

CORROSION TESTS OF LWR FUELS – NUCLIDE RELEASE

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Corrosion Tests of LWR Fuels – Nuclide Release

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ABSTRACT

Two BWR fuels [64 and 71 (MWd)/kgU], one of which contained 2% Gd, and two PWR fuels [30 and 45 (MWd)/kgU], are tested by dripping groundwater on the fuels under oxidizing and hydrologically unsaturated conditions for times ranging from 2.4 to 8.2 yr at 90°C. The ^{99}Tc , ^{129}I , ^{137}Cs , ^{97}Mo , and ^{90}Sr releases are presented to show the effects of long reaction times and of gadolinium on nuclide release. This investigation showed that the five nuclides at long reaction times have similar fractional release rates and that the presence of 2% Gd reduced the ^{99}Tc cumulative release fraction by about an order of magnitude over that of a fuel with a similar burnup.

INTRODUCTION

A potential site for the U.S. high-level waste repository is in the hydrologically unsaturated volcanic tuff beds at Yucca Mountain, Nevada. To define the source term, the release behavior of different types of spent fuels under hydrologically unsaturated and oxidizing conditions is needed. For over eight years, PWR fuels with burnups of 30 and 45 MWd/kgU have been tested under hydrologically unsaturated and oxidizing conditions. Both fuels oxidized and formed alteration phases in less than two years; the phase composition depends on the presence of large amounts of silicate in the groundwater.

To examine possible effects of burnable poisons on nuclide release behavior, two BWR fuels, one containing Gd, were placed under test conditions in late 1998. The radionuclide release data for the first 2.4 yr of reaction of the two fuels is summarized to show differences due to the presence of Gd. Of particular interest are the release behaviors of ^{99}Tc and ^{129}I , which are the primary contributors to the dose rate at the Yucca Mountain site boundary for storage times up to 40,000 yr, and ^{90}Sr , which “monitors” the corrosion of the fuel matrix [1].

EXPERIMENTAL DETAILS

Some characteristics of the four fuels under test are listed in table I. Additional information is found in the references cited. The PWR fuels are lower burnup fuels, 30 and 45 (MWd)/kg U; the BWR fuels, are higher burnup, 71 and 64 (MWd)/kg U.

Table I. Characteristics of four fuels being tested.

Fuel	Fuel Type	Burnup (MWd/kgU)	Fission Gas Release (%)	Gadolinium (%)
ATM-103 ^a	PWR	30	0.25	---
ATM-106 ^b	PWR	45	11	---
ATM-109A ^c	BWR	71	4.4	---
ATM-109C ^c	BWR	64	3.5	2

^a Reference 2

^b Reference 3

^c Reference 4

The test configuration is designed to expose an 8-g fuel sample in the form of fragments to humid air and to a twice-weekly injection of simulated groundwater (“EJ-13”). Details of the test configuration are described elsewhere [5].

Water from well J-13 near Yucca Mountain, which has a chemistry representative of the saturated zone below Yucca Mountain, Nevada, is conditioned for eighty days at 90°C with crushed core samples of Topopah Spring tuff. The resulting liquid, which is designated EJ-13, has a pH of 8.4 to 8.6.

The fuel fragments are placed in a Zircaloy-4 holder having a retainer with 10- μ m-diameter holes at its base, except at the 7.7 and 8.2 yr test intervals, when a gold retainer with 200- μ m-diameter holes is used. The fuel holders are housed in type-304L stainless steel vessels. At the start of each test interval, the vessel contains approximately 5 mL of EJ-13. Every 3 to 4 days, approximately 0.75 mL of EJ-13 is injected onto the fuel. At six-month intervals, the tests are interrupted to remove the leachate. The test vessel is cooled and opened, and the fuel holder is removed from the vessel. The reacted fuel is examined visually and photographed to qualitatively determine the degree of corrosion and look for evidence of alteration phase formation. The fuel holder is then placed in a clean vessel and the test is resumed.

The leachate is removed from the used vessel and the interior of the vessel is acid-stripped to collect nuclides fixed on the walls. Aliquots of the leachate and the acid-strip solution are analyzed by high-resolution gamma spectroscopy to determine ¹³⁷Cs and by inductively coupled plasma-mass spectroscopy (ICP-MS) to determine ⁹⁹Tc, ⁹⁰Sr, ¹²⁹I, ¹⁵⁷Gd, and ⁹⁷Mo. The analytical accuracy is estimated to be ± 20 to $\pm 50\%$ depending on the nuclide. The Gd release is below ICP-MS detection limits at all but the first test interval for the ATM-109C fuel, which is consistent with retention of Gd.

A nuclide that is entrained by fluid from the fuel holder is defined as being released. The release includes the nuclides in the leachate solution, in colloids suspended in the leachate, and fixed on the vessel interior surfaces; the latter are recovered through an acid strip of the vessel interior. Radionuclides that form alteration phases on the fuel fragments or are sorbed by fuel fragments, alteration phases, or the fuel holder are not included in the total release. The release of each nuclide is normalized to the nuclide content in a fuel sample. The latter is obtained from ORIGEN code calculations for ATM-103 and from analyses of samples similar to those under test for ATM-109A and ATM-109C. The release fraction, R, is

$$R = \frac{(\text{g nuclide in the leachate} + \text{g nuclide in the acid-strip})}{(\text{g nuclide/g fuel}) (\text{g sample})} \quad (1)$$

The cumulative fraction is the sum of the nuclide release in sequential test intervals. The release rate is the release fraction R divided by the duration in days of a test interval.

DISCUSSION

⁹⁹Tc, ¹²⁹I, ¹³⁷Cs, ⁹⁷Mo, and ⁹⁰Sr Release in ATM-103 and ATM-106 Tests

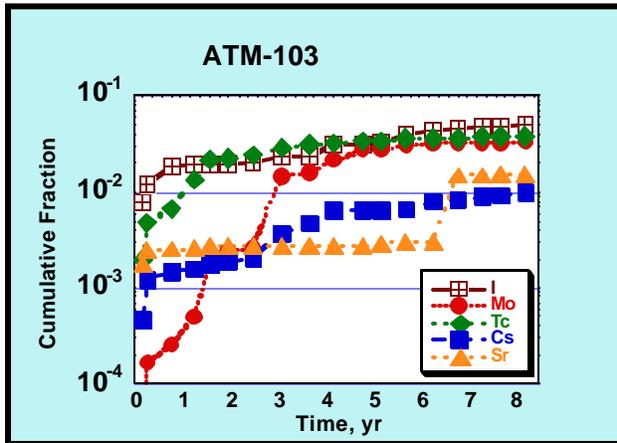


Figure 1. The ATM-103 ¹²⁹I, ⁹⁷Mo, ⁹⁹Tc, ¹³⁷Cs, and ⁹⁰Sr cumulative release fractions

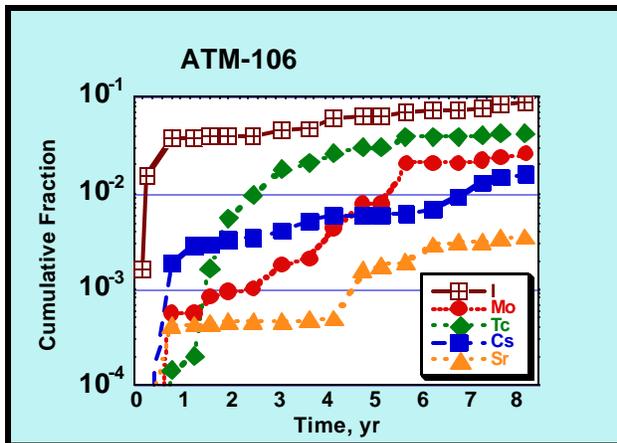


Figure 2. The ATM-106 ¹²⁹I, ⁹⁷Mo, ⁹⁹Tc, ¹³⁷Cs, and ⁹⁰Sr cumulative release fractions

Figures 1 and 2 summarize the cumulative release fractions of ^{129}I , ^{97}Mo , ^{99}Tc , ^{137}Cs , and ^{90}Sr over 8.2 years of reaction for the ATM-103 and ATM-106 tests, respectively. For the two PWR fuels, a general corrosion reaction occurs at the fuel surface [6]. As the fuel reacts and dissolves, over 95% of the uranium is precipitated as uranyl alteration phases on the fuel surface. Nuclides, which are soluble under unsaturated and oxidizing conditions, are released to the leachate. As the reaction progresses, the contribution of the matrix to nuclide release is expected to dominate, whereas at early reaction times, the contribution to radionuclide release from the grain boundaries may dominate.

To evaluate the nuclide release rate at long reaction times, a linear least squares fit was done for each nuclide in figures 1 and 2 for the period between 6.2 and 8.2 years. The slope of each fit, in units of mass fraction per year, and the fitting parameter R^2 , are summarized in table II.

Table II. ATM-103 and ATM-106 release rates between 6.2-8.2 yr. Slopes are derived from the linear least squares fit of the cumulative release fractions for the time period between 6.2 and 8.2 yr.

Nuclide	ATM-103 (fraction/yr)	R^2	ATM-106 (fraction/yr)	R^2
^{129}I	0.0034	0.93	0.0082	0.92
^{99}Tc	0.0010	0.91	0.0019	0.95
^{97}Mo	0.0007	0.91	0.0026	0.89
^{137}Cs	0.0009	0.98	0.0050	0.97
^{90}Sr	0.0003 ^a	0.97	0.0003	0.96

^aFor the period between 6.8 to 8.2 yr.

The rates of release of the different nuclides vary within a factor of 10 for ATM-103 and within a factor of 30 for ATM-106. For a given nuclide, the rates of release vary within a factor of two to five. There is less variation in the rate of release of a given nuclide for two different PWR fuels than in the rate of release of several nuclides of a given fuel.

Note the similar fractional release rates for ^{99}Tc and ^{97}Mo , which are consistent with their release being from corroded epsilon phase particles in the fuel matrix. After more than eight years of reaction the fractional release rates of ^{129}I , ^{137}Cs , and ^{90}Sr are in the order $^{129}\text{I} > ^{137}\text{Cs} > ^{90}\text{Sr}$, which suggests that either there is preferential release of ^{129}I for more than eight years or that there is retention of some of the ^{137}Cs and the ^{90}Sr in alteration phases. Despite the noted differences in the nuclide release rates, the trend in the long-term release rates of the five nuclides suggests that matrix corrosion is becoming ever more important in controlling nuclide release rates.

Gadolinium's effect on nuclide release

The cumulative release fractions of ^{137}Cs , ^{90}Sr , ^{99}Tc , ^{97}Mo , and ^{129}I during the first 2.4 yr of reaction are shown in figures 3 and 4 for ATM-109A and ATM-109C, respectively. The ^{129}I cumulative release fractions for both fuels are similar in magnitude as are the ^{90}Sr cumulative release fractions for both fuels, (i.e. the ^{129}I and ^{90}Sr releases are not affected by the presence of 2% Gd). In contrast, the ATM-109C ^{137}Cs cumulative release fraction is ten times larger than that of ATM-109A; however, most of the difference is due to a very large ^{137}Cs release for the ATM-109C fuel at the first test interval. The two nuclides that appear to be affected at each test interval by the presence of Gd are ^{97}Mo and ^{99}Tc . After 2.4 yr, the ATM-109A ^{97}Mo and ^{99}Tc cumulative release fractions are over an order of magnitude larger than the corresponding ATM-109C cumulative release fractions.

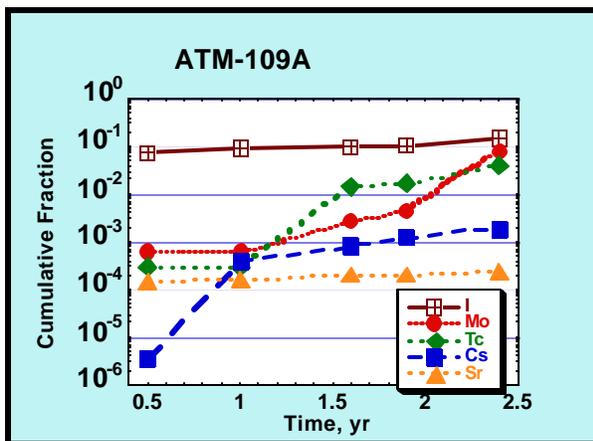


Figure 3. The ATM-109A ^{129}I , ^{97}Mo , ^{99}Tc , ^{137}Cs , and ^{90}Sr cumulative release fractions

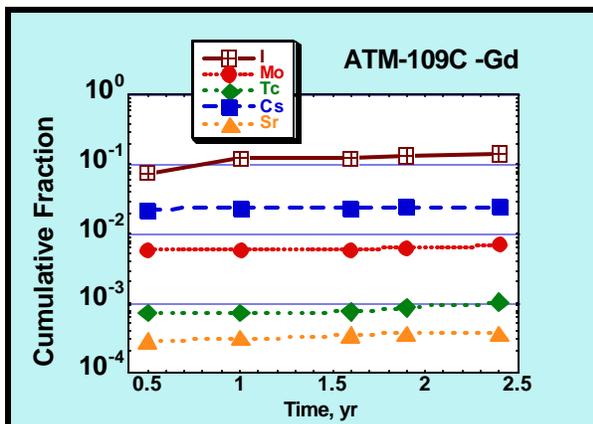


Figure 4. The ATM-109C ^{129}I , ^{97}Mo , ^{99}Tc , ^{137}Cs , and ^{90}Sr cumulative release fractions

As seen in figure 5, the ATM-103, ATM-106, and ATM-109A ^{99}Tc cumulative release fractions are similar in magnitude at 2.4 yr, but all three are at least an order of magnitude larger than the cumulative release fraction of the ATM-109C fuel, which contains Gd. In effect, a

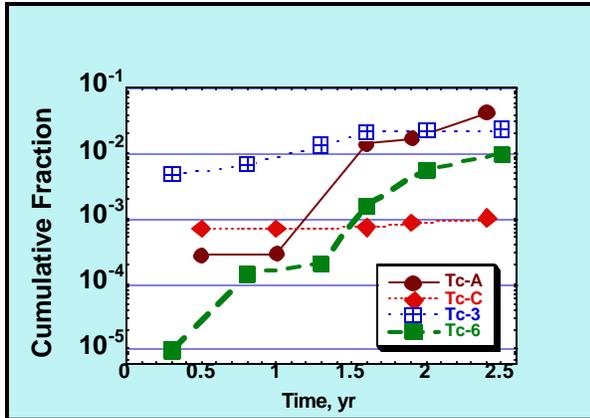


Figure 5. The ATM-109A, ATM-109C, ATM-103, and ATM-106 ^{99}Tc cumulative release fractions

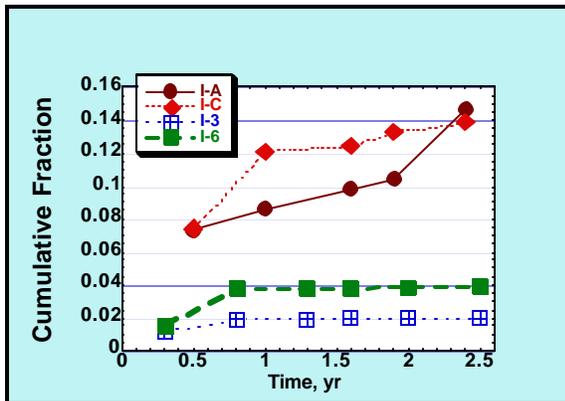


Figure 6. The ATM-109A, ATM-109C, ATM-103, and ATM-106 ^{129}I cumulative release fractions

significant reduction in the ^{99}Tc release is found in the presence of Gd.

Figure 6 shows that the ^{129}I cumulative release fractions of both BWR fuels, which have burnups of 64 and 71 (MWd)/kgU, are similar. The BWR ^{129}I cumulative release fractions at 2.4 yr are ten times larger than the ^{129}I cumulative release fractions of the lower burnup PWR fuels, ATM-103 (30 (MWd)/kgU) and ATM-106 (45 (MWd)/kgU). The larger BWR ^{129}I cumulative release fractions compared to the smaller PWR ^{129}I cumulative release fractions suggest that a larger fraction of the ^{129}I may be available for release from the gap and/or grain boundary regions of the BWR fuels. Whether this is a characteristic of BWR fuels cannot be ascertained given the limited number of fuels tested.

Post-irradiation examination of other irradiated urania-gadolinia fuels [7] showed no fuel

restructuring, but rods with 3.4% fission gas release had more interconnected porosity than those with 1.5% fission gas release. Thus, there may be a potential pathway along the interconnected porosity for water to react with the urania-gadolinia fuel. Although the cumulative release fraction data suggest that the presence of Gd may limit ^{99}Tc release, its presence has a limited effect, if any, on ^{129}I release.

Long-term data are needed before the nuclide release fractions can be interpreted in terms of the possible effects of Gd on the rate of fuel matrix corrosion, grain boundary corrosion, or retention of radionuclides in alteration phases. Resolution of the cause of the lower ^{99}Tc release is important because ^{99}Tc is the main contributor to the dose rate for the resident population at the boundary of the potential Yucca Mountain repository at storage times of less than 40,000 years.

CONCLUSIONS

The study has shown that the trend in the long-term release rates of ^{129}I , ^{97}Mo , ^{99}Tc , ^{137}Cs , and ^{90}Sr for the PWR fuels is consistent with matrix corrosion becoming ever more important in controlling nuclide release rates. There is less variation in the rate of release of a given nuclide for two different PWR fuels than in the rate of release of several nuclides of a given fuel. After more than eight years of reaction the fractional release rates of ^{129}I , ^{137}Cs , and ^{90}Sr are in the order $^{129}\text{I} > ^{137}\text{Cs} > ^{90}\text{Sr}$, which suggests that either there is preferential release of ^{129}I for more than eight years or that there is retention of some of the ^{137}Cs and the ^{90}Sr in alteration phases. For the BWR fuels, the presence of 2% Gd reduces the ^{99}Tc cumulative release fraction by over an order of magnitude compared to the ^{99}Tc release of a fuel without Gd but with a similar burnup. The BWR fuels, which have a high burnup [64 and 71 (MWd)/kgU], have ten times larger ^{129}I release fractions than the ^{129}I release fractions for lower burnup PWR fuels [30 and 45 (MWd)/kgU].

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REFERENCES

1. R. S. Forsyth, L. O. Werme, "Spent Fuel Corrosion and Dissolution," *J. Nucl. Mat.* 190, 3-19 (1992).
2. R. J. Guenther et al., Characterization of Spent Fuel Approved Testing Material - ATM-103, Pacific Northwest Laboratory Report PNL-5109-103 (1988).
3. R. J. Guenther et al., Characterization of Spent Fuel Approved Testing Material - ATM-103, Pacific Northwest Laboratory Report PNL-5109-106 (1988).
4. S. Vaidyanathan et al., "High Burnup BWR Fuel Pellet Performance," *Proc. 1997 Intl. Topical Meeting on LWR Fuel Performance* 471-477 (1997).
5. P. A. Finn et al., "Colloidal Products and Actinide Species in Leachate from Spent Nuclear Fuel," *Radiochimica Acta* 66/67, 189-195 (1994).
6. P. A. Finn, R. J. Finch, E. C. Buck, J. K. Bates, "Corrosion Mechanisms of Spent Fuel under Oxidizing Conditions," *MRS Symp. Proc.* 506, 123 (1998).
7. L. W. Newman, Qualification of the B&W Mark B Fuel Assembly for High Burnup and Development of an Advanced Design Incorporating Urania-Gadolinia, Babcock and Wilcox Report DOE/ET/34212-57 (1991).