Elements in the N2 Solution

Figure 70 shows the total cumulative mass release of lithium and boron in the vessel rinse from the N2 tests into solution as a function of time. The term "release" is used throughout this report to indicate elements that have left the WPA and are either dissolved in solution, suspended as colloids, or sorbed onto the test vessel. The release of these elements is an important gauge of the glass corrosion, as they are not expected to form secondary phases, are not major components of EJ-13 water, and are not present in the steel. Negligible amounts of lithium and boron are measured in the acid strip solutions. Normalized release rates for these elements appear in Fig. 71. Note the nearly identical behavior of these two elements, an indication that they are remaining in solution (dissolved) and are released from the glass congruently. Note also that while the data from the three replicate samples in the test may differ, the N2-10 sample releases both lithium and boron the fastest, while the N2-9 sample releases both elements the slowest (not including N2-11). The differences in measured reaction rate are real and are reflections of the reproducibility of this type of test over a 10-year period. The composition of the unfiltered N2-10 vessel rinse test solution from the June 17, 1996, sampling, which includes plutonium and americium contributions from colloids, appears in Table 23.



Fig. 70. Cumulative Release of Boron and Lithium from the N2 Tests as a Function of Elapsed Time (Note the increased release rate from N2-10 relative to the other tests. The test N2-11 is a blank test, and the release data from the N2-11 test are upper bounds due to detection limits.)



Fig. 71. Normalized Cumulative Release of Boron and Lithium from the N2 Tests as a Function of Elapsed Time (Note the increased release rate from N2-10 relative to the other tests. Note also that the normalized releases of these elements are in excellent agreement.)

			Concentration	n (μg/mL)		
Li	B	Na	Al	Si	K	Ca
31200	6300	329000	10300	153000	54600	17500
			Concentration	$(\mu g/mL)$		
Cr	Fe	Ni	U	Np	Pu	Am
1800	30500	6500	2040	35	63	1.0

Table 23. Composition of the Unfiltered Test Solution Collected from N2-10 on June 17, 1996.^a

These values are typical of what is observed in the N2 series over the past 3 years.

Uranium release from the N2 tests appears in Fig. 72. Note that the uranium normalized release is about half (or less) that of lithium and boron (Fig. 71), and that the N2-10 test appears to be releasing uranium at a much higher rate than the other two tests. These plots do not include uranium from the acid strip of the test vessel, which has only been measured since the December 1993 sampling; extrapolating from present trends, the acid strip data would add about 30% to the observed release of uranium and are included in the normalized uranium release rates of Table 24. From this table, it is apparent that the normalized uranium release from N2-10 is

approximately the same as the normalized lithium or boron release, whereas the N2-9 and -12 tests are releasing uranium somewhat more slowly. A release mechanism by solution-borne colloids is proposed later in this section as a likely explanation for such variations among samples.



Fig. 72. Cumulative Uranium Release from the N2 Tests as a Function of Time (Left, total mass release; and right, normalized release.)

Normalized Release Rates ^b (g m ⁻² day ⁻¹)						
Test Series	Li	В	U	Np	Pu	Am
N2-9	1.6 x 10 ⁻³	0.9 x 10 ⁻³	4.0 x 10 ⁻⁴	1.0 x 10 ⁻⁴	3.0 x 10 ⁻⁵	4.4 x 10 ⁻⁵
N2-10	2.8 x 10 ⁻³	2.2 x 10 ⁻³	1.3 x 10 ⁻³	3.4 x 10 ⁻³	1.4 x 10 ⁻³	1.4 x 10 ⁻³
N2-12	1.7 x 10 ⁻³	1.1 x 10 ⁻³	3.2 x 10 ⁻⁴	4.0 x 10 ⁻⁴	0.8 x 10 ⁻⁴	0.9 x 10⁻⁵
Average	2.1 x 10 ⁻³	1.4 x 10 ⁻³	6.7 x 10 ⁻⁴	1.6 x 10 ⁻³	4.8 x 10 ⁻⁴	5.0 x 10 ⁻⁴

Table 24. Normalized Release Rates over the Latest 2.5-year Period for Selected Elements from the N2 Test Series^a

The rates include data from the period between December 1993 and December 1995. The above rates are for vessel rinse only, except the rates for U, Pu and Am, which include the acid strip.
^bError is approximately ±30% for each rate. These rates reflect the latest glass composition analysis by ICP-MS (Table 21).

The elements in the acid strip solution (except for the actinides plus Fe, Ni, and Cr from the stainless steel test vessel itself) are present at very low amounts relative to the vessel rinse solution. Neptunium, Pu, and Am in the acid strip have been monitored by high-resolution alpha spectroscopy since the tests were initiated, and these data have been periodically reported [BATES-1990, -1994a, b; FORTNER-1996], and are updated in this report. Uranium levels in the acid strip were not measurable by the alpha spectroscopy procedure, and have only recently become available with the ICP-MS data.

The release of the transuranic elements Np, Pu, and Am into solution is plotted in Figs. 73 and 74 for the N2 test series. Neptunium is highly soluble and does not sorb substantially onto the stainless steel, a fact confirmed by measurements of the acid strip solutions.



Fig. 73. Cumulative Mass Releases for the Transuranic Elements Np, Pu, and Am from the N2 Tests: N2-9 (circles), N2-10 (rectangles) and N2-12 (diamonds)



Fig. 74. Normalized Actinide Release from the N2 Tests: N2-9 (circles), N2-10 (rectangles) and N2-12 (diamonds) (Note the retention of Am and Pu relative to Np.)

The reported values for Np, like those of Li and B, thus include only the vessel rinse. Plutonium and Am, on the other hand, are known to sorb onto the stainless steel from which the test vessel is made and may also be incorporated into the clay layer and alteration phases (see, for instance, [BATES-1992]). The Pu and Am data in the figures represent the sum of the vessel rinse and acid strip results, where there are comparable contributions from each. Typically, 60-70% of the Pu and Am is from the vessel rinse, with the remaining 30-40% from the acid strip.

The sharp increase in Pu and Am release rates seen in some of the latest data are a result of some actinide-bearing secondary phases spalling off of the glass and appearing in the test solution. These increases correlate with the visual observations, where the N2-10 test is observed to undergo the greatest corrosion of the metal and spalling of clay from the glass into the test solution of the N2 series tests. A comparison of the normalized releases of B, Np, Pu, and Am appear in Fig. 75. For the first 8 years, the release of the soluble B and Np was more than two orders of magnitude greater than that of the relatively insoluble plutonium and americium. During the latest 2 years, the release rate of the Pu and Am has nearly equaled that of the soluble elements (Table 24). Note that the Np release does not experience the recent jumps observed for Pu and Am but continues the smoothly as do the Li and B releases. This behavior is consistent with the clay alteration layer being depleted in these elements; release of Pu and Am is thus unaffected by spalling of the clay. Continued spalling of the clay will ultimately cause the normalized release of Pu and Am (as solution-borne solid phases) to approach that of the Li and B. These lower rates are due to incorporation of elements into secondary phases, many of which remain attached to the WPA [BATES-1990; FORTNER-1995, -1996]. The spalling off of these phases then controls the release of the incorporated elements from the glass. These spalled-off phases may then become suspended in solution as colloids. The role of colloidal solids in solution is also reflected in the sequential filtering data, where substantial Pu and Am often appear on the filters and are removed from the filtered solution. Recent use of ultracentrification filtration has shown that nearly 100% of the Np is recovered in the filtered solution from the N2 tests, while less than 10% of the Pu and Am passes as through the filter. A more detailed analysis of the filtered solutions will be prepared as more data are compiled and analyzed. The concentrations of truly dissolved actinides from the N2-12 test sampled December 18, 1995, appear in Table 25. It is clear from these data (and other data) that little of the Np in solution is associated with undissolved solids, while a majority of the Am and Pu are incorporated into particulates and colloids. Examples of solid phases observed from the N2 test components appear in Table 26.

b. <u>Elements in the N3 Solution</u>

The cumulative release of boron and lithium from the N3 tests appears in Fig. 76, with normalized release plotted in Fig. 77. As with the N2 tests, the normalized release of these elements is nearly identical for each test in the N3 series, consistent with congruent dissolution of the glass and complete solubility of the lithium and boron under the test conditions.

Transuranic release appears in Figs. 78 and 79 as total mass release and normalized release, respectively. From these figures it is apparent that the release rate for plutonium and americium has increased by nearly a factor of two during the past 2 years, but they still remain well below the release rate for the soluble elements (Table 27), rather than jumping by an order of magnitude as was observed in the N2-10 test.



Fig. 75. Normalized Release of Np, B, Am, and Pu from a Single Test Series, N2-10, which Displayed Evidence of Excessive Clay Spallation. Note the sudden increase in release of the insoluble elements plutonium and americium, without an accompanying disruption in the release of the more soluble neptunium and boron. This is likely due to the release of the americium and plutonium as solids (colloids or larger particulates), potentially leading to near-congruent release of elements.

Element in solution (ng)						
Np (unfiltered)	Np (filtered)	Pu (unfiltered)	Pu (filtered)	Am (unfiltered)	Am (filtered)	
5 1	<u>5 2^b</u>	0.844	0.002	0.0115	0.0003	

Table 25. Comparison of Transuranic Content in Unfiltered and Ultracentrifuge-Filtered Solutions^a from the N2-12 Test Sampled December 18, 1995

*The solution volume recovered was 1.42 mL.

^bThe recovery of more than 100% of the neptunium is an artifact of statistical error.

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Table 20. Alter	Table 20. Alteration Thases reclumed on 112 Sond Components					
Phase	Nominal Composition	Comments				
Ferrihydrate	5Fe ₂ O ₃ 9H ₂ O					
Iron	FeOOH					
oxyhydroxide						
Sodium feldspar	NaAlSi ₃ O ₈	Precipitate				
Cristobalite	SiO ₂	Precipitate				
Orthoclase	KAĪSi ₃ O ₈	Precipitate				
Smectite clay	Layered aluminosilicate with interlayer Fe and Mg	Variable composition				

Table 26. Alteration Phases Identified on N2 Solid Components





Fig. 76. Cumulative Release of Boron and Lithium from the N3 Tests as a Function of Elapsed Time (The test N3-11 is a blank test, and the release data from the N3-11 test are upper bounds due to detection limits.)



Fig. 77. Normalized Cumulative Release of Boron and Lithium from the N3 Tests as a Function of Elapsed Time (Note also that the normalized releases of these elements are in excellent agreement with one another.)



Fig. 78. Cumulative Mass Releases for the Transuranic Elements Np, Pu, and Am from the N3 Tests: N3-9 (circles), N3-10 (rectangles), and N3-12 (diamonds)



Fig. 79. Normalized Actinide Release from the N3 Tests: N3-9 (circles), N3-10 (rectangles) and N3-12 (diamonds) (Note the retention of americium and plutonium relative to neptunium.)

Normalized Release Rates ^b (g m ⁻² day ⁻¹)							
Test Series	Li	B	Th	U	Np	Pu	Am
N3-9	4.0 x 10 ⁻³	3.4 x 10 ⁻³	1.3 x 10 ⁻⁵	2.6 x 10 ⁻⁴	9.6 x 10 ⁻⁴	4.7 x 10 ⁻⁵	3.0 x 10 ⁻⁵
N3-10	1.8 x 10 ⁻³	1.7 x 10 ⁻³	2.1 x 10 ⁻⁵	4.3 x 10 ⁻⁴	6.6 x 10 ⁻⁴	4.7 x 10 ⁻⁵	2.2 x 10 ⁻⁵
N3-12	2.6 x 10 ⁻³	2.3 x 10 ⁻³	1.1 x 10 ⁻⁵	3.7 x 10 ⁻⁴	4.9 x 10 ⁻⁴	1.0 x 10 ⁻⁴	3.6 x 10 ⁻⁵
Average	2.8 x 10 ⁻³	2.5 x 10 ⁻³	1.5 x 10 ⁻⁵	3.5 x 10 ⁻⁴	7.0 x 10 ⁻⁴	6.5 x 10 ⁻⁵	3.0 x 10 ⁻⁵

Table 27. Normalized Release Rates over the Latest 2.5-year Period for Selected Elements from the N3 Tests Series^a

*The rates include data from the period between January 1994 and July 1996. The above rates are for vessel rinse only, except the rates for Th, U, Pu, and Am, which include the acid strip. ^bError is approximately ±30% for each of the above rates.

The West Valley-type glass used in the N3 tests is unusual in that it contains a large amount of the actinide element thorium relative to most other waste glasses. This element is found to concentrate in alteration phases [BATES-1992; FORTNER-1995, -1996]. The N3 tests continue to release thorium at the relatively low rate of 1.5 (± 0.5) $\times 10^{-5}$ g/(m² day), about 100 times less than the normalized release rates for boron and lithium (Table 27). This low release rate suggests that the thorium alteration phases are mostly remaining with the waste package, although they have been observed in colloidal particles from the test solution [BATES-1992; FORTNER-1996]. Alteration phases observed on components from the N3 test series are summarized in Table 28.

2. <u>Colloidal Particle Analyses</u>

Since the December 1993 and January 1994 samplings of the N2 and N3 tests, respectively, small portions ($\sim 5 \mu$ l) of the test solution have been wicked through a porous or "holey" carbon transmission electron microscope grid to allow AEM examination of suspended particles.

In both the N2 and N3 tests, the majority of colloidal particles observed by AEM have been either a smectite-type clay or a variety of iron-silicates. Both clays and iron silicates can sorb actinides and for entrain actinide containing phases, and thus these colloids represent potential transport mechanisms for insoluble elements. As stated previously, more than 90% of the plutonium and americium in solution from the N2 and N3 Tests appears to be associated with particulate matter that will not pass through a 1 μ m filter. In the N2 Tests, both the clay and iron-silicate colloids are sometimes observed to contain small amounts of uranium. Uranium is also observed on occasion in the clays and iron-silicates from the N3 Tests; thorium is generally detected only in an alteration phase such as brockite [BATES-1992; FORTNER-1995, -1996], and not in the clay itself.

Phase	Location	Identification	Comments
Smectite clays	A layer on all glass surfaces. Spalled fragments located sporadically on 304L retainer components	EDS, electron diffraction, lattice imaging	A ubiquitous layer that grew with test duration. The more advanced growths displayed a "backbone" structure.
Brockite (CaThPO ₄)	Copious amounts found on most glass surfaces. Clusters found on most 304L retainer surfaces except those of shortest test duration.	EDS, electron diffraction, EELS	Appeared to form as separate crystallites in or on outer layer of clay. Entrained rare earth elements, uranium, and probably transuranics. This phase was amorphous or partly amorphized.
Uranium silicates	Very sparsely located on glass and 304L retainer surfaces. More likely to be observed where 304L retainer interacted with glass.	EDS	Positive phase identification of these rarely-encountered crystallites was not possible; they did not appear in any AEM samples.
Iron silicates, iron silicate hydrates, and iron oxyhydrates	In some cases, iron- rich layers grew on glass where it contacted 304L retainer. Separate material and crystals found on most glass and 304L retainer surfaces.	EDS, electron diffraction	Electron diffraction generally found these materials to be amorphous. Fayalite was identified in one instance by electron diffraction.
Thorium titanium iron silicate	Appeared to precipitate colloidally between glass and clay layer or in other regions of restricted water flow.	EDS, EELS	This material was amorphous and grew as wisps that were usually mixed with the clay. The clay appeared to serve as a barrier, trapping this material between the glass and the clay "backbone"
Zeolites	Rarely encountered (possibly artifacts).	EDS, electron diffraction	Only two instances observed; once in the SEM (N3#8 glass top) and once in the AEM (N3#3 glass bottom). Electron diffraction identified the latter as a member of the heulandite subgroup.
Amorphous silica	Occasional white surface particulates.	EDS, EELS, electron diffraction (as diffuse rings)	The conditions that cause silica rather than clay formation are unknown.

Table 28. Summary of Alteration Phases Noted on the N3 Test Components Surfaces

Source: FORTNER-1997.

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E. <u>Summary</u>

Drip tests designed to replicate the synergistic interactions between waste glass, repository groundwater, water vapor, and sensitized 304L stainless steel in the proposed Yucca Mountain Repository have been in progress for over 10 years with actinide-doped glasses. The N2 Test Series on DWPF-type glass has clearly demonstrated the importance of alteration phases in controlling actinide release from the corroding waste glass. These alteration phases may be spalled from the glass surface, releasing the actinides as solution-borne colloids and particulates. The N3 Tests on WVDP-type glass has formed unusual actinide-containing phases, several of which have been identified. As in the N2 Tests, the N3 Tests initially retain actinides in alteration phases, later releasing them by layer spallation as glass corrosion progresses. This alteration/spallation process effectively results in near-congruent release of elements from the glass, regardless of their solubilities.

F. Ongoing Work

The N2 and N3 Tests will continue through FY 1998, and updates of data and interpretations will be made in reports and publications in refereed journals. Detailed analysis of the sequentially filtered solution data and AEM examination of colloids will be performed. As it appears from recent data that the spallation rate is increasing for actinide-bearing phases from the waste package, the role of colloidal particles in controlling release rates is expected to become correspondingly more important. An example of data now available but previously unpublished include technetium release, which is available for sample periods since 1993. Total mass release rates for technetium from the N2 and N3 Tests appear in Table 29. We are currently reanalyzing archival test glasses to accurately determine technetium content so that these data may be interpreted and reported as normalized release rates.

Technedulii Hom die 112	recimentalit from the NZ and NJ rests Series					
Test Series	Tc Release Rate (ng year ⁻¹)					
<u>N2-9</u>	2.9					
N2-10	25					
N2-12	15					
N3-9	15					
N3-10	3.3					
N3-12	16					

Table 29. Release Rates over the Latest 2.5-year Period for Technetium from the N2 and N3 Tests Series

IX. VAPOR HYDRATION TESTING OF GLASS

A. <u>Introduction</u>

In an unsaturated environment such as that projected at the potential repository at Yucca Mountain, HLW glass will be subjected to a range of hydrologic conditions after the waste package and pour canister have been breached. However, water vapor, prior to liquid water, will contact the glass, and previous studies have shown that the glass reacts when contacted by water vapor [1-5]. The importance of water vapor corrosion is that vapor-hydrated glass reacts differently with liquid water than does as-cast glass. Thus, the initial reaction between liquid water and the glass HLW form will be with hydrated glass. To accurately predict what the release from a hydrated glass will be, it is necessary to know the extent of hydration that will occur as a function of time, temperature, and glass composition.

Previous studies [ABRAJAN0-1989, BATES-1982, POINSSOT-1996, EBERT-1991, GONG-1996] have shown that HLW glass reacts initially with vapor via a process that converts the glass to a smectite clay. While the mechanism of this initial reaction is not known, the kinetics of the reaction for SRL 131 glass have a $t^{1/2}$ time dependence for a temperature range between 75 and 240°C and for relative humidities greater than 80%. The thickness of the reaction layer is used as a measure of glass reaction in these tests.

After the initial reaction, a new set of alteration phases form, which typically include zeolites and calcium silicates. At this time, the reaction rate accelerates. In liquid water the same effect in duality in rates is observed [WRONKIEWICZ-1993, BOUCIER-1994, EBERT-1993, ADBELOUAS-1997, FENG-1993, VERNAZ-1992], where the accelerated rate has linear kinetics. However, in vapor, there has been considerable scatter in the measured thickness of the alteration layer during the time period when the accelerated reaction occurs. This scatter is likely due to variance in the onset of phase nucleation. It is believed that when the second set of alteration phases form, the rate increases because the chemical potential for the reaction increases. If phase nucleation occurs at a uniform stage during the reaction progress, then the accelerated reaction would be initiated at the same time, and the rate of reaction would be straightforward to determine. However, since phase nucleation does not occur at a uniform time during the reaction progress, then data scatter related to the formation of the second set of alteration products occurs, which can be described as an offset of the x axis of a reaction layer thickness (y axis) vs. time (x axis) plot.

To accurately measure the reaction rate for a glass, either a sufficient number of tests must be performed such that the precision in the data is improved to an acceptable level, or the onset of nucleation must be controlled. It may be possible to control the onset of nucleation by seeding the glass surfaces with reaction products taken from another highly reacted glass sample of the same composition.

In this task, work will be performed to determine the rate of reaction between water vapor and several nuclear waste glass formulations as a function of temperature. This information is needed to calculate the amount of reaction that glass will undergo prior to contact with liquid water. Previous studies have indicated that the nucleation of secondary phases will be important in determining the long-term rate of vapor hydration, and efforts will be made to control this part of the reaction to obtain reproducible values for the rate constants.

B. <u>Objective</u>

The objective of the vapor hydration test (VHT) is to determine the rate of reaction between water vapor and glass in a water-vapor-saturated air atmosphere as a function of glass composition and temperature. Based on these measurements, it will be possible to calculate an activation energy and rate constant for each glass, and from this information it will be possible to extrapolate the reaction of glass in saturated water vapor to different temperatures as required by repository performance assessment calculations. A procedure will be developed and documented that can be used to perform the VHT to provide quantitative rate information. As part of the VHT, the alteration phases that form on the surface of the glass will be identified. While it is recognized that radiation may affect the rate of vapor hydration of glass, the bulk of the tests will be performed using glasses containing no fission products. The glasses may contain U or Th. Some tests will be done using a sludge-based radioactive glass to confirm the results generated with the nonradioactive glass.

C. <u>Technical Approach</u>

A test procedure will be developed to determine uniform reaction kinetics for the accelerated stage of reaction. Since the actual procedure is not known at this time, an exact test matrix cannot be given. However, the approach to be used in gathering the required information is outlined below.

Three nonradioactive glasses with different compositions will be reacted at temperatures between 70 and 200°C at 100% relative humidity (RH). The glasses to be tested are designated as 202U, 200S, and 165U. One sludge-based radioactive glass will be tested at 100% RH at one temperature to be determined later to confirm the results on the nonradioactive glass of the same nominal composition. Initially, the existing "Procedure for Performing Vapor Hydration Tests" will be issued as a YMP procedure and it will be used on one glass (200S) to determine the best method to obtain quantitative kinetic information. Then, the procedure will be revised on the basis of the resulting data. The new procedure will be applied to all of the glasses over a complete temperature range. The initial test matrix is shown in Table 30. Two glass monoliths are used in each test, and tests will be done both with a seeded glass to control the onset of phase alteration and with fresh glass as a control. The test matrix with simulated glasses is shown in Table 31. A similar test matrix will be performed with all three glasses. The test matrix to be used with radioactive glass is shown in Table 32.

Table 30. Initial Test Matrix for 200S Glass (Procedure Development)					
Test ID	Glass ID	(T, °C/t, days)			
Fresh Glass					
VHT(200)-1	200S-20/21	200/3			
VHT(200)-2	200S-22/23	200/7			
VHT(200)-3	200S-24/25	200/10			
VHT(200)-4	2008-26/27	200/14			
VHT(200)-5	200S-28/29	200/17			
VHT(200)-6	2008-30/31	200/21			
Seeded Glass					
VHT(200)-11	200S-20/21	200/3			
VHT(200)-12	200S-22/23	200/7			
VHT(200)-13	200S-24/25	200/10			
VHT(200)-14	200S-26/27	200/14			
VHT(200)-15	2005-28/29	200/17			
VHT(200)-16	200S-30/31	200/21			

		Fresh Glass			Seeded Glass
Test ID	Glass ID	(T, °C/t, days)	Test ID	Glass ID	(T, °C/t, days)
VHT(70)-1	2005-1/2	70/182	VHT(70)-11	200S-20/21	70/182
VHT(70)-2	200S-3/4	70/364	VHT(70)-12	200S-22/23	70/364
VHT(70)-3	2005-5/6	70/728	VHT(70)-13	200S-24/25	70/728
VHT(70)-4	200S-7/8	70/1092	VHT(70)-14	200S-26/27	70/1092
VHT(70)-5	2005-9/10	70/1456	VHT(70)-15	200S-28/29	70/1456
VHT(70)-6	2005-11/12	70/1820	VHT(70)-16	200S-30/31	70/1820
VHT(70)-7	2005-12/13	70/TBD	VHT(70)-17	200S-32/33	70/TBD
VHT(70)-8	2005-14/15	70/TBD	VHT(70)-18	200S-34/35	70/TBD
VHT(70)-9	2005-16/17	70/TBD	VHT(70)-19	200S-36/37	70/TBD
VHT(70)-10	2005-18/19	70/TBD	VHT(70)-20	200S-38/39	70/TBD
VHT(90)-1	2005-20/21	90/91	VHT(90)-11	2008-20/21	90/91
VHT(90)-2	2005-22/23	90/182	VHT(90)-12	2008-22/23	90/182
VHT(90)-3	2005-24/25	90/364	VHT(90)-13	2008-24/25	90/365
VHT(90)-4	2005-26/27	90/728	VHT(90)-14	2008-26/27	90/728
VHT(90)-5	2005-28/29	90/1092	VHT(90)-15	2005-28/29	90/1092
VHT(90)-6	2005-30/31	90/1456	VHT(90)-16	2005-30/31	90/1456
VHT(90)-7	2005-32/33	90/1820	VHT(90)-17	2008-32/33	90/1820
VHT(90)-8	2005-34/35	90/TBD	VHT(90)-18	2008-34/35	90/TBD
VHT(90)-9	2005-36/37	90/TBD	VHT(90)-19	2008-36/37	90/TBD
VHT(90)-10	2005-38/39	90/TBD	VHT(90)-20	2005-38/39	90/TBD
VHT(125)-1	2005-20/21	125/56		2005-20/21	125/56
VHT(125)-1	2005-20/21	125/91	VHT(125)-12	2008-22/23	125/91
VHT(125)-2	2005-22/25	125/182	VHT(125)-12	2008-24/25	125/182
VHT(125)-3	2005-24/23	125/364	VHT(125)-14	2008-26/27	125/364
VHT(125)-4	2005-20/27	125/728	VHT(125)-15	2005-28/29	125/728
VHT(125)-5	2005-20/21	125/1092	VHT(125)-16	2005-30/31	125/1092
VHT(125)-7	2005-32/33	125/1456	VHT(125)-17	2005-32/33	125/1456
VHT(125)-8	2005-34/35	125/TBD	VHT(125)-18	2005-34/35	125/TBD
VHT(125)-9	2005-36/37	125/TBD	VHT(125)-19	2005-36/37	125/TBD
VHT(125)-10	2005-38/39	125/TBD	VHT(125)-20	2005-38/39	125/TBD
VHT(150)-1	2005-20/21	150/28		2005-20/21	150/28
VHT(150)-7	2005-20/21	150/56	VHT(150)-12	2005-22/23	150/56
VHT(150)-3	2005-24/25	150/91	VHT(150)-13	2005-24/25	150/91
VHT(150)-4	2005-26/27	125/182	VHT(150)-14	2005-26/27	150/182
VHT(150)-5	2005-28/29	1507364	VHT(150)-15	200S-28/29	150/364
VHT(150)-6	200S-30/31	150/728	VHT(150)-16	200S-30/31	150/728
VHT(150)-7	2005-32/33	150/1092	VHT(150)-17	200S-32/33	150/1092
VHT(150)-8	2008-34/35	150/TBD	VHT(150)-18	200S-34/35	150/TBD
VHT(150)-9	2005-36/37	150/TBD	VHT(150)-19	200S-36/37	150/TBD
VHT(150)-10	200S-38/39	150/TBD	VHT(150)-20	200S-38/39	150/TBD
VHT(200)-1	2005-20/21	200/3	VHT(200)-11	200S-20/21	200/3
VHT(200)-2	200S-22/23	200/7	VHT(200)-12	200S-22/23	200/7
VHT(200)-3	200S-24/25	200/10	VHT(200)-13	200S-24/25	200/10
VHT(200)-4	2005-26/27	200/14	VHT(200)-14	200S-26/27	200/14
VHT(200)-5	200S-28/29	200/17	VHT(200)-15	200S-28/29	200/17
VHT(200)-6	200S-30/31	200/21	VHT(200)-16	200S-30/31	200/21
VHT(200)-7	2008-32/33	200/35	VHT(200)-17	200S-32/33	200/35
VHT(200)-8	200S-34/35	200/TBD	VHT(200)-18	200S-34/35	200/TBD
VHT(200)-9	2005-36/37	200/TBD	VHT(200)-19	200S-36/37	200/TBD
VHT(200)-10	2005-38/39	200/TBD	VHT(200)-20	200S-38/39	200/TBD

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Table 31. Test Matrix for 200S, 202U, and 165U Glasses^a

*A similar test matrix will be developed for each glass. The time periods may very depending on the character of the glass.

Test ID	Glass ID	T, °C/t, days
Fresh Glass		
VHTR(TBD)-1	202R-20/21	TBD/TBD
VHTR(TBD)-2	202R-22/23	TBD/TBD
VHTR(TBD)-3	202R-24/25	TBD/TBD
VHTR(TBD)-4	202R-26/27	TBD/TBD
VHTR(TBD)-5	202R-28/29	TBD/TBD
VHTR(TBD)-6	202R-30/31	TBD/TBD
Seeded Glass		
VHT(200)-11	200R-20/21	TBD/TBD
VHT(200)-12	200R-22/23	TBD/TBD
VHT(200)-13	200R-24/25	TBD/TBD
VHT(200)-14	200R-26/27	TBD/TBD
VHT(200)-15	200R-28/29	TBD/TBD
VHT(200)-16	200R-30/31	TBD/TBD

Table 32. Proposed Test Matrix for 202R Glass

Three simulated glasses and one fully radioactive glass will be tested. These glasses are available at ANL and have been used previously in testing supported by the Environmental Restoration branch of the DOE. These glasses are identified in the ANL Glass Reference Data Base as glasses 200R, 200S, 202S, and 165S and have been analyzed at ANL. The compositions are given in Table 33. These glasses were chosen because they are representative of a range of compositions that may be produced at the DWPF, and they have been tested at ANL under a variety of conditions.

Each test will be carried out in a certified Type 304L stainless steel reaction vessel manufactured by Parr Instrument Co., Moline, IL. These vessels have a compression-type closure and will be sealed with a flat annealed copper gasket. The experiments will be performed in forced-air electrically heated ovens, whose temperatures will be controlled $\pm 2^{\circ}$ C and monitored with a data logger that will periodically record the temperature . Uniformity of the temperature inside each oven will be mapped using thermocouples that have been calibrated prior to use against thermometers traceable to NIST standards.

The thickness of the alteration layers will be plotted as a function of time and temperature to determine the rate of reaction during the different stages in the reaction progress and to determine the energy of activation of the reactions. The phases formed will be compared to determine whether the same phases form at different temperature, and thereby determine the effect of phase formation on the rate of reaction. The samples will be analyzed to examine the mechanism of reaction and ascertain whether the mechanism changes as a function of temperature. If the mechanism changes, the activation energy should also change, which would be indicated in the data plots.

If no change in the reaction mechanism is observed, then the data can be extrapolated to longer time periods over the temperature range studied. Also, the tests with the fully radioactive glass will be started to confirm that both the simulated and radioactive glasses hydrated follow the same process and rate.

	Composition			
-	51R*	51S	202S	165S
Element				
Al	4.82	4.99	3.9	4.5
В	6.41	7.08	8.0	6.7
Ba			0.21	0.03
Ca	1.38	1.33	1.3	1.6
Ce	— –		<0.01	<0.01
Cr	0.44	0.41	0.12	0.02
Cu			0.41	ND⁵
Fe	13.10	11.71	11.9	12.2
K	1.56	1.33	3.7	0.20
La	0.55	0.52	0.11	<0.01
Li	4.50	4.34	4.4	4.5
Mg	2.05	1.96	1.4	0.73
Mn	1.54	1.35	2.2	2.8
Мо			0.05	0.01
Na	9.35	9.18	7.8	11.4
Nd		<u> </u>	<0.01	ND
Ni	0.29	0.26	0.85	0.85
Р	0.60	0.54		
Pb			0.01	0.01
Rh		—	<0.01	<0.01
Ru			<0.01	0.01
Si	52.16	53.81	50.2	52.4
Sr	0.0060		0.03	0.11
Th	0.02	0.02	0.28	ND
Ti		<u> </u>	0.93	0.15
U	1.09	1.05	2.0	1.1
Zn	0.14	0.11	0.29	0.02
Zr		<u> </u>	0.06	0.70
²⁴¹ Am	7.4E-5	_	4.4E-4	1.8E-4
²⁴⁴ Cm	1.1E-5		ND	ND
⁶⁰ Co	NR°		ND	ND
¹³⁷ Cs	2.2E-5	—	ND	ND
¹⁵⁴ Eu	NR		ND	ND
¹⁵⁵ Eu	NR	—	ND	ND
²³⁷ Np	4.2E-4	—	1.4E-2	1.4E-2
²³⁸ Pu	1.1E-4	<u> </u>	ND	ND
²³⁹ Pu	2.2E-3		1.3E-2	8.7E-3
²⁴⁰ Pu	3.0E-4		ND	ND
¹²⁵ Sb	NR		ND	ND
⁹⁹ Tc	3.8E-4		3.0E-3	1.5E-3

Table 33. Compositions of Glass to be Used in the Vapor Hydration Tests (element wt%)

^aSource: BIBLER-1994 ^bND = no data exist for that element. ^cNR = not reported.

Results and Ongoing Effort D.

At this time, the test vessels and glasses have been prepared and the tests are to be initiated shortly.



X. DEVELOPMENT OF METHODS TO STUDY WASTE FORM COLLOIDS

A. <u>Introduction</u>

The present work is being conducted to complement and enhance currently used techniques (such as sequential filtration and AEM) in the characterization of colloidal properties. Methods developed in this study include dynamic light scattering (DLS), electrophoretic light scattering (ELS), and autoradiography (AR) to study colloids formed from the reaction of glass or spent fuel with groundwater under potential repository conditions at Yucca Mountain. This year a task plan, operating procedure, and a report were issued for the DLS technique. Leachate samples from a variety of waste form tests have been analyzed with DLS, and these analyses will continue as samples become available from ongoing tests. Task plans have been issued and developmental work is ongoing for the ELS and AR techniques.

B. <u>Objective</u>

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The objective of this task is to develop such methods as DLS, ELS, and AR to characterize colloids formed from the reaction of radioactive waste forms (glass or spent fuel) with groundwater under potential repository conditions at Yucca Mountain. Particle size distributions of the colloids present in the waste form leachate solutions will be determined with DLS. The data obtained by ELS will reveal surface charge properties of the colloids, which are related to the mobility and stability of the colloids. Autoradiography will be combined with small-particle-handling techniques and AEM to identify the radionuclide-bearing phases.

C. <u>Technical Approach</u>

Dynamic light scattering has been developed as a method for the characterization of colloidal size distributions that result from waste form corrosion, while work is continuing in the development of ELS and AR. An experimental procedure for performing DLS on waste form colloids was developed. The DLS method was used to analyze colloids that were formed under a variety of laboratory test conditions that simulate waste form reaction in a repository environment. Leachate samples from ongoing Yucca Mountain activities and other glass corrosion tests with EJ-13 groundwater were examined with DLS for testing and developing this method. The particle size distribution and concentration of colloids were examined *in situ* with DLS.

1. Instrumentation

The DLS apparatus consists of a modified 4700c Photon Correlation Spectrometer from Malvern Instruments Ltd. The light scattering unit includes a Siemens 35 mW HeNe laser and a Uniphase 3-75 mW argon ion laser. All components of the system and associated optics are mounted on an enclosed optical table.

2. <u>Service and Maintenance</u>

The DLS unit has been serviced to receive sample solutions from both simulant and radioactive tests. Service of the DLS system included alignment of the lasers and the photomultiplier tube (PMT), cleaning the sample chamber and pump system, calibration of the unit with NIST traceable standards, and performance of other routine maintenance tasks on the unit. In addition, the optical bench and associated optics were cleaned and are kept free of dust and contaminants. All glassware and sample cells were stringently cleaned.
3. <u>Calibration</u>

Laser light scattering system calibration was performed with a series of NIST traceable polystyrene latex standards (32, 74, and 304 nm) from Duke Scientific Corp. Standard solutions were sampled according to certification instructions using filtered deionized water. Measurements were made with the argon ion laser at 3 mW and the HeNe laser at 24 mW.

4. DLS Measurements on Waste Form Solutions

The test sampling or termination was dependent on the ongoing test; however, the general DLS measurement procedure was to take an unfiltered sample aliquot of approximately 500 mL from the test solution. A "clean" DLS cell (8 mm OD.) was used for the DLS aliquot. Minimal handling of the DLS cell occurred during loading into the system's sample chamber. Test solutions were measured with the DLS unit as soon as possible after running the test sampling or termination solution. Laser power and other experimental parameters were adjusted for collecting DLS data. The correlator is able to record the scattering intensity from small volumes in time intervals as short as 50 ns. Such a short time interval enables the motion of colloids in solution to be monitored. The time interval or fundamental sample time (t) is dependent on the size of the colloidal particles present in each sample.

5. Data Analysis

Data analysis involves the LaPlace inversion of the correlation function. The particle sizing data are fit by well-accepted methods: cumulants and CONTIN [CHU-1991; HARDING-1992; PROVENCHER-1984; STOCK-1985]. The raw data can be fit to the cumulants method using the cumulant expansion, which is a power series expansion of the form given in Equation X-1 [CHU-1991],

$$\Gamma(t) = A + Ab \left[\exp(2(-\Gamma t + (1/2!)\mu_{2}t^{2} - (1/3!)\mu_{3}t^{3} + ...)) \right]$$
(38)

where $\Gamma(t)$ is the measured intensity correlation function, t is the delay time, A is the baseline, b is an instrumental constant, Γ is the mean decay constant (related to the particle size), and μ_2/Γ^2 is the polydispersity or the width of the particle size distribution. The value of Γ is directly related to the diffusion coefficient (D) by Eq. 39.

$$D = \Gamma / q^2 \tag{39}$$

The scattering vector (q) is defined by Eq. 40,

$$q = (4\pi\eta/\lambda)\sin(\theta/2)$$
(40)

where λ is the laser wavelength (λ for Ar⁺ = 5.145 x 10⁻⁵ cm⁻¹), θ is the scattering angle, and η is the solvent or solution viscosity (η for H₂O = 8.95 x 10⁻³ g cm⁻¹sec⁻¹). Applying the Stokes-Einstein relationship (Eq. 41), the mean diameter (d) of the colloid is obtained.

$$d = k_{\rm B} T / 3\pi \eta D \tag{41}$$

where the Boltzmann's constant is k_B (1.381 x 10⁻¹⁶ g cm²sec⁻²K⁻¹) and T is the absolute temperature (Kelvin). The cumulants analysis gives the mean particle size and width of the distribution.

CONTIN is a well-known and powerful program for the analysis of photon correlation spectroscopy (or DLS) data. Polydisperse data (indicated by a variance greater than 0.3 from the cumulants analysis [CHU-1991]) were analyzed with Malvern's CONTIN Processor. This program is a constrained regularization method that is model independent to avoid the bias of fixed form models. A more detailed explanation of the program's capabilities are available in the CONTIN User Manual [PROVENCHER-1984].

D. <u>Results</u>

Developmental work has been performed to characterize waste form colloids with DLS. As part of this work, an operating procedure for analysis of waste form colloids with DLS has been written. The DLS unit is operational (i.e., the system has been aligned and calibrated). Samples from ongoing, waste form, corrosion tests were examined as they became available.

1. <u>Calibration Using Polystyrene Standards</u>

Polystyrene (PS) nanospheres (NIST traceable standards) of various sizes (i.e., 32, 74, 304 nm) were used to calibrate the instrument. These are accepted standards for DLS measurements and are stable for long periods of time. To date, there do not exist nonspherical standards for DLS measurements. The literature contains light-scattering measurements on rod-and disc-shaped biological molecules (DNA fragments, viruses, etc.). However, due to purification and preparation requirements (i.e., dialysis, sonication, buffer solution, etc.) which can greatly affect the size and shape of the biological molecules, these types of molecules are not recommended for calibration. Static light scattering measurements can be made as a function of scattering angle to determine the shape of the particles (i.e., spherical, rod-shaped, etc).

Dynamic light scattering measurements of the polystyrene standards exhibited narrow size distributions that were in excellent agreement with the manufacturer's specifications. Table 34 lists the results of multiple measurements on each standard solution by both lasers. The data were fit by the cumulants method.

	Mean Diameter (nm)		Standard Deviation (nm)	
No. of Measurement	Certified	Measured	Certified	Measured
4	32	32.0	1.3	0.7
4	74	74.0	2.7	0.5
5	30 4	305.7	6	2.3

Table 34. Particle Size of Polystyrene Standards Measured by DLS System

In addition, polystyrene standards were diluted to several different concentrations and the solutions were measured with DLS. A linear relationship between count rate and concentration was obtained for both standards (Fig. 80). This plot can be used to estimate unknown colloid concentrations, but it should be used to provide a range with noted limitations. Such estimated concentrations would be an approximate concentration range and not an absolute value due to scattering differences between the standard and the unknown sample, polydispersity effects, and other factors. The PS standards are spherical particles that scatter light very efficiently; this may not be the case with waste form colloids. In general, Fig. 80 shows that particles which scatter light efficiently (e.g., good scattering contrast between the particle and the suspending medium) can be detected quite easily in the parts per million concentration range. Particle sizing measurements can be made on concentrations of particles as low as 0.2 ppm. However, DLS measurements can be severely limited by the presence of dust and foreign material, especially at sub-ppm concentrations. A small amount of dust will distort the measured correlation function, in that dust partially blocks the incident beam and scatters the laser light very strongly in comparison to dilute weakly scattering systems.



Fig. 80. Correlation between Count Rate and Concentration for 74 and 304 nm PS Standards

2. Leachate from Long-Term, Intermittent, Flow Test on Radioactive Glass

Modified drip tests using a pre-aged, radioactive, sludge-based, Savannah River Laboratory (SRL) 200R glass have been ongoing for five years (N4-2 test series) under a program performed for EM. The standard drip test (unsaturated test procedure) was modified to include the effects of aging both the glass and metal components. The drip tests follow the unsaturated test procedure and are described elsewhere [BATES-1986; BATES-1990]. A monolith glass sample of SRL 200R and the stainless steel holder were pre-aged for four weeks in 200°C water vapor. The drip tests were performed with tuff-equilibrated groundwater (EJ-13) slowly dripping on the waste glass sample, and stainless steel holder in an unsaturated water vapor atmosphere at 90°C. A sampling of this test occurred on September 23, 1996 [Sample ID: N4-2 (9-23-96)], and an aliquot was taken for DLS measurements.

Dynamic light scattering measurements were made over the course of 10 days on the N4-2 (9-23-96) leachate to monitor the stability of the colloids. The sample remained in a temperature-controlled water bath at 25°C during the 10-day period. Initial data from the correlator that were measured within hours of the sampling are shown in Fig. 81. The data could not be fit by the cumulants method and were analyzed by CONTIN [CHU-1991; HARDING-1992]. The results from DLS indicated a broad or polydisperse distribution for the several hour measurement. CONTIN was able to resolve a bimodal distribution (Fig. 82). The largest suspended fraction (99%, based on the intensity distribution) is attributed to particles in the size range of 20-306 nm with a mean diameter of approximately 200 nm. A smaller fraction (1%) of particles in the size

range of 1640-2500 nm with a mean diameter greater than 3000 nm (3 micrometers) was also found suspended in the sample.







Fig. 82. Particle Size Distribution for Leachate Sample N4-2 (9-23-96) (Measurement with DLS was made several hours after sampling.)

Correlator data for the 10-day measurement on the N4-2 (9-23-96) leachate are shown in Fig. 83. A monomodal distribution was obtained for the 10-day measurement with particles in the range of 50-530 nm and a mean diameter of approximately 200 nm (Fig. 84). The contribution from the larger size fraction that was observed in initial measurements of the leachate was absent from the 10-day measurement and can be attributed to settling of the larger particles.







Fig. 84. Particle Size Distribution for Leachate Sample N4-2 (9-23-96) (Measurement with DLS was made 10-days after sampling.)

The count rate from three DLS measurements made within several hours of the N4-2 (9-23-96) sampling at 3 mW with the argon ion laser was 194 ± 10 kilocounts/second (kc/s). Ten days later, three DLS measurements made on the N4-2 (9-23-96) leachate had a steady count rate of 150 ± 1 kc/s. The same settings were used for the 10-day measurements as for the initial, several hour measurements. Concentration range estimates for the sample at several hours and at 10 days did not vary significantly (2-6 and 2-5 ppm, respectively), which was expected since the several hour measurement contained only a small fraction (1%) of micrometer-sized particles. By means of the DLS analyses on the N4-2 (9-23-96) leachate over the 10-day period, we were able to monitor

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the stability of the colloids, where the micron-sized particles were shown to settle out of solution, leaving the stable nanometer fraction suspended in solution.

3. Leachate from Long-Term, Static Test on Radioactive Glass

An ongoing (70-day), product consistency test (PCT) of an actinide-doped borosilicate waste glass (SRL 131A) at a surface-area-to-volume ratio of 2000 m⁻¹ was terminated and the leachate was available for DLS measurements. Dynamic light scattering measurements were performed on the leachate sample, and representative data from the correlator are shown in Fig. 85. Cumulants analysis of the data indicated a fairly broad distribution with a variance of 0.3, and therefore, CONTIN analysis was performed on the data. Results for the DLS measurements on the leachate solution indicate a monomodal distribution, with particles in the range of 15-320 nm and a mean diameter of approximately 100 nm (Fig. 86). Initial and two-day measurements had count rates of 155 and 151 kc/s, respectively. Even after 10-days, the colloidal sample was quite stable, as indicated by a count rate of 159 kc/s. This count rate corresponds to a concentration range of 2-5 ppm for this sample. Sequential filtration and alpha spectroscopy results from a previously terminated PCT conducted under the same reaction conditions as the test on the SRL 131A glass just terminated indicated a colloidal actinide fraction between 6 and 450 nm [EBERT-1993]. The DLS results are consistent with the filtration data of Ebert and Bates [EBERT-1993], and give additional information on the colloids that was not available from previous analysis methods (i.e., particle size distribution and concentration estimates of the colloids in solution). In addition, in situ DLS measurements were used to monitor the stability of the colloids over a 10-day period, which could not have been done by other methods.



Fig. 85. Intensity Autocorrelation Function Data for Leachate Solution from Reaction of SRL 131A Glass with EJ-13 Groundwater at 2000 m⁻¹ for 70 Days (A fundamental sample time of 45 ms was used to collect the data.)



Fig. 86. Particle Size Distribution for Leachate Solution from Reaction of SRL 131A Glass with EJ-13 Groundwater at 2000 m⁻¹ for 70 Days (CONTIN was used to analyze the data.)

4. Spent Fuel Leachate

An unsaturated leach test with irradiated UO_2 was sampled at 49 months, and an aliquot was taken for DLS measurements. This test was designed to evaluate the performance of ATM-103 irradiated fuel (burnup of 30 MW d/kgU) in unsaturated conditions similar to those expected at Yucca Mountain. The test was performed on the irradiated UO_2 at 90°C under high-drip-rate conditions with EJ-13 groundwater (water velocity of 5 mm/yr). Dynamic light scattering measurements on the sample did not indicate any colloids above the detection limits of the system. The count rate for the spent fuel leachate was comparable to background levels. In any event, colloids were not expected in this sample due to sequential filtration results from previous sampling events.

E. <u>Conclusions</u>

Development of colloid characterization techniques will provide essential information on colloids generated from waste form reactions in tests that simulate the expected conditions for the repository. Dynamic light scattering has been demonstrated as a technique to examine and monitor waste form colloids. This work shows that DLS measurements can provide useful information on the particle size distribution and concentration of colloidal species that form during the corrosion of waste forms. Test solutions from ongoing tests on glass and spent fuel have been examined by DLS. *In situ* DLS measurements have shown that waste form colloids exist as stable species (for 10-days in two of the cases examined in this study). Dynamic light scattering is a technique that can minimize disadvantages in studying colloids due to poor statistical representation of the leachate colloids, possible sample preparation artifacts with AEM and interactions with filter membranes with sequential filtration techniques.

F. Ongoing Work

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Further work is needed to understand the behavior of colloids in the waste form environment. While it has been established that radioactive waste forms can release radionuclides via colloids, details of the role of the colloids are not well-documented. Using combination of DLS, ELS, and AR to examine solutions from the testing of either spent fuel or glass samples would provide a firm technical basis for understanding fundamental properties of waste form colloids and the mechanism by which they form. In situ, ELS measurements would determine the mobility of charged colloids in solution and surface charge properties related to stability and transport. Characterization of surface charge properties of radionuclide-bearing colloids would allow examination of attractive and repulsive tendencies of the waste form colloids towards other charged particles and surfaces as a function of groundwater properties. Thus, zeta potential measurements would determine stable and unstable solution conditions for colloidal species. In addition, the development of an AR technique to isolate radionuclide-bearing colloids will be essential to characterizing the disposition of radionuclides in colloidal phases. Autoradiography employs a nuclear emulsion to locate radionuclide-bearing colloids. These colloids are then isolated by small-particle-handling techniques, and the composition of the phases are identified with TEM. Development of ELS and AR techniques will be advanced in ongoing work to fully characterize waste form colloids (conditions promoting colloid formation, relationship of those conditions to the proposed storage site, and characterization of the waste form colloids). Experimentally determined colloid properties (size distribution, colloid surface charge characteristics, colloid aggregation processes, and radionuclide-bearing phases) obtained from DLS, ELS, and AR measurements are essential in assessing the stability and mobility of waste form colloids.



XI. ACKNOWLEDGMENTS

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