

PNL-SA--18263

DE91 005177

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November 1990

Received by OSTI
DEC 18 1990

Paper for presentation at
Materials Research Society Symposium
Scientific Basis for Nuclear Waste Management XIV
Boston, Massachusetts
November 26-29, 1990

Work supported by
the U.S. Department of Energy
Office of Civilian Radioactive Waste Management
under Contract DE-AC06-76RLO 1830

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RESULTS FROM LONG-TERM DISSOLUTION TESTS USING OXIDIZED SPENT FUEL

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ABSTRACT

Two semi-static dissolution tests using oxidized PWR spent fuel specimens are being conducted under ambient hot cell conditions in Nevada Test Site J-13 well water and unsealed fused silica vessels. The test specimens were oxidized at 250°C in air to bulk oxygen-to-metal (O/M) values of 2.21 and 2.33. Following an initial 191-day test cycle, the specimens were restarted in fresh J-13 water for a second long-term test cycle. Results through the first 40 months of Cycle 2 are compared with results from similar tests at 25°C and 85°C using unoxidized spent fuel specimens.

Increased concentrations of U, Am, Cm and Np were measured in 0.4- μ m filtered samples from the oxidized fuel tests compared to the unoxidized fuel tested at 25°C; Pu concentrations were not affected by the fuel oxidation state. Most of the Am and Cm, and a portion of the Pu, measured in 0.4- μ m filtered samples was removed by 2-nm filtration. Fission product release results were normalized to specimen inventories and reported as fractional release. No attempt was made to normalize the data to surface area. Initial ^{99}Tc release was greatly increased, and prolonged increases in the fractional release rates of ^{99}Tc and ^{129}I occurred as a result of fuel oxidation. Fractional release rates for ^{137}Cs and ^{90}Sr from oxidized fuel eventually decreased to levels similar to those observed with unoxidized fuel after equivalent testing times, suggesting that matrix dissolution rates normalized to fuel mass were not increased as a result of oxidation.

INTRODUCTION

Spent fuel disposed of in a geological site located above the water table in the unsaturated zone, such as the Yucca Mountain site under investigation in the state of Nevada, may be exposed to oxidizing conditions (air) for extended periods prior to contact by water. Under such conditions spent fuel may potentially be degraded or altered as a result of oxidation of the UO_2 fuel matrix. With the exception of ^{14}C , which may be transported in the vapor phase, dissolution and transport as a result of groundwater flow is generally accepted as the primary mechanism by which radionuclides could be released from a repository to the biosphere[1]. Laboratory studies of spent fuel dissolution and radionuclide release behavior have typically been conducted using unoxidized specimens prepared from freshly sectioned fuel rod segments. Two scoping tests using air oxidized spent fuel specimens were started in August 1986 in support of the Waste Package Task of the U.S. Department of Energy Nevada Nuclear Waste Storage Investigations (NNWSI)^(b). The purpose of these tests was to provide preliminary data on the dissolution behavior of oxidized fuel prior to testing with fuel specimens from long-term low-temperature spent fuel oxidation tests [2], which were in progress at that time and are continuing as of this reporting.

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- (a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.
(b) Renamed the Yucca Mountain Project, the Waste Package Task is managed by Lawrence Livermore National Laboratory.

TEST DESCRIPTION

The oxidized fuel scoping tests were similar to the NNWSI Series 2 Bare Fuel Tests [3], which were conducted at ambient hot cell temperature in 250 mL of Nevada Test Site J-13 well water. Ambient hot cell temperature varied over a range of about 22°C to 28°C depending on time of day and time of year and is estimated to have averaged 25°C. Turkey Point fuel particles were oxidized in air at 250°C for time periods of 45 hours and 116 hours producing test specimens having bulk oxygen-to-metal (O/M) stoichiometries of 2.21 and 2.33 based on weight gain. Burnup was approximately 27,000 MWd/MTU and fission gas release was reported to be 0.3% for this fuel. The fuel particles were screened to +10 mesh prior to test specimen preparation, and geometric surface area is estimated at about 2 cm²/g before oxidation.

Microstructures of fuel particles removed during Cycle 2 of each test are shown in Figure 1. The particle from the O/M = 2.33 test appears to be relatively uniformly oxidized. The surface of this ceramographic section was double impregnated to reduce grain pull out during preparation. Only a few of the larger grains in the higher magnification photographs of this particle show unoxidized UO₂ visible as a darker gray phase at the center of the grains. The bright areas in the lower magnification photograph of the particle from the O/M = 2.21 test are areas where the UO₂ fuel matrix did not oxidize. The higher magnification composite strip shows fracturing and pull out of the more oxidized grains near the particle edge. A larger average grain size in this particle may indicate that the particle was from the center of a fuel pellet where a higher irradiation temperature induced grain growth, although other examinations of fuel from this fuel assembly have suggested variations in the as-fabricated fuel microstructure. The highest magnification photograph of this particle shows oxidation occurring initially along the grain boundaries forming oxidized shells surrounding unoxidized UO₂ grain cores. Oxidation appears to have caused grain cracking and the loss of several loose grains during sample preparation.

Solution samples (20 mL) were periodically removed from the vessels for analysis and the solution sample volume replaced with fresh J-13 well water to maintain a constant water volume during the tests. The first test cycle was terminated after 191 days, and the fuel specimens were restarted in new vessels and fresh J-13 well water for a second test cycle. Cycle 2 was not terminated and is still in progress as of this reporting. Samples were divided to provide unfiltered, 0.4- μ m filtered and 2-nm filtered aliquots for analysis. The unfiltered aliquots were typically analyzed for pH, U, ²³⁹⁺²⁴⁰Pu, ²⁴⁴Cm and ¹²⁹I. The 0.4- μ m filtered aliquots were typically analyzed for U, ²³⁹⁺²⁴⁰Pu, ²⁴¹Am, ²⁴⁴Cm, ²³⁷Np, ¹³⁷Cs, ⁹⁰Sr and ⁹⁹Tc. The 2-nm filtered aliquots of Cycle 2 samples were typically analyzed for ²³⁹⁺²⁴⁰Pu, ²⁴¹Am and ²⁴⁴Cm. Nonradiochemical inorganic analyses were also performed on 0.4- μ m filtered aliquots by inductively coupled plasma (ICP) emission spectrometry, ion chromatography, and for HCO₃⁻. J-13 well water is a relatively pure low-ionic-strength groundwater containing about 170 μ g/mL dissolved NaHCO₃, 12 μ g/mL Ca and 30 μ g/mL Si as its major dissolved components. Very little change in the J-13 water nonradiochemical inorganic analyses occurred during the 25°C tests and pH remained in a range of 7.9 to 8.5. Partial precipitation of Ca and Si and reduction in bicarbonate concentration was noted in the 85°C test.

Results from the two oxidized fuel dissolution tests are compared to results from the 25°C Series 2 and 85°C Series 3 tests using unoxidized (O/M = 2.00) Turkey Point fuel specimens from the same fuel assembly [3,4]. The two oxidized fuel specimens were tested in unsealed fused silica vessels identical to those used in the Series 2 tests, whereas the 85°C Series 3 test was conducted in a sealed stainless steel vessel. The oxidized fuel specimens weighed approximately 10 g each. The Series 2 specimen weighed about 27 g and the Series 3 specimen weighed about 85 g. The Series 2 and 3 specimens were unscreened and included the empty cladding hulls; the oxidized fuel tests did not include cladding. The Series 2 specimen ran for

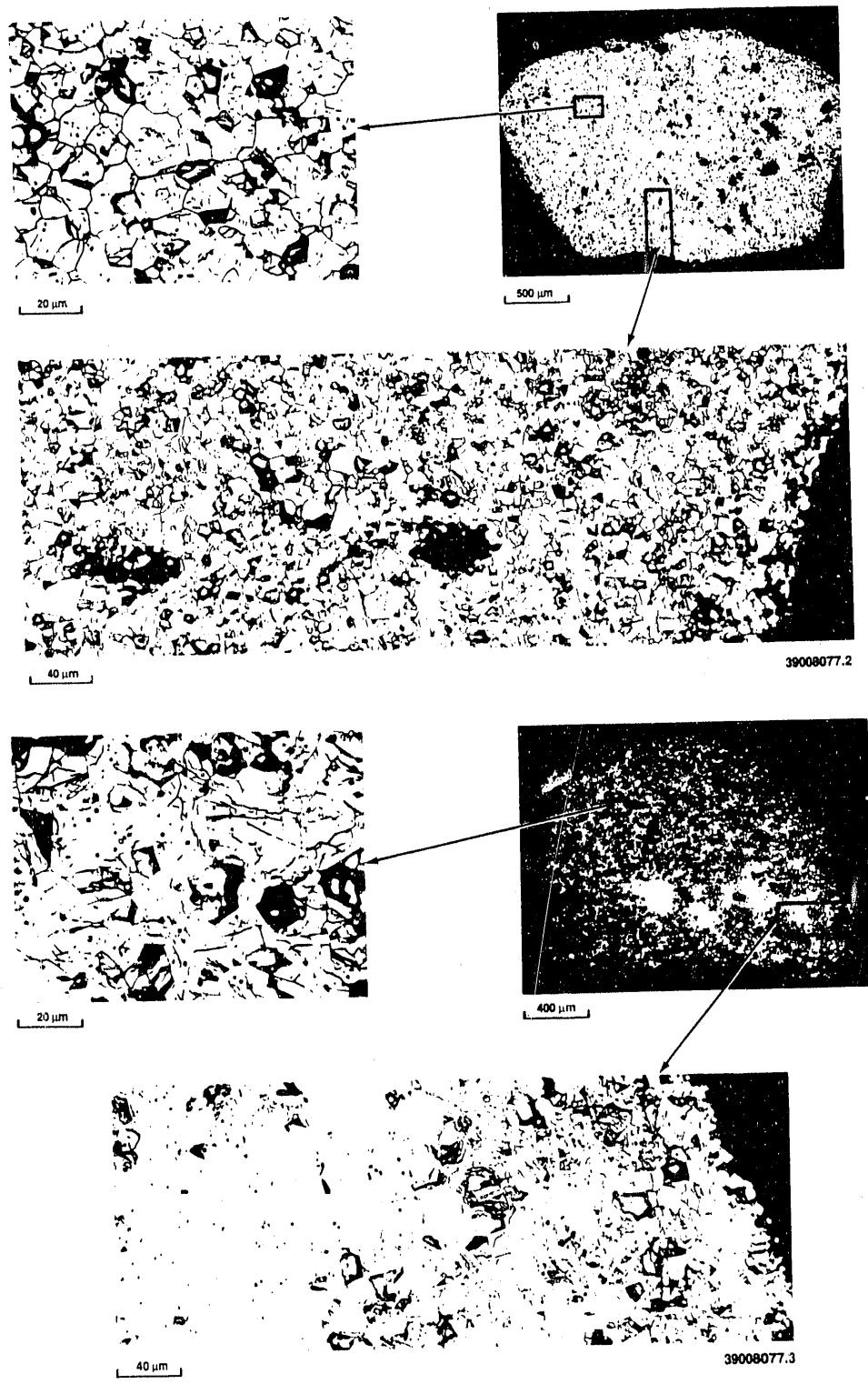


Figure 1. Ceramographic Sections of Fuel Particles Removed after the 1196-day Cycle 2 Solution Samples. Particle from the O/M = 2.33 test shown above, and particle from the O/M = 2.21 test shown below. Etched 85% H₂O₂ - 15% H₂SO₄.

five test cycles of 181, 195, 224, 240, and 132 days. The Series 3 specimen ran for three test cycles of 174, 181, and 97 days.

RESULTS AND DISCUSSION

The actinides (U, Np, Pu, Am and Cm) have low solubilities in neutral aqueous solutions and reached solubility-limited steady-state concentrations during the tests. The solution concentrations of U and activities of $^{239+240}\text{Pu}$ and ^{241}Am measured in 0.4- μm filtered samples are plotted in Figure 2. Maximum U concentrations in the oxidized fuel tests reached about 20 $\mu\text{g}/\text{mL}$ during Cycles 1 and 2, decreasing to about 10 $\mu\text{g}/\text{mL}$ later in Cycle 2. With unoxidized fuel at 25°C, U concentrations decreased from about 4 $\mu\text{g}/\text{mL}$ during Cycle 1 to about 1 $\mu\text{g}/\text{mL}$ at the end of Cycle 5, with lower values measured in the initial samples from each of the later test cycles. Lower U concentrations in the range of 0.1 to 0.2 $\mu\text{g}/\text{mL}$ in the 85°C test are attributed to precipitation secondary uranium phases. Uranophane, a calcium-uranium-silicate phase, was identified in the 85°C test [4]. Fuel oxidation did not affect the 100-200 pCi/mL $^{239+240}\text{Pu}$ activities measured in 0.4- μm filtered samples at 25°C. However, $^{239+240}\text{Pu}$ activities decreased to less than 1 pCi/mL in the 85°C test. A similar effect of temperature was observed on ^{241}Am activities. Activities measured for ^{244}Cm were very similar to those measured for ^{241}Am in all samples.

Approximate concentrations at which the actinide elements appeared to stabilize during later test cycles are compared in Table I for the 0.4- μm and 2-nm filtrations. These data suggest that about 40-80% of the Pu and more than 90% of the Am measured in 0.4- μm filtered samples from the 25°C tests were associated with colloids. Lower concentrations and reduced effects of filtration in the 85°C test suggest that formation of non-suspended stable secondary phases was favored over colloid formation at the higher temperature.

Fission product release data were normalized to specimen inventory to obtain fractional release results. Results for ^{137}Cs , ^{90}Sr , and ^{99}Tc are plotted in Figure 3. Each plotted data point includes the inventory fraction in the 250 mL of water in the test on the sampling day plus the inventory fractions calculated to have been removed in prior samples from the test cycle. Cumulative release is plotted for Cycles 2-5 of the 25°C and Cycles 2 and 3 of the 85°C unoxidized fuel tests. Fractional releases measured during Cycle 1 are given in Table II. The effect of temperature on initial releases of ^{137}Cs appeared to be greater than the effect of oxidation. However, initial ^{137}Cs release may have been reduced in the oxidized

Table I. Actinide Concentrations, Log($\mu\text{g}/\text{mL}$)

Actinide	Filter	O/M=2.33	O/M=2.21	O/M=2.00	O/M=2.00
		25°C	25°C	25°C	85°C
U	0.4 μm	1.1	1.1	0.0	-0.8
	2 nm	--	--	0.0	-0.8
Pu	0.4 μm	-2.7	-2.7	-2.7	-5.0
	2 nm	-3.3	-3.5	-2.9	-5.0
Am	0.4 μm	-4.1	-4.0	-4.7	-7.0
	2 nm	-5.4	-5.4	-6.1	-7.3
Np	0.4 μm	-2.6	-2.6	-3.2	-3.8
	2 nm	--	--	-3.2	<-3.6

Estimated steady-state concentrations based on Cycle 2 data for the oxidized fuel tests, Cycles 2-5 of the O/M = 2.00 25°C test and Cycles 2 and 3 of the O/M = 2.00 85°C test.

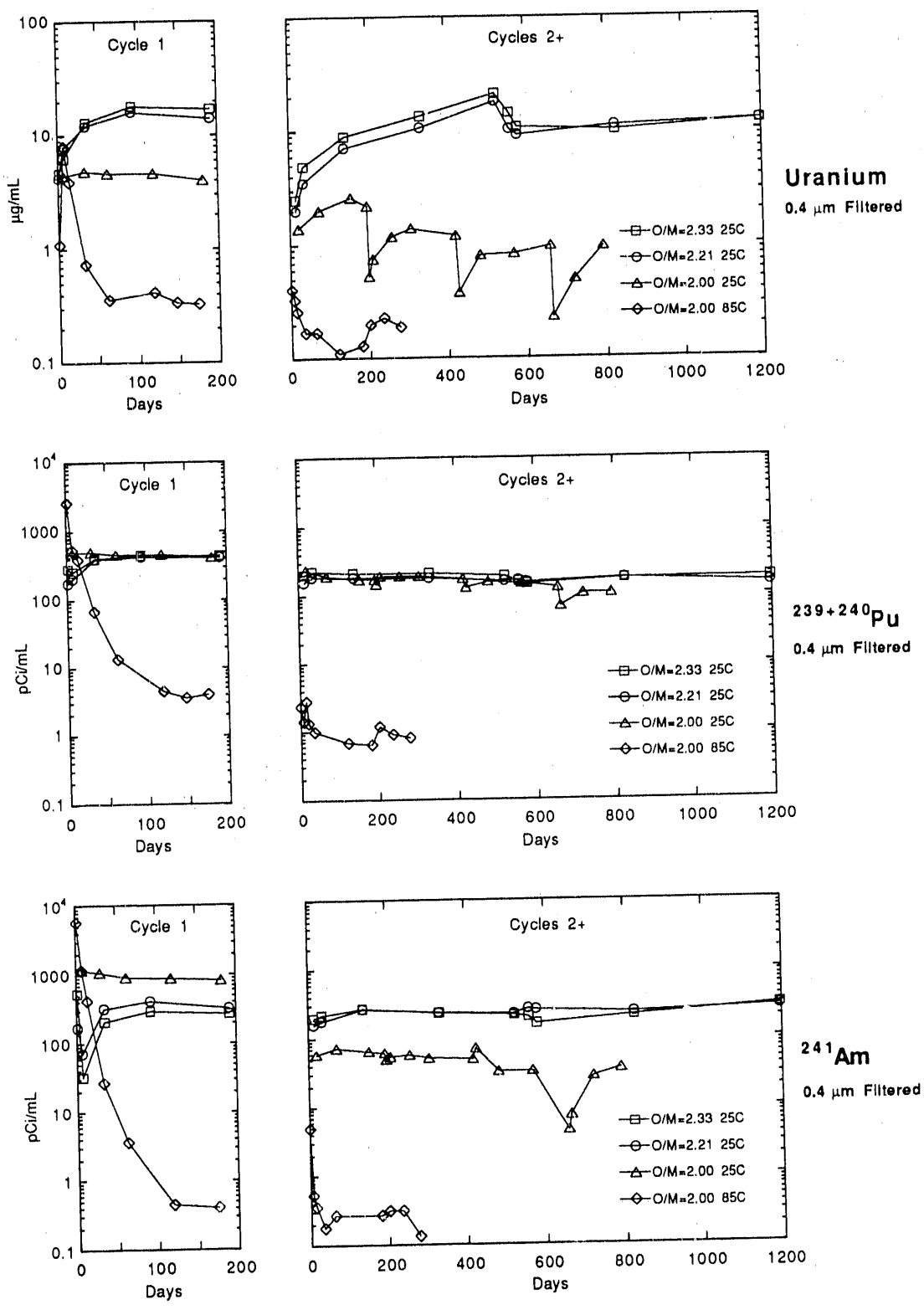


Figure 2. Uranium Concentrations and Activities of $^{239+240}\text{Pu}$ and ^{241}Am Measured in 0.4- μm Filtered Solution Samples. Mass basis conversion factors are $1 \text{ pCi } ^{239+240}\text{Pu} = 1.1 \times 10^{-5} \mu\text{g Pu}$ and $1 \text{ pCi } ^{241}\text{Am} = 3.6 \times 10^{-7} \mu\text{g Am}$.

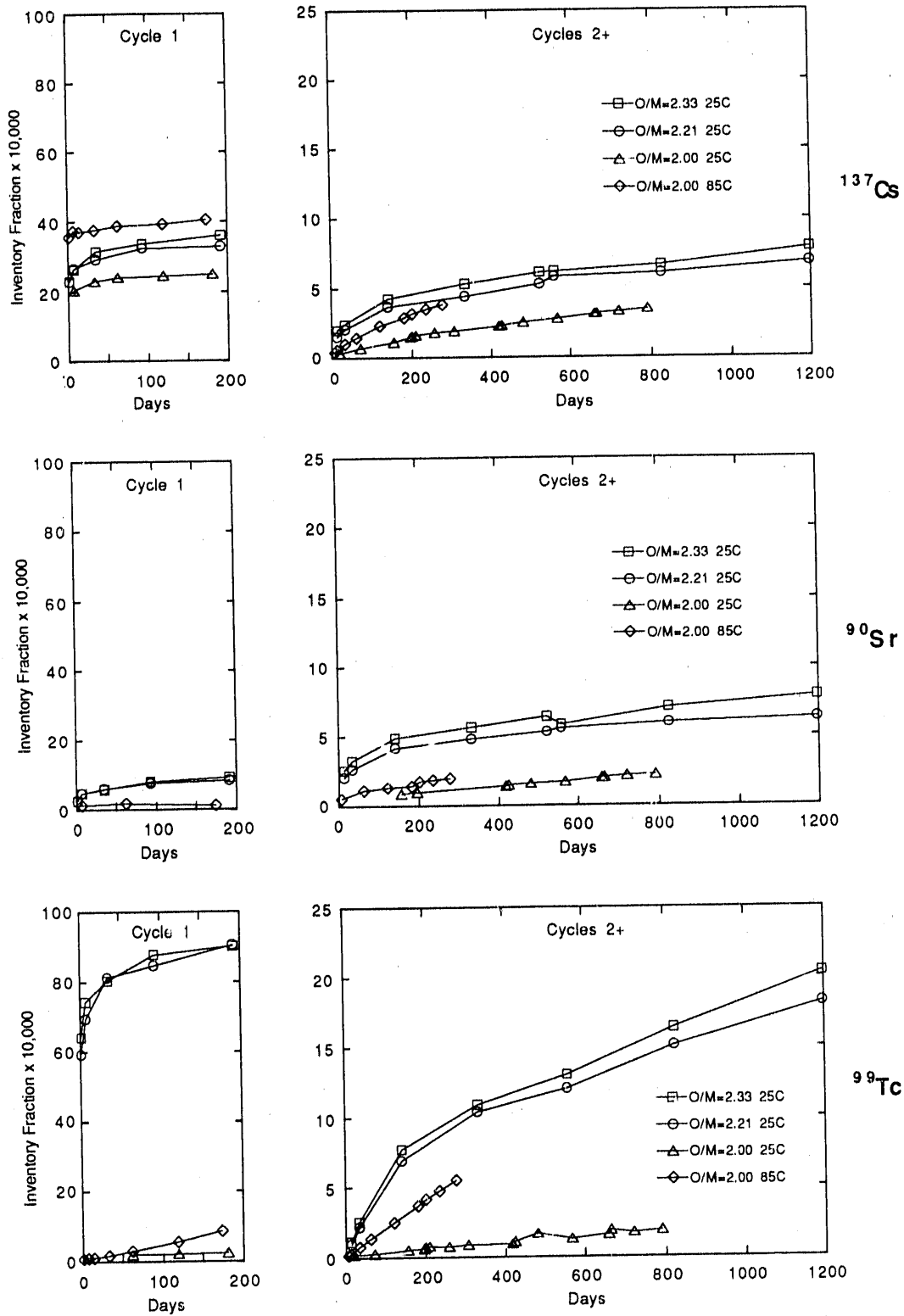


Figure 3. Fractional Releases of Soluble Fission Product Radionuclides ¹³⁷Cs, ⁹⁰Sr, and ⁹⁹Tc

fuel tests due to the lack of cladding in these tests. Initial ^{129}I release was increased both as a result of oxidation and increased temperature. ^{90}Sr was not measured during Cycle 1 of the 25°C unoxidized fuel test and precipitated during the 85°C tests.

The substantial increase in ^{99}Tc release as a result of oxidation is thought primarily to be the result of increased release from grain boundaries. Gray and Strachan [5] have also observed increased ^{99}Tc release from separated fuel grains as a result of fuel oxidation, indicating that the increased release is not entirely due to increased water penetration of grain boundaries as a result of oxidation. One hypothesis is that Tc is concentrated in finely dispersed metallic phases present at the grain boundaries that are insoluble in their reduced state, and that the solubility of these particles is also increased when the fuel is oxidized.

Table III gives annual fractional release rates for the soluble fission product radionuclides during later time periods of the tests after much of the initial enhanced release from exposed gap and grain boundary inventories had been completed. An unexpected result is that the ^{137}Cs and ^{90}Sr fractional release rates in the oxidized fuel tests eventually decreased to levels similar to those observed with unoxidized fuel after equivalent testing times, even though grain boundary opening may have increased wettable fuel surface area as a result of oxidation. If ^{137}Cs and ^{90}Sr release rates are indicative of fuel matrix dissolution rates at later time periods of the tests, these data suggest that inventory normalized matrix dissolution rates were not increased by oxidation, and that matrix dissolution rates normalized to surface area were not increased as a result of oxidation. However, matrix dissolution rates measured in water types such as J-13 well water, which contains dissolved Ca, Si, NaHCO_3 and O_2 , may be ambiguous. Flow-through tests with unirradiated UO_2 in such water types have suggested that the dissolution rate of UO_2 may decrease with time as result of Ca and/or Si incorporation with the UO_2 surface [6].

Table II. Cycle 1 Fractional Releases x 100,000

Nuclide	O/M=2.33 25°C	O/M=2.21 25°C	O/M=2.00 25°C	O/M=2.00 85°C
^{137}Cs	362	330	251	406
^{90}Sr	92	84	--	--
^{99}Tc	903	906	25	88
^{129}I	159	129	29	104

Table III. Annual Fractional Release Rates x 100,000

Nuclide	O/M=2.33 25°C	O/M=2.21 25°C	O/M=2.00 25°C	O/M=2.00 85°C
^{137}Cs	12	11	12	46
^{90}Sr	10	8	8	--
^{99}Tc	44	39	7	73
^{129}I	62*	58*	8	43

Average rates for days 140-1196 of cycle 2 for oxidized fuel tests, cycles 3 through 5 for the O/M = 2.00 25°C test, and cycles 2 and 3 for the O/M = 2.00 85°C test.

* Average for days 0-1196 of Cycle 2.

CONCLUSIONS

Fuel oxidation appeared to cause moderate increases in the eventual steady-state concentrations measured for the actinide elements U, Am, Cm and Np at 25°C. Pu concentration was not affected by fuel oxidation. Am and Cm, and to a lesser extent Pu, appeared to associate with colloids in the 25°C tests. Lower actinide concentrations were generally measured in the 85°C test where kinetic factors appeared to favor formation of nonsuspended secondary phases. Fuel oxidation resulted in a substantial increase in the initial release of ⁹⁹Tc, and in greater fractional release rates for ⁹⁹Tc and ¹²⁹I over the duration of the tests. Fractional release rates measured for ¹³⁷Cs and ⁹⁰Sr in the oxidized fuel tests eventually decreased to levels similar to those measured with unoxidized fuel after equivalent testing times, suggesting that inventory normalized fuel matrix dissolution rates in J-13 well water were not increased as a result of oxidation. Fractional release rates for the soluble fission products ¹³⁷Cs, ⁹⁹Tc and ¹²⁹I from unoxidized fuel increased by factors ranging from about 4 to 10 when temperature was increased from 25°C to 85°C.

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ACKNOWLEDGMENT

This work was performed in support of the Yucca Mountain Project (YMP) and was funded through the YMP Waste Package Task at Lawrence Livermore National Laboratory. The YMP is managed by the Yucca Mountain Project Office of the U.S. Department of Energy (DOE), Nevada Operations Office, under the DOE Office of Civilian Radioactive Waste Management.

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