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ABSTRACT

Drip tests to measure radionuclide release from spent nuclear fuel are being performed at 90°C at a drip rate of 0.75 mL/3.5 days; the test conditions are designed to simulate the behavior of spent fuel under the unsaturated and oxidizing conditions expected in the potential repository at Yucca Mountain. This paper presents measurements of the actinide, ^{137}Cs, ^{90}Sr, ^{99}Tc, and ^{129}I contents in the leachates after 581 days of testing at 90°C. These values provide an estimate of the source term for the long-lived radionuclide release under these test conditions. Comparisons are made between our results and those of other researchers.

INTRODUCTION

Radioisotope release scenarios for the potential repository at Yucca Mountain assume that the cladding has failed, and that water contacts the fuel as vapor or liquid. Drip tests that simulate the unsaturated and oxidizing conditions expected at Yucca Mountain are in progress to evaluate the long-term behavior of spent nuclear fuel. The tests are performed at 90°C at a drip rate of 0.75 mL/3.5 days. We use the results from the drip tests to monitor the reaction rate of the fuel, the corresponding release rates for individual radionuclides, as well as the solution chemistry. The information from these tests can be used to estimate the magnitude of the potential radionuclide source term at the exterior of the fuel cladding, and the changes that can be expected in water chemistry due to groundwater interaction with the spent fuel.

In this paper we report the actinide, ^{137}Cs, ^{90}Sr, ^{99}Tc, and ^{129}I contents in the leachate during the first 581 days of drip testing of two pressurized-water-reactor fuels at 90°C. Measurements were made after intervals of 120, 155, 207, and 99 days (total fuel reaction times of 120, 275, 482, and 581 days for one fuel) and 113, 158, 211, and 99 days for the other fuel.

Testing of the fuels is still in progress. The ATM-103 fuel showed evidence of significant oxidation (1), i.e., the formation of a yellowish-white coating on the fuel after 748 days of reaction. Similar oxidation on the ATM-106 fuel was noted six months later. If oxidation is crucial in effecting release of some of the radionuclides, we would expect that release fractions for the ATM-103 fuel would be larger than those for the ATM-106 fuel.

Different radionuclides were examined to provide a measure of the release from five different chemical groups within the spent fuel. Uranium release may provide a measure of matrix dissolution; plutonium release may indicate its congruency with uranium release; cesium release demonstrates the behavior of oxide precipitates; strontium release provides an indication of the behavior of elements dissolved in the fuel matrix; and technetium release demonstrates the behavior of metallic precipitates. Finally, iodine release provides an indication of the behavior of the fission gases. Taken together, our values provide an estimate of the source term for the long-lived radionuclides released from spent fuel under dripping water conditions. Comparisons are made between our results and those of other researchers (2-4).

EXPERIMENTAL

The two pressurized-water-reactor fuels used in the tests were ATM-103, which has a burnup value of 30 MW•d/kg U, and ATM-106, which has a burnup of 43 MW•d/kg U. The fuels were in the form of large fragments with an estimated geometric surface area of 2.1 cm^2/g. The groundwater, which came from well J-13 near Yucca Mountain, was equilibrated at 90°C for 80 days with crushed core samples of Topopah Spring tuff and is designated EJ-13. The EJ-13 water had a pH of 8.4. Its major cations (mM) were: K$^+$ (0.18), Ca^{2+} (0.18), Al^{3+} (0.04), Na$^+$ (2.35) and Si^{4+} (1.64); its major anions were: Cl$^-$ (0.23), F$^-$ (0.11), NO$_3^-$ (0.16), SO$_4^{2-}$ (0.21), CO$_3^{2-}$ (0.33). The experimental configuration has been described elsewhere (5).

Aliquots (the leachate and the acid solutions used to strip the test vessel) from the first four time intervals as well as the EJ-13 blank, were characterized semi-quantitatively using inductively coupled plasma-mass spectrometry (ICP-MS) in scan mode with an indium internal standard. All measurements

were performed in duplicate. This technique provides accurate results for the isotopes in the middle mass range (80-160 atomic mass units), but results for the actinides may vary by ±50%. The duplicate measurements varied by 0.6-2% for concentrations above 0.5 ppb and by 13-17% below 0.5 ppb. Cesium data, obtained from gamma spectrometry of aliquot samples, were included for comparison.

ICP-MS Methodology -- Two spreadsheet programs were developed to convert the ICP-MS data from the form "integrated counts per mass unit" to "grams per given element", taking into account the non-natural isotopic abundances that were present in the leachate samples and the need for extensive dilution of some samples. The first program converts the integrated counts per mass unit to grams per mass unit, taking account of dilution factors, blank subtraction, and potential impurities in the diluent. The second program is used to assign the grams per mass unit to a particular elemental isotope, allowing for the non-natural distribution in spent fuel samples, as well as the presence of natural elemental distribution from the EJ-13 leachant. This second program is developed in small blocks, i.e., there are separate calculations for the actinides, for isotopes with mass units 83-105, etc. The non-natural distributions for the spent fuel were calculated from results (6,7) obtained using the ORIGEN code. The natural distribution in EJ-13 was determined for a nonradioactive sample.

RESULTS AND DISCUSSION

The total mass (g) of isotopes measured in the leachate (defined here as the liquid collected in the base of the 304L stainless steel test vessel) and in the acid solutions used to strip the test vessel are listed in Table 1 for the four reaction intervals. (These values do not include material sorbed on the Zircaloy or in alteration products on the spent fuel.) The data were interpreted in several ways. First, we calculated the release of each isotope as a fraction of the total material in the fuel fragment. Second, we calculated the daily fractional release rate for each test interval (fraction/d) to determine if any radionuclides were released congruently with uranium. Third, we calculated for each isotope the cumulative release fraction after 581 days of reaction and compared these fractions to that of uranium to determine if we could

separate matrix dissolution from gap and/or grain boundary release. Results of these calculations are discussed below.

Fraction of Material Released – The fractional releases and corresponding daily release rates for ^{137}Cs, ^{238}U, ^{239}Pu, ^{90}Sr, ^{99}Tc, and ^{129}I are listed in Table 2. The ^{137}Cs release from the ATM-103 fuel was relatively constant during the first 581 days of reaction (Table 2) while for the ATM-106 fuel, significant release only occurred after 113 days of reaction. The ^{238}U and ^{239}Pu release fractions were comparable for the ATM-106 fuel for the first three time intervals, while, for the ATM-103 fuel, all three ^{239}Pu release fractions were less than the ^{238}U release fraction. At the 581 day interval, the ^{239}Pu release fraction for both fuels was two orders of magnitude less than their respective ^{238}U releases. These results suggest that as the reaction time increases, release of plutonium decreases significantly from that of uranium. For both fuels, the strontium release fractions were larger than or comparable to, the cesium fractions. The strontium fractional release rate (Table 2) fluctuated between 10^{-5} and 10^{-7}/d in the ATM-106 test and fell from an initial value of 2×10^{-4} to 4×10^{-6}/d in the ATM-103 test. Our technetium release fractions were comparable to the cesium fractions for the ATM-106 fuel, but they were orders of magnitude larger than the cesium fractions for the ATM-103 fuel. Our iodine release fractions for both fuels were orders of magnitude larger than those for uranium.

Table 3 shows the cumulative release fraction for each radionuclide after 581 days of reaction (the tests have been in progress for three years), the ratio of these fractions for the two fuels, and for each fuel, the ratio of the fractions of each radionuclide to that of uranium. Also shown are the same ratios for the last test interval after 581 days of reaction.

The cumulative release fraction for uranium was smaller by several orders of magnitude than the fractions of all the other radionuclides except plutonium. Since extensive oxidation of the fuel was noted later (1) in the tests, the uranium results may indicate that there was significant uranium secondary phase formation, i.e., precipitation of uranium alteration products. The plutonium cumulative fraction, which was lower than uranium's in the case of ATM-103 fuel, may indicate that there was significantly more precipitation of plutonium alteration products. For cesium and iodine, for which gap and grain boundary

releases would be important, higher cumulative release fractions were found as expected. The very high technetium and strontium cumulative release fractions were surprising since these isotopes were expected to be released congruently with uranium. However, these fractions, once gap and grain boundary contributions are subtracted, may indicate the extent of matrix dissolution under the conditions of our test.

The differences in cumulative release fractions for the same isotope may reflect the rates at which the two fuels react under conditions of oxidative dissolution. For both ^{90}Sr and ^{99}Tc, a larger cumulative release fraction was found for the ATM-103 fuel than for the ATM-106 fuel. However, for both ^{137}Cs and ^{129}I, the cumulative release fraction from the ATM-106 fuel was three times that from the ATM-103 fuel, i.e., a ratio of 3. The uranium and plutonium cumulative release fractions were also larger for the ATM-106 fuel.

To estimate the contribution of gap and grain boundary release on our cumulative release fractions, we examined the release fractions at the 581-day interval. The ^{238}U, ^{90}Sr, ^{239}Pu, and ^{99}Tc release fractions for the ATM-106 fuel were smaller than those for the ATM-103 fuel. Only the ^{137}Cs and ^{129}I fractions were larger. We then examined the difference between the cumulative fraction and the interval fraction for uranium and iodine, since the latter should be most influenced by gap release. For ATM-103 fuel, both uranium fractions were the same order of magnitude which indicated that uranium release was constant over the first 581 days. The ^{129}I fraction had significantly decreased at the 581-day interval which suggested that release from the gap no longer contributed significantly. Similar ^{129}I behavior was noted for the ATM-106 fuel. We were unable to separate grain boundary release from matrix release using these differences.

Comparisons with Other Tests -- We compared our release fractions from the drip tests with those from static tests (2-3) and flow-through tests (4). Some of the parameters in these tests are shown in Table 4. The discussion will deal first with the static tests.

The ^{137}Cs fractional release rate for both fuels was 1-2 x 10^{-6} fraction/d at 581 days which is similar to that reported by Forsyth and Werme (2) after 400 days of reaction. For ATM-106 fuel, the ^{137}Cs cumulative release fraction (see Table 3) after 581 days was three times that for ATM-103, the fuel with the

lower burnup. Forsyth and Werme (2), found that the cesium release fraction was a function of fuel burnup, i.e., the cumulative fraction at 40-46 MW•d/kgU was twice that at 30 MW•d/kgU.

Their ^{90}Sr fractional release rate had decreased from 10^{-5}/d to 10^{-6}/d after 100 days of static testing, and steadily decreased to 10^{-7}/d after 1000 days of testing. The ^{90}Sr release fraction reported by Wilson (3) for 150-day-cycle static tests decreased from 4×10^{-4} to 6×10^{-5}/d over his three cycles. Both fuels in our drip tests had a release rate of 10^{-6}/d by the 581-day interval.

For ^{99}Tc, Forsyth and Werme (2) reported a constant fractional release rate of 10^{-5} to 10^{-6}/d even after 1000 days of reaction. They speculated that the ^{99}Tc release was controlled by the oxidation of metallic inclusions that are known to be present in spent fuel. The ^{99}Tc release rate from the ATM-103 fuel ranged from $1-6 \times 10^{-4}$/d, which was an order of magnitude larger than theirs, but our rates for the ATM-106 fuel were similar to theirs. Since release and reaction for the ATM-106 fuel has been slower than that for the ATM-103 fuel, this latter result may indicate that oxidation of the spent fuel enhances the release of technetium.

The ^{99}Tc release fractions for the ATM-103 fuel were two orders of magnitude larger than those reported by Wilson (3), which ranged from $1-9 \times 10^{-4}$. His fractions were similar to the fractions for the ATM-106 test, except that in our last test interval our fraction rose to 10^{-2}, which may again indicate the importance of oxidation.

Wilson (3) measured release fractions for ^{129}I of 1×10^{-4} in his third cycle but 3×10^{-3} in his first cycle. For both fuels, our fractions at 120 days and 275 days were one to two orders of magnitude larger than Wilson's; our release fractions at 581 days were $2-4 \times 10^{-3}$. Our large initial release fractions may reflect the release of ^{129}I from the gap and grain boundaries, while later release fractions may indicate the release of ^{129}I from the grains in the matrix.

In flow-through tests (4) at 25°C, which separated the effects of gap and grain boundary inventory from that of the uranium matrix, the rates (fraction/day) of technetium and strontium release for the matrix were of the same order of magnitude as the uranium rate (1×10^{-5}/d); the fractional cesium release rate was about twice the uranium rate. If release rates scale with temperature, then at 90°C, one would expect a uranium release rate of ~6×10^{-4}/d.

Our rates for the ATM-103 fuel at the 581-day time interval were: ^{137}Cs, 2 x 10^{-6}/d; ^{238}U, 2 x 10^{-7}/d; ^{90}Sr, 3 x 10^{-6}/d; ^{99}Tc, 6 x 10^{-4}/d; and ^{129}I, 2 x 10^{-5}. If one speculates that at 581 days, release is primarily from the uranium matrix, and that Gray's (4) results are representative of matrix dissolution, then our technetium release may reflect the magnitude of matrix dissolution under our test conditions. Since most of the dissolved uranium appears to form alteration products (1), a substantial amount of strontium and cesium may also be found in the alteration products. We hope to confirm this hypothesis when we characterize the alteration products on the fuel.

CONCLUSIONS

Since the fuels in our tests have undergone significant alteration since the 581-day time interval, the magnitude of the radionuclide source term in these tests is clearly a function of several parameters including time. The following preliminary conclusions are drawn from our results. Further data and interpretation of the results will be presented elsewhere.

In general, congruent release of the radionuclides with uranium was not noted during the first 581 days of reaction. An exception was the ^{239}Pu release from the ATM-106 fuel. The uranium release fractions were much lower than those for the other reported radioisotopes. Since macroscopic evidence for the formation of alteration products was found after the 581-day time interval, the release results may indicate that the fuel matrix dissolved congruently under the conditions of our test, but, because of the low water inventory in the drip tests, many of the radionuclides were reprecipitated on the fuel or the Zircaloy fuel holder. Only those isotopes with very high solubilities in acidic solutions, were found in the leachate collected in the test vessel.

The different release fractions observed for the different radioisotopes suggest that the four fission products (Cs, Sr, Tc, I) are affected differently by the conditions, i.e., water chemistry, etc., present in these tests. The cumulative and 581-day interval ^{90}Sr release fractions were comparable to the ^{137}Cs release fractions for both fuels. The ^{99}Tc release fractions were two orders of magnitude larger than the ^{137}Cs release fractions. The larger ^{99}Tc release fractions for the ATM-103 fuel may be due its to more rapid oxidation. The cumulative ^{129}I release fractions were two orders of magnitude larger than the ^{137}Cs release

fractions for both fuels. Release in the earlier reaction intervals, which had the highest ^{139}I release fractions, may be dominated by release from the gap and grain boundaries. Later release fractions may be dominated by release from the UO_2 matrix. The large fractional releases for ^{99}Tc may then reflect actual matrix dissolution under the conditions present in our tests. These results would then suggest that uranium release rates do not reflect matrix dissolution, nor the release rate of highly soluble species. This observation may impact some of the assumptions made concerning the magnitude of the source term in performance assessments studies.

ACKNOWLEDGMENTS

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Table 1. Total Mass[a] of Elements Collected in Leachate and Acid Strip Solutions

Fuel	Total Reaction Time, d	Mass, g								
		^{238}U	^{239}Pu	^{237}Np	^{241}Am	^{244}Cm	^{137}Cs	^{90}Sr	^{99}Tc	^{129}I
ATM-106	113	1E-4	8E-7	7E-8	2E-7	3E-8	3E-7	1E-7	7E-8	3E-5
	271	1E-3	3E-6	4E-7	1E-6	2E-7	1E-5	1E-6	9E-7	4E-5
	482	5E-5	3E-7	3E-8	5E-8	6E-9	7E-6	4E-8	4E-7	3E-7
	581	9E-6	1E-9	8E-10	5E-9	2E-9	1E-6	8E-8	1E-5	1E-6
ATM-103	120	4E-4	1E-7	4E-6	1E-5	7E-7	7E-6	6E-6	3E-5	2E-5
	275	4E-5	1E-7	1E-8	7E-8	2E-9	1E-6	1E-7	1E-5	9E-6
	482	6E-5	7E-8	4E-10	4E-7	2E-9	5E-7	3E-7	4E-5	4E-7
	581	2E-4	7E-9	5E-9	8E-8	4E-9	1E-6	8E-8	4E-5	4E-7

[a]Mass values are listed for each time interval.

Table 2. Fractional Releases of Isotopes: Spent Fuel Drip Tests

| | ATM-103 | | | ATM-106 | | |
Isotope	Total Reaction Time, d	Fractional Release[a]	Release Rate,[b] fraction/d	Total Reaction Time, d	Fractional Release	Release Rate, fraction/d
^{137}Cs	120	7E-4	1E-5	113	4E-5	1E-6
	275	2E-4	1E-6	271	2E-3	1E-5
	482	9E-5	4E-7	482	1E-3	5E-6
	581	2E-4	2E-6	581	2E-4	2E-6
^{238}U	120	5E-5	4E-7	113	2E-5	2E-7
	275	5E-6	3E-8	271	1E-4	9E-7
	482	8E-6	4E-8	482	7E-6	4E-8
	581	2E-5	2E-7	581	1E-6	1E-8
^{239}Pu	120	3E-6	3E-8	113	2E-5	2E-7
	275	3E-6	2E-8	271	8E-5	5E-7
	482	2E-6	9E-9	482	8E-6	4E-8
	581	2E-7	2E-9	581	3E-8	3E-10
^{90}Sr	120	2E-2	2E-4	113	4E-4	3E-6
	275	4E-4	2E-6	271	3E-3	2E-5
	482	9E-4	4E-6	482	9E-5	4E-7
	581	3E-4	3E-6	581	2E-4	2E-6
^{99}Tc	120	4E-2	3E-4	113	7E-5	6E-7
	275	1E-2	1E-4	271	9E-4	6E-6
	482	5E-2	2E-4	482	4E-4	2E-6
	581	6E-2	6E-4	581	1E-2	1E-4
^{129}I	120	9E-2	8E-4	113	1E-1	9E-4
	275	5E-2	3E-4	271	2E-1	1E-3
	482	2E-3	1E-5	482	1E-3	6E-6
	581	2E-3	2E-5	581	4E-3	4E-5

[a]Interval fraction is the ratio of material released in an interval to that originally in the spent fuel sample.
[b]Rate is the ratio of the interval fraction divided by the length of the time interval.

Table 3. Comparison Release Fractions after 581 Days of Reaction

Species	ATM-103		ATM-106		Ratio 106/103[a]
	Cumulative Fraction	Species/U	Cumulative Fraction	Species/U	
^{137}Cs	1E-3	12.5	3E-3	30	3
^{238}U	8E-5	1	1E-4	1	1.25
^{239}Pu	8E-6	0.1	1E-4	1	1.25
^{90}Sr	2E-2	250	4E-3	40	0.2
^{99}Tc	2E-1	2500	1E-2	100	0.05
^{129}I	1E-1	1250	3E-1	3000	3

Species	ATM-103		ATM-106		Ratio 106/103
	Interval[b] Fraction	Species/U	Interval Fraction	Species/U	
^{137}Cs	2E-4	10	2E-4	200	1
^{238}U	2E-5	1	1E-6	1	0.5
^{239}Pu	2E-7	0.01	3E-8	0.03	0.15
^{90}Sr	3E-4	15	2E-4	200	0.5
^{99}Tc	6E-2	3000	1E-2	1000	0.16
^{129}I	2E-3	2	4E-3	100	2

[a]Ratio of the cumulative fractions for the two fuels.
[b]The 581-day interval's release fraction.

Table 4. Comparison of Experimental Conditions for Spent Fuel Tests

Fuel Type	Burnup, (MW•d/kg U)	Groundwater	pH	Temp., °C	Experimental Conditions	Reference
PWR/BWR	43/42	J-13 like	8	20-25	Static, 200 mL, >1 yr, oxid.	1
PWR	30	J-13	8	85	Static, 250 mL, 150 d cycles, oxid.	2
PWR[a]	30/45	Carbonate	8	25	Flow-through, 150 d, ≥0.2 mL/min, oxid.	3
PWR[a]	30/45	EJ-13	<4-7	90	Drip, 0.75 mL/3.5 d, >581 d, oxid.	b

[a]Same fuels were used.
[b]This study.