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INTRODUCTION

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. This paper examines the corrosion behavior of the spent fuel matrix under conditions in which water is introduced at a rate of 1.5 mL every 7 days. Our recent results suggest a rapid reaction rate of the spent fuel matrix, the formation of alteration products that are similar to the sequence found in ore deposits in uranium mines, and the presence of colloidal species in the leachate. These results are compared to results from two models developed for a potential repository in an unsaturated zone.

DESCRIPTION

The drip tests examine the leach/dissolution behavior at 90°C of two types of well-characterized irradiated pressurized water reactor fuels, ATM-103 and ATM-106, and have been in progress for two years. The experimental configuration and earlier results have been reported elsewhere [1-2]. The groundwater came from well J-13 near Yucca Mountain, which has a chemistry representative of the saturated zone and was equilibrated at 90°C for 80 days with crushed core samples of Topopah Spring tuff. After successive intervals of 120, 155, 207, 100, and 167 days, the tests were interrupted to collect accumulated fluid, acid strip the stainless steel test vessel, and restart the test in a new vessel.

At the end of each interval, aliquots of the leachate were characterized for soluble, colloidal, and precipitated content. Phases in the solid residue on the Zircaloy retainer, upon which the spent fuel rests, were identified by transmission and scanning electron microscopy (TEM and SEM).

RESULTS

Fuel Alteration - Striking evidence of a physical change in the appearance of the ATM-103 fuel after 748 days of reaction was noted. All edges of the fuel fragments were rounded; all surfaces were covered by an ~100 µm thick white coating. The coating probably is comprised of different types of uranyl oxide hydrates, and possibly uranyl silicate phases. (This needs corroboration.) Six months earlier, a few white dots along the edge of a fragment may have been evidence of the presence of nucleation sites. The short time, six months, required to achieve that dramatic change demonstrates that spent fuel reaction rates can be quite rapid.

Some of the phases formed when the spent fuel matrix reacts were identified by examining the residue on the Zircaloy retainer. Schoepite, $UO_3 \cdot 2H_2O$, was found attached to one spent fuel particle which was itself identified as UO_2. There was evidence that La, Ce, Pr, Nd, Sm, Am, and Cm were present in the UO_2. A second phase had a distinctive morphology consisting of elongated crystallites. The phase incorporated Cs, Ba, and Mo, and the electron diffraction results matched best with the becquerelite group minerals, particularly billietite which is a barium-bearing uranyl hydroxide hydrate of the form $M(UO_2)_5O_4(OH)_6 \cdot 8H_2O$.

Within the spent fuel leachate, both schoepite and soddyite, the latter being a uranyl silicate phase, have been identified as colloidal species. These phases were also identified as alteration products in ore deposits of uranium mines and in dissolution tests with unirradiated UO_2.

Cesium and Actinide Release - Table 1 gives the ratios (maximum fraction) of the sum of material released (ionic, colloidal, and precipitated material) to the total in the fuel for the actinides and cesium at four reaction times. The materials leached have a higher proportion of Am and Cm than Pu. The plutonium fraction for ATM-103 after 581 days of reaction was an order of magnitude greater than that for ATM-106; a large fraction of the plutonium in the former test was in colloidal form. Since the cesium fraction was the same order of magnitude for both fuels, a greater percentage of the actinides were released to the leachate for ATM-103 fuel.

Table 1. Maximum Fraction (%) for Drip Tests

	Reaction Time, days			
	113	271	482	581
	ATM-106			
Am-241	2E-5	7E-5	6E-5	4E-5
Cm-244	2E-5	2E-4	1E-4	1E-4
Np-237	N.A.[a]	N.A.	2E-3	7E-4
Pu-239	8E-6	2E-5	5E-5	1E-5
U-238	7E-6	4E-5	N.A.	N.A.
Cs-137	1E-4	1E-3	9E-3	2E-2
	Reaction Time, days			
	120	275	482	581
	ATM-103			
Am-241	6E-4	2E-6	7E-6	1E-3
Cm-244	8E-3	2E-5	2E-5	4E-3
Np-237	N.A.	N.A.	7E-4	3E-2
Pu-239	1E-6	2E-7	8E-7	9E-5
U-238	1E-5	1E-6	N.A.	N.A.
Cs-137	5E-4	1E-4	8E-4	2E-2

We have estimated the reaction rate for the uranium in the spent fuel matrix. We compared this rate to that reported for unirradiated UO_2 reacted under saturated and unsaturated conditions for periods in which the uranium release is slowest. The rates are shown in Table 2 as is the dissolution rate for spent fuel under dynamic high-flow conditions.

Table 2. Uranium Dissolution Rate

Material	mg/m^{2}d	Test Type	Reference
UO_2	0.002	Saturated	[3]
UO_2	0.04	Saturated	[4]
UO_2	0.1-0.3	Unsaturated	—
ATM-103[a]	0.04-0.5	Unsaturated	This work
ATM-106[a]	0.3-1.2	Unsaturated	This work
Spent Fuel	8.4	Flow	[5]

[a] Geometric surface area.

The 0.5 and 1.2 mg/m^{2}d rates for ATM-103 and ATM-106 are minimums, since they are calculated for 113 and 275 days of reaction, times at which the smallest amounts of cesium were released (Table 1) and the fuel showed no visible changes. The rates at 581 days and 747 days are expected to be at least one to two orders of magnitude higher to match the cesium release.

Actinide Composition of Colloidal Species - The actinide content of the colloids was determined as a function of size fractionation after 581 days of reaction. (Both leachates had a pH of 6.9.) For ATM-103, the percentage of Am, Cm, Np, and Pu which passed through a 4-nm filter was 8, 15, 40, and 2%, respectively, of the total colloidal and ionic content. Except for neptunium, the majority of the transuranic elements in the leachate was associated with colloids. For Am and Cm, large percentages of the colloidal material, 52 and 42%, respectively, were in the fraction between 4 and 50 nm. These percentages will be reexamined in future test intervals.

For ATM-106, the percentage of Am, Cm, Np, and Pu which passed through a 4-nm filter was 9, 15, 61, and 20%, respectively. Large percentages of the Am and Cm, 22 and 41%, occurred in the fraction between 4 and 50 nm. Since most models for transport of radionuclides in the repository assume that transport is solubility-limited [6,7], these results indicate that over 80% of the potential transportable transuranic material is not being considered.

DISCUSSION

Our results have shown that dissolution of the spent fuel matrix occurs, with evidence of the formation of alteration products noted in less than 60 days [1]. The uranium reaction rate after the formation of alteration products appears to be faster than that observed under either saturated or flow conditions. (This needs verification.) The alteration products on the fuel are part of the same paragenetic sequence noted for ore deposits in uranium mines and the unsaturated dissolution of unirradiated UO_2. Our tests have also shown that colloids are a significant means of release for the transuranics, a mode of potential transport which has been ignored in many models.

Most models assume that release of the individual radionuclides is congruent with that of the spent fuel matrix. The two limiting cases [7] are then bulk flow, which is solubility limited, and water saturation, which is diffusion limited. Such models predict that the yearly fractional release rate for water saturation is two to three orders of magnitude greater than that for bulk flow. The fractional release that we have observed at 120 days for ATM-103 is an order of magnitude higher and that at 275 days for ATM-106 is two orders of magnitude higher than that for the water saturation case. If the uranium release at 747 days is two orders of magnitude higher than the former values, then current models are not estimating the magnitude of the potential source term in an unsaturated repository.

CONCLUSIONS

Our tests which simulated the unsaturated environment appear to indicate that current models for the reaction of spent fuel and the subsequent release of actinides and other radionuclides do not result in conservative limits. The presence of colloidal material which was noted in our tests appears to have significant consequences for transport of radionuclide material under long-term storage conditions.

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