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ABSTRACT

The release fractions of the five elements in the ε-phase (^{99}Tc, ^{97}Mo, Ru, Rh, and Pd) as well as that of ^{238}U are reported for the reaction of two oxide fuels (ATM-103 and ATM-106) in unsaturated tests under oxidizing conditions. The ^{99}Tc release fractions provide a lower limit for the magnitude of the spent fuel reaction. The ^{99}Tc release fractions indicate that a surface reaction might be the rate controlling mechanism for fuel reaction under unsaturated conditions and the oxidant is possibly H_2O_2, a product of alpha radiolysis of water.

INTRODUCTION

A potential site for the U.S. high-level waste repository is in the volcanic tuff beds at Yucca Mountain, Nevada, a hydrologically unsaturated zone. To qualify this site for licensing, information on the corrosion behavior of spent fuel under unsaturated and oxidizing conditions is needed. Performance assessment calculations are needed to license this site and radionuclide release rates are needed as the source term in these calculations. Laboratory testing of spent fuel under unsaturated conditions, i.e., those with limited water, provides the information necessary to determine the magnitude of the potential radionuclide source term at the boundary of the fuel's cladding after the cladding has failed and water as vapor or liquid contacts the fuel.

Tests that simulate the presence of limited water and oxidizing conditions are in progress to evaluate the long-term behavior of commercial spent nuclear fuel at 90°C. In the tests, a thin film of water, which is supplied by saturated water vapor at 90°C, continuously contacts and reacts with the fuel. Water that is dripped on the fuel provides sufficient liquid to transport reacted material beyond the fuel holder.

The purpose of the experiments is to determine the relationship between the rate of fuel alteration and the release rate of different radionuclides under unsaturated conditions. Therefore, the extent of spent fuel alteration, e.g. dissolution, under unsaturated conditions is assessed as is the effect of fuel alteration on radionuclide release. This paper examines the reaction of spent fuel, specifically the ε-phase (Tc, Mo, Ru, Rh, Pd) in high drip rate tests for the first 3.1 years of reaction. The release of ^{99}Tc appears to be a marker for matrix dissolution. The magnitude of the ^{99}Tc interval release fractions as a function of time suggest that the spent fuel reaction is controlled by a surface reaction in which oxidants supplied from alpha radiolysis of water may play an important role.

EXPERIMENTAL

Samples of two pressurized-water-reactor fuels, ATM-103, [1], and ATM-106 [2], with burnups of 30 and 45 MW•d/kg U, respectively, are used in the tests. The grain sizes are 17-20 and 6-16 μm, respectively. The fuel samples, 7-8.5 g each, are fragments with masses in the range of 0.3 to 1.2 g. The average geometric surface area of the fragments is 2.1 x 10^{-4} m^2/g. The measured percent distribution of ^{99}Tc [3] for both fuels in the gap, grain-boundary, and fuel matrix is <0.1, <0.1, and >99.8%, respectively. The reported distribution [4] of ^{99}Tc in ε-phase particles in ATM-103 is as follows. Most ε-phase particles are within the grains and their diameter varies as a function of radial position, being 20 nm diameter at the pellet edge and 50-100 nm diameter in the pellet mid- and center sections. Particles on the grain boundaries are ≤1 μm diameter and are located in the mid- and center sections. For ATM-106 fuel [5], the ε-phase particles within the grains are 20 to 100 nm diameter in the mid- section. Near the pellet center 3 to 10 μm diameter particles were found along the grain boundaries. These particles also contained gas bubbles and secondary precipitates.

The test procedures used for the high drip rate tests have been given previously [6]. Groundwater from well J-13 near Yucca Mountain was equilibrated for eighty days at 90°C with crushed core samples of Topopah Spring tuff and is designated EJ-13. Solution compositions were analyzed with inductively coupled plasma-mass spectrometry (ICP-MS) in the single standard scan mode with an indium internal standard. For samples after 2.5 years of reaction, bismuth is used as the internal standard for actinides. This technique provides accurate results (±15%) for the isotopes in the middle mass range (80-160 atomic mass units), but results for the actinides and the light elements might vary by ±50%. Individual mass concentrations for duplicates of the different samples varied by 0.6-2% for concentrations above 0.5 ppb and by 13-17% below 0.5 ppb. The uncertainties in the ICP-MS data are a maximum of ±50% depending on radionuclide concentration. The assignment of a mass unit to a particular isotope is done by comparison with the isotopic distribution given in results [1,2] from ORIGEN code calculations.

Terminology — The term "interval" refers to the total number of days during which spent fuel is reacted in a given sequential reaction period. The "interval release fraction" for a given radionuclide is defined as the ratio of the mass of radionuclide collected in a given interval, i.e., the sum in the leachate and the acid strip, divided by the amount of the same radionuclide calculated [1,2] to be in the fuel. The material in alteration products, adsorbed on the Zircaloy holder or on the spent fuel is not included. The radionuclide with the largest interval release fractions provides a lower estimate for the spent fuel reaction rate. The interval release fractions are used to compare the releases for various radionuclides for the same interval and for the same test for different intervals. The "cumulative release fraction" is the sum of the interval release fractions.

RESULTS

The fractional releases of ^{99}Tc, ^{97}Mo, and ^{238}U are reported as is the physical appearance of the fuel. Parameters that may control spent fuel reaction and radionuclide release are discussed.

The ε-Phase — Table I provides a summary for successive reaction intervals of the release behavior of the five elements in the ε-phase (Tc, Mo, Ru, Rh, Pd) for tests with ATM-103. The information includes: (1) the released amounts (μg) for the isotope of each element with minimal interference from other elements; (2) the total released amount of each element based on the measured isotope and the element's isotopic distribution; (3) the calculated amount of the ε-phase that reacted based on the ^{99}Tc release and the distribution [1,5] of each element in the ε-phase; and (4) the amount of each element that was retained on the spent fuel based on the difference between the material released (column 2) and that calculated to have reacted (column 3). For ATM-103 at each reaction interval, and for ATM-106, ^{99}Tc was the dominant element released; 10% of the Mo and only trace amounts of the other three elements were detected.

Reaction and dissolution of the ε-phase particles with later incorporation of the non-Tc elements in alteration products is indicated by three additional pieces of data. First, large amounts of Mo were found in a cesium uranyl oxide that was attached to a reacted fuel grain [7]. Second, 1-2 wt% amounts of Ru and Mo were incorporated into a uranyl silicate alteration product, while only ppm of Tc were found. Third, corrosion of ε-phase particles as fuel grains dissolve is evident in Fig. 1 in which individual ε-phase particles <10 nm diameter are shown.

Since the ε-phase particles are homogeneously dispersed in the ATM-103 fuel matrix [1] and both fuels have similar ^{99}Tc release behavior, the use of ^{99}Tc release fractions as an indicator of the minimum extent of the reaction of the fuel matrix is proposed. Observations of ^{99}Tc release behavior in saturated tests were as follows. Forsyth and Werme[8] found that after 2.7 years of reaction under oxidizing conditions ^{99}Tc was the only radionuclide whose release fraction had remained constant. They suggested that ^{99}Tc was oxidized and released as the matrix around the ε-phase particles reacted. Wilson[9] suggested that Tc was oxidized prior to release.

Reaction Progress — Uranium interval release fractions were examined to determine the extent of uranium retention based on ^{99}Tc release fractions as a measure of the extent of fuel reaction. The interval release fractions for ^{99}Tc, ^{97}Mo, and ^{238}U (Table II), and their cumulative release fractions (Table III) indicate that for both fuels, cumulative ^{238}U release fractions were smaller by several orders of magnitude than the ^{99}Tc cumulative release fractions; and, the difference increased as reaction time increased. Alteration products incorporated over 99% of the reacted uranium; a minor amount may have sorbed on the Zircaloy fuel holder.

Table I. Disposition of Elements in ε-Phase for Selected Intervals — ATM-103 High Drip Test

Isotope	Measured[a] Released Element[b] (μg)	Calculated Released Element[c] (μg)	Calculated Amount Reacted (μg)	Element[d] Retained (mass %)
		0.3 Years Reaction		
^{99}Tc	20	20	20	—
^{97}Mo	0.9	4	50	93
^{101}Ru	0.02	0.07	50	100
^{103}Rh	0.6	0.6	7	92
^{105}Pd	0.04	0.1	0.5	75
		0.8 Years Reaction		
^{99}Tc	10	10	10	—
^{97}Mo	0.05	2	30	94
^{101}Ru	6E-5	2E-4	40	100
^{103}Rh	0.06	0.06	5	99
^{105}Pd	ND[e]	ND	0.3	100
		1.6 Years Reaction		
^{99}Tc	40	40	40	—
^{97}Mo	8	30	100	77
^{101}Ru	2E-3	7E-3	200	100
^{103}Rh	0.02	0.02	20	100
^{105}Pd	2E-3	9E-3	1	100
		2.1 Years Reaction		
^{99}Tc	5	5	5	—
^{97}Mo	2	10	20	44
^{101}Ru	8E-5	2E-4	20	100
^{103}Rh	7E-3	7E-3	3	100
^{105}Pd	8E-3	0.03	0.2	83
		2.5 Years Reaction		
^{99}Tc	10	10	10	—
^{97}Mo	1	6	30	82
^{101}Ru	6E-4	2E-3	30	100
^{103}Rh	0.02	0.02	5	100
^{105}Pd	5E-3	0.02	0.3	94

[a]Measured mass in leachate. Values were rounded to one significant figure.
[b]The isotopic distribution for each element and the mass of the measured isotope was used to determine the total mass released.
[c]For ATM-103, the wt%s in the ε-phase are: [1]: Tc(11.8); Mo(39.9); Ru(42.3); Rh(5.6); Pd(0.4). The released ^{99}Tc was the basis for the reacted amount of a given element.
[d]This is the minimum amount retained and is based on ^{99}Tc and its wt% in the ε-phase.
[e]ND = not detected.

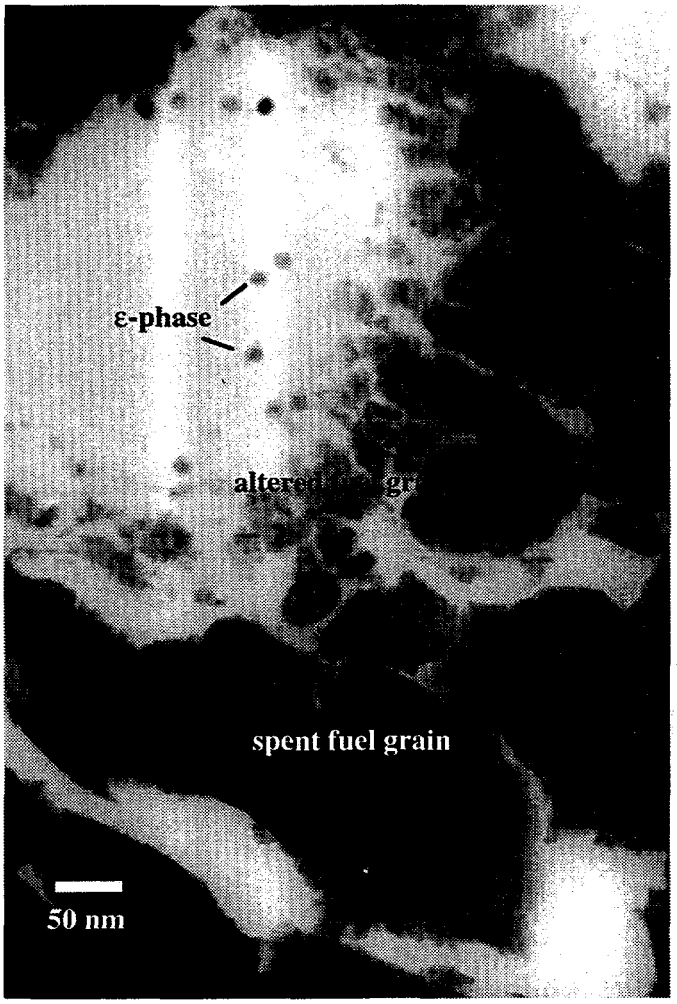

Fig. 1.

Image of corroded pit in altered fuel grain with reacted ε-phase particles at fuel surface.

Table II. Interval Release Fractions — High Drip Rate Tests

Time (yr)	Interval Release Fraction		
	^{99}Tc	^{97}Mo	^{238}U
ATM-103			
0.2	2E-3	1E-5	3E-5
0.3	3E-3	2E-4	2E-5
0.8	2E-3	9E-5	5E-6
1.3	7E-3	2E-4	9E-6
1.6	8E-3	1E-3	2E-5
2.1	1E-3	4E-4	2E-6
2.5	2E-3	3E-4	8E-7
3.1	5E-3	1E-2	3E-6
ATM-106			
0.2	0	0	1E-9
0.3	1E-5	6E-6	2E-5
0.8	1E-4	6E-4	2E-4
1.3	6E-5	9E-6	8E-6
1.6	1E-3	3E-4	1E-6
2.1	4E-3	9E-5	1E-7
2.5	4E-3	9E-5	3E-7
3.1	8E-3	8E-4	3E-7

Table III. Cumulative Release Fractions — High Drip Rate Tests

	^{99}Tc	^{97}Mo	^{238}U
1.6 Year			
ATM-103	2E-2	2E-3	9E-5
ATM-106	2E-3	8E-4	2E-4
2.5 Year			
ATM-103	2E-2	3E-3	9E-5
ATM-106	1E-2	1E-3	2E-4
3.1 Year			
ATM-103	3E-2	1E-2	9E-5
ATM-106	2E-2	2E-3	2E-4

The ^{97}Mo cumulative release fractions increased as a function of reaction time and were also orders of magnitude larger than the ^{238}U cumulative release fractions. No definitive trends can be suggested at this time on the basis of available data.

The ^{99}Tc interval release fractions for both fuels were the same order of magnitude 1×10^{-3} to 8×10^{-3} after the 1.6 year reaction interval, although earlier the release fractions for the ATM-106 fuel had been smaller, i.e., an induction period had been required for the ATM-106. Since as reaction time increased, the ^{99}Tc interval release fraction was unchanged, this suggests that reaction and dissolution occurs only at the outer grain surface, i.e., the effective surface area for radionuclide release is unchanged although oxidation occurs along the grain boundaries.

Alteration Products — Yellow alteration products were observed on the spent fuel surface after 2.5 years of reaction [7]. Examination of the fuel fragments after 3.7 years of reaction(leachate results are not yet available) indicated that there were two layers of light-yellow alteration products. The outer layer could be easily manipulated with a fine tungsten needle but a thinner layer immediately adjacent to the fuel was denser and adhered tenaciously to the surface. Electron microscopy showed that both layers are uranyl silicates structurally related to uranophane type minerals.

A fragment of reacted ATM-103 fuel was extremely friable and disintegrated under examination producing four smaller pieces and black fuel grains . One of the smaller pieces was reduced to a smear of black-like powder. This behavior indicated that reaction had proceeded down the grain boundaries and into individual grains after less than four years at 90°C. The disintegration of the ATM-103 fragment was similar to fuel behavior in oxidation tests done at 200°C [10] in the presence of water vapor. There, schoepite formed in grain boundaries, but, did not impede further reaction progress throughout the grain-boundary network. Since our tests use a silicate-groundwater, yellow uranyl silicates form on the fuel surface, but our analyses to date, show no reaction products in the grain boundaries.

DISCUSSION

The ε-Phase — The presence of soluble forms of ^{99}Tc and ^{97}Mo in the leachate (pH 7 at room temperature) indicated that the fuel matrix surrounding the ε-phase particles had dissolved exposing them to an oxidizing environment. Kleykamp [11] noted that complete dissolution of the ε-phase occurred with boiling nitric acid but that long reaction times were required, i.e. for particles 0.15 to 1.5 μm in diameter, eight hours was needed for complete dissolution. Thus, ε-phase particles (<1 nm to 100 nm diameter) could react and release ^{99}Tc in each 0.5 year reaction interval, but larger particles (1 μm) might not completely react (see Fig. 1).

Water vapor at 90°C supplies a continuous thin film of water on the spent fuel surface in each test, a film that may be over 50 nm thick. Allen noted that the primary yield of H_2O_2 from alpha radiolysis of water was 1.2 times that from gamma radiolysis of water [12]. The H_2O_2 is produced in dense tracks within the first 30 μm (the alpha particle range) of the fuel surface. Shoesmith et al. [13] noted that for reaction of unirradiated UO_2 at pH 9.5 with an alpha source 30 μm away, the redox potential was 0.11 V versus a saturated calomel electrode, a value similar

to that in an equivalent H_2O_2 solution or in a saturated O_2-containing solution. (The corresponding corrosion potential would be -0.14 V.)

The corrosion potential in the unsaturated tests was estimated by considering the Eh required to form soluble ions of Tc, Mo, Ru, Rh, and Pd based on Eh/pH diagrams [14]. For Mo and Tc at pH 7, a minimum Eh of 0 and 0.3 V, respectively, is needed to form TcO_4^- and $HMoO_4^{2-}$, whereas for Pd and Ru, a minimum Eh of 0.5 and 0.6 V, respectively, is needed. For Rh, a soluble form is noted only at pH 4 and an Eh of 0.65 V. If one assumes that these diagrams are appropriate for the conditions of the unsaturated tests, then the oxidation potential at the fuel surface may be as high as 0.6 V since Ru dissolved and was incorporated into alteration products.

An analogue for the behavior of the elements in the ε-phase is the behavior of these elements at the Oklo natural reactor site in Gabon, Africa. Although the natural reactor had an upper temperature of 450°C, out-of-pile experiments showed that the ε-phase can form at temperatures as low as 450°C [15] and thus it was probably present at Oklo. Most of the soluble radionuclides (Tc, Cs, Mo, and Ru) were diminished in the reactor zones with over 50% of the Tc and Ru mass missing. The three release mechanisms suggested [16] were: fission recoil, dissolution of the uraninite grains, and solid-state diffusion. Curtis and Gancarz [17] proposed that oxidative dissolution of the uraninite was caused by water radiolysis in the reactor zones that led to the production of species that oxidized uraninite, dissolved the ε-phase, and permitted transport of soluble species from the reactor zone.

Potential Mechanism in the Spent Fuel Reaction — Grambow et al. [18] found that for unirradiated UO_2 the reaction rate depended only on the concentration of the oxidant and concluded that even under an initially anoxic conditions, the spent fuel dissolution process was oxidative. Therefore, the local steady-state concentration of oxidants at the surface is of key importance and provides an upper limit on reaction.

In the unsaturated tests, there is a steady-state concentration of H_2O_2, as well as other radiolysis products, in the thin film of water at the fuel surface. Reaction with the oxidant occurs at the surface and proceeds down the grain boundaries as shown by the friable nature of the ATM-103 fragment. The alteration products do not form a protective layer that decreases fuel dissolution since the ^{99}Tc interval release fractions were constant over 3.1 years of reaction. Since ppm amounts of ^{99}Tc were present in the alteration phases, the fuel reaction rate is higher than that measured from ^{99}Tc interval release fractions.

If one accepts ^{99}Tc release as a measure of fuel reaction, then it can be used to examine five suggested mechanisms [19]. These are: (1) solubility limited dissolution of alteration products, (2) transport of oxygen to the UO_2 surface, (3) growth of alteration products, (4) the rate of formation of oxidants by radiolysis, and (5) a surface reaction.

For solubility limited dissolution to control rate, radionuclide release has to decrease significantly as a function of time. This might control ^{238}U release but not its reaction since ^{99}Tc release fractions did not decrease as a function of time.

For oxygen transport to control rate, a diffusion process has to be established. Diffusion does not appear to control rate since the best fit of ^{99}Tc cumulative release was found with a linear dependence on time (see Fig. 2).

For the growth of alteration products to control rate, release should be constant or should increase as the surface area increased, i.e., as grain boundaries opened. For both unsaturated tests, no increase was noted in the ^{99}Tc release fractions as a function of time although the surface area increased, instead, the ^{99}Tc release fractions for ATM-103 were the same order of magnitude during 3.1 years of reaction. Thus, this mechanism does not appear to control the rate.

The rate of formation of oxidants by radiolysis also does not appear to control rate since Grambow et al. noted [18] that even in a reducing environment radiolysis supplied sufficient oxidants to oxidize spent fuel. However, if the rate of a surface reaction is faster than the rate of oxidant formation, this mechanism could be rate controlling.

Since the reaction rate, defined by the ^{99}Tc interval release fractions, remained constant with time a surface reaction appears to be the rate controlling mechanism. Support for control of the rate by a surface reaction was provided by Ericksen et al who observed in tests [20] with spent fuel that nearly 100% of the oxidants from radiolysis was taken up by the fuel surface.

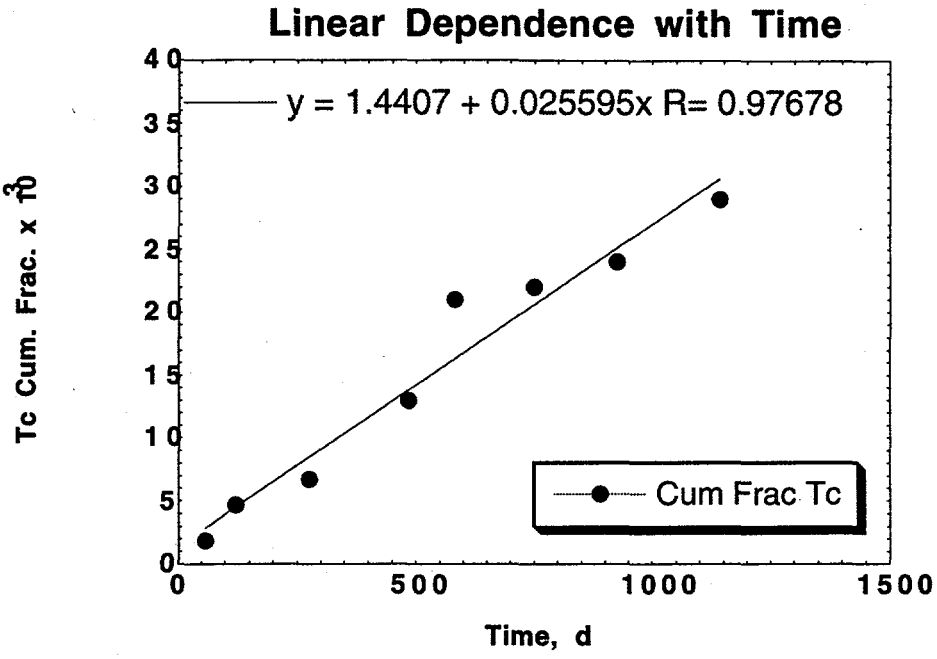

Fig. 2. The linear time dependence of ^{99}Tc cumulative release fractions in the ATM-103 high drip rate test. (Equation is the linear least squares fit.)

CONCLUSIONS

Our conclusions for the high drip rate tests are these. (1) The ^{99}Tc interval release fractions provide a lower limit for the spent fuel reaction. (2) The friability of a spent fuel fragment after less than four years provides support for the use of ^{99}Tc release fractions as a lower limit for reaction. (3) Oxidation of the ε-phase suggests that the oxidizing potential at the fuel surface may be as high as 0.6 V. The oxidant may be H_2O_2, a product of alpha radiolysis of water. (4) The non-variability of the ^{99}Tc release fractions over 3.1 years of reaction provides support for a surface reaction as the rate-controlling mechanism for fuel reaction under unsaturated conditions.

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