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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, IL 60439

**LEACHING ACTION OF EJ-13 WATER ON UNIRRADIATED UO_2
SURFACES UNDER UNSATURATED CONDITIONS AT 90°C:
INTERIM REPORT**

by

David J. Wronkiewicz, John K. Bates,
Thomas J. Gerding, Ewald Veleckis,
and Benjamin S. Tani
(Activity #D-20-42, QA level III)

Chemical Technology Division

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LEACHING ACTION OF EJ-13 WATER ON UNIRRADIATED UO_2 SURFACES UNDER UNSATURATED CONDITIONS AT 90°C: INTERIM REPORT

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ABSTRACT

A set of experiments, based on the application of the Unsaturated Test method to the reaction of UO_2 with EJ-13 water, has been conducted over a period of 182.5 weeks. One half of the experiments have been terminated, while one half are still ongoing. Solutions that have dripped from UO_2 specimens have been analyzed for all experiments, while the reacted UO_2 surfaces have been examined for only the terminated experiments. A pulse of uranium release from the UO_2 solid, in conjunction with the formation of dehydrated schoepite on the surface of the UO_2 , was observed during the 39- to 96-week period. Thereafter, the uranium release decreased and a second set of secondary phases was observed. The latter phases incorporate cations from the EJ-13 water and include boltwoodite, uranophane, sklodowskite, compregnacite, and schoepite. The experiments are being continued to monitor for additional changes in solution composition and secondary phase formation, and have now reached the 319-week period.

LEACHING ACTION OF EJ-13 WATER ON UNIRRADIATED UO_2 SURFACES UNDER UNSATURATED CONDITIONS AT 90°C: INTERIM REPORT

I. INTRODUCTION

The unsaturated tuff beds of Yucca Mountain, Nevada, are being investigated as a potential site for the permanent disposal of high-level nuclear waste. A description of the repository horizon and of issues that need to be considered when evaluating the performance of waste forms has been provided in the Site Characterization Plan [1]. Contact of the waste by humid air and by small amounts of water after container breach is one scenario that has received particular attention because of the small volumes of water anticipated to exist in the waste package environment. The Unsaturated Test Method [2] has been specifically developed to investigate waste form reactions under such conditions.

This method has been applied extensively to glass [3,4], where the ratio of waste form surface area to volume of water is larger than that found in typical leach tests, and has resulted in the identification of several materials interactions that might affect glass reaction. While the goal of the method is to provide descriptive details of several reaction processes (e.g., reactions between waste and humid air, reactions between the waste and small quantities of intermittently recharged water, as well as reactions between the waste, water, and metal container), measurements of total elemental releases from the waste are also provided.

It is also possible that spent reactor fuel water form will be exposed to similar unsaturated conditions. Reactions of the UO_2 matrix under these conditions could be significantly different from those observed in spent fuel leach tests because of the oxidizing environment that will exist in the former case and because of the reduced volume of solution available for reaction. To demonstrate the feasibility of utilizing the Unsaturated Test Method with spent fuel, a set of experiments has been undertaken using unirradiated UO_2 . While it is recognized that such experiments cannot be used to predict spent fuel behavior, the gross processes observed in the breakdown of the UO_2 matrix may be relevant in the spent fuel testing, especially with respect to the identification of secondary mineral phases formed during the reaction.

II. EXPERIMENTAL

A. Materials

Normal uranium oxide pellets used in the experiments were obtained from the vaults of Argonne National Laboratory (SPM Batch No. 4-4-110). The isotopic composition of the uranium was determined by a mass spectrometric isotopic dilution to be <0.0005 wt % ^{233}U , 0.0055 ± 0.0005 wt % ^{234}U , 0.7118 ± 0.0005 wt % ^{235}U , <0.0005 wt % ^{236}U , and 99.283 ± 0.002 wt % ^{238}U . The uranium assay, measured by the same technique, was

88.20 $\pm$ 0.01 wt % U. The oxygen/metal ratio was determined to be 2.000 $\pm$ 0.002 by heating a weighed amount of UO_2 at 850°C for one hour in an open crucible to convert the material to U_3O_8 , followed by cooling in a dessicator and reweighing. The concentration of impurities in UO_2 ($>0.1 \mu\text{g/g}$ UO_2) is listed in Table 1.

The pellets were prepared for the experiments in one of three ways: (1) they were cut into 1.75-mm thick slices, (2) crushed in a mortar and pestle to collect -60+80 mesh fraction of the granules, or (3) cut into 10-mm-high cylinders. An Isomet rotary diamond saw (Buehler, Ltd.) was used for cutting. All operations were performed in air.

Zircaloy-4 tubing (13.9-mm ID, 0.38-mm wall) was used to contain UO_2 specimens and to simulate fuel cladding. The tubing was cut into 20.0 and 31.8-mm lengths to accommodate the two different sample heights used in the experiments.

The leachant for the experiments was groundwater from well J-13 located near Yucca Mountain, Nevada. Before use, the water was equilibrated with Topopah Spring tuff at 90°C according to a procedure described elsewhere [3]. Briefly, the procedure consisted of soaking 10 g of <100 mesh tuff granules in a polyethylene (PE) bottle containing 1 L of J-13 water for two weeks at 90°C, followed by filtration and storage in a dark place. The equilibrated water (EJ-13 water) has been demonstrated to be more representative of the vadose water in the repository rock than the water from J-13 well [5]. The composition of EJ-13 water is presented in Table 2.

Table 1. Impurity Content of UO_2 Pellets in $\mu\text{g/g}$ UO_2^a

Al	4	Cu	3	S	0.9
As	0.5	F	0.1	Sc	<0.06
B	1	Fe	20	Si	<2
Ba	0.4	K	0.3	Th	15
Bi	<0.2	Mg	<0.7	Ti	0.4
Ca	2	Mn	0.3	V	0.3
Cl	0.2	Na	0.9	Y	0.4
Co	0.2	Ni	2	Zn	0.3
Cr	0.7	P	0.8	Zr	<0.5

^aSpark source mass spectrometric analysis performed by the Northern Analytical Laboratory, Amherst, New Hampshire. A factor of 2 is the estimated accuracy.

Table 2. Composition of EJ-13 Water ($\mu\text{g/mL}$)

pH	8.10	Sr	0.045
Al	0.63	U	0.0024
B	0.16	F ⁻	2.40
Ca	9.08	Cl ⁻	7.15
Fe	0.01	NO ₃ ⁻	7.60
K	NA	NO ₂ ⁻	<0.5
Li	0.044	SO ₄ ⁼	17.3
Mg	0.96	C (org)	5.0
Na	46.5	C (inorg)	26.5
Si	34.4	HCO ₃ ⁻	134.7

NA = Not analyzed because of insufficient sample volume.

B. Apparatus

The main portion of the apparatus is shown in Fig. 1. It consists of a stainless steel (304L) vessel manufactured by the Parr Instrument Company, Moline, Illinois and modified for the present application by ANL. The vessel provides for the collection and containment of the liquid, as well as for support of the specimen. The specimen-Zircaloy assemblage rests on a TeflonTM-PFA stand, the top of which consists of a grating of crossed bars. There is about a 1/8" space between the bottom surface of the UO₂ and the bottom circumference of the Zircaloy that rests on the TeflonTM stand. In none of the experiments was the UO₂ directly in contact with the TeflonTM. A tightly fitting stainless steel washer is installed around the top portion of the Zircaloy cladding to stabilize and to center the specimen. The vessel is sealed with a matching cap by means of a compression fitting (not shown in Fig. 1) and a 1.6-mm-thick TeflonTM gasket. The seal is secured by placing

Fig. 1.
Schematic Diagram of
Experimental Assembly

the vessel in a special vise and by tightening the fitting at ~20 foot-pound torque. The assembled vessels are placed in an oven (model Blue M, General Signal Co., Blue Island, Illinois) that is controlled at 90°C to within ±1°C.

Water is introduced into the vessel through an injection system that is comprised of a 250-μL Unimetrics syringe (Alltech Associates, Inc., Deerfield, Illinois) with a TeflonTM-tipped plunger, a low-volume TeflonTM-body Mininert valve, a feedthrough into the oven, another feedthrough in the vessel cap, and approximately 45 cm of connecting 1.6-mm OD stainless steel tubing. The injection nozzle inside the vessel is directed towards the center of the exposed top UO₂ surface. The total estimated volume of the injection system (excluding the syringe) is 0.2mL.

C. Procedure

The experiments were performed on eight natural UO₂ specimens each of which has been encased in Zircaloy cladding, placed on a TeflonTM stand, and sealed in an air-tight stainless steel vessel. Accurately measured quantities of EJ-13 water were periodically dripped on the specimen from the injection system. All tests were performed in the same oven at 90°C. Three different specimen configurations were employed:

- (1) a stack of eleven as-cut pellet discs (13.7-mm dia, 1.75-mm thick);
- (2) ~19-mm-high column of crushed UO₂, vertically sandwiched between two 1.75-mm-thick as-cut discs; and
- (3) ~30-mm-high stack of three 13.7-mm dia UO₂ pellets.

The top and bottom specimen surfaces in all experiments were the original as-formed pellet surfaces. The as-cut surfaces were always directed toward the inside of the waste form assemblage.

Duplicate experiments were conducted for these three configurations at a water injection rate of 0.075 mL every 3.5 days. For configuration 3, an additional pair of experiments was performed at a lower injection rate of 0.0375 mL every 7 days. The matrix of experimental parameters is given in Table 3. Specimen volumes and surface areas shown in the matrix were calculated from the geometry of the corresponding configuration. In the case of granulated specimens (experiments #3 and #4), they were calculated assuming spherical close-packed particles (26% void space) with diameters that match the apertures of a 70-mesh sieve (212 μm).

The experiments were initiated according to the following procedure. A small amount of EJ-13 water (200 μL) was deposited into the vessel to be installed to provide an initial atmosphere that is saturated in water vapor. The vessel was then assembled as shown in Fig. 1, sealed by tightening the compression fitting, weighed, placed in the oven, and was connected to the water injection line. Injections were made according to the rate schedule, given in Table 3, by the following steps: (1) the 250-μL syringe was filled with the required amount of EJ-13 water, (2) the Luer tip of the syringe was

Table 3. Experimental Parameter Matrix

Experiment Number	Specimen Configuration ^a	Weight of UO ₂ (g)	Surface of UO ₂ (cm ²)	Volume of UO ₂ (cm ³)	Weight of Zircaloy (g)	EJ-13 Water Injection Rate	
						Volume (mL)	Interval (days)
1	1	29.522	40.7	2.83	2.365	0.075	3.5
2	1	29.166	40.6	2.80	2.401	0.075	3.5
3	2	19.856	486	2.21	2.368	0.075	3.5
4	2	18.258	467	2.14	2.376	0.075	3.5
5	3	47.955	22.1	4.54	3.839	0.075	3.5
6	3	48.360	22.2	4.58	3.854	0.075	3.5
7	3	47.596	21.9	4.48	3.840	0.0375	7
8	3	47.773	22.1	4.54	3.850	0.0375	7

^aConfigurations defined in text.

coupled with the matching hub of the TeflonTM-body valve, (3) the valve was momentarily opened to allow the injection of the syringe contents, and (4) steps 1-3 were repeated by injecting 250 μ L of air into the system to clear the lines and to repressurize the vessel.

A semi-continuous leaching mode was adopted for the experiments. At predetermined intervals (approximately every 6.5, 13, or 26 weeks), an experiment was interrupted to collect the accumulated liquid in the vessel according to the following procedure. First, the vessel was disconnected from the water injection system by momentarily disassembling a connector near the vessel top and by plugging its exposed end with a cap. (The amount of water escaping during this operation is considered to be negligible.) The vessel was then removed from the oven, cooled in an ice bath, weighed, and was opened by disengaging the compression fitting. The specimen-Zircaloy assemblage was lifted from the vessel and observations were made regarding the appearance of the exposed surfaces. The assemblage was temporarily stored in a covered TeflonTM container. Approximately 10 mL of deionized water (DIW), acidified with five drops of concentrated HNO₃ (Ultrex), was added to the vessel reaching a level just above the TeflonTM-PFA stand. After a 10-min soak at room temperature the resulting solution was decanted into a PE bottle. The vessel, still containing the stand, was rinsed with DIW and was allowed to dry in a stream of nitrogen (the rinse water was discarded). After an addition of 200 μ L of EJ-13 water, the specimen-Zircaloy assemblage was returned to the vessel which was then resealed, weighed, and put back in the oven on the water injection system until the next sampling date.

D. Analytical Methods

The analytical methods used for the solution samples were as follows: uranium was analyzed by the Atomic Fluorescence Spectroscopy, cations by the Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES), and anions by Ion Chromatography (IC). Carbon was determined with the Dohrmann Total Carbon Analyzer, and pH with the Brinkmann Metrohm Meter.

III. SOLUTION RESULTS

The Unsaturated Test Method treats all uranium outside the UO_2 -Zircaloy assembly as having been released. This includes the uranium that is in solution, that which is sorbed into the vessel walls, and that which is deposited on the TeflonTM stand. The latter two uranium sources are largely recovered through solubilization during the 10-min acid strip. The portion that is not recovered is incorporated back into the test through reuse of the vessel and the TeflonTM stand. Only with a more thorough acid strip during termination can an essentially complete uranium retrieval be accomplished. Therefore, the periodic uranium releases reported in this study simply represent the quantity of uranium that was retrieved for analysis during the corresponding period.

Because of low water injection rates, the amount of liquid found in the vessel at the end of shorter sampling periods was quite small. For this reason, most of the analyses were limited to the uranium content, which could be readily determined from acidified rinse solutions. Extensive surface reactions occurring during the first two years of testing prompted us to make changes in the subsequent sampling procedures to establish the contribution of aqueous species to the secondary phase formation: (1) analyses for major cations were included in all acidified samples submitted for uranium determination, and (2) anion analyses were performed where possible on small samples withdrawn from the leachate solutions prior to acidification. Also, after the first year of testing, the length of sampling periods was increased to yield larger solution volumes.

The release of various species to the leachate solution is reported in the following manner.

- (1) For uranium, the release data are reported in terms of mass units because of its plate-out tendency in dilute solutions. The contribution of the uranium introduced with 0.2 mL of EJ-13 water is negligible because of low concentrations.
- (2) Cations other than uranium do not plate-out and their release can be reported in terms of concentration units that are calculated from the mass released and solution volume. Cation contributions from 0.2 mL of added EJ-13 water are significant and must be corrected.

- (3) Releases of anions, carbon, and the unplated portion of uranium were determined by analyzing small aliquots from the solution before acidification. The results are also reported in concentration units. The 0.2-mL water corrections were applied to the anions but not to uranium and carbon. For the uranium the correction is negligible whereas the carbon content in 0.2 mL of EJ-13 water exceeds that of the samples themselves.

A. Uranium Release

The sampling matrices for uranium are given in Tables 4 to 7. The first six experiments, carried out at the higher water injection rate (7.8 mL/yr), are comprised of 12 or 13 sampling periods with the exception of experiment #4, which had to be terminated after nine periods because of a plugged water line. For experiments #7 and #8, which were performed at a lower injection rate (1.95 mL/yr), the initial 6.5-week sampling periods were extended to 13 weeks to provide larger sample sizes.

The quantity of liquid present in the vessel at the end of a sampling period was determined from the measured weight gain of the vessel. The fraction of liquid recovered, i.e., the ratio of weight gain to volume of water injected during that period, shows a considerable scatter, but the average fraction recovered was ~75%. There are several paths by which the water loss can occur: from losses in the pressurized water feed system during injections, though TeflonTM seal between the pressurized vessel and its cap, and from leakage occurring during vessel disengagement from the injection system inside the oven at the end of a sampling period. Our experience has indicated that the first of these paths can be considered to be a prime suspect. Line plugging has been discovered in several cases that required moving the vessel to another feed line. The normal measure of the amount of water introduced into the vessel was taken to be the vessel weight gain before and after a sampling period.

In some of the later sampling operations, the solution volumes were more accurately measured by weighing only the bottom portion of the vessel (with and without solution) after removing the compression fitting, vessel cap, and specimen during the normal vessel disassembly steps, but retaining the TeflonTM stand. Results of these measurements are identified in Tables 4 to 7 by footnotes.

The mass of uranium released, listed in column 14 of Tables 4 to 7 and shown in Figs. 2-5, was calculated according to the formula given in table footnotes. The procedure, however, had to be somewhat modified for the final two sampling periods of experiments #1, #2, #3, #5, and #6 in which small samples were taken directly from the original liquid for the pH (typically 0.1 mL), carbon (0.5 mL), anions (0.5 mL), and uranium (0.1 mL) determinations, prior to its transfer from the vessel and subsequent acidification. For these special cases, the transferred liquid was prepared for the uranium and cation analyses in the usual manner, except that

Table 4. Sampling Matrix and Uranium Release for Unsaturated Experiments #1 and #2

Specimen Configuration: Stack of 11 UO₂ Discs
 EJ-13 Water Flow Rate: 0.075 mL/3.5 d

Expt 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) ^a	Total U Release (μg)
1	4/25/85	6/20/85	8.0	8.0	355.13	355.97	0.84	0.0	11.93	0.0	TF-174	2.2	26.2	26.2
	6/20/85	7/25/85	5.0	13.0	355.41	356.16	0.75	0.0	14.22	0.0	TF-189	1.516	21.6	47.8
	7/25/85	9/09/85	6.6	19.5	355.49	356.26	0.77	0.0	9.94	0.0	TF-214	45.2	449.3	497.1
	9/09/85	10/24/85	6.4	26.0	355.36	356.14	0.78	0.0	16.48	0.0	TF-229	16.0	263.7	760.8
	10/24/85	12/09/85	6.6	32.5	356.27	356.94	0.67	0.0	10.05	10.0	TF-245	6.45	129.3	890.1
	12/09/85	1/23/86	6.4	39.0	356.17	356.81	0.64	0.0	11.39	0.0	TF-260	6.54	74.5	964.6
	1/23/86	3/10/86	6.6	45.5	356.18	356.84	0.66	0.0	14.12	0.0	TF-276	70.9	1001	1966
	3/10/86	4/24/86	6.4	52.0	356.18	356.92	0.74	0.0	16.74	0.0	TF-294	129	2159	4125
	4/24/86	10/23/86	26.0	78.0	356.25	359.46	3.21	0.0	11.95	0.0	TF-356	22.9	273.7	4399
	10/23/86	4/28/87	26.7	104.7	356.39	359.42	3.03	0.0	8.34	5.0	TF-432	12.6	168.1	4567
	4/28/87	11/16/87	28.9	133.5	356.36	359.65	3.29	0.0	9.97	10.0	TF-518	7.26	145.0	4712
	11/16/87	4/25/88	23.0	156.5	356.25	358.83	2.58	1.0	8.86	10.0	TF-596	4.03	124.1	4836
	4/25/88	10/24/88	26.0	182.5	356.04	358.81	2.77	1.2	8.37	10.0	TF-700	5.05	163.7	5000
Terminated on 10/24/88														
2	4/25/85	6/20/85	8.0	8.0	355.34	356.15	0.81	0.0	15.68	0.0	TF-175	0.703	11.0	11.0
	6/20/85	7/25/85	5.0	13.0	355.47	356.11	0.64	0.0	12.35	0.0	TF-190	2.083	25.7	36.7
	7/25/85	9/09/85	6.6	19.5	355.00	356.61	1.01	0.0	10.49	0.0	TF-215	37	388.1	424.9
	9/09/85	10/24/85	6.4	26.0	355.64	356.57	0.93	0.0	15.25	0.0	TF-230	13.2	201.3	626.2
	10/24/85	12/09/85	6.6	32.5	356.00	356.89	0.81	0.0	9.10	10.0	TF-246	2.94	56.2	682.3
	12/09/85	1/23/86	6.4	39.0	355.73	356.56	0.83	0.0	12.98	0.0	TF-261	2.95	38.3	720.6
	1/23/86	3/10/86	6.6	45.5	355.72	356.38	0.66	0.0	13.56	0.0	TF-277	3.46	46.9	767.5
	3/10/86	4/24/86	6.4	52.0	355.74	356.54	0.80	0.0	15.63	0.0	TF-295	92.5	1446	2213
	4/24/86	10/23/86	26.0	78.0	355.70	358.33	2.63	0.0	11.49	0.0	TF-357	130	1494	3707
	10/23/86	4/28/87	26.7	104.7	355.67	359.07	3.40	0.0	8.59	5.0	TF-433	7.71	104.8	3812
	4/28/87	11/16/87	28.9	133.5	355.53	359.18	3.65	0.0	8.12	10.0	TF-519	3.84	69.6	3881
	11/16/87	4/25/88	23.0	156.5	355.55	358.77	3.22	1.0	7.85	10.0	TF-597	6.72	174.0	4055
	4/25/88	10/24/88	26.0	182.5	355.43	359.01	3.41 ^b	1.2	7.17	10.0	TF-701	2.79	73.9	4129

^aThe mass of uranium released, M (column 14), is calculated according to formula $M = V * C * (A+D)/(V-v) - 0.2 * s$ where,

V = solution volume in the vessel (column 8),

v = solution volume removed for analysis before acidification (column 9),

A = volume after acidification (column 10),

D = volume of DIW added to acidified solution before analysis (column 11),

C = uranium concentration reported by the ACL (column 13), and

s = uranium concentration in EJ-13 water (see Table 2).

^bCalculated from the weight difference in the bottom portion of the vessel.

Table 5. Sampling Matrix and Uranium Release for Unsaturated Experiments #3 and #4

Specimen Configuration: Crushed UO₂ Pellets between Two UO₂ Discs
 EJ-13 Water Flow Rate: 0.075 mL/3.5 d

Expt 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) ^a	Total U Release (μg)
3	4/25/85	6/20/85	8.0	8.0	345.54	346.32	0.78	0.0	15.73	0.0	TF-176	0.0178	0.280	0.280
	6/20/85	7/25/85	5.0	13.0	346.29	346.87	0.58	0.0	14.58	0.0	TF-191	0.403	5.88	6.16
	7/25/85	9/09/85	6.6	19.5	346.55	347.34	0.79	0.0	9.89	0.0	TF-216	7.21	71.3	77.5
	9/09/85	10/24/85	6.4	26.0	346.66	347.44	0.78	0.0	13.91	0.0	TF-231	9.08	126.3	203.8
	10/24/85	12/09/85	6.6	32.5	346.79	347.54	0.75	0.0	12.38	10.0	TF-247	3.97	88.8	292.6
	12/09/85	1/23/86	6.4	39.0	346.74	347.56	0.82	0.0	13.31	0.0	TF-262	2.34	31.1	323.8
	1/23/86	3/10/86	6.6	45.5	346.76	347.61	0.85	0.0	13.61	0.0	TF-278	14.3	194.6	518.4
	3/10/86	4/24/86	6.4	52.0	347.00	347.63	0.63	0.0	17.22	0.0	TF-296	7.59	130.7	649.1
	4/24/86	10/23/86	26.0	78.0	346.84	350.26	3.42	0.0	14.14	0.0	TF-358	18.8	265.8	914.9
	10/23/86	4/28/87	26.7	104.7	346.62	349.93	3.31	0.0	8.33	5.0	TF-434	10.4	138.6	1054
	4/28/87	11/16/87	28.9	133.5	346.73	350.25	3.52	0.0	9.18	10.0	TF-520	2.65	50.8	1104
	11/16/87	4/25/88	23.0	156.5	346.83	349.89	3.06	1.0	11.14	10.0	TF-598	9.15	287.3	1392
	4/25/88	10/24/88	26.0	182.5	346.65	349.91	3.26	1.2	7.08	10.0	TF-702	6.35	171.6	1563
4	4/25/85	6/20/85	8.0	8.0	342.14	342.95	0.81	0.0	15.25	0.0	TF-177	0.176	2.68	2.68
	6/20/85	7/25/85	5.0	13.0	342.86	343.50	0.64	0.0	16.08	0.0	TF-192	0.480	7.72	10.4
	7/25/85	9/09/85	6.6	19.5	343.34	344.17	0.83	0.0	10.26	0.0	TF-217	0.897	9.20	19.6
	9/09/85	10/24/85	6.4	26.0	343.46	344.27	0.81	0.0	11.39	0.0	TF-232	0.849	9.67	29.3
	10/24/85	12/09/85	6.6	32.5	343.43	344.18	0.75	0.0	11.50	10.0	TF-248	8.98	193.1	222.3
	12/09/85	1/23/86	6.4	39.0	343.36	344.17	0.81	0.0	12.12	0.0	TF-263	9.34	113.2	335.5
	1/23/86	3/10/86	6.6	45.5	343.50	344.13	0.63	0.0	13.16	0.0	TF-279	47.4	623.8	959.3
	3/10/86	4/24/86	6.4	52.0	343.25	343.50	0.25	0.0	13.92	0.0	TF-297	69.5	967.4	1927
	4/25/86	10/24/86	26.0	76.0	343.68	345.25	1.57	0.0	10.61	0.0	TF-359	132	1401	3327
Terminated on 10/24/86														

^aThe mass of uranium released, M (column 14), is calculated according to formula $M = V * C * (A+D)/(V-v) - 0.2 * s$ where,

V = solution volume in the vessel (column 8),

v = solution volume removed for analysis before acidification (column 9),

A = volume after acidification (column 10),

D = volume of DIW added to acidified solution before analysis (column 11),

C = uranium concentration reported by the ACL (column 13), and

s = uranium concentration in EJ-13 water (see Table 2).

Table 6. Sampling Matrix and Uranium Release for Unsaturated Experiments #5 and #6

Specimen Configuration: Stack of Three UO₂ Pellets
EJ-13 Water Flow Rate: 0.075 mL/3.5 d

Expt 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) ^a	Total U Release (μg)
5	4/25/85	6/20/85	8.0	8.0	368.47	369.22	0.75	0.0	18.02	0.0	TF-178	0.158	2.85	2.85
	6/20/85	7/25/85	5.0	13.0	368.67	369.25	0.58	0.0	14.14	0.0	TF-193	0.0864	1.22	4.07
	7/25/85	9/09/85	6.6	19.5	368.76	369.61	0.85	0.0	12.83	0.0	TF-218	8.53	109.4	113.5
	9/09/85	10/24/85	6.4	26.0	368.88	369.64	0.76	0.0	13.93	0.0	TF-233	2.59	36.1	149.6
	10/24/85	12/09/85	6.6	32.5	368.97	369.74	0.77	0.0	16.72	0.0	TF-249	3.5	33.8	183.4
	12/09/85	1/23/86	6.4	39.0	368.75	369.52	0.77	0.0	11.68	0.0	TF-264	1.68	19.4	202.7
	1/23/86	3/10/86	6.6	45.5	368.85	369.92	1.07	0.0	11.17	0.0	TF-280	28.8	321.7	524.4
	3/10/86	4/24/86	6.4	52.0	368.97	369.89	0.92	0.0	14.48	0.0	TF-298	5.02	72.7	597.1
	4/24/86	10/23/86	26.0	78.0	369.02	372.64	3.62	0.0	9.82	0.0	TF-360	10.5	103.1	700.2
	10/23/86	4/28/87	26.7	104.7	368.82	372.23	3.41	0.0	8.47	5.0	TF-435	3.55	47.8	748.1
	4/28/87	11/16/87	28.9	133.5	368.95	372.30	3.35	0.0	8.37	10.0	TF-521	3.77	69.3	817.3
	11/16/87	4/25/88	23.0	156.5	368.81	370.35	1.54	1.0	8.23	10.0	TF-599	1.12	58.2	875.5
	4/25/88	10/24/88	26.0	182.5	368.77	370.01	1.24	0.4	7.72	10.0	TF-703	1.19	31.1	906.7
Terminated on 10/24/88														
6	4/25/85	6/20/85	8.0	8.0	375.45	376.32	0.87	0.0	14.65	0.0	TF-179	0.178	2.61	2.61
	6/20/85	7/25/85	5.0	13.0	375.81	376.47	0.66	0.0	17.65	0.0	TF-194	0.167	2.95	5.56
	7/25/85	9/09/85	6.6	19.5	375.88	376.66	0.78	0.0	11.40	0.0	TF-219	2.67	30.4	36.0
	9/09/85	10/24/85	6.4	26.0	375.88	376.65	0.77	0.0	11.95	0.0	TF-234	3.51	41.9	77.9
	10/24/85	12/09/85	6.6	32.5	376.00	376.70	0.70	0.0	10.85	0.0	TF-250	73.6	798.6	876.5
	12/09/85	1/23/86	6.4	39.0	375.73	376.49	0.76	0.0	14.25	0.0	TF-265	97.6	1391	2287
	1/23/86	3/10/86	6.6	45.5	375.84	376.27	0.43	0.0	15.66	0.0	TF-281	3.58	55.7	2323
	3/10/86	4/24/86	6.4	52.0	375.93	376.15	0.22	0.0	13.78	0.0	TF-299	43.1	593.1	2916
	4/24/86	10/23/86	26.0	78.0	376.01	378.98	2.95	0.0	11.45	0.0	TF-361	324	3710	6626
	10/23/86	4/28/87	26.7	104.7	375.61	378.75	3.14	0.0	8.46	5.0	TF-436	28.9	389.0	7015
	4/28/87	4/25/88	51.9	156.5	375.66	382.18	6.52	1.0	8.39	10.0	TF-600	20.7	449.6	7465
	4/25/88	10/24/88	26.0	182.5	375.63	378.84	3.48 ^b	1.2	8.09	10.0	TF-715	3.08	85.0	7550

^aThe mass of uranium released, M (column 14), is calculated according to formula $M = V * C * (A-D)/(V-v) - 0.2 * s$ where,
V = solution volume in the vessel (column 8),
v = solution volume removed for analysis before acidification (column 9),
A = volume after acidification (column 10),
D = volume of DIW added to acidified solution before analysis (column 11),
C = uranium concentration reported by the ACL (column 13), and
s = uranium concentration in EJ-13 water (see Table 2).

^bCalculated from the weight difference in the bottom portion of the vessel.

Table 7. Sampling Matrix and Uranium Release for Unsaturated Experiments #7 and #8

Specimen Configuration: Stack of Three UO₂ Pellets
 EJ-13 Water Flow Rate: 0.0375 mL/7 d

Expt 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) ^a	Total U Release (μg)
7	4/25/85	7/25/85	13.0	13.0	374.68	374.98	0.30	0.0	15.35	0.0	TF-195	0.069	1.06	1.06
	7/25/85	10/24/85	13.0	26.0	374.89	375.56	0.67	0.0	15.17	0.0	TF-235	19.9	301.9	302.9
	10/24/85	1/23/86	13.0	39.0	375.17	ND	ND	0.0	12.95	0.0	TF-266	7.38	95.3	398.3
	1/23/86	4/24/86	13.0	52.0	375.01	375.40	0.39	0.0	14.39	0.0	TF-300	46.2	664.8	1063
	4/24/86	10/23/86	26.0	78.0	375.19	375.91	0.72	0.0	9.77	0.0	TF-362	110	1074.7	2138
	10/23/86	4/28/87	26.7	104.7	375.06	375.58	0.52	0.0	5.86	10.0	TF-437	14.2	225.2	2363
	4/28/87	11/16/87	28.9	133.5	375.03	375.16	0.13	0.0	7.79	10.0	TF-522	4.46	79.3	2442
	11/16/87	4/25/88	23.0	156.5	375.16	375.80	0.64	0.0	10.53	10.0	TF-601	5.50	112.9	2555
	4/25/88	10/24/88	26.0	182.5	375.00	375.94	1.05 ^b	0.0	7.95	10.0	TF-704	5.90	105.9	2661
8	4/25/85	7/25/85	13.0	13.0	374.76	375.11	0.35	0.0	10.01	0.0	TF-196	0.0486	0.875	0.875
	7/25/85	10/24/85	13.0	26.0	375.08	375.59	0.51	0.0	15.72	0.0	TF-236	33.4	525.0	525.9
	10/24/85	1/23/86	13.0	39.0	375.66	376.00	0.34	0.0	14.09	0.0	TF-267	17.5	246.6	772.5
	1/23/86	4/24/86	13.0	52.0	375.16	375.79	0.63	0.0	14.98	0.0	TF-301	17.6	263.6	1036
	4/24/86	10/23/86	26.0	78.0	375.35	376.13	0.78	0.0	15.41	0.0	TF-363	386	5948	6984
	10/23/86	4/28/87	26.7	104.7	375.32	375.89	0.57	0.0	5.61	10.0	TF-438	135	2107	9092
	4/28/87	7/20/87	11.9	116.5	375.39	375.90	0.51	0.0	9.28	5.0	TF-457	732	10324	19416
	Terminated on 7/20/87													

^aThe mass of uranium released, M (column 14), is calculated according to formula $M = V * C * (A+D)/(V-v) - 0.2 * s$ where,
 V = solution volume in the vessel (column 8),
 v = solution volume removed for analysis before acidification (column 9),
 A = volume after acidification (column 10),
 D = volume of DIW added to acidified solution before analysis (column 11),
 C = uranium concentration reported by the ACL (column 13), and
 s = uranium concentration in EJ-13 water (see Table 2).

^bCalculated from the weight difference in the bottom portion of the vessel.

ND = Not Determined.

Fig. 2. Cumulative Uranium Release for Experiments #1 and #2 (11 UO₂ Discs; 0.075 mL/3.5 d Flow Rate)

Fig. 3. Cumulative Uranium Release for Experiments #3 and #4 (Crushed UO₂ Pellet; 0.075 mL/3.5 d Flow Rate)

Fig. 4. Cumulative Uranium Release for Experiments #5 and #6 (Three UO_2 Pellets; 0.075 mL/3.5 d Flow Rate)

Fig. 5. Cumulative Uranium Release for Experiments #7 and #8 (Three UO_2 Pellets; 0.0375 mL/7 d Flow Rate)

corrections had to be applied to the analytical results to account for the removed material. Also, for experiments #1 and #5, which were terminated on 10/24/88 (as well as for experiment #8 terminated on 7/20/87), the acid rinse/soak step was performed overnight at 90°C.

The samples that were taken from the original liquid, on the other hand, were submitted for their individual analysis according to the matrix presented in Table 8. The uranium results of this table can be used in assessing the extent to which uranium plate-out occurs during the corresponding leach periods. The mass of uranium in each sample, calculated from columns 3 and 6 of Table 8, was compared with the uranium release for the same sampling period in Tables 4 to 7. In spite of a large scatter, the comparison showed that only $9 \pm 7\%$ of the released uranium resides in the leachate, the remainder being plated out on the vessel walls and the TeflonTM stand. This finding reinforces the need for acid rinses of apparatus components when evaluating the total uranium release from a waste form. It also points out that breached containment vessels can serve as barriers for the migrating heavy nuclides.

B. Solution Chemistry

Because of small volumes of the leachates collected, only a limited number of solution analyses could be performed. The results for the pH, carbon, and anion determinations, made on samples taken directly from the original leachates, are given in Table 8. Those for the cation analysis, determined from the diluted and acidified solutions, are given in Table 9. In both cases, the raw analytical data were converted to concentration units according to the formulas given in footnotes (a) of Tables 8 and 9.

The pH measurements showed some instability in that there was an initial rapid decline that was followed by a slow ascent to an uncertain final value. For consistency, the minimum pH values were recorded. They indicate slightly more acidic values than that of EJ-13 water itself. The results for total carbon (TC) show that it originates mainly from organic species (TOC). TeflonTM is the only organic component in the apparatus, but the lack of an accompanying increase in the fluoride concentration and the intrinsic stability of TeflonTM makes this choice unlikely. The EJ-13 water is likely the source of organic carbon because over the course of the experiments the organic carbon content of the EJ-13 water increased from ~5 ppm to ~15 ppm. There are slight increases in the concentrations of Cl^- , NO_3^- , and SO_4^{2-} ions over those in the starting EJ-13 water. Sample TF-703 of experiment #5 shows an anomalous result: low unplated uranium and high anion concentrations. A probable reason for this is the inadequate fraction of the liquid recovered for this sample (Table 6), that required a tenfold dilution to produce valid IC analyses.

Table 8. Concentrations of Uranium, Carbon, and Anions in Unacidified Solutions

Expt No.	Sampling Date	Solution Volume (mL) ^b	Sample Number	pH	Uranium Conc. (μg/mL)	Carbon (μg/mL)				Anions (μg/mL) ^a			
						TC	TOC	TIC	HCO ₃ ⁻	Cl ⁻	F ⁻	NO ₃ ⁻	SO ₄ ⁼
1	4/25/88	2.58	TF-596	7.3	NA	30.2	27.0	3.2	16.3	NA	NA	NA	NA
	10/24/88	2.77	TF-700	6.8	1.7	29.5	25.0	4.5	22.9	17	2.0	19	39
2	4/25/88	3.22	TF-597	7.0	NA	26.4	22.2	4.2	21.3	NA	NA	NA	NA
	10/24/88	3.41	TF-701	6.9	2.3	29.2	25.4	3.8	19.3	16	2.0	18	37
3	4/25/88	3.06	TF-598	6.6	NA	22.7	19.2	3.5	17.8	NA	NA	NA	NA
	10/24/88	3.26	TF-702	6.3	2.5	26.7	24.9	1.8	9.1	16	<1.6	22	37
5	4/25/88	1.54	TF-599	6.7	NA	19.6	17.4	2.2	11.2	NA	NA	NA	NA
	10/24/88	1.24	TF-703	6.9	1.2	NA	NA	NA	NA	78	<8.4	161	187
6	4/25/88	6.52	TF-600	7.9	NA	27.1	20.1	7.0	35.6	NA	NA	NA	NA
	10/24/88	3.48	TF-715	6.5	4.6	27.3	22.0	5.3	26.9	15	<1.7	22	31

^aThe concentration of a given anion, CA (columns 11-14) is calculated according to the formula $CA = C - 0.2 \cdot s/V$ where,
V = solution volume in the vessel (column 3),
C = anion concentration reported by the ACL (see Table 10),
s = anion concentration in EJ-13 water (see Table 2).

^bVolumes of liquid determined from vessel deltas given in column 8 of Tables 4-6.

NA = Not analyzed.

Table 9. Concentration of Cations Released into Solution from UO₂ Specimen^a

Expt No.	Sampling Date	Solution Volume (mL) ^b	Portion Removed (mL)	Acidified Volume (mL)	DIW Added (mL)	Sample Number	Cation Concentration (μg/mL) ^c										
							Al	B	Ca	Fe	K	Li	Mg	Mn	Na	Ni	Si
1	4/28/87	3.03	0.0	8.34	5	TF-432	0.44	0.28	0.60	0.07	NA	0.063	0.21	0.14	52.0	0.75	15.4
	4/25/88	2.58	1.0	8.86	10	TF-596			0.64	0.18			0.06		41.2	0.24	20.8
	10/24/88	2.77	1.2	8.37	10	TF-700	1.48		0.40	12.9			0.12	0.15	40.5	1.64	23.1
2	4/28/87	3.40	0.0	8.59	5	TF-433		0.24	0.87	0.10	NA	0.065	0.24	0.06	44.8	0.44	17.4
	4/25/88	3.22	1.0	7.85	10	TF-597			0.72	0.15			0.09		31.0	0.17	16.8
	10/24/88	3.41	1.2	7.17	10	TF-701		0.22	1.02	0.31			0.11		31.9		16.7
3	4/28/87	3.31	0.0	8.33	5	TF-434		0.41	0.66	0.15	NA	0.24	1.11	0.17	51.8	0.64	7.91
	4/25/88	3.06	1.0	11.14	10	TF-598			0.84	0.16			0.36	0.12	27.4	0.56	7.60
	10/24/88	3.26	1.2	7.08	10	TF-702		0.26	0.77	0.17		0.089	0.43	0.07	28.0	0.37	7.42
5	4/28/87	3.41	0.0	8.47	5	TF-435		2.8	0.18	0.15	NA	0.061	0.19	0.35	53.4	2.09	13.5
	4/25/88	1.54	1.0	8.23	10	TF-599									19.3		1.61
	10/24/88	1.24	0.4	7.72	10	TF-703		3.8	1.07	19.4	11.8		0.29	1.01	68.9	5.70	9.22
6	4/28/87	3.14	0.0	8.46	5	TF-436	0.86	0.32	1.14	0.12	NA	0.057	0.20	0.077	52.3	0.40	15.5
	4/25/88	6.52	1.0	8.39	10	TF-600		0.22	0.01	0.04		0.052	0.09	0.023	41.2	0.13	15.8
	10/24/88	3.48	1.2	8.09	10	TF-715		0.23	0.27				0.03	0.10	29.8	0.27	14.2
7	4/28/87	0.52	0.0	5.86	10	TF-437	3.11	0.91	9.01	1.09	NA		0.45	3.36	90.1	18.0	8.12
	4/25/88	0.64	0.0	10.53	10	TF-601			1.97	0.35			0.15	1.92	65.7	11.9	12.7
	10/24/88	1.05	0.0	7.95	10	TF-704		1.51	1.52	0.29			0.07	0.26	37.5	0.63	6.27
8	4/28/87	0.37	0.0	5.61	10	TF-438	35.9	5.86	5.64	2.10	NA		0.66	1.86	83.3	22.8	13.0

^aThe concentration of a given cation, CC (columns 8-14), is calculated according to the formula $CC = C * (A+D)/(V-V) - 0.2 * s/V$ where,
V = solution volume in the vessel (column 3),
v = solution volume removed for analysis before acidification (column 4),
A = volume after acidification (column 5),
D = volume of DIW added to acidified solution before analysis (column 6),
C = cation concentration reported by the ACL (see Table 10), and
s = cation concentration in EJ-13 water (see Table 2).

^bVolumes of the liquid determined from vessel deltas given in column 8 of Tables 4-7.

^cBlank spaces indicate that the cations in diluted analytical samples were below their detection limits.

NA = Not analyzed.

Table 10. Raw Concentration Data for Cations and Anions as Reported by the ACL^a

Expt No.	Sample Number	Cations (µg/mL)										Anions (µg/mL)				
		Al	B	Ca	Fe	K	Li	Mg	Mn	Na	Ni	Si	Cl ⁻	F ⁻	NO ₃ ⁻	SO ₄ ⁻
1	TF-432	0.11	0.065	0.250	0.017		0.015	0.063	0.032	13.3	0.170	4.01				
	TF-596	<0.1	<0.03	0.104	0.015	<0.3	<0.01	0.011	<0.005	3.75	0.020	1.97				
	TF-700	0.13	<0.03	0.090	1.100	<0.3	<0.01	0.016	0.013	3.75	0.140	2.19	18	2.2	20	40
2	TF-433	<0.1	0.063	0.350	0.024		0.017	0.073	0.015	11.9	0.110	4.86				
	TF-597	<0.1	<0.03	0.160	0.019	<0.3	<0.01	0.019	<0.005	4.21	0.021	2.35				
	TF-701	<0.1	<0.03	0.200	0.040	<0.3	<0.01	0.021	<0.005	4.46	<0.02	2.41	17	2.1	18	38
3	TF-434	<0.1	3.103	0.300	0.037		0.06	0.290	0.042	13.5	0.160	2.48				
	TF-598	<0.1	<0.03	0.140	0.016	<0.3	<0.01	0.040	0.012	2.97	0.055	0.960				
	TF-702	<0.1	0.032	0.160	0.020	<0.3	0.011	0.059	0.009	3.72	0.044	1.15	16	<1.8	22	38
5	TF-435	<0.1	0.072	0.180	0.039		0.016	0.062	0.009	14.2	0.530	3.93				
	TF-599	<0.1	<0.03	0.021	<0.01	<0.3	<0.01	<0.005	<0.005	0.750	<0.02	0.180				
	TF-703	<0.1	0.18	0.120	0.920	0.58	<0.01	0.021	0.048	3.62	0.270	0.700	79	<8.8	162	190
6	TF-436	0.21	0.077	0.400	0.027		0.014	0.060	0.018	12.9	0.094	4.13				
	TF-600	<0.1	0.067	0.087	0.013	<0.3	0.016	0.035	0.007	12.8	0.039	5.07				
	TF-715	<0.1	0.030	0.100	<0.01	<0.3	<0.01	0.011	0.013	4.09	0.034	2.04	15	<1.8	22	32
7	TF-437	0.11	0.032	0.410	0.036		<0.01	0.027	0.110	3.54	0.590	0.700				
	TF-601	<0.1	<0.03	0.150	0.011	<0.3	<0.01	0.014	0.060	2.50	0.370	0.730				
	TF-704	<0.1	<0.03	0.190	0.017	<0.3	<0.01	0.015	0.015	2.71	0.037	0.750				
8	TF-450	0.08	0.141	0.250	0.050		<0.01	0.028	0.044	2.57	0.540	0.750				

^aBlank spaces indicate that no sample was submitted for analysis.

For the cations, the minute concentrations of Al, B, Fe, and Li show little change from those in EJ-13 water except for few spurious numbers for Fe. The sodium is slightly depleted. The concentrations of Ca, Mg, and Si, however, indicate significant decreases, probably because of their participation in forming secondary phases with the uranium (see Section IV). Anomalies in the cation data appear mostly in tests with lower flow rates. Sample TF-438, which also had a low fraction of the liquid recovered (Table 7), is particularly noticeable.

IV. SURFACE ANALYSIS RESULTS

As noted in Tables 4 to 7, four of the experiments have been terminated. Experiment #8 was terminated because the inlet line had become plugged. The other experiments were terminated to allow the inspection of sample surfaces. Of particular interest was the identification of the secondary phases that were clearly visible in all experiments. The samples were analyzed initially by carefully observing and mapping the surfaces using a stereomicroscope with magnification up to 150X. Color photographs were taken to provide a record of the surface. Crystallites with unique appearances, as indicated by their morphology or color, were carefully removed from the surface for analysis using X-ray diffraction (XRD) or Fourier transform infrared (FTIR) spectroscopy. The crystallographic data were obtained with a Phillips XRD powder diffraction camera of 114.6 mm diameter using a filtered $\text{CuK}\alpha$ or $\text{FeK}\alpha$ radiation. Intensities of the diffraction lines were visually estimated and normalized to the strongest line intensity. In some cases, after XRD had been performed, the crystal samples were placed on a carbon-coated aluminum stub and analyzed using a scanning electron microscope with associated energy dispersive x-ray spectroscopy (SEM/EDS). In other cases, samples taken from the same region of the surface as that analyzed by XRD, were directly studied using SEM/EDS. For experiment #8, the UO_2 pellet was cross-sectioned after removal from the test vessel and the entire bottom surface was examined using SEM/EDS. The detailed surface examination results for the four experiments are presented in the following subsections.

A. Experiment #1

This sample, consisting of 11 stacked discs with as-formed surfaces comprising the top and bottom faces of the stack, was terminated after 182.5 weeks. The observations made during the sampling and termination of this experiment are recorded in Table 11. The top surface was nearly always wet with scattered water droplets. Yellow precipitates were first noted during the 19.5-week sampling period, but it was not until the 78-week period that they became prominent. The bottom surface was always quite wet. The TeflonTM stand retained its original appearance.

During analysis, the entire sample was kept intact and only the top and bottom faces of the entire stack were inspected. The top surface (Fig. 6a) was highly altered with the central region being dominated by a dirty white mat and the near perimeter regions having more isolated coverage of yellow islands punctuated with irregular white feathers that formed upward from the

Table 11. Observations Made during Sampling and Termination of Experiments

Test #1 Elapsed Weeks	Observations			
	Top	Metal Collar ^a	Bottom ^a	Teflon Stand
8.0	Dry	Drops	Soaking	
13.0	No observations recorded			
19.5	One large drop, several small wet areas, dry area yellow ppt	Drops	Wet	
26.0	Little drops	Drops	Wet	
32.5	Quite wet with small drops	Drops	Wet	
39.0	Fair-sized drops all over	Drops		
45.5	Large individual drops	Wet	Wet	
52.0	Large drops	Drops	Soaked	
78.0	Drop of water, yellow solid ~3 mm dia, white needles	Drops	Very wet	
104.7	Damp with small drops, yellowish smear, fine white crystals	Drops	Soaked	
133.5	Slightly damp with small drops, diffuse yellow with small white needles		Soaked	Slight yellow discoloration
156.6	Small droplets, yellow patches, ~50% of surface scatter white needles			
182.5	Large drop about the size of a dime, yellow tinge, clear crystals		Soaked	
terminate				

Cont'd

Table 11 (Cont'd)

Test #5 Elapsed Weeks	Observations			
	Top	Metal Collar ^a	Bottom ^a	Teflon Stand
8.0	2-3 small areas damp	Drops	Wet	
13.0	Dry with hint of a yellowish tinge	Drops	Wet	
19.5	Almost dry, a small portion had a thin film of water	Dry	Wet	
26.0	Slightly damp, could see water drying	Drops	Wet	
32.5	Small amount of water at Zircaloy contact, top dry, sparkly ppts	Drops	Wet	
39.0	Dry except at Zircaloy contact where it is damp	Dry	Soaked	
45.5	Slightly damp, whitish solid on one side, light colored circular formation in center of top		Wet	
52.0	Dry, round area in center has a yellowish tinge with fine crystals. Appears to be a flow pathway which is yellow	Drops		Soaked
78.0	Dry with yellow and white patches looks like drop contact and spreading		Soaked	Yellow to clear crystals
104.7	Damp with yellow area near center			
133.5	Dry except at Zircaloy contact where it is slightly damp, top has a clearly defined pattern	Drops	Soaked	
terminate				

Table 11 (Cont'd)

Test #7 Elapsed Weeks	Observations			
	Top	Metal Collar ^a	Bottom ^a	Teflon Stand
13.0	Dry	Drop	Two small damp areas	
26.0	Dry with greenish sparkly appearance	Dry	Wet	
39.0	Damp with yellow area as water evaporates	Dry		
52.0	Dry with a uniform yellowish appearance		Soaked	
78.0	Dry with green crystals	Drops	Wet	
104.7	Few small drops on the outside, irregular yellowish area in the center, small crystals all over the yellow area	Drops	Wet	Yellowish tinge didn't dissolve during soak
133.5	Dry with faint yellow circular mark		Soaked	Brown and yellow crud
156.6	Dry with 1/2" yellow center spot			
182.5	Dry, yellow center circle		Wet	

Cont'd

Table 11 (Cont'd)

Test #8 Elapsed Weeks	Observations			
	Top	Metal Collar ^a	Bottom ^a	Teflon Stand
13.0	One drop of water	Dry	Dry	
26.0	Dry	Dry	Wet	
39.0	Covered with little drops	Drops		
52.0	Dry with yellow phases forming top and bottom pellets fell out, the pellets are wet, replaced	Wet		
78.0	Dry, yellow green solid at perimeter near Zircaloy			
104.7	Dry with bright yellow splotches	Wet	Soaked	Bright yellow but didn't dissolve in acid soak
116.5	Several small drops, bright yellow in places	Wet and Yellow	Wet and Yellow	Yellow, cleaned up during overnight acid soak

^aWet indicates the sample was damp, soaking indicates there was standing water, and drops indicates there were discrete drops remaining on the surface.

Fig. 6. Optical Photograph of the (a) Top and (b) Bottom Surfaces from Experiment #1. Magnification = 4.5X. Scale bar = 1 cm

surface but were interconnected by fine threads on the surface. The connected length of these white feathers ranged upwards to several millimeters. Also in this near perimeter was a stack of gray plates that were intermixed with a group of feathers, and one distinctly blue strand. The far perimeter region near the Zircaloy cladding had sparse coverage of distinct yellow crystals that had a block-like appearance with reflective faces. These blocks were intermixed with the white feathers. Samples for XRD analysis were taken of the yellow block crystals (1A), the yellow islands (1B), the white feathers (1C), the white central mat (1D), and the gray plates (1E). A separate sample of the white feathers (1C) was taken for FTIR analysis, and separate samples of each phase were taken for SEM/EDS analysis. An EDS spectrum of UO_2 is given for reference in Fig. 7a. The phases identified during these analyses and their formula are given in Table 12.

Yellow Blocks (1A)

These blocks were very difficult to remove from the surface. A micropick attached to a micromanipulator was used to dislodge the block sample which was then picked up with an XRD glass capillary that had been coated with a thin film of grease. When the blocks were dislodged they tended to fracture, but retained most of their integrity. Only a few blocks could be picked up on an XRD capillary because of their proximity to Zircaloy cladding. There were many blocks located on the side of UO_2 specimen. These grew in the space between the Zircaloy and UO_2 , were attached to both the Zircaloy and the UO_2 , and were not available for microscopic inspection because of their inaccessible location.

Fig. 7. EDS Spectra of (a) UO₂ Solid for Reference, (b) Yellow Block (Sample 1A), (c) Another Yellow Block (Sample 1A), and (d) White Feather (Sample 1C), (e, f, and g) Center White Mat (Sample 1D), and (h) Needle in Gray Plate (Sample 1E)

Fig. 7. (Cont'd)

Table 12. Phases Identified on Reacted UO_2 Surface

Phase	Formula
Schoepite	$\text{UO}_3 \cdot 2\text{H}_2\text{O}$
Dehydrated Schoepite	$\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$
Compreignacite	$\text{K}_2\text{U}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}$
Uranophane	$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Boltwoodite	$\text{K}(\text{H}_3\text{O})\text{UO}_2(\text{SiO}_4) \cdot n\text{H}_2\text{O}$
Sklodowskite	$\text{Mg}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Becquerelite	$\text{CaU}_6\text{O}_{19} \cdot 10\text{H}_2\text{O}$
Teflon	Not determined

The XRD pattern of the blocks was spotty, typical of a single crystal. Without a larger number of crystals, an identification of this phase is only speculative; however, the phases shown in Table 13 have JCPDS patterns that could account for the observed XRD data. Compositional information obtained using EDS indicates that the yellow blocks contain U, Ca, and possibly K (Fig. 7b,c).

Figure 7b clearly shows the presence of U and Ca, although the CaK α line is not fully resolved from the U lines. The presence of K in sample 1A is difficult to assess using EDS because the U(M α and M β) lines overlap with those of K(K α and K β) lines. However, as shown in Fig. 7c, there is an indication, based on the relative peak heights of the U lines compared with that of UO $_2$ (Fig. 7a), that sample 1A also may contain K. Additional EDS spectra collected from sample 1A match closely with that shown in Fig. 7a suggesting that a U-only phase also exists. The XRD and EDS data do not lead to an unambiguous identification of the phases that make up sample 1A. Of the phases indicated by XRD (Table 13) only sodium uranite can be ruled out because no Na was detected in the sample using EDS. Thus, it appears that sample 1A consists of phases with a range of compositions, varying from U-only to U/K and U/Ca or a phase containing U/Ca/K. The best XRD and EDS matches are schoepite, becquerelite, and compreignacite.

Additional samples of blocks with this physical appearance were collected from the bottom face of sample #5 and the identification of this phase will be discussed in more detail later.

Table 13. XRD Identification^a of Yellow Blocks (1A)

Phase	Structure	JCPDS Number
Becquerelite	CaU $_6$ O $_{19}$ •10H $_2$ O	29-389
Becquerelite	CaU $_6$ O $_{19}$ •11H $_2$ O	13-405
Compreignacite	K $_2$ U $_6$ O $_{19}$ •11H $_2$ O	33-1049
Sodium Uranite	Na $_2$ U $_7$ O $_{22}$	5-0132
Schoepite	UO $_3$ •2H $_2$ O	29-1379

^aBecause of the spotty nature of the XRD pattern, no XRD data were reported and no absolute identification was made.

Yellow Islands (1B)

The yellow islands also required dislodging using the micropick. These islands took on varying shades of yellow depending on the degree of mixing with the white center mat material. The samples studied were taken from the regions that had the greatest intensity of yellow. Samples were taken for XRD and SEM/EDS and the results are given in Fig. 8a and Table 14.

XRD patterns were collected from two separate samples taken from region 1B. The patterns are characterized by a strong line at 7.47 Å similar to that observed for sample 1A, which is characteristic of the becquerelite or schoepite groups (see discussion for sample 5I). However, in comparison, the rest of the pattern is somewhat different from 1A indicating a variable amount of dehydrated schoepite in the two samples. There is also a possibility that a clay phase is present in sample 1B. The EDS spectrum is similar to that shown in Figs. 7a and 7c which is suggestive of schoepite (U only) or compreignacite (U + K).

White Feathers (1C)

The white feathers were only loosely held to the surface, but because the feathers were all interconnected and intergrown with the yellow islands, they were difficult to remove from the surface. The feathers were very pliable and stretched as they were pulled from the surface. Samples were submitted for XRD, SEM/EDS, and latter for FTIR analysis. The results are shown in Figs. 7d, 8b, and 9 and Table 15. The XRD pattern clearly identified the sample as a fluoropolymer; however, the type of fluoropolymer (PFA, PTFE, FEP, etc.) could not be determined. The presence of a fluoropolymer on the UO_2 surface was a surprising result, but it was confirmed by the FTIR (Fig. 9) and EDS spectra. The FTIR spectra of the sample collected at ANL matched closely with the FTIR spectra of a small piece of the Teflon™ stand, while the EDS spectrum (Fig. 7d) showed a strong F peak. The photomicrograph shows that the fluoropolymer formed together with the U-bearing phases as indicated by the incorporation of the U phases (both 1A and 1D) throughout the sample. The pattern of the stand sample also showed a minor UO_2 phase to be present.

Because the formation of a fluoropolymer was unexpected, the DuPont Company was contacted, and they agreed to perform analysis of the sample to try and identify the type of fluoropolymer. The ideal method for this determination is differential scanning calorimetry. However, this technique requires ~500 mg of sample, far more than was available. Thus, they performed FTIR spectroscopy on a speck of a white feather producing results that were similar to those obtained at ANL (Fig. 9). The spectrum confirmed that the speck is a fluoropolymer, but the sample was too small to identify its type. There is a small peak that would support its identification as PFA and another small peak that would support it as FEP. The signal-to-noise ratio would have to be improved to provide a more definite identification.

(a)

(b)

Fig. 8. SEM Photomicrograph of (a) the Yellow Island (Sample 1B), Micron Marker = 10 μm ; (b) the White Feather with U-Rich Inclusions (Sample 1C), the Right Side of the Micrograph was Taken Using Backscattered Electrons, Micron Marker = 10 μm

(c)

(d)

Fig. 8. (Cont'd)
SEM Photomicrograph of (c) Center White Mat (Sample 1D),
Micron Marker = 1 μm ; and (d) Gray Plate with U-Rich Needles,
Micron Marker = 10 μm

Table 14. XRD Identification^a of Yellow Islands (1B)

I ^b	First Sample 1B d(obs) ^c	I ^b	Second Sample 1B d(obs) ^c	I	Dehydrated Schoepite Sample 1F d(obs)	Comments
100	7.47	100	7.47			
5	6.80					
1	5.90	10	6.35			
5	5.00	30	5.07	80	5.09	
		5	4.75			
10d	4.45	30	4.52			Clay?
25	4.15	30	4.15			(grease)
1	3.98					
10d	3.80	25d	3.78			(grease)
10d	3.70	25d	3.70			
20sp	3.50	10	3.51			
15sp	3.42	40	3.44	100	3.44	
5sp	3.35	1	3.33			
20sp	3.27	5	3.26			
15vsp	3.18	5	3.19			
20	3.10	10	3.10			
15	2.99	15	2.99			
5d	2.89					
1d	2.85	15vd	2.86	40	2.849	
5	2.73	15	2.71			
5vd	2.57	5	2.55	25	2.546	
5vd	2.50					Clay?
		35d	2.48	40	2.488	
		1	2.25			
		1	2.15	15	2.157	
5	2.11	5	2.10			
1	2.03	10	2.03	20	2.046	
		25	1.985	50	1.986	
		1	1.905			
		5	1.865			
		1	1.82	20	1.828	
1	1.795					
		10	1.78	35	1.779	
1	1.68	5	1.64	5	1.647	
1	1.497	1	1.52			Clay?

^aThe XRD pattern obtained for Sample 1B is presented, and lines assigned to dehydrated schoepite are identified. The assignment of the remaining lines is discussed more fully with Sample 5I.

^bI = estimated intensity measured from the observed pattern.

^cd = diffuse, sp = spotty, vsp = very spotty, and vd = very diffuse.

Fig. 9. FTIR Spectrum of (a) Sample 1C; (b) Sample 1C, Expanded Scale; and (c) TFE Standard

Table 15. XRD Identification of White Feathers (1C) and Gray Plate (5H)

Teflon Stand			PMP8U 1C		PMP 5H		Teflon Standard # 7066	
I	CuK α d		I	CuK α d	I	CuK α d	I	d
1000	4.9	Teflon	1000	4.9	1000	4.9	1000	4.9
1	4.1	Grease	1	4.15	10	4.15		
5	3.4	vsp			5	3.72		
10	3.15	UO ₂						
1	2.98	vsp						
10	2.84	d Teflon	10	2.83	5	2.83	20	2.83
1	2.74	UO ₂			10vsp	2.75		
10	2.46	Teflon	10d	2.43	5d	2.43	30	2.43
5	2.35	vd						
	2.15	vd	10	2.18	5vd	2.18	25	2.18
1	1.97	vsp					1	1.98
5	1.93	UO ₂						
1	1.87	Teflon	1	1.86			5	1.85
1	1.67	vsp						
10	1.645	UO ₂					5	1.63
1	1.58	UO ₂					1	1.415
1	1.366	UO ₂					2	1.362
			1	1.30	1	1.305	10	1.302
1	1.255	UO ₂						
1	1.222	UO ₂						
1	1.924	UO ₂						
1	0.911	UO ₂						

vsp = very spotty,
vd = very diffuse, and
d = diffuse.

Center White Mat (1D)

The center white mat adhered tightly to the surface and had to be chipped or scraped using the micropick. The shade of white of this mat varied depending on the underlying substrate which turned out to be a yellow mat. Thus, the samples collected, which were very fine needles plus flat rectangular phases (Fig. 8c), were a mixture of the yellow and white phases. Two separate samples were submitted for XRD, both being taken from what appeared to be the whitish region of the mat. XRD and SEM/EDS results are shown in Figs. 7e-g and Table 16.

Table 16. XRD Identification of Sample 1D (Center White Mat)

1 ^a PMP8U 1D Sample 1 CuK _α I	2 ^b PMP8U 1D Sample 2 CuK _α I	3 ^c PMP8U 1D Sample 2 FeK I	4 ^d PMP8U 1D Sample 2 d(obs)	5 ^e	6 ^f JCPDS 29-1026 Boltwoodite I	JCPDS 8-442 Uranophane I d	Comments
30	60	70	7.93			7.88	
		10	7.53	sp	7.53		
100vsp	40	20	7.45				in 1A and 1B
35	100	100	6.87		6.81		
1	1	15	6.60	sp		6.61	
10	35	25	6.40		6.40		
1	1	1	6.00	d			
25	30	30	5.42		5.45	5.42	
30	40	25	4.80	sp		4.76	
		35	4.73		4.74		
10	15	30	4.30		4.32	4.29	
30	5	20	4.17		4.11		
25	30	30	3.94		3.91	3.94	
	1	1	3.78	d	3.75		
20sp	2	1	3.72	d			
15sp	15	25	3.59			3.60	
40sp	40	35	3.52		3.54	3.51	
20	20	30	3.395		3.40	3.41	
vsp						3.35	
40	20	20	3.205			3.20	
30	20	15	3.120		3.13		
5	15	20	2.990		3.07	2.99	
30	45	35	2.940		2.95		
30	45	30	2.920		2.91	2.91	
15			2.740				
15	10	5	2.690		2.69	2.69	
5	5	5	2.625			2.63	

Cont'd

Table 16 (Cont'd)

1 ^a PMP8U 1D Sample 1 CuK _α I	2 ^b PMP8U 1D Sample 2 CuK _α I	3 ^c PMP8U 1D Sample 2 FeK I	4 ^d PMP8U 1D Sample 2 d(obs)	5 ^e	6 ^f JCPDS 29-1026 Boltwoodite I	JCPDS 8-442 Uranophane I d	Comments
		5	2.540	d		2.57	
	10	5	2.530	d	2.53	2.52	
	5	5	2.480				
	1	1	2.455		2.45	2.40	
					2.34		
	5	5	2.265	d	2.26	2.26	
20	25	25	2.200		2.21	2.20	
		5	2.140		2.13		
15	15	20	2.100		2.11	2.10	
10	10	15	2.045		2.05	2.06	
	1	1	1.990	vd	1.994		
	5	1	1.960	vd	1.950	1.969	
	5	1	1.940	vd	1.935		
	30	25	1.910	d	1.900	1.906	
		1	1.897			1.889	
	5	1	1.870		1.874	1.867	
	5	1	1.825		1.820	1.827	

^aCol. 1 is the observed intensity data with CuK_α radiation from sample 1 for d's in Col. 4. From this data set the first three lines could be due to 1, 2, or 3 phases.

^bCol. 2 is intensity data for the second sampling of 1D. Thus the two intensity data sets suggest by their variation that there may be at least three phases present.

^cCol. 3 is the intensity data for sample 2 using Fe K radiation for better "d" resolution.

^dCol. 4 are the observed "d" values using the Fe radiation.

^eCol. 5 is the "d" values line character notation, sp = spotty, d = diffuse, vd = very diffuse.

^fCol. 6 is the JCPDS file data for comparison with the observed data in col. 2, 3, and 4. There are three JCPDS data for boltwoodite, 13-218, 29-1026, and 35-490. All three JCPDS data are useful for comparison and cross checking the data match. 35-490 states that the 7.53 peak is probably gypsum and boltwoodite is the uranophane group.

XRD analysis, based on a comparison of two patterns, indicated that there are at least three and possibly four phases present. Two of these phases account for most of the pattern. They include a boltwoodite type, with a strong line at 6.8 Å and a uranophane type with a strong line at 7.8 Å. The third phase with a distinct line at 7.45 Å is similar to that observed in samples 1A and 1B. This identification was strengthened by the compositional information obtained using SEM/EDS, which showed the phases to contain Ca, Si, U (Fig. 7e), K, Si, U (Fig. 7f), U only or U,K (Fig. 7g). The strength of the XRD patterns together with the overall EDS spectra indicate that the majority phase in the white region is uranophane.

Gray Plate (1E)

These plates had more rigidity than the Teflon™ feathers but were pliable and tended to stick together (Fig. 8d). They were easily removed from the surface and were analyzed using XRD and SEM/EDS. The results are shown in Fig. 7h and Table 17. The major pattern corresponded to that of a fluoropolymer; however, there was a very minor set of spotty lines possibly due to sklodowskite. A spotty pattern indicates that the material was crystalline. Estimated line intensities are being determined. The presence of Mg in the phase was confirmed by EDS (Fig. 7h).

Table 17. XRD Identification of Sample 1E (Gray Plate)

PMP8U 1E		Sklodowskite		
Fe K		JCPDS 29-875		
I	d(obs)	I	d(obs)	Comments
35	8.35	100	8.42	vsp
5	6.8			Boltwoodite?
5	6.35	20	6.37	
10	5.9	50	5.91	sp
100	4.9	40	4.82	Teflon
5	4.52	10	4.51	d
5	4.32	40	4.33	sp
30	4.18	80	4.19	Grease
10	4.02	50	4.00	
5	3.51	60	3.52	sp
1	3.25	70	3.27	
5	2.99	60	3.00	sp
1	2.85	50	2.87	
		20	2.80	
		20	2.74	
		10	2.70	
		10	2.66	
		10	2.52	
1	2.34	20	2.34	
		5	2.27	
		20	2.22	
1	2.19	20	2.19	

sp = spotty; v = very; d = diffuse

The bottom surface of sample #1 was examined in the same manner as the top surface and a photograph of the surface is shown in Fig. 6b. This surface was covered by far fewer and less diverse reaction products. Essentially, there were clusters of yellow crystals and discrete larger yellow blocks. There also were several isolated groups of a whitish material. This material had a rounded cube-like morphology with several cubes grouped together. Samples were collected for XRD and SEM/EDS analysis of the yellow crystals (1F) and of the white cubes (1G).

Yellow Crystals (1F)

These samples were also difficult to remove from the surface. The XRD results are shown in Tables 18, 19, and 20. The pattern obtained is given in Table 18 together with some line identifications. No JCPDS data matched the pattern for 1F exactly; instead there appeared to be slight variations between line positions of the patterns. Lattice constants were then derived for the

Table 18. XRD Identification of Bottom Yellow Crystals (1F)

I	PMP8U 1F d(obs)		Comments
	7.45	v	1A/5I
80	5.08		
20	4.14	g	grease
	3.70	v	1A/5I
	3.59	v	1A/5I
	3.50	v	1A/5I
100	3.443		
	3.22	v	1A/5I
	3.18	v	1A/5I
40	2.852		
1	2.75		
25	2.548		
40	2.488		
15	2.159		
20	2.047		
50	1.986		
	1.970	v	1A/5I
20	1.828		
35	1.778		
30	1.740		
10	1.720		
5	1.695		
5	1.646		
10	1.627		
15	1.522		
15	1.486		

v = very spotty, intensity poor.

Table 19. Comparison of Derived Lattice Constants for Sample 1F (Bottom Yellow Crystals) with JCPDS Data

Lattice Constants			Sample	Source
a	b	c		
10.183(12)	6.875(8)	4.319(5)	Yellow crystals	PMP 8U 1F
10.19	6.86	4.27	UO ₃ •H ₂ O? Schoepite, dehydrated basic uranium oxide	JCPDS 13-242
10.23	6.89	4.28	UO ₃ •0.8H ₂ O uranium oxide hydrate	JCPDS 10-309
10.302	6.868	4.242	Alpha-UO ₂ (OH) ₂ uranyl hydroxide	JCPDS 25-1116

Table 20. Comparison of 1F Data with JCPDS Patterns^a

hkl	PMP8U 1F Yellow ppt, U		d(calc)	do-dc	UO ₃ •0.8H ₂ O JCPDS 10-309		UO ₃ •H ₂ O JCPDS 13-242		α-UO ₂ (OH) ₂ JCPDS 25-1116	
	I	d(obs)			d	do-d	d	do-d	d	do-d
200	80	5.08	5.09	-0.010	5.110	-0.030	5.090	-0.010	5.151	-0.071
020	100	3.443	3.438	0.005	3.450	-0.007	3.450	-0.007	3.434	0.009
111		3.443	3.442	0.001	3.430	0.013	3.390	0.053	3.406	0.037
220	40	2.852	2.849	0.003	2.857	-0.005	2.890	-0.038	2.857	-0.005
400	25	2.548	2.546	0.002	2.557	-0.009	2.542	0.006	2.575	-0.027
311	40	2.488	2.488	0.000	2.487	0.001	2.480	0.008	2.488	0.000
002	15	2.159	2.159	0.000	2.138	0.021	2.110	0.049	2.121	0.038
420	20	2.047	2.046	0.001	2.053	-0.006	2.060	-0.013	2.060	-0.013
131	50	1.986	1.986	0.000	1.986	0.000	1.993	-0.007	1.977	0.009
202		1.986	1.988	-0.002	1.971	0.015	1.954	0.032	1.961	0.025
022	20	1.828	1.828	0.000	1.817	0.011	1.826	0.002	1.804	0.024
511	35	1.778	1.779	-0.001	1.782	-0.004	1.774	0.004	1.789	-0.011
331	30	1.740	1.739	0.001	1.740	0.000			1.738	0.002
222	10	1.720	1.721	-0.001	1.721	-0.001	1.720	0.00	1.717	0.003
600	5	1.695	1.697	-0.002	1.704	-0.009	1.698	-0.003	1.703	-0.008
402	5	1.646	1.647	-0.001	1.641	0.005			1.637	0.009
240	10	1.627	1.628	-0.001	1.632	-0.005	1.630	-0.003	1.628	-0.001
620	15	1.522	1.522	0.000	1.528	-0.006	1.541	-0.019	1.536	-0.014
422	15	1.486	1.485	0.001	1.481	0.005	1.484	0.002	1.478	0.008
Sum of Deviations				0.032		0.153		0.256		0.314
Average Deviation				0.002		0.008		0.016		0.011

^aThis table shows that the calculated orthorhombic cell is the better match to the sample 1F than JCPDS data. The closest next match is for UO₃•0.8H₂O. Absorption correction would improve the 1F fit but not the JCPDS fit.

1F pattern, which was indexed based on the basis of an orthorhombic cell. A comparison of lattice constants is shown in Table 19. Then, based on the derived lattice constants, a new set of calculated XRD data was derived and compared to the 1F pattern and other literature data (Table 20). The best fit to the 1F (major phase) observed data is with the new reindexed cell data. These cell constants are within the variation reported in the literature for the so-called "dehydrated" schoepite. The slight XRD pattern differences that exist among all the data sets may be due to compositional differences and/or thermal history. The closest JCPDS data fit is with $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$. The variation in the lattice constants may be due to slight compositional differences and is most notable in the XRD pattern of the hkl: (020) and (111), which are resolved in the JCPDS data, but not in the 1F pattern. The EDS spectrum indicated that only U was present in the phase. Also present in sample 1F, as indicated by XRD, was a minor phase that corresponded to that identified as schoepite in sample 1A.

White Cube (1G)

These samples were easily removed from the surface as discrete groups, but were not easily deformed. Samples collected from two different locations had a similar appearance. The XRD and SEM/EDS results are shown in Fig. 10 and Table 21. The XRD results indicated that the closest match of the patterns was with polyethylene. SEM/EDS results indicated that the samples differed in their compositions: one indicated the presence of Al/Si/Zr/Cl and the other Mg/Al/Si/Ca. Neither of these compositions support too well their XRD pattern similarity to polyethylene, thus no firm identification of this material can be made at this time. It is likely that the white cubes formed on the surface during the test period because the stored samples did have dehydrated schoepite incorporated in the cubes.

B. Experiment #5

The specimen in this experiment consisted of three stacked pellets with as-formed surfaces making up the top and bottom faces. During analysis, the specimens remained intact within the Zircaloy cladding. The top surface was highly altered having an appearance dominated by what could be described as a restricted flow pattern (Fig. 11a), i.e., the water drop contacts the surface in the center and spreads out in a circular pattern covering about 50% of the distance to the perimeter. This inner circular region is comprised of large dark yellow crystals that are intermixed with small white needles. The needles are isolated on the gray surface and cluster upwards in the center of the sample into clumps that take on a white-yellow color. In the middle of this central area there is a nest of gray platelets rising upwards from the surface.

Surrounding this circular pattern is a halo of fine white needles. These needles form a nearly continuous mat and do not seem to be a mix of yellow and white as was observed in sample #1. Scattered throughout this white mat, however, are many large individual yellow crystals. Outside the halo

(a)

(b)

(c)

Fig. 10. SEM Photomicrograph (a) of White Cube Taken from the Bottom Surface of Sample #1 and EDS Spectra (b and c) of Two Different Samples Identified as White Cubes (1G). Micron marker = 100 μm

Table 21. XRD Identification of Bottom White Cubes (1G)

I	White Chunk PMP8U 1G d(obs)		Polyethylene 11-834		Comments
			I	d	
50	5.07	v	30	4.6	r = $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ type
5	4.50				
10	4.30				
20	4.15				
100	4.08		100	4.1	grease
10	3.70				
30	3.62				
40	3.45				
20	2.85	v			r
20	2.49	(v)	40	2.49	r
10	2.25		30	2.30	
1	2.13	v	30	2.07	r
5	1.985	v	20	1.76	r

v = very spotty

(a)

(b)

Fig. 11. Optical Photograph of the (a) Top and (b) Bottom Surfaces from Experiment #5. Magnification = 4.5X. Scale bar = 1 cm

there is a region of intermixed white and yellow needles (with the white usually covering the yellow) and also a mixture of strands and clumps of what appears to be a fluoropolymer that is combined with small clumps of yellow crystals as well as with one flat reddish plate standing on end.

Since most of the phases observed on the top surface of experiment #5 had an appearance similar to that already identified in experiment #1, several samples were taken from various regions of the surface and examined using SEM/EDS. The gray plates were also submitted for XRD analysis (sample 5H). The areas to be examined included the white needles from the halo region, the gray plate from the central region, yellow crystals from the central region, a sample from the white-gray region, and yellow plates from the perimeter region.

White Needles

The white needles are shown in Fig. 12a and have an EDS spectrum containing Si/U/Ca, similar to that shown in Fig. 7e. These needles are probably uranophane.

Gray Plate

The gray plate from the central region is shown in Fig. 12b. The EDS spectra taken from different regions of this sample indicate the presence of F/Al/Si/U/Ca/Ti/Fe/Ni in varying amounts depending on where the beam is focused. The XRD data, shown in Table 15, indicate that the gray plates are mainly a fluoropolymer.

Yellow Crystal

The yellow crystals from the central region are shown in Fig. 12c. The EDS spectra indicate that the block substrate contains U/Ca and perhaps K, while the fine needles on the surface of the crystal are Si/U/Ca. These crystals appear similar to those observed in experiment #1, which were identified as schoepite, becquerelite, and compreignacite.

White-Gray Region

The white-gray halo region was a mixture of fine needles and larger blocks. The fine needles were composed of Si/U/Ca (uranophane) and the blocks were U or U/K (schoepite or compreignacite).

Yellow Plates

The yellow plates from the perimeter region were also composed of U or U/K, similar to those observed in the white-gray region.

Fig. 12. SEM Photomicrograph of Different Regions from Sample #5; (a) the White Needles from the Halo Region, Micron Marker = $1\ \mu\text{m}$; (b) Gray Plate from the Central Region, Micron Marker = $100\ \mu\text{m}$

(c)

(d)

Fig. 12 (Cont'd)
SEM Photomicrograph of Different Regions from Sample #5
(c) Yellow Crystals from the Central Region, Micron
Marker = 10 μm ; and (d) Yellow Crystals from the Bottom
Surface, Micron Marker = 10 μm

The bottom surface of the sample of experiment #5 (Fig. 11b) was strikingly less reacted when compared to that of experiment #1. Only a ring of yellow blocks provided any evidence for reaction. These blocks (sample 5I), which had an appearance similar to those of sample 1A, were removed for XRD and EDS analysis. The blocks are composed of a series of stacked plates (Fig. 12d). The XRD pattern shown in Table 22 appears to be similar to compreignacite. The XRD lines were indexed on this basis and the derived orthorhombic lattice constants are listed in Table 23 together with comparative literature values. Table 22 shows the calculated vs. observed d values for sample 5I. One weak line, $d = 3.66$, was not accounted for by the index and could be due to a minor amount of schoepite (JCPDS 13-241). The intensity data represent only qualitative estimates due to the spotty line character of the pattern.

Compreignacite is classified as a member in the becquerelite group, which includes the calcium and barium forms of uranyl hydroxy hydrates. These compounds are closely related to schoepite [6]. The variations in lattice constants reported by different investigators may be due to compositional differences that depend on sample history. It is also possible that there are mixed ions compounds in this group since ion exchange experiments have been performed on becquerelite group compounds [7].

C. Experiment #8

The specimen consisted of three stacked pellets with reduced water contact, and was terminated after 116.5 weeks because the input line was plugged and because it was of interest to investigate the nature of the reacted surfaces (see Table 11 for observations). The pellets were carefully removed from the Zircaloy sleeve and the top and bottom surfaces were sectioned from the pellets for further examination.

The top surface was first examined optically and is shown in Fig. 13. The surface has a central circular yellow region about $0.8\ \mu\text{m}$ in diameter. The bulk of the material observed at magnifications up to 150X does not appear crystalline and the color ranges from light to dark yellow. Interspersed among the amorphous backdrop are several highly reflectant specks that may indicate the presence of a crystalline material. However, no discrete blocks or crystals could be observed. The yellow material was not continuous and exposed several patches of UO_2 base surface.

Surrounding the central yellow region is an area where the UO_2 surface is prominent. Spread over the UO_2 surface area are many reflectant surfaces that clearly are associated with small crystals. Unlike the previous samples where the reflectant faces could be associated with yellow blocks, with this sample the surfaces seemed to exist almost with no additional bulk. At higher magnification, however, there were thin black discontinuous lines that could have corresponded to the edges of unique crystals.

Table 22. XRD Identification of Sample 5I
(Yellow Crystals, Bottom Surface)

I(obs)	PMP 5I		hkl
	CuK d(obs)	d(calc)	
2	9.43	9.33	011
100	7.39	7.40	002
2	6.45	6.46	101
1	6.02	6.01	020
5	5.70	5.69	111
2	4.677	4.667	022
10	4.565	4.564	013
60	3.704	3.700	004
15	3.660	**	
60	3.593	3.592	200
50	3.507	3.501	130
15	3.367	3.369	123
60	3.229	3.231	202
60	3.162	3.165	132
15	3.025	3.019	221
15	2.878	2.874	015
30	2.579	2.577	204
40	2.544	2.543	134
20	2.492	2.491	125
5	2.466	2.467	006
1	2.375	2.375	051
15	2.322	2.320	311
5	2.280	2.282	026
5	2.241	2.244	215
5	2.201	2.201	242
5	2.179	2.180	152
5	2.172	2.175	126
5	2.119	2.121	313
20	2.084	2.082	017
20	2.055	2.056	330
20	2.028	2.028	107
30	2.016	2.016	136
20	2.001	2.005	060
20	1.982	1.981	332
20	1.928	1.926	226
20	1.923	1.922	127
20	1.851	1.850	008
25	1.798	1.797	334
20	1.745	1.745	402

$$a = 7.184 \pm 0.008$$

$$b = 12.029 \pm 0.014$$

$$c = 14.801 \pm 0.017$$

**Schoepite

JCPDS 13-241

Table 23. Comparison of Derived Lattice Constants with Reported Constants

5I	Compreignacite ^a	Compreignacite ^b
a = 7.184 ± 0.008	a = 7.16 ± 0.02	a = 7.161
b = 12.029 ± 0.014	b = 12.16 ± 0.05	b = 12.190
c = 14.801 ± 0.017	c = 14.88 ± 0.05	c = 14.847

^aJ. Protas, Bull. Soc. Franc. Min. Crist. 87, 365-371 (1964).

Mineral form $K_2O \cdot 6UO_3 \cdot 11H_2O$. The XRD mineral powder data is also in JCPDS 17-167 as $K_2(UO_2)_6(OH)_{14} \cdot 4H_2O$.

^bBrindley et al. JCPDS 33-1049 as $K_2U_6O_{19} \cdot 11H_2O$. Synthetic preparation from uranyl acetate and KOH at room temperature.

Fig. 13. Optical Photograph of the Top Surface from Experiment #8. Magnification = 4.5X. Scale bar = 1 cm

The outer perimeter of the surface was comprised of a darker yellow material interspersed with the single crystals. There were two discrete chunks of white material and several regions where the yellow substrate was replaced by a brown material that varied in color from dark brown to light brown. These brownish regions were similar in appearance to the gray plates identified in the previous samples as a fluoropolymer. There were only a few places which appeared to be similar to the white feathers of the previous samples. If these regions were indeed fluoropolymer, the amount was far less than that observed in experiments #5 or #1.

Samples were taken from the surface for XRD and SEM/EDS analysis from the white chunk (8J), the light yellow substrate from the central region (8K), the dark yellow substrate with crystals from the outer perimeter (8L), and the brown clump from the outer perimeter (8M).

White Chunk (8J)

There were two white chunks that had a similar appearance. Both were loosely connected to the surface and were easily removed. One sample was used for XRD analysis and the other for SEM/EDS. There is no assurance that these are equivalent samples, but they appeared to be similar in the optical microscope.

The sample that was examined with SEM/EDS was clearly inhomogeneous, containing various inclusions in an amorphous matrix (Fig. 14a). These inclusions were composed of Fe (Fig. 15a) and Si (Fig. 15b), while the matrix was mainly Mg, Si, and Ti (Fig. 15c) with some areas also containing Ca (Fig. 15d).

The XRD results are shown in Table 24. The patterns show a good match with rutile (TiO_2) and talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$]. The fact that the XRD results match closely with the SEM/EDS results suggests that the white chunks were formed on the surface during reactions, as opposed to artifacts that might have collected on the surface due to handling.

Light Yellow Substrate (8K)

This sample was taken from the central region in an area that had a lighter yellow color than the surrounding material. It was dislodged from the surface with the micropick using a moderate force. In the SEM/EDS, this sample (Fig. 14b) appears to be comprised mainly of agglomerated small particles with a few larger surfaces that were beginning to have sharp edges and smooth faces. The EDS spectrum of either the particles or the smooth surfaces were identical and showed only U to be present.

The XRD pattern indicated the sample to be dehydrated schoepite, which matches the EDS compositional information.

Fig. 14. SEM Photomicrograph of (a) the White Chunk (8J), Micron Marker = 10 μm ; (b) the Light Yellow Center Substrate, Micron Marker = 10 μm (8K)

Fig. 14 (Cont'd)
SEM Photomicrograph of (c) the Darker Yellow Substrate from the Outer Perimeter, Micron Marker = $10\ \mu\text{m}$ (8L); (d) the Darker Yellow Substrate Plus Some Discrete Crystals, Micron Marker = $10\ \mu\text{m}$ (8L)

Fig. 14 (Cont'd)
SEM Photomicrograph of (e) the Brown Clump, Micron
Marker = 10 μm (8M)

Fig. 15. EDS Spectra of (a) the Phase on the Left Center of Fig. 14a; (b) the Triangular Inclusion in the Right Center of Fig. 14a; (c) the Substrate of the White Chunk (8J); (d) Isolated Bright Regions in the White Chunk (8J), see Fig. 14a Center; and (e) the Brown Clump (8M)

Table 24. XRD Identification of White Chunk (8J)

PMP 8U 95250-2 8J		
I	d(obs)	Comments
80	9.4	Talc
20	4.7 d	Talc
40	4.52	Talc
40	4.15	Grease
100	3.23	TiO ₂
35	3.12	Talc
10	2.62	
15	2.59	Talc
65	2.48	TiO ₂
5	2.47 d	Talc
10	2.29	TiO ₂
5	2.22 d	Talc
30	2.18	TiO ₂
5	2.11 d	Talc
10	2.05	TiO ₂
5	1.87 d	Talc
5	1.722 d	Talc
60	1.685	TiO ₂
30	1.623	TiO ₂
5	1.565 d	Talc
25	1.525	Talc
5	1.480	TiO ₂
10	1.450	TiO ₂
5	1.400 vd	
20	1.360	TiO ₂
10	1.345	TiO ₂

Match within errors of measurement with
TiO₂ JCPDS 21-1276; Talc JCPD 29-1493.

d = diffuse

v = very.

Dark Yellow Substrate (8L)

This material also had to be removed with the micropick and was comprised of dark yellow material with some crystalline edges. The sample is shown in Figs. 14c,d where its crystalline nature is apparent. The EDS spectrum indicated only U to be present and the XRD results were similar to those observed in sample 8K, except that the pattern was decidedly more spotty in the present case due to a larger number of crystals present. This material is also dehydrated schoepite.

Brown Clump (8M)

Several regions of the surface near one section of the perimeter had a puffy appearance as though the material was being erupted from the surface. The material was brittle and was easily dislodged. Part of a clump that appeared amorphous is shown in Fig. 14e. Its composition was fairly uniform and gave the spectrum shown in Fig. 15e. Uranium is the major component and there may be some Si present. The XRD results (Table 25) indicate that the material is a mixture of UO_2 , schoepite, and dehydrated schoepite.

The bottom surface (Fig. 13b) was examined optically, and several discrete regions were selected for further examination with SEM/EDS. The surface is the most extensively reacted bottom surface of the samples examined thus far. The reaction coverage is random with clumps of yellow material forming on the outer edges and the central region. There were many reflective faces but no yellow blocks observed in the previous samples. The reflective faces appeared similar to those observed on the top surface of the specimen. A portion of the surface material was collected for XRD analysis. Intermixed with the yellow material were interwoven strands of a white filament. Several areas of the original UO_2 surface were also visible.

Table 25. XRD Identification of Brown Clump (8M)

PMP 8M 95250-4 8M		
I	d(obs)	Comments
20	7.4	1 $\bar{A}$ /5I
30	5.05 v	r
30	4.15	Grease
50	3.44 v	r
70	3.16	' UO_2 '
15	2.84 v	r
10	2.76	()
20	2.73	' UO_2 '
100	2.35	Ag
60	2.04	Ag
5	1.985 v	r
5	1.960	()
30	1.930	' UO_2 '
5	1.780	r
5	1.740	r
5	1.710	r
35	1.645	Ag
5	1.580	' UO_2 '
40	1.442	Ag

v = very spotty.

r = $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ type.

Ag as per JCPDS 4-783.

' UO_2 ' type close to Fe cubic cell may be tetragonal which may account for extra lines ().

The SEM/EDS examination revealed that the surface of the UO_2 is covered with a very finely grained mat (Fig. 16a). Based on the EDS analysis, the mat contains only U. Intermixed with and forming from the mat are many crystalline phases (Fig. 16b). These are also composed only of U. In a few areas, the crystalline material is mixed with a non-crystalline material (Fig. 16c), which is black when examined with backscattered electrons and contains Mg, Si, and Fe (Fig. 17a) in addition to U. The intertwining filaments containing mainly F are likely to be the fluoropolymer identified in the previous samples. Finally, there were several regions of the surface that had a bluish appearance. These regions contained U and Cu as shown in Fig. 17b. Unfortunately, these blue phases could not be isolated for XRD analysis and their identity is unknown.

V. DISCUSSION

The solution results indicate that for the initial 26 weeks, all experiments released very little uranium ranging from ~ 1 to $760 \mu\text{gm}$. Between the 26- and 52-week periods, however, all experiments showed an increase in the rate of U release. The magnitude of the increase was similar in duplicate experiments #1 and #2, but there was a significant disparity in the other pairs of duplicate experiments. After about 70 weeks, the rate of U release in all experiments (except #8 which was terminated at 116.5 weeks) had decreased to near the initial 26-week rates.

The release of other ions to the solution was not measured until after the U release pulse had abated. At that time, the analyses indicated that in all experiments the solutions were markedly depleted in Ca, K, Mg, and Si, and marginally in Na, the concentrations of Cl^- , NO_3^- , and $\text{SO}_4^{=}$ showed an increase of about 100%, and the concentrations of F^- remained constant. Over the duration of the experiments, the amount of total carbon in solution remained fairly constant, but there was an increase in the organic carbon content and a decrease in the inorganic carbon content (see latter discussion).

It does not appear from the solution results that the test configurations had a significant effect on the releases. For example, contrary to expectations, experiment #8, which had the smallest surface area and the lowest flow, had the largest U release. In themselves, the solution results are difficult to interpret. However, in combination with the observations and analyses of the reacted surfaces, the reaction process can be made clearer. While some visible alteration of the surface was evident as early as 19 weeks, the most dramatic changes occurred in the 52-104 week period. After that time, any further changes in the surface appearance were difficult to detect. Some of the samples showed clear evidence of a restricted flow pattern on the top surface as marked by a circular region of phases where the drop contacted the surface but did not spread over the entire surface. Other samples had more random distribution of phases indicating that the water had access to the entire surface. For these latter samples, there was also more phase formation on the bottom surface in conjunction with more total U release from the sample. However, for all samples the extent of reaction of the top surface

Fig. 16 SEM Photomicrographs of (a) the Finely Grained Mat on the UO_2 Surface, Micron Marker = $10\ \mu\text{m}$; (b) Discrete Crystalline Phase, Micron Marker = $10\ \mu\text{m}$

Fig. 16 (Cont'd)
SEM Photomicrograph of (c) the Surface with Backscattered
Electrons Showing the Dark Material Next to the Crystalline Phase,
Micron Marker = 10 μm . The surface examined was the bottom
surface of sample PMP8 E8

Fig. 17. EDS Spectra of (a) Dark Area Shown in Fig. 16c, and (b) Regions with a Bluish Appearance

was qualitatively similar. Thus, the measured U release appears to be more a function of whether the water that contacted the top surface flowed over the sides to the bottom surface and then dripped off of the sample, or whether the water contacted the top surface and evaporated to the vessel walls before it could drip from the sample. This release control mechanism may also explain the large variations in U release between duplicate sample pairs. Evaporation will occur despite the saturated environment if localized temperature differences exist between the UO_2 and the vessel walls.

The onset of U release and phase formation occurred at nearly the same time in all samples. The analysis of sample #8, which was terminated during the U release pulse, indicated that the only U-bearing phases present on the surface were dehydrated schoepite, and a minor amount of schoepite. No phases containing Si, Ca, K, or Mg were identified during the pulse period.

After ~104 weeks, the pulse subsided and in the samples examined at 182.5 weeks, several new phases were identified. These phases all contained elements present in the EJ-13 water, which in turn showed a depletion in the same elements. These results suggest that the initial reaction of the UO_2 is the formation of dehydrated schoepite with a concurrent increase in the release of U to solution. After continued reaction, however, the dehydrated schoepite appears to transform into more stable phases that contain elements from the EJ-13 water. Evidence for paragenetic sequencing has been observed in additional SEM analysis performed on sample 5, and the results will be presented elsewhere.

The resulting excess hydrogen ions may also complex with HCO_3^- from EJ-13 water, thereby reducing the anionic concentration of this species in solution. The carbonic acid formed by this reaction will dissociate into CO_2 and H_2O under atmospheric conditions (Eq. 1).

A second mechanism which results in a decrease in pH and HCO_3^- concentration is carbonate complexation of U (Eq. 2).

However, the low concentration of U in solution implies that this reaction may account for <10% of the observed HCO_3^- decrease.

A final mechanism that can explain both decreased pH and HCO_3^- concentrations is the formation of formic and oxalic acids from HCO_3^- . Limited solution analyses indicate that inorganic carbon is being converted into organic carbon, whereas total carbon concentrations remain constant. Concentrations of CHO_2^- (9-19 mg/L) and $\text{C}_2\text{O}_4^{2-}$ (2-4 mg/L) in the leachate solution confirms this suspicion. The exact cause of this conversion is uncertain but may involve radiolytic effects from the UO_2 samples. Organic acid generation probably has gone undetected in previous batch tests due to the diluting effects of relatively large volumes of water used in these experiments. Identification of organics in solution may be important in that these species readily complex with actinide species and thus may play an important role in radionuclide migration.

The observed pH decrease may conceivably result from the dissociation of water molecules and incorporation of hydroxide ions in secondary mineral phases that form on the UO_2 surface (Eqs. 3 and 4).

The formation of secondary phases during the dissolution of spent fuel has been the subject of modeling investigations using the EQ3/6 geochemical code [8,9]. In these studies, modeling was applied to the dissolution of spent fuel in the presence of relatively large volumes of water where the formation of secondary phases was limited. The present results offer an opportunity to apply the code in a situation where a sequence of phase formation appears to exist, and where the U release seems to be a function of the phases that exist at a given time. The experiments in progress will be continued to monitor both the solution compositions and the appearance of the sample to determine whether any additional transformations occur.

VI. CONCLUSIONS

A set of eight experiments have been conducted in which UO_2 pellets in various configurations were contacted by an intermittent flow of dripping EJ-13 water. Little reaction occurred for the first 26 weeks. After this time, however, the surfaces of the pellets began to transform, producing visible reaction products and a large pulse of U released from the samples. The pulse corresponded to the formation of dehydrated schoepite on the sample surfaces. After about 104 weeks, the pulse subsided and U was released at a decreased rate. A sequence of phases was observed on the longer-reacted samples that suggested that the dehydrated schoepite had partially transformed to more stable phases that contained, in addition to U, some of the cation components of the EJ-13 water.

While the data collected during the early portions of the reaction sequence were limited by the scope of the experiments, the more detailed solution and surface results suggest that a well-defined sequence of secondary phases produced through reactions of UO_2 with EJ-13 water can be postulated. This sequence of reaction progress should be amenable to validation of the EQ3/6 modeling code, and could provide confidence that long-term performance of spent fuel in an unsaturated repository environment can be understood.

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