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Yucca Mountain Project – Argonne National Laboratory Annual Progress Report, FY 1994

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

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LABORATORY, ANNUAL PROGRESS REPORT, FY 1994**

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Chemical Technology Division

February 1995

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ABSTRACT

This document reports on the work done by the Nuclear Waste Management Section of the Chemical Technology Division (CMT), Argonne National Laboratory, in the period October 1993-September 1994. Studies have been performed to evaluate the performance of nuclear waste glass and spent fuel samples under 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 simulated waste glasses have been in progress for over eight years and demonstrate that actinides from initially fresh glass surfaces will be released as a result of the spallation of reacted glass layers from the surface, as the small volume of water passes over the waste form. The glass reaction appears to follow nearly linear reaction kinetics for the time period of testing and does not exhibit the decrease that is commonly observed during the intermediate stage of reaction in tests done with large volumes of water.

Studies are also underway to evaluate the performance of spent fuel samples and unirradiated UO_2 in projected repository conditions. Tests with UO_2 have been ongoing for nine years and show that the oxidation of UO_2 occurs rapidly, and the resulting paragenetic sequence of secondary phases that form on the sample surface is similar to that observed in natural analogues. The reaction of spent fuel samples under conditions similar to those used with UO_2 have been in progress for nearly two years, and the results suggest that spent fuel follows the same reaction progress as UO_2 . The release of individual fission products and transuranic elements was not congruent, with the release being controlled by the formation of small particles or colloids that are suspended in solution and transported away from the waste form. The reaction progress depends on the composition of the spent fuel samples used and, likely, on the composition of the groundwater that contacts the waste form.

EXECUTIVE SUMMARY

The volcanic tuff beds at Yucca Mountain, Nevada, are being studied as a potential site for the U.S. high-level nuclear waste repository. The potential site at Yucca Mountain lies several hundred meters above the local water table in a hydrologically unsaturated zone. Because only water vapor or small volumes of liquid water in the repository horizon are expected to contact the waste forms, we have designed test methods which represent the expected repository environment. We are using these methods to study the waste/repository interactions that may occur and to project the long-term behavior of emplaced waste (glass and spent fuel).

These tests are being performed to provide realistic bounding release input for performance assessment studies and model validation. It is often assumed that waste forms will react most rapidly when contacted with large volumes of water. However, our tests with low volumes of water resulted in more rapid alteration of the waste forms and a non-solubility-limited release of radionuclides from the waste form. That is, the reaction of waste under conditions of low volume water contact rapidly saturates the solution with released elements, accelerates secondary mineral phase formation, and results in a distribution of radionuclides in solution that is completely different from that observed in tests with large volumes of water. Long-term tests are underway with transuranic-doped glasses, spent fuel samples, and unirradiated UO_2 .

Tests are being performed with transuranic-doped glasses that represent versions of reference compositions which may be produced at the Defense Waste Processing Facility (DWPF) and the West Valley Demonstration Project (WVDP). The tests are being conducted with dripping J-13 groundwater that has been equilibrated with tuff at 90°C (EJ-13 water). This water is altered from the composition of J-13 water to provide a potentially more realistic reaction condition. These tests are being conducted with as-cast glass at 90°C and have been ongoing for periods of up to eight years.

The results with both DWPF and WVDP glasses are similar in that the reaction as measured by the release of the soluble components of the glass (e.g., B, Li) is nearly linear as a function of time, but the release of individual elements differs depending on the reaction mechanism that controls the glass reaction and the formation of secondary reaction products. For both glasses, the release of transuranic elements is controlled by the rate at which the reacted layer that is formed by glass/water contact is rinsed away from the glass and spalls into solution. This spalled reaction layer retains the majority of transuranic elements, remains suspended in solution, and thus forms a means by which actinide elements can be transported through the engineered barrier system. For DWPF glass, the reacted layer is composed mainly of a smectite-type clay, which retains the transuranic elements, while the layer for the WVDP glass is made up of the mineral brockite surrounded by clay. The brockite forms very early in the reaction sequence and incorporates Am and Pu into its structure. The brockite is found both in the test solution as suspended particles or colloids and the reacted layer itself. Portions of the reacted layer are also found in solution.

Additional tests must be performed on prehydrated glass, or glass that has been exposed to water vapor prior to liquid water contact, so that the radionuclide release rate can be fully bounded. Additionally, the rate at which the glass reacts when exposed to water vapor must be determined as a function of glass composition, time, and temperature. This information is necessary to predict the extent of prehydration that will occur before liquid water contact. Preliminary assessments of glass reaction when compared to spent fuel have shown that the release from glass may be a significant contributor to the overall release of radionuclides from the engineered barrier system. Thorough knowledge of the reaction of glass under realistic conditions is essential to further refine this comparison and improve on the performance assessment calculations.

Long-term tests at 90°C are also underway with EJ-13 well water and two types of spent fuel, ATM-103 and ATM-106. In tests up to 581 days, both the leachate and the physical appearance of the spent fuel have been visibly characterized. Colloids formed during spent fuel dissolution were characterized by analyzing the leachate. The major colloid phases present appear similar to the secondary phases that form on the spent fuel itself. These phases are rich in fission products and transuranic elements and include schoepite and soddyite. Also, a smectite clay was found in several of the tests.

The amount of Am and Cm released from the two fuels was one to two orders of magnitude greater than that released from spent fuel under saturated conditions. The cause of the difference in behavior has not been identified. However, it could be due to the presence of large amounts of colloids which contained actinides in the leachate of the unsaturated tests.

While spent fuel tests have been underway for a relatively short time, it is apparent that under conditions of low-volume water contact, such as will occur under unsaturated conditions, spent fuel undergoes alteration in a manner where the entire reaction process is accelerated compared to that observed under saturated conditions. That is, the conversion of the UO₂ matrix to oxidized secondary phases occurs instantly in terms of repository time frames. This results in the individual fission products and actinide elements being released noncongruently, with release of most radionuclides being controlled by the formation of particulates in solution. These particulates may be colloidal analogues of the phases identified on the Zircaloy retainer or partially dissolved grains of spent fuel itself. The results also indicate that the spent fuel reaction and radionuclide release depend on the spent fuel type or composition. This suggests that developing an acceptable bounding release scenario by testing only a few fuel types may not be possible. Furthermore, extrapolation from the reaction progress time line indicates that the fuel reaction will be very dependent on the groundwater composition. As the fuel oxidizes, it transforms into secondary phases that depend on the cation content of the groundwater. It is possible that groundwaters more concentrated in specific cations (e.g., Si, Na, K) may promote the formation of secondary phases and accelerate the reaction of spent fuel. Finally, the rate at which the fuel oxidizes in the presence of small volumes of water and air is so rapid that prior oxidation of the fuel during storage is unlikely to affect total radionuclide release; however, dry oxidation that results in cladding rupture would expose a greater surface area of fuel to reaction. However, if no credit can be given to the cladding as a barrier, even this prior oxidation becomes less important.

In addition to spent fuel studies, drip tests with UO₂ pellets (nonirradiated) and EJ-13 well water have been ongoing for 7.5 to 8.8 years. Results from these tests show that oxidation of UO₂ occurs rapidly and suggest that the sequence of altered phases (e.g., schoepite and soddyite) that form on the pellets is similar to that observed in natural analogues. This finding suggests that tests with low volume of water accurately simulate reaction processes that occur in nature and provide information essential for evaluating the performance of an unsaturated repository.

I. INTRODUCTION

Ash-flow tuff beds at Yucca Mountain, Nevada, are currently being investigated as a potential site for the permanent disposal of high-level nuclear waste. The proposed repository horizon is to be located in an unsaturated environment, approximately 200 to 400 m above the present-day water table. Matrix flow is expected to be the dominant water transport mechanism, with only limited amounts of water being available to corrode the waste packages and transport the available radionuclides. In the event of eventual breaching of the waste containers, the nuclear waste forms are most likely to be exposed to humid air and limited amounts of flowing water, which may contact the waste by dripping onto the waste package or through wicking of water from the geologic media to the waste form through a bridge of solid materials that may have fallen or been emplaced in the waste package bore hole.

Because only water vapor or small volumes of liquid water in the repository horizon are expected to contact the waste forms, we have designed test methods which represent the expected repository environment. We are using these methods to study the waste/repository interactions that may occur and to project the long-term behavior of emplaced waste (glass and spent fuel). These tests are being performed to provide realistic bounding release input for performance assessment studies and model validation.

II. UNSATURATED TESTS WITH GLASS

A. Introduction

The Unsaturated Glass Testing Program was upgraded to Quality Affecting in February 1986, when tests with a Defense Waste Processing Facility (DWPF) glass (SRL 165) were begun. These tests are still ongoing and are called the "N2 tests." The tests are performed in a batch mode, where tests are terminated at specific time periods up to one year, and a continuous mode, where tests continue but the leachate is sampled at intermittent intervals. A report [1] was issued after the batch tests were completed, and sampling in the continuous test has continued. This year data were analyzed and are reported for the continuous tests.

A second set of Unsaturated Tests began in July 1987 using a West Valley Demonstration Plant (WVDP) glass (ATM-10). These tests (eight batch mode, four continuous mode) are termed the "N3 tests," and up to this year no results of these tests have been reported, other than a description of some particulates found in the test solution [2]. This year the data from the last seven years have been compiled and are, in part, reported below.

B. Objective

The objective of this task is to use the Unsaturated Test procedure to determine the reaction progress of glass under conditions that are likely to exist at the potential Yucca Mountain repository site. These conditions are where as-cast glass is exposed to intermittent dripping water. During the tests the leachates are monitored for the release of glass components, such as B and Li, and for radionuclides. The former provides an indication of the glass reaction, and the latter provides information regarding how the transuranic elements such as Np, Pu, and Am are released from the glass. Also examined are the interactions between the glass and the 304L type stainless steel which makes up the retainer that holds the glass during the test.

C. Technical Approach

Both the N2 and N3 tests were performed according to the NNWSI Unsaturated Test Procedure (NNWSI-05-011, Rev. 1, see reference [1]), as specified in the approved Test Plans. The procedure has remained unchanged, except for additional analyses that can now be performed due to improved techniques. These techniques were developed to analyze the small volumes of water that are generated during the test periods and include the analysis of anions and particulate or colloidal material in solution. The colloidal analysis involves determining the size fraction distribution of radionuclides as collected on filters of varying sizes and using analytical electron microscopy (AEM) to characterize solid particulates that have been collected on a "holey" (perforated) carbon grid through which test leachate has passed. Neither of these techniques provides a full characterization of the colloidal properties of the particulates. The sequential filtering can be used to determine size fractions during test conditions and also, if required, the identity and radionuclide content of the particles. In the N2 and N3 test series, sequential filtering has been done, but the colloids trapped on the filters have not been studied. The filters have been retained for further examination if desired.

During the first sampling periods this year for both test series, there was sufficient water for additional water/material interaction tests because the tests had not been sampled for approximately three years. This water was retained in the original test vessels until these vessels were needed for the second sampling period. At that time, the leachate was removed from the original test vessel and stored in a glass vial, and the original test vessels were acid stripped to determine the amount of cations and transuranic elements that had sorbed to the vessel walls. These results have not been completely analyzed, so the updated results reported below do not

fully reflect the total reaction of the glass or release of radionuclides from the glass. The data reported below are those that have been compiled to date. Emphasis has been placed on the N3 series because no data from that test series have been reported previously.

D. Results

1. N2 Tests

The N2 tests are being performed with SRL 165 glass that has been doped with the transuranic elements Np, Pu, and Am and with Tc. The composition of this glass is given in Table 1. The N2 tests were sampled on 12/21/93 after a period of 190 weeks without sampling. The results from the N2 tests were reported at the International High-Level Radioactive Waste Management Conference held in Las Vegas, May 16-22, 1994. The N2 results up to the 12/21/93 sampling period are presented there.

The second sampling of the N2 tests occurred on 6/20/94, which was a period of 26 weeks since the previous sampling. The results from the 6/20/94 sampling period are not complete, and no additional data are reported. The tests are continuing with obvious interaction between the glass and the metal retainer sections. From our earlier results, we know that this results in the formation of iron silicate particles, which are released to solution. Also, the glass reacts in a manner such that the alteration layer that forms on the glass is not firmly attached to the glass. During the minor water flow that occurs during testing, sections of the reacted layer are released from the glass and enter the solution as colloidal suspensions. This released layer retains most of the Pu and Am in the glass, and thus these elements are released from the glass as particulates suspended in solution. The properties of these particles could be determined under a range of solution conditions (pH, ionic strength, etc.) if the information were required.

2. N3 Tests

The N3 test vessels have been sampled periodically since test initiation, with the exception of a long interval between September 1993 and January 1994 when no guidance for sampling was given. Sampling was last done on 1/12/94 and 7/14/94. The composition of the actinide-doped ATM-10 glass used in the N3 tests is given in Table 2.

Table 1. SRL 165 Glass Composition (oxide wt %) Used in the N2 Test Series

Element	SRL 165 Glass	Element	SRL 165 Glass
Al	4.08	Sr	0.11
B	6.76	Ti	0.14
Ba	0.06	Zn	0.04
Ca	1.62	Zr	0.66
Cr	<0.01	U	0.92
Fe	11.74	Tc	0.02
K	0.19	²³⁷ Np	0.01
Li	4.18	²³⁸ Pu	--
Mg	0.70	²³⁹ Pu	0.01
Mn	2.79	²⁴¹ Am	0.0004
Na	10.85	²⁴⁴ Cm	--
Ni	0.85	¹³⁷ Cs	--
Si	52.86		

Table 2. ATM-10 Glass Composition^a Used in the N3 Test Series

Oxide	Mean wt%	wt% Std. Dev.
Al ₂ O ₃	6.65	0.0209
AmO ₂	0.0064	0.000073
B ₂ O ₃	9.17	0.082
BaO	0.045	0.00131
CaO	0.60	0.0354
CeO ₂	0.072	0.00127
Cr ₂ O ₃	0.253	0.0107
CsO ₂	0.062	0.0015
Fe ₂ O ₃	11.5	0.2065
K ₂ O	3.34	0.125
La ₂ O ₃	0.025	0.0020
Li ₂ O	2.88	0.0281
MgO	1.15	0.0296
MnO ₂	1.29	0.0219
Na ₂ O	10.5	0.150
Nd ₂ O ₃	0.168	0.0023
NiO	0.296	0.0135
NpO ₂	0.021	0.00041
P ₂ O ₅	2.34	0.258
PuO ₂	0.0081	0.000527
RhO ₂	0.012	0.0018
RuO ₂	0.061	0.0108
SO ₃	0.31	0.090
SiO ₂	45.8	2.391
SrO	0.025	0.00096
Tc ₂ O ₇	0.0031	0.000083
ThO ₂	3.29	0.0336
TiO ₂	0.858	0.0245
UO ₂	0.527	0.0171
Y ₂ O ₃	0.017	0.00082
ZrO ₂	0.247	0.00513
Total	101.5	

^aFrom Maupin et al. (Ref. 3).

The N3 series consists of 12 tests, eight of which were terminated in pairs within the first year at roughly 13-week intervals. The remaining four, N3 #9 through N3 #12, have been running in continuous mode. One of these, N3 #11, is a blank test containing no glass or stainless steel waste form holder. Table 3 lists the tests, along with sampling dates and solution volume information, through the July 1994 sampling.

The liquid collected with each sampling was initially analyzed for cations by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). After the 1990 samplings, the more sensitive technique of inductively coupled plasma-mass spectroscopy (ICP-MS) was used to determine elemental concentrations in solution. The concentrations of the transuranic elements

Table 3. N3 Test Sample Identification

Test #	Description	Date Started	Date Sampled	Cumulative Test Period (weeks)	EJ-13 Water Injected (mL)	Solution Recovered (mL)
N3 #1	Batch	07/06/87	10/01/87	12.5	2.38	
N3 #2	Batch	07/06/87	10/01/87	12.5	2.38	
N3 #3	Batch	07/06/87	01/04/88	26	4.40	2.58
N3 #4	Batch	07/06/87	01/04/88	26	4.40	3.01
N3 #5	Batch	07/06/87	04/04/88	39	6.35	3.64
N3 #6	Batch	07/06/87	04/04/88	39	6.35	4.19
N3 #7	Batch	07/06/87	07/04/88	52	8.3	5.64
N3 #8	Batch	07/06/87	07/04/88	52	8.3	5.57
N3 #9	Continuous	07/06/87	08/24/87	6.5	1.47	0.66
	Continuous	08/02/87	10/01/87	12.5	1.47	0.73
	Continuous	10/01/87	11/19/87	19.5	1.47	1.05
	Continuous	11/19/87	01/04/88	26	1.47	0.95
	Continuous	01/04/88	02/22/88	33	1.47	1.01
	Continuous	02/22/88	04/04/88	39	1.47	0.88
	Continuous	04/04/88	05/19/88	45.5	1.47	1.07
	Continuous	05/19/88	07/05/88	52	1.47	1.32
	Continuous	07/05/88	10/03/88	65	2.45	1.83
	Continuous	10/03/88	01/05/88	78.5	2.52	1.14
	Continuous	01/05/88	04/03/89	91	2.38	0.96
	Continuous	04/03/89	07/06/89	104.5	2.52	0.99
	Continuous	07/06/89	01/08/90	131	4.47	2.59
	Continuous	01/08/90	09/10/90	166	5.75	1.58
	Continuous	09/10/90	01/12/94	340.5	26.67	7.99
	Continuous	01/12/94	07/14/94	366.5	4.4	0.58
N3 #10	Continuous	07/06/87	08/24/87	6.5	1.47	1.01
	Continuous	08/02/87	10/01/87	12.5	1.47	0.72
	Continuous	10/01/87	11/19/87	19.5	1.47	1.15
	Continuous	11/19/87	01/04/88	26	1.47	0.95
	Continuous	01/04/88	02/22/88	33	1.47	1.14
	Continuous	02/22/88	04/04/88	39	1.47	1.05
	Continuous	04/04/88	05/19/88	45.5	1.47	0.62
	Continuous	05/19/88	07/05/88	52	1.47	0.90
	Continuous	07/05/88	10/03/88	65	2.45	1.79
	Continuous	10/03/88	01/05/89	78.5	2.52	1.69
	Continuous	01/05/88	04/03/89	91	2.38	1.23
	Continuous	04/03/89	07/06/89	104.5	2.52	1.37
	Continuous	07/06/89	01/08/90	131	4.47	3.02
	Continuous	01/08/90	09/10/90	166	5.75	4.79
	Continuous	09/10/90	01/12/94	340.5	26.67	13.16
	Continuous	01/12/94	07/14/94	366.5	4.40	3.01

(contd.)

Table 3 contd.

Test #	Description	Date Started	Date Sampled	Cumulative Test Period (weeks)	EJ-13 Water Injected (mL)	Solution Recovered (mL)
N3 #11 (Blank)	Continuous	07/06/87	08/24/87	6.5	1.47	1.06
	Continuous	08/02/87	10/01/87	12.5	1.47	0.82
	Continuous	10/01/87	11/19/87	19.5	1.47	1.09
	Continuous	11/19/87	01/04/88	26	1.47	1.04
	Continuous	01/04/88	02/22/88	33	1.47	1.12
	Continuous	02/22/88	04/04/88	39	1.47	1.08
	Continuous	04/04/88	05/19/88	45.5	1.47	1.09
	Continuous	05/19/88	07/05/88	52	1.47	1.20
	Continuous	07/05/88	08/25/88	59	1.62	1.35
	Continuous	08/25/88	10/03/88	65	1.32	1.01
	Continuous	10/03/88	01/05/88	78.5	2.52	1.71
	Continuous	01/05/88	04/03/89	91	2.38	1.55
	Continuous	04/03/89	07/06/89	104.5	2.52	1.83
	Continuous	07/06/89	01/08/90	131	4.47	3.08
	Continuous	01/08/90	09/10/90	166	5.75	4.31
	Continuous	09/10/90	01/13/94	340.5	26.67	8.39
	Continuous	01/12/94	07/14/94	366.5	4.40	1.83
N3 #12	Continuous	10/06/87	11/19/87	6.5	1.47	1.04
	Continuous	11/19/87	01/04/88	13	1.47	1.05
	Continuous	01/04/88	02/22/88	20	1.47	1.16
	Continuous	02/22/88	04/04/88	26	1.47	1.09
	Continuous	04/04/88	05/19/88	32.5	1.47	1.12
	Continuous	05/19/88	07/05/88	39	1.47	1.00
	Continuous	07/05/88	08/25/88	46.5	1.47	1.13
	Continuous	08/25/88	10/03/88	52	1.47	0.7
	Continuous	10/03/88	01/05/89	65.5	2.52	1.27
	Continuous	01/05/89	04/03/89	78	2.38	0.74
	Continuous	04/03/89	07/06/89	91.5	2.52	1.2
	Continuous	07/06/89	01/08/90	118	4.47	1.28
	Continuous	01/08/90	09/10/90	153	5.75	3.8
	Continuous	09/10/90	01/13/94	327.5	26.67	5.16
	Continuous	01/12/94	07/14/94	353.3	4.40	2.20

Np, Pu, and Am in solution were determined by alpha spectroscopy. The alpha spectroscopy procedure was modified prior to the January 1994 samplings to include electroplating of the solution, *in addition to* the usual evaporation method. Electroplating affords higher energy resolution (by reducing the inelastic scattering that plagues thick samples), but the results are somewhat more difficult to normalize because it is not clear whether all the elements of interest are plated onto the planchet. A combination of evaporated and electroplated alpha spectra allows use of peak areas from the former to be interpreted in light of relative peak heights from the latter. Note that the ICP-MS method also detects these transuranic elements, and the agreement is generally quite good, although Am and Pu concentrations are generally near ICP-MS detection limits.

The analytical data from the solutions are reported as a concentration in the submitted volume. Mass release of an element during the test period was calculated with a corrected solution volume, which accounts for any dilutions performed. Solution volume for determining total elemental mass release was determined by the formula

$$V = V_c \cdot \frac{(V_c - s) + d}{(V_c - s)} \quad (1)$$

where V_c is the volume of solution collected, s is the total volume of all samples removed prior to dilution (such as samples for pH, carbon, colloid, and anion analyses), and d is the volume of dilutions (distilled water and, where applicable, dilute nitric acid). If more than one dilution was performed with additional sampling between dilutions, then Eq. 1 was applied recursively, i.e., V calculated for the first dilution was used as V_c for the second dilution, etc.

The pH levels were measured periodically; however, the pH behavior was found to be correlated with the stainless steel test vessel where the solution was collected and did not correlate with any other measurements.

Starting with the January 1994 samplings, the solutions have also been tested for carbon (both organic and total carbon) and anion content. Also starting in January 1994, solutions have been sampled for colloidal material and analyzed by analytical transmission electron microscopy.

a. Solution Analyses

Masses of dissolved elements are shown in Figs. 1-5 for the continuous tests. The solution data can be roughly divided into three categories: (1) $M_g \gg M_b$ or M_{EJ-13} , (2) $M_g \sim M_b \sim M_{EJ-13}$, and (3) $M_g \sim M_b \gg M_{EJ-13}$, where M_g is the solution mass from the glass tests (N3 #9, N3 #10, and N3 #12), M_b is the solution mass from the blank test (N3 #11), and M_{EJ-13} is the mass in the volume of injected EJ-13 water. Category (1) includes Li, B, Mg, Mn, U, Np, Pu, and Am, and the data clearly indicate elemental release trends from the glass. The data from Category (2), which includes Na, Si, K, and Ca, are more difficult to interpret, and the observed trends are presumably due to competing effects of sorption, reaction, and spallation or redissolution. Category (3) includes Fe and Ni. These elements appear from the stainless steel test vessel in which the solution resides for extended periods, and their release into solution poses difficulty in evaluating the glass performance.

In Fig. 1, the cumulative solution mass of Li, B, Mg, Mn, and U is plotted as a function of elapsed time through the January 1994 samplings. The release for N3 #10 during the gap in sampling between September 1990 and January 1994 is systematically higher than for N3 #9 and N3 #12, except for Mg and Mn, which are components of stainless steel; these appear

Fig. 1. Cumulative Mass Release of (a) Lithium, (b) Boron, (c) Magnesium, (d) Manganese, and (e) Uranium from the N3 Test Series through 340 Weeks

Fig. 2. Cumulative Mass Release for (a) Neptunium, (b) Plutonium, and (c) Americium from the N3 Test Series. The plutonium and americium plots are a sum of solution plus acid wash results, and are only available through 166 weeks.

Fig. 3. Cumulative Mass in Solution of (a) Sodium, (b) Silicon, (c) Potassium, and (d) Calcium from the N3 Test Series through 340 Weeks

Fig. 4. Cumulative Mass Release of (a) Sodium, (b) Silicon, (c) Potassium, and (d) Calcium from the N3 Test Series, Corrected for EJ-13 Injection Contributions, through 340 Weeks

Fig. 5. Cumulative Mass in Solution of (a) Iron and (b) Nickel from the N3 Test Series through 340 Weeks

to be released more rapidly from the N3 #9 test, where more severe reaction with the stainless steel waste form holder was observed. A few further comments on the Mg and Mn data are in order: the magnesium in the N3 #11 (blank) test solution is well above detection limits and matches very closely with the amount expected simply from injection (labeled EJ-13 in the legend). The manganese in solution from the N3 #11 test is well above that from the EJ-13 water, where this element was below detection limits.

In Fig. 2, the cumulative solution mass of the transuranic elements Np, Pu, and Am is plotted for the glass tests through the January 1994 samplings. At present, acid-strip results are available only through the September 1990 samplings. Neptunium was not observed above background in the acid strip solutions, suggesting that it does not form insoluble phases.

Table 4 lists average release rates, $\Delta M_i/\Delta t$, through 340 weeks for Li, B, U, Np, Pu, and Am, plus a concentration-corrected or fractional release rate, $R_i = \frac{\Delta M_i}{\Delta t \cdot M_i}$, where ΔM_i is the mass loss over time Δt , and M_i is the total mass of element i in the glass (from Table 2 and an average glass sample weight of 10.4 g). These data allow comparison of releases by elements present in the glass in widely varying concentrations. The data have not yet been normalized to the surface area of the glass.

Boron release is useful as a benchmark of glass corrosion, as it is not expected to form secondary phases. As can be seen from the rates R , the fractional releases of B and Li are the greatest, followed closely by Np. Uranium, plutonium, and americium have fractional releases an order of magnitude (or more) lower, strongly suggesting incorporation into secondary phases or sorption onto the glass or stainless steel waste form holder. Formation of uranium phases was previously observed in several test series [4]. The transuranics may be incorporated into any number of phases, a likely candidate being brockite, a calcium-thorium-phosphate phase. Unfortunately, thorium, which is present in this glass at 3.29 oxide wt %, was not reported in solution by ICP-AES, and data were thus not available prior to the January 1994 samplings.

Table 4. Release Rates for Selected Elements from the N3 Series through 340 Weeks

Test	Li		B		U	
	Release Rate (ng/day)	R (day ⁻¹)	Release Rate (ng/day)	R (day ⁻¹)	Release Rate (ng/day)	R (day ⁻¹)
N3 #9	75	5.4×10^{-7}	120	4×10^{-7}	2.5	5×10^{-8}
N3 #10	100	7.2×10^{-7}	180	6×10^{-7}	3	6×10^{-8}
N3 #12	75	5.4×10^{-7}	120	4×10^{-7}	2.5	5×10^{-8}

Test	Np		Pu ^a		Am ^a	
	Release Rate (ng/day)	R (day ⁻¹)	Release Rate (ng/day)	R (day ⁻¹)	Release Rate (ng/day)	R (day ⁻¹)
N3 #9	0.35	1.9×10^{-7}	3.6×10^{-3}	4.8×10^{-9}	1×10^{-3}	1.7×10^{-9}
N3 #10	0.65	3.5×10^{-7}	3.9×10^{-3}	5.2×10^{-9}	3×10^{-4}	5.1×10^{-10}
N3 #12	0.33	1.8×10^{-7}	2.6×10^{-3}	2.5×10^{-9}	1.2×10^{-3}	2×10^{-9}

^aCalculated for total (solution plus acid strip) through 166 weeks only.

In Fig. 3, the cumulative solution mass of the category (2) elements (Na, Si, K, and Ca) is plotted as a function of elapsed time through the January 1994 samplings. Note that the blank N3 #11 test has cumulative solution mass values comparable to those of the glass-containing tests. This suggests that more complex processes are taking place.

Figure 4 plots the same elements as in Fig. 3, but with the total mass due to the injected EJ-13 water subtracted. By comparing Figs. 3 and 4, we determined that the alkali ions Na and K are released at a level of about 10% of the total concentration in the solution. The negative release of these elements observed for the blank N3 #11 is probably real, indicating their sorption onto the stainless steel test vessel. Note that Na and K are released at much greater levels between the 166- and 340-week samplings for N3 #10, as was observed for B, Li, U, Np, Pu, and Am.

Calcium is sorbed or incorporated by reaction into solid phases attached to the waste package assemblage (WPA) for all the tests, the blank test sorbing somewhat less (suggesting interaction of calcium with the glass). For the first 50 weeks or so, a slight positive release of calcium is indicated for the WPA-bearing tests.

Silicon shows an initial release from the WPA-bearing tests for the first 100 weeks, followed by sorption (except for the N3 #10 test). The blank test shows continuous, strong sorption; note that the amount of silicon sorbed after 340 weeks is comparable to the total silicon in solution, i.e., about one-third of the injected silicon is sorbed or unaccounted for in N3 #11.

Figure 5 shows cumulative Fe and Ni release in solution for the continuous tests. As mentioned above, the mass in solution far exceeds that injected with the EJ-13 water. The blank test behaving virtually the same as the WPA-bearing tests indicates that the observed masses are caused by the test vessel and are not of great use in evaluating the glass. However, there was more rust-colored material, indicating stainless steel corrosion, visible on the waste form holder of the N3 #9 test than on the holders of the N3 #10 and N3 #12 tests during the January and July 1994 samplings. This qualitative observation appears to be reflected by the data in Fig. 5.

As mentioned above, data for thorium were not reported prior to the use of the ICP-MS in the procedure. Reports since January 1994 have included thorium, as well as the previously unreported (or undetected) elements Tc and Sr. These data are presented in Table 5. Trends in their release cannot be inferred at this time but will be reported at a later time as more data are collected.

Figure 6 is a plot of measured solution pH versus total elapsed time. The arrow indicates the pH of the EJ-13 water that has been injected recently. Over the term of the test, the starting pH of the EJ-13 water has varied between ~8 and 9. Attempts to find a correlation between pH and element releases proved unsuccessful; it is probable that the pH is affected by interaction with the test vessel and does not completely reflect glass behavior in these tests.

b. Analysis of Colloidal Particles in Solution

For the sample periods ending in January and July 1994, specimens of colloidal material from the solutions were prepared for AEM analysis. Samples were prepared by wicking between 5 and 15 μL of solution from the test vessel through "holey" carbon TEM grids. These were then submitted for analysis by the standard procedure. The material that is trapped on the grid represents the colloids present in only a small volume of solution, and does not provide a complete representation of colloids that may be in solution.

Table 5. Strontium, Technetium, and Thorium in Solution after 174.5-Week Interval

Test	Element in Solution (ng)		
	Sr	Tc	Th
N3 #9	733	3	10
N3 #10	1144	87	1
N3 #11	525	0	0
N3 #12	654	10	8

Fig. 6. Solution pH in N3 Test versus Time

The colloid material was found to be mostly smectite-type clay particles of 1-10 μm diameter (Fig. 7). The clay particles frequently incorporated a variety of elements or precipitated phases, including a calcium-thorium phosphate, calcium silicates, iron oxide, uranium oxides, and occasional Pb, Zn, Sn, or Ba. A complete description of the phases will be given later, and a partial description of the phases found in the 1990 sampling has been reported by Bates [2].

E. Ongoing Work

The N2 and N3 tests are continuing. They represent the longest term tests in progress which provide quality approved input to the Yucca Mountain Project. The data are required to validate modeling codes and to determine the form by which radionuclides are released to solution. Since the volume of solution that is collected can be varied, depending on the sampling interval, leachate can be collected and used in further studies of colloidal material released from the waste form and in integrated tests involving the effects of other engineered materials. The tests will be continued in FY 1995, and the data from both test series compiled and published in refereed journals.

It is important to recognize that prior to the contact of glass with liquid water in an unsaturated environment, glass will first be exposed to water vapor, creating a pre-aged glass. In the repository the main release scenario will occur because of reaction between liquid water and pre-aged glass. Preliminary performance assessment studies [5] that compare the release of radionuclides for glass and spent fuel have concluded that glass can provide a significant proportion of the radionuclide release for the overall repository. To refine this assessment and to provide a bounding limit to radionuclide release, further testing of pre-aged glass must be performed. Two issues are paramount: (1) what is the rate at which the glass will react with water vapor as a function of glass composition, time, and temperature? and (2) when the pre-aged glass contacts liquid water, what will be the manner and rate by which radionuclides are released to solution? Without this information, a credible performance assessment of release from the engineered barrier system cannot be done.

Fig. 7. EDS Spectra from Analytical Transmission Electron Microscopy Study of N3 Series Colloids: (a) Clay Material with Evidence of Uranium Silicate Formation and (b) Clay Material with Evidence of Brockite (a Ca-Th-P Bearing Mineral) Formation (inset)

III. UNSATURATED TESTS WITH IRRADIATED SPENT FUEL

A. Introduction

The Unsaturated Spent Fuel Testing Program in CMT provides technical support to DOE's Yucca Mountain Site Characterization Project (YMP), which is investigating the tuff beds of Yucca Mountain as a potential location for a high-level radioactive waste repository. As part of the waste package development portion of this project, which is directed by Lawrence Livermore National Laboratory, this program was initiated in 1994 to evaluate factors likely to affect spent fuel reaction in an unsaturated environment. The data resulting from this program will provide a firm basis for the Yucca Mountain modeling and performance assessment programs, accounting for important physical parameters which affect spent fuel dissolution in an unsaturated environment and relating the mechanistic basis of spent fuel reaction to conditions which will exist in an unsaturated environment. Without this information, it will not be possible to validate spent fuel reaction models generated to predict long-term performance. Results from the program will also be used to validate models generated to predict long-term performance.

The tasks of the Unsaturated Spent Fuel Testing Program are to (1) develop and perform a test to measure spent fuel behavior in unsaturated conditions, (2) characterize both the leachate and the spent fuel surfaces during these tests, (3) perform testing to quantify the effects of variables deemed important in spent fuel performance, and (4) characterize spent fuel performance under a range of bounding repository conditions. The information provided by these tasks, when combined with data generated by the YMP, will form the basis of a well-founded program that will qualify the spent fuel waste packages for repository disposal.

Under the geologically unsaturated conditions expected at the proposed Yucca Mountain repository, the most likely scenario for water contact on buried spent fuel is that thin films of water could condense on the fuel. The limited quantities of solution expected to condense would preclude volumetric dilution of the radiolytic and fuel dissolution products. Rapid increases in the concentrations of fuel dissolution products would result in the leachate becoming saturated with certain secondary alteration minerals, accelerating the precipitation of secondary phases. This may or may not promote additional dissolution of the spent fuel and/or preferential release of some of the radionuclides within the spent fuel.

This section reports on our tests of the release behavior of radionuclides from spent fuel under unsaturated conditions. The emphasis is on recent results, with some discussion of release under unsaturated versus saturated conditions. The topics addressed are the released fraction of cesium and actinides; the amount, size distribution, and observed phases of colloids in the leachate; the ionic fraction in the leachate; and the appearance of the fuel.

B. Objective

The objective of this task is to use unsaturated tests to measure the reactivity of spent fuel under a range of potential repository conditions. Data from the tests will yield information of the (1) chemistry of the solutions after contact with the spent fuel as a function of time, (2) the dissolution rate of the spent fuel matrix, (3) the form of the released radionuclides, (4) the release rate of the radionuclides, and (5) the type of alteration products formed as a function of total reaction time.

C. Technical Approach

The leach/dissolution behavior of two types of irradiated fuels, ATM-103 and ATM-106, is being determined in two tests with a saturated water vapor atmosphere, two with a drip rate of 0.075 mL/3.5 d, and two with a drip rate of 0.75 mL/3.5 d. A control test without fuel but with a drip rate of 0.075 mL/3.5 d is also included.

The experimental configuration and initial results for these tests have been reported elsewhere [6,7]. The two fuels are well-characterized [8,9] and came from the pressurized water reactor at Calvert Cliffs. The ATM-103 has a burnup of 30 MW-d/kg U and a grain size of 9-19 μm . The ATM-106 has a burnup of 43 MW-d/kg U and a grain size of 6-14 μm . Fragments of the spent fuel were placed inside a Zircaloy holder with a 20- μm -thick base drilled with ~ 10 μm holes. The base, which retains the fuel but releases the leached water, is designated as the "retainer." The groundwater came from well J-13 near Yucca Mountain, which has a chemistry representative of the saturated zone. The water was equilibrated at 90°C for 80 days with crushed core samples of Topopah Spring tuff and is designated EJ-13. This water is more concentrated in Si and Na than J-13 and is a surrogate for water that may contact spent fuel in a repository environment. After reaction times of 120, 275, 482, and 581 days, the tests were interrupted to collect accumulated fluid, acid strip the stainless steel test vessel, and restart each test in a new vessel. (The fuel transfer is accomplished in approximately two hours.) After an acid strip, an acid wash was done on each test vessel. Total time each fuel sample was reacted under unsaturated conditions was 581 days. The last two intervals (275 to 482 days and 482 days to 581 days) occurred this fiscal year.

The spent fuel test matrix is shown in Table 6. The test vessels of the two tests at high drip rate were sampled at the end of the third (482 days) and the fourth interval (581 days); the other five unsaturated tests were only sampled at 120, 275, and 581 days (three intervals). The spent fuel was visually examined by using a camera with 10X magnification; video records were kept. The dry appearance of the fuel after the third interval (482 days) differed from that previously observed and may indicate that the injection of water had been partially reduced during this interval. In addition, only two-thirds of the expected fluid was present in the test vessels.

Aliquots of the leachate taken at each interval were characterized with regard to pH, carbon content, anion content, radionuclide content as dissolved and suspended material, total radionuclide content, and elemental release. At 581 days, aliquots from the high drip-rate tests were passed sequentially through 1000, 100, and 50 nm filters to determine the distribution of the colloidal material. The filters were saved for future autoradiographic and AEM analysis of the colloids [10]. The fluid was analyzed by gamma spectroscopy and ICP-MS; filters were analyzed by alpha spectroscopy.

Table 6. Experimental Matrix for Spent Fuel Tests at 90°C

Test Number	Fuel	Water Form	Vol. EJ-13/3.5 d
S3-1J1	ATM-103	Inject	0.075 mL
S6-1J1	ATM-106	Inject	0.075 mL
S3-2J1	ATM-103	Inject	0.75 mL
S6-2J1	ATM-106	Inject	0.75 mL
S3-V1	ATM-103	Vapor	---
S6-V1	ATM-106	Vapor	---
CC-1J1	None	Inject	0.075 mL

D. Results

1. Solution Chemistry

The pH and carbon analyses for all seven tests at the end of the fourth interval are shown in Table 7. The two vapor tests have the lowest pH's of all the tests, 6.1 and 6.7. The pH was 6.9 for the high drip-rate tests and 7.1 for the low drip-rate tests, while during the fourth interval the pH of the EJ-13 leachant ranged between 8.4 and 7.3. An acidic solution was present in the control test (pH = 3.2), but this may represent the effect of the pH of the EJ-13, which had been used for 16 months. In general, radiolysis and the formation of nitrogen-based acids appear to be responsible for the change in pH, especially that in the leachant [6,7].

For the high drip-rate tests at 581 days, the organic and inorganic carbon contents had decreased compared to the starting EJ-13 water to ~3 ppm each (Table 7). For the two vapor and the two low drip-rate tests, the organic carbon had increased to 11-26 ppm, and the inorganic carbon had decreased to ~3 ppm. The increase in organic carbon was also observed in the control test.

2. Radionuclide Release Rates for High Drip-Rate Tests

The amount of transuranics and cesium measured in the two high drip-rate tests at 581 days is shown in Table 8. Also reported are the unprecipitated fraction and the maximum fraction of each radionuclide. The unprecipitated fraction is the ratio of the material not deposited on the vessel walls (both dissolved and suspended material) to the total amount of material

Table 7. Carbon Content and pH Results for Spent Fuel Leachate at ~581 Days

Test	pH	Content, ppm ^a			Test Condition
		Organic	Inorganic	Total	
S6-V1-574	6.7	26	3	30	Vapor
S3-V1-580	6.1	11	4	15	Vapor
S3-2J1-581 ^b	6.9	3	3	6	High Drip Rate
S6-2J1-581 ^b	6.9	3	2	6	High Drip Rate
S3-1J1-568 ^c	7.1	12	4	16	Low Drip Rate
S6-1J1-569 ^c	7.1	11	2	13	Low Drip Rate
CC-1J1-569 ^{c,d}	3.2	39	13	52	Control
EJ-13 (0) ^e	8.4	5	20	26	---
EJ-13 (+3) ^f	7.3	7	22	28	---

^aAt concentrations ≤ 5 ppm, the carbon analysis has a $\pm 50\%$ precision.

^bThese tests were interrupted at 482 days, the leachate removed, and the test restarted. A new bottle of EJ-13 was introduced.

^cTwo different bottles of EJ-13 were used.

^dThe control test was injected with the same EJ-13 each time other tests were injected. The control test is in a radiation environment, which can affect the pH and the carbon content of the fluid.

^eNew bottle of EJ-13 at month 0.

^fAliquots from new EJ-13 after three-month interval, i.e., (+3).

Table 8. Transuranic^a and Cesium Measured in High Drip-Rate Tests at 581 Days

Isotope	Mass (g)				Unprecip. Frac. (%)	Maximum Frac. (%)
	Leachate	Strip	Wash	Total		
ATM-106						
Am-241 ^b	3(-11)	2(-9) ^c	1(-10)	2(-9)	2	4(-5)
Am-243	--- ^d	6(-10)	---	6(-10)	---	4(-5)
Cm-244	5(-12)	4(-10)	7(-12)	4(-10)	1	1(-4)
Np-237	5(-9)	2(-8)	---	2(-8)	25	7(-4)
Pu-239	8(-11)	4(-9)	1(-9)	5(-9)	2	1(-5)
Cs-137	1(-6)	7(-8)	---	1(-6)	94	2(-2) ^e
ATM-103						
Am-241 ^b	5(-10)	6(-8) ^c	3(-10)	6(-8)	<1	1(-3)
Am-243	---	1(-8)	---	1(-8)	---	2(-3)
Cm-244	1(-10)	4(-9)	3(-11)	4(-9)	2	4(-3)
Np-237	2(-7)	6(-7)	6(-10)	8(-7)	25	3(-2)
Pu-239	2(-8)	1(-8)	4(-9)	3(-8)	59	9(-5)
Cs-137	1(-6)	5(-8)	---	1(-6)	96	2(-2) ^e

^aThe values are results from alpha analysis of electroplated samples. In some cases, the higher counts were found for evaporated samples. Numbers in parentheses indicate powers of ten.

^bThe americium content is an estimate of its contribution since the Pu-238 and the Am-241 peaks from alpha spectroscopy cannot be separated. A measurement of Am-241 can be obtained from the gamma spectroscopy results.

^cThis is the Am-241 measured value.

^dDashes indicate non-detection of this isotope.

^eValue is equivalent to 10^{-6} fraction/day during the fourth interval.

measured as released from the spent fuel. Note that the measured amount of material released from the spent fuel includes all material that is no longer directly associated with the spent fuel and includes material in solution and material sorbed to the stainless steel vessels. The total release should also include the material that has accumulated on the Zircaloy retainer or alteration products on the spent fuel fragments. However, to date, we have not quantitatively measured the material associated with the Zircaloy retainer or alteration products on the spent fuel. The maximum fraction is the ratio between the total measured amount of isotope released in a given test interval and the expected amount of the isotope in the fuel under test. Similar data sets were collected for all tests at each test interval.

From the data in Table 8, the relative release characteristics of the two different fuels can be compared. In the ATM-106 test, most of the transuranics had precipitated except for neptunium. Most of the cesium was in solution. The order of the maximum fraction for the transuranics was Np $\sim$ Cm > Am > Pu. The cesium maximum fraction was two to three orders of magnitude greater than the actinide fractions and corresponds to approximately 10^{-6} fraction/day during the fourth interval. This value is comparable to that found in Swedish leaching experiments [11]. Because we did not consider any additional material associated with secondary phases on the Zircaloy retainer or the spent fuel fragments, this comparison must be viewed cautiously.

In the ATM-103 sample, a large fraction of the plutonium had not precipitated. The order of the maximum fractions was $\text{Np} > \text{Cm} \sim \text{Am} \gg \text{Pu}$. The cesium fraction was nearly the same as the neptunium fraction. Since the measured cesium fraction was the same for ATM-103 and ATM-106, the release of the actinides to the leachate appears to be significantly faster from ATM-103 than ATM-106. (This observation may be modified if a greater fraction of the cesium is incorporated in secondary phases associated with either the Zircaloy retainer or the spent fuel.)

The maximum fractions for the transuranics and cesium measured in the two high drip-rate tests are shown in Table 9 for the four time intervals. For the ATM-106 fuel, the measured amount of cesium released increased with time, while the amount of the transuranics released did not appear to increase. There was a spread of two orders of magnitude in the maximum fractions for the transuranics, with plutonium being the species with the minimal release. For the ATM-103 fuel, the amount of cesium released increased substantially in the fourth interval, as did all the actinide releases. There was greater than two orders of magnitude range in the maximum fractions for all the actinides. In addition, the plutonium fraction was an order of magnitude greater for ATM-103 than ATM-106.

The results for the high drip-rate tests indicate that the radionuclides that accumulate in the test vessel as a result of corrosion of the fuel fragments release at a consistent rate during the first year and a half of continuous testing. Also, the solutions analyzed in the test vessel have a higher proportion of Am and Cm compared with Pu.

Table 9. Maximum Nuclide Fraction at Successive Time Intervals for High Drip-Rate Tests^a

	ATM-106 Nuclide Fraction			
	113 d	271 d	482 d	581 d
Am-241	2(-5)	7(-5)	6(-5)	4(-5)
Am-243	2(-5)	1(-4)	7(-5)	4(-5)
Cm-244	2(-5)	2(-4)	1(-4)	1(-4)
Np-237	N.A. ^b	N.A.	2(-3)	7(-4)
Pu-239	8(-6)	2(-5)	5(-5)	1(-5)
U-238	7(-6)	4(-5)	N.A.	N.A.
Cs-137	1(-4)	1(-3)	9(-3)	2(-2)

	ATM-103 Nuclide Fraction			
	120 d	275 d	432 d	581 d
Am-241	6(-4)	2(-6)	7(-6)	1(-3)
Am-243	1(-3)	1(-5)	1(-5)	2(-3)
Cm-244	8(-3)	2(-5)	2(-5)	4(-3)
Np-237	N.A.	N.A.	7(-4)	3(-2)
Pu-239	1(-6)	2(-7)	8(-7)	9(-5)
U-238	1(-5)	1(-6)	N.A.	N.A.
Cs-137	5(-4)	1(-4)	8(-4)	2(-2)

^aThe radionuclide content associated with the Zircaloy retainer is not included.

^bN.A. indicates not available.

3. Colloidal Composition

For the first two intervals, the americium release was not congruent with the uranium release. From earlier data [6,7], much of the americium was determined to be in a colloidal form within the leachate. The presence of large quantities of colloidal material has potential significant consequences for transport of radionuclide material under long-term storage conditions. Since results from these tests can be applied to the conditions expected for long-term storage of DOE spent nuclear fuel, we performed a limited study of the actinide content of the colloids formed in our tests.

Aliquots of the leachate from the two high drip-rate tests at 581 days were sequentially passed through 1000, 100, and 50 nm filters to determine the composition of the colloidal material. Cesium passed through all three filters. The filtration behavior of the actinides for ATM-103 and ATM-106 exhibited two similarities: (1) a bimodal distribution for curium, with 50% of the content being $\geq 1000 \mu\text{m}$ and 50% being $< 50 \text{ nm}$, and (2) neptunium species $< 100 \text{ nm}$. The difference was that the Am and Pu species were $< 100 \text{ nm}$ for ATM-103 but $> 100 \text{ nm}$ for ATM-106 fuel. Also, the distribution of the actinides in the colloidal fraction appears to be unique for each actinide, as shown in Table 10.

Also shown in Table 10 is the calculated concentration of each actinide in the final filtered solution. These values can be compared to the expected ionic concentrations at $\text{pH} = 6.9$. The expected concentrations (in units of mol/L) for Pu, Np, and Am are 9×10^{-9} [11], 5×10^{-8} [11], and 1×10^{-7} [12], respectively. The values in Table 10 are comparable to the reported values for Pu and Np but are orders of magnitude lower than the americium concentration. The latter observation may indicate that americium forms colloidal species under unsaturated conditions.

Table 10. Actinides in Leachate^a and Material on Filters Determined by Alpha Spectroscopy

Isotope	Mass (g)				Final Filt. Sln. ^b	
	Unfil. Sln.	1000 nm	100 nm	50 nm	g	mol/L
ATM-106						
Am-241 ^c	3(-11)	1(-11)	8(-12)	1(-12)	8(-12)	3(-11)
Cm-244	5(-12)	2(-12)	6(-13)	3(-14)	3(-12)	1(-11)
Np-237	5(-9)	---	2(-9)	1(-9)	2(-9)	8(-9)
Pu-239	3(-10) ^e	2(-10)	1(-10)	2(-11)	3(-11)	1(-10)
ATM-103						
Am-241 ^c	5(-10)	---	$< 8(-10)$	---	---	---
Cm-244	1(-10)	4(-12)	3(-11)	5(-12)	6(-11)	2(-10)
Np-237	2(-7)	---	3(-7)	2(-7)	---	---
Pu-239	2(-8)	1(-9)	1(-8)	6(-9)	3(-9)	9(-9)

^aThe pH's of the two leachates for ATM-106 and ATM-103 were both 6.9.

^bCalculated value. Remainder after content of each filter was subtracted from the unfiltered solution.

^cCorrection for Pu-238 content.

^dDashes indicate non-detection of this isotope.

^eThis value is that for an evaporated sample that was analyzed by alpha spectroscopy.

4. Fuel Alteration

The surface appearance of the ATM-106 fuel at 271, 482, and 581 days of testing is shown in Fig. 8. The lighter colored areas may indicate the formation of alteration products on the surface. A trefoil shape is readily apparent at 581 days (see Figs. 8 and 9). Its appearance can be noted as early as 271 days. This change at the fuel surface may be evidence of the rate of material removal.

The visual appearance of the material on the Zircaloy retainer at 271 days is shown in Fig. 10. This retainer was examined after it was dry. The findings were the following.

An optical microscopic examination of the alteration minerals on the Zircaloy retainer revealed an abundance of yellow alteration minerals with minor amounts of small black particles. The yellow crystals display a crystal morphology and EDS composition that are consistent with the presence of uranyl oxide hydrates (Figs. 11a and 11b). These mineral types were also prevalent during the early alteration of UO_2 pellets, as discussed in Sec. IV. The uranyl oxide hydrates also have incorporated radioactive Cs and, to a lesser extent, Ba and Mo from the dissolving spent nuclear fuel (Fig. 11c). The black particles observed during the optical examinations display a surface morphology that is reminiscent of spalled UO_2 granules from the UO_2 drip tests (Sec. IV). The SEM/EDS and AEM/EDS spectra from these samples reveal a uranium-dominated composition, with lesser Cs and Mo, as well as trace amounts of light rare earth elements (Figs. 11b-11e). These particulates may represent fines produced from mechanically damaged spent fuel particles. More likely, they may represent granules that have been loosened and dislodged from the spent fuel particles as the intergrain boundary regions have corroded.

5. Low Drip-Rate and Vapor Tests

The release behavior of cesium and the transuranics in the four other fuel tests and the control test is reported in Table 11. The values for the isotopes in the control tests are used as base values to eliminate any influence of cross-contamination from hot cell equipment.

The leachate in the low drip-rate and the vapor tests contained four orders of magnitude less cesium than that in the high drip-rate tests, and the transuranic release rate for the low drip-rate tests was two orders of magnitude lower. For the low drip-rate tests, the maximum fraction of Am and Cm released in the ATM-103 test was an order of magnitude greater than that in the ATM-106 test. This difference was also noted in the high drip-rate tests, but its cause has not been found.

For the vapor test with ATM-103, no release of cesium and the transuranics appears to have occurred if the results are compared to those from the control test. For the vapor test with ATM-106 fuel, the fraction of transuranics found in the vessel strip was an order of magnitude greater than that found in any of the three other tests. A possible reason may be that this vessel had not been acid stripped for 441 days.

E. Discussion

Tables 12 and 13 present the unprecipitated and maximum fractions, respectively, for cesium and the actinides for the following cases: the sum of the first two test intervals (120 and 275 days) for the high drip-rate tests with ATM-103 and ATM-106, the fourth test interval for these same tests, and saturated tests conducted by Wilson [13]. The total test time for Wilson was 540 days, versus 275 days at our second test sampling and 581 days (100-day interval) at our fourth sampling. The test temperatures are similar. The ratio of fuel weight to total volume of

Fig. 8. Visual Appearance of ATM-106 Fuel in High Drip-Rate Test (10X Magnification) at (a) 271 Days, (b) 482 Days, and (c) 581 Days. Note light-colored areas at 581 days and pronounced shape of trefoil at lower left.

Fig. 9. Visual Appearance of ATM-106 Trefoil at 581 Days (20X Magnification). Light-colored areas are more pronounced and may be alteration products.

Fig. 10. Visual Appearance of Zircaloy Filter from High Drip-Rate Test with ATM-106 Sample at 271 Days. The light-colored regions were identified from SEM and TEM as possibly billietite, a barium-containing member of the becquerelite group.

Fig. 11. Results from Analysis of ATM-106 after 581 Days of Testing: (a) SEM Image, (b and c) EDS Spectra of Uranyl Oxide Hydrates and Spent Fuel Particles, (d) AEM Characterization of Uranium Oxide Particles Found in Spent Fuel Test, and (e) EDS Analysis of Uranium Oxide Fuel

Table 11. Distribution of Cesium and Transuranics in Low Drip-Rate and Vapor Tests after ~581 Days

	Mass (g)				Unprecip. Frac. (%)	Maximum Frac. (%)
	Leachate	Strip	Wash ^a	Total		
ATM-106 - Low Drip Rate						
Am-241 ^b	1(-11)	1(-10)	1(-11)	1(-10)	8	2(-6)
Cm-244	4(-13)	2(-11)	5(-13)	2(-11)	2	5(-6)
Np-237	2(-10)	4(-8)	3(-8)	7(-8)	<1	2(-3)
Pu-239	2(-11)	9(-10)	4(-10)	1(-9)	2	3(-6)
Cs-137	7(-10)	3(-9)	---	4(-9)	20	6(-5)
ATM-106 - Vapor ^c						
Am-241 ^b	1(-12)	2(-9)	5(-10)	3(-9)	<1	4(-5)
Am-243	---	3(-10)	2(-10)	5(-10)	<1	3(-5)
Cm-244	4(-14)	1(-10)	3(-11)	1(-10)	<1	2(-5)
Np-237	1(-9)	2(-8)	3(-8)	5(-8)	2	2(-3)
Pu-239	3(-11)	1(-8)	5(-9)	2(-8)	<1	7(-5)
Cs-137	1(-10)	1(-8)	---	1(-8)	1	2(-4)
ATM-103 - Low Drip Rate						
Am-241 ^b	5(-12)	7(-10)	6(-11)	8(-10)	<1	2(-5)
Am-243	---	3(-10)	---	3(-10)	<1	5(-5)
Cm-244	8(-14)	5(-11)	3(-12)	5(-11)	<1	4(-5)
Np-237	2(-9)	2(-8)	7(-9)	3(-8)	7	1(-3)
Pu-239	1(-11)	7(-10)	6(-10)	1(-9)	1	3(-6)
Cs-137	3(-10)	2(-9)	---	2(-9)	13	3(-5)
ATM-103 - Vapor						
Am-241 ^b	3(-12)	9(-11)	6(-11)	2(-10)	2	5(-6)
Cm-244	1(-14)	1(-12)	6(-13)	2(-12)	<1	2(-6)
Np-237	3(-10)	7(-9)	---	7(-9)	4	2(-4)
Pu-239	2(-11)	3(-10)	1(-10)	4(-10)	5	9(-7)
Cs-137	3(-10)	6(-11)	---	4(-10)	83	7(-6)
Control - Low Drip Rate						
Am-241 ^b	2(-12)	4(-11)	6(-11)	1(-10)	2	---
Cm-244	6(-14)	1(-12)	4(-12)	5(-12)	1	---
Np-237	3(-9)	5(-9)	5(-9)	1(-8)	23	---
Pu-239	6(-11)	2(-10)	2(-10)	5(-10)	12	---
Cs-137	4(-13)	5(-10)	---	5(-10)	<1	---

^aThe acid wash contributed 40-60% of the total plutonium and up to 30% of the total Am, Np, and Cm.

^bThe americium content is an estimate, based on subtraction of the Pu-238 present.

^cThe test vessel had not been stripped for 441 days. Therefore, the values for the strip and the wash are elevated compared to those for the other test vessels.

Table 12. Average Unprecipitated Fractions (%) for Unsaturated High Drip-Rate versus Saturated Tests

	U	Pu	Am	Cm	Cs
ATM-103 (275 d) ^a	50	40	50	70	98
ATM-103 (100 d) ^b	N.A. ^c	59	<1	2	96
ATM-106 (275 d) ^a	20	50	10	30	60
ATM-106 (100 d) ^b	N.A.	2	2	1	94
Wilson (540 d) ^d	10	5	3	3	85

^aThis is total time for first two test intervals.

^bFourth test interval.

^cN.A. = not yet available.

^dReference 12; bare fuel for three test periods at 85°C.

Table 13. Maximum Fraction (%) for Unsaturated High Drip-Rate versus Saturated Tests

	U	Pu	Am	Cm	Cs
ATM-103 (275 d) ^a	1(-5)	1(-6)	6(-4)	7(-3)	6(-4)
ATM-103 (100 d) ^b	N.A.	9(-5)	1(-3)	4(-3)	2(-2)
ATM-106 (275 d) ^a	5(-5)	3(-5)	9(-5)	2(-4)	1(-3)
ATM-106 (100 d) ^b	N.A.	1(-5)	4(-5)	1(-4)	2(-2)
Wilson (540 d) ^c	1(-4)	1(-4)	2(-4)	4(-5)	1(-2)
Werme ^d	1(-4)	---	---	---	8(-3)

^aThis is total time and total fractions for first two test intervals.

^bFourth test interval.

^cReference 12; bare fuel for three test periods at 85°C.

^dReference 10.

fluid in contact with the fuel was slightly greater for the unsaturated tests at the end of the second interval. Therefore, we assumed that fluid was in contact with the fuel either as a film of water or as a pool of liquid in the fuel holder during our tests.

By comparing our 275-day data to those of Wilson, we noted three major differences. These noted differences do not reflect the material released from the spent fuel but retained by the Zircaloy. First, a much larger fraction of the material was unprecipitated in the unsaturated tests. The one exception was cesium in the ATM-106 test. The low cesium release is confirmed by incorporation of cesium into the uranyl hydrate phase described previously (Sec. III.D.4) and is consistent with cesium uranate phases that have been reported in the literature [11,14]. Second, the maximum fraction of Cs, U, and Pu released for the unsaturated tests is approximately an order of magnitude less than that in the saturated tests. Third, the maximum fraction of Cm and Am released in the unsaturated tests is about an order of magnitude greater than that in the saturated tests. These differences appear to be linked to the higher unprecipitated fraction in the unsaturated tests.

By comparing our 100-day data to that of Wilson, we found that the fraction of cesium released is comparable for all three fuels. However, for the ATM-103 fuel, the fraction of Am and Cm released is one and two orders of magnitude greater, respectively, than that observed in Wilson's test. The plutonium release is comparable. For the ATM-106 fuel, the curium release is an order of magnitude greater than Wilson's, and the Am and Pu release is an order of magnitude less.

The amount of Am and Cm released from the two fuels was one to two orders of magnitude greater than that released from spent fuel under saturated conditions. The cause of these differences has not been identified. However, uranium may form insoluble alteration products in which transuranics are not incorporated. The transuranics could then be carried by the fluid, either as soluble species or as colloids, away from the site of the uranium alteration products. This mechanism suggests the existence of different transport routes for uranium and for the transuranics. This potential difference would have to be considered in any modeling efforts.

F. Conclusions

In the high drip-rate tests, actinides appeared to have been released from the fuel fragments at a consistent rate during 581 days of testing. The leachates contained a higher proportion of Am and Cm than Pu. The distribution of the actinides in the colloidal fraction appears to differ for each actinide and for each fuel type. The leachates for both ATM-103 and ATM-106 had a bimodal distribution for curium, with 50% of the content being $\geq 1000 \mu\text{m}$ and 50% being $< 50 \text{ nm}$, and the neptunium species were $< 100 \text{ nm}$. The Am and Pu species were $< 100 \text{ nm}$ for ATM-103 but $> 100 \text{ nm}$ for ATM-106.

The leachate in the low drip-rate and the vapor tests had four orders of magnitude less cesium than that in the high drip-rate tests. The actinide release rate for the low drip-rate tests was two orders of magnitude lower than that in the high drip-rate tests. For the low drip-rate tests, the maximum fraction of Am and Cm released in the ATM-103 test was an order of magnitude greater than that in the ATM-106 test. This difference in release behavior for the two fuels was also noted in the high drip-rate tests, but its cause has not been elucidated.

The amount of Am and Cm released from the two fuels under unsaturated conditions was one to two orders of magnitude greater than that released from spent fuel under saturated conditions. The cause of the difference has not been identified. However, uranium may form insoluble alteration products in which transuranics are not incorporated. This could result in different transport routes for uranium and for the transuranics.

Uranyl oxide hydrate minerals containing Cs and lesser amounts of Mo and Ba were found on the Zircaloy retainer used for the first 270 days in the high-drip rate test with ATM-106. The occurrence of uranyl oxide hydrates is similar to patterns observed during initial stages of UO_2 alteration in unsaturated tests, as well as initial stages of alteration of naturally occurring uraninite. These phases may retard the migration of fission products during the corrosion of spent nuclear fuel. Small ($\sim 5 \mu\text{m}$) particles of spent fuel interspersed within the uranyl oxide hydrate crystals were also observed. The genesis of these particles is not known.

G. Ongoing Work

All of the unsaturated tests remain in progress. 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 composition, form, and quantity of the radionuclides. The full suite of radionuclides and fission products released during the tests will be reported (see below).

Limited studies by AEM on the formation and characterization of colloids in the leachate will continue, with emphasis on the impact of colloids on fuel dissolution. Colloids in solution could also be examined by using more detailed techniques to determine the actinide content of individual colloidal species, as well as the composition of the colloids in solution, as a function of ionic strength and pH, but this information requires an additional commitment from the Yucca Mountain Project.

Data collected on leachate samples with ICP-MS have not yet been analyzed due to the need for data on the non-natural isotopic distributions for the spent fuel. Work has begun on acquiring the needed data and will continue.

Samples of alteration phases produced in these tests will continue to be monitored with reference to mineral paragenetic trends and retardation mechanisms for spent fuel corrosion products. A more detailed Test Plan will be written to address new issues that have been identified during the above-described testing of spent fuel under low water volume conditions. This Test Plan will use a fuller range of spent fuel samples and reaction conditions than used in our initial tests, and the results from the newly planned tests should be directly interpretable in terms of information needed to conduct realistic performance assessment of engineered barrier performance.

IV. UNSATURATED TESTS WITH UO₂

A. Introduction

The present tests with UO₂ are being conducted to examine the feasibility of using the unsaturated drip test method on spent nuclear fuel (see Sec. III). Because direct testing of spent fuel is difficult due to its high level of radioactivity, unirradiated UO₂ is being used as a surrogate for spent fuel. While these experiments are not completely analogous to spent fuel behavior, the reaction processes occurring during the corrosion of spent fuel and UO₂ may be similar since spent fuel contains >95% UO₂. Therefore, the gross processes observed in the UO₂ experiments should be relevant to spent fuel behavior, especially with respect to the identification of secondary alteration products and modes of waste form degradation.

B. Objective

The objective of this project is to evaluate the reaction of UO₂ after exposure to dripping EJ-13 water at 90°C (Unsaturated Test Method). These tests will thus examine the alteration behavior of UO₂ under a potential unsaturated repository scenario, where limited amounts of groundwater contact and migrate across the waste material. More specifically, these tests are designed to examine the dissolution behavior of the UO₂ pellets, identify long-term alteration mineral paragenetic trends, describe parameters that control the release of uranium from the UO₂ pellets, and serve as a pilot study for similar tests with spent nuclear fuel.

C. Experimental Approach

The experimental procedure for these tests is described in detail by Wronkiewicz et al. [15] and will be summarized here. Sample pellets were fabricated from pressed and sintered UO₂ granules with a natural isotopic composition. Trace element abundances are minor: the B, Si, Ca, Ni, Cu, and Al concentrations are between 1 and 5 ppm and the Cl, Th, and Fe concentrations are 10, 15, and 20 ppm, respectively. All other trace constituents were <1 ppm each. The overall oxygen/metal ratio was determined to be 2.000 ± 0.002 by measuring the weight difference of a sample both before and after open-air heating to 850°C. The effect of variable sample surface area on the dissolution rate has been examined by preparing several different sample pellet, disk, and granule configurations (bottom of Table 14). All sample assemblies were encased in a sleeve of Zircaloy-4 tubing with the assembled UO₂ surfaces exposed on the tops and bottoms to allow fluids to flow across the samples. The Zircaloy tube bottoms were pinched to keep the UO₂ assembly from coming in direct contact with the vessel support plate.

The experiments were conducted in stainless steel (304L) vessels that provided a stable atmosphere for the containment and collection of the leachate and support of the specimen assembly (Fig. 12). Tests were conducted at $90 \pm 2^\circ\text{C}$. The leachant for the tests is equilibrated J-13 groundwater (EJ-13), which was prepared in the same manner as described in Sec. III.C. The EJ-13 leachant was periodically dripped onto the tops of the UO₂ samples via a stainless steel/Teflon injection line. Water contact occurred on the top sample surfaces, with the fluids then flowing along the sides of the samples and dripping from the bottom UO₂ surface into the test vessel chamber, where the leachate was collected. Two water injection rates were employed for the samples: 0.075 mL/3.5 days (six tests) and 0.0375 mL/7 days (two tests). Of the eight tests, five have been terminated at various time intervals to allow for a detailed examination of the reacted solid surfaces, and the remaining three tests have been continuously in operation for over nine years.

Table 14. Total Uranium Release in Unsaturated Tests with UO₂ Samples^a

Elapsed Time (wks)	Sample #1			Sample #2			Sample #3			Sample #4		
	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)
8.0	0.84	26.2	26.2	0.81	11	11	0.78	0.28	0.28	0.81	2.7	2.7
13.0	0.19	21.6	47.8	0.64	25.7	36.7	0.58	5.88	6.16	0.64	7.7	10.4
19.6	0.77	449	497	1.01	388	425	0.79	71.3	77.5	0.83	9.2	19.6
26.0	0.78	264	761	0.93	201	626	0.78	126	204	0.81	9.7	29.3
32.6	0.67	129	890	0.81	56.2	682	0.75	88.8	293	0.75	193	222
39.0	0.64	74.5	965	0.83	38.3	721	0.82	31.1	324	0.81	113	336
45.6	0.66	1001	1966	0.66	46.9	768	0.85	195	518	0.63	624	959
52.0	0.74	2159	4125	0.80	1446	2214	0.83	131	649	0.25	967	1927
78.0	3.21	274	4398	2.63	1494	3708	3.42	266	915	1.57 1401 3328 Terminated after 78 weeks		
105	3.03	168	4566	3.40	105	3812	3.31	139	1053			
134	3.29	145	4711	3.65	69.6	3882	3.52	50.8	1104			
157	2.58	124	4836	3.22	174	4056	3.06	287	1391			
183	2.77 164 4999 Terminated after 183 weeks			3.41	73.9	4130	3.26	172	1563			
211				2.09	193	4323	3.32	250	1813			
238				1.87	71.6	4394	2.38	97.7	1911			
291				5.43	38.1	4432	6.14	106	2017			
358				6.70	266	4698	8.15	424	2441			
417				4.47	325	5023	5.88	301	2742			
469							4.24	298	3040			
Terminated after 417 weeks												
Drip Rate	0.075 mL/3.5 days			0.075 mL/3.5 days			0.075 mL/3.5 days			0.075 mL/3.5 days		
Configuration	11 disks			11 disks			Crushed UO ₂			Crushed UO ₂		
Sample Wt (g)	29.52			29.17			19.86			18.26		
Sample SA (m ²)	40.7			40.6			486			467		
Sample Vol. (m ³)	2.83			2.80			2.21			2.14		

(contd.)

Table 14 (contd.)

Elapsed Time (wks)	Sample #5			Sample #6			Sample #7			Sample #8		
	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)	Sol. Vol. (mL)	U Release (μg)	Cum. U Release (μg)
8.0	0.75	2.85	2.85	0.87	2.61	2.61						
13.0	0.58	1.22	4.07	0.66	2.95	5.56	0.30	1.06	1.06	0.35	0.88	0.88
19.6	0.85	109	113	0.78	30.4	36.0						
26.0	0.76	36.1	150	0.77	41.9	77.9	0.67	302	303	0.51	525	526
32.6	0.77	33.8	183	0.70	799	876						
39.0	0.77	19.4	203	0.76	1391	2267		95.3	398	0.34	247	772
45.6	1.07	322	524	0.43	55.7	2323						
52.0	0.92	72.7	597	0.22	593	2916	0.39	565	1063	0.63	264	1036
78.0	3.62	103	700	2.95	3710	6626	0.72	1075	2138	0.78	5948	6984
105	3.41	47.8	748	3.14	389	7015	0.52	225	2363	0.37	2107	9091
134	3.35	69.3	817				0.13	79.3	2442	0.51	10324	19415
157	1.54	58.2	876	6.52	450	7465	0.64	113	2555			
183	1.24	31.1	907	3.48	85.0	7550	1.05	106	2661	Terminated after 117 Weeks		
211				1.16	424	7974	2.53	110	2771			
238	Terminated after 183 weeks			2.37	56.0	8030	0.61	11.9	2783			
291				6.09	76.2	8106	1.50	14.4	2797			
358				7.79	97.0	8203	2.28	42.8	2840			
417				5.98	162.0	8365	1.88	56.8	2897			
469				4.80	198.0	8562	1.58	159.0	3056			
Drip Rate		0.075 mL/3.5 days			0.075 mL/3.5 days			0.0375 mL/7 days			0.0375 mL/7 days	
Configuration		3 Pellets			3 Pellets			3 Pellets			3 Pellets	
Sample Wt (g)		47.96			48.36			47.60			47.77	
Sample SA (m ²)		22.1			22.2			21.9			22.1	
Sample Vol. (m ³)		4.54			4.58			4.48			4.54	

*Values represent total uranium released from sample, excluding portion that reprecipitates on the UO₂-Zircaloy assembly. Solution volumes determined by weight differences measured between the beginning and end of each cycle. Terminated tests are indicated, while remaining experiments are continuing. Blanks indicate no analysis performed. Horizontal bars separate per annum intervals. Water injection schedule and sample configuration explained in the text. All experiments were conducted at 90°C. Determinations made from collected acid strip solution of the test vessels.

Fig. 12. Schematic Diagram of Experimental Assembly Showing Three-Pellet Sample Configuration

Solution samples have been periodically collected from these tests by opening the test vessels and collecting the accumulated leachate solution. Leachate aliquots have been analyzed for cations, anions, carbon, and pH. Uranium concentrations have been determined for several different solution aliquots, including an acid strip of the test vessel plus accumulated fluid, an unfiltered solution, and a 5-nm filtered solution.

D. Results

Results for cumulative release of uranium from samples for periods up to nine years are summarized in Table 14, as are the details of the individual sample periods (Table 15). Figure 13 depicts the cumulative release of uranium from the samples, as recovered during a 10-min nitric acid strip of the test vessel components. All samples display a rapid increase in the rate of uranium released in the first 1-2 years. Uranium release rates during this interval ranged up to $14 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (Table 16), with most of this release being attributed to the spallation of UO_2 granules from the sample surface [14]. The value of $14 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ is probably a minimum because the 10-min acid strip would not have completely dissolved the released grains. The final analysis for sample PMP8U-8 indicates a normalized release of $56 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. This higher value is believed to arise from a more complete dissolution of secondary uranyl minerals during the final overnight acid strip of the test vessel components. Analytical results that received between 2 and 9 years of testing indicate a decrease in the rate of uranium release from the samples relative to earlier periods (Fig. 13). Subsequent to the rapid release period, release rates for most tests decreased to an average of approximately 0.10 to $0.30 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. This level of release has remained relatively constant throughout the remaining tests. Sample PMP8U-3 is an exception to the overall trend, with normalized uranium release rates remaining below $0.10 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ throughout the tests.

Table 15. Results for Eight Unsaturated Tests with UO₂ Samples (DIW = deionized water)

Exp. No.	Date Started	Date Stopped/ Sampled	Sampling Period (weeks)	Elapsed Time (weeks)	Vessel In (g)	Vessel Out (g)	Vessel Delta (g)	Portion Removed (mL)	Acidified Volume (mL)	DIW Added (mL)	Sample Number	U Conc. Reported (µg/mL)	Uranium Release (µg)	Total Release (µg)
1	04/25/85	06/20/85	8.0	8.0	355.13	355.97	0.84	0.00	11.93	0.00	TF-174	2.2	26.246	26.246
	06/20/85	07/25/85	5.0	13.0	355.41	356.16	0.75	0.00	14.22	0.00	TF-189	1.516	21.557	47.803
	07/25/85	09/09/85	6.6	19.6	355.49	356.26	0.77	0.00	9.94	0.00	TF-214	45.2	449.288	497.090
	09/09/85	10/24/85	6.4	26.0	355.36	356.14	0.78	0.00	16.48	0.00	TF-229	16	263.680	760.770
	10/24/85	12/09/85	6.6	32.6	356.27	356.94	0.67	0.00	10.05	10.00	TF-245	6.45	129.322	890.092
	12/09/85	01/23/86	6.4	39.0	356.17	356.81	0.64	0.00	11.39	0.00	TF-260	6.54	74.490	964.582
	01/23/86	03/10/86	6.6	45.6	356.18	356.84	0.66	0.00	14.12	0.00	TF-276	70.9	1001.108	1965.689
	03/10/86	04/24/86	6.4	52.0	356.18	356.92	0.74	0.00	16.74	0.00	TF-294	129	2159.460	4125.149
	04/24/86	10/23/86	26.0	78.0	356.25	359.46	3.21	0.00	11.95	0.00	TF-356	22.9	273.655	4398.803
	10/23/86	04/28/87	26.7	104.7	356.39	359.42	3.03	0.00	8.34	5.00	TF-432	12.6	168.084	4566.887
	04/28/87	11/16/87	28.9	133.6	356.36	359.65	3.29	0.00	9.97	10.00	TF-518	7.26	144.982	4711.869
	11/16/87	04/25/88	23.0	156.6	356.25	358.83	2.58	1.00	8.86	10.00	TF-596	4.03	124.110	4835.979
	04/25/88	10/24/88	26.0	182.6	356.04	358.81	2.77	1.20	8.37	10.00	TF-700	5.05	163.674	4999.653
Terminated on 10/24/88														
2	04/25/85	06/20/85	8.0	8.0	355.34	356.15	0.81	0.00	15.68	0.00	TF-175	0.703	11.023	11.023
	06/20/85	07/25/85	5.0	13.0	355.47	356.11	0.64	0.00	12.35	0.00	TF-190	2.083	25.725	36.747
	07/25/85	09/09/85	6.6	19.6	355.60	356.61	1.01	0.00	10.49	0.00	TF-215	37	388.130	424.877
	09/09/85	10/24/85	6.4	26.0	355.64	356.57	0.93	0.00	15.25	0.00	TF-230	13.2	201.300	626.176
	10/24/85	12/09/85	6.6	32.6	356.08	356.89	0.81	0.00	9.10	10.00	TF-246	2.94	56.154	682.330
	12/09/85	01/23/86	6.4	39.0	355.73	356.56	0.83	0.00	12.98	0.00	TF-261	2.95	38.291	720.620
	01/23/86	03/10/86	6.6	45.6	355.72	356.38	0.66	0.00	13.56	0.00	TF-277	3.46	46.917	767.537
	03/10/86	04/24/86	6.4	52.0	355.74	356.54	0.80	0.00	15.63	0.00	TF-295	92.5	1445.775	2213.312
	04/24/86	10/23/86	26.0	78.0	355.70	358.33	2.63	0.00	11.49	0.00	TF-357	130	1493.700	3707.011
	10/23/86	04/28/87	26.7	104.7	355.67	359.07	3.40	0.00	8.59	5.00	TF-433	7.71	104.778	3811.790
	04/28/87	11/16/87	28.9	133.6	355.53	359.18	3.65	0.00	8.12	10.00	TF-519	3.84	69.580	3881.370
	11/16/87	04/25/88	23.0	156.6	355.55	358.77	3.22	1.00	7.85	10.00	TF-597	6.72	173.984	4055.354
	04/25/88	10/24/88	26.0	182.6	355.43	359.01	3.41	1.20	7.17	10.00	TF-701	2.79	73.915	4129.269
	10/24/88	05/08/89	28.0	210.6	355.39	357.41	2.09	0.80	7.79	4.00	TF-797	10.1	192.926	4322.195
	05/08/89	11/13/89	27.0	237.6	355.90	357.56	1.87	0.30	10.18	5.00	DW-9	3.96	71.599	4393.794
	11/13/89	11/19/90	53.0	290.6	346.47	360.41	5.43	0.70	9.61	7.00	DW-58	2	38.136	4431.930
	11/19/90	03/05/92	67.3	357.9	180.49	187.19	6.70	2.76	7.91	0.00	DW-72a	19.78	266.061	4697.990
	03/05/92	04/26/93	59.4	417.3	180.64	185.11	4.47	1.74	8.59	0.00	DW-82	23.119	325.167	5023.157
Terminated on 4/26/93														

(contd.)

Table 15 (contd.)

Exp. No.	Date Started	Date Stopped/ Sampled	Sampling Period (weeks)	Elapsed Time (weeks)	Vessel In (g)	Vessel Out (g)	Vessel Delta (g)	Portion Removed (mL)	Acidified Volume (mL)	DIW Added (mL)	Sample Number	U Conc. Reported (µg/mL)	Uranium Release (µg)	Total Release (µg)
3	04/25/85	06/20/85	8.0	8.0	345.54	346.32	0.78	0.00	15.73	0.00	TF-176	0.0178	0.280	0.280
	06/20/85	07/25/85	5.0	13.0	346.29	346.87	0.58	0.00	14.58	0.00	TF-191	0.403	5.875	6.155
	07/25/85	09/09/85	6.6	19.6	346.55	347.34	0.79	0.00	9.89	0.00	TF-216	7.21	71.306	77.461
	09/09/85	10/24/85	6.4	26.0	346.66	347.44	0.78	0.00	13.91	0.00	TF-231	9.08	126.302	203.764
	10/24/85	12/09/85	6.6	32.6	346.79	347.54	0.75	0.00	12.38	10.00	TF-247	3.97	88.848	292.612
	12/09/85	01/23/86	6.4	39.0	346.74	347.56	0.82	0.00	13.31	0.00	TF-262	2.34	31.145	323.757
	01/23/86	03/10/86	6.6	45.6	346.76	347.61	0.85	0.00	13.61	0.00	TF-278	14.3	194.623	518.379
	03/10/86	04/24/86	6.4	52.0	347.00	347.83	0.83	0.00	17.22	0.00	TF-296	7.59	130.699	649.078
	04/24/86	10/23/86	26.0	78.0	346.84	350.26	3.42	0.00	14.14	0.00	TF-358	18.8	265.832	914.910
	10/23/86	04/28/87	26.7	104.7	346.62	349.93	3.31	0.00	8.33	5.00	TF-434	10.4	138.632	1053.541
	04/28/87	11/16/87	28.9	133.6	346.73	350.25	3.52	0.00	9.18	10.00	TF-520	2.65	50.827	1104.368
	11/16/87	04/25/88	23.0	156.6	346.83	349.89	3.06	1.00	11.14	10.00	TF-598	9.15	287.329	1391.697
	04/25/88	10/24/88	26.0	182.6	346.65	349.91	3.26	1.20	7.08	10.00	TF-702	6.35	171.637	1563.334
	10/24/88	05/08/89	28.0	210.6	346.64	350.01	3.32	0.80	9.36	4.00	TF-798	14.2	249.938	1813.272
	05/08/89	11/13/89	27.0	237.6	346.50	348.95	2.38	0.30	8.52	8.00	DW-10	5.17	97.726	1910.998
	11/13/89	11/19/90	53.0	290.6	338.65	352.89	6.14	0.70	9.28	7.00	DW-59	5.77	106.022	2017.020
	11/19/90	03/05/92	67.3	357.9	172.44	180.59	8.15	2.76	8.08	0.00	DW-73a	34.708	424.042	2441.063
	03/05/92	04/26/93	59.4	417.3	172.58	178.46	5.88	1.84	7.99	0.00	DW-83	25.895	301.133	2742.196
	04/26/93	04/25/94	52.0	469.3	172.58	178.46	4.24	0.70	9.70	0.00	DW-102	25.630	297.771	3039.966
4	04/25/85	06/20/85	8.0	75.3	342.14	342.95	0.81	0.00	15.25	0.00	TF-177	0.176	2.684	2443.746
	06/20/85	07/25/85	5.0	80.3	342.86	343.50	0.64	0.00	16.08	0.00	TF-192	0.48	7.718	2451.464
	07/25/85	09/09/85	6.6	86.9	343.34	344.17	0.83	0.00	10.26	0.00	TF-217	0.897	9.203	2460.667
	09/09/85	10/24/85	6.4	93.3	343.46	344.27	0.81	0.00	11.39	0.00	TF-232	0.849	9.670	2470.337
	10/24/85	12/09/85	6.6	99.9	343.43	344.18	0.75	0.00	11.50	10.00	TF-248	8.98	193.070	2663.406
	12/09/85	01/23/86	6.4	106.3	343.36	344.17	0.81	0.00	12.12	0.00	TF-263	9.34	113.200	2776.606
	01/23/86	03/10/86	6.6	112.9	343.50	344.13	0.63	0.00	13.16	0.00	TF-279	47.4	623.784	3400.390
	03/10/86	04/24/86	6.4	119.3	343.25	343.50	0.25	0.00	13.92	0.00	TF-297	69.5	967.440	4367.829
	04/24/86	10/23/86	26.0	145.3	343.68	345.25	1.57	0.00	10.61	0.00	TF-359	132	1400.520	5768.349

Terminated on 10/23/86

(contd.)

Table 15 (contd.)

Exp. No.	Date Started	Date Stopped/ Sampled	Sampling Period (weeks)	Elapsed Time (weeks)	Vessel In (g)	Vessel Out (g)	Vessel Delta (g)	Portion Removed (mL)	Acidified Volume (mL)	DIW Added (mL)	Sample Number	U Conc. Reported (µg/mL)	Uranium Release (µg)	Total Release (µg)
5	04/25/85	06/20/85	8.0	8.0	368.47	369.22	0.75	0.00	18.02	0.00	TF-178	0.158	2.847	2.847
	06/20/85	07/25/85	5.0	13.0	368.67	369.25	0.58	0.00	14.14	0.00	TF-193	0.0864	1.221	4.068
	07/25/85	09/09/85	6.6	19.6	368.76	369.61	0.85	0.00	12.83	0.00	TF-218	8.53	109.439	113.507
	09/09/85	10/24/85	6.4	26.0	368.88	369.64	0.76	0.00	13.93	0.00	TF-233	2.59	36.078	149.586
	10/24/85	12/09/85	6.6	32.6	368.97	369.74	0.77	0.00	10.72	0.00	TF-249	3.15	33.768	183.353
	12/09/85	01/23/86	6.4	39.0	368.75	369.52	0.77	0.00	11.68	0.00	TF-264	1.66	19.388	202.741
	01/23/86	03/10/86	6.6	45.6	368.85	369.92	1.07	0.00	11.17	0.00	TF-280	28.8	321.696	524.437
	03/10/86	04/24/86	6.4	52.0	368.97	369.89	0.92	0.00	14.48	0.00	TF-298	5.02	72.689	597.126
	04/24/86	10/23/86	26.0	78.0	369.02	372.64	3.62	0.00	9.82	0.00	TF-360	10.5	103.110	700.236
	10/23/86	04/28/87	26.7	104.7	368.82	372.23	3.41	0.00	8.47	5.00	TF-435	3.55	47.818	748.054
	04/28/87	11/16/87	28.9	133.6	368.95	372.30	3.35	0.00	8.37	10.00	TF-521	3.77	69.254	817.308
	11/16/87	04/25/88	23.0	156.6	368.81	370.35	1.54	1.00	8.23	10.00	TF-599	1.12	58.227	875.535
	04/25/88	10/24/88	26.0	182.6	368.77	370.01	1.24	0.40	7.72	10.00	TF-703	1.19	31.128	906.663
Terminated on 10/24/88														
6	04/25/85	06/20/85	8.0	8.0	375.45	376.32	0.87	0.00	14.65	0.00	TF-179	0.178	2.607	2.607
	06/20/85	07/25/85	5.0	13.0	375.81	376.47	0.66	0.00	17.65	0.00	TF-194	0.167	2.947	5.554
	07/25/85	09/09/85	6.6	19.6	375.88	376.66	0.78	0.00	11.40	0.00	TF-219	2.67	30.438	35.992
	09/09/85	10/24/85	6.4	26.0	375.88	376.65	0.77	0.00	11.95	0.00	TF-234	3.51	41.944	77.936
	10/24/85	12/09/85	6.6	32.6	376.00	376.70	0.70	0.00	10.85	0.00	TF-250	73.6	798.560	876.495
	12/09/85	01/23/86	6.4	39.0	375.73	376.49	0.76	0.00	14.25	0.00	TF-265	97.6	1390.800	2267.295
	01/23/86	03/10/86	6.6	45.6	375.84	376.27	0.43	0.00	15.66	0.00	TF-281	3.56	55.749	2323.044
	03/10/86	04/24/86	6.4	52.0	375.93	376.15	0.22	0.00	13.76	0.00	TF-299	43.1	593.056	2916.100
	04/24/86	10/23/86	26.0	78.0	376.01	378.96	2.95	0.00	11.45	0.00	TF-361	324	3709.800	6625.899
	10/23/86	04/28/87	26.7	104.7	375.61	378.75	3.14	0.00	8.46	5.00	TF-436	28.9	388.994	7014.893
	04/28/87	04/25/88	51.9	156.6	375.66	382.18	6.52	1.00	8.39	10.00	TF-600	20.7	449.635	7464.528
	04/25/88	10/24/88	26.0	182.6	375.63	378.84	3.48	1.20	8.09	10.00	TF-715	3.08	85.042	7549.569
	10/24/88	05/08/89	28.0	210.6	375.46	376.79	1.16	0.30	7.55	4.00	TF-799	27.2	423.750	7973.319
	05/08/89	11/13/89	27.0	237.6	375.48	377.82	2.37	0.30	7.47	8.00	DW-11	3.16	55.970	8029.289
	11/13/89	11/19/90	53.0	290.6	367.45	382.11	6.09	0.70	9.45	7.00	DW-60	4.1	76.204	8105.492
	11/19/90	03/05/92	67.3	357.9	201.07	208.86	7.79	2.77	8.07	0.00	DW-74a	7.745	96.990	8202.482
	3/5/92	04/26/93	59.4	417.3	201.12	207.10	5.98	1.88	8.34	0.00	DW-84	13.301	161.795	8364.278
	4/26/93	04/25/94	52.0	469.3	172.49	176.73	4.80	0.70	8.82	0.00	DW-103	19.180	198.049	8562.327

(contd.)

Table 15 (contd.)

Exp. No.	Date Started	Date Stopped/ Sampled	Sampling Period (weeks)	Elapsed Time (weeks)	Vessel In (g)	Vessel Out (g)	Vessel Delta (g)	Portion Removed (mL)	Acidified Volume (mL)	DIW Added (mL)	Sample Number	U Conc. Reported (µg/mL)	Uranium Release (µg)	Total Release (µg)
7	04/25/85	07/25/85	13.0	13.0	374.68	378.98	0.30	0.00	15.35	0.00	TF-195	0.069	1.059	1.059
	07/25/85	10/24/85	13.0	26.0	374.89	375.56	0.67	0.00	15.17	0.00	TF-235	19.9	301.883	302.941
	10/24/85	01/23/86	13.0	39.0	375.17	ND	ND	0.00	12.95	0.00	TF-266	7.36	95.312	398.253
	01/23/86	04/24/86	13.0	52.0	375.01	375.40	0.39	0.00	14.39	0.00	TF-300	46.2	664.818	1063.070
	04/24/86	10/23/86	26.0	78.0	375.19	375.91	0.72	0.00	9.77	0.00	TF-362	110	1074.700	2137.770
	10/23/86	04/28/87	26.7	104.7	375.06	375.58	0.52	0.00	5.86	10.00	TF-437	14.2	225.212	2362.981
	04/28/87	11/16/87	28.9	133.6	375.03	375.16	0.13	0.00	7.79	10.00	TF-522	4.46	79.343	2442.324
	11/16/87	04/25/88	23.0	156.6	375.16	375.80	0.64	0.00	10.53	10.00	TF-601	5.5	112.915	2555.239
	04/25/88	10/24/88	26.0	182.6	375.00	375.94	1.05	0.00	7.95	10.00	TF-704	5.9	105.905	2661.143
	10/24/88	05/08/89	28.0	210.6	374.94	377.43	2.53	0.80	8.54	4.00	TF-800	5.99	109.849	2770.992
	05/08/89	11/13/89	27.0	237.6	374.62	375.23	0.61	0.10	9.82	5.00	DW-12	0.673	11.929	2782.921
	11/13/89	11/19/90	53.0	290.6	377.71	367.74	1.50	0.70	9.06	7.00	DW-61	0.477	14.363	2797.285
	11/19/90	03/05/92	67.3	357.9	200.62	202.90	2.28	0.80	9.06	0.00	DW-75a	3.0647	42.774	2840.059
	03/05/92	04/26/93	59.4	417.3	200.66	202.54	1.88	0.62	7.72	0.00	DW-85	4.9322	56.812	2896.871
	04/26/93	04/25/94	52.0	469.3	200.64	202.22	1.58	0.70	8.78	0.00	DW-104	10.100	159.217	3056.088
8	04/25/85	07/25/85	13.0	13.0	374.76	375.11	0.35	0.00	18.01	0.00	TF-196	0.0486	0.875	2840.934
	07/25/85	10/24/85	13.0	26.0	375.08	375.59	0.51	0.00	15.72	0.00	TF-236	33.4	525.048	3365.981
	10/24/85	01/23/86	13.0	39.0	375.66	376.00	0.34	0.00	14.09	0.00	TF-267	17.5	246.575	3612.556
	01/23/86	04/24/86	13.0	52.0	375.16	375.79	0.63	0.00	14.98	0.00	TF-301	17.6	263.648	3876.203
	04/24/86	10/23/86	26.0	78.0	375.35	376.13	0.78	0.00	15.41	0.00	TF-363	386	5948.260	9824.463
	10/23/86	04/28/87	26.7	104.7	375.32	375.69	0.37	0.00	5.61	10.00	TF-438	135	2107.350	11931.81
	04/28/87	07/20/87	11.9	116.6	375.39	375.90	0.51	0.00	9.28	5.00	TF-457	723	10324.44	22256.25
Terminated on 7/20/87

Fig. 13. Cumulative Uranium Release in Milligrams as Measured after a Ten-Minute Acid Strip of the Test Vessel Plus Contained Fluids. Blackened symbols represent tests that have been terminated.

Table 16. Normalized Release Rate for UO₂ Samples in Unsaturated Tests

	Pellet Surface Area (m ²)	Normalized Periodic Release (mg/m ² /day)	Sampling Period (weeks)	Normalized Cumulative Release (mg/m ² /day)	Elapsed Time (weeks)		Pellet Surface Area (m ²)	Normalized Periodic Release (mg/m ² /day)	Sampling Period (weeks)	Normalized Cumulative Release (mg/m ² /day)	Elapsed Time (weeks)
PMP8U-1	0.00407	0.11515	8.0	0.11515	8.0	PMP8U-3	0.0486	0.00010	8.0	0.00010	8.0
		0.15133	5.0	0.12907	13.0			0.00345	5.0	0.00139	13.0
		2.39978	6.6	0.89150	19.6			0.03190	6.6	0.01163	19.6
		1.43969	6.4	1.02704	26.0			0.05775	6.4	0.02304	26.0
		0.69075	6.6	0.95919	32.6			0.03974	6.6	0.02641	32.6
		0.40672	6.4	0.86812	39.0			0.01424	6.4	0.02440	39.0
		5.34723	6.6	1.51401	45.6			0.08706	6.6	0.03344	45.6
		11.79066	6.4	2.78448	52.0			0.05976	6.4	0.03669	52.0
		0.36943	26.0	1.97946	78.0			0.03005	26.0	0.03488	78.0
		0.22085	26.7	1.53081	104.7			0.01525	26.7	0.02957	104.7
		0.17635	28.9	1.23819	133.6			0.00518	28.9	0.02430	133.6
		0.18940	23.0	1.08413	156.6			0.03672	23.0	0.02613	156.6
		0.22096	26.0	0.96120	182.6			0.01940	26.0	0.02517	182.6
								0.02624	28.0	0.02531	210.6
PMP8U-2	0.00406	0.04848	8.0	0.04848	8.0	PMP8U-4	0.0467	0.01064	27.0	0.02364	237.6
		0.18103	5.0	0.09946	13.0			0.00588	53.0	0.02040	290.6
		2.07823	6.6	0.76386	19.6			0.01852	67.4	0.02005	357.9
		1.10180	6.4	0.84742	26.0			0.01490	59.6	0.01932	417.3
		0.30067	6.6	0.73711	32.6			0.01683	52.0	0.01904	469.3
		0.20958	6.4	0.65016	39.0			0.00103	8.0	0.09928	8.0
		0.25122	6.6	0.59263	45.6			0.00472	5.0	0.09339	80.3
		7.91338	6.4	1.49767	52.0			0.00428	6.6	0.08665	86.9
		2.02146	26.0	1.67227	78.0			0.00460	6.4	0.08100	93.3
		0.13801	26.7	1.28085	104.7			0.08988	6.6	0.08158	99.9
		0.08484	28.9	1.02246	133.6			0.05387	6.4	0.07990	106.3
		0.26617	23.0	0.91136	156.6			0.29037	6.6	0.09216	112.9
		0.10003	26.0	0.79582	182.6			0.46036	6.4	0.11200	119.3
		0.24244	28.0	0.72224	210.6			0.16478	26.0	0.12144	145.3
		0.09331	27.0	0.65076	237.6						
		0.02532	53.0	0.53668	290.6						
		0.13910	67.4	0.46191	357.9						
		0.19262	59.6	0.42358	417.3						

(contd.)

Table 16 contd.

	Pellet Surface Area (m ²)	Normalized Periodic Release (mg/m ² /day)	Sampling Period (weeks)	Normalized Cumulative Release (mg/m ² /day)	Elapsed Time (weeks)		Pellet Surface Area (m ²)	Normalized Periodic Release (mg/m ² /day)	Sampling Period (weeks)	Normalized Cumulative Release (mg/m ² /day)	Elapsed Time (weeks)
PMP8U-5	0.00221	0.02300	8.0	0.02300	8.0	PMP8U-7	0.00219	0.00531	13.0	0.00531	13.0
		0.01579	5.0	0.02023	13.0			1.51479	13.0	0.76005	26.0
		1.07652	6.6	0.37490	19.6			0.47826	13.0	0.66612	39.0
		0.36278	6.4	0.37190	26.0			3.33593	13.0	1.33357	52.0
		0.33216	6.6	0.36388	32.6			2.69632	26.0	1.78782	78.0
		0.19496	6.4	0.33604	39.0			0.54993	26.7	1.47201	104.7
		3.16443	6.6	0.74389	45.6			0.17935	28.9	1.19274	133.6
		0.73091	6.4	0.74229	52.0			0.32024	23.0	1.06458	156.6
		0.25635	26.0	0.58031	78.0			0.26570	26.0	0.95081	182.6
		0.11571	26.7	0.46178	104.7			0.25592	28.0	0.85841	210.6
		0.15513	28.9	0.39553	133.6			0.02882	27.0	0.76413	237.6
		0.16365	23.0	0.36147	156.6			0.01768	53.0	0.62797	290.6
		0.07739	26.0	0.32101	182.6			0.04146	67.4	0.51768	357.9
								0.06239	59.6	0.45286	417.3
								0.19973	52.0	0.42481	469.3
PMP8U-6	0.00222	0.02097	8.0	0.02097	8.0	PMP8U-8	0.00221	0.00435	13.0	14.12627	13.0
		0.03793	5.0	0.02749	13.0			2.61075	13.0	8.36851	26.0
		0.29806	6.6	0.11834	19.6			1.22607	13.0	5.98769	39.0
		0.41986	6.4	0.19289	26.0			1.31096	13.0	4.81851	52.0
		7.81982	6.6	1.73166	32.6			14.78857	26.0	8.14187	78.0
		13.92192	6.4	3.74104	39.0			5.09921	26.7	7.36563	104.7
		0.54592	6.6	3.28030	45.6			56.28545	11.9	12.34155	116.6
		5.93649	6.4	3.60868	52.0						
		9.18176	26.0	5.46637	78.0						
		0.93702	26.7	4.31086	104.7						
		0.55796	51.9	3.06788	156.6						
		0.21048	26.0	2.66096	182.6						
		0.97387	28.0	2.43663	210.6						
		0.13339	27.0	2.17486	237.6						
		0.09252	53.0	1.79505	290.6						
		0.09274	67.4	1.47492	357.9						
		0.17528	59.6	1.28991	417.3						
		0.24509	52.0	1.17413	469.3						

Size-fractionated uranium release trends have also been examined for a few samples (Fig. 14). A comparison of filtered and nonfiltered solution aliquots from the 8- and 9-year tests indicates that only 2 to 6% of the released uranium passed through a 5 nm filter, with the remaining fraction being released in particulate form or reprecipitating as secondary uranyl phases on the test vessel walls. The acid strip component represents the largest recovered uranium fraction from the tests (80 to 98%). The suspended fraction represents all uranium suspended in solution, less the fraction passing through the 5 nm filter. This suspended fraction represents from 1 to 15% of the total release, with the relatively high variability probably resulting from the resuspension of particulate material during the vessel opening and sampling processes. Examinations of filtered residues from these tests reveal the presence of elongated uranium silicate grains (Fig. 15). These phases probably formed as crystalline alteration phases on the sample surface and became dislodged by dripping water during the biweekly leachant injection.

The results from solution cation analyses are presented in Fig. 16. Leachate concentrations of Mg, Ca, K, and Si are depleted relative to the starting EJ-13 leachant (Figs. 16a to 16d). Magnesium is generally depleted to the greatest extent, with leachate concentrations typically reduced to ~10% of the initial EJ-13 values. Calcium and potassium are generally depleted to ~30% of the original EJ-13 compositions, while silicon is depleted to a level that is within 50 to 60% of the original EJ-13 composition. Analytical results from the last several test periods have also revealed a gradual increase in calcium concentrations. Sodium concentrations are similar to those of the starting EJ-13 solution (Fig. 16e), a finding consistent with the absence of any discrete sodium uranyl phases on the UO_2 pellet surfaces. Solution pH values are also noted to decrease for all samples relative to the initial 8.2 value for the EJ-13 leachant (Fig. 16f).

Fig. 14. Fractional Release of Uranium for Eight- and Nine-Year Solutions from Test Number PMP8U-3. Plate out represents release portion recovered after 10-min acid strip of test vessel less suspended and <5 nm fractions, suspended fraction represents unfiltered leachate concentration minus the <5 nm fraction, and <5 nm represents fraction of uranium passing through 5 nm filter.

Fig. 15. Suspended Fraction in Solution from Unsaturated Tests with UO_2 after Eight Years:
(a) AEM Photomicrograph of Rod-Shaped Uranium Silicate Colloid Particle and
(b) Selected Area Electron Diffraction Pattern from Uranium Silicate Crystal

Fig. 16. Leachate Concentrations Normalized to the Concentration of the Starting EJ-13 Leachant in Unsaturated Tests with UO_2 Samples: (a) Magnesium, (b) Calcium, (c) Potassium, (d) Silicon, (e) Sodium, and (f) Solution pH Values

Detailed SEM/EDS analyses of the surfaces of samples terminated during the initial 1-2 year period, during which pulsed uranium release occurred, have revealed the presence of micron-sized fragments of uranium-rich material, apparently produced as corroded and dislodged UO_{2+x} granules were washed from the sample surface during the biweekly leachant injection. An examination of the altered UO_{2+x} pellet surfaces has also revealed highly corroded grain boundaries, with individual grains becoming detached from the samples with severe sample corrosion. Detailed photomicrographs of these samples and the reacted UO_{2+x} surface have been presented in previous ANL reports and by Wronkiewicz et al. [15]. A decrease in the abundance of loosened particulate material was observed during SEM examinations of the post-two-year samples. The SEM/EDS investigations also indicated that the Mg, Ca, Si, and K depletions noted in the solution analyses are paralleled by the incorporation of these elements into uranyl oxide hydrate and uranyl silicate phases that formed on the UO_{2+x} pellet surfaces.

The top surface of a sample terminated after eight years was dominated by the uranyl alkaline silicate phase, boltwoodite (Fig. 17a) $[\text{K}(\text{H}_3\text{O})\text{UO}_2(\text{SiO}_4) \cdot n\text{H}_2\text{O}]$. Also present were dehydrated schoepite (Fig. 17b) $[\text{UO}_3 \cdot 0.8\text{H}_2\text{O}]$, uranophane (Fig. 17b) $[\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}]$, soddyite (Fig. 17c) $[\text{U}_6\text{Si}_2\text{O}_{16} \cdot \text{H}_2\text{O}]$, and hollow-shaped Mg-Al-Si tubes believed to be the clay-mineral palygorskite (attapulgite) (Fig. 17d). This tube-shaped phase had not been observed on any previous samples and helps to explain the "sink" for the magnesium in the EJ-13 leachant, which was strongly depleted in the solutions dripping from the UO_2 samples (Fig. 16a). The bottom surface of the sample was characterized by the formation of schoepite (Fig. 18a) $[\text{UO}_3 \cdot 2\text{H}_2\text{O}]$, dehydrated schoepite (Figs. 18b and 18c), and compregnacite (Figs. 18c and 18d) $[\text{K}_2\text{U}_6\text{O}_{19} \cdot 10\text{H}_2\text{O}]$.

Experimental results from these tests have been presented at several conferences the past year, including the 1993 Spent Nuclear Fuels Conference in Santa Fe, New Mexico; the 1993 Geological Society of America's annual meeting in Boston, Massachusetts; and the 1994 Spent Nuclear Fuels Conference in Montebello, Quebec.

E. Discussion

The decrease in released uranium after the 1-2 year period is thought to result from the formation of a dense surface mat of uranyl silicate phases, which significantly lessened the amount of released particulate material from the UO_2 pellet surfaces. After 8-9 years, however, it still appears that uranium release is being dominated by particulate material release, despite the reduction in total uranium loss and the disappearance of micron-sized particulate material from the sample surfaces. With these later tests, it appears that the particulates are finer-grained than those of the 1-2 year samples.

The covering of secondary minerals also does not appear to act as a complete barrier for fluid access to the UO_{2+x} pellet surface. During SEM examinations of the samples, the granular UO_2 surface could still be observed in many locations, even in regions where thick mats of alteration minerals have accumulated.

The SEM/EDS investigations also indicate that these cation components have been incorporated into distinct uranyl-bearing phases that formed on the UO_{2+x} pellet surfaces. Mineral trends indicate the following paragenetic sequence for the top UO_{2+x} surfaces over the past eight years: uraninite $\rightarrow$ uranyl oxide hydrates $\rightarrow$ uranyl silicates $\rightarrow$ uranyl alkaline silicates. This trend is identical to the pattern of uraninite alteration observed in naturally occurring weathered uraninite deposits (Fig. 19) and indicates that the experimental conditions used in these tests replicated the UO_2 corrosion process expected to occur in natural geologic systems.

(a)

(b)

(c)

(d)

Fig.17. SEM Photomicrographs for the Top Surface of UO_2 Pellet after Eight Years of Reaction: (a) Dense Mat of Boltwoodite Needles, (b) Uranophane Needles and Dehydrated Schoepite "Book-Shaped"-Hexagonal Crystals, (c) Bladed Soddyite Crystals, and (d) Palygorskite Tubes and Dehydrated Schoepite

(a)

(b)

(c)

(d)

Fig. 18. SEM Photomicrographs for the Bottom Surface of UO_2 Pellet after Eight Years of Reaction: (a) Schoepite Crystals Showing Evidence for Dissolution Pitting, (b) Dehydrated Schoepite "Book-Shaped"-Hexagonal Crystals, (c) Reacted UO_{2+x} Surface Showing both Grain and Grain Boundary Dissolution as well as Dislodged Granules, and (d) Compreignacite Crystals

Fig. 19. Paragenetic Sequence for Uranyl Minerals Formed under Oxidizing Conditions:
 (a) Experimental Sequence Formed in Unsaturated Drip Tests with UO_2 and
 (b) Natural Geologic Sequence Formed during the Alteration of Uraninite in the
 Nopal I, Mexico, Deposit [16]

It would also be of interest to study in detail the reaction that is occurring at the grain boundaries, with emphasis on the depth into the pellet which the reaction has penetrated. To accomplish this would require a change in the Test Plan governing the work.

F. Conclusions

The following conclusions were derived from the study of UO_2 reactions with dripping EJ-13 groundwater:

- (1) During the first 1-2 years, the pulsed release of uranium occurred mainly because of the spallation of UO_2 granules from the sample surface. The spallation of UO_2 granules, in turn, results from the rapid corrosion of intergrain boundary regions. This rapid corrosion of the intergrain boundaries probably results from energetically favorable lattice deformations produced during the press sintering of the UO_2 pellets.
- (2) After two years of reaction, the uranium release rate subsided to the present rate of ~ 0.1 to $0.3 \text{ mg} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$. The reduction of spalled material probably results from the formation of a cohesive net of alteration minerals on the sample surface that entrap the UO_2 granules.
- (3) At the rate of 0.1 to $0.3 \text{ mg} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ observed in the longer term tests, $<6\%$ of the released uranium will pass through a 5 nm filter.
- (4) A distinct sequence of secondary alteration minerals formed on the reacted sample surfaces, starting with uranyl oxide hydrates, followed by uranyl silicates, and finally, uranyl alkali and alkaline earth silicates. This paragenetic sequence of alteration minerals is identical to that found in oxidized zones of naturally occurring uranium deposits. This similarity indicates that the unsaturated drip test method has accurately replicated alteration conditions expected in natural geologic systems, while accelerating the paragenetic sequence of alteration phases formed in natural systems into reasonably short time periods.
- (5) The replication of a naturally occurring paragenetic sequence for uranium alteration minerals in these tests provides the first documented evidence for the bridging of short-term laboratory tests with natural analogue systems for uraninite minerals. The replication of naturally occurring geologic phenomenon in these tests will also provide public confidence in the experimental results that are obtained for spent nuclear fuel studies.

G. Ongoing Work

Three of the initial eight tests are continuing into their ninth year of operation. These samples will continue to be monitored for long-term reaction trends with respect to the release of uranium from the samples and the formation of secondary alteration products. Archived samples will also be cross-sectioned to examine grain boundary corrosion features, formation of alteration minerals within the grain boundaries, and depth of alteration into the samples, if guidance is received from the YMP to do so.

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