Contract No. W-7405-eng-26

Consolidated Fuel Reprocessing Program

HEAD-END REPROCESSING STUDIES OF H. B. ROBINSON-2 FUEL: II. PARAMETRIC

VOLOXIDATION STUDIES

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Date Published - May 1980

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ABSTRACT

A series of hot-cell tests was conducted with UO_2 that had been irradiated to an average of 28,000 MWd/t in the H. B. Robinson-2 reactor of the Carolina Power and Light Company. The tests examined the effects of temperature and of the rate of oxygen supply on the release of gaseous and semivolatile fission products, while the fuel fragments were tumbled at 12 rpm during voloxidation — the high-temperature oxidation of UO_2 to U_3O_8 . The experiments showed that >99.9% of the tritium in the irradiated UO_2 was released to the off-gas stream at temperatures of 480 and 550°C and at oxygen feed rates ranging from 0.1 to 1.2 mol/h. The release of ^{85}Kr varied from 2 to 7% of the fuel inventory. The U_3O_8 product (~99% smaller than 44 μm) was easily dissolved in 7 M HNO_3 . One 2-h leach in 7 M HNO_3 dissolved ~99.5% of the heavy metals; a second 2-h leach in 7 M HNO_3 brought the total to >99.98%. Voloxidation did not affect the final solubility of the uranium and plutonium but did increase the weight of the insoluble fission product residue from 0.18% of the irradiated UO_2 to ~0.62%.

1. INTRODUCTION

The Chemical Technology Division of the Oak Ridge National Laboratory is conducting hot-cell experiments on proposed methods for the containment during reprocessing of gaseous and semivolatile fission products that are present in irradiated heavy-metal oxide fuels. One proposal for the release and isolation of the beta-emitting hydrogen isotope, tritium, is voloxidation — the high-temperature oxidation of the fuel. During voloxidation, the UO_2 in light-water reactor (LWR) fuels is converted to U_3O_8 and the tritium to tritiated water, HTO. Exploratory studies using UO_2 from the H. B. Robinson-2 reactor indicated that >99% of the tritium, ~50% of the ^{14}C , ~6% of the ^{85}Kr , and smaller quantities of other nuclides were volatilized when the UO_2 was oxidized to U_3O_8 in air at 480°C for ~4 h.¹ The larger surface area of the U_3O_8 increased the rate of dissolution of the fuel in nitric acid. A larger

amount of nitric acid-insoluble residue was found when the voloxidized fuels were dissolved.

The successful preliminary tests indicated that additional study of process variables was warranted in order to determine optimum conditions for the removal of these long-lived gaseous fission products. This document describes experiments in which two oxidation temperatures (480 and 550°C) were used; the atmosphere was varied between air and O_2 , and the speed of rotation of the voloxidizer was held at 12 rpm. In most of the experiments, unclad UO_2 was used. The off-gases were collected and analyzed during the oxidation and during the subsequent dissolution of the oxide in nitric acid. Complete material balances were made on the uranium, plutonium, and fission products.

2. EXPERIMENTAL

2.1 Fuel Specimens

The fuel used in these voloxidation-dissolution experiments was taken from three H. B. Robinson-2 rods: G-10, J-6, and J-10 (see Table 1). A detailed description of the H. B. Robinson fuel and the baseline studies (Runs LWR-1, 2, and 3) with UO_2 from rod G-10 has been reported.¹ For comparison purposes, the fuel used in the parametric experiments and in three supplemental experiments was taken from the center segments of rods with an average burnup of $\sim 28,000$ MWd/t. (Gamma scans indicated that except for the ends, the burnup along the length of the 12-ft rods was essentially constant.)

Sections from each rod were cut into short pieces with a single-rod hydraulic shear to provide unclad UO_2 . Most of the Zircaloy fines and all of the larger fragments were removed from the dislodged fuel prior to its sieve analysis. The dislodged fuel was divided into replicate (~ 100 -g sized) samples. Midsections of Rod G-10 were cut into 1-in.-long pieces to provide clad fuel specimens.

Unclad fuel from segment G-10-2 was used in a separate set of tests to determine the amount of tritium evolving as HT during the voloxidation process. The fuel in that segment was 18 in. from the end of the rod (a slightly lower burnup level was indicated); however, the tritium content of the UO_2 was the same as that from more centrally located rod segments.

Table 1. Fuel specimens for voloxidation experiments

Rod segments (Assembly B05)	Experiments (LWR Run No.)	Condition of UO ₂	Av. burnup (MWD/ton)
G-10-5 and G-10-6	Baseline (1,2) Baseline (3) Supplemental(15)	Clad (1-in.-long pieces) Unclad Clad (1-in.-long pieces)	28,000
J-6-7, J-6-8, G-10-3, G-10-4, G-10-7, J-10-5, and J-10-6	Parametric and supplemental ^a (4,5,6,7,8,9, 10, ^a 11 ^a)	Unclad	28,000
G-10-2	Supplemental (12, 13, 14)	Unclad	~24,000
Unirradiated UO ₂	Supplemental (A, B, C, D, E)	Pellets (3/8 in. long)	Unirradiated

^aSupplemental runs.

Supplemental voloxidations of unirradiated prototype UO_2 were run in the hot cell and in the laboratory hood to verify some aspects of the oxidation process observed during the parametric experiments.

2.2 Equipment and Procedures

The voloxidations were conducted in a purged, rotating, stainless steel chamber that was equipped with sintered stainless steel filters (35- μm porosity) at the gas inlet and outlet. Several thin, removable stainless steel sheets were inserted between the flights. Each covered about one-sixth of the voloxidizer interior. Periodically one was removed to measure the amounts of deposited semivolatile fission products. A stainless steel tube was inserted downstream of the sintered-metal filters in the off-gas tube to measure the deposition of semivolatiles in the off-gas cooling zone. Beyond that point, heated tubing carried the off-gas to a heated filter pack (containing filters to trap particles and charcoal beds for ^{129}I). This was followed by a HEPA filter, a tritium oxidizer (heated CuO), silica-gel beds for sorption of tritiated water vapor, a multichannel analyzer (MCA) for gamma spectroscopy (^{85}Kr release rate), and a flow splitter to divert one-tenth of the total off-gas flow to a special plastic bag for a cumulative measurement. Purge flow rates and oxygen concentrations in the off-gas were continuously monitored.

The operation of the voloxidizer, the feed and off-gas systems, and the sampling apparatus was primarily the same as during the earlier baseline experiments.¹ The greatest changes to the system were in data logging and reduction. A Hewlett-Packard 3050B data acquisition system with a 9825A automated calculator was brought on-line for the simultaneous recording and processing of oxygen consumption and gaseous release rate information. Flow instrumentation, thermocouples, the oxygen analyzer, and the multichannel analyzer (MCA) were monitored at selected short (1-, 2-, 5-, or 10-min) intervals, depending on the rate at which the oxidation reaction was proceeding. During the parametric experiments and during most of the supplemental voloxidations, flowing-stream gas samples were extracted from the off-gas line and counted for ^{85}Kr as a calibration check for the MCA measurements. To

ensure completeness of reaction under the chosen voloxidation conditions, each experiment was continued beyond the point at which oxygen consumption had ended, and the ^{85}Kr concentration in the off-gas had returned to about system background levels. There were some indications that the ^3H release processes were not finished when the runs were terminated. However, the final release rates were very low.

The primary dissolution equipment consisted of a series of Pyrex vessels arranged such that a stream of purge air carried the dissolution off-gases from the dissolver, through a reflux condenser, a sodium hydroxide scrubber, and an in-line high-efficiency particulate (HEPA) filter before the gas passed out of the hot cell. Outside of the hot cell, the gases flowed through a multichannel gamma spectrometer for determination of the ^{85}Kr content and were finally all collected in a bag as a cumulative sample. The flows of the gases into and out of the system were also recorded. A clinical centrifuge was used to separate the insoluble residues from the leach solutions; the residues were thoroughly washed with 3 M HNO_3 after each leach. The second and third leaches were conducted in the same centrifuge cone fitted with a reflux condenser. The residue was dried in the centrifuge cone for determination of its weight; the residue was fused with Na_2CO_3 for analysis.

3. RESULTS AND DISCUSSION

3.1 Shearing

The data taken during shearing of H. B. Robinson fuel have been presented.^{1,2} The second report presents detailed shearing information such as the forces required to shear the rods, the releases from cladding, the size distributions of dislodged materials, and others, for a variety of irradiated reactor fuels, in addition to the H. B. Robinson fuel.

3.2 Voloxidation

3.2.1 General

A series of exploratory and parametric voloxidation tests was run to characterize the Robinson fuel and to determine fission product

behavior during the oxidation process. The principal objective was to define the effects of the UO_2 oxidation rate on the rate of evolution and yield of tritium. Other responses, such as the fates of ^{85}Kr , ^{14}C , and semivolatile fission products were also monitored. A summary of the run conditions is shown in Table 2.

Several voloxidations were run under standardized conditions (unclad fuel, 480°C , air, 12 rpm) to determine fuel and system responses and to form the baseline for comparison studies. Parametric experiments to characterize the oxidation rate effects were made at two temperature levels (480 and 550°C) with oxygen feed rates (air or pure O_2) ranging from 0.1 to 1.20 mol/h. In four instances (Runs 6, 7, 9, and 15), oxidation rates were increased to the limit of the apparatus in a vain attempt to cause maloperation (fuel sintering).

One experiment (LWR-10) was interrupted to yield a partially oxidized product for the confirmation of the presence of U_4O_9 as an intermediary to the UO_2 to U_3O_8 conversion. These were followed by parallel studies using unirradiated UO_2 (A, B, C, D, E).

Hindered modes of tritium release were also investigated. In addition to clad fuel, the effect of bed depth was studied in LWR-11. In this run, a 3:1 mixture of U_3O_8 to UO_2 was used to simulate mixing conditions at a position downstream from the feed point in a continuous rotary voloxidizer. The bed depth during that experiment was 1.23 in. (about one-third the inside diameter of the voloxidizer), compared to about 0.23 in a typical experiment. The effects of cladding coverage and different oxygen feed rates (0.1 and 0.75 mol/h) were briefly studied in experiments 1, 2, and 15.

In the final set of experiments (LWR-12, -13, and -14), flows of voloxidizer off-gas were selectively either passed through heated CuO before tritium collection on silica gel or were collected without using the CuO traps. In theory, any unoxidized tritium (i.e., in the HT form) would not be trapped on the silica gel, and the amount of HT could be determined by the differences in recovered tritium. In practice, things did not work out as predicted.

Table 2. Voloxidation of H. B. Robinson-2 fuel

Run No.	Charged to voloxidizer		Voloxidation conditions					
	Fuel	U + Pu ^a (g)	Temp. (°C)	Time ^b (min)	Atmos.	Purge flow rate (cm ³ /min)	O ₂ feed rate (mol/h)	Rotation (rpm)
LWR-1	UO ₂ (1-in. clad)	99.17	480	240	Air	200-220	~0.10	12
LWR-2	UO ₂ (1-in. clad)	86.09	480	270	Air	200-220	~0.10	12
LWR-3	UO ₂ (unclad)	64.07	480	280	Air	300	0.15	12
LWR-4	UO ₂ (unclad)	82.19	480	140	O ₂	230	0.55	12
LWR-5	UO ₂ (unclad)	83.45	480	160	O ₂	~200-225	0.55	12
LWR-6	UO ₂ (unclad)	83.29	480	120	O ₂	500	1.20	12
LWR-7	UO ₂ (unclad)	79.35	550	150	O ₂	300	0.75	12
LWR-8	UO ₂ (unclad)	86.30	550	170	Air	300	0.15	12
LWR-9	UO ₂ (unclad)	87.52	550	110	O ₂	300	0.75	12
LWR-10	UO ₂ (unclad)	83.76	480	40	Air	300	0.15	12
LWR-11	UO ₂ /U ₃ O ₈ ^c	86.74/263.1	480	230	Air	300	0.15	12
LWR-12	UO ₂ (unclad)	90.35	480	180	Air	220	0.11	12
LWR-13	UO ₂ (unclad)	~85 ^d	480	150	Air	300	0.15	12
LWR-14	UO ₂ (unclad)	~85 ^d	480	180	Air	~270	~0.135	12
LWR-15	UO ₂ (1-in. clad)	78.20	480	180	O ₂	300	0.75	12

^aBased on recoveries of dissolved product.

^bTime at temperature.

^cMixture of unclad fuel (UO₂ to U₃O₈ ~ 1:3).

^dEstimated; product not dissolved.

3.2.2 Material balances and weight gains during voloxidation

The high yields (99.2 to 100.2%) of voloxidized products demonstrated the handling losses of the materials were very low. However, each 0.1% loss is equivalent to $\sim 2.5\%$ conversion. We think the Robinson UO_2 was converted to U_3O_8 with relatively little difficulty (see Table 3), but we obtained only an average oxide conversion of 91.8% for 14 experiments. This low measured conversion could be explained by an average handling loss of ~ 0.3 wt %. Measured oxide conversions in the runs having high oxygen feed rates (pure O_2) tended to be slightly greater than for the air runs (94.3% vs 89.9%). However, in the LWR-8 experiment (550°C, air) a 98.7% conversion was measured, and in the LWR-2 run where clad fuel was voloxidized for 4.5 h (480°C, air), a slight excess (106%) to the theoretical yield was obtained.

Calculated conversions based on amount of oxygen consumed generally were higher; an average conversion value of 112.1% was obtained for the same experiments. This may be due to accumulating errors in on-line flow rate and concentration measurements.

The product from the shortened run (Run LWR-10, 40 min at temperature) showed a 1.44% weight increase, which is $\sim 35\%$ of the amount required for complete conversion to U_3O_8 . That weight gain corresponds to the 1.48% weight increase necessary for conversion to U_4O_9 . Samples of the product were analyzed by x-ray diffraction (see Sect. 3.2.8).

3.2.3 Fuel comminution

Size distributions for the unclad fuel charged to and recovered from the voloxidizer during the parametric experiments are listed in Table 4. No data were taken for Runs 13 and 14. In the earlier experiments (LWR-1, -2, and -3), it was shown that oxidation of the fuel resulted in essentially complete pulverization of the oxide, irrespective of whether the UO_2 feed was in cladding or not. The same results were seen in these tests. In each case where sufficient reaction time was allowed, $99.6 \pm 0.2\%$ of the product was found below the 44- μm -sized sieve. More detailed sieve analyses on the voloxidized products from other UO_2 fuels have shown that $>99\%$ were sized $<20 \mu\text{m}$.

Table 3. Material balances on voloxidation of H. B. Robinson-2 fuel

Run No.	Input total (g)	Output total (g)	Weight gain (g)	Yield ^a (%)	Oxide conversion	
					Measured ^a (%)	Calculated ^b (%)
LWR-1	135.9 ^c	139.6 ^c	3.7	99.4	83.1	112.0
LWR-2	120.6 ^c	124.7 ^c	4.1	100.2	106.0	115.0
LWR-3	72.7	75.2	2.5	99.5	87.1	80.0
LWR-4	100.2	103.7	3.5	99.2	91.0	118.3
LWR-5	100.0	103.8	3.8	99.9	99.0	118.5
LWR-6	100.3	103.9	3.6	99.8	96.0	111.8
LWR-7	100.4	103.7	3.3	99.5	86.8	120.7
LWR-8	100.4	104.2	3.8	99.9	98.7	112.4
LWR-9	100.1	104.1	4.0	100.0	100.0	115.0
LWR-10	100.2	101.6	1.4	97.7	36.4	63.4
LWR-11	99.7/310.6	413.5	3.2	99.4	83.6	100.1
LWR-12	100.0	103.2	3.2	99.4	83.3	104.4
LWR-13	100.0	103.4	3.4	99.6	88.6	126.2
LWR-14	100.0	103.4	3.4	99.6	88.6	107.7
LWR-15	115.8 ^c	119.1 ^c	3.3	99.8	92.9	127.0

^aBased on 3.95% increase in UO₂ weight (excluding fission products and insolubles) for 100% theoretical yield.

^bDetermined from oxygen consumption measurements.

^cTotals include cladding weight: LWR-1 (23.3 g), LWR-2 (22.9 g), and LWR-15 (23.3 g).

Table 4. Fuel comminution during voloxidation

Mesh size	Opening (μm)	Size distribution, % of fuel remaining on indicated screen										
		Unoxidized feed ^a	Voloxidized product									
			LWR (4)	LWR (5)	LWR (6)	LWR (7)	LWR (8)	LWR (9)	LWR (10) ^b	LWR (11) ^c	LWR (12)	LWR (15) ^d
20	841	43.41										
35	500								55.50			
40	420	24.30										
100	149	19.69							20.60			
	<149	12.60										
200	74								6.50			
325	44		0.97	0.51	0.39	0.25	0.50	0.38	2.80	0.10	0.50	0.40
	<44		99.03	99.49	99.61	99.75	99.50	99.62	14.60	99.90	99.50	99.60

^aUnclad UO_2 in 100-g-sized batches.

^bTerminated after 40 min at temperature.

^cFeed included 310.6 g of U_3O_8 .

^dFeed was UO_2 clad in 1-in.-long pieces.

Apparently, operating temperature, oxygen feed rate, or the presence of cladding (over the ranges studied) had no significant effects on the final size distributions, although the number of runs was small. The fuel product from the mixed-bed experiment showed slightly more comminution, as expected, since it experienced more processing (tumbling and oxidizing) than usual. In LWR-10, only limited amounts of pulverization were evident after 80 min (40 min at 480°C) of rotary voloxidation in air.

3.2.4 Fission product contents of H. B. Robinson UO₂

The inventory of fission products in H. B. Robinson UO₂ was determined by (1) dissolution of unvoloxidized and voloxidized segments and fragments of fuel, and (2) analyzing the solutions, insoluble residues, and gas streams. The best values for the fission product content are listed in Table 5; these concentrations form the basis of the calculated releases of fission products.

3.2.5 Release of gaseous fission products

Fission product releases from the UO₂ during voloxidation are presented in Table 6 as percentages of the total measured fuel contents. Tritium release fractions were obtained by differences in the dissolver solutions with or without prior voloxidation. The recoveries of tritium from the silica-gel traps generally ranged from 75 to 85% of the total amounts found by difference.

The tritium releases were high in all cases, and, except for one clad fuel run and the shortened experiment, they averaged $\geq 99.9\%$ of the fuel inventories. The parametric variables (temperature, oxygen feed rate, bed depth, and the presence of cladding) apparently had little effect on the total amounts evolved in these tests. These results indicate that 3 to 4 h of voloxidation in air at 480°C, with agitation, should be sufficient to quantitatively remove the tritium from unclad UO₂ fuel. Less time would be required in a pure oxygen atmosphere.

Krypton releases were typically low, ranging from ~ 2.2 to 7.2% of the amount in the fuel. The amounts released to the voloxidizer off-gases were about twice as great for the experiments in air, probably due to the longer times at temperature in those runs. Only the mixed-bed effect (LWR-11) appeared to significantly inhibit ⁸⁵Kr release.

Table 5. Fission product recoveries from H. B. Robinson-2 UO₂ (based on the date of 4-1-77)

Run No.	(U + Pu) (g)	dis sec ⁻¹ g (U + Pu) ⁻¹								
		³ H x 10 ⁶	¹⁴ C x 10 ⁴	⁸⁵ Kr x 10 ⁸	¹⁰⁶ Ru x 10 ⁴	¹²⁵ Sb x 10 ⁷	¹²⁹ I ^a	¹³⁴ Cs x 10 ⁹	¹³⁷ Cs x 10 ⁹	¹⁴⁴ Ce x 10 ⁹
1A ^b	25.95	9.80	1.15 ^c	3.23	2.52	c	12.6 ^c	1.77	3.50	2.64
1B	15.58	7.43	1.48 ^c	c	2.81	8.67	75.6 ^c	1.79	3.41	2.58
1C	82.16	7.74 ^c	1.62 ^c	d	2.13	7.79	54.2 ^c	1.70	3.27	2.39
2A	16.32	7.19 ^c	1.61 ^c	3.33	2.03	6.44 ^c	79.1 ^c	1.78	3.38	2.65
3A	64.64	6.62 ^c	1.69 ^c	d	2.59	10.30	146.6 ^c	1.62	3.12	2.46
3B ^b	25.26	10.90 ^c	2.05	3.88	2.07	9.60	21.9 ^c	1.34 ^c	2.55 ^c	1.98 ^c
4	82.19	9.33 ^c	1.46 ^c	d	1.54 ^c	5.13 ^c	129.0 ^c	1.81	3.45	2.79
5	20.26	8.90 ^c	2.13	d	1.77 ^c	0.65 ^c	157.0	1.57	2.87 ^c	2.17
6	20.04	9.96 ^c	0.32 ^c	d	2.12	8.37	11.9 ^c	1.78	3.29	2.50
7	18.81	8.95 ^c	2.19	3.44	1.63 ^c	0.01	38.2 ^c	1.91	3.67	2.83
8	21.07	8.90 ^c	0.67 ^c	3.26	2.20	10.20	d	1.61	2.98	2.17
9-1	21.60	6.95 ^c	bc	d	2.29	8.91	d	1.73	3.18	2.55
9-2	21.53	6.95 ^c	1.66 ^c	d	2.18	11.60	d	1.86	3.40	2.85
9-3	21.23	6.95 ^c	bc	d	0.32 ^c	8.98	d	1.88	3.45	2.79
9-4	16.82	6.95 ^c	bc	d	0.49 ^c	8.69	d	3.59 ^e	6.54 ^e	5.19 ^e
10	20.61	6.25 ^c	3.22	3.50	1.44 ^c	10.80	d	1.42	3.59	2.68
11-1	18.75	8.08 ^c	c	1.67 ^c	2.27	c	d	1.89	3.63	2.78
11-2	20.82	8.08 ^c	1.78 ^c	1.99 ^c	c	c	d	1.83	3.37	2.68
11-3	18.41	8.08 ^c	d	d	c	c	d	d	d	d
11-4	c	d	d	d	c	c	d	d	d	d
11-5	c	d	d	d	c	c	d	d	d	d
11-6	c	d	d	d	c	c	d	d	d	d
12A ^f	23.61	7.11	1.02 ^f	1.95 ^f	1.67	7.24 ^f	d	1.19 ^f	2.55 ^f	2.32
12B ^f	22.53	f	1.36 ^f	1.74 ^f	f	f	d	1.23 ^f	2.56 ^f	2.30
15A	20.32	c	1.82 ^f	2.09 ^c	2.35	16.30	d	1.89	3.51	2.80
15C	20.60	c	d	2.27 ^c	1.96	9.15	d	0.96	3.12	0.51 ^c
"Best"	-	1.02+0.06	2.15+0.07	3.44+0.24	2.37+0.24	9.87+2.23	157	1.76+0.15	3.30+0.28	2.55+0.25
value		x 10 ⁷	x 10 ⁴	x 10 ⁸	x 10 ⁹	x 10 ⁷		x 10 ⁹	x 10 ⁹	x 10 ⁹

^a μg/g (U + Pu).

^b No voloxidation.

^c Incomplete recovery; not used in average.

^d Not measured.

^e Not used in average; see text.

^f Low burnup, end segments.

Table 6. Gaseous release totals during voloxidation

Run No.	Temp. (°C)	Atmos.	O ₂ feed rate (mol/h)	Released (% of UO ₂ inventory)		
				³ H ^a	¹⁴ C ^a	⁸⁵ Kr ^b
LWR-1 ^c	480	Air	0.10	97.2	>32.0	6.5
LWR-2 ^c	480	Air	0.10	99.9	52.0	6.1
LWR-3	480	Air	0.15	>99.9	>81.0 ^b	4.3
LWR-8	550	Air	0.15	99.9	67.4	4.5
LWR-10 ^d	480	Air	0.15	40.6	7.6 ^b	2.2
LWR-11 ^e	480	Air	0.15	99.9	43.8	2.2
LWR-12	480	Air	0.11	>99.9	19.2	4.8
LWR-13	480	Air	0.15	99.9	f	7.2
LWR-14	480	Air	0.135	99.9	f	7.2
LWR-4	480	O ₂	0.55	99.9	32.9	3.9
LWR-5	480	O ₂	0.55	>99.9	28.1	3.8
LWR-6	480	O ₂	1.20	>99.9	>15.5 ^b	5.3
LWR-7	550	O ₂	0.75	99.9	19.1 ^b	5.2
LWR-9	550	O ₂	0.75	99.9	19.2	4.8
LWR-15 ^c	480	O ₂	0.75	99.9	11.4	5.4

^aBased on residual content of voloxidized oxide except where noted for ¹⁴C.

^bDetermined from collected voloxidizer off-gas.

^cCladding present.

^dTerminated after 40 min at temperature.

^eMixed bed of UO₂ + U₃O₈. Releases based on UO₂ contents.

^fNot analyzed. Tritium release estimated from off-gas recoveries.

Approximately the same amount (2.2%) was evolved from the fresh UO_2 in the $\text{UO}_2\text{-U}_3\text{O}_8$ mixture after 4 h as was evolved during the shortened UO_2 run.

Releases of ^{14}C during voloxidation were quite variable, ranging from 11 to 81%. Much of the scatter in the ^{14}C release totals (Table 6) can be attributed to difficulties with recovery and analysis of the carbon isotope. (A CO_2 carrier in the voloxidizer purge gas and improved analytical techniques were adopted after these runs were completed.) As with krypton, the apparent higher releases during the runs in air might be caused by the longer times at temperature; for example, after 40 min at 480°C , only 7.6% of the ^{14}C had been evolved (LWR-10).

The experiments (12 to 14) to determine the fraction of tritium released as HT, vs HTO , did not yield the HT content of the off-gas. It was found that any HT present was less than the "noise" due to variability between experiments with and without the CuO oxidizers. One concludes that the amount of HT in the off-gas is small, probably $<1\%$ of the total, but the exact amount has not been established.

3.2.6 Gaseous release profiles

Gas evolution and oxygen consumption occurred more rapidly in the higher O_2 feed rate runs at 480°C . There was some indication that the rate of release in pure oxygen was slightly slower at 550 than at 480°C . Concentration profiles and consumption-release curves are shown for typical runs of each type: air (LWR-8) and O_2 (LWR-7) in Figs. 1 and 2, respectively. Both sets of curves show close correspondence between oxygen-utilization rates and the release of gas from the UO_2 . Tritium collection on the traps usually lagged behind release of ^{85}Kr by 10 to 30 min, indicating a slower transport through the heated lines. All air runs (O_2 feed rate 0.1 to 0.15 mol/h) showed double-peaked oxygen-consumption curves with corresponding double-peaked releases of ^{85}Kr . This phenomenon is thought to be related to the two-stage oxidation of UO_2 to U_4O_9 , then U_3O_8 (see Sect. 3.2.8).

The relationships between off-gas concentration peaks and oxygen spikes (consumption maximums) are shown in Table 7. Tritium and krypton peak heights were related to the rate of oxygen consumption: generally,

Fig. 1 (a) Voloxidizer off-gas concentration profiles for tritium, krypton, and oxygen (LWR-8; air); (b) gaseous release and oxygen consumption during voloxidation (LWR-8).

Fig. 2 (a) Oxygen consumption rate and tritium and krypton off-gas concentration profiles (LWR-7; O_2); (b) gaseous release and oxygen consumption during voloxidation (LWR-7).

Table 7. Gaseous release and oxygen consumption during voloxidation of H. B. Robinson fuel (all times include an approximate 40-min heatup to operating temperature)

Run No.	Voloxidation conditions			O ₂ utilization Peak rate (mol/h)	³ H in off-gas		Cumulative O ₂ ^a		Time (min)		
	Atmos.	Temp. (°C)	O ₂ feed rate (mol/h)		Max. conc. (dis s ⁻¹ cm ⁻³)	Time (min)	50%	100%	Tritium release		
									50%	90%	100%
LWR-1 ^c	Air	480	0.1	0.08	1.03 E+04	165	130	280	340 ^d	420 ^d	
LWR-2 ^c	Air	480	0.1	0.07	4.07 E+04	140	135	290	120	200	280
LWR-3	Air	480	0.15	0.07	2.95 E+04	95	85	140	95	125	180
LWR-8	Air	550	0.15	0.12	6.92 E+04	83	82	155	85	127	180
LWR-10 ^e	Air	480	0.15	0.11	3.25 E+04	80	f		f		
LWR-11 ^g	Air	480	0.15	0.11	7.71 E+04	112	85	165	100	140	210
LWR-12 ^h	Air	480	0.11	0.08			100	168			
LWR-13 ^h	Air	480	0.15	0.11			73	180			
LWR-14 ^h	Air	480	0.135	0.10			75	180			
LWR-4	O ₂	480	0.55	0.46	2.34 E+05	82	67	88	84	92	180
LWR-5 ⁱ	O ₂	480	0.55	0.43	1.16 E+05	115	67	90	120	j	j
LWR-6	O ₂	480	1.20	0.71 _k	1.23 E+05	78	70	85	80	95	130
LWR-7	O ₂	550	0.75	0.75 _k	1.05 E+05	67	57	65	77	90	165
LWR-9	~O ₂	550	0.75	0.75 _k	8.28 E+04	63	56	70	73	83	150
LWR-15 ^c	O ₂	480	0.75	0.75 _k	9.98 E+04	68	46	60	66	74	170

^aPercentage of total oxygen consumed during experiment.

^bRelease of indicated percentage of tritium contained by the UO₂.

^cCladding present.

^dRecoveries delayed by condensation of ³H₂O in off-gas system.

^eTerminated after 40-min at temperature.

^fAt termination product wt gain was 36% of theoretical value; about 41% of the tritium inventory had been released.

^gMixed bed of UO₂ and U₃O₈.

^hTritium release rates not measured.

ⁱLow purge rate due to system backpressure after first 80 min.

^jApproximately 66% of the tritium was recovered on silica gel during voloxidation; the remainder was recovered during a 2-h purge after the run.

^kAt maximum utilization, output flow from voloxidizer was zero.

the off-gas concentrations were 2 to 3 times greater in the pure O_2 experiments. The effects of bed depth and cladding were more substantial in the air runs. Release curves for the mixed-bed experiment [Run 11, Figs. 3(a) and 3(b)] show profiles extended ~ 45 min in comparison with other experiments (see Fig. 4). Tritium releases from the 1-in.-clad fuel was delayed when air was the oxidant purge. The cumulative release in LWR-2 lagged from 60 to 100 min behind that of runs with unclad fuel (Fig. 5). Oxidation and tritium evolution in the higher oxygen feed rate experiments apparently proceeded normally when this 1-in. length of cladding was present (Fig. 6). The pronounced second peaks seen in off-gas ^3H concentrations whenever clad fuel was voloxidized have not been fully explained. While this could be explained by release of ^3H from the Zircaloy cladding, and recoveries on silica gel during the clad runs were a few percent higher in two of three instances, analysis of the voloxidized cladding did not conclusively verify a decrease in its tritium content. We are continuing to investigate with other Zircaloy-clad UO_2 fuels.

3.2.7 Rate of O_2 consumption

As shown in Table 7 and Figs. 1 and 2 from Sect. 3.2.5 during the pure O_2 runs, the peak oxidation rates were generally four to seven times greater than in air. Typically, in both cases (air and O_2) at least 70 to 85% of the oxygen in the feed stream was consumed during the periods of the maximum conversion rates. In three runs with oxygen (Nos. 7, 9, and 15), the outflow from the voloxidizer fell to zero, indicating that 100% utilization of the oxygen was attained at those times. In Run 6, having the highest feed rate, the peak oxygen utilization rate was approximately the same (0.71 mol/h). This might indicate that the maximum rate of oxygen consumption had been reached for this fuel.

There was some indication that the higher temperature level (550°C) decreased the tritium release rate at one higher oxygen flow rate. Utilization of oxygen by the UO_2 - U_3O_8 mixed bed was slightly inhibited (the consumption curve in Fig. 3 was not as sharply peaked). Tritium release during that run was also slowed. The presence of cladding appeared to significantly delay the oxidation process. Total cumulative consumption times were approximately doubled, increasing from ~ 165 to 290 min.

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Fig. 3 (a) Voloxidizer off-gas concentration profiles for tritium, krypton, and oxygen (LWR-11; air, mixed bed); (b) gaseous release and oxygen consumption during voloxidation (LWR-11).

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Fig. 4. Bed depth effects on tritium release.

Fig. 5. Tritium concentration profiles in air.

Fig. 6. Tritium concentration profiles in oxygen.

3.2.8 X-ray diffraction analysis of voloxidized UO_2

Samples of the partially voloxidized product from LWR-10 were submitted to the High-Radiation-Level Examination Laboratory for determination of the uranium oxide form by x-ray diffraction. A representation of the diffraction scans appears in Fig. 7. Experiment 10 was interrupted at a point on the double-peaked oxygen curve corresponding to the position of sample Nos. 3 and 4. Fuel from the +200 and -325 mesh fractions were each submitted. Voloxidized fuel (samples Nos. 2 and 5) was submitted along with a portion of unvoloxidized UO_2 (sample No. 1). Peaks on the scans at the indicated Bragg diffraction angles (top) were used to calculate d-lattice spacings for each sample.

$$\lambda = 2d \sin \theta,$$

where

$$\text{Bragg angle} = 2\theta$$

$$\lambda = \text{wavelength of copper } \alpha\text{-line} = 1.5418 \text{ \AA}$$

$$d = \text{lattice spacing.}$$

The spacings (peak locations) indicate that although there is not a large definition between the UO_2 and U_4O_9 spacing alignments, both samples 3 and 4 showed peaks corresponding to the U_4O_9 standard configuration rather than one for the UO_2 standard as did sample 1. The completely voloxidized fuel had an entirely different lattice structure and was analyzed as U_3O_8 - α . Voloxidized and partially voloxidized samples of unirradiated fuel from Runs LWR-A, B, C, D, and E showed diffraction results similar to those from the Robinson fuel.

These results, considered along with the weight gain measured on the LWR-10 product (Sect. 3.2.2), tend to verify the presence of U_4O_9 and suggest that its formation is connected with the double-peaked consumption pattern seen during voloxidation of UO_2 at low oxygen feed rates.

3.2.9 Fission product distribution

Experimentally determined inventories of fission products in H. B. Robinson fuel were listed in Table 5. Fission product amounts remaining on voloxidizer walls and on samples located in the off-gas system were determined following voloxidation at several conditions.

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Fig. 7. X-ray diffraction scans of voloxidized H. B. Robinson fuel.

Selected recoveries are shown in Table 8 as percentages of inventories listed in Table 5. No samples were analyzed for Runs LWR-13 and -14. The results for LWR-12 are for deposition and entrainment samples remaining in the system for Runs 10, 11, and 12.

Generally, <0.1% of the total ^{106}Ru , ^{125}Sb , $^{134-137}\text{Cs}$, and ^{144}Ce left the fuel and was found in the system after voloxidation in air or O_2 at either temperature level. Apparently, the leach solution for the LWR-15 voloxidizer sheet sample was contaminated or some of the loose (nondeposited) fuel was left on the sample prior to leaching. (Brushing or ultrasonic washing of the sheets usually provides adequate precleaning.)

Higher temperatures and purge flow rates tended to increase fission product volatilization. With the exception of ^{129}I (excluding LWR-5, low flow rate) and to some extent ^{106}Ru , most of the recovered fission products were deposited on sample surfaces within the voloxidizer. Amounts of cesium, cerium, and antimony transferring to the off-gas system were typically <0.001% of the fuel contents. Recoveries of volatilized iodine were usually on the order of 1 to 2% of the total fuel inventories, nearly all of which were located on downstream charcoal beds heated to 125°C (Table 9). Most of the other fission products reporting to the off-gas system were deposited on tubing specimens immediately beyond the exit-gas frit. Apparently the higher oxidation rates and higher temperature (LWR-7 at 550°C) caused more cesium to reach the secondary HEPA filters as fine (<0.3- μm -sized) particulates.

Under the conditions studied, the ruthenium released from the fuel evidently acted somewhat differently from other fission products. Approximately the same amount of ^{106}Ru was found on off-gas system samples as was recovered from inside the voloxidizer. Most of the released ruthenium was retained on tubing specimens, where surface temperatures ranged from $>400^\circ\text{C}$ down to $\sim 100^\circ\text{C}$ (Fig. 8). Increased quantities of ^{106}Ru were deposited during runs with more severe oxidizing conditions. Usually less ^{137}Cs was on the tubing samples from runs with high-temperatures and high- O_2 feed rates than was found on samples from oxidations at the baseline conditions (480°C , air). A comparison of fission product ratios shown in Table 10 indicates that ^{106}Ru was volatilized as RuO_2 to a greater extent than the other semi-volatile fission product oxides. It is possible that oxidation to the

Table 8. Selected fission product recoveries from the voloxidizer and off-gas system

Nuclide	Run No.	Temp. (°C)	Atmosphere	Distribution (% of UO ₂ inventory)	
				Voloxidizer walls	Off-gas system
¹⁰⁶ Ru	LWR-1 ^a	480	Air	0.007	<0.001
	LWR-2 ^a	480	Air	0.007	<0.001
	LWR-3	480	Air	0.007	0.003
	LWR-8	550	Air	0.047	0.014
	LWR-12 ^b	480	Air	0.047	0.003
	LWR-4	480	O ₂	0.020	0.030
	LWR-5	480	O ₂	0.030	0.040
	LWR-6	480	O ₂	0.040	0.050
	LWR-7	550	O ₂	0.080	0.080
	LWR-9	550	O ₂	0.168	0.104
	LWR-15 ^a	480	O ₂	0.038 ^c	0.080
¹²⁵ Sb	LWR-1 ^a	480	Air	0.026	<0.001
	LWR-2 ^a	480	Air	0.026	<0.001
	LWR-3	480	Air	0.025	0.001
	LWR-8	550	Air	0.110	0.001
	LWR-12 ^b	480	Air	0.086	<0.001
	LWR-4	480	O ₂	0.020	<0.001
	LWR-5	480	O ₂	0.068	<0.001
	LWR-6	480	O ₂	0.068	<0.001
	LWR-7	550	O ₂	0.122	<0.001
	LWR-9	550	O ₂	0.263	<0.001
	LWR-15 ^a	480	O ₂	0.119 ^c	<0.001
¹²⁹ I	LWR-1 ^a	480	Air	0.22	0.66
	LWR-2 ^a	480	Air	0.22	0.04 ^d
	LWR-3	480	Air	0.22	1.08
	LWR-8	550	Air	0.06	1.60
	LWR-12 ^b	480	Air	1.44	0.29
	LWR-4	480	O ₂	0.09	0.56
	LWR-5	480	O ₂	e	0.30
	LWR-6	480	O ₂	e	2.36
	LWR-7	550	O ₂	e	1.40
	LWR-9	550	O ₂	0.06 ^c	1.56
	LWR-15 ^a	480	O ₂	21.2	1.17

Table 8 (Continued)

Nuclide	Run No.	Temp. (°C)	Atmosphere	Distribution (% of UO ₂ inventory)	
				Voloxidizer walls	Off-gas system
¹³⁴ Cs	LWR-1 ^a	480	Air	0.017	<0.001
	LWR-2 ^a	480	Air	0.017	<0.001
	LWR-3	480	Air	0.017	<0.001
	LWR-8	550	Air	0.040	0.002
	LWR-12 ^b	480	Air	0.022	<0.001
	LWR-4	480	O ₂	0.024	<0.001
	LWR-5	480	O ₂	0.013	<0.001
	LWR-6	480	O ₂	0.038	<0.001
	LWR-7	550	O ₂	0.055	<0.001
	LWR-9	550	O ₂	0.074	<0.001
	LWR-15 ^a	480	O ₂	0.246 ^c	<0.001
¹³⁷ Cs	LWR-1 ^a	480	Air	0.021	<0.001
	LWR-2 ^a	480	Air	0.021	<0.001
	LWR-3	480	Air	0.021	0.002
	LWR-8	550	Air	0.039	0.002
	LWR-12 ^b	480	Air	0.024	<0.001
	LWR-4	480	O ₂	0.025	<0.001
	LWR-5	480	O ₂	0.012	<0.001
	LWR-6	480	O ₂	0.038	<0.001
	LWR-7	550	O ₂	0.055	<0.001
	LWR-9	550	O ₂	0.073	<0.001
	LWR-15 ^a	480	O ₂	0.323 ^c	<0.001
¹⁴⁴ Ce	LWR-1 ^a	480	Air	0.014	<0.001
	LWR-2 ^a	480	Air	0.014	<0.001
	LWR-3	480	Air	0.014	<0.001
	LWR-8	550	Air	0.034	0.001
	LWR-12 ^b	480	Air	0.026	<0.001
	LWR-4	480	O ₂	0.003	<0.001
	LWR-5	480	O ₂	0.014	<0.001
	LWR-6	480	O ₂	0.033	<0.001
	LWR-7	550	O ₂	0.043	<0.001
	LWR-9	550	O ₂	0.064	<0.001
	LWR-15 ^a	480	O ₂	0.233 ^c	<0.001

^aCladding present.

^bDeposition and entrainment samples remained in the system for Runs 10, 11, and 12.

^cThese results appear to be in error; see text.

^dCharcoal paper used instead of charcoal bed.

^eNot detected.

Table 9. Distribution of selected fission products in the voloxidizer off-gas system

Nuclide	Run No.	System distribution (% of total released from voloxidizer)					Total found in off-gas system [dis·sec ⁻¹ g(U + Pu) ⁻¹]
		Deposition tubing	Graded filter papers (>5 μm)	(0.3 μm)	Charcoal bed	HEPA filter	
¹⁰⁶ Ru	LWR-3	99.86	0.03	0.01	0.07	0.04	5.76E4
	LWR-8	99.96	0.02	0.01	a	a	3.11E5
	LWR-4	99.91	0.03	0.03	b	0.04	6.30E5
	LWR-7 ^c	99.77	0.23		b	b	1.81E6
	LWR-15 ^c	99.96	0.02	0.01	a	a	1.83E6
¹²⁹ I	LWR-3	5.75	b	b	94.25	b	1.634 ^d
	LWR-8	e	e	e	100.0	e	2.430 ^d
	LWR-4	b	b	b	100.0	b	0.849 ^d
	LWR-7 ^c	2.40	e	e	97.60	e	1.730 ^d
	LWR-15 ^c	e	e	e	100.0	e	1.780 ^d
¹³⁴ Cs	LWR-3	98.54	0.35	0.04	0.50	0.57	3.55E3 ^f
	LWR-8	99.71	0.21	0.07		0.01	2.68E2
	LWR-4	61.15	10.81	12.94	0.83	14.27	3.23E2
	LWR-7 ^c	80.97	16.12	1.05		1.86	8.81E1
	LWR-15 ^c	97.74	1.46	0.29	0.21	0.29	1.10E2
¹³⁷ Cs	LWR-3	99.59	0.10	0.01	0.19	0.11	6.52E4 ^f
	LWR-8	99.56	0.24	0.11	0.03	0.05	1.24E3
	LWR-4	86.71	5.26	5.23	0.14	2.67	7.05E3
	LWR-7 ^c	63.53	11.78	9.96	0.04	14.69	2.86E2
	LWR-15 ^c	96.83	1.03	0.27	1.45	0.42	3.59E2

^aTrace quantities.^bUndetected.^cCladding present.^dValues in μg/g.^eNo analysis.^fCesium ratios for LWR-3 indicated residual contamination in system from fast irradiated fuel.

Fig. 8. Fission product deposition from voloxidizer off-gas.

Table 10. Ratios of ruthenium to selected fission products recovered from the voloxidizer system

Nuclides	Run	Voloxidation conditions			Ratio (location)		
		Temp. (°C)	Atmos.	O ₂ feed rate (mol/h)	Fuel	Voloxidizer ^a	Off-gas system ^a
¹⁰⁶ Ru/ ¹³⁷ Cs	LWR-3	480	Air	0.15	0.692	0.262	0.883
	LWR-8	550	Air	0.15	0.663	0.824	250.0
	LWR-4	480	O ₂	0.55	0.663	0.426	31.5
	LWR-9	550	O ₂	0.75	0.663	1.60	3699.0
	LWR-15 ^b	480	O ₂	0.75	0.692	0.081	5097.0
¹⁰⁶ Ru/ ¹⁴⁴ Ce	LWR-3	480	Air	0.15	0.906	0.50	36.7
	LWR-8	550	Air	0.15	0.854	1.15	c
	LWR-4	480	O ₂	0.55	0.854	4.14	230.0
	LWR-9	550	O ₂	0.75	0.854	2.37	c
	LWR-15 ^b	480	O ₂	0.75	0.906	0.146	c

^aRatios determined from total fission product recoveries on voloxidizer walls and in the off-gas system following voloxidation.

^bCladding present.

^cCerium amounts below detection limits.

the more volatile RuO_4 would be enhanced by the increase in temperature and oxidation rate.

3.2.10 Actinide and fission product accumulation

The continuing buildup of fission products and entrapped heavy-metal oxides within the voloxidizer could be troublesome over a period of time. Sheet samples remaining in the voloxidizer through several runs were analyzed for accumulated species (see Table 11). The results seem to indicate that no significant amount of deposition had occurred after periods of up to 21.7 h of operation [763 g(U + Pu) throughput]. Actinide recoveries were on the order of 0.01 to 0.02% of the cumulative amounts processed. Fission product deposition was also minimal and showed no significant increase after four runs [348 g(U + Pu) throughput]. We are continuing to look at this problem with other fuels and particularly after a number of runs at severe oxidizing (plateout) conditions.

3.3 Dissolution

3.3.1 General

The effects of the voloxidation variables on the release of tritium, krypton, and other fission products from the fuel were measured by dissolving the UO_2 or U_3O_8 in nitric acid and analyzing the gases, solutions, and undissolved residues. The dissolution — usually a series of three leaches in nitric acid, with centrifugation and washing between — was also used to compare any effects on the solubility of the untreated and oxidized fuel due to the voloxidation. Earlier studies with the Robinson fuel indicated that voloxidation in air at 480°C increased the total amount of insoluble residue from ~ 0.2 wt % of the UO_2 that was dissolved to ~ 0.6 wt %. Greater than 99.9% of the fuel usually dissolved in the first 2-h leach in 7 M HNO_3 .¹

In order to eliminate possible effects due to the presence of the Zircaloy cladding, the fuel was separated from its cladding prior to voloxidation in all of the tests except the early baseline studies (Runs 1A, 1C, and 3B) and in Run 15.

The voloxidation variables and dissolution conditions are listed in Tables 12 and 13. Runs 1A, 3B, and 12A were the baseline dissolutions of unvoloxidized UO_2 ; Runs 1BC, 3A, 12B, and 15A represent dissolutions of

Table 11. Accumulation of actinides and fission products in the voloxidizer

Run Nos.	Σ (U + Pu) (g)	Σ Time (hr)	Amounts deposited on voloxidizer walls				
			U (mg)	Pu (mg)	¹⁰⁶ Ru (dis/sec)	¹³⁷ Cs (dis/sec)	¹⁴⁴ Ce (dis/sec)
6 to 8	248.9	7.33	38.7	0.32	5.65E7	1.28E8	8.47E7
9 to 12	348.4	9.33	69.1	0.62	3.77E8	2.79E8	2.29E8
4 to 12	763.0	21.66	76.4	0.68	1.93E8	2.85E8	2.58E8

Table 12. Voloxidation variables for H. B. Robinson fuel used in hot-cell dissolution tests

Voloxidation conditions				
None	480°C		550°C	
	Air	Oxygen	Air	Oxygen
Run 1A	Run 1BC	Run 4	Run 8	Run 7
Run 3B	Run 3A	Run 5		Run 9
	Runs 10, ^a 11	Run 6		
Run 12A	Run 12B	Run 15A		

^aVoloxidized to U_4O_9 stage and stopped.

the U_3O_8 product from voloxidation Runs 1, 3, 12, and 15, as did Runs 4 through 8. The U_3O_8 products from voloxidation Runs 9 and 11 were divided into ~25 g aliquots, and dissolved or leached in dissolution Runs 9-1, 9-2, 11-1, 11-2, etc.

In Runs 9-1, 9-2, 9-3, and 9-4, successively smaller volumes of 7 M HNO_3 were used to determine what effect that had on the centrifugation of the insoluble residue from the first leach. In Runs 11-1, 11-2, 11-3, 11-4, the volume of the first leach was held constant, and the moles of nitric acid were decreased in successive runs. Runs 11-5 and 11-6 were tests on the effect of the presence of $UO_2(NO_3)_2$ and lower concentrations of HNO_3 on the dissolution rate of the U_3O_8 . Runs 12A and 12B were made with UO_2 from the lower-burnup end segments of the Robinson fuel rods. The primary dissolution conditions are shown in Table 13.

3.3.2 Material balances

The material balances for the experiments are listed in Table 14. The recoveries are based upon the weight of total uranium, plutonium, and residue found plus a calculated average amount of soluble fission products [0.018 g/g (U + Pu)]. The soluble fission product content of the H. B. Robinson-2 fuel was determined by spark source mass spectrometric (SSMS) analyses of first (concentrated) leach solutions. The plutonium content was calculated on the basis of a specific plutonium alpha activity of 4.35×10^8 alpha counts $min^{-1} mg^{-1}$; that counting rate was based upon the isotopic composition of the plutonium, determined by mass spectrometer analysis.

The material balances for 20 experiments, discounting four obviously low values, were $100.4 \pm 2.4\%$, well within weighing and analytical errors. The amount of insoluble residue (last column in Table 14) increased from 0.18 wt % of the $(U,Pu)O_2$ in solution for three runs with unvoloxidized fuel to 0.62 ± 0.16 wt % for the 19 experiments with voloxidized fuel (all conditions). This is in agreement with the earlier baseline studies with the H. B. Robinson-2 fuel.¹

Table 13. Dissolution conditions for first leach of H. B. Robinson-2 fuel (92 to 95°C, 2-h each)

Run No.	Equiv. UO_2 (g)	U (mol)	HNO ₃ supplied for DS-1		
			Volume (ml)	Concentration (M)	mol H ⁺ /mol U
1A ^a	29.8	0.110	75	7.0	4.8
1B	17.8	0.066	100	7.9	12.0
1C ^a	94.2	0.396	250	7.4	4.7
2A	18.3	0.068	50	7.0	5.2
3A	72.4	0.268	200	7.9	5.9
3B ^a	30.0	0.111	80	7.0	5.0
4	98.2	0.363	265	7.9	5.7
5	24.3	0.090	66	7.0	5.1
6	24.1	0.089	66	7.0	5.2
7	23.7	0.088	66	7.0	5.3
8	24.8	0.092	67	7.0	5.1
9-1	24.3	0.090	66	7.0	5.1
9-2	25.0	0.093	60	7.0	4.5
9-3	25.5	0.094	53	7.0	4.0
9-4	25.0	0.093	44	7.0	3.3
10 ^b	24.1	0.091	62	7.0	4.8
11-1	24.3	0.090	63	7.0	4.9
11-2	23.8	0.088	63	6.3	4.5
11-3	24.1	0.089	62	5.6	3.9
11-4	24.2	0.089	62	5.1	3.5
11-5	24.1	0.089	150 ^c	4.2	7.1
11-6	23.7	0.088	100 ^d	5.1	5.8
12A	26.2	0.097	66	7.0	4.8
15A	24.1	0.089	100	7.0	7.9

^aCladding present during dissolution.

^bIncomplete voloxidation - stopped at U_4O_9 -stage ($\text{U} = 0.869 \times \text{wt.}$).

^cDissolvent was 151 g U per liter - 4.2 M HNO_3 .

^dDissolvent was 76 g U per liter - 5.1 M HNO_3 .

Table 14. Material balances for dissolution experiments (H. B. Robinson-2)

Run No.	Dissolved ^a		Recovered					
	UO ₂ (g)	UO ₂ (g)	PuO ₂ (g)	Residue (g)	Sol. F. P. (g)	Total (g)	% Input	Residue % of (U,Pu)O ₂
1A	29.8	29.20	0.25	0.05	0.52	30.02	100.7	0.18
1B	17.8	17.53	0.14	0.11	0.32	18.10	101.7	0.62
1C	94.2	92.33	0.82	0.42	1.66	95.23	101.1	0.45
2A	18.3	18.36	0.16	0.11	0.33	18.96	103.6	0.57
3A	72.4	72.87	0.50	0.53	1.33	75.22	103.9	0.72
3B	29.6	28.41	0.26	0.06	0.52	29.25	98.8	0.20
4	98.2	92.49	0.80	0.28	2.57	96.14	97.9	0.30
5	24.3	22.82	0.18	0.03	0.43	23.46	96.7	0.13
6	24.1	22.57	0.17	0.10	0.41	23.25	96.6	0.46
7	23.7	21.15	0.20	0.13	0.40	21.88	93.3	0.61
8	24.8	23.74	0.18	0.41	0.43	24.76	99.8	0.68
9-1	24.3	24.31	0.21	0.23	0.44	25.18	103.6	0.90
9-2	25.0	24.23	0.22	0.19	0.44	25.08	100.3	0.71
9-3	25.5	23.90	0.21	0.15	0.43	24.69	96.8	0.56
9-4	25.0	18.93	0.15	0.19	0.34	19.62	78.5 ^b	0.68
10	24.1	23.19	0.21	0.04	0.42	23.86	99.0	0.17
11-1	24.3	21.12	0.20	0.13	0.38	21.83	89.7	0.61
11-2	23.8	23.42	0.20	0.16	0.42	24.20	101.7	0.55
11-3	24.1	20.71	0.19	0.13	0.37	21.40	88.8	0.62
11-4	24.2	24.01	0.18	0.12	0.43	34.74	102.2	0.49
11-5	24.1	23.44	0.22	0.24	0.42	24.32	100.9	1.02
11-6	23.7	22.62	0.19	0.16	0.41	23.38	98.7	0.71
12A	26.2	26.66	0.14	0.02	0.48	27.30	104.2	0.06
15A	24.1	23.28	0.19	0.11	0.42	24.00	99.9	0.47

^a UO₂ or (U₃O₈ x 0.963).

^b Supersaturated solution.

3.4 Solubility of Uranium and Plutonium

The relative quantities of uranium and plutonium found in each leach and in the insoluble residues are listed in Table 15. Two hours in 7 M HNO_3 at 95°C dissolved >99.5% of the uranium and plutonium; a second 2-h leach in fresh 7 M HNO_3 reduced the amounts of undissolved uranium and plutonium in the residue to ~0.01% and ~0.02% respectively. Voloxidation of this fuel apparently did not affect the solubility of the uranium or plutonium in nitric acid.

3.5 Consumption of Nitric Acid

Data from dissolutions in which the first leach was removed by centrifugation (and not diluted by nitric acid rinses) are summarized in Table 16. The average consumption of nitric acid during the dissolution, using an air purge, was ~2.45 mol H^+ per mol of uranium dissolved.

The oxides of nitrogen reacted with the oxygen in the air purge (as in "fumeless" dissolving) and affected the gas flow rates. In the data from a typical experiment (below), the off-gas volume first increased due to the generation of oxides of nitrogen and then decreased as the oxides react:

Time (min)	Inlet flow (cm ³ /min)	Outlet flow (cm ³ /min)
0	100	106
2	100	102
4	100	106
6	100	107
8	100	117
10	100	114
12	100	127
14	100	89 ^a
16	100	93
18	100	96
20	100	103
22	100	103

^aLowest flow rate 83 cm³/min at 14.5 min.

Table 15. Solubility of H. B. Robinson-2 fuel in nitric acid^a

Run No.	First leach		Second leach		Third leach		Residue	
	U (%)	Pu (%)	U (%)	Pu (%)	U (%)	Pu (%)	U (%)	Pu (%)
1-3	99.98	99.97	0.01	0.01	0.01	0.01	0.01	0.02
4	99.96	99.95	0.04	<0.01	<0.01	0.02	<0.01	0.03
5	99.99	99.96	b	-	-	-	<0.01	0.04
6	99.81	99.74	0.18	0.21	<0.01	0.03	<0.01	0.01
7	99.69	99.69	0.29	0.21	0.02	0.07	0.01	0.02
8	99.81	99.65	0.14	0.24	<0.01	0.03	0.02	0.08
9-1	99.83	99.87	0.14	0.05	0.03	0.07	<0.01	0.01
9-2	99.74	99.58	0.25	0.38	0.01	0.04	<0.01	0.02
9-3	99.61	99.60	0.34	0.34	0.05	0.05	<0.01	0.02
10	99.83	99.88	0.09	0.09	0.09	<0.01	<0.01	0.02
11-1	99.99	99.99	-	-	-	-	<0.01	0.01
11-2	99.21	99.62	0.78	0.33	0.01	0.05	<0.01	<0.01
11-4	99.99	99.86	-	-	-	-	<0.01	0.14
12A	99.99	99.99	0.01	0.01	<0.01	<0.01	<0.01	<0.01
12B	99.86	99.83	0.13	0.13	<0.01	0.02	0.01	0.02
15A	99.95	99.85	0.04	0.13	-	-	<0.01	0.01

^aFirst leach: 7 M HNO₃, 2 h, 95°C; second leach: 3 M HNO₃, 2 h, 95°C; third leach: 7 M HNO₃, 2 h, 95°C.

^bThe sign (-) signifies leach has been omitted.

Table 16. Consumption of nitric acid during dissolution

Run No.	U diss. (mol)	HNO ₃ added (mol)	Final HNO ₃ (mol)	HNO ₃ consumed (mol H ⁺ /mol U)
1B	0.066	0.740	0.615	2.65
4	0.363	2.085	1.144	2.59
6	0.089	0.462	0.285	1.99
8	0.092	0.469	0.285	2.00
9-1	0.090	0.463	0.193	2.96
9-2	0.093	0.419	0.159	2.86
9-3	0.094	0.371	0.151	2.47
9-4	0.093	0.309	0.149	2.25
11-1	0.090	0.441	0.208	2.59
11-5	0.089	0.510	0.295	2.41
12B	0.092	0.441	0.241	2.17
Mean				2.45 ± 0.32

3.6 Effect of Voloxidation on the Residue

As mentioned above, voloxidation increased the amount of nitric acid-insoluble fission product residue about three-fold over that remaining from unvoloxidized fuel. The effect of voloxidation conditions on the total amount of residue is shown in Table 17. The higher temperature of 550°C may have produced slightly more residue than voloxidation at 480°C, but the confidence limits do overlap (Fig. 9). The use of air or oxygen apparently had little effect on the amount of residue formed. Tables 18 and 19 summarize the effect of the voloxidation variables on the amounts of uranium and plutonium that did not dissolve; there appears to be no effect due to the variations in conditions. (The high plutonium values in Runs 5, 8, 10, and 11-4 of Table 19 appear to be due to contamination of the sample since they are so much different than the other results.)

The effect of the variables on the distribution of ruthenium during dissolution, discussed above in Sect. 3, is indicated further in Table 20. The data clearly illustrate the differences by the decreased solubility of the voloxidized ruthenium.

About 70 to 80% of the unvoloxidized ruthenium is soluble, and about 80 to 90% is insoluble after voloxidation. The different voloxidation condition used in these tests, however, had little effect.

3.7 Residue Composition

The exploratory studies¹ showed that the insoluble dissolution residues from voloxidized or unvoloxidized fuels was a variable mixture of 30 to 55 wt % ruthenium, 10 to 30% molybdenum, 6 to 12% palladium, $\leq 14\%$ rhodium, $\leq 8\%$ technetium, plus traces of zirconium, antimony, and other elements. Calculations based on the radiochemical analyses for ^{106}Ru in each of the residues from Runs 4-7, the specific activity of ^{106}Ru (2.95×10^{-4} g/Ci), and on the isotopic fraction of ^{106}Ru to the total ruthenium (0.01031) indicated that voloxidation in oxygen at 480°C or 550°C yielded about the same amount of ruthenium in the residue as voloxidation in air (i.e., 0.275 g of Ru per g of residue from oxygen runs vs 0.272 g Ru per g of residue from air runs).

Table 17. Effect of voloxidation conditions on amount of insoluble residues

Run No.	Amount of residue [wt % (U,Pu)O ₂ dissolved]				
	None	Temperature = 480°C		Temperature = 550°C	
		Air	O ₂	Air	O ₂
1A	0.18				
1B		0.60			
1C		0.45			
2A		0.57			
3A		0.72			
3B	0.20				
4			0.30		
5					
6			0.46		
7					0.61
8				0.68	
9-1					0.90
9-2					0.72
9-3					0.56
9-4					0.68
10	0.17 ^a				
11-1		0.61			
11-2		0.55			
11-3		0.62			
11-4		0.49			
15A			0.47		
Mean	0.183	0.576	0.410	0.68	0.694
Range (95%)	± 0.038	± 0.070	± 0.237	-	± 0.162

^aVoloxidized to U₄O₉ stage and stopped.

Fig. 9. The effect of voloxidation temperature on the amount of insoluble residue for H. B. Robinson-2 fuel (28,000 MWd/ton).

Table 18. Effect of voloxidation conditions on amount of uranium in residue

Run No.	Amount of uranium in residue (mg U/g residue)				
	None	Temperature = 480°C		Temperature = 550°C	
		Air	O ₂	Air	O ₂
1A	48.5 ^a				
1B		15.0			
1C		6.7			
2A		18.3			
3A		21.7			
4			8.2		
5			20.6		
6			6.7		
7					16.5
8				24.0	
9-1					8.5
9-2					10.9
9-3					13.3
9-4					16.6
10	2.6 ^b				
11-1		13.3			
11-2		7.1			
11-3		8.3			
11-4		12.8			
15A			12.2		
Average	2.6	12.90	11.92	24.0	18.16
Range (95%, t)		+4.52	+9.91	-	+4.38

^aOmitted from average.

^bVoloxidized to U₄O₉ stage and stopped.

Table 19. Effect of voloxidation conditions on amount of plutonium in residue

Run No.	Amount of plutonium in residue (mg Pu/g residue)				
	None	Temperature = 480°C		Temperature = 550°C	
		Air	O ₂	Air	O ₂
1A	0.15				
1B		0.45			
1C		0.16			
2A		0.26			
3A		0.21			
3B	0.15				
4			0.64		
5			2.01 ^a		
6			0.10		
7					0.16
8				0.94 ^a	
9-1					0.06
9-2					0.12
9-3					0.10
9-4					
10	1.01 ^b				
11-1		0.15			
11-2		0.07			
11-3		0.11			
11-4		1.79 ^a			
15A			0.19		
Average	0.15	0.201	0.310	0.94	0.110
Range (95%)		+0.117	+0.719		+0.066

^aOmitted from average due to single very large values.

^bOmitted from average since the voloxidation was incomplete.

Table 20. Effect of voloxidation on the distribution of ruthenium during dissolution

Run No.	Voloxidation		¹⁰⁶ Ru distribution, % of total				¹⁰⁶ Ru total found [dis s ⁻¹ g (U + Pu) ⁻¹]
	Temp. (°C)	Atmos.	DS-1 ^a	DS-2	DS-3	R1	
1A	None	None	73.03	n.a.	n.a.	26.69	2.52 x 10 ⁹
3B	None	None	63.99	0.03	3.64	32.36	2.07 x 10 ⁹
10 ^{b,c}	480	Air	87.74	2.55	7.02	1.44 ^c	1.44 x 10 ^{9c}
12A	None	None	82.78	1.36	3.52	12.72	1.67 x 10 ^{9c}
Average			76.1 ^d			23.9	
1BC	480	Air	14.99	0.48	0.71	83.67	2.29 x 10 ⁹
2A	480	Air	18.90	n.a.	n.a.	81.13	2.03 x 10 ⁹
11-1	480	Air	14.31	0.05	n.a.	85.92	2.27 x 10 ⁹
8	550	Air	11.91	0.08	0.12	87.59	2.20 x 10 ⁹
Average			15.4 ^d			84.6	
4	480	O ₂	22.62	0.30	1.07	75.71	1.54 x 10 ^{9c}
6	480	O ₂	21.62	0.01	0.49	79.77	2.12 x 10 ^{9c}
7	550	O ₂	18.41	0.06	0.14	81.17	1.63 x 10 ⁹
9-1	550	O ₂	10.71	n.a.	0.11	88.89	2.29 x 10 ⁹
Average			18.3 ^d			81.4	

^aDS-1 is first leach in 7 M HNO₃; DS-2 is second leach in 3 M HNO₃; DS-3 is third leach in 7 M HNO₃; R-1 is insoluble residue.

^bVoloxidation interrupted at U₄O₉ stage; not completed to U₃O₈-alpha stage.

^cOmitted from averages.

^dAverage for sum of all solutions.

3.8 Release of Gaseous Fission Products During Dissolution

The U_3O_8 voloxidizer product contains residual ^3H , ^{14}C , ^{85}Kr , and other fission products that were not volatilized. Since dissolution of the U_3O_8 releases these elements, the fate of these fission products was investigated. The dissolution off-gas system consisted of an air-purged Pyrex dissolver, a Pyrex reflux condenser, and a length of rubber tubing leading to an empty spray trap. The gases then were bubbled through 3 M NaOH in a gas scrubber or washing bottle.

Radiochemical analyses showed the following distribution for the volatile fission products during the dissolution:

	Dissolver	Trap	Scrubber	Off-gas
^3H	97.9	1.0	1.0	a
^{14}C	<0.5	<0.1	>99.5	a
^{85}Kr	a	a	a	100
^{106}Ru	99.9	0.002	<0.001	a
^{125}I	7	a	93	a

^aNo analysis was made.

These results supplement earlier similar data and confirm that the tritium, ruthenium, and other nonvolatile elements remain in the dissolver solution, except for entrainment. The ^{14}C and ^{129}I were volatilized and were removed by a caustic scrubber. Experiments by Collins and Benker² indicated that boiling, sparging, or other treatments would remove essentially all of the iodine from the dissolver solution. The ^{85}Kr and other gases were collected in a gas bag.

The dissolution equipment was modified near the end of this series of experiments to remove excess holdup volume. This would permit the multichannel gamma spectrometer (MCA) to more closely reflect the dissolution rate of the uranium oxide by measuring the instantaneous release rates of ^{85}Kr . This change resulted in an MCA response time of ~4 min in contrast to the 27-min delay in the earlier experiments.

Figure 10 shows the instantaneous ^{85}Kr concentration in the off-gas (expressed as dps/cm³) vs time. All of the ^{85}Kr was released before 25 min elapsed, indicating that the dissolution of the bulk of the U_3O_8 had been completed. Visually, the reaction started at room temperature, with oxides of nitrogen being generated after the acid was added. The solution was boiling ~10 min after the hot plate was turned on. The evolution of nitrogen oxides had ceased in another 10 min. The krypton release curve (Fig. 10) indicates that the ^{85}Kr evolution ceased around the 25-min mark. (The flat portions of the concentration curve represent counter background.)

3.9 Dissolution of U_3O_8 in $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ Solutions

An attempt was made to simulate downstream stages of a continuous dissolver and determine the dissolution rates of the U_3O_8 voloxidation product in two concentrations of uranyl nitrate-nitric acid solutions. Runs 11-5 and 11-6 were conducted by adding about 25 g of U_3O_8 to the dissolver, adding two concentrations of the $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solution to the powder (76 g U/l-5.1 M HNO_3 and 151 g/l-4.2 M HNO_3), and periodically removing 3-ml samples of solution with a transfer pipet. Each sample was replaced with an approximately equal volume of the original $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ dissolvent to minimize any depletion effects. The dissolution reaction started slowly when the ambient temperature acid contacted the U_3O_8 ; this was indicated by bubbling and evolution of oxides of nitrogen plus a color change of the solutions. The hot plate was turned on as soon as the dissolvent was in the Pyrex dissolver, and reached the 95°C dissolution temperature in about 30 min. Experimental conditions and results are summarized in Table 21.

Examination of the data indicate that there was little difference in the dissolution rate in the two uranyl nitrate-nitric acid solutions. The reaction proceeded slowly until the temperature reached 80 to 85°C, and then reacted rapidly for about 30 min (Fig. 11).

A graphic representation of the reaction is presented in Fig. 12, where the dissolution rate (mg/min) is shown as a function of time. After an initial rate of about 1 g U per min when the very finest particles were dissolved in the ambient temperature acid, the rate slowed until the temperature increased, and then reached a peak of ~1 g U per min at ~95°C.

Fig. 10. Krypton release during dissolution.

Table 21. Dissolution of U_3O_8 in the $UO_2(NO_3)_2-HNO_3$

	Run 11-5		Run 11-6	
Dissolvent U, mg/ml	150.5		76.1	
Dissolvent H ⁺ , <u>M</u>	4.2		5.1	
Volume, ml	150.0		100.0	
U ₃ O ₈ , g	25.1		24.8	
Sample time, min	Undissolved, %		Undissolved, %	
	U	Pu	U	Pu
0	100.0	100.0	100.0 ^a	100.0 ^a
2	89.54	93.17	86.94	91.07
5	87.17 ^a	92.18 ^a	86.94	90.54
10	85.69	90.54	86.35	88.74
20	93.28	86.90	82.39	83.74
30	71.15 ^b	79.62 ^b	57.37 ^b	64.81 ^b
45	6.97	23.98	5.17	9.71
60	0.00	8.78	3.71	9.71
90	0.00	8.78	3.08	0.00
120	0.00	0.00	0.10	0.00
Final volume, ml	142.0		94.0	
Final H ⁺ , <u>M</u>	2.1		N.A.	
Final U, mg/ml			262.9	

^aHeat turned on hot plate.

^bSimmering ($\sim 95^\circ C$).

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Fig. 11. Dissolubility of uranium and plutonium in $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solutions.

Fig. 12. Dissolution rate of U_3O_8 in $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solutions.

3.10 Actinide Content of First Leach Solutions

The average concentrations of the actinides in the first leach solutions are tabulated in Table 22. The mean plutonium content of the fuel was 3.64×10^9 Pu alpha counts $\text{min}^{-1} \text{ g (U)}^{-1}$, or 8.37 mg plutonium per g of uranium. The mean gross alpha activity of the fuel was $\sim 7 \times 10^9$ gross alpha counts $\text{min}^{-1} \text{ g (U)}^{-1}$:

Plutonium alpha:	3.64×10^9 counts $\text{min}^{-1} \text{ g (U)}^{-1}$
Americium alpha:	0.53×10^9 counts $\text{min}^{-1} \text{ g (U)}^{-1}$
Curium alpha:	2.80×10^9 counts $\text{min}^{-1} \text{ g (U)}^{-1}$
Total alpha:	6.97×10^9 counts $\text{min}^{-1} \text{ g (U)}^{-1}$

3.11 Fission Product Content of First Leach Solutions

The fission product contents of the first leach solutions are listed in Table 23. The principal point of interest was brought out in the earlier report¹ — that the bulk of the tritium present in the unvoloxidized fuel (Runs 1A, 3B, 10, and 12A) was not present in the voloxidizer product leach solutions (all other runs). About five times as much ^{106}Ru was present in the unvoloxidized fuel solution as in the voloxidized fuel solution [1.42×10^6 dis $\text{sec}^{-1} \text{ mg (U)}^{-1}$ vs $\sim 3.1 \times 10^5$ dis $\text{sec}^{-1} \text{ mg (U)}^{-1}$]. A large fraction of the ^{125}Sb also did not dissolve; it remained with the ruthenium in the insoluble residue.

Note in Run 19-4 that the concentrations of the soluble $^{134-137}\text{Cs}$ and ^{144}Ce are about twice that of the other samples. This is due to the supersaturation and precipitation of $\text{UO}_2(\text{NO}_3)_2$, leaving the soluble fission products in solution.

The data of Table 24 illustrate that oxidation of the UO_2 to U_3O_8 released essentially all of the tritium in the fuel. (A final tritium concentration of 1×10^3 dis $\text{sec}^{-1} \text{ g(U + Pu)}^{-1}$ represents a removal of 99.99% of the tritium.) Partial oxidation (Run 10) to U_4O_9 released only about half of the radionuclide.

The presence of the Zircaloy cladding during the leach apparently contributes more tritium to the leach solution [Runs 1A, 1C, 3B, and 15B] even from cladding that has been through voloxidation. This may represent dissolution of a small fraction of the cladding that contains up to 40% of the total tritium generated in the fuel.

Table 22. Concentrations of the actinides in the first leach solutions,
H. B. Robinson-2 reactor, EOC-3

Run No.	HNO ₃ M	U (mg/ml)	Pu alpha (counts min ⁻¹ ml ⁻¹)	Gross alpha (counts min ⁻¹ ml ⁻¹)	Pu alpha [counts min ⁻¹ mg (U) ⁻¹]	Gross alpha [counts min ⁻¹ mg (U) ⁻¹]
1A	4.53	316.6	1.17 x 10 ⁹	2.34 x 10 ⁹	3.70 x 10 ⁶	7.39 x 10 ⁶
1B	6.28	157.6	5.64 x 10 ⁸	1.13 x 10 ⁹	3.58 x 10 ⁶	7.17 x 10 ⁶
1C	4.56	316.1	1.22 x 10 ⁴	2.35 x 10 ⁹	3.86 x 10 ⁶	7.43 x 10 ⁶
2A	4.58	319.7	1.23 x 10 ⁹	2.42 x 10 ⁴	3.85 x 10 ⁶	7.57 x 10 ⁶
3A	5.42	273.7	8.01 x 10 ⁸	1.99 x 10 ⁹	2.93 x 10 ⁶	7.27 x 10 ⁶
3B	a	307.9	1.24 x 10 ⁹	2.29 x 10 ⁹	4.03 x 10 ⁶	7.44 x 10 ⁶
4	4.22	293.5	1.13 x 10 ⁹	2.04 x 10 ⁹	3.85 x 10 ⁶	6.59 x 10 ⁶
5	4.09	267.5	9.33 x 10 ⁸	1.70 x 10 ⁹	3.49 x 10 ⁶	6.36 x 10 ⁶
6	4.52	308.2	9.85 x 10 ⁸	1.96 x 10 ⁹	3.20 x 10 ⁶	6.36 x 10 ⁶
7	4.75	282.9	1.20 x 10 ⁹		4.24 x 10 ⁶	
8	4.13	296.7	1.00 x 10 ⁹		3.37 x 10 ⁶	
9-1	2.84	307.6	1.19 x 10 ⁹		3.74 x 10 ⁶	
9-2	2.69	351.3	1.37 x 10 ⁹		3.90 x 10 ⁶	
9-3	2.91	397.0	1.48 x 10 ⁵		3.73 x 10 ⁶	
9-4	3.32	363.4	1.28 x 10 ⁹		3.52 x 10 ⁶	
10	2.41	322.5	1.26 x 10 ⁹		3.91 x 10 ⁶	
11-1	3.47	304.1	1.25 x 10 ⁹		4.11 x 10 ⁶	
11-2		333.8	1.26 x 10 ⁹		3.78 x 10 ⁶	
11-3		198.7(?)	5.82 x 10 ⁹		2.92 x 10 ⁶	
11-4		341.3	1.08 x 10 ⁹		3.16 x 10 ⁶	
11-5	2.08	277.6	3.82 x 10 ⁸		1.37 x 10 ⁶	
11-6		263.0	5.32 x 10 ⁸		2.02 x 10 ⁶	
12A		355.6	8.00 x 10 ⁸		2.25 x 10 ⁶	
12B	3.83	352.5	1.09 x 10 ⁹		3.09 x 10 ⁶	
15A		201.8	7.20 x 10 ⁸		3.57 x 10 ⁶	
Average =					3.64 x 10 ⁶	7.06 x 10 ⁶

^aNo analysis was made.

Table 23. Concentrations of fission products in the first leach solutions

Run No.	U conc. (mg/ml)	Fission product concentration [dis sec ⁻¹ (mg U) ⁻¹] ^a					
		³ H	¹⁰⁶ Ru	¹²⁵ Sb	¹³⁴ Cs	¹³⁷ Cs	¹⁴⁴ Ce
1A	316.6	9.79 x 10 ³	1.86 x 10 ⁶	<7.9 x 10 ⁴	1.81 x 10 ⁶	3.47 x 10 ⁶	2.64 x 10 ⁶
1B	157.6	4.03 x 10 ¹	4.64 x 10 ⁵	<4.3 x 10 ⁴	1.80 x 10 ⁶	3.44 x 10 ⁶	2.60 x 10 ⁶
1C	316.1	3.48 x 10 ²	3.16 x 10 ⁵	<1.2 x 10 ⁵	1.71 x 10 ⁶	3.29 x 10 ⁶	2.41 x 10 ⁶
2A	319.7	1.14 x 10 ¹	3.57 x 10 ⁵	<5.3 x 10 ⁴	1.70 x 10 ⁶	3.41 x 10 ⁶	2.35 x 10 ⁶
3A	273.7	<1.0 x 10 ¹	3.50 x 10 ⁵	<4.8 x 10 ⁴	1.63 x 10 ⁶	3.23 x 10 ⁶	2.49 x 10 ⁶
3B	307.9	1.09 x 10 ⁴	1.12 x 10 ⁶	8.03 x 10 ⁴	1.37 x 10 ⁶	2.60 x 10 ⁶	2.03 x 10 ⁶
4	293.5	1.17	3.58 x 10 ⁵	<10 ⁴	1.83 x 10 ⁶	3.44 x 10 ⁶	2.82 x 10 ⁶
5	267.5	<1	<3.36 x 10 ⁵	<2.2 x 10 ⁴	1.64 x 10 ⁶	3.02 x 10 ⁶	2.28 x 10 ⁶
6	308.2	1.0	4.22 x 10 ⁵	<6.5 x 10 ⁴	1.79 x 10 ⁶	3.31 x 10 ⁶	2.52 x 10 ⁶
7	282.9	~2.5	3.18 x 10 ⁵	<7.0 x 10 ⁴	1.97 x 10 ⁶	3.78 x 10 ⁶	2.93 x 10 ⁶
8	296.7	~2.6	2.70 x 10 ⁵	<2.7 x 10 ⁴	1.62 x 10 ⁶	2.94 x 10 ⁶	2.18 x 10 ⁶
9-1	307.6	<1	<2.60 x 10 ⁵	<6.5 x 10 ⁴	1.75 x 10 ⁶	3.21 x 10 ⁶	2.57 x 10 ⁶
9-2	351.3	<1	<9.7 x 10 ⁵	<5.7 x 10 ⁴	1.87 x 10 ⁶	3.42 x 10 ⁶	2.88 x 10 ⁶
9-3	398.9	~1.1	2.52 x 10 ⁵	<1 x 10 ⁵	1.93 x 10 ⁶	3.55 x 10 ⁶	2.87 x 10 ⁶
9-4	363.4	b	~5.5 x 10 ⁵	<1.1 x 10 ⁵	3.69 x 10 ⁶	6.71 x 10 ⁶	5.34 x 10 ⁶
10	322.5	6.25 x 10 ³	1.30 x 10 ⁶	9.3 x 10 ⁴	1.94 x 10 ⁶	3.63 x 10 ⁶	2.70 x 10 ⁶
11-1	304.1	<1	3.29 x 10 ⁵	<6.6 x 10 ⁴	1.95 x 10 ⁶	3.68 x 10 ⁶	2.87 x 10 ⁶
11-2	333.8	~3.3	3.0 x 10 ⁵	<6.0 x 10 ⁴	1.88 x 10 ⁶	3.48 x 10 ⁶	2.76 x 10 ⁶
11-3	198.7	~1.1	<2.0 x 10 ⁵	<1.0 x 10 ⁵	1.83 x 10 ⁶	3.41 x 10 ⁶	2.52 x 10 ⁶
11-4	341.3	~1	2.93 x 10 ⁴	<6 x 10 ⁴	1.75 x 10 ⁶	3.19 x 10 ⁶	2.47 x 10 ⁶
11-5	277.6	<1	1.44 x 10 ⁵	<2 x 10 ⁴	8.12 x 10 ⁵	1.5 x 10 ⁶	1.12 x 10 ⁶
12A	355.6	7.26 x 10 ³	1.39 x 10 ⁶	7.03 x 10 ⁴	1.20 x 10 ⁶	2.55 x 10 ⁶	2.33 x 10 ⁶
12B	352.5	<10	2.84 x 10 ⁵	<6 x 10 ⁴	1.23 x 10 ⁶	2.54 x 10 ⁶	2.29 x 10 ⁶
15A	201.8	~1	<2 x 10 ⁵	<2 x 10 ⁴	9.12 x 10 ⁵	1.70 x 10 ⁶	1.25 x 10 ⁶

^aValues as of April 1, 1977.^bNo analysis was made.

Table 24. Effect of voloxidation conditions on the amounts of residual tritium

Run No.	Tritium content of fuel [dis sec ⁻¹ g((U + Pu) ⁻¹]				
	None	Temperature = 480°C		Temperature = 550°C	
		Air	Oxygen	Air	Oxygen
1A ^a	9.79 x 10 ⁶				
1B		4.03 x 10 ⁴			
1C ^a		3.48 x 10 ⁵			
2A		1.11 x 10 ⁴			
3A ^a		<3.10 x 10 ²			
3B ^a	1.09 x 10 ⁷				
4			1.17 x 10 ³		
5			2.78 x 10 ⁴		
6			2.52 x 10 ²		
7					2.51 x 10 ³
8				2.56 x 10 ³	
9-1					5.44 x 10 ²
9-2					5.37 x 10 ²
9-3					1.13 x 10 ³
10 ^b	6.25 x 10 ⁶				
11-1		2.76 x 10 ²			
11-2		3.29 x 10 ³			
11-3		1.05 x 10 ³			
11-4		9.44 x 10 ²			
12A	7.11 x 10 ⁶				
12B		<1.77 x 10 ³			
15A ^{a,c}			1.14 x 10 ³		
15B ^{a,c}			1.84 x 10 ³		

^aCladding present in leaches.

^bPartial oxidation of UO₂ to U₄O₉.

^cCladding only from the LWR-15 (23.4 g) and adherent U₃O₈.

4. CONCLUSIONS

1. During voloxidation in air, oxygen usage was completed in 2 h for unclad fuel and in ~ 4 h for 1-in.-clad fuel. Oxygen consumption in pure oxygen was completed in $< 1\frac{1}{2}$ h in unclad and clad UO_2 .
2. The weight gains and oxygen consumption during voloxidation indicated good conversions to U_3O_8 . Fuel dislodgement from the cladding was complete; the oxide product was a fine powder (more than 99% $< 44 \mu\text{m}$).
3. A temporary reduction in the rate of oxygen consumption at low oxygen feed rates is related to the formation of U_4O_9 as an intermediary during fuel voloxidation.
4. Tritium releases from the UO_2 during voloxidation were essentially quantitative (i.e., $> 99.9\%$ at 480 and 550°C using oxygen feed rates in the range 0.1 to 1.20 mol/h). Release of ^{85}Kr was ~ 2 to 7% of the inventory.
5. A deeper bed (3:1 U_3O_8 to UO_2) or cladding on the UO_2 inhibit fuel oxidation and tritium release rates, but not the completeness of reaction; however, the total ^{85}Kr release may have been reduced.
6. Volatilization of fission product solids and semivolatiles was not extensive during oxidation in air or pure O_2 at either temperature (480 or 550°C). Less than $\sim 0.1\%$ of the inventories of ruthenium, cesium, and cerium were deposited inside the voloxidizer. Except for ^{106}Ru and ^{129}I , the quantities recovered downstream in the off-gas system were $< 0.001\%$ of the fuel contents. As much as 2% of the total ^{129}I was recovered from the off-gas equipment. In addition, up to $\sim 0.1\%$ of the total ^{106}Ru was found deposited on surfaces in the voloxidizer off-gas system. This suggests that at the higher temperatures and O_2 flows, ruthenium may have a higher volatility than the other fission products.
8. Voloxidation increased HNO_3 -insoluble fission product residues from $\sim 0.18\%$ to $\sim 0.62\%$ of the weight of the irradiated UO_2 dissolved. The extra weight was due to fission products. Ruthenium changed from 75 to 80% soluble to 80 to 90% insoluble as a result of voloxidation. The residue also contains molybdenum, rhodium, technetium, antimony, etc. The different conditions for voloxidation tested had little

effect on the amount of uranium or plutonium in the residue (mg/g).

9. In our equipment, 2.45 moles HNO_3 were required to dissolve 1 mole of UO_2 .
10. A 2-h leach in 7 M HNO_3 dissolved >99.5% of the heavy metals; the second leach in 7 M brought the total to >99.98%.
11. During dissolution ^{14}C and ^{129}I reported to the NaOH scrubber; any residual ^3H stays in solution as HTO (>99%).

5. ACKNOWLEDGMENTS

The authors wish to acknowledge the efforts of the talented technicians of the Chemical Development Section of the Chemical Technology Division who performed the hot-cell manipulations: E. C. Hendren, J. R. Travis, and C. S. Webster. Stewart Dismuke, ORNL Metals and Ceramics Division, supervised the x-ray diffraction work on the UO_2 , U_4O_9 , and U_3O_8 samples. The many analyses were performed by ORNL Analytical Chemistry Division personnel.

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