

RADIONUCLIDE RELEASE FROM PWR FUELS IN A REFERENCE

TUFF REPOSITORY GROUNDWATER

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ABSTRACT

The Nevada Nuclear Waste Storage Investigations Project (NNWSI) is studying the suitability of the welded devitrified Topopah Spring tuff at Yucca Mountain, Nye County, Nevada, for potential use as a high level nuclear waste repository. In support of the Waste Package task of NNWSI, tests have been conducted under ambient air environment to measure radionuclide release from two pressurized water reactor (PWR) spent fuels in water obtained from the J-13 well near the Yucca Mountain site. Four specimen types, representing a range of fuel physical conditions that may exist in a failed waste canister containing a limited amount of water were tested. The specimen types were: 1) fuel rod sections split open to expose bare fuel particles; 2) rod sections with water-tight end fittings with a 2.5-cm long by 150- μ m wide slit through the cladding; 3) rod sections with water-tight end fittings and two 200- μ m diameter holes through the cladding; and 4) undefected rod segments with water-tight end fittings.

Radionuclide release results from the first 223-day test runs on H. B. Robinson spent fuel specimens in J-13 water are reported and compared to results from a previous test series in which similar Turkey Point reactor spent fuel specimens were tested in deionized water. Selected initial results are also given for Turkey Point fuel specimens tested in J-13 water. Results suggest that the actinides Pu, Am, Cm and Np are released congruently with U as the UO₂ spent fuel matrix dissolves. Fractional release of ¹³⁷Cs and ⁹⁹Tc was greater than that measured for the actinides. Generally, lower radionuclide releases were measured for the H. B. Robinson fuel in J-13 water than for Turkey Point Fuel in deionized water.

INTRODUCTION

The candidate repository horizon for the Nevada Nuclear Waste Storage Investigations (NNWSI) Project is a welded devitrified tuff above the water table. A limited amount of water infiltrating the rock may provide a potential mechanism for transporting radionuclides to the underlying water table. NNWSI spent fuel canisters are being designed to meet the 10 CFR 60 requirement¹ that containment of all radionuclides within the waste package be "substantially complete for a period ... not less than 300 years nor more than 1000 years after closure of the geologic repository." During most of this "containment period," repository temperature will be above the boiling point of water and the repository atmosphere will be air-steam. During the post-containment period, a limited amount of water could enter a breached canister and contact the spent fuel. The condition of the fuel rods at that time is not easily predicted. A majority of the rods may be intact. A significant number of rods may be breached, containing fine holes or cracks in the cladding. More severe fuel rod degradation may occur as a result of cladding corrosion, or splitting of the cladding as fuel within breached rods slowly oxidizes.

The 10 CFR 60 requirement for the post-containment period is that "the release rate of any radionuclide ... shall not exceed one part in 10⁶ per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure" of the repository. Typical fractional radionuclide inventories calculated for a 1000-year old PWR spent fuel² are given in Table I. More than one half of the 1000-year curie activity results from

americium isotopes, and americium plus plutonium isotopes account for approximately 98% of the 1000-year activity. The next isotope in Table I, ⁹⁹Tc, has a 212,000 year half-life, accounts for approximately one percent of the total 1000-year activity, and is predicted to be soluble in groundwater³. The fourth group of isotopes in Table I are primarily activation products. Of these, ¹⁴C is of special interest because of its potential mobility as carbonate in groundwaters and incorporation into the biosphere. At lower fractional activity levels, isotopes in the last group may be of concern based on potential mobility and/or potential for incorporation in the biosphere. In the NNWSI Spent Fuel Leaching/Dissolution Tests, which are the subject of this paper, release of U, ²³⁹⁺²⁴⁰Pu, ²⁴¹Am, ⁹⁹Tc, ¹⁴C, ²³⁷Np, ¹²⁹I, ¹³⁷Cs and ²⁴⁴Cm are measured. Results from these tests will be used in the evaluation of potential waste package source term release rates relative to 10 CFR 60 requirements (one part in 10⁶ annual release rate).

The actual chemical state of spent fuel is not well characterized on the microscopic scale and the long term stability of spent fuel under proposed repository conditions is not well understood. The UO₂ microstructure is affected by irradiation. Unirradiated UO₂ is a hard ceramic material which exhibits transgranular cleavage when fractured. SEM photographs of the fracture surface of unirradiated fuel and the Turkey Point fuel used for the presently described tests are shown in Fig. 1. The irradiated fuel is very friable and fractures along grain boundaries, which are easily resolved by the SEM. Accumulation of noble metal, alkali, and gaseous fission

TABLE I

PWR SPENT FUEL ASSEMBLY RADIONUCLIDE INVENTORIES AT 1000 YEARS^(a)

Radionuclide ^(b)	% of Total 1000-Year Activity	Cumulative %
Am-241	51.84	51.84
Am-243	1.75 ^(c)	53.59
Pu-240	26.87	80.46
Pu-239	17.37	97.83
Pu-242	0.10	97.93
Pu-238	0.06	97.99
Tc-99	0.77	98.76
Ni-59	0.252	
Ni-63	0.021	
Zr-93	0.181	
Nb-94	0.074	
C-14	0.076 ^(d)	
U-234	0.113	
U-238	0.018	
U-236	0.015	
Np-237	0.058	
Sn-126	0.045	
Se-79	0.023	
Cs-135	0.022	
Sm-151	0.013	
Pd-107	0.006	
I-129	0.0018	

(a) Based on ORIGEN data reported in ORNL/TM-6008⁽²⁾ for 33,000 MWD/MTM burnup PWR Assembly.

(b) Radionuclides with 1000-year activity less than ¹²⁹I or half-life less than 1 year omitted.

(c) Includes activity of ²³⁹Np daughter product.

(d) ¹⁴C activity may vary considerably depending on as-fabricated nitrogen impurities.

products at the grain boundaries is thought to occur during irradiation, resulting in a non-homogeneous chemical microstructure, from which radionuclides may be preferentially released during leaching/dissolution. Some fission products, such as Cs and possibly I, partially migrate out of the fuel to the free rod internal volume during irradiation and may be rapidly released with initial contact by water. Additional segregation of radionuclides from the fuel structure may result from slow degradation of the fuel matrix by oxidation. A better understanding of the physical/chemical state of spent fuel and its potential long term interactions with the repository environment will be useful for detailed repository source term modeling. (Testing of spent fuel resistance to degradation by oxidation under NNWSI proposed post-containment conditions is discussed by Einziger and Woodley in Ref. 4.)

In the NNWSI spent fuel leaching/dissolution testing program, radionuclide release is measured from spent fuel specimens representing a range of possible fuel degradation states thought to be possible during the post-containment period. Series 1 Tests used Turkey Point reactor spent fuel in deionized water under ambient hot cell air atmosphere. Initial results from the Series 1 Tests were reported at the Waste Management 84 conference⁵ and complete results are contained in Ref. 6. Series 2A

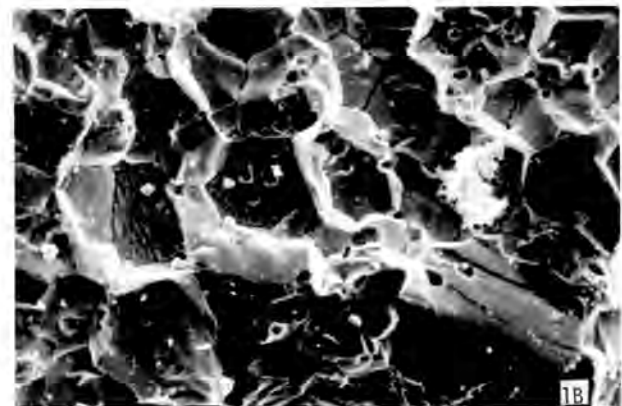


Fig. 1. SEM photographs of fracture surfaces of (A) unirradiated UO₂ fuel exhibiting primarily cleavage fracture through grains, and (B) Turkey Point irradiated fuel exhibiting primarily fracture along grain boundaries.

Tests used H. B. Robinson reactor spent fuel in NNWSI J-13 well water under conditions similar to those of the Series 1 Tests. This report contains primarily results from the First 223-day test run on the Series 2A specimens. Series 2B Tests use Turkey Point fuel specimens in J-13 water. Planned Series 3 Tests will use the H. B. Robinson fuel in J-13 water at higher temperatures. Additional planned tests will use oxidized spent fuel specimens.

TEST DESCRIPTION

Four test specimen types were tested in each test series:

- Bare fuel plus split cladding hulls.
- Slit defect, 2.5 cm long by 150 μm wide.
- Hole defects, two laser-drilled holes ~200 μm diameter.
- Undefected rod sections.

The ends of the slit defect, hole defects, and undefected specimens were sealed using specially fabricated 316 stainless steel fittings incorporating ethylene propylene O-rings. The tests were run in air at ambient hot cell temperature. The test apparatus and specimen configurations are shown in Fig. 2.

Each test vessel was initially filled with 250 ml of J-13 water (or deionized water for Series 1). Solution samples (10-25 ml depending on required

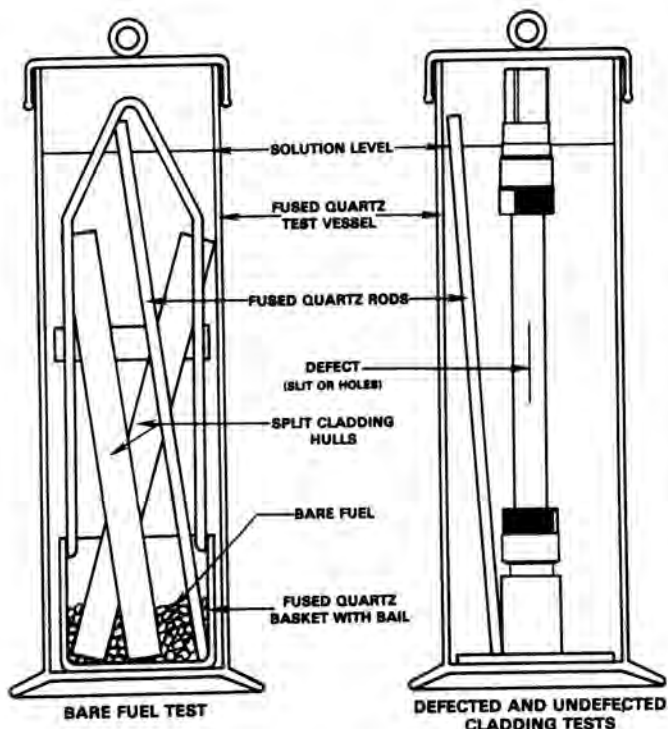


Fig. 2. Test Apparatus.

analyses) were periodically removed and replaced with fresh J-13 water (or deionized water for Series 1). Evaporation losses were made up using deionized water. Fused quartz rod samples were also periodically removed to monitor progression of radionuclide "plate-out." At the end of a test run, final solution and quartz rod specimens were taken and the specimens and apparatus were rinsed. Samples of the bare fuel and any observed residues were taken for microstructural examination. The test vessels, along with specimen pedestals and the bare fuel test fused quartz baskets, were stripped with 8 M HNO₃. The following sample types were analyzed:

- Periodic solution samples.
- Periodic quartz rod samples.
- Terminal specimen and apparatus rinse samples.
- Terminal 8 M HNO₃ vessel strip solutions.
- Bare fuel particles for metallographic examination.

The test specimens were then restarted in fresh J-13 water (deionized water for Series 1).

Test specimens were prepared using five inch long sections cut from PWR spent fuel rods from two reactors. Characteristics of the two PWR fuels used are contained in Table II. Both fuels were of similar vintage from the same vendor and were essentially identical (except for a small difference in burnup) prior to post-irradiation sectioning. The Series 2A H. B. Robinson fuel⁷ specimens were sectioned from the central region of a single rod (rod C-5, assembly B0-5), avoiding rod positions adjacent to spacer grid locations in order to assure uniform burnup specimens. The Turkey point specimens had been previously sectioned⁸ and stored in sealed steel tubes. Approximately one inch of fuel had been removed from each end of the Turkey Point fuel specimens during original sectioning. The resulting differences in specimen fuel content (~43g for Turkey

TABLE II

CHARACTERISTICS OF H. B. ROBINSON UNIT 2 AND TURKEY POINT UNIT 3 FUELS

Characteristic	H. B. Robinson	Turkey Point
Fuel Type	PWR 15 x 15	PWR 15 x 15
Discharged	May, 1974	November, 1975
Estimated Burnup	31 Mwd/kgM	27 Mwd/kgM
Fission Gas Release	~0.2%	~0.3%
Initial Enrichment	2.55 wt% ²³⁵ U	2.559 wt% ²³⁵ U
Initial Pellet Density	92% TD (UO ₂)	92% TD (UO ₂)
Rod Diameter	10.7 mm	10.7 mm
Cladding	Zircaloy-4	Zircaloy-4
Specimen Section Length	5 inches	5 inches
Specimen Fuel Length	5 inches	2-3 inches

Point versus ~80g for H. B. Robinson Specimens), and the corresponding increase in specimen internal void volume for the Turkey Point "slit defect" and "hole defects" specimens, are likely the most significant differences between the specimens of the two fuel types.

RESULTS AND DISCUSSION

Results from the first run of the Series 2A H. B. Robinson fuel in J-13 water (J-13/HBR) tests are presented and compared to results from the first run of the previously completed Series 1 Turkey Point fuel in deionized water (DIW/TP) tests. Some initial solution sample results from Turkey Point fuel in J-13 water (J-13/TP) are also presented. Second run J-13/HBR and J-13/TP Series 2 tests are in progress and will be reported later. Second run DIW/TP results are contained in Ref. 6.

Uranium, ²³⁹+²⁴⁰Pu and ¹³⁷Cs contents in unfiltered solution samples are plotted in Figs. 3 through 5 for the four J-13/HBR tests and the J-13/TP and DIW/TP bare fuel tests. Solution levels which would result if 10⁻³ of the three bare fuel specimen inventories were dissolved in the 250 ml of test solution are also shown. Uranium concentration in the J-13/TP bare fuel test remained nearly constant at 4 to 5 µg/ml. For the J-13/HBR bare fuel test, uranium concentration decreased from a maximum value of 4.5 µg/ml measured in the 6-day solution sample to 1.2 µg/ml when the test was terminated at 223 days.

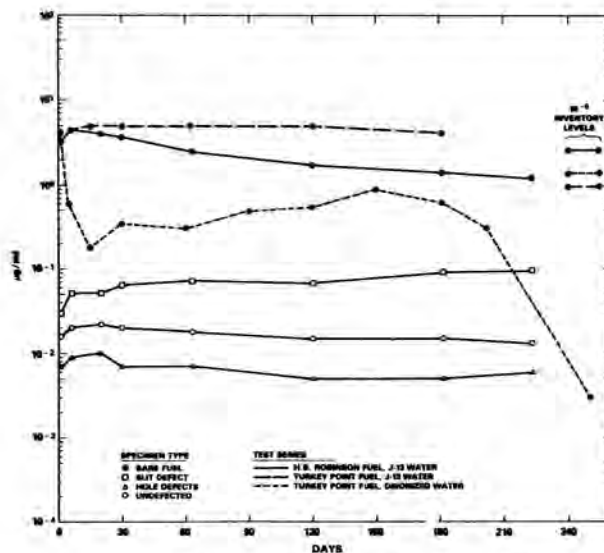


Fig. 3. Uranium in unfiltered solution.

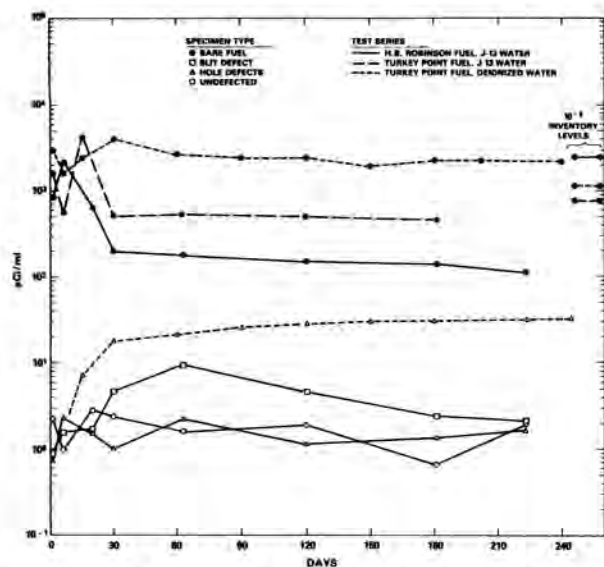


Fig. 4. $^{239+240}\text{Pu}$ activity in unfiltered solution.

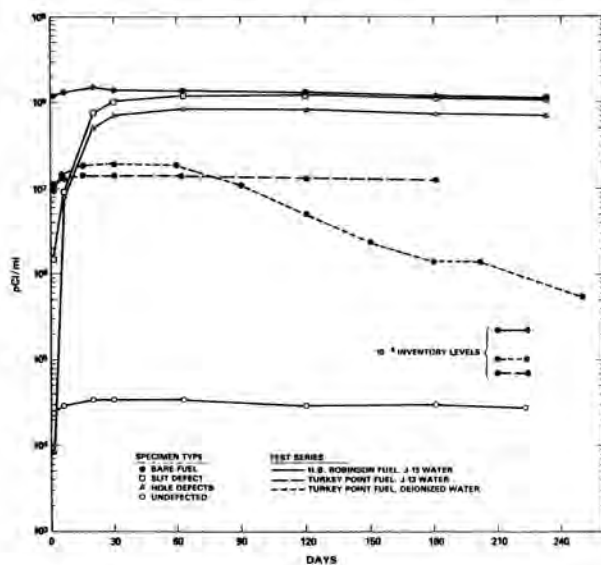


Fig. 5. ^{137}Cs activity in unfiltered solution.

Essentially all of the uranium in these solution samples from tests using J-13 water passed through both 0.4 μm and 18A filters, indicating true solution.

Unfiltered solution uranium content fluctuated to a greater extent in the DIW/TP bare fuel test, dropping to 0.003 $\mu\text{g/ml}$ at 250 days when the test was terminated. Filtration of the 202-day solution sample from this test (when uranium in the unfiltered solution was 0.3 $\mu\text{g/ml}$) suggested that most of the uranium was colloidal or present in fine undissolved particles. Between the 202-day and final 250-day samples from the DIW/TP bare fuel test, it appears that much of this colloidal phase may have precipitated. As with uranium, a significant reduction in ^{241}Am and ^{244}Cm solution activity was also noted between the 202-day and 250-day samples from this test and most of the ^{241}Am and ^{244}Cm activity in the 202-day sample was removed by filtration. The effect of 0.4 μm and 18A filtration on radiochemical results from the 223-day terminal J-13/HBR bare fuel solution sample and the 202-day DIW/TP bare fuel solution sample are compared in Table III.

TABLE III
EFFECTS OF FILTRATION ON 223-DAY J-13/HBR
AND 202-DAY DIW/TP BARE FUEL TEST SOLUTION SAMPLES

	Series	Unfiltered	0.4 μm	18A
Uranium ($\mu\text{g/ml}$)	J-13/HBR	1.2	1.2	1.2
	DIW/TP	0.3	0.003	0.002
$^{239+240}\text{Pu}$ (pCi/ml)	J-13/HBR	112	75	26
	DIW/TP	2240	2180	1810
^{241}Am (pCi/ml)	J-13/HBR	286	151	3.6
	DIW/TP	9860	1430	97
^{244}Cm (pCi/ml)	J-13/HBR	410	231	0.9
	DIW/TP	21,100	2860	163
^{99}Tc (pCi/ml)	J-13/HBR	450	490	450
	DIW/TP*	2250	2250	2200

*250 Day solution sample; ^{99}Tc was not analyzed in the 202-day DIW/TP solution sample

Uranium levels measured in unfiltered solution from the J-13/HBR slit defect test reached a maximum level of ~ 0.1 $\mu\text{g/ml}$ at the end of the 223-day test run, while uranium in the hole defects test fluctuated between 0.005 and 0.01 $\mu\text{g/ml}$. Uranium in the J-13/HBR undefected test remained at about 0.02 $\mu\text{g/ml}$ during the test, which is slightly higher than observed in the hole defects test, indicating that decontamination(a) of the cladding exterior during specimen preparation was not as effective with the undefected specimen. Integrity of the J-13/HBR undefected specimen is shown by the ^{137}Cs data in Fig. 5, which indicates that the J-13 water was not in contact with the interior of the undefected specimen, but did contact the interior of the other specimens. In the DIW/TP and J-13/TP test series, uranium and all other radionuclides were at their lowest levels in the undefected tests. It is interesting to note that, in the J-13/HBR tests, more actinide release is observed from a presumably small microscopic amount of contamination on the cladding exterior than is released through the 200- μm holes in the cladding.

Plutonium solution activities in the DIW/TP tests were in general about an order of magnitude higher than those measured in the J-13 water tests. The $^{239+240}\text{Pu}$ solution activities measured in the J-13/HBR slit defect, hole defects and undefected tests were not much above the detection limits for measurement. A higher fraction of the $^{239+240}\text{Pu}$ solution activity was retained on filters in J-13 water bare fuel tests and solution-to-plateout activity ratios were lower in the J-13 bare fuel tests relative to the DIW/TP tests.

Due to the high free activity and solubility of ^{137}Cs in the fuel-cladding gap, ^{137}Cs solution activity provides a means to monitor test performance. The relatively fast buildup of ^{137}Cs solution activity in the slit defect and hole defects tests to levels approximately equal to that in the bare fuel tests indicated that the water entered and filled these test specimens. No increase in ^{137}Cs solution activity in the undefected tests indicated that these specimens did not leak. Solution ^{137}Cs content at 30 days was $\sim 0.2\%$ of specimen inventory in the J-13/TP and DIW/TP

(a) Prior to final specimen assembly, slit defect, hole defects, and undefected fuel rod segments were decontaminated by wiping with alcohol dampened cloths until smearable alpha activity from the cladding surface read below 50 cpm.

tests and ~0.6% of specimen inventory in the J-13/HBR tests. Based on similar reported ^{7,8} percentage fission gas release values for these fuels, similar ¹³⁷Cs release from gap inventories would be expected. Loss of some of the ¹³⁷Cs gap inventory during post-sectioning handling and storage of the Turkey Point fuel may be indicated. A most interesting, and yet to be explained, observation was the decrease in ¹³⁷Cs activity after 60 days in the DIW/TP bare fuel test. The ¹³⁷Cs which left the solution in this test was not accounted for in the terminal rinse or strip solution samples. Procedures used for rinsing and collection of rinse solutions for analysis were changed after the DIW/TP tests to avoid loss of settled particles which may have contained the ¹³⁷Cs. However, no similar drop in ¹³⁷Cs solution activity was observed in any of the other tests.

Iodine-129 was determined by neutron activation analysis on unfiltered fractions of the J-13/HBR 63-day and 223-day solution samples. Results of these ¹²⁹I analyses are given in Table IV. The fractions of specimen ¹²⁹I inventory measured in solution in the bare fuel and slit defect tests were comparable to the total fractional actinide release determined at the end of the bare fuel test (i.e., 5 to 8 x 10⁻⁵ inventory). Fractional ¹²⁹I in solution from the hole defects test was not significantly different from that measured for the undetected test, which is an unexpected result, considering the respective fractional ¹³⁷Cs solution activities in these two tests.

TABLE IV

¹²⁹I MEASURED IN J-13/HBR SOLUTION SAMPLES

Test	Days	¹²⁹ I (pCi/ml)*	±10 ⁻⁵ Inventory**
Bare Fuel	63	0.52	5.6
	223	0.72	7.5
Slit Defect	63	0.29	3.0
	223	0.38	4.0
Hole Defects	63	0.0019	0.020
	223	0.0050	0.053
Undetected	63	0.0060	0.064
	223	0.0054	0.057

*Average for 2 replicate samples measured by neutron activation analysis.

** (pCi/ml)(250 ml)/(10⁻⁵ of specimen inventory).

An accounting for several of the radionuclides (and uranium) analyzed was made in order to estimate total release as a fraction of inventory for each test in each series. The uranium release accounting for the J-13/HBR tests is given in Table V. Measured release accounting data for ²³⁹⁺²⁴⁰Pu, ²⁴¹Am, ²⁴⁴Cm and ⁹⁹Tc in the J-13/HBR bare fuel test are contained in Table VI. Similar measured release accounting data for the J-13/HBR slit defect test are contained in Table VII. In the bottom line of each accounting, total measured release (∑ above) is divided by 10⁻⁵ of the radionuclide inventory calculated by ORIGEN-2 to be present in each specimen ⁷. The resulting fractional releases for each radionuclide are given in Table VIII for each of the J-13/HBR and DIW/TP tests.

Three general conclusions from the Table VIII fractional release data are that: 1) greater release occurred in the DIW/TP tests relative to the J-13/HBR

TABLE V

H. B. ROBINSON FUEL IN J-13 WATER
URANIUM RELEASE DATA (μg)

	Bare Fuel	Slit Defect	Hole Defects	Undetected
∑ Solution Samples	211	4.3	0.50	1.26
∑ Rod Samples	34	0.3	<0.17	<0.19
Final Solution [U (μg/ml)]*	300 (1.2)	23.8 (0.095)	1.50 (0.006)	3.25 (0.013)
Strip	2700	1.5	0.60	0.60
Rinse**	550	1.8	0.60	0.27
∑ Above	3795	31.7	<3.37	<5.57
Divided by 10 ⁻⁵ Inv.	5.42	0.044	<0.0047	<0.008

*Unfiltered 223-day final solution uranium content in μg/ml given in parentheses.

**Bare fuel rinse solution was 0.4 μm filtered prior to analysis.

TABLE VI

RELEASE DATA FOR H. B. ROBINSON
BARE FUEL IN J-13 WATER (nCi)

	²³⁹⁺²⁴⁰ Pu	²⁴¹ Am	²⁴⁴ Cm	⁹⁹ Tc
	∑ Solution Samples*	42.9	93.9	125.0
∑ Rod Samples	56.2	125.1	138.2	<0.6
Final Solution	27.9	71.5	102.5	112.5
Strip	4054.1	9600.0	8970.0	28.4
Rinse**	253.8	532.0	564.6	18.6
∑ Above	4434.9	10,422.5	9900.3	183.6
Divided by 10 ⁻⁵ Inv.	7.04	7.76	6.54	20.2

*Last solution sample included in "Final Solution" value.

**Rinse solution 0.4 μm filtered.

TABLE VII

RELEASE DATA FOR H. B. ROBINSON SLIT DEFECT
SPECIMEN IN J-13 WATER (nCi)

	²³⁹⁺²⁴⁰ Pu	²⁴¹ Am	²⁴⁴ Cm	⁹⁹ Tc
	∑ Solution Samples*	0.251	0.625	0.702
∑ Rod Samples	0.322	0.702	1.167	--
Final Solution	0.495	1.352	0.980	7.32
Strip	2.568	5.940	5.820	3.51
Rinse	1.703	2.700	2.676	10.56
∑ Above	5.339	11.319	11.345	22.89
Divided by 10 ⁻⁵ Inv.	0.0082	0.0082	0.0073	2.46

*Last solution sample included in "Final Solution" value.

tests; 2) actinides appear to be released congruently; and 3) ¹³⁷Cs and ⁹⁹Tc are released preferentially relative to the actinides.

Except for ¹³⁷Cs, lower absolute μg and nCi releases occurred in the J-13/HBR tests relative to the DIW/TP tests, even though the J-13/HBR specimen inventories were about twice that of the DIW/TP inventories. Initial data from the J-13/TP tests suggest that the observed differences in release are due to the different leaching solutions (i.e., DIW vs J-13 water) rather than the difference in fuel types. Chemistry of the J-13 water, as shown by Table IX for

TABLE VIII
TOTAL MEASURED RELEASE
DIVIDED BY 10⁻⁵ INVENTORY

	SERIES	BARE FUEL	SLIT DEFECT	HOLE DEFECTS	UNDEFECTED
Uranium	J-13/HBR	5.42	0.044	<0.005	<0.008
	DIW/TP	21.2	0.065	0.032	0.010
***Pu	J-13/HBR	7.04	0.008	<0.002	<0.002
	DIW/TP	22.4	0.20	0.042	0.021
**Am	J-13/HBR	7.76	0.008	<0.002	<0.003
	DIW/TP	17.2	0.152	0.019	<0.008
***Cm	J-13/HBR	6.54	0.007	0.001	<0.002
	DIW/TP	21.5	0.35	0.026	0.006
***Np	J-13/HBR	~6.4	--	--	--
	DIW/TP	~18	~0.2	--	--
**Cs	J-13/HBR	683	567	362	<0.7
	DIW/TP	~230	110	50	0.04
**Tc	H-13/HBR	20.2	2.46	~1	--
	DIW/TP	152	8.1	--	--

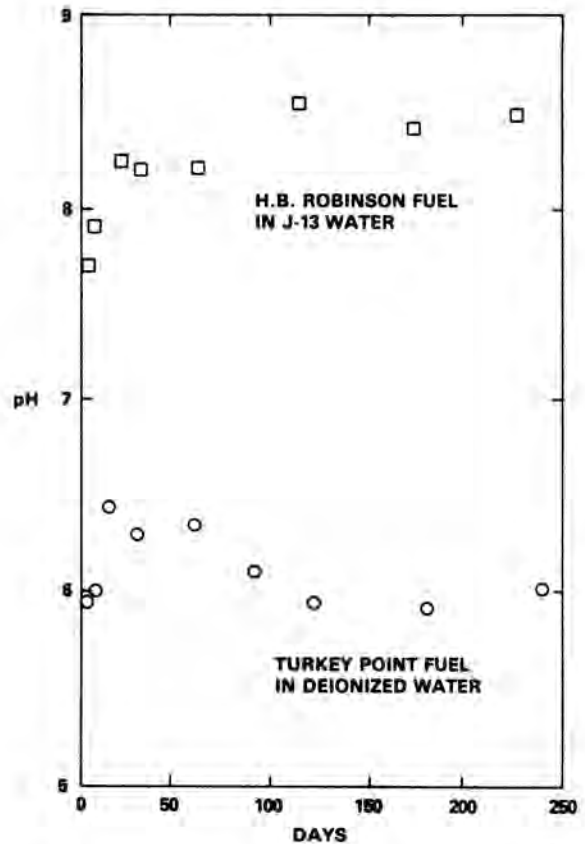
TABLE IX

SOLUTION CHEMISTRY* FOR THE
H. B. ROBINSON BARE FUEL TEST IN J-13 WATER

	STARTING J-13 WATER	30 DAYS	120 DAYS	223 DAYS
pH	7.2	8.2	8.5	8.5
Al	0.11	0.09	0.10	<0.08
Ca	15.0	12.7	12.1	12.3
Fe	--	0.21	0.15	0.08
K	5.5	4.5	2.8	2.2
Mg	2.1	1.8	2.1	2.0
Mo	--	0.26	0.21	0.20
Na	49.5	41.6	44.5	45.5
Sr	--	--	--	0.06
Si	31.9	24.5	26.2	32.7
Cl	7.3	7.8	7.3	7.6
F	2.7	2.4	2.1	2.2
PO ₄	2.8	--	--	--
NO ₂	--	--	~0.5	~0.6
NO ₃	8.7	7.4	8.1	8.3
SO ₄	18.8	18.8	18.6	18.5
CO ₃	118.0	--	120.0	118.0

*Units in µg/ml, 0.4 µm filtered.

the J-13/HBR bare fuel test, was relatively constant for the duration of the tests. The J-13 water, containing about 120 µg/ml bicarbonate, became slightly basic during the tests, while the deionized water became slightly acidic. Test solution pH values for each sample taken from the J-13/HBR and DIW/TP bare fuel tests are plotted in Fig. 6. Essentially identical pH behavior was observed for all eight tests in the J-13/HBR and J-13/TP test series, where after about 15 days, pH was between about 8.2 and 8.5 for the remainder of the tests. Similarly, pH of all four tests in the DIW/TP test series dropped into a range of about 6.4 to 5.7 and remained in this range for the duration of the tests. Lower pH in the deionized water tests may have resulted from radiolysis of dissolved air producing HNO₃. The NO₃ concentration in all four of the DIW/TP tests was found to be approximately 2 µg/ml when these tests were terminated. This small amount of HNO₃ radiolysis product would probably not have had a significant effect on the J-13 water pH because of buffering by the bicarbonate.



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Fig. 6. pH of solution samples taken from the H. B. Robinson fuel in J-13 water and Turkey Point fuel in deionized water -- bare fuel tests.

Some additional insight into differences in spent fuel leaching/dissolution behavior in J-13 water and deionized water was provided by metallographic examination of post-test fuel particles from the J-13/HBR, J-13/TP and DIW/TP bare fuel tests. Micrographs of polished sections of bare fuel particles tested in deionized water and J-13 water are shown in Fig. 7. The bare fuel tested in deionized water exhibited extensive grain boundary attack, while no significant grain boundary attack was observed in bare fuel particles tested in J-13 water. Since **Tc may partially segregate to grain boundaries during irradiation, more extensive grain boundary attack in deionized water likely accounts for the higher fractional **Tc release relative to the fractional actinide release observed in the deionized water bare fuel test.

CONCLUSIONS

Comparative semi-static leach tests were conducted on PWR spent fuel specimens in NNWSI reference J-13 well water and in deionized water under hot cell ambient air and temperature conditions. Four spent fuel specimen configurations were tested in both water types: 1) bare fuel plus the cladding; 2) fuel rod segments with sealed ends and a slit defect through the cladding; 3) fuel rod segments with sealed ends and small (~200 µm) laser-drilled holes through the cladding; and 4) undefected fuel rod segments with sealed ends. Principal conclusions based on initial results from these tests are:

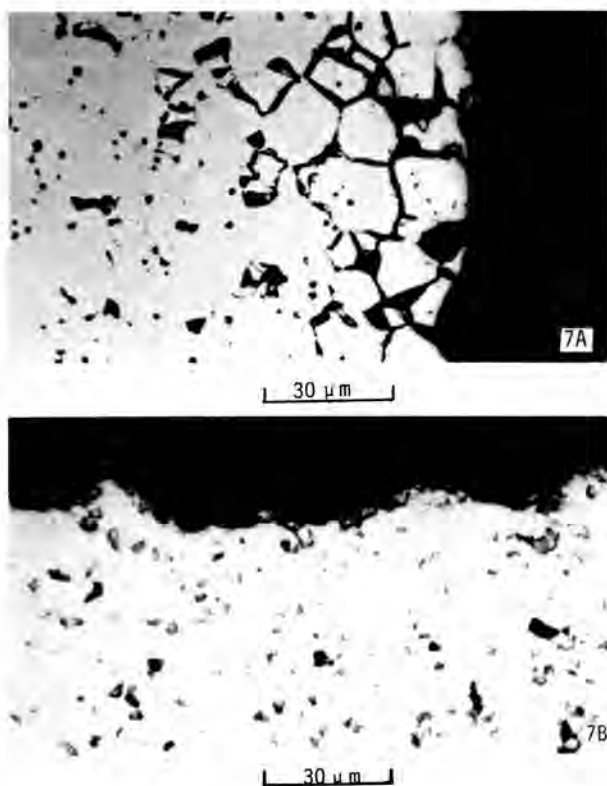


Fig. 7. Polished sections of fuel particles from (A) Turkey Point bare fuel tested in deionized water showing grain boundary attack, and (B) H. B. Robinson bare fuel tested in J-13 water showing an absence of grain boundary attack.

- 1) Within the probable accuracy of total release measurements and specimen inventory calculations, the actinides U, Pu, Am, Cm and most likely Np, appear to be released congruently.
- 2) ^{99}Tc and ^{137}Cs are released preferentially relative to the actinides. Preferential ^{99}Tc release is of particular interest, since it is predicted to be relatively soluble in groundwater and is one of the major radionuclides of interest with respect to the requirements of 10 CFR 60 (10^{-5} of 1000-year inventory maximum permitted annual release).

- 3) Much greater total release was observed in both J-13 and deionized water for bare fuel versus the same quantity of fuel contained in defected cladding.
- 4) Lower actinide release was observed in J-13 well water than in deionized water. Greater actinide and ^{99}Tc release from bare fuel in deionized water appeared to be caused by grain boundary dissolution. Carbonate buffering of the J-13 water to alkaline pH, while deionized water becomes slightly acidic from radiolysis, may account for the observed differences in actinide release.

REFERENCES

1. Code of Federal Regulations, *Disposal of High-Level Radioactive Wastes in Geologic Repositories - Licensing Procedures*, Title 10, Chapter 1, Part 60, June 30, 1983 (cited as 10 CFR 60).
2. C. W. ALEXANDER et al., "Projections of Spent Fuel to Be Discharged by the US Nuclear Power Industry," ORNL/TM-6008, Oak Ridge National Laboratory, Oak Ridge, TN, October 1977.
3. J. F. KERRISK, "Solubility Limits on Radionuclide Dissolution at a Yucca Mountain Repository," LA-9995-MS, Los Alamos National Laboratory, Los Alamos, NM, May 1984.
4. R. E. EINZIGER, R. E. WOODLEY, "Low Temperature Spent Fuel Oxidation Under Tuff Repository Conditions," *Paper presented at Waste Management 85 Conference*, Tucson, AZ, March 28, 1985, (HEDL-SA-3271).
5. C. N. WILSON, V. M. OVERSBY, *Proceedings of the Symposium on Waste Management, Tucson, Arizona, March 11-15, 1984*, R. G. Post Editor, Volume 1, pp. 569-572.
6. C. N. WILSON, "Results from NNWSI Series 1 Spent Fuel Leach Tests," HEDL-TME 84-30, Hanford Engineering Development Laboratory, Richland, WA, April 1985.
7. J. O. BARNER, "Characterization of LWR Spent Fuel MCC-Approved Testing Material ATM-101," PNL-5109, Pacific Northwest Laboratory, Richland, WA, June 1984.
8. R. B. DAVIS and V. PASUPATHI, "Data Summary Report for the Destructive Examination of Rods G7, G9, J8, I9 and H6 from Turkey Point Fuel Assembly B17," HEDL-TME 80-85, Hanford Engineering Development Laboratory, Richland, WA, April 1981.