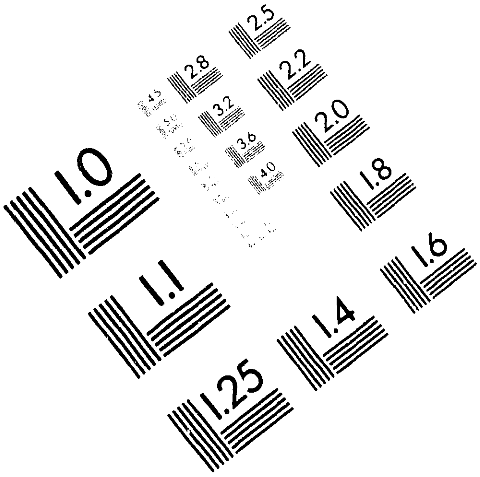

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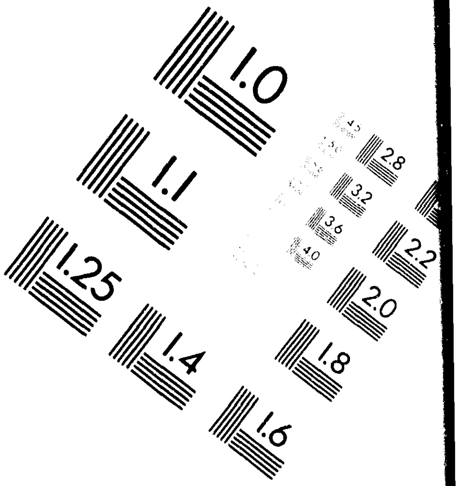

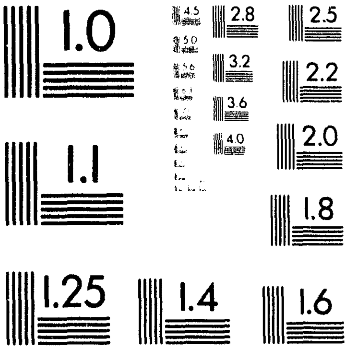

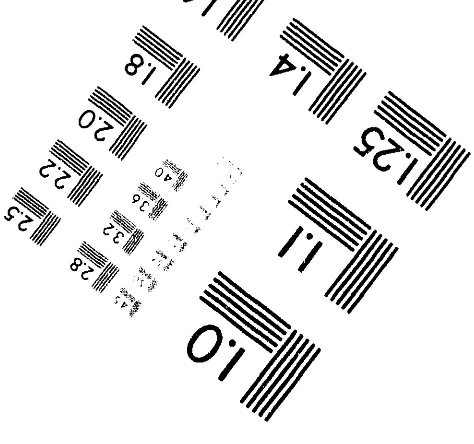

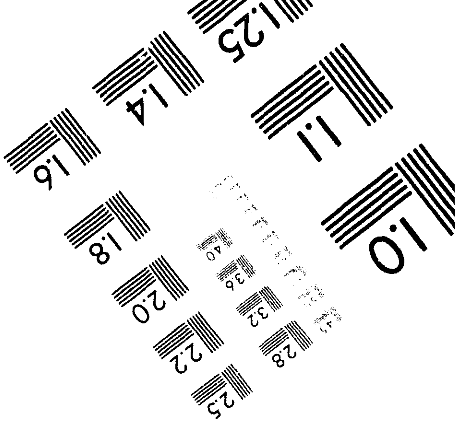

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THE EFFECT OF FUEL TYPE IN UNSATURATED SPENT FUEL TESTS

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THE EFFECT OF FUEL TYPE IN UNSATURATED SPENT FUEL TESTS

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ABSTRACT

Two well-characterized types of spent nuclear fuel (ATM-103 and ATM-106) were tested under simulated unsaturated conditions with simulated groundwater at 90°C. The actinides present in the leachate were measured after periods of approximately 60, 120, and 275 days.

The vessels were acid stripped after 120 and 275 days. Both colloidal and soluble actinide species were detected in the leachates which had pHs ranging from 4 to 7. Alpha spectroscopy studies of filtered and unfiltered leachates showed that large amounts of actinides may be bound in colloids. The uranium phases identified in the colloids were schoepite and soddyite.

The actinide release behavior of the two fuels appears to be different. The ATM-106 fuel began to release actinides later than the ATM-103 fuel, but after 275 days, it had released more. The amount of americium released from the two fuels was a higher percentage of the maximum amount of americium present than was the percentage of the simultaneous amount of uranium released.

I. INTRODUCTION

A potential repository for spent nuclear fuel may be sited in an unsaturated zone at Yucca Mountain, Nevada. Since the repository site may be in an unsaturated zone, waste package container and cladding failures would expose the fuel to air in an unsaturated water environment.

In a saturated water environment in which the matrix dissolved slowly, the actinide solubility limit was suggested to depend on matrix dissolution.[1-3] However, the importance of unsaturated conditions has recently been demonstrated.[4] In moist air, dissolution and precipitation reactions produced U_3O_8 and UO_3 hydrates at the spent fuel surface via a thin film of water that condensed on the exposed spent fuel. The oxidation-dissolution/redeposition reactions appeared to be accelerated by the products from interaction with air and/or moisture. In saturated tests, these products would be washed away so their effects would not be observed. Therefore, the performance of spent fuel needs to be tested under conditions that simulate an unsaturated environment.

To simulate this environment, we have initiated ongoing unsaturated tests in which two types of spent fuel are exposed to small, intermittent amounts of a simulated groundwater (0.75 mL injected once every 3.5 days). Our unsaturated leach tests are designed to simulate and monitor the release of radio-nuclides from the spent fuel as a function of spent fuel type. They yield information on (1) the chemistry of the solutions after contact with the spent fuel as a function of time, (2) the dissolution rate of the spent fuel matrix, (3) the species form and type (ion, colloid) of the released radionuclides, and (4) the release rate of the radionuclides. The results from these tests identify processes that depend on spent fuel type. The results also provide data to validate models that predict long-term behavior of spent fuel for an unsaturated repository.

II. EXPERIMENTAL

Two types of well-characterized spent fuel from the pressurized water reactor at Calvert Cliffs were tested: ATM-103 with a burnup of 30 MW-d/kg U and ATM-106 with a burnup of 43 MW-d/kg U.[5,6] The grain sizes of the irradiated fuel were 9-19 and 6-14 µm, respectively.[5,6] The as-received fuel fragments (0.3- to 1.2-g each) had an average geometric surface area of 2.1 cm^2/g. Prior to use, the fragments were dry-screened with a 20-mesh sieve (840 µm) to remove fines. The tests on ATM-103 fuel were designated S32J1, and those on ATM-106 fuel S62J1. See Table 1. (A number after the test designation indicates the length of the interval or the acid strip done; for example, a leachate sample labeled S32J1-57 was removed after 57 days of testing, while S32J1-S1 is the first acid strip.)

The groundwater which came from well J-13 had a chemistry representative of the saturated zone below Yucca Mountain, Nevada. It was equilibrated at 90°C for 80 days with crushed core samples of Topopah Spring tuff. The resulting water, designated EJ-13, had the following composition (µg/mL): Al (0.68), B (0.19), Ca (6.95), K (6.67), Li (0.03), Mg (0.08), Na (53.6), Si (45.5), NO_3^- (10), NO_2^- (0.12), SO_4^{2-} (20), Cl (7.5), F (2.4), total carbon (25), and organic carbon (5). The pH was 8.4.

The experiments were done in stainless steel (type 304L) vessels. A small amount (5 mL) of EJ-13 water was initially deposited in the base of the vessel to ensure a humid atmosphere. The spent fuel was placed inside a Zircaloy-4 sample holder. The holder consisted of a 1.33-cm-diameter tube that was press-fitted into a 2.6-cm-square plate, which contained a 20-µm-thick filter with 7-µm-diameter holes. The fuel assembly was set on a ledge inside the test vessel and the vessel was sealed. The test vessels were held at 90°C in an oven inside a hot cell. A small quantity of premeasured EJ-13 water (0.75 mL) was periodically dripped every 3.5 days from a reservoir onto the top of the spent fuel in the holder. Air was flushed through the lines to ensure that the water left the lines and contacted the fuel.

After intervals of approximately 60, 120, and 275 days, the experiments were interrupted to collect the accumulated liquid and to visually examine the spent fuel samples. The volume of fluid present was determined by measuring the difference in vessel weight between the beginning and the end of each test interval. On average about 90-92% of the calculated injected fluid was in the test vessel. The vessel was disengaged from the injection system, cooled rapidly, and then opened. The spent fuel assembly was removed from the vessel and examined visually (a videotape was retained). The assembly was then returned to the vessel after the leachate was removed or introduced into a new test vessel if the used vessel was to be acid stripped. When the same vessel was used, the assembly was kept in a moist environment while the leachate was removed from the test vessel.

When the test vessel was acid stripped, it was filled with 1% nitric acid (a mixture of Ultrex and deionized water) and heated at 90°C for 16 hours to remove any species that had adhered to the vessel walls. Aliquots of the acidified solution were then analyzed by gamma and alpha spectroscopy and inductively coupled plasma-mass spectrometry (ICP-MS).

Aliquots of the leachate were taken and examined for the following: pH (Brinkmann Metrohm Meter); carbon content (Dohrmann Total Carbon Analyzer); anion content (ion chromatography); radionuclide content in dissolved and suspended material (alpha spectroscopy of unfiltered and filtered leachate [3.6-nm filter, which was prewetted with deionized water]); radionuclide content (gamma spectroscopy); and elemental release (Fisons ICP-MS). Suspended material was characterized using a JEOL 2000 FXII transmission electron microscope (TEM) operated at 200 kV and equipped with X-ray energy dispersive spectrometry (EDS) and parallel electron energy loss spectrometry (EELS). Electron diffraction data were compared to X-ray diffraction standards to assist in identification of phases.

III. RESULTS AND DISCUSSION

A. Evidence of Colloidal Species

Table 1 shows the concentrations of the transuranic species identified by alpha spectroscopy in unfiltered and filtered (3.6-nm filter) spent fuel leachate samples. The amount of material (80 to 90% of the total) that was trapped by the filter is calculated to be the difference in content between the unfiltered and the filtered leachate samples. This trapped material is most likely colloidal since colloidal species have been identified by TEM.[7,8] A TEM sample from leachate S32J1-57 (ATM-103 fuel) contained two major intermixed uranium phases, which also contained rare earth elements (REEs). One phase contained individual particles that were 50-100 nm in diameter. Partially crystalline uranium silicate colloids were identified by selected area electron diffraction (SAED) analysis and EDS compositional data as soddyite, a uranyl silicate with a U/Si ratio of 1:1. The second uranium-containing phase consisted of 20-50 nm particles in agglomerates that were themselves 3-5 µm in diameter. It contained very little silicon but did have a small amount of a mixture of REEs. The phase was not crystalline, but its elemental composition suggested a schoepite phase (a uranyl hydrate species). The identified REEs were La, Ce, Pr, Nd, Sm, and Eu.

The uranium phases found in colloids in the leachate tests form part of the paragenic sequence found for unirradiated UO_2 dissolution.[9] The presence of both schoepite and soddyite indicates that the uranium in the spent fuel matrix is dissolving in a manner similar to that found for unirradiated UO_2. However, the transuranics in the spent fuel do not appear to be released congruently with the uranium matrix.

Note that the release behavior of the two fuels, ATM-103 and ATM-106, differ, as does the behavior of individual transuranics as a function of leach time. First, no transuranic species were observed at the 60-day interval for ATM-106 fuel. However, by the end of the third interval (271 days total leach time), the total transuranic release from ATM-106 fuel was greater than that from the ATM-103 fuel; that is, the release rate for the ATM-103 fuel had decreased while that for the ATM-106 fuel had significantly increased. Second, the release behavior of americium and plutonium was quite different for the two fuels. For the ATM-103 fuel, substantial amounts of americium and a small amount of plutonium were released,[8] while a large amount of plutonium and only a small amount of americium were released for the ATM-106 fuel.[8] Third, significant amounts of neptunium were detected only after 275 days and then in the acid strip of the test vessel. In this case, the amount detected for ATM-106 fuel was 100 times greater than that for the ATM-103 fuel.

B. Solution Composition

The pH of the four leachate samples (calculated to eliminate dilution effects) was lower than that of EJ-13 (pH 8.4). For the test with ATM-103 fuel (S32J1), the leachate had a pH of 6.0 at 57 days, 6.3 at 120 days, and 6.4 at 275 days. For the test with ATM-106 fuel (S62J1), the leachate had a pH of 6.2 at 55 days, 4.7 at 113 days, and 6.2 at 271 days. The change in the anion composition at the end of 60 and 120 days has been reported previously.[7] The major change noted was that the formate ion content increased in parallel with a decrease in bicarbonate and an increase in nitrite. During the third interval, the decrease in bicarbonate content (1×10^{-5} mol for S32J1 and 7×10^{-6} mol for S62J1) paralleled an increase in the sum of the carbon in the formate and oxalate ion content (8×10^{-6} mol for S32J1 and 6×10^{-6} mol for S62J1). The nitrite content was relatively unchanged; however, for both the S32J1 and the S62J1 test, the nitrite content decreased 4 and 1×10^{-6} mol, respectively.

The presence of formate species may serve to make some of the actinide species, like UO_2^{2+}, Pu^{4+}, and PuO_2^{2+}, more soluble in the leach solutions.[10] However, as shown in Table 1, a large fraction of the americium appears to be present as a colloid. Kim[11] found that americium was strongly sorbed on groundwater colloids, which could be filtered at ~1 nm (removing ~95-98% of the americium activity). When ethylene diamine tetraacetic acid (EDTA) was added to the groundwater, americium was not sorbed on the groundwater colloids. The importance of these different effects have not yet been ascertained for these unsaturated tests.

C. Quantification of Actinide Release

Tables 2 and 3 show the fraction of maximum material release for each actinide during the three test intervals. The maximum material release is defined as the total quantity of a given isotope in the spent fuel sample. The ratio between the amount of material detected in the leachate versus the total released from the fuel which includes that material which adhered to the stainless steel vessel wall is also shown for each isotope. This ratio is labeled "unprecipitated fraction"; it represents the material not deposited on the vessel walls and includes all dissolved material (colloidal, ionic, etc.).

The information in Table 2 is the basis for the following observations for ATM-106 fuel. (1) During the first 60 days, only a minor actinide release was detected in the ATM-106 leachate. However, the amount released steadily rose. At 270 days, six times more uranium had been released than that released in the first 120 days. (2) The fraction of maximum transuranic released was ten times greater than the fraction of maximum uranium released, thus, the transuranics were not released congruently with uranium except for plutonium. (3) Most of the transuranics (columns 3-6 of Table 2) that were released appear to be deposited on the walls of the vessel (the rows labeled acid strip). One transuranic, Cm-244, appeared to have a large unprecipitated fraction (0.23 for the first 120 days). At 270 days, the unprecipitated fraction increased for both uranium and plutonium.

The information in Table 3 is the basis for the following observations for ATM-103 fuel. (1) The major actinide release occurred in the first 60 days and steadily decreased thereafter. The actinide release significantly decreased at 270 days. (2) The fraction of maximum actinide released was not the same for all actinides. The fractions for plutonium and uranium were equivalent ($\sim 10^{-5}$) but both were three orders of magnitude smaller than the fraction for americium and curium ($\sim 10^{-3}$). (3) The unprecipitated fraction was high for the ATM-103 fuel, ranging from 0.44 to 0.88 for the first two test periods; the opposite behavior was found for the ATM-106 fuel. The amounts of americium-241 in the leachate during the first two intervals were 2 and 0.2 µg, respectively, while the amount in the first acid strip was 1 µg. This high unprecipitated fraction persisted at 270 days, although the amount dissolved had decreased.

There was an additional difference between transuranic release behavior for the two fuels. Using the fraction of maximum uranium release as a basis of comparison, less material was released from the ATM-106 fuel over the first two test periods than from the ATM-103 fuel. However, during the third test period, the ATM-106 fuel released a fraction forty times that of the ATM-103 fuel. The two fuels had different burnup histories, which may have had an influence on their release behavior. However, other variables such as the inhomogeneity of the fuels and the time interval for water contact may also play a role in these results. Further testing will be required to separate these effects.

IV. CONCLUSIONS

The uranium and transuranic release from samples of two different spent fuels, ATM-103 and ATM-106, under unsaturated conditions appear to depend on the fuel characteristics. Differences were noted for the total amount of material released, the relative amount of each isotope released compared to the uranium release, and the amount and type of release as a function of leach time. The following should be noted. First, an induction period of approximately 60 days was found for ATM-106 fuel. Second, the two fuels had different transuranic release patterns. For ATM-103, the major transuranic released was americium, whereas for ATM-106, plutonium and americium were released in equal amounts for the first and second test periods. Third, neptunium release was not substantial for both fuels until after 275 days.

We suspect that actinide release from the waste form can be affected by the composition of the leachate. Under unsaturated conditions, radiolysis products are not diluted; therefore, they decrease the leachate pH which results in higher actinide solubilities.[12] In addition, the organic species formed (e.g., formate) may also influence actinide solubility. In saturated tests, these effects are masked by the large volume of liquid.

Last, a large percentage of the transuranics (ten times the unprecipitated fraction for americium and curium) may be bound in colloids, as evidenced by the unfiltered and filtered results from alpha spectroscopy. Two uranium species identified in these colloids were schoepite and soddyite, phases identified as part of the paragenic sequence of UO_2 dissolution. If the transuranic behavior (high release rate, formation of colloidal species) is verified in future test intervals, their contribution will need to be addressed in transport models for the proposed repository system.

ACKNOWLEDGMENTS

This task was performed under the guidance of the Yucca Mountain Site Characterization Project (YMP) and is part of activity D-20-43 in the YMP/Lawrence Livermore National Laboratory Spent Fuel Scientific Investigation Plan. The work was initiated and funded with internal Argonne National Laboratory research and development funding. Work supported by the U.S. Department of Energy, under contract W-31-109-ENG-38.

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Table 1. Actinide Species Detected by Alpha Spectroscopy for Successive Unfiltered and Filtered[a] Leachate Samples

		Content of Sample (g/L)					
Fuel	Test No.[b]	Cm-244	Am-241	Am-243	Pu-239	Np-237	Pu-238
Unfiltered Samples							
ATM-103	S32J1-57	4.9E-6	3.6E-5	8.5E-6	ND[c]	ND	ND
ATM-103	S32J1-120	2.0E-6	1.3E-5	ND	ND	ND	ND
ATM-103[d]	S32J-S1	1.2E-6	2.5E-5	ND	ND	ND	ND
ATM-103	S32J1-275	3.0E-9	2.8E-8[e]	ND	1.7E-8	ND	NC[e]
ATM-103[d]	S32J1-S2	1.1E-8	1.5E-7[e]	ND	6.7E-7	6.2E-5	NC[e]
ATM-106	S62J1-55	ND	ND	ND	ND	ND	ND
ATM-106	S62J1-113	4.1E-8	2.1E-7	3.4E-7	ND	ND	ND
ATM-106[d]	S62J1-S1	2.8E-7	NA[f]	ND	1.0E-5	ND	4.2E-7
ATM-106	S62J1-271	5.0E-7	NA[f]	ND	1.3E-5	ND	5.5E-7
ATM-106[d]	S62J1-S2	7.7E-7	NB[g]	ND	1.4E-5	2.9E-3	1.5E-6[g]
Filtered Samples							
ATM-103	S32J1-57	1.7E-7	1.2E-6	6.4E-8	4.5E-7	1.1E-4	ND
ATM-103	S32J1-120	2.1E-7	9.1E-7	4.8E-8	2.9E-7	2.2E-5	ND
ATM-103	S32J1-275	1.0E-10	6.2E-10[e]	ND	2.9E-9	ND	NC[e]
ATM-106	S62J1-55	ND	ND	ND	ND	ND	ND
ATM-106	S62J1-113	4.7E-9	4.5E-9	ND	ND	ND	ND
ATM-106	S62J1-271	1.0E-7	NA[f]	ND	ND	ND	4.4E-8

[a] Filtered through 3.6-nm filter.

[b] Number following hyphen is test time in days when aliquot was taken.

[c] ND = No species were detected.

[d] Volume of strip solution was 52-57 mL. The volume of the leachate ranged from 15-32 mL.

[e] NC indicates that Pu-238 was present but was masked by the Am-241 peak.

[f] Because of the magnitude of the Pu-239 species, the species at 5.5 MeV were assigned to Pu-238. The acronym NA = not assigned.

[g] NB indicates that Am-241 was present but was masked by the Pu-238 peak; the latter value is thus greater than the actual value.

Table 2. ATM-106 Test Results[a]

	U-238	Pu-239	Am-241	Am-243	Cm-244	Cs-137
<u>First Two Intervals</u>						
Leachate 60 d	7E-10	1E-11	5E-12	1E-11	1E-11	2E-9
Leachate 120 d	4E-6	1E-8	9E-9	3E-9	3E-9	9E-7
Acid Strip	5E-5	3E-7	1E-7	3E-8	1E-8	5E-7
Total	5E-5[b]	3E-7	1E-7	3E-8	1E-8	1E-6
Unprecip. Fraction[c]	0.07	0.03	0.09	0.09	0.23	0.64
Fraction of Maximum[d]	7E-6	8E-6	2E-5	2E-5	2E-5	1E-4
<u>Third Interval</u>						
Leachate 270 d	1E-4	7E-7	8E-8	2E-8	4E-8	5E-6
Acid Strip	2E-4	4E-7	4E-7	2E-7	4E-8	4E-6
Total	3E-4	1E-6	4E-7	2E-7	8E-8	9E-6
Unprecip. Fraction[c]	0.34	0.62	0.16	0.12	0.48	0.57
Fraction of Maximum[d]	4E-5	2E-5	7E-5	1E-4	2E-4	1E-3

[a] Values are derived from semi-quantitative ICP-MS results.

[b] The uranium release corresponds to 0.26 mg/m^2-d for ATM-106 for an estimated average surface area.

[c] The fraction of isotope present in the leachate and not deposited on the vessel walls.

[d] The fraction of the maximum amount of isotope present in the spent fuel sample.

Table 3. ATM-103 Test Results[a]

	U-238	Pu-239	Am-241	Am-243	Cm-244	Cs-137
<u>First Two Intervals</u>						
Leachate 60 d	4E-5	1E-8	2E-6	4E-7	7E-7	9E-7
Leachate 120 d	1E-5	6E-9	2E-7	4E-8	2E-8	2E-6
Acid Strip	5E-5	2E-8	1E-6	3E-7	1E-7	1E-7
Total	1E-4[b]	4E-8	3E-6	7E-7	8E-7	3E-6
Unprecip. Fraction[c]	0.50	0.44	0.69	0.59	0.88	0.97
Fraction of Maximum[d]	1E-5	1E-6	6E-4	1E-3	8E-3	5E-4
<u>Third Interval</u>						
Leachate 270 d	6E-6	7E-9	3E-9	6E-9	2E-9	8E-7
Acid Strip	5E-6	1E-10	6E-9	1E-9	8E-10	1E-8
Total	1E-5	7E-9	9E-9	8E-9	2E-9	8E-7
Unprecip. Fraction[c]	0.56	0.98	0.37	0.83	0.66	0.99
Fraction of Maximum[d]	1E-6	2E-7	2E-6	1E-5	2E-5	1E-4

[a] Values are derived from semi-quantitative ICP-MS results.

[b] The uranium release corresponds to 0.46 mg/m^2-d for ATM-103 for an estimated average surface area.

[c] The fraction of isotope present in the leachate and not deposited on the vessel walls.

[d] The fraction of the maximum amount of isotope present in the spent fuel sample.

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