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Initial Results from Dissolution Rate Testing of N-Reactor Spent Fuel Over a Range of Potential Geologic Repository Aqueous Conditions

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Initial Results from Dissolution Rate Testing of N-Reactor Spent Fuel Over a Range of Potential Geologic Repository Aqueous Conditions

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Summary

Hanford N-Reactor spent nuclear fuel (HSNF) may ultimately be placed in a geologic repository for permanent disposal. To determine whether the engineered barrier system that will be designed for emplacement of light-water-reactor (LWR) spent fuel will also suffice for HSNF, aqueous dissolution rate measurements were conducted on the HSNF. The purpose of these tests was to determine whether HSNF dissolves faster or slower than LWR spent fuel under some limited repository-relevant water chemistry conditions.

The tests were conducted using a flowthrough method that allows the dissolution rate of the uranium matrix to be measured without interference by secondary precipitation reactions that would confuse interpretation of the results (i.e., uranium concentrations were kept below the solubility limit). Similar tests had been conducted earlier with LWR spent fuel, thereby allowing direct comparisons.

Six undamaged HSNF test specimens (one of the six specimens was treated to produce a thin oxide surface layer) were tested using 10 different water chemistry conditions. Six tests were conducted simultaneously, and then the water chemistries were changed to conduct the remaining four tests. In addition, two auxiliary tests were conducted to investigate one possible cause of the Stage 2 corrosion noted below.

Two distinct corrosion modes were observed during the course of these 12 tests. The first, Stage 1, involved no visible corrosion of the test specimen and produced no undissolved corrosion products. The second, Stage 2, resulted in both visible corrosion of the test specimen and left behind undissolved corrosion products.

During Stage 1, the rate of dissolution could be readily determined because the dissolved uranium and associated fission products remained in solution where they could be quantitatively analyzed. The measured rates were much faster than has been observed for LWR spent fuel under all conditions tested to date when normalized to the exposed test specimen surface areas. Application of these results to repository conditions, however, requires some comparison of the physical conditions of the different fuels. The surface area of LWR fuel that could potentially be exposed to repository groundwater is estimated to be approximately 100 times greater than HSNF. Therefore, when compared on the basis of mass, which is more relevant to repository conditions, the HSNF and LWR spent fuel dissolve at similar rates. Also, the concentrations of fission products and actinides are about 10 times lower in HSNF than in LWR spent fuel. Thus, for equal dissolution rates (the rate obtained when the intrinsic rate is multiplied by an appropriate surface area), radionuclide release rates from HSNF would be only about 10% of the LWR release rates.

During Stage 2 corrosion, much of the corroded metal remained undissolved as uranium oxides (sludge). As the U metal oxidizes, all of the fission products and actinides are apparently made accessible to the water and potentially could be released in large part from the sludge. In

the present study, as the U metal was converted to oxide form, the majority of some fission products (the only ones analyzed were Cs, Tc, and Sr) was released. However, the two actinides analyzed (Pu and Am) were quantitatively retained by the sludge.

Stage 2 corrosion rates were much higher than was observed during Stage 1. In one case, the difference was a factor of nearly 2000. Further testing and analysis will be required to determine what triggers the onset of Stage 2 corrosion and what the implications may be for geologic storage.

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1.0 Introduction

Hanford N-Reactor spent nuclear fuel (HSNF) is currently stored in the K-Reactor basins and is being prepared for long-term dry storage. Eventually, it is expected that the fuel will be disposed of in a suitable geologic repository subject to design and regulatory requirements similar to those required for disposal of light-water-reactor (LWR) spent fuel. The most likely mechanism for release of radionuclides from a geologic repository into the biosphere is slow dissolution and transport by groundwater. To determine whether the engineered barrier system that will be designed for LWR spent fuel is also acceptable for HSNF, tests were conducted at Pacific Northwest National Laboratory (PNNL) to judge whether HSNF dissolves faster or slower than LWR fuel under some limited water chemistries that may represent bounding conditions for a potential repository site at Yucca Mountain, Nevada.

Regulations [10 CFR 60] promulgated by the U.S. Environmental Protection Agency (EPA) and the U.S. Nuclear Regulatory Commission (NRC) put limits on the release of radionuclides from the repository. In addition, the NRC has put a requirement on the release of radionuclides from the engineered barrier system (EBS), which includes the HSNF, canister, overpack, and any other manmade barrier up to the undisturbed rock wall. By 10 CFR 60, LWR spent fuel was declared an acceptable waste form, and no requirement exists per se on the dissolution rate from the LWR fuel itself other than it be known or bounded. The Office of Civilian Radioactive Waste Management (RW) is designing a barrier system, based on the expected dissolution rate of radionuclides from spent LWR fuel, that would ensure that the release-rate requirements are met.

A subgroup of the RW/Environmental Restoration and Waste Management (EM) repository task team, consisting of representatives of both RW and EM, reviewed the regulations governing placement of HSNF in a repository. It was determined that the potential for radionuclide dissolution from the fuel, if it were sufficiently high, might prevent RW from including HSNF in its license application. The tests described in this report were designed to show whether HSNF dissolves faster or slower than LWR fuel under certain limited water chemistry conditions. The results of these tests will be used to help determine whether the EBS that will be designed for LWR fuel can also be used for HSNF.

2.0 Experimental Description

To make the comparison between HSNF and LWR fuel, the same flowthrough test method and apparatus were used for the HSNF tests as had been used previously to test LWR fuel [Wilson and Gray 1990; Gray et al. 1992; Steward and Gray 1994; Gray and Wilson 1995]. Test results on portions of a single batch of unirradiated UO_2 by three different laboratories had shown that the flowthrough test method can provide average steady-state dissolution rates that are repeatable to within a factor of about two [Gray et al. 1994]. A similar level of uncertainty was expected to apply to the tests with HSNF. To enable direct comparisons, some of the test conditions (temperature, pH, solution chemistry) in the HSNF tests were the same as in some of the earlier LWR tests.

It was anticipated that the HSNF (metallic U) could be more reactive under the different test conditions than the UO_2 LWR fuel. Therefore, the size of the HSNF test coupons was chosen so that the surface area exposed to the test solutions was small and was expected to keep the amount of dissolving U from exceeding the U solubility limit. Keeping the U concentrations below the solubility limit was expected to prevent the formation of secondary-phase corrosion-products within the specimen test cells, which was what had been observed in the LWR tests (i.e., no secondary phases have been observed in the LWR tests). Under these conditions, only small fractions of the test coupons were expected to dissolve during the testing period, and their surfaces were expected to dissolve rather uniformly. Under these conditions, the effective surface areas of the test specimens were not expected to change significantly. In addition, the chemical composition of the test-coupon surfaces was not expected to change beyond the possible formation of a very thin (a few atom layers) oxide film that would have been expected to form immediately upon exposure to aerated water in the flowthrough test and perhaps even before the test started as a result of exposure to humid air.

These expected conditions were apparently realized throughout the course of several of the tests judging from the nearly pristine visual appearance of the test coupons following the tests. However, in other tests, an unexpected rapid corrosion mode was encountered, which prevented their completion under the originally planned test conditions (8 of 12 planned tests were completed). Characterization of this unexpected corrosion mode was pursued as far as was possible within the scope of this project. However, many questions were left unanswered. Suggestions of work that should be pursued to answer some of these questions are outlined in Section 6.0.

The following subsections describe the preparation of the test specimens, the nature of the test equipment and procedures, and the test matrix. Also, two subsections address special issues, one on specimen surface areas and the other on a change in test procedure that was implemented on the basis of unexpected test results.

2.1 HSNF Fuel Description

All of the HSNF fuel elements consisted of two concentric tubes made of relatively pure U metal that was co-extruded into Zircaloy-2 cladding [Abrefah et al. 1994]. The outer tube, from which test specimens for this project were cut, was approximately 6.2 cm OD x 4.3 cm ID x 66 cm long. When the fuel elements were discharged from the reactor, they sustained various degrees of cladding damage, including fuel-element breakage, that exposed some of the U metal to the pool water. Some of the exposed U oxidized, and a portion of the oxidized U sloughed off to form a sludge. To prevent further contamination of the basin, a number of fuel elements were put in sealed, water-filled containers in the K-West basin from 1982 to 1984 [Johnson and Burke 1995]. Although the extent of existing fuel corrosion is expected to be an important variable from a dissolution standpoint, only fuel that was considered to be undamaged was investigated in these scoping tests to provide a baseline of radionuclide release rate data for the irradiated metallic fuel.

As the fuel is prepared for storage, it will be dried and possibly conditioned to form an oxide layer (e.g., UO_2) on exposed U surfaces [WHC 1995]. Because of the possibility that the fuel will be conditioned before storage, both conditioned and as-received (dried) fuel was tested to determine the possible benefit of conditioning on limiting the radionuclide release rate.

2.2 Test Specimens

The test specimens were cut from a 105-N Reactor Mark IV fuel element, which is described by Abrefah et al. [1994]. The particular spent fuel element chosen had one end damaged such that the U metal had been exposed to water in the K-Basin pool. However, it was expected that the effects of corrosion near the damaged end of the element would not have extended to the center of the 66-cm-long fuel element. The test specimens were prepared from a 2.5-cm-long section that was cut from the center of the outer spent-fuel element. Figure 1a is a schematic representation of this section showing the location of the six $\sim 22.5^\circ$ wedge-shaped specimens that were prepared. Further, each 22.5° segment was cut (see Figure 1b) to remove the outer cladding and reduce the size of the specimen so that it would fit into the 1.3-cm-ID specimen cell. Following this last cut, specimen dimensions were measured with a dial caliper across both the large and small edges of the wedge, along the length, and along the dimension labeled as "a" in Figure 1b. These dimensions were used to calculate the geometric surface area of exposed U metal fuel (all surfaces except the inside radius, which still had the Zircaloy cladding attached). Cladding was left on the inside radius of the specimens so that any galvanic effects (due to the dissimilar metals) on the measured dissolution rates would be retained.

The cut represented in Figure 1b was made in air using a slow-speed wafering saw with no cutting fluid. All other cuts were made with a milling machine under vortex cooling by argon gas, which was intended both to cool the specimen and exclude O_2 . The efficacy of specimen cooling and O_2 exclusion was not evaluated, but the O_2 exclusion in particular was expected to be less than complete.

All specimens, other than P, were tested in the as-cut condition. After cutting, specimen P was passivated by exposing it to a flowing gas stream consisting of 2% O₂/98% Ar at 250°C for 4 hours. This treatment was calculated to have produced an oxide (UO₂) film on the bare U surfaces ~2 μm thick^(a) based on rates obtained from Ritchie [1981]. However, this calculation was not confirmed by metallography or other measurement. The intent was to determine whether the passivation *process* had any influence on subsequent dissolution rates, not to determine the thickness nor the adherency of the resulting oxide coating.

In addition to any galvanic interaction that may occur between the Zircaloy cladding and the U metal as mentioned above, the possibility exists of galvanic interaction between either of these metals and the stainless steel specimen cell. Because a similar interaction may be possible between the spent fuel and its container in a repository environment, we decided to allow for this interaction during the course of these tests. Either the Zircaloy or the U, or both, is expected to have been in continuous direct contact with the stainless steel specimen cell during the entire test duration. Both metals are expected to have a negative electrical potential relative to the stainless steel and, therefore, could corrode (dissolve) faster than in the absence of such galvanic interaction.

2.3 Test Equipment

The experiments were based on a flowthrough method developed at PNNL for measuring the dissolution kinetics of LWR spent fuel and unirradiated UO₂ [Wilson and Gray 1990]. The flowthrough test apparatus is shown schematically in Figure 2. The feedwater was continuously sparged with air containing the appropriate concentration of CO₂ to maintain the pH at the desired value. Positive displacement piston pumps capable of generating pulsed-flow average flow rates in the range of 0.04 to 0.4 mL/min forced the water from the feedwater container through the 1.3-cm-ID x 5-cm-long specimen cells. The specimen cells were made of type 316 stainless steel and were capped at both ends by type 316 stainless steel frits with openings of approximately 2 μm.^(b) The sparge-gas cylinder, feedwater container, and pump were located outside the hot-cell, and the specimen cell and sample collection container were located inside the hot-cell. Stainless steel tubing (1.6 mm OD) connected the pump to the specimen cell, penetrating through the hot-cell wall, and also extended from the specimen cell to the sample collection vial. Tygon tubing was used between the feedwater container and the pump.

-
- a) If passivation treatment is chosen, it is anticipated that a process will be defined that is intended to coat the exposed areas of the metallic fuel with a thin (~2 μm) layer of oxide, just as was done with specimen P.
 - b) The test apparatus used in earlier tests with LWR fuels was identical except that the specimen cells were 0.64-cm ID and the stainless steel frits had openings of approximately 0.5 μm.

2.4 Test Matrix

Table 1 shows the conditions for the 10 tests that were completed and identifies the test specimen used in each. Two additional tests described below were planned, but not completed. As indicated in Table 1, Specimen K was used first in Test 1 and then in Test 5. This was done simply by changing the water chemistry and the sparge gas so that the water flowing through the specimen cell changed from pH = 8 (Test 1) to pH = 5 (Test 5). Similarly, Specimen L was used first in Test 2 and then in Test 6, and so on. Using a single test specimen in more than one test condition was considered to be legitimate based on tests with LWR fuel that were conducted to confirm the methodology [Gray and Wilson 1995]. So long as the HSNF test specimen remained in a visibly uncorroded condition, use in more than one test was probably appropriate. As shown in Table 2, Specimen K was visibly uncorroded after use in Tests 1, 5, and 7. Specimen L was found to be uncorroded midway through Test 6 (after first being used in Test 2), although it was slightly corroded at the end of Test 6. Specimen N was uncorroded after use in Tests 4 and 8.

The first four tests in Table 1 were chosen because they include the extremes of high and low carbonate concentration, which was expected to be one of the more important variables based on tests with LWR spent fuel, and they replicate some of the conditions used in testing LWR fuel [Gray et al. 1992; Steward and Gray 1994]. The test solutions had total carbonate/bicarbonate concentrations in the range 2×10^{-4} to 2×10^{-2} mol/L with the carbonate/bicarbonate ratio adjusted to be compatible with a constant pH of 8 or 10. The CO₂ concentration in the sparge gas was set to maintain the pH at the desired values. Tests 5 and 6 were added to extend the pH range to 5 while maintaining the total carbonate concentrations in the same range as Tests 1 to 4. Again, the CO₂ concentration in the sparge gas was set to maintain the pH at the desired value.

Tests 7 and 8 were conducted with dilute HNO₃ solutions to evaluate the effect that radiolytically generated HNO₃ might have on the dissolution rate. Note that any change in the dissolution rate that may result from simply changing from carbonate to HNO₃ solution while holding the pH constant can be determined by comparing the results from Tests 5 and 7.

Tests 9 and 10 were conducted with both as-received fuel and passivated (surface oxidized) fuel using simulated J-13 well water (Table 3). Well J-13 is located near the potential repository site at Yucca Mountain, and, therefore, its composition is expected to be representative of water that could be present in the repository. The simulated J-13 water was made up from reagent grade laboratory chemicals based on analysis of actual well water.

Two additional tests were originally planned in which the temperature for Specimen O would be raised to 75°C and the temperature for Specimen P would be lowered to 25°C. However, neither of these tests was conducted because the specimens were severely corroded during Tests 9 and 10.

2.5 Test Specimen Surface Areas

A major objective of this study was to compare the dissolution rates of HSNF with rates observed in previous tests with LWR spent fuel. Consequently, wherever LWR test results are available under conditions identical to those used with the HSNF tests, they were included in Table 1 to allow this comparison. To reliably compare dissolution rates for different test specimens, the data must be normalized to the surface area contacted by the water. Methods used to measure the surface areas for the different types of test specimens are described below.

Dissolution rates listed in Table 1 for the HSNF specimens were based on the measured geometric surface areas with no roughness factor applied. This was done because the surfaces are relatively smooth saw cuts, not irregular particles as in the case of LWR spent-fuel specimens. However, on a fine scale, the saw-cut surfaces will obviously exhibit some irregularity. Thus, it might be supposed that surface roughness factors in the range of two to three might apply. If so, then the rates listed in Table 1 should be divided by a factor of two to three.

The surface areas of the grain-size powder specimens used for the LWR spent fuel tests, which were conducted under conditions identical to those in Tests 1 to 4, were measured using the method developed by Brunauer, Emmett, and Teller [1938] (BET method). For powder specimens with no internal pores or grain boundaries, this method provides a reliable measurement of the surface area that is actually contacted by the water.

The LWR specimen used for a test under conditions identical to those in Test 9 consisted of 1- to 5-mm fragments. The surface area was estimated by measuring the size distribution of the fragments and calculating the total geometric surface area by assuming a cubical geometry for each fragment. This geometric surface area was then multiplied by a surface roughness factor of three. However, it is known that the roughness factor of three underestimates the surface actually contacted by water because it does not adequately account for the partial penetration of water into the grain boundaries. Some information exists that would suggest a roughness factor closer to 15 might be more appropriate. Nevertheless, the dissolution rate listed in Table 1 ($3 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) was based on a roughness factor of three [Gray and Wilson 1995]. If, instead, the rate were based on a roughness factor of 15, its value would be 5 times lower.

2.6 Test Procedure

The first six tests (Tests 1, 2, 3, 4, 9, and 10) were started with water flowing upward for several minutes to purge air from the specimen cells. Then the cells were inverted so that water was flowing downward. Downward flow has the potential advantage that dissolved gases (O_2 and CO_2 , in particular) are trapped in solution (i.e., the system acts like a closed system). This guarantees that their concentrations remain unchanged from the equilibrium values, which were established by sparging the feedwater containers (at ambient temperature, $\sim 25^\circ\text{C}$) with gas containing 20% O_2 plus CO_2 concentrations meant to maintain the desired pH.

The effluent from each test was sampled 1 to 3 times per week. Each sample was analyzed for U; selected samples were analyzed for Cs, Tc, and Pu.

Generally, each test was expected to run 3 to 6 months until a steady-state dissolution rate persisted for a few weeks. Determining when the dissolution rate has been sufficiently steady to justify termination of a test is rather subjective. In general, one looks for U rates over a few weeks that fall within a band not wider than about $\pm 30\%$ and with no (or very little) trend either higher or lower. The $\pm 30\%$ value was somewhat arbitrarily set at about three times less than the factor-of-two repeatability between labs for this method [Gray et al. 1994]. However, as described in Section 4.0, some of the test specimens experienced an unexpected corrosion mode, and steady-state rates were observed only briefly or not at all. Data analysis for the different corrosion modes is described in Section 5.0.

During the first several weeks of the initial six tests, results for some of the tests were much more irregular than has commonly been observed in our testing program with LWR spent fuel [Gray and Wilson 1995]. Since water was flowing downward through the specimen cells, it was suspected, though never confirmed by opening the cells for inspection, that gas spaces were developing in the upper portions of the cells and causing the unstable results by uncovering a portion of the specimen surface. Therefore, the three cells operating at ambient temperature (Tests 1, 4, and 9) were inverted so that the water was flowing upward. These three cells were selected simply because they were physically easier to invert, and they included two of the cells producing irregular data. Eventually, the remaining three cells (Tests 2, 3, and 10) were also inverted. The remaining tests (5 to 8), which were started later, were conducted with water flowing only upward. Changing the direction of water flow is expected to have caused relatively minor changes in pH and dissolved O_2 , as discussed below.

2.7 Consequences of Inverting Specimen Cells

The advantage of downward flow is that the system is effectively closed, and dissolved gases such as O_2 and CO_2 are therefore trapped in solution. Changing the water flow to the upward direction effectively opens the system and potentially allows dissolved O_2 and CO_2 concentrations to decrease, particularly at elevated temperatures. However, the following analyses indicate that the changes are expected to be minor in these tests.

For cells that operate at $75^\circ C$, the O_2 and CO_2 concentrations will tend to decrease because of lower solubilities at higher temperature. However, the O_2 and CO_2 concentrations may not have a chance to completely reestablish equilibrium at the elevated temperature because the systems are not completely open, and the residence time of the water in the specimen cells is relatively short (~ 30 min.).

The solubility of O_2 decreases from 8 mg/L to 5 mg/L in going from $25^\circ C$ to $75^\circ C$, but, as noted above, the actual decrease in O_2 was likely to have been less than the maximum. However,

Baker et al. [1966] reported that the inhibiting effect of O₂ on the aqueous corrosion of U was independent of pressure down to the lowest pressures measured (~1 Torr). Thus, the possible decrease in O₂ concentration when the specimen cells were inverted probably had little effect on the observed dissolution rates.

The change in pH that may have resulted from inverting the specimen cells operating at 75°C cannot be calculated rigorously because the partial pressure of CO₂ gas in the system is not known with certainty. However, two cases that probably bracket the actual situation were calculated. One assumed that the CO₂ partial pressure was the same as in the sparge gas used to condition the water in the supply jug, and the other assumed atmospheric CO₂ partial pressure (~300 ppm). For Test 2, with a nominal pH of 10, the re-equilibrated pH values based on these two assumptions were calculated to be between 9.6 and 10.0. For Test 3, with a nominal pH of 8, the re-equilibrated pH values were calculated to be between 8.0 and 8.3. Thus, it appears that the pH was not changed very much by inverting the specimen cells. An even smaller effect is expected for the cells that operate at ambient temperature.

Another possible concern regarding the inversion of the specimen cells involves the question of whether the surfaces of the test specimens that had been exposed only to water were the same as surfaces that may have been exposed to humid air during part of the initial testing period. If the nature of the specimen surfaces were dependent on this difference, then results obtained after the flow was changed to the upward direction could be suspect. Probably the most important counter argument is that the specimen surfaces had already been exposed to air with some level of humidity before the start of the tests. Therefore, it seems hardly tenable that re-exposure of the specimen surfaces to air within the specimen cells during downward water flow would result in an irreversibly changed surface condition. Another counter argument is that visible inspection of specimens after the inversions of the specimen cells had taken place revealed no evidence for any type of boundary region between opposites ends of the specimens. Granted that visible inspection does not constitute any kind of detailed surface analysis, at least there was no visible evidence to support any difference between opposite ends of the specimens. Finally, Section 4.10 describes the results of two tests with water flowing upward in one test and downward in the other test. The test with downward flow was started in a manner to ensure that the specimen was exposed to dripping water in an air environment. In the end, there was no discernable difference in the extent of corrosion between the two tests.

3.0 Description of Flowthrough Test Results

A complete description of results from the individual tests is given in the following subsections. The order of the test descriptions follows the actual chronology of testing so any changes in test results that occurred as a result of changing from one set of test conditions to another can be seen. First, however, some general test results are given below.

The chronology of testing is summarized in Table 2, and results from the ten tests that were completed are plotted in Figures 3 to 15. Initial testing included Tests 1, 2, 3, 4, 9, and 10. Several weeks after the start of testing, the direction of water flow was changed, as described in Sections 3.5 and 3.6. Figures 3, 6, 9, 10, 12, and 13 include a vertical line, which shows when the change occurred. Later, the conditions in Tests 1, 2, and 4 were changed to start Tests 5, 6, and 8.

A few weeks after inverting the specimen cells to allow for upward water flow, the U dissolution rate in Test 3 (Figure 9) began to decrease markedly. This prompted interruption of the test for visual inspection of the specimen, which was found to be badly corroded. In addition, the specimen cell contained a large quantity of corrosion products that consisted of a black sludge. Consequently, all remaining ongoing tests (5, 6, 8, 9, and 10) were also interrupted for visual inspection of the specimens. Specimens O and P in Tests 9 and 10 were found to be moderately corroded while Specimens K, L, and N in Tests 5, 6, and 8 had no visible signs of corrosion. Therefore, Tests 5, 6, and 8 were resumed, but Tests 9 and 10 were terminated. Subsequently, the conditions in Test 5 were changed to start Test 7.

These results made it clear that two distinct corrosion modes occurred during the course of these tests. The first, Stage 1, involved no visible corrosion of the test specimen and produced no undissolved corrosion products. The second, Stage 2, resulted in both visible corrosion of the test specimen and left behind undissolved corrosion products (sludge). During Stage 1, the rate of dissolution could be readily determined because the dissolved U and associated fission products remained in solution where they could be quantitatively analyzed. In Stage 2, much of the corroded metal remained undissolved as U oxides (Section 5.2).

At this point, there was no obvious reason why some of the test specimens had visibly corroded and others had not. One possibility was that gas spaces had developed in the upper portion of some of the specimen cells during the early testing while the water was flowing downward as was mentioned above. If that had happened, then the specimens would have been exposed to dripping water in a water-vapor saturated air environment rather than being completely submerged in water as was intended. It was possible, although it was never confirmed by opening the specimen cells for inspection, that some cells had developed gas spaces and others had not. Therefore, a decision was made to conduct two additional tests designed to determine whether dripping water in a water-vapor saturated air environment was more corrosive than complete submersion in water.

Specimens for the two additional tests were obtained from Tests 7 and 8, the dissolution rates of which were judged to be stable enough to justify termination of these tests. Visual inspection of the specimens (K and N) from those two tests indicated that they were still free of corrosion. The conditions established for the additional tests were the same as in Test 3 in which the greatest amount of corrosion had been found. One of the new tests was operated with the water dripping downward through a cell that was purposely not filled with water, i.e., the environment was essentially air that was saturated with water vapor. The second additional test was operated with the water flowing upward through a cell that was completely filled with water. These two tests were labeled 3A and 3B, respectively. Periodically, these tests were interrupted for visual inspection of the specimens to check for corrosion.

3.1 Test 1 (Figure 3)

During the first few weeks of this test, the U results were actually quite steady and the test was presumed to be operating normally. However, because of the irregularity in some other tests as described in Section 3.5, the specimen cells for the three tests operating at ambient temperature were inverted. After the cell in this test was inverted, the U rate actually became a bit less steady, but the average dissolution rate increased, which may be an indication that only part of the specimen surface had been exposed to the test solution before the change. Because of that possibility, the U data were averaged only over the 64- to 137-day period and reported in Table 1 as the Stage 1 dissolution rate for this test.

The Cs dissolution rates were nearly congruent with the U rates throughout the duration of this test. This is the expected result for Stage 1 dissolution.

During initial analysis of samples for Pu concentrations, two samples from this test and two samples from Test 2 were analyzed merely to get an indication of how well the data would correlate with the U data. The second sample in each case showed that the Pu dissolved approximately congruently with the U, and no further samples from either of these two tests were analyzed for Pu.

After 137 days, the U results in this test were judged (see Section 3.5) to be stable enough to justify changing the water chemistry conditions to begin Test 5.

3.2 Test 5 (Figure 4)

The only change in conditions between Test 1 and Test 5 was to drop the pH from 8 to 5. This caused the U dissolution rate to decrease from an average of $150 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ to an average of $63 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. On day 68, the test specimen was visually inspected and found to be uncorroded, so the test was resumed for a few days.

The Cs rates were considerably higher than the U rates in Test 5, which is a possible indicator of Stage 2 corrosion (see Section 5.3). Nevertheless, because the U rates were steady and the specimen was not visibly corroded, the conditions were next changed to Test 7.

3.3 Test 7 (Figure 5)

The change in conditions between Test 5 and Test 7 involved changing from a carbonate solution to a nitric acid solution while maintaining the pH at 5 and the temperature at 25°C. This caused the U dissolution rate to decrease from an average of $63 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ to an average of $38 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. The higher rate in carbonate solution may have resulted from the stronger tendency of carbonate to form U complexes. No radionuclides other than U were analyzed in this test.

When this test was terminated after 36 days, the specimen still showed no signs of visible corrosion. Therefore, the specimen was used in a repeat of Test 3, which is described in Section 4.10.

3.4 Test 2 (Figure 6)

During the first few weeks of this test, the U results were reasonably steady, although there was a slight upward trend. However, because of the irregularity in some other tests as described in Section 3.5, all specimen cells were eventually inverted so that the water was flowing upward. The U dissolution rate experienced a sharp transient after the cell inversion and then settled down to an average rate that was not much different from where the results were trending before the inversion.

The Cs data in this test seem inconsistent. In addition to the initial sample in which the Cs data commonly differ from the U data, the two samples at 46 and 81 days also show Cs rates that are much higher than the U rates. However, the Cs dissolved nearly congruently with the U after the specimen cell was inverted, and because of the reasonably steady U rates following the cell inversion, the test conditions were changed from Test 2 to Test 6.

As noted in Section 4.1, two samples from this test and two from Test 1 were initially analyzed for Pu. Because the second sample in each case showed that the Pu dissolved approximately congruently with the U, no further samples from either of these two tests were analyzed for Pu.

3.5 Test 6 (Figures 7 and 8)

In changing from Test 2 to Test 6 conditions, the carbonate concentration was decreased by a factor of 100, and the pH was dropped from 10 to 5. The temperature remained the same at 75°C. Figure 7 shows that after an initial transient, the U rate settled down to a reasonably stable rate for a few weeks at a value about 10 times lower than during Test 2.

As was noted in Section 4.0, all ongoing tests at the time were interrupted for inspection of the test specimens because advanced (Stage 2) corrosion had been discovered in some of the other tests. The specimen in this test was not visibly corroded, so the test was continued. Immediately following the visual inspection, both the U and Cs rates increased dramatically. Some of the Cs and Tc rates are off scale in Figure 7, but they are shown in Figure 8. In contrast to the Cs and Tc, the Pu rates following the visual inspection dropped to near detection limits whereas they had been nearly congruent with the U before the inspection.

When the test was terminated after 113 days, the specimen was found to be slightly corroded. Based on the change in dissolution rates, it seems likely that Stage 2 corrosion began after the first visual inspection at 67 days. There is no known reason for the visual inspection to have been associated with the Stage 2 corrosion that apparently began soon after the inspection, and as nearly as can be determined at this time was simply coincidental.

3.6 Test 3 (Figure 9)

This test produced the most highly corroded specimen (Figure 16). Before the specimen cell was inverted, the U rates had been fairly stable for a few weeks, but then began to increase about 3 weeks before the cell inversion. After the cell inversion, the U rates jumped up, but soon began to decrease and finally fell precipitously to near detection limits after 154 days. This prompted the visual inspection of this and all other test specimens.

The Cs rates began to exceed the U rates after about 40 days and then increased very dramatically about the same time the U rates dropped sharply after 154 days. All the Tc rates except the ones at 60, 171, and 185 days are above the break in the axis of Figure 9 and range between 600 and 3800 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. The Pu rates are below the U rates during the entire test and fall below detection limits following the cell inversion.

3.7 Test 4 (Figure 10)

Following the initially high rate (off scale in this figure), the U rates went through a minimum before the cell inversion and then began to increase. After the inversion, the average rate was about the same as it had been just before the inversion. The U rates stabilized after 96 days, so the average was calculated over this period and recorded in Table 1.

Although the Cs rates in this test were generally somewhat higher than the U rates, the difference was not large enough to suggest Stage 2 corrosion. The Pu data in this test are not very informative since only the first and fifth samples were analyzed. The Pu rate was higher than the U rate for the first sample (off scale in this expanded graph), which is common, whereas the Pu rate for the fifth sample was well below the U rate. The same specimen was used in Test 8, as described below, and the Pu rates were congruent with the U rates throughout that test as expected for Stage 1 dissolution.

3.8 Test 8 (Figure 11)

In changing from Test 4 to Test 8 conditions, the solution was changed from carbonate to nitric acid, and the pH was dropped from 10 to 3. The temperature remained at 25°C. This change caused an initially high transient U rate, but then the rate stabilized at a value about 2½ times higher than it had been in Test 4. Except for the high Cs value at 61 days, both the Cs and Pu rates were reasonably congruent with the U rates as expected for Stage 1 dissolution. The test specimen was not visibly corroded at the end of the test. Therefore, the specimen was used in a repeat of Test 3, which is described in Section 4.10.

3.9 Tests 9 and 10 (Figures 12 and 13)

These tests were conducted with as-received and passivated (see Section 3.1) specimens, respectively, in simulated J-13 well water (Table 3). The original plan called for switching the test temperatures, 25°C and 75°C, after the dissolution rates had stabilized, but this was not done because the specimens were found to be corroded after about 180 days. The U rate never stabilized in Test 9. In test 10, the U rate was reasonably stable both before and after the specimen cell was inverted, but the rate approximately tripled after the inversion. At the time, the increase in U rate was thought to indicate that only part of the specimen surface had been exposed to the test solution before the cell was inverted. The Cs rates were erratic and well above the U rates in both tests, which has been taken to be indicative of Stage 2 corrosion.

3.10 Tests 3A and 3B (Figures 14 and 15)

It was noted in Section 4.0 that two additional tests were conducted using Specimens K and N from Tests 7 and 8. The conditions were the same as in Test 3, one with water dripping downward across the specimen in a water vapor saturated air environment and the other with the water flowing upward so that the specimen was completely covered with the water. Callouts in both figures indicate the conditions of the test specimens during periodic visual inspections. During most of the test period, the specimen with downward flow (Figure 14) was the more corroded one, but at the end of the tests when both specimens were badly corroded, the extent of corrosion was visually indistinguishable.

Because the specimen in Test 3B (Figure 15) was not visibly corroded when it was first inspected, and because the U rates were reasonably stable for about 30 days before that, the rates were averaged over that period, and the result was recorded in Table 1 as being representative of the Stage 1 dissolution rate for Test 3 conditions.

The Cs rates were above the U rates from the start of both tests, but began to exceed the U rates by very large margins only after the specimens started to become more visibly corroded. Finally, near the end of both tests, the Cs rates went up dramatically and the U rates dropped to very low values. Similar Cs and U results were observed in Test 3 (Figure 9). At the end of Tests 3A and 3B, both specimens were badly corroded (Figures 17 and 18), and there was no discernable difference between them. The appearance of the specimens and the sludge from the specimen cells was similar to that shown for Specimen M in Figure 16. Thus, these two auxiliary tests have shown that the extent and approximate rate of Stage 2 corrosion is reproducible and, with the possible exception of short times, independent of water-flow mode.

4.0 Additional Results and Discussion

Stage 1 and Stage 2 dissolution rates are described here as well as characterization of some of the Stage 2 corrosion products. Comparisons with literature are discussed along with the implications of the results of these tests for repository performance.

4.1 Stage 1 Dissolution Rates

Table 1 lists the average Stage 1 dissolution rates for eight of the ten test conditions. These averages are for the times when water was flowing upward so that the entire specimen was exposed to the water and when approximately steady-state rates were being observed. Also, these averages are for times when the test specimens were believed not to be experiencing visible corrosion as determined by inspecting the specimens following the testing, even though, in some cases, high Cs results suggest that Stage 2 corrosion may have slowly started. The exact times used for calculating the average dissolution rates are indicated in Figures 3, 4, 5, 6, 7, 10, 11, and 15. Dissolution rates measured for LWR spent fuel [Gray and Wilson 1995] under some of the same test conditions are listed in Table 1 for comparison.

Three different specimens (K, M, and N) were subjected to Test 3 conditions. The dissolution rate listed in Table 1 was taken from the data in Figure 15 (Specimen N). Data for Test 3 conditions in Figure 9 (Specimen M) were rejected, even though the observed rates were reasonably steady between about 20 and 60 days because the water was flowing downward, which introduces the possibility that the specimen surfaces were not entirely covered by the water. If that were true, then the data would not represent dissolution from the entire surface of the specimen as is assumed in calculating the rate per unit surface area. Data for Test 3 conditions in Figure 14 (Specimen K) were rejected mainly because the specimen was slightly corroded when inspected on day 33. Also, the high Cs rates suggest the specimen was undergoing Stage 2 corrosion during that period. Although the Cs data in Figure 15 (Specimen N) are also a little high during the first 33 days, the specimen was not visibly corroded when it was inspected on day 33. Also, the U dissolution rate was reasonably steady during this period. For these reasons, the data in Figure 15 were considered to be the most reliable for Test 3 conditions.

In the case of Test 6 (Figures 7 and 8), although the specimen did experience Stage 2 corrosion in the latter days of the test, there was no visible corrosion when the specimen was inspected on day 67. Therefore, the steady state rate observed between days 18 and 61 was considered to represent a reliable Stage 1 dissolution rate.

Regressing on data from the first four tests in Table 1 shows that the dissolution rates, R, can be expressed by the following equations for Hanford and LWR spent fuel, respectively:

$$\log(R)_{\text{HSNF}} = 7.17 + 0.413\log[\text{CO}_3] + 0.160\text{pH} - 1654/T \quad (1)$$

$$\log(R)_{LWR} = 9.03 + 0.267\log[CO_3] - 0.194pH - 1911/T \quad (2)$$

where R is in units of $mg \cdot m^{-2} \cdot d^{-1}$, $[CO_3]$ is in units of mol/L, and T is in Kelvins. It should be remembered that each of the four points for both fuels are actually averages of data taken over periods of many days. This allows estimates of the in-test uncertainties and adds legitimacy to the equations above, despite the fact that four points are the minimum required to fit an equation with three independent variables. Equation (2) is further legitimized by the observation that its coefficients were not greatly different when the fit was made using nine different tests with six different test conditions [Steward and Gray 1994]. Similarly, the coefficients of Equation (1) did not change much when the data from six tests were used to generate Equation (3) below. Equations (1) and (2) were fit with just four points each because those were the four test conditions that were identical for the two fuels.

Aside from the initial constant, the fit parameters of the equations above are fairly similar and thus show that the dissolution rates of the two spent fuels respond similarly to changes in the test variables. The small values for the pH parameters show that the dissolution rates were almost independent of pH over the range 8 to 10. Actually, a very weak dependence in opposite directions is manifested by the opposite signs of the pH parameters. The dissolution rates exhibit a somewhat greater although still modest dependence on carbonate/bicarbonate concentration with the HSNF being influenced nearly twice as strongly as the LWR spent fuel. The two fuels exhibit similar activation energies, 7.6 kcal/mol and 8.8 kcal/mol, for HSNF and LWR, respectively. Similar activation energies might suggest similar reaction mechanisms. However, evidence to the contrary is presented in Section 5.4. Also, these activation energies are about half that represented by the aqueous corrosion data reviewed and presented by Ballinger et al. [1994], 17.1 kcal/mol, which may indicate that the mechanisms of corrosion and dissolution are different for U metal.

Regressing on all six HSNF tests with carbonate solutions yields Equation 3 with an R^2 value of 0.94.^(a) Except for the constant, the parameters did not change much, and the calculated activation energy is still low, 8.8 kcal/mol.

$$\log(R)_{HSNF} = 8.52 + 0.347\log[CO_3] + 0.088pH - 1929/T \quad (3)$$

It is interesting to compare the results of Tests 5 and 7 (Table 1). The only difference between these two tests is that one used a carbonate solution and the other a nitric acid solution. The pH and temperature was the same for the two tests. The results in Table 1 show that the dissolution rate in the carbonate solution (Test 5) was 66% higher, which is not surprising since carbonate forms known complexes with U(VI).

a) $R^2 = 1$ and is meaningless for Equations 1 and 2 because four tests are the minimum number that can be fit with a 4-parameter equation.

As an independent check on the measured U dissolution rates, two specimens that had apparently not experienced Stage 2 corrosion were weighed, and the loss in weight was compared with the total U dissolved. Specimen K was used in Tests 1, 5, and 7. It was weighed only before the start of Test 1 and at the end of Test 7. During that time, the total weight lost was 21.8 mg, which compares favorably with the total U dissolved, 19.4 mg, as determined by integrating the areas under the U plots in Figures 3 to 5. Specimen N was used in Tests 4 and 8. It was weighed only before the start of Test 4 and at the end of Test 8. During that time, the total weight lost was 23.4 mg, which again compares favorably with the total U dissolved, 20.0 mg, as determined by integrating the areas under the U plots in Figures 10 and 11.

4.2 Characterization of Stage 2 Corrosion Products from Tests 3, 9, and 10

When Tests 3, 9, and 10 (Specimens M, O, and P) were opened for inspection, the water was found to be thick with black corrosion products (sludge). Of the three, Specimen M was the most corroded. Figure 16 shows the appearance of Specimen M and associated sludge when first discharged from the specimen cell. The picture shows that portions of the ends of the specimen, which originally was approximately in the shape of a parallelepiped, were corroded away. The sludge associated with Specimens O and P was similar in appearance, but the specimens themselves had not deteriorated to such a large extent.

After drying in air at ambient hotcell conditions, the sludge from all three tests consisted of a fine black powder. Portions of the powder from each test were characterized by x-ray diffraction (XRD) and by total dissolution and analysis for selected radionuclides (U, Am, Pu, Cs, Tc, and Sr).

Figure 19 is a composite XRD plot for all three specimens (M, O, and P) labeled HM-3, HO-9, and HP-10. Also shown in the figure are standard stick-figures for UO_2 , $\text{UO}_{2.25}$ (U_4O_9), and $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. Careful analyses of the data showed that sludges from Specimens O and P were essentially pure $\text{UO}_{2.25}$ (U_4O_9). Sludge from Specimen M consisted of $\text{UO}_{2.25}$ (U_4O_9) plus Schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$). The XRD data show no evidence for other compounds, such as U hydride, in any of the specimens.

The different composition of sludge from Specimen M may be related to a difference in the water chemistry. Specimen M was exposed to a pure carbonate/bicarbonate solution while Specimens O and P were both exposed to simulated J-13 well water. However, a more important quality of the different sludges is the deficiency of radionuclides compared to their original inventory in the U metal, as described below.

To obtain the inventory of radionuclides originally present in the metal test specimens for comparison with the sludge, one of the actual test specimens (Specimen L) was analyzed after the flowthrough testing was completed. Multiple samples were obtained by partially dissolving the specimen in stepwise fashion in nitric acid. Because Specimen L had experienced some Stage 2

corrosion during the latter phase of testing (see Section 4.5 and Table 2), the solution from the first partial dissolution was discarded. Thereafter, the specimen was placed three times in nitric acid for short periods sufficient to dissolve approximately one gram of metal each time. In between each exposure to acid, the specimen was dried and weighed. Each of the three nitric acid solutions was analyzed, and the results are shown in Table 4. The fact that all three U analyses were very close to the expected value for pure U metal, 1000 mg/g, demonstrated that all surface corrosion products had been removed and discarded during the first partial dissolution. The agreement among the three analyses for each of the other radionuclides was generally within the expected range of analytical uncertainties and demonstrates that there was little or no composition gradient across the specimen.

Table 4 also contains inventory information calculated with the ORIGEN code [Bergsman 1992] and measured for a piece of fuel that was cut from the end of the same element from which the flowthrough test specimens were obtained. Agreement is fair between the ORIGEN calculations and the fuel sample taken from the end of the element. However, there are large differences between either of these and the actual test specimen that was analyzed. These differences illustrate the importance of obtaining inventory data from actual test specimens, or from specimens that are cut from areas directly adjacent to the actual test specimens.

Radionuclide contents of the replicate sludge samples are given in Tables 5 and 6. Agreement between the replicate samples is quite good, which is an indication that the sludge samples were homogeneous oxides and that none of the samples contained pieces of unoxidized metal, for example. The second and third columns of Table 5 show the measured U and Cs contents. The fourth column of Table 5 shows the Cs/U ratio, and the fifth column lists Cs retention, which is given by the Cs/U ratio divided by the Cs content of the metal (column 5 in Table 4). The sixth column shows that the sludge from Specimen M retained 38% of the Cs on average while the sludge from Specimens O and P retained only 11 to 13% of the original Cs. For reference, the table also shows some of the test conditions together with an indication of the extent of corrosion as well as identification of the oxides present in the different sludges.

Retention of other radionuclides was determined in the same manner as was done with the Cs, and the results are listed in Table 6. Once again for reference, some of the test conditions are listed along with indications of the extent of corrosion and identification of the oxides present in the different sludges. The table shows that retention of Am and Pu by the three sludges was essentially complete. Actually, most of the values exceed 100%. Perhaps these can be attributed to analytical uncertainties. Alternatively, it is possible that the extra Am and Pu in the sludge may have come from Am and Pu that originally dissolved congruently along with Stage 1 U dissolution and then reprecipitated as secondary phases within the sludge because of their low solubility.

Retention of Tc was near 54% for all three sludges. However, the sludge from Specimen M retained higher percentages of both Cs and Sr than did the sludges from Specimens O and P. As stated above, the sludge from Specimen M was also different from the other sludges in that it contained Schoepite. These differences also appear to correlate with the different test solutions,

the pure carbonate solution for Specimen M and J-13 water for Specimens O and P. Whether these apparent correlations have some unifying principle or are just coincidental is not known.

Tyfield [1988], by comparison, stated that essentially none of the Cs was retained by the corrosion products in his studies with Magnox spent fuel in dilute sodium hydroxide solutions. However, he provided no actual experimental results, so it is not known whether the absence of Cs was complete. Tyfield also assigned a release fraction of 0.25 (75% retention) to Sr, but it appears that he did not actually measure the Sr release. Finally, Tyfield stated that the other major fission products and activation products were effectively insoluble in the alkaline solutions and, thereby, implied that they were not released from the corrosion products. Again, he provided no evidence that actual measurements were made. However, the Am and Pu results from the present study lend support to Tyfield's statement

4.3 Stage 2 Corrosion Rates

It should be noted that the following Stage 2 corrosion rates were based on the original geometric surface areas of the test specimens. Clearly, the Stage 2 sludge added a very large amount to the total surface area. However, the Cs was presumably being released from the U metal as it corroded, and the surface area of the corroding metal may have been not that much different from the original geometric area. Although the specimen surface was getting rougher, the amount of specimen would have been shrinking, which would have tended to compensate for the increased roughness. Granted, the increasing uncertainty in the true surface area increases the uncertainty in the derived corrosion rates, but the magnitude of the uncertainty appears to be not nearly so large as if the surface area of the sludge had to be taken into account.

Stage 2 corrosion rates can be estimated from the Cs data in these tests because a known fraction of the Cs was retained by the sludge, and the rest is presumed to have been dissolved in the effluent from the specimen cells. The Cs data may even provide an indication of when the Stage 2 corrosion phase began. Looking at Figure 9, for example, it is clear that the normalized Cs dissolution rate began to increase markedly relative to the U rate beginning about 40 to 60 days into the test, which is probably an indication that the Stage 2 corrosion started at that time. Toward the end of the test, the Cs dissolution rate had increased to $180,000 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Because Table 5 shows that ~38% of the Cs remained in the sludge, the actual corrosion rate of the fuel would have exceeded the observed Cs dissolution rate by a factor of $1/(0.62)$, i.e., $290,000 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

Data for Specimen O (Figure 12) are less clear cut. The Cs dissolution rate was always higher than the U dissolution rate, but the difference was less dramatic than the latter portion of Test 3 (Figure 9). Because the Cs dissolved faster than the U for the entire test, perhaps this is an indication that the Stage 2 corrosion began almost immediately in this test. If one takes the Cs data to be an indication of the rate of Stage 2 corrosion, then that rate appears to be generally in the range of $9,000$ to $13,000 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Because Table 5 shows that only 11% of the Cs

remained in the sludge for this test, the Stage 2 corrosion rate of the fuel would have been about 11% higher than the Cs dissolution rate, i.e., 10,000 to 15,000 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

Data for Specimen P (Figure 13) are similar to that for Specimen O in that the Cs dissolution rate was always higher than the U dissolution rate, which indicates that the Stage 2 corrosion began almost immediately in this test also. The Cs dissolution rate in the latter days of this test was 52,000 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Table 5 shows that only ~13% of the Cs remained in the sludge so the Stage 2 corrosion rate would have been ~60,000 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

Data for Specimen L in Test 6 (Figures 7 and 8) provide additional evidence that the onset of Stage 2 corrosion is marked by an increase in the Cs dissolution rate relative to the U rate. In this case, the specimen was visually inspected on day 67 and found to be uncorroded. Following that inspection, the U rate went up, but the Cs rate went up even faster. Toward the end of the test, the Cs dissolution rate was 23,000 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, and the specimen was found to be slightly corroded when the test was terminated after a total of 117 days. It seems likely that the Stage 2 corrosion began shortly after the specimen was inspected on day 67. The sludge from this test was not analyzed, so there is no measure of the fraction of the Cs that was retained by the sludge and, therefore, no indication of how well the Cs data may represent the rate of Stage 2 corrosion. However, based on results from Tests 3, 9, and 10, it is expected that the Stage 2 corrosion rate would have been somewhat higher than the Cs dissolution rate.

4.4 Comparison with Literature

A compilation of data pertaining to aqueous corrosion of unirradiated U metal by Ballinger et al. [1994], shows weight-gain rates in aerated water of about 8×10^{-5} and 5×10^{-3} $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ at 25°C and 75°C, respectively. These weight gains are for the reaction

where the asterisk indicates a reported exchange of dissolved O_2 with the water [Baker et al. 1966]. However, a more recent study indicates that the UO_2 contains O_2 from both the water and the dissolved O_2 [McGillivray et al. 1994]. For present purposes, the exact mechanism is unimportant because, in either case, the overall reaction can be written

and the corresponding amount of reacted U is obtained by multiplying the above rates by 238/32 to give 6.0×10^{-4} $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ and 3.7×10^{-2} $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ at 25°C and 75°C, respectively.

In completely separate studies, it has been found that the oxidative dissolution of UO_2 can be written [Shoesmith and Sunder 1992]:

If it is supposed that the dissolution of U metal involves the intermediate product, UO_2 , then the overall dissolution of U metal should be given by combining Reactions 5 and 6 to give

However, even if Reaction 7 adequately represents the net dissolution of U metal, the mechanism must not involve UO_2 as an intermediate product because the results of the present study have shown that the dissolution of U metal (e.g., Reaction 7) is faster than the dissolution of UO_2 (Reaction 6).

Whatever the mechanism of U metal dissolution, it is interesting to compare the dissolution rates measured in this study with the rates reported for aerated corrosion of U metal (Reaction 5). After converting units, the reported rates cited above by Ballinger et al. are $140 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and $8900 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ at 25° and 75°C , which are the same order of magnitude as the values listed for HSNF in Table 1. However, the activation energy represented by the values in the Ballinger et al. review, 17.1 kcal/mol , is more than double the value, 7.6 kcal/mol , given by Equation 1. Thus, although the rates are similar, the difference in activation energies provides evidence that the mechanisms involved in corrosion and dissolution are different.

The discussion so far has focused on reported corrosion rates in aerated water and on the dissolution rates of U metal observed during Stage 1 dissolution. Turning now to the Stage 2 corrosion rates, which were derived from the observed Cs dissolution rates, note that they were generally much higher than the aerated corrosion rates compiled by Ballinger et al. [1994]. In fact, the highest rates derived from the Cs data in Figure 9, $290,000 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, are somewhat higher than the deaerated rate of $178,000 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ given by Ballinger et al. [1994] at 75°C . The proximity of these two results suggests that the Stage 2 corrosion may have involved the following deaerated reaction, which is much faster than the aerated reaction (4 or 5) [Ballinger et al. 1994]:

That Stage 2 corrosion may involve deaerated reaction is supported by the following analysis, which shows that O_2 in the specimen cells would have been consumed faster than it was being supplied. As stated above, the literature suggests that the predominant reaction in aerated water can be written as Equation (5). Water equilibrated with air contains $8 \text{ }\mu\text{g/mL}$ of dissolved O_2 . Since air-saturated water was pumped through the specimen cells at $\sim 0.2 \text{ mL/min}$, it thereby delivered O_2 at the rate of $1.6 \text{ }\mu\text{g/min}$. This amount of O_2 is capable of oxidizing $1.6 \times 238/32 = 12 \text{ }\mu\text{g/min} = 17 \text{ mg/d}$ of U metal. Since the original surface area of the test specimens was $\sim 7 \times 10^{-4} \text{ m}^2$, the maximum rate of corrosion supported by the dissolved O_2 would be $(17 \text{ mg/d})/(7 \times 10^{-4} \text{ m}^2) = 24,500 \text{ mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. This is well below the corrosion rates derived from the Cs data in Figure 9 for times beyond ~ 150 days. Thus, in the case of Test 3 (Figure 9),

it appears that as the corrosion rate increased, it began to consume all of the incoming dissolved O₂. As that happened, the corrosion rate accelerated even more and approximately equaled the anoxic rate at 75°C cited by Ballinger et al. [1994].

Further support for this scenario is provided by both the U and the Tc data in Figure 9. First, it is important to note that UO₂ is not oxidized by water, but requires an oxidant such as dissolved O₂ to dissolve according to Reaction 6. Because of the requirement for an oxidant, the rate of UO₂ dissolution decreases approximately in proportion to the square root of dissolved O₂ concentration [Steward and Gray 1994; Gray and Wilson 1995]. Therefore, the decrease in the U dissolution rate beyond about 130 days in Figure 9 is consistent with depletion of O₂ in the water. Furthermore, the decrease in the dissolution rate of Tc beyond about 160 days is also consistent with depletion of the dissolved O₂ because the solubility of Tc in its lower oxidation states is markedly lower [Rard 1983; Meyer, Arnold, and Case 1985].

The case for anoxic (deaerated) corrosion in the other three tests where Stage 2 corrosion was observed (Tests 6, 9, and 10) is less persuasive. In Test 6 (Figures 7 and 8), Stage 2 corrosion was evident from the presence of black sludge at the end of the test. No sludge was visually apparent when the specimen was inspected on day 67, but the Cs results suggest that Stage 2 corrosion began shortly thereafter. However, only at the end of the test did the corrosion rate implied by the Cs dissolution rate approach the maximum rate of 24,500 mg•m⁻²•d⁻¹ allowed by the incoming dissolved O₂. Also, the corrosion rate implied by the Cs data never came close to approaching the anoxic corrosion rate at 75°C of 178,000 mg•m⁻²•d⁻¹. Finally, the U dissolution rate remained high, which would not be expected if the dissolved O₂ were depleted.

In the case of Test 9 (Figure 12), the situation is muddled because the anoxic corrosion rate at 25°C is about 2800 mg•m⁻²•d⁻¹ according to the compilation of Ballinger, Johnson, and Simpson [1994]. Although the corrosion rates implied by the Cs data are higher than that (as is much of the U data), they do not exceed the maximum rate allowed by the incoming dissolved O₂, 24,500 mg•m⁻²•d⁻¹.

The highest corrosion rates implied by the Cs data in Test 10 (Figure 13) well exceed the maximum rate of 24,500 mg•m⁻²•d⁻¹ allowed by the incoming dissolved O₂. Again however, the U dissolution rate remained relatively high, which would not be expected if the dissolved O₂ were depleted. Thus, the evidence for anoxic corrosion in all three tests (6, 9, and 10) is less clear than it is for Test 3.

It is hard to tie all the results from this limited study together into a self-consistent story. It seems inescapable that the dissolution of the U metal spent fuel must be a complex process that may involve two or more processes going on simultaneously. To show that there must be at least two processes, one need only consider that the rate of Stage 2 corrosion is too high in some cases to be supported by oxic corrosion, i.e., the calculations above showed that incoming dissolved O₂ was insufficient to explain the high corrosion rate. But, at the same time, there must be oxic corrosion in progress to consume the incoming dissolved O₂. Additional studies will obviously be

required to sort this out. From a purely pragmatic standpoint, additional studies are particularly important to determine what triggers the start of Stage 2 corrosion because the fission products and actinides associated with the corroded U metal clearly become accessible for reaction with and transport by the water.

4.5 Implication of Test Results for Repository Performance

The most important thing learned during the course of these tests is that HSNF can corrode at a very rapid rate, called Stage 2 corrosion. During Stage 2 corrosion, the corroded U metal does not completely dissolve. Instead, a portion of the corroded metal is converted to U oxide sludge. In the present study, a major portion of some soluble fission products such as Cs, which were originally contained within the U metal, dissolved and were transported out of the specimen cells by the water. However, the actinides (only Pu and Am were measured) appeared to have been quantitatively retained within the U oxide sludge. This is due, at least in part, to the fact that the actinides are quite insoluble. However, there was some evidence in this study that, once the U oxide sludge began to form, the Pu concentrations in the effluent from the specimen cells dropped. This suggests that the actinides may be partially sorbed from solution by the sludge in addition to forming secondary precipitation phases.

Stage 2 corrosion has not been well characterized by this study in terms of (1) the rate of corrosion, (2) how it varies with temperature and water chemistry, and (3) what leads to the transition between Stage 1 and Stage 2 corrosion. Further studies will be required to assess the magnitude and variability of Stage 2 corrosion as a function of potential repository conditions.

If Stage 2 corrosion can be shown to be unlikely to occur under repository conditions, then the dissolution rates measured in this study during Stage 1 will apply. To use the intrinsic dissolution rates measured during Stage 1 in performance assessment calculations, the rates given in Figures 3 to 15 and in Table 1 must be multiplied by an applicable surface area. By way of comparison with dissolution rates for LWR spent fuel, Gray and Wilson [1995] suggested that a reasonable surface area to apply to LWR fuel might include the original UO_2 pellet surface area, plus the surface area that results from cracks that develop during reactor operation, plus a roughness factor that allows for some penetration of water into the grain boundaries. This is based on the assumption that, once the cladding is breached, no further credit will be taken for protection of the fuel by the cladding. This is the same as assuming that the cladding simply vanishes once it has been breached. The surface area estimated on this basis for LWR spent fuel was approximately $4 \times 10^{-3} \text{ m}^2/\text{g}$.

If the same reasoning were applied to the HSNF (i.e., assume the cladding vanishes once it has been breached), the exposed surface of an undamaged fuel element would simply be a solid U metal tube once the cladding had been breached. Varying somewhat with the type of fuel element and whether it is an inner or outer element, the specific geometric surface area would be approximately $1.5 \times 10^{-5} \text{ m}^2/\text{g}$. Even if this were multiplied by a surface roughness factor of two

to three, it would still be approximately 100 times smaller than the value estimated above for LWR spent fuel. Thus, when intrinsic dissolution rates are multiplied by "repository relevant" surface areas, the two fuels would dissolve at more nearly equal rates. In addition, the burnup of the HSNF is approximately 10 times less than LWR fuel, meaning that the concentrations of actinides and fission products (curies per gram of fuel) are also about 10 times less. Thus, for equal dissolution rates as defined above, radionuclide release rates from HSNF would be only about 10% of the LWR release rates.

The above estimate for a repository relevant release rate is based on an undamaged fuel element. Following container and cladding breach, corrosion of the fuel element could lead to increased surface roughness and cracks. The associated increase in exposed surface area could lead to substantially increased release rates.

5.0 Conclusions

The most important thing learned during the course of these tests that HSNF can corrode at a very rapid rate, called Stage 2 corrosion. During Stage 2 corrosion, the corroded U metal did not completely dissolve. Instead, a portion of the corroded metal was converted to U oxide sludge that retained only a portion of the soluble fission products, such as Cs, which were originally contained within the U metal.

If Stage 2 corrosion can be shown to be unlikely to occur under repository conditions, then the dissolution rates measured in this study during Stage 1 dissolution will apply and the following items become relevant:

- The intrinsic dissolution rate (rate normalized on the basis of surface area) of HSNF is much higher than LWR fuel under the conditions tested so far.
- The dissolution rates of HSNF and LWR fuel are approximately the same order of magnitude when compared on the basis of mass because the potentially exposed specific surface area of HSNF in a repository environment is expected to be approximately 100 times lower than for LWR spent fuel.
- The burnup of the HSNF is approximately 10 times less than LWR fuel, which means that the concentrations of actinides and fission products (curies per gram of fuel) are also about 10 times less. Thus, for equal dissolution rates, radionuclide release rates from HSNF would be only about 10% of the LWR release rates.

Radionuclide inventories measured for samples taken from the end and from the center of the same fuel element were quite different. This shows that it is very important for interpretation of results to use inventories measured for samples taken from near the actual specimens used in the dissolution testing.

6.0 Future Work

It is not currently known what caused the transition from Stage 1 to Stage 2 corrosion. Two possibilities have been considered. One is galvanic interaction between the U metal and the Zircaloy cladding and/or the stainless steel specimen cell. The second is the possibility that the reaction between the U metal and water somehow switched from an oxic mode to the faster anoxic mode. Testing planned by the National Spent Nuclear Fuel Program will evaluate both of these possibilities.

Tests to evaluate the potential for galvanic corrosion will include flowthrough tests with HSNF specimens with and without the Zircaloy cladding attached. Flowthrough tests will also be conducted with and without a glass liner in the specimen cell to evaluate the impact of galvanic interaction with the specimen cell. In addition, electrochemical tests will be conducted with unirradiated U metal plus Zircaloy and stainless steel to provide a mechanistic basis for interpretation of the flowthrough test results.

To address the question of anoxic corrosion, flowthrough tests will be conducted with unirradiated U metal using flowthrough apparatus modified to monitor hydrogen evolution. This will provide a measure of the reaction of U with water according to Reaction 1. In the presence of dissolved O_2 , Reaction 1 is inhibited, and the reaction proceeds according to Reaction 2, and no hydrogen is evolved. It is possible that, under some circumstances, Reactions 1 and 2 occur simultaneously. Monitoring the hydrogen evolution during the flowthrough testing will enable determination of the relative importance of each reaction as a function of dissolved O_2 concentration. Such tests may show whether some type of transition from Reaction 2 to Reaction 1 was involved in the transition from Stage 1 to Stage 2 corrosion in the present tests.

In addition to the tests described above, at least three of the corroded specimens from this program will be cross-sectioned, polished, and examined by optical microscopy to look for evidence of corrosion modes, such as cracking, pitting, hydriding, and preferential corrosion near the fuel/cladding interface. For comparison, an as-cut specimen will also be examined.

7.0 References

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Table 1. Test Matrix and Steady-State Stage 1 Dissolution Rates^(a)

Test No.	Specimen ^(d)	Temp. (°C)	Carbonate ^(b)		Dissolution Rate (mg•m ⁻² •d ⁻¹) ^(e)	
			(molar)	pH	HSNF	LWR ^(e)
1	K(1)	25	2 x 10 ⁻²	8	160	4.1
2	L(1)	75	2 x 10 ⁻²	10	2100	14
3	N(3) ^(f)	75	2 x 10 ⁻⁴	8	150	10
4	N(1)	25	2 x 10 ⁻⁴	10	50	0.49
5	K(2)	25	2 x 10 ⁻²	5	63	NM ^(g)
6	L(2)	75	2 x 10 ⁻⁴	5	200	NM
<hr/>						
			HNO ₃ (molar)			
7	K(3)	25	1 x 10 ⁻⁵	5	38	NM
8	N(2)	25	1 x 10 ⁻³	3	130	NM
<hr/>						
9	O(1)	25	J-13 well water ⁽ⁱ⁾	8.5	j	3.0
10	P(1) ^(h)	75	J-13 well water ⁽ⁱ⁾	8.5	j	NM

- (a) These rates are based on the U data and on the surface areas of the fuel exposed to the test solutions. Data for HSNF were taken only during Stage 1 dissolution, i.e., during times when Stage 2 corrosion was believed not to be occurring at a significant rate. It should be noted that estimates of the specific surface areas of spent fuel that might be exposed to groundwater under geologic disposal conditions are very much larger for LWR fuels than for HSNF. When that difference is taken into account, the rates for HSNF and LWR are of the same order (see Section 4.10).
- (b) Made up using appropriate amounts of Na₂CO₃ and NaHCO₃ (except for J-13, see Table 3).
- (c) Geometric surface area for HSNF; BET [Brunauer et al. 1938] surface area for LWR Tests 1 to 4; Geometric surface area multiplied by surface roughness factor of 3 for LWR Test 9. See Section 3.4 and Note (e).
- (d) Numbers in parentheses indicate whether this was the first, second, or third test in which the specimen was used. For example, specimen K was used first in Test 1, second in Test 5, and so on. Also see Table 2 for testing chronology.
- (e) ATM-103 (grain-size powder) for Tests 1 to 4; ATM-101 (1 to 5 mm fragments) for Test 9. See Guenther et al. [1988] and Barner [1985] for descriptions of these two LWR spent fuel test materials.
- (f) The listed dissolution rate was obtained from the data for Specimen N. Specimens M and K were also tested at these conditions. See Table 2.
- (g) Not Measured.
- (h) Passivated specimen. See Section 3.1.
- (i) Carbonate concentration is approximately 2 x 10⁻³ molar. See Table 3.
- (j) These tests apparently experienced only Stage 2 corrosion during the entire test period.

Table 2. Chronology of Testing

<u>Test</u>	<u>Specimen</u>	<u>Figure</u>	<u>Start</u>	<u>Specimen Cell</u>	<u>Visual</u>	<u>End</u>	<u>Corrosion</u>	<u>Follow-On Testing</u>
				<u>Inverted</u>	<u>Inspection</u>			
1	K	3	6/20/96	8/15/96	None	11/7/96	NA	Changed to Test 5 on 11/7/96
2	L	6	6/20/96	9/13/96	None	11/7/96	NA	Changed to Test 6 on 11/7/96
3	M	9	6/6/96	9/16/96	12/13/96	12/13/96	Extensive	Corrosion Products Analyzed
4	N	10	6/13/96	8/15/96	None	11/7/96	NA	Changed to Test 8 on 11/7/96
5	K	4	11/7/96	NA	1/13/97	1/23/97	None	Changed to Test 7 on 1/23/97
6	L	7, 8	11/7/96	NA	1/13/97	3/4/97	Slight	Apparently started to corrode after inspection on 1/13/97 and found to be corroded on 3/4/97
7	K	5	1/23/97	NA	3/4/97	3/4/97	None	Started Test 3A on 3/5/97
8	N	11	11/7/96	NA	1/10/97	3/4/97	None	Started Test 3B on 3/5/97
9	O	12	6/13/96	8/15/96	12/18/96	12/18/96	Moderate	Corrosion Products Analyzed
10	P	13	7/18/96	9/13/96	1/10/97	1/10/97	Moderate	Corrosion Products Analyzed
3A	K	14	3/5/97	NA	Periodic	9/5/97	Extensive	None
3B	N	15	3/5/97	NA	Periodic	9/5/97	Extensive	None

Table 3. Nominal Composition of J-13 Well Water

<u>Component</u>	<u>Concentration (mg/L)</u>
Ca	13
K	5.3
Mg	1.9
Na	44
Si	33
Cl	7.1
F	2.3
NO ₃	8.1
SO ₄	18
HCO ₃	120
pH	~8.5

Table 4. Inventories of Selected Radionuclides in Metal Specimens

<u>U (mg/g)</u>	<u>²⁴¹Am (μCi/g)</u>	<u>²³⁹ + ²⁴⁰Pu (μCi/g)</u>	<u>²³⁸Pu (μCi/g)</u>	<u>¹³⁷Cs (μCi/g)</u>	<u>⁹⁹Tc (μCi/g)</u>	<u>⁹⁰Sr (μCi/g)</u>
-----Specimen L ^(a) -----						
1010	2.48	38.4	1.38	1450	0.451	1110
993	3.55	40.6	1.46	1520	0.420	1150
996	2.78	38.9	1.52	1460	0.499	1200

Avg. 1000	3.10	39.3	1.45	1480	0.457	1150
-----End Specimen ^(b) -----						
945	12.5	70.8	4.31	2490	0.620	2160
-----ORIGEN ^(c) -----						
not listed	10.8	70.4	7.12	2790	not listed	2390

- 36 (a) This was one of the actual test specimens, which was partially dissolved in stepwise fashion in nitric acid (approximately one gram of material was dissolved in each step) after flowthrough testing was completed. The first partial dissolution, which would have contained some corroded surface material, was discarded. Only data from this specimen were used to normalize the flowthrough dissolution rates and for calculating the percentages of radionuclides retained by the sludge specimens in Tables 5 and 6.
- (b) This specimen, which was completely dissolved in nitric acid, was taken from the end of the same fuel element. The U data (945 mg/g rather than the expected value of 1000 mg/g) indicate that the surface of the specimen may have been slightly corroded, i.e., not pure U metal. Values listed for the other radionuclides have been corrected for this small deviation from the expected U value to give ratios of μCi of radionuclide per gram of U metal. Data for this specimen are included in this table merely to illustrate how much the radionuclide concentrations can vary even within a single fuel element.
- (c) Calculated for 6% ²³⁸Pu in the Pu and 10 years since reactor shut down [Bergsman 1992]. These calculations are in reasonable agreement with measurements for the end specimen, but not for Specimen L.

Table 5. Cs Retention after Corrosion

Specimen	U(mg/g) ^(a)	¹³⁷ Cs (μCi/g)	Cs/U (μCi/g)	%Cs	Corrosion	Temp.	Water	Oxide
M	897	515	574	38.3	Extensive	75	Carbonate	U ₄ O ₉ + Schoepite
M	823	449	546	36.9				
M	863	478	554	37.4				
Avg.				37.5				
O	753	113	150	10.1	Moderate	25	J-13	U ₄ O ₉
O	737	131	178	12.0				
Avg.				11.1				
P	779	130	167	11.3	Moderate	75	J-13	U ₄ O ₉
P	661	137	207	14.0				
Avg.				12.6				

- (a) The U concentrations in the sludge specimens were less than 1000 mg/g because, as shown by XRD, they were oxides. The Cs/U ratios (Column 4) are given by the measured Cs concentration divided by the fraction of U in the specimen, e.g., 0.897 for the first M specimen.

Table 6. Am, Pu, Cs, Tc, Sr Retention after Corrosion

Specimen	%Am	%Pu ^(a)	%Cs	%Tc	%Sr	Corrosion	Temp.	Water	Oxide
M	144	91.0	38.9	55.1	78.5	Extensive	75	Carbonate	U ₄ O ₉ + Schoepite
M	105	115	37.0	58.0	107				
M	160	111	37.5	55.8	88.5				
Avg.	136	106	37.8	56.3	91.2				
O	79.7	101	10.2	56.9	20.7	Moderate	25	J-13	U ₄ O ₉
O	99.0	133	12.1	52.3	25.4				
Avg.	89.4	117	11.1	54.6	23.1				
P	104	117	11.3	50.5	33.7	Moderate	75	J-13	U ₄ O ₉
P	125	121	14.0	51.6	34.3				
Avg.	114	118	12.7	51.1	34.0				

(a) Average of ²³⁹+²⁴⁰Pu and ²³⁸Pu

Figure 1. Specimen Cutting Diagram: a) End View of 2.5-cm-Long Section Cut from Center of 66-cm-Long Fuel Element SFEC10, 4366-S4. Six $\sim 22.5^\circ$ wedge-shaped specimens were cut and designated as shown; b) perspective view of wedge specimen showing cut (dotted line) made to remove outer cladding.

Figure 2. Schematic Diagram of Flowthrough Testing Apparatus

Figure 3. Dissolution Rate of Specimen K in 2×10^{-2} M Carbonate, pH = 8, 25°C (Test 1)

Figure 4. Dissolution Rate of Specimen K in 2×10^{-2} M Carbonate, pH = 5, 25°C (Test 5)

Figure 5. Dissolution Rate of Specimen K in 2×10^{-5} M Nitric Acid, pH = 5, 25°C (Test 7)

Figure 6. Dissolution Rate of Specimen L in 2×10^{-2} M Carbonate, pH = 10, 75°C (Test 2)

Figure 7. Dissolution Rate of Specimen L in $2 \times 10^{-4} \text{ M}$ Carbonate, $\text{pH} = 5$, 75°C (Test 6). Expansion of Figure 8.

Figure 8. Dissolution Rate of Specimen L in 2×10^{-4} M Carbonate, pH = 5, 75°C (Test 6).

Figure 9. Dissolution Rate of Specimen M in 2×10^{-4} M Carbonate, pH = 8, 75°C (Test 3)

Figure 10. Dissolution Rate of Specimen N in 2×10^{-4} M Carbonate, pH = 10, 25°C (Test 4)

Figure 11. Dissolution Rate of Specimen in $2 \times 10^{-3} \text{ M}$ Nitric Acid, $\text{pH} = 3$, 25°C (Test 8)

Figure 12. Dissolution Rate of Specimen O in J-13 Well Water at 25°C (Test 9)

Figure 13. Dissolution Rate of Specimen P (Passivated) in J-13 Well Water at 75°C (Test 10)

Figure 14. Dissolution Rate of Specimen K in 2×10^{-4} M Carbonate, pH = 8, 75°C (Test 3A)

Figure 15. Dissolution Rate of Specimen N in $2 \times 10^{-4} \text{ M}$ Carbonate, $\text{pH} = 8$, 75°C (Test 3B)

Figure 16. Specimen M Plus Slurry of Uranium Oxide Sludge Poured from Specimen Cell Following Test 3 (Top Photo). Expanded View of Specimen M (Bottom Photo).

Figure 17. Two Views of Specimen K Following Test 3A. A Small Amount of the Sludge Poured from the Specimen Cell is Visible in the Top Photo.

Figure 18. Two Views of Specimen N Following Test 3B. Some of the Sludge Poured from the Specimen Cell is Visible, Particularly in the Top Photo.

<970121A.DIF> HP-10, Scan: 5.0-65.0/0.05, Dwell=3(sec), Anode=CU(45 kV, 40 mA), 01-21-97@11:04
 <970109A.DIF> HO-9, Scan: 5.0-65.0/0.05, Dwell=3(sec), Anode=CU(45 kV, 40 mA), 01-10-97@09:47
 <961220B.DIF> HM-3, FUEL SAMPLE, Scan: 5.0-75.0/0.02, Dwell=20(sec), Anode=CU(45 kV, 40 mA), 01-06-97@09:46

Figure 19. Composite XDR plot for sludge from Specimen M (HM-3), O (HO-9), and P (HP-10). Stick figures for UO_2 , $\text{UO}_{2.25}$ (U_4O_9), and $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ are also shown for comparison.