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ABSTRACT

In the potential repository at Yucca Mountain, failure of the waste package container and the cladding of the spent nuclear fuel would expose the fuel to water under oxidizing conditions. To simulate the release behavior of radionuclides from spent fuel, dynamic drip and vapor tests with spent nuclear fuel have been ongoing for 2.5 years. Rapid alteration of the spent fuel has been noted with concurrent release of radionuclides. Colloidal species containing americium and plutonium have been found in the leachate. This observation suggests that colloidal transport of radionuclides should be included in the performance assessment of a potential repository.

INTRODUCTION

Laboratory testing of the behavior of spent fuel under the conditions expected in a repository provides the information necessary to determine the magnitude of the potential radionuclide source term at the boundary of the fuel's cladding. In scenarios for the potential Yucca Mountain repository, it is assumed that the cladding has failed and water as vapor or liquid contacts the fuel. Several drip tests which simulate the unsaturated conditions expected in the potential repository at Yucca Mountain are in progress to evaluate the long-term performance of spent fuel (1-5). The purpose of the experiments is to determine if the rate of fuel alteration affects the release rate of different radionuclides under unsaturated conditions.

This paper examines the corrosion behavior of the spent fuel matrix (irradiated UO_2) in long-term drip and vapor tests at 90°C and compares it to that found for unirradiated UO_2 in similar drip tests (5,6) and to irradiated fuel reactions at higher temperatures (7-9). It also examines the release rates of some transuranics and compares them to those for uranium. Last, it examines the potential for colloidal radionuclide transport.

EXPERIMENTAL

Drip and vapor tests at 90°C have been in progress over 2.5 years to determine the dissolution behavior of well-characterized irradiated fuels. The drip tests use two rates: 0.075 mL/3.5 d and 0.75 mL/3.5 d. The vapor test uses a saturated water atmosphere. A control test without fuel is also underway at a drip rate of 0.075 mL/3.5 d. The two pressurized-water fuels used are: ATM-103 which has a burnup of 30 MW-d/kg U and ATM-106 which has a burnup of 43 MW-d/kg U. Both fuels are in the form of large fragments with a geometric surface area of 2.1 cm^2/g. The groundwater, which came from well J-13 near Yucca Mountain, is equilibrated at 90°C for 80 days with crushed core samples of Topopah Spring tuff, and is designated EJ-13. The EJ-13 has a pH of 8.4. Its major cations are: K (7 ppm), Ca (7 ppm), Al (1 ppm), Na (54 ppm) and Si (46 ppm); its major anions are: Cl (8 ppm), F (2 ppm), NO_3

(10 ppm), SO_4 (20 ppm), CO_3 (20 ppm). The experimental configuration and earlier results have been reported elsewhere (1-5).

After successive reaction intervals (120, 155, 205, 100, 165, and 176 days), the tests were interrupted to collect accumulated fluid, acid strip the stainless steel test vessel, and restart the test in a new vessel. (Only data from the first four intervals have been analyzed.) At the end of each interval, aliquots of the leachate were characterized for soluble, colloidal and sorbed content. The physical appearance of the spent fuel at each interval was recorded on video tape by using a macro lens with 10-19X magnification. At the end of the 176 day-interval, a fragment of fuel from each of the tests was removed for further characterization. During removal, holes were created in the thicker layers (i.e., alteration products), which were used to estimate the thickness of the individual layers.

Leachate aliquots were characterized as to pH, carbon content, anion content, radionuclide and elemental content by using gamma and alpha spectroscopy and inductively-coupled plasma-mass spectrometry (ICP-MS). Sequential filtering through 1000, 100, and 50 nm filters was done to determine colloid particle size distributions. Colloids and other solid phases were characterized by using transmission electron microscopy and scanning electron microscopy. Values are updated as more accurate information becomes available.

FUEL ALTERATION

Evidence for oxidation/dissolution of unirradiated and irradiated nuclear fuel has been noted by Taylor (7-9) under high-moisture oxidation conditions, i.e. in the presence of unsaturated steam. Detectable quantities of UO_3 hydrate, schoepite, appeared within 5 days at 225°C, and 20 days at 200°C on unirradiated spent fuel (7). For spent fuel, schoepite's presence did not appear to hamper leaching (9), since formation of recrystallized oxidation products in the grain boundaries did not impede further progress of the oxidation process throughout the grain-boundary network (9). The oxidation process needs water for mobilization of uranium. Our tests provide a similar high-moisture oxidation environment. Our results indicate that oxidation/dissolution of the spent fuel occurs rapidly at 90°C under the unsaturated conditions of the tests. Four types of evidence for reaction of the spent fuel are discussed: the phases identified in the leachate and/or the fuel holder, the physical appearance of the fuel, the successive weight gain for the fuel fragments, and the cumulative amount of uranium found in the leachate.

In our tests, alteration products were noted in <60 days. Both schoepite and soddyite, the latter a uranyl silicate phase, were identified within the spent fuel leachate as colloids (1,3). Within the fuel holder (4,5) used in the test assembly, schoepite, $UO_3 \cdot 2H_2O$, was found attached to a spent fuel particle identified as UO_2. (The particle also contained La, Ce, Pr, Nd, Sm, Am, and Cm.) A second phase identified on a spent fuel particle incorporated Cs, Ba, and Mo. Electron diffraction results matched the becquerelite minerals, particularly billietite, which is a barium-bearing uranyl hydroxide hydrate of the form $Ba(UO_2)_6O_4(OH)_6 \cdot 8H_2O$.

The ATM-103 fuel's appearance in the high drip rate test experienced a drastic change after 748 days of reaction. The fuel was bright white to yellow-white. The edges of all fuel fragments were rounded, and the surfaces were covered by a ~0.1-mm-thick layer. At 925 d, the layer on the ATM-103 fuel was thicker and the fragments appeared to be loosely bonded together. A twisting motion on the forceps was required to remove a fragment. This procedure produced a hole in the upper layer of the alteration products. The thickness of the alteration layer was estimated by estimating the depth of the hole, ~0.5 mm. The ATM-106 fuel in the other high drip rate test had a similar layer. See Table I for a description of the fuel's appearance in the different tests. Also listed in Table I are some potential phases which may be

present based on their physical similarity to phases found in a similar set of ongoing drip tests (Table II) with unirradiated UO_2 (5,6). For the fuel fragments, the phase identifications have not yet been confirmed by TEM and SEM characterization of the layers.

Table 1. Fuel Appearance after 2.5 Years of Reaction

High Drip Rate Tests		
Fuel Surface	-	white or yellowish mat; fuel fragments adhering to each other
	-	fragment edges rounded, with fine needles extending outwards
	-	thickness of mat, ~0.5 mm
Potential Phases	-	uranophane (white needles, continuous mats) $Ca(UO_2)_2(SiO_3OH)_2 \cdot 2H_2O$
	-	boltwoodite (yellow needles, continuous mats) $K(H_3O)UO_2(SiO_4) \cdot nH_2O$
Low Drip Rate Tests		
Fuel Surface	-	light yellow layer on darker yellow layer, crystalline phases
	-	light yellow layer with drip pattern down side of fuel fragment
	-	thickness of light yellow layer, ~0.05 mm
Potential Phases	-	schoepite (dark yellow crystals) $UO_3 \cdot 2H_2O$
	-	same phases as for high drip rate tests
Vapor Tests[a]		
Fuel Surface	-	light yellow layer
	-	thickness is unknown
Potential Phases	-	schoepite

[a]Vapor test results demonstrate that a water film on the fuel is sufficient for oxidation.

Table II. Identified Phases[a] in Unirradiated UO_2 Drip Tests (References 5,6)

Reaction Time (yr)	Uranium Phases[b] - Appearance
1.5	Dehydrated schoepite - yellow to green crystals [soddyite (Si) - white buttons]
2.25	Dehydrated schoepite - green mats
3.5	Uranophane (Ca,Si) - fine white needles in mats [boltwoodite (K,Si), sklodowskite (Mg,Si), becquerelite (Ca)]
8	Boltwoodite (K,Si) - fine yellow needles in mats [uranophane (Ca,Si), soddyite (Si), dehydrated schoepite]

[a]The phase identifications were made using TEM and SEM results.
[b]Elements other than U and O for each phase are shown in parentheses. Minor phases are in brackets.

The fuel in each test was weighed at the end of each reaction interval. The cumulative increase in weight for the last two reaction intervals is given in Table III. (The weight increase for the control test has been subtracted.) We assumed that the weight increase was due to the formation of a continuous layer of schoepite. The thickness of this layer was calculated using the geometric surface area, 2.1 cm^2/g for the spent fuel, the density of schoepite, 7.29 g/cm^3, and a porosity of 99%. (A very high porosity was used to account for the measured thickness of the layer in optical photographs at 747 days.) The calculated thicknesses are shown in Table III. The calculated thicknesses at 924 days are the same order of magnitude as the thicknesses measured for the holes produced in the layers during handling.

Table III. Weight Change and Estimated Thickness of Reaction Product[a]

	High Drip Rate		Low Drip Rate		Vapor	
Values	ATM-103	ATM-106	ATM-103	ATM-106	ATM-103	ATM-106
			After 747 d			
Weight Increase (mg)	25	14	7	9	19	10
Layer Thickness (mm)	0.2	0.1	0.05	0.08	0.1	0.08
			After 924 d			
Weight Increase (mg)	36	44	16	17	26	12
Layer Thickness (mm)	0.3	0.4	0.1	0.2	0.2	0.1

[a]The mass of uranium which would be incorporated in the reaction product is ten times the cumulative total in the leachate.

Table IV. Released Fraction[a] of Uranium-238 for High Drip Rate Tests. Determined from ICP-MS Results.

	ATM-106		ATM-103	
	Fraction	Rate, $mg/m^2 \cdot d$	Fraction	Rate, $mg/m^2 \cdot d$
0-120	2E-5	0.8	5E-5	1.9
120-275	2E-4	4.7	6E-6	0.2
275-482	8E-6	0.2	8E-6	0.2
482-581	1E-6	0.06	2E-5	1.1
0-581[b]	2E-4		8E-5	
Average Rate		1.5		0.7

[a]Fraction denotes the amount of uranium collected divided by that initially present in the fuel.
[b]Cumulative fraction released after 581 days of reaction.

Another means to determine alteration of the spent fuel matrix is by the fraction of material released into the leachate. The released fraction in the high drip tests is tabulated in Table IV for four reaction intervals for which data is available, and for the cumulative reaction time. (Fraction denotes the amount of a material collected divided by that initially present in the fuel used in the test.) The cumulative uranium fraction for the ATM-106 fuel is approximately twice that for the ATM-103 fuel. Using the geometric surface area of the spent fuel fragments, 2.1 cm^2/g, the uranium release rate ($mg/m^2 \cdot d$) was calculated for each test interval (Table IV). Table V gives the average dissolution rate along with the dissolution rates previously reported for UO_2 and spent fuel under saturated or flow-through conditions. The rates for saturated tests are orders of magnitude less than those for unsaturated or flow-through tests. For unsaturated UO_2 tests, a range of dissolution rates was noted for different test intervals; some were as high as 12-14 $mg/m^2 \cdot d$. For spent fuel, the dissolution rates for unsaturated tests are the same order of magnitude as those for a flow-through test. The unsaturated rates are minimums since the alteration products on the fuel surface and material in the fuel holder are not included. The

results for the flow-through test were assumed to demonstrate conditions for maximum dissolution but our unsaturated results for spent fuel suggest that flow-through tests may not provide conservative limits. In addition, our results suggest that significant dissolution will occur under the conditions expected in the potential Yucca Mountain repository.

Table V. Uranium Dissolution Rates

Material	Test Type[a]	Average Dissolution Rate, $mg/m^2 \cdot d$	Reference
Unirradiated UO_2	Saturated	0.002; 0.04	[10]
Unirradiated UO_2	Unsaturated	0.1-0.3	[5]
ATM-103	Flow-Through	8.4	[11]
ATM-103/ATM-106[b]	Unsaturated	0.7-1.5	This work

[a]Each test was done with different water chemistries.
[b]This is the minimum dissolution rate since alteration products on the fuel's surface are not included.

CUMULATIVE RELEASE FRACTIONS

Reaction of the spent fuel matrix releases radionuclides into the leachate. The leachate after the 482-581 day interval contained different fractions of Am, Np, and Pu for both fuels. (See Table VI.) For the two high drip rate tests, the respective fractions were 1E-6, 2E-7, and 3E-8 for ATM-106 and 2E-5, 2E-6, and 3E-7 for ATM-103. The respective fractions for cesium and uranium were 2E-4 and 1E-6 for ATM-106 and 2E-4 and 2E-5 for ATM-103. Thus, in this interval, the released fractions of actinides for the lower burn-up fuel were an order of magnitude greater than those for the high burn-up fuel. However, the cesium release was the same for both fuels and 10-100 times greater than the uranium release. For both ATM-103 and ATM-106, the neptunium and plutonium were released at 10^{-1} to 10^{-2} the rate of uranium, whereas americium was released at the same rate.

Table VI. Cumulative Released Fraction for High Drip Rate Tests after 581 Days of Reaction

	Released Fraction	
	ATM-106	ATM-103
Cs-137	3E-4	2E-4
U-238	2E-4	8E-5
Np-237	1E-4	1E-3
Pu-239	1E-4	1E-5
Am-241	3E-4	3E-3

The cumulative released fractions for the first 581 days of reaction are tabulated in Table VI. These results indicate that for the ATM-106 fuel, transuranics are released congruently with uranium, while for the ATM-103 fuel, both neptunium and americium appear to be released at 10 times the rate of uranium, and plutonium appears to be released at 10^{-1} the rate of uranium. The cumulative cesium fraction is comparable to uranium's for both fuels. However, as noted above, the cesium release fraction is not the same as the uranium fraction for a given interval. Since cesium is much more soluble than uranium, one might expect that the cesium released fraction would always be greater than the uranium fraction. However, cesium can be incorporated into alteration products, i.e. billietite, as we noted earlier. This mixed behavior suggests that cesium's release may not always correspond to that of a soluble species. These observations may be significant for modeling the release behavior of Cs-135 which has a longer half-life than Cs-137.

Most transport models assume that release of the individual radionuclides contained within the spent fuel matrix is congruent with that of the matrix. From our results we can neither confirm nor negate this assumption. Additional testing is required to determine if the variable releases at the 482-581 day interval are representative of long term release behavior.

COLLOIDS IN THE LEACHATE

Uranium phases were found in the colloids collected from the leachate. To determine the colloidal distribution of the transuranics in the leachate, the leachates from the two high drip rate tests from the 482-581 day interval, were passed through a series of sequential filters (1000, 100, and 50 nm). The percentage of transuranics in each colloidal fraction, as well as the sorbed and ionic percentages are listed in Table VII. Over 50% of the uranium and plutonium was sorbed on the steel test vessel for both fuels. The original form of this material could have been ionic or colloidal. However, because 28% of the plutonium colloids for ATM-106 and 49% of those for ATM-103 were >50 nm in size, this suggests that the sorbed plutonium may have been colloidal when it was transported from the spent fuel holder to the base of the test vessel by the leachate.

The behavior of the released americium was similar. Although 88% of the americium for ATM-103 and 26% for ATM-106 was sorbed, the majority of the remaining americium was again found in the colloidal fractions: 5% for ATM-103 and 51% for ATM-106. The ionic fractions were 1% and 7%, respectively. Again, these results suggest that the sorbed americium may have been colloidal when it was transported from the spent fuel holder. Thus, most of the transuranics in the leachate appear to be associated with colloids.

The concentrations of species collected in the base of the test vessel are also given in Table VII. (This calculation assumes that all are ionic.) For uranium, the concentration is of the order of 10^{-5} to 10^{-6} M. For the transuranics, it ranges from 10^{-8} to 10^{-10} M. These molarities are lower than some of the suggested solubilities for the transuranics. The lower molarities could be caused by non-saturation of the leachant, common ion effects which would lower solubility, the presence of other isotopes, and species incorporation in alteration products on the fuel surface. There is insufficient data to determine which if any of these factors is dominant.

Table VII. Radionuclide Distribution[a] for High Drip Rate Tests during 482-581 Day Interval (ICP-MS Results for Totals)

Species	Total Collected, µg	Drip[b] Concen., M	Sorbed, %	Ionic, %	Colloidal, % 1000 nm	100 nm	50 nm
			ATM-106				
Am-241	5.3E-3	1.3E-9	26	7	30	19	2
Np-237	8.9E-4	2.2E-10	11	<89	ND[c]	ND	ND
Pu-239	9.5E-4	2.4E-10	55	6	16	10	2
Cs-137	2.2	9.5E-7	6	94	ND	ND	ND
U-238	8.7	2.2E-6	56	<44	ND	ND	ND
			ATM-103				
Am-241	8.2E-2	1.7E-8	88	1	0.2	4	1
Np-237	6.0E-3	1.3E-9	18	<82	ND	ND	ND
Pu-239	1.2E-2	2.6E-9	50	1	3	28	18
Cs-137	6.4E-1	2.4E-7	4	96	ND	ND	ND
U-238	1.7E2	3.7E-5	59	<41	ND	ND	ND

[a]Percentages do not add to 100 because different analytical procedures and different aliquot sizes were used.
[b]Concentration equals total collected of isotope listed/leachant volume.
[c]ND = not detected.

Our experimental results do suggest that colloids will be present in the leachate in significant quantities. The need to include the effect of colloidal transport in future versions of performance assessment models for the Yucca Mountain repository has been recognized. However, the effect of colloidal transport may be complex as suggested by two early papers (12,13) which examined solute and colloid coupling interactions for diffusive transport through porous rock and through fractures. For diffusive flow, coupling of colloidal and solute transport resulted in a reduction in the maximum distance traveled for colloidal species but doubled the distance for solute transport (12). For fracture flow, both fronts appeared to be significantly accelerated if there was coupling (13). The coupling interactions should be reevaluated with upgraded parameters for the Yucca Mountain repository. If the effects are confirmed, colloids formed from degradation of the spent fuel matrix could be a transport mode for radionuclides. This mode needs to be evaluated to assess performance of the engineered barrier system of a repository.

CONCLUSIONS

Oxidation/dissolution of the spent fuel occurred rapidly in drip tests at 90°C under the unsaturated conditions expected at Yucca Mountain. Four types of evidence were presented to characterize the alteration process.

Most transport models assume that release of the individual radionuclides is congruent with that of the spent fuel matrix. From our results we can neither confirm nor negate this assumption. Additional testing is required to determine if the variable releases at the 482-581 day interval are representative of long term release behavior.

These drip rate tests, which simulate the unsaturated geological environment, indicate that significant quantities of colloids form and may provide a significant mode of transport for the transuranics. Therefore, the incorporation of colloidal transport in performance assessment

models is needed to ensure that the models have conservative transport limits. The presence of colloidal material may have significant consequences for transport of radionuclide material under long-term storage conditions.

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