UCRL- 94633
PREPRINTExperimental Study of the Dissolution
Spent Fuel at 85°C
in Natural Ground WaterC. N. Wilson
H. F. ShawReceived by OST
MAR 02 1987Materials Research Society Symposium
Boston, MASS
December 1-5, 1986

December 1986

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EXPERIMENTAL STUDY OF THE DISSOLUTION OF
SPENT FUEL AT 85°C IN NATURAL GROUND WATER*

CHARLES N. WILSON* AND HENRY F. SHAW**

*Westinghouse Hanford Company, Richland, WA 99352

**Lawrence Livermore National Laboratory, Livermore, CA 94550

ABSTRACT

Semi-static dissolution tests using pressurized water reactor spent fuel rod segments and NMWSI reference J-13 well water in sealed stainless steel vessels at 85°C are being conducted in support of the Waste Package Task of the NMWSI Project. Test specimens include: bare fuel plus the empty cladding hulls, fuel rod segments with artificially induced cladding defects and water-tight end caps, and undefected fuel rod segments with water-tight end caps. The test conditions approximate those expected in the proposed NMWSI Project repository when the waste package has cooled sufficiently to allow water to enter a breached container and contact the fuel rods, some of which may exhibit various degrees of cladding failure. Periodic solution samples (unfiltered and filtered) were analyzed for most radionuclides for which cumulative release limits are listed by the U.S. Environmental Protection Agency. Results from the first six-month cycle of the 85°C tests are presented and are compared with results from the first cycle of a previous test series run at 25°C in fused silica test vessels.

INTRODUCTION

The Nevada Nuclear Waste Storage Investigations (NMWSI) Project is investigating the suitability of the Topopah Spring Tuff at Yucca Mountain, Nye County, Nevada, as a candidate disposal site for high-level nuclear waste. The repository horizon under study is a densely welded devitrified volcanic tuff formation that lies ~200 meters to 400 meters above the water table in the unsaturated zone. The predominant waste form in the repository will be spent LWR fuel either in the form of intact assemblies or consolidated rods and hardware. Contact of the spent fuel by water will not occur until the repository has cooled to below the 95°C boiling temperature at the repository elevation. At that time, which is predicted to be hundreds of years after disposal, a limited quantity of water infiltrating the rock could potentially enter a failed waste container and contact the spent fuel where cladding failures have occurred. Migration of a limited quantity of such water that may become contaminated by contact with a failed waste package is considered to be the most probable mechanism for radionuclide release from the disposal container (with the exception of ¹⁴C, which may be released as gaseous ¹⁴CO₂).

Tests are being conducted under NMWSI-relevant conditions to measure radionuclide release to water from spent fuel specimens with failed cladding. Series 3 of these tests is being conducted at 85°C with NMWSI J-13 well water in sealed stainless steel (SS) vessels. Stainless steel (304L) is the reference NMWSI spent fuel container material and the chemistry of J-13 well water approximates that of the small amount of water that would be expected to infiltrate the repository. Cycle 1 of the Series 3 tests was started in February 1986 and terminated after 174 days. The specimens were then restarted for Cycle 2 with fresh J-13 well water in new 304L SS vessels. Results from Cycle 1 of the Series 3 tests are presented and discussed in this paper. These results are also compared with results from Cycle 1 of the Series 2 tests (run at 25°C in fused silica vessels) to correlate release behavior with temperature and container material.

*Work performed under the auspices of the U.S. Department of Energy
by the Lawrence Livermore National Laboratory under Contract
W-7405-Eng-48.

MASTER

GSC

TEST DESCRIPTION

Four test specimen configurations were used in both the Series 2 and Series 3 tests. The four specimen configurations were:

- Undefected Specimens containing intact cladding and water-tight end fittings.
- Hole Defect Specimens containing two (~ 0.01 in. diameter) laser-drilled holes through the cladding, and water-tight end fittings.
- Slit Defect Specimens containing a machined (~ 0.006 in. by 1 in.) slit through the cladding, and water-tight end fittings.
- Bare Fuel Specimens prepared by axially splitting the cladding and removing the fuel pellet fragments; the empty cladding hulls are included in the test vessel.

Six specimens were prepared for the Series 3 tests: One of each configuration from an H. B. Robinson (hence referred to as HBR) Unit 2 reactor spent fuel rod for testing at 85°C, an additional bare fuel specimen from the HBR rod for testing at 25°C so that the effects of temperature in the sealed SS vessels could be evaluated, and a bare fuel specimen from a Turkey Point (hence referred to as TP) Unit 3 reactor spent fuel rod for testing at 85°C. One specimen of each configuration from both the HBR and TP spent fuels was tested at 25°C in the Series 2 tests. Results from the Series 2 HBR bare fuel test are presented for comparison in this paper. More detailed results from the Series 2 tests are presented in [1-3]. The seven specimens to be discussed in this report are described in Table I.

All test specimens were prepared from five-inch-long fuel rod sections. Both the HBR and TP fuels are low gas release (0.1% to 0.3%) pressurized water reactor (PWR) fuels of ~ 30 MWd/kgU burnup. Additional characterization data for these two fuels are given in [4,5]. The external surfaces of the cladding were decontaminated to less than 50 cps smearable alpha activity before testing to remove residual contamination resulting from specimen preparation and handling in contaminated hot cells. The water-tight end fittings were fabricated from stainless steel vacuum adapters using ethylene propylene O-rings to seal against the cladding. Two test vessel internal configurations were used and are shown in Fig. 1 for the Series 3 tests. The Series 2 tests used fused silica vessels with loose-fitting glass lids and specimen configurations similar to those used in Series 3.

TABLE I: TEST SPECIMENS

<u>Identification*</u>	<u>Description</u>
BF/HBR-3-85	Bare Fuel Specimen/H. B. Robinson-Series 3-Run at 85°C
BF/TP-3-85	Bare Fuel Specimen/Turkey Point-Series 3-Run at 85°C
BF/HBR-3-25	Bare Fuel Specimen/H. B. Robinson-Series 3-Run at 25°C
SD/HBR-3-85	Slit Defect Specimen/H. B. Robinson-Series 3-Run at 85°C
HD/HBR-3-85	Hole Defect Specimen/H. B. Robinson-Series 3-Run at 85°C
UD/HBR-3-85	Undefected Specimen/H. B. Robinson-Series 3-Run at 85°C
BF/HBR-2-25	Bare Fuel Specimen/H. B. Robinson-Series 2-Run at 25°C**

*Identification for reporting, not actual laboratory identification.

**One of eight Series 2 specimens.

In the semi-static testing method used, periodic solution samples were taken during the tests and the sample volume (10 to 30 ml) was replaced with an equal volume of fresh J-13 well water. This method provides radionuclide concentration data as a function of time and simulates the flow-through that may occur in the repository if a failed container were to fill with water. At the end of a test cycle, the specimens' and the apparatus' internal surfaces were rinsed with J-13 well water, and the vessel interior and internal components (less the specimen) were stripped with 8 M HNO₃. The specimens were then restarted in fresh J-13 well water for subsequent test cycles. The periodic solution samples were split into unfiltered, 0.4- μ m filtered, and 18- μ m filtered fractions for analysis. The terminal rinse and the acid strip samples were also analyzed. In addition to solution chemistry and uranium, radionuclides analyzed included ²³⁹⁺²⁴⁰Pu, ²⁴¹Am, ²⁴⁴Cm, ²³⁷Np, ¹³⁷Cs, ¹²⁹I, ¹²⁶Sn, ⁹⁹Tc, ⁹⁰Sr and ¹⁴C.

RESULTS AND DISCUSSION

Uranium concentrations measured in unfiltered periodic solution samples are shown in Fig. 2. The concentration that would result if 10⁻⁵ of the specimen uranium inventory were dissolved in the 250-ml test solution volume is shown for correlation to fractional dissolution. Concentrations measured in filtered sample fractions were not significantly different from those measured in unfiltered fractions. However, the laser-excited fluorescence method used is not sensitive to uranium contained in fine solid particles that may have initially been present in the unfiltered fractions. Uranium concentration peaked early in the Series 3 bare fuel tests at 16 μ g/ml in the BF/HBR-3-85 test (Day 7), at 8.3 μ g/ml in the BF/TP-3-85 test (Day 7), and at 13 μ g/ml in the BF/HBR-3-25 test (Day 1). Uranium concentration then fell by ~1.3 orders of magnitude (to 0.4 μ g/ml on Day 119) in the BF/TP-3-85

Fig. 1. Series 3 Test Configurations. Neg 8600029-1

test, by 1.8 orders of magnitude (to 0.2 $\mu\text{g/ml}$ on Day 62) in BF/HBR-3-25 tests, and by 3.1 orders of magnitude (to 0.012 $\mu\text{g/ml}$ on Day 147) in the BF/HBR-3-85 test. In comparison, uranium peaked at 4.5 $\mu\text{g/ml}$ and decreased to a minimum of 1.2 $\mu\text{g/ml}$ in Cycle 1 of the Series 2 BF/HBR-2-25 test.

The test vessel type appears to be a more significant factor in determining the solution chemistry than either fuel type or test temperature. Table II lists the iron concentrations, measured by inductively coupled plasma (ICP) analysis, of solution samples during the Series 3 tests. Iron began to appear in solution in the 33-day samples from all the bare fuel tests, corresponding to the time when significant reductions in the solution uranium concentrations were occurring in these tests. The only sources of iron in the experiment are the test vessel components. The fact that the bare fuel tests and not the other specimen configurations showed the most significant iron concentrations in solution suggests that corrosion of the weld-sensitized areas of the 304 SS specimen baskets used to hold the fuel fragments was the main source of the iron.

Corrosion of the 304 SS could have affected the solution concentrations of species released from the fuel in two ways: 1) through the production of insoluble iron oxy-hydroxide corrosion products that scavenge or coprecipitate other ions (such as U^{6+}), thus removing them from solution; and 2) through the consumption of oxygen in the sealed test vessel as the solution attempts to equilibrate with the vessel, thus lowering the oxygen potential of the solution. The second possibility actually involves two separate mechanisms, one being the reduction of U, Tc and Pu species in solution to less soluble oxidation states; the other involves a retardation in the dissolution rate itself because of the consumption of dissolved oxygen in the leachant.

The quantities of uranium measured in periodic solution samples, final solution, terminal rinse solution, and terminal acid strip solution are summed in Table III and the total is divided by 10^{-5} of the specimen uranium inventory to calculate fractional release. The measured fractional uranium release in the Series 3 bare fuel tests was ~ 5 times greater at 85°C than at 25°C, with most of the difference being in the quantity of uranium in the terminal acid strip solution. At 25°C, greater fractional release was measured in the Series 2 test than in the Series 3 test. This may be related to the dissolution of more fine particles of fuel or precipitates in the strip sample and/or to the greater air access to the test solution in the Series 2 test. Both Table III and Fig. 2 indicate much less extensive dissolution of fuel contained in defected cladding than with bare fuel particles. In fact, uranium concentrations in neither the slit defect nor hole defects tests were significantly different from those observed in the undefected test during much of the test cycle.

TABLE II. SERIES 3 SOLUTION IRON CONCENTRATION

Test	Iron Concentration ($\mu\text{g/ml}$)*			
	0 Days	33 Days	147 Days	174 Days
BF/HBR-3-85	<0.010	0.136	0.450	0.026
BF/TP-3-85	<0.010	0.142	<0.010	<0.010
BF/HBR-3-25	<0.010	0.125	0.030	0.051
SD/HBR-3-85	<0.010	<0.010	<0.010	<0.010
HD/HBR-3-85	<0.010	0.029	<0.010	<0.010
UD/HBR-3-85	<0.010	<0.010	<0.010	<0.010

*Determined by ICP analysis, 0.4- μm filtered.

Activities of $^{239+240}\text{Pu}$ measured in $0.4\text{-}\mu\text{m}$ filtered solution samples are shown in Fig. 3. Initial activities in the Series 3 bare fuel tests were significantly greater than in the Series 2 test. However, activities decreased to much lower levels by the end of the test cycle in the two 85°C Series 3 bare fuel tests. Quantities of $^{239+240}\text{Pu}$ activity measured in each test are summed in Table IV and fractional releases are calculated. The Series 3 Pu fractional release and percent in solution values were generally similar to those for uranium and show much higher fractional release for bare fuel than for fuel in defected cladding. Note that the fractional release of U is slightly lower than that of Pu for the HBR specimens, but the reverse is true for the TP specimen. This difference may be due to the presence of a more highly oxidized fuel surface for the TP specimen [3]. Solution activity

TABLE III: URANIUM RELEASE DATA (μg)

	BF/HBR -3-85	BF/TP -3-85	BF/HBR -3-25	BF/HBR -2-25	SD/HBR -3-85	HD/HBR -3-85	UD/HBR -3-85
Solution Samples	666	274	522	253	2.03	1.34	1.15
Final Solution [U ($\mu\text{g/ml}$)]	4 (0.016)	115 (0.46)	65 (0.26)	300 (1.2)	2.75 (0.011)	1.75 (0.007)	3.25 (0.013)
Rinse	330	108	396	660	<0.6	66	0.6
Strip	4950	6330	405	2736	30.	4.8	2.4
Total	5950	6827	1388	3949	<35.4	73.9	7.4
$\times 10^{-5}$ Inv.	8.37	9.05	1.83	5.66	0.047	0.10	0.010
% in Solution	11.3	5.7	42.3	14.0	~14	4.2	59.5

Fig. 2. Uranium Measured in Unfiltered Solution Samples.

Fig. 3. $^{239+240}\text{Pu}$ Activities Measured in $0.4\text{-}\mu\text{m}$ Filtered Solution Samples.

TABLE IV: $^{239+240}\text{Pu}$ RELEASE DATA (nCi)

	BF/HBR -3-85	BF/TP -3-85	BF/HBR -3-25	BF/HBR -2-25	SD/HBR -3-85	HD/HBR -3-85	UD/HBR -3-85
Solution Samples	765	85.3	673	41	0.29	0.63	0.04
Final Solution [Pu (ng/ml)]	16.3 (0.27)	2.1 (0.09)	247 (10.4)	28 (1.2)	1.91 (0.08)	0.06 (0.002)	0.08 (0.003)
Rinse	97	24.3	188	254	0.08	0.11	---
Strip	5400	3550	1530	4113	37.3	6.35	7.84
Total	6268	3662	2638	4436	39.6	6.55	7.90
$\pm 10^{-5}$ Inv.	10.45	6.08	4.11	7.18	0.062	0.011	0.013
% in Solution	12.1	2.4	34.9	1.6	5.6	1.4	1.5

data for ^{241}Am and ^{244}Cm were very similar to those plotted in Fig. 3 for Pu, except that Am and Cm activities in the SD/HBR-3-85 test were higher (just above the BF/TP-3-85 data after 119 days) than in the other tests.

Activities of ^{99}Tc measured in unfiltered solution samples are shown in Fig. 4. The 0.4- μm and 18- μm filtered ^{99}Tc activities were essentially identical to the unfiltered activities. The dramatic drop in solution ^{99}Tc activity in the BF/HBR-3-85 test after the 62-day sample is thought to be related to the weld corrosion that appeared to have occurred in this test during this time. Tc was likely initially released as soluble TcO_4^- , which was later either sorbed onto corrosion products or was reduced to a less soluble species as more extensive oxidation of Fe occurred in this test relative to the other tests. Activities of the ^{99}Tc dropped below the detection limit (~ 9 pCi/ml) after 119 days in the four tests showing the lowest activities at 119 days in Fig. 4. Quantities of ^{99}Tc measured in each test and the calculated fractional release are given in Table V. These data indicate preferential Tc release relative to the actinides in all of the bare fuel tests.

Cesium-137 release in the Series 3 tests was essentially identical to that in the Series 2 tests, with about 0.7% of the HBR specimen inventory and about 0.3% of the TP specimen inventory being rapidly released from the bare fuel and defected cladding specimens. Cesium activity was ~ 4 orders of magnitude less in the undefected test, indicating that the end fittings did not leak during the test. The fractional release observed for Cs was the highest of that for any radionuclide measured and is attributed to rapid dissolution of the gap inventory as well as a lesser release of Cs present in the grain boundary inventory. As in Series 2 tests, all of the fission product radionuclides measured appeared to be preferentially released relative to the actinides.

Activities of activation product ^{14}C , measured in solution samples, are plotted in Fig. 5. Inventory of ^{14}C was measured radiochemically on two samples from the HBR fuel rod. Averaging the results of these two measurements gave 0.49 $\mu\text{Ci/g}$ for the fuel and 0.53 $\mu\text{Ci/g}$ for the cladding. The 10^{-5} of specimen inventory in solution level shown in Fig. 5 is based on these values. Lower activities in the BF/HBR-2-25 test relative to the BF/HBR-3-25 test may be explained by loss of ^{14}C as volatile CO_2 from the unsealed Series 2 test vessel. Most of the measured ^{14}C release appears to originate from the fuel or cladding interior in the HBR fuel tests, but a significant release may also originate from the cladding exterior, as indicated by the UD/HBR-3-85 data. The TP bare fuel released about an order of magnitude more ^{14}C than did the HBR bare fuel at 85°C.

Fig. 4. ^{99}Tc Activities Measured in Unfiltered Solution Samples.

Fig. 5. ^{14}C Activities Measured in Unfiltered Solution Samples.

TABLE V: ^{99}Tc RELEASE DATA (nCi)

	BF/HBR -3-85	BF/TP -3-85	BF/HBR -3-25	BF/HBR -2-25	SD/HBR -3-85	HD/HBR -3-85	UD/HBR -3-85
Solution Samples	54	109	60.1	43*	<2.4	<1.7	1.1
Final Solution [Tc (ng/ml)]	<2.3 (<0.5)	600 (141)	153 (36)	113 (26)	<2.3 (<0.5)	<2.3 (<0.5)	2.3 (<0.5)
Rinse	22.4	24.1	10.3	18	<5.4	8.4	<5.4
Strip	24.3	12.3	4.6	28	<2.7	<2.7	<2.7
Total	~100**	745	228	~200	<12.8	<15.1	<11.5
+ 10^{-5} Inv.	12.2**	89.4	25.2	~32	<1.4	<2.2	<1.2
% in Solution	~56	95	93	~80			

*Based on average activity from three samples.

**Including the ~146 nCi of ^{99}Tc known to have dropped out of solution in this test and not found in rinse or strip, total is ~200 and + 10^{-5} inventory is ~24.

The chemistry of the J-13 well water remained relatively unchanged during the Series 2 and the 25°C Series 3 tests. An analysis of J-13 well water from the storage barrel is given in Table VI. Significant reductions in Ca, Mg, Si and HCO_3^- concentrations were noted in the 85°C tests. The HCO_3^- reductions were to the 60 to 100 $\mu\text{g/ml}$ range. Reductions in Ca, Mg and Si were relatively more significant, amounting to 60% to 80% in several samples. An

increase in SO_4 to the 20 to 30 $\mu\text{g}/\text{ml}$ range was also observed during the 85°C tests. An apparent silica gel layer was observed on the surface of post-test bare fuel particles in both the Series 2 and Series 3 tests. Dissolution of the fused silica vessel probably occurred to maintain constant Si concentration during the Series 2 tests.

CONCLUSIONS

Key conclusions drawn from the Series 3 results obtained to date, along with the major differences noted between the Series 3 and Series 2 results are summarized below:

- Uranium concentrations peaked early in the Series 3 bare fuel tests at levels higher than in the Series 2 tests and then fell to much lower levels. Plutonium activities in the 85°C Series 3 bare fuel tests similarly dropped to levels below those observed in Series 2.
- Corrosion of the stainless steel vessels appears to have affected solution chemistry during the Series 3 tests. Coprecipitation with iron oxy-hydroxide corrosion products and/or reduced solubility as a result of reduced oxygen potential may account for observed drops in actinide and Tc concentrations in these tests.
- Temperature (85°C vs 25°C) did not have a consistent effect on fuel dissolution behavior in the bare fuel tests. Other factors, such as vessel type (sealed stainless steel vs unsealed silica) and fuel type (HBR vs TP) also appeared to affect concentrations and total measured release values.
- Chemistry of the J-13 well water was relatively stable at 25°C in both the Series 2 and Series 3 tests, whereas reductions in Ca, Mg, Si and HCO_3 concentrations were observed in the 85°C Series 3 tests.
- Much greater release was observed from bare fuel than from fuel in defected cladding in both the Series 2 and Series 3 tests.

TABLE VI: J-13 WELL WATER ANALYSIS ($\mu\text{g}/\text{ml}$)

B	0.29
Ca	15
K	4.7
Mg	2.8
Na	42
Si	38
Cl	7.0
F	2.1
NO_3	7.9
SO_4	18.0
HCO_3	123
pH	8.0

REFERENCES

1. C.N. Wilson and V.M. Oversby, in Waste Management 85, Ed. R.G. Post, vol 1, pp. 497-504 (also UCRL-91484, March 1985).
2. V.M. Oversby and C.N. Wilson, in Scientific Basis for Nuclear Waste Management IX, Ed. L.O. Werne (Materials Research Society, Pittsburgh, PA, 1986) pp. 337-346.
3. C.N. Wilson, Results from Cycles 1 and 2 of NMMSI Spent Fuel Dissolution Tests, HEDL-TME 85-22, Hanford Engineering Development Laboratory, Richland, WA (anticipated publication date of February 1987).
4. R.D. Davis and V. Pasupathi, Data Summary Report for the Destructive Examination of Rods G7, G9, J8, J9 and H6 from Turkey Point Fuel Assembly B17, HEDL-TME 80-85, Hanford Engineering Development Laboratory, Richland, WA (April 1981).
5. J.O. Barner, Characterization of LWR Spent Fuel MCC-Approved Testing Material ATM-101, PNL-5109, Pacific Northwest Laboratory, Richland, WA, (1984).