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IDENTIFICATION OF SECONDARY PHASES FORMED DURING UNSATURATED REACTION OF UO_2 WITH EJ-13 WATER

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ABSTRACT

A set of experiments, wherein UO_2 has been contacted by dripping water, has been conducted over a period of 182.5 weeks. The experiments are being conducted to develop procedures to study spent fuel reaction under unsaturated conditions that are expected to exist over the lifetime of the proposed Yucca Mountain repository site. One half of the experiments have been terminated, while one half are ongoing. Analyses of solutions that have dripped from the reacted UO_2 have been performed for all experiments, while the reacted UO_2 surfaces have been examined for the terminated experiments. A pulse of uranium release from the UO_2 solid, combined with the formation of schoepite on the surface of the UO_2, was observed between 39 and 96 weeks of reaction. Thereafter, the uranium release decreased and a second set of secondary phases was observed. The latter phases incorporated cations from the EJ-13 water and included boltwoodite, uranophane, sklodowskite, compreignacite, and schoepite. The experiments are continuing to monitor whether additional changes in solution chemistry or secondary phase formation occurs.

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 developed to investigate waste form reactions under such conditions.

This method, which involves periodically dripping repository water on the waste form, has been applied extensively to study the reaction of glass [3,4]. With glass, it is found that the increased SA/V (surface area of the waste form to volume of liquid) at which the test is performed, accentuates interactions that occur to transform the glass into secondary phases, compared to what is observed in standard leach tests. While the goal of the method is to provide descriptive detail of several reaction processes (e.g., reaction between waste and humid air, the reaction between the waste and small quantities of intermittently recharged water, as well as the 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 will be exposed to unsaturated conditions. Reactions of the UO_2 matrix under such 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 performing 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, it is possible that the reaction processes involved in the breakdown of the UO_2 matrix could be comparable. Therefore, the gross processes observed in the UO_2 experiments may also be relevant in the spent fuel testing, especially with respect to the identification of secondary mineral phases formed during the reaction.

EXPERIMENTAL

Normal uranium oxide pellets were used in the experiments. The oxygen/metal ratio was established to be 2.000 ± 0.002 with the major impurities being (μg/g of UO_2) Fe (2), Th (15), Al (4), Cu (3), Ni (2), and Ca (2). 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 in 10-mm-high cylinders. An Isomet rotary diamond saw (Buehler, Ltd.) was used for cutting. All operations were performed in air and complete details of the experimental setup are provided elsewhere [5].

The prepared UO_2 samples were used in eight tests. The tests were performed in duplicate and utilized the following configurations:

(1) a stack of eleven as-cut pellet discs (13.7-mm dia, 1.75-mm thick);
(2) ~19-mm-high column of crushed UO_2, vertically sandwiched between two 1.75-mm-thick as-cut discs; and
(3) ~30-mm-high stack of three 13.7-mm dia UO_2 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.

The UO_2 specimens were encased in Zircaloy cladding, placed on a Teflon^{TM} stand, and sealed in an air-tight stainless steel vessel. Accurately measured quantities of EJ-13 (J-13 water that had been equilibrated with tuff at 90°C) were periodically dripped on the specimen from the inject system. All tests were performed at 90°C. Duplicate experiments were conducted for the 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. Thus, four sets of experiments were performed. After initiation of the tests, the solution that collected in the bottom of the vessel was analyzed at 6.5-, 13-, or 26-week intervals. At the same time, the UO_2 surfaces were visually examined for evidence of reaction. When it became clear that the UO_2 was undergoing reaction, one test in each set was terminated for more detailed examination of the reacted surfaces. The other test in each set was allowed to continue.

RESULTS

Solution Analyses

Throughout the sampling periods, the test solutions were analyzed for U. Two types of measurements were made. First, all of the U released from the UO_2-Zircaloy assembly was determined by performing an acid strip of the vessel and the Teflon^{TM} stand. This information was obtained during every sampling period. Secondly, at some of the long-term test sampling periods, the U in solution was determined by taking an aliquot of test solution prior to the acid strip.

The total amount of uranium released is shown in Fig. 1. Duplicate experiments are shown in each plot and the blocked value indicates the test was terminated. The amount of U in solution ranged from 1-4 ppm, indicating that most of the U released from the UO_2 was associated either with secondary phases that formed on the Teflon^{TM} stand, or was sorbed to the stainless steel.

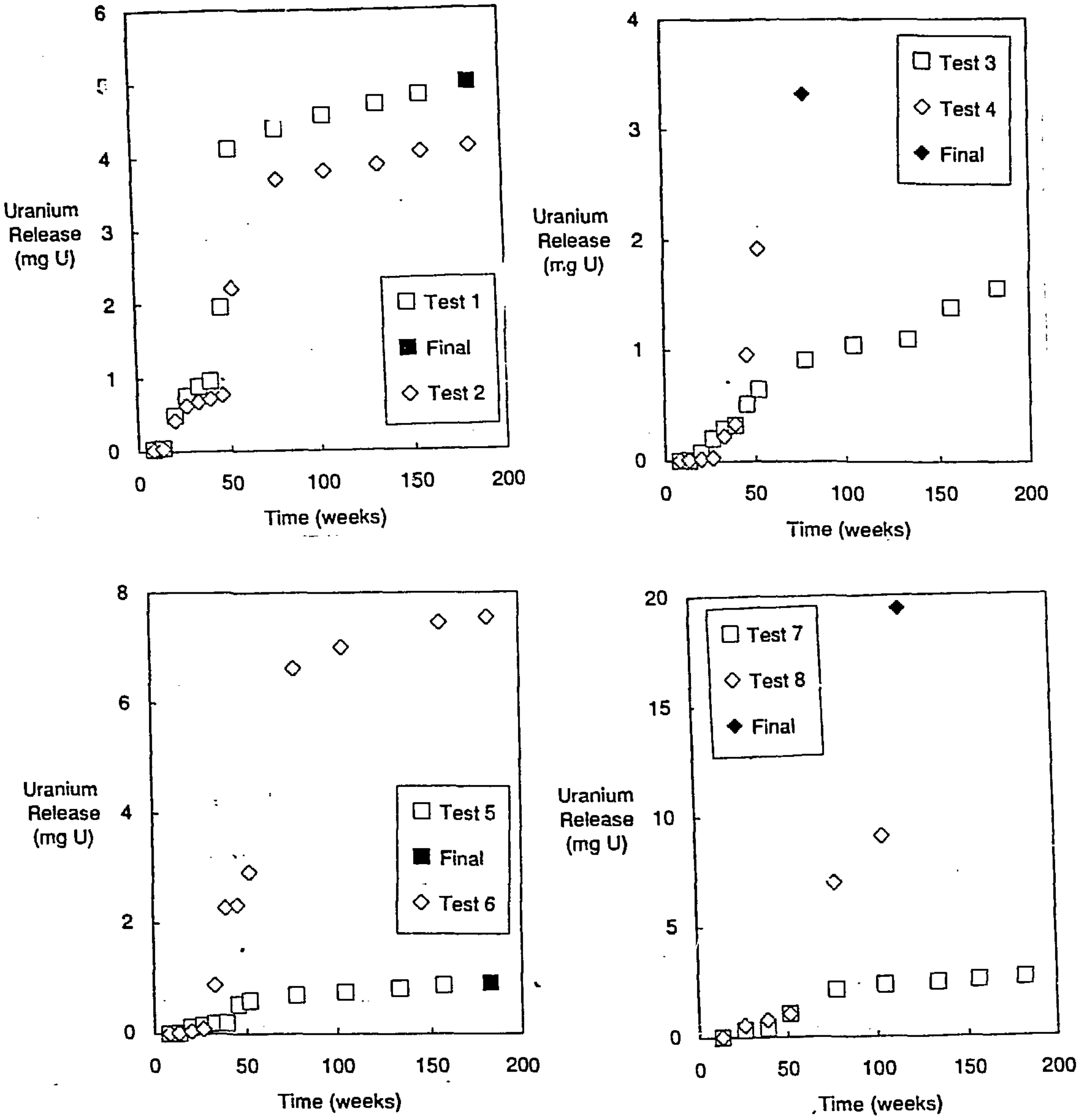

Fig. 1. Cumulative Release of Uranium from Experiments (1) #1 and #2 (11 UO_2 discs; 0.075 mL/3.5 day); (b) #3 and #4 (crushed UO_2 pellet; 0.075 mL/3.5 days); (c) #5 and #6 (three UO_3 pellets; 0.075 mL/3.5 days); and (d) #7 and #8 (three UO_2 pellets; 0.0375 mL/7 days). The blocked points are for tests that were terminated.

Because of the small volumes of the leachates collected, only a limited number of solution analyses could be performed. The results for pH, carbon, anion, and cation determinations, made on samples taken directly from the original leachates, are given in Table I.

The pH measurements showed some instability in that there was an initial rapid decline that was followed by a slow ascent. For consistency, the minimum pH values were recorded. In all cases, the pH values are only slightly lower than that of the starting EJ-13 water.

TABLE I
Leachate Analyses for Unsaturated UO_2 Tests

Test #	Sampling Period (weeks)	Concentration (μg/mL)										
		pH	HCO_3^-	Cl^-	F^-	NO_3^-	$SO_4^=$	Ca	Mg	Na	Si	U
Starting EJ-13	-	8.1	135	7.2	2.4	7.6	17	9.1	1.0	46.5	34.4	0.0024
#1	182.5	6.8	22.9	17	2.0	19	39	0.4	0.1	40	23	1.7
#2	182.5	6.9	19.3	16	2.0	18	37	1.0	0.1	32	17	2.3
#3	182.5	6.3	9.1	18	<1.6	22	37	0.8	0.4	28	7.4	2.5
#4	78.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
#5	182.5	6.9	ND	78	<8.4	161	187	1.1	0.3	69	9.2	1.2
#6	182.5	6.5	26.0	15	<1.7	22	31	0.3	0.0	30	14	4.6
#7	182.5	ND	ND	ND	ND	ND	ND	1.5	0.1	38	6.3	ND
#8	116.5	ND	ND	ND	ND	ND	ND	5.6	0.7	83	13	ND

ND = Not determined.

For the cations, the minute concentrations of Al, B, Fe, and Li show no changes from those in EJ-13 water. The sodium concentration is slightly depleted in the test solutions. The concentrations of Ca, Mg, and Si, however, indicate significant decreases, probably because of their participation in forming secondary phases with the uranium (see below).

Surface Analyses

As noted, four of the tests have been terminated to allow the sample surfaces to be analyzed. Of particular interest is the identification of the secondary phases that are 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. Phases with unique appearances as indicated by morphology or color were carefully removed from the surface for analysis using x-ray diffraction (XRD) or Fourier transform infrared (FTIR) spectroscopy. In some cases, after XRD had been performed, the samples were transferred to an aluminum stub, carbon coated, and analyzed using scanning electron microscopy with associated energy dispersive x-ray spectroscopy (SEM/EDS). In other cases, samples from the same region of the surface as was analyzing using 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.

Each sample developed a unique appearance depending on the disposition of water after it contacted the surface. In some cases, the formation of secondary phases suggested that the water drop, after contacting the surface, remained near the center of the pellet and evaporated and/or reacted with the UO_2 before reaching the perimeter of the sample and flowing down the sides to collect on the bottom. These samples were marked by a significant buildup of reaction products in the center of the sample surrounded by rings of precipitates of varying colors. An example of this type of reacted surface is sample #5 where the top surface was highly altered, having an appearance dominated by what could best be described as a restricted flow pattern (Fig. 2). The water appears to have contacted the surface in the center and the spread out in a circular pattern that extends about 50% of the distance to the perimeter. This inner circular region is comprised of large dark yellow crystals intermixed with small white needles. The needles are isolated on the gray surface and cluster upwards in the center of the sample into clumps of needles that take on a white-yellow color. In the middle of this central area is a nest of gray platelets forming upwards from the surface.

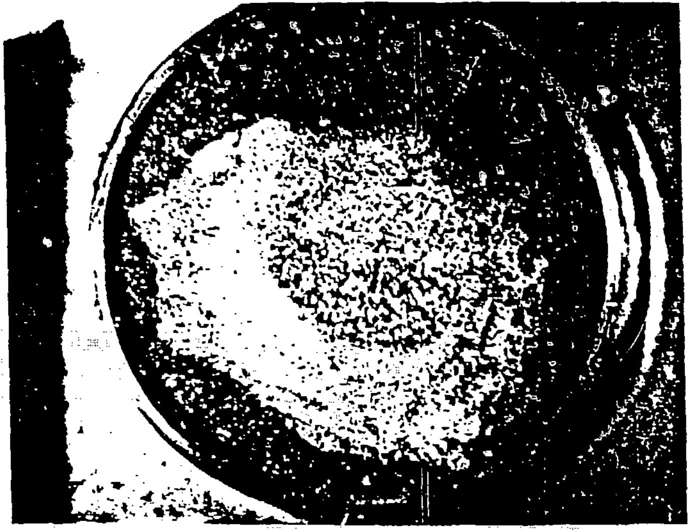

Fig. 2. Top Surface of UO_2 from Test #5 Showing Restricted Flow Pattern of Secondary Phase Formation, Magnification = 3X

Surrounding this circular pattern is a halo of fine white needles. These needles form a fairly continuous mat and do not form a white/yellow mix as was observed in the central region. However, scattered throughout this white mat are many large individual yellow crystals. At the perimeter of the halo is a region of intermixed white and yellow needles with the white usually covering the yellow.

Outside of the halo is a mixture of strands and clumps of what looks like irregularly shaped white feathers that form upwards from the surface but were interconnected by fine white threads. The connected length of these white feathers ranged upwards to several millimeters. The bottom surface for samples of this type showed little evidence of reaction, with at most small clusters of yellow crystals evident. Samples #5, #7, and to a lesser extent #3, had this type of appearance.

The remaining samples had the top and bottom surfaces reacted to essentially the same extent based on the amount of precipitates observed. The phases were of the same morphology as described above, but they were randomly spread over the surface. There was no evidence of restricted water flow on these samples, and in most cases, the Teflon^{TM} stand took on a yellow appearance.

The secondary phases identified are listed in Table II. Uranophane, boltwoodite, sklodowskite, and becquerelite were identified with XRD, and EDS was used to confirm the chemical characteristics of the phase. Dehydrated schoepite was identified with XRD with the EDS showing only U. Schoepite and compreignacite were difficult to differentiate because they have very similar XRD patterns, and it is also difficult to distinguish between the x-ray lines of U and K, even with wavelength dispersive spectroscopy. Based on background subtraction of EDS spectra, the identification of schoepite is certain, while the existence of compreignacite is more tenuous. Additional compositional information obtained using ion-microprobe spectroscopy will be required to confirm the identification. The fluoropolymer was identified by XRD and micro infrared spectroscopy; however, the exact identity of the polymer could not be ascertained.

TABLE II
Phases Identified on Reacted UO_2 Surface

Phase	Formula	Appearance
Schoepite	$UO_3 \cdot 2H_2O$	Dark yellow crystals
Dehydrated Schoepite	$UO_3 \cdot 0.8H_2O$	Yellow crystals with reflective face
Compreignacite	$K_2U_6O_{19} \cdot 11H_2O$	Yellow crystals
Uranophane	$Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$	Fine white needles
Boltwoodite	$K(H_3O)UO_2(SiO_4) \cdot nH_2O$	Yellow crystals
Sklodowskite	$Mg(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$	Fine needles
Becquerelite	$CaU_6O_{19} \cdot 10H_2O$	Dark yellow crystals
Fluoropolymer	Not determined	White feathers

DISCUSSION

The reaction of the UO_2 pellets in all of the experiments showed identical trends. For the first 26-39 weeks, there was very little U release, and the UO_2 surfaces remain essentially pristine. Between weeks 39 and ~100, there was a pulse of U release that corresponded to the appearance of yellow precipitates on the top UO_2 surface and, in some cases, a yellow staining of the Teflon^{TM} stand. Thereafter, there was a slowing in the rate of U release, and additional phases, including the white appearing uranophane, began to form. Those experiments that showed the largest U release, had evidence of reaction on the top and bottom surfaces with some precipitates forming on the Teflon^{TM} stand. Those experiments with the smallest U release had the phases clustered on the top surface with little evidence of reaction on the bottom surface.

These results can be described by a sequence of events starting with the formation of schoepite as in the oxidizing environment of the experiments, the UO_2 matrix breaks down. A large release pulse is observed because schoepite has a relatively large solubility (compared to the other phases that formed) [6] in water, and because in those experiments where there was unrestricted flow, the Teflon^{TM} stands were partially stripped of yellow precipitates during the acid wash process.

After the initial formation of schoepite, phases that contain cations from the EJ-13 water begin to form. These phases have a much lower solubility limit in water, as evidenced by the 1-4 ppm content of the unacidified test solutions. Additionally, the test solutions were depleted to a significant extent in Mg, Ca, and Si, each of which are incorporated into stable phases. In those experiments where the water flow was restricted, the Mg-, Ca-, and Si-bearing phases formed in the center of the pellet surface. Any water that eventually did reach the perimeter and flow down the sides and collected on the bottom was depleted in cations and the main phase to form was dehydrated schoepite. The disparity in U release between duplicate experiments was due to the water flow pathway. Within the parmaeters of the experimental design used, e.g., U surface area and water drip rate, the release of U was dominated by water flow and not by the surface area or drip rate/volume. In fact, the largest release was observed in experiment #3, which had the smallest SA and the reduced water input.

CONCLUSION

A set of experiments has been performed where repository water was dripped onto UO_2 over a period of 3-1/2 years under oxidizing conditions. The experiments were done to develop an experimental procedure to test the reaction of spent fuel under unsaturated conditions anticipated for the proposed tuff repository. These experiments indicated that the UO_2 matrix was transformed into a series of secondary phases. The phases appear to have formed in a sequence with the first phase, schoepite, having a relatively large U solubility, leading to a pulse of U release. Thereafter, the phases that formed incorporated cations from the water into their structure and had a lower solubility, thereby reducing the rate at which U was released from the pellet. The experiments are continuing to observe whether any additional phases will form as the reaction process continues.

ACKNOWLEDGMENTS

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