ORNL/TM-7103
Dist. Category UC-86
~~(Applied)~~

Contract No. W-7405-eng-26

CONSOLIDATED FUEL REPROCESSING PROGRAM

COMPARISON STUDIES OF HEAD-END REPROCESSING USING THREE LWR FUELS

J. H. Goode
R. G. Stacy
V. C. A. Vaughen

Chemical Technology Division

Date Published: June 1980

NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

RELEASED FOR ANNOUNCEMENT IN ALDR.
Distribution limited to participants in the
Consolidated Fuel Reprocessing Program.
Others request from Program Mgr.
CFRP, OROO.

DISCLAIMER

CONTENTS

COMPARISON STUDIES OF HEAD-END REPROCESSING USING THREE LWR FUELS

J. H. Goode
R. G. Stacy
V. C. A. Vaughen

ABSTRACT

The removal of ^3H by voloxidation and the dissolution behavior of two PWR and one BWR fuels were compared in hot-cell studies. The experiments showed that >99% of the ^3H contained in the irradiated UO_2 was volatilized by oxidation in air at 753 K (480°C). The oxidation did not affect the dissolution of the uranium and plutonium in 7 M HNO_3 (0.02 to 0.03% insoluble plutonium) but did create a fission-product residue that was two to three times more insoluble. From 40 to 69% of the ternary fission-product ^3H was found in the Zircaloy cladding of the fuel rods. Voloxidation had little effect on the ^3H held in the Zircaloy cladding; oxidation for 6 h at 753 K released only 0.05% of the ^3H.

1. INTRODUCTION

Hot-cell tests are being conducted at Oak Ridge National Laboratory (ORNL) on different phases of the head-end steps — that is, pre-solvent extraction — of proposed reprocessing flowsheets for light water-moderated nuclear reactor (LWR) fuels. Two series of earlier hot-cell tests were conducted with UO_2 that had been irradiated to an average burnup of 2.419 E+03 GJ/kg heavy metal (28,000 MWd/ton) in the H. B. Robinson-2 reactor of the Carolina Power and Light Company.[1,2] Those tests examined the effects of temperature and 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 (^3H) in the irradiated UO_2 was released to the off-gas stream at temperatures of 753 and 823 K (480 and 550°C) and at oxygen feed rates ranging from 0.1 to 1.2 moles/h. The release of ^{85}Kr varied from 2 to 7% of the fuel inventory. The U_3O_8 product was easily dissolved in 7 M HNO_3. (Greater than 99% of the product was smaller than 44 μm.) 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 dissolution 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%.

In order to make the studies more general, we examined the voloxidation and dissolution of UO_2 from a second pressurized water reactor (PWR), Oconee-1, and from a boiling water reactor (BWR), Dresden-3, in our hot cells. These three reactors, each designed, fabricated, and fueled by different suppliers (Table 1), represent a cross section of typical fuels from the U.S. nuclear industry. They should thus represent the typical fuel supply for a reprocessing plant.

Table 1. Light water reactor fuels tested in hot cells

Utility-Owner	Commonwealth Edison	Duke Power Company	Carolina Power and Light
Location	Morris, Ill.	Seneca, S.C.	Hartsville,S.C.
Reactor	Dresden-3	Oconee-1	H. B. Robinson-2
Net MW(e)	800	871	665
Type	BWR	PWR	PWR
Supplier	GE	B&W	Westinghouse
End of cycle, GJ/kg M	3 1.538 E+03	2 2.046 E+03	3 2.678 E+03
Peak burnup, MWd/ton	17,800	23,680	31,000
Discharge date	4/75	2/76	5/74
Linear heat rating, kW/m (kW/ft)	∿44.0 (∿13.4)	∿18.1 (∿5.5)	∿18.1 (∿5.5)

2. EXPERIMENTAL

2.1 Equipment and Procedures

The operation of the voloxidizer, the feed and off-gas systems, and the sampling apparatus was primarily the same as that of 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 near-system background levels.

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. One was periodically removed to measure the amounts of semivolatile fission products that had been deposited. 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 particulates and charcoal beds for ^{129}I). This was followed by a high-efficiency particulate (HEPA) filter, a ^{3}H oxidizer (heated CuO), silica gel beds for sorption of tritiated water vapor, a 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 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 NaOH scrubber, and an in-line HEPA filter before the gas passed out of the hot cell. Outside the hot cell, the gases flowed through a multichannel gamma spectrometer for determination of the ^{85}Kr content. The total off-gas was collected in a bag as a cumulative sample. The flows of the gases into and out of the dissolution and trap systems were also recorded.

A clinical centrifuge was used to separate the insoluble residues from the leach solutions; the residues were thoroughly washed with 3 $\underline{M}$ HNO_3 after each leach. The second and third leaches were conducted in this centrifuge cone which was fitted with a reflux condenser. The residue was dried in the centrifuge cone for determination of its weight; the residue was then fused with Na_2CO_3 for analysis.

Dissolution of the fuel is made so that the heavy-metal and fission-product inventory can be determined before and after voloxidation. The UO_2 is also dissolved to determine whether the head-end processing steps have changed the solubility characteristics of the uranium and plutonium in 7 $\underline{M}$ HNO_3 (the process dissolvent). The first dissolutions were to an arbitrary final concentration of 200 g U/ℓ. In most of the experiments, a series of three 2-h leaches in boiling 7 $\underline{M}$ HNO_3 was used to simulate the contacting of fuel, cladding, and insoluble residues with fresh acid. In a few experiments, however, only one to two leaches were used, primarily to determine the fission product contents.

2.2 Fuel Description

Each of the fuels tested in the hot cell was furnished to ORNL after post-irradiation examinations at other facilities. The Dresden-3 fuel rods were obtained from the Battelle-Columbus Laboratory after examination by General Electric and Argonne National Laboratory in an EPRI program;[3] the Oconee-1 rods came from a facility of the Babcock and Wilcox Company located in Lynchburg, Virginia; and the Robinson-2 rods were from an EG&G-Idaho hot-cell facility at Idaho National Engineering Laboratory (INEL). The different fuels are described in Table 2. The

Table 2. Fuel description

Reactor	Dresden-3	Oconee-1	H. B. Robinson-2
Rod No.	KE-3038	32028	G-10
Assembly	DD-710	1C56	B05
Average burnup, MWd/ton)	∿13,900	18,711	∿28,000
Cladding type	Zr-2	Zr-4	Zr-4
O.D., in.	0.563	0.430	0.423
Wall thickness, in.	0.032	0.026	0.024
UO_2 pellet OD, in.	0.487	0.370	0.367
Length, in.		0.717	0.600
Initial enrichment, % U-235	1.69-2.44	2.00 (av)	1.83-3.10
Cladding, g/in.	5.82	3.61	3.31

12-ft-long rods were cut into 4-ft segments at the different sites and then further cut into 1-ft lengths at the ORNL High-Radiation Level Examination Laboratory (HRLEL) before being transferred to our hot cells for the experiments.

3. RESULTS AND DISCUSSION

3.1 Shearing

The data taken during the shearing of light water reactor (LWR) fuels have been presented.[1,4,5] Detailed shearing information (such as the forces required to shear the rods, the releases from cladding, the size distributions of dislodged materials, etc.) for a variety of irradiated reactor fuels is given in ORNL/TM-6835.[4] A nonlinear least-squares analysis of the particle size distributions from sheared irradiated and unirradiated LWR fuels is described in ORNL/NUREG-60.[5]

3.2 Voloxidation

3.2.1 General

A series of exploratory voloxidation tests was run to characterize fuel from the Oconee-1 (PWR) and Dresden-3 (BWR) reactors and to determine fission product behavior during the oxidation process. The principal objective was to scout the effects of fuel fabrication and reactor type on the UO_2 oxidation rate and the rate of evolution and yield of ^{3}H, ^{85}Kr, ^{14}C, and semivolatile fission products. The results were compared to those obtained from selected tests[1,2] with fuel from the H. B. Robinson-2 reactor (PWR). A summary of the run conditions is shown in Table 3.

Several voloxidations were run under standardized conditions (unclad fuel, 480°C, air, 12 rpm) to determine baseline responses for each reactor fuel. Voloxidations were also made on clad pieces of fuel to test the effects of cladding coverage. The smaller-diameter (0.42-in. OD) PWR fuels were voloxidized in 1-in. sheared lengths. Less than 15% of the Robinson UO_2 was dislodged during shearing; however, ∿55% of the Oconee fuel had become dislodged from the 1-in.-long pieces prior to the voloxidation run (LWR-17). Since none of the Dresden BWR fuel remained in 1-in.-long sheared hulls (0.56-in. OD), 2-in.-long clad fuel pieces were selected for that test (LWR-19). One additional fuel-in-cladding voloxidation (LWR-15) was made with the Robinson UO_2 using a pure oxygen purge to study the effects of oxygen feed rate on the fuel oxidation-^{3}H release process.

During runs LWR-16 to 19, an air-5% CO_2 purge gas was used instead of air. The additional CO_2 served as a carrier for the ^{14}C that was released to the voloxidizer off-gas (Sect. 3.2.5).

3.2.2 Material balances and weight gains during voloxidation

The high yields (99.5 to 100.2%) of voloxidized products indicated that the UO_2 was oxidized in each case with relatively little difficulty, and that not much material was lost by spillage, entrainment in the gas phase, etc. (Table 4). Although the measured oxide weight gains for seven experiments indicated an average conversion of only 94.6% (based on oxidation of the UO_2 to U_3O_8), the apparent low conversion might be

Table 3. Voloxidation of light water reactor fuel

Run No.	Charged to voloxidizer		Voloxidation conditions				
	Fuel	U + Pu[a] (g)	Temperature (°C)	Time[b] (min)	Purge flow rate (ml/min)	O_2 feed rate (moles/h)	Rotation (rpm)
H. B. Robinson-2							
LWR-2	1-in. clad	86.09	480	270	200-220	∿0.10	12
LWR-3	Unclad	64.07	480	180	300	0.15	12
LWR-15[c]	1-in. clad	78.20	480	180	300	0.75	12
Oconee-1							
LWR-16	Unclad	91.59	480	240	∿300	0.15	12
LWR-17	1-in. clad + unclad	110.73	480	240	∿300	0.15	12
Dresden-3							
LWR-18	Unclad	88.66	480	240	∿300	0.15	12
LWR-19	2-in. clad	131.57	480	240	∿300	0.15	12

[a] Based on recoveries of dissolved product.
[b] Time at temperature.
[c] Pure oxygen purge; all other runs made in air or in air-5% CO_2.

Table 4. Material balances for voloxidation of LWR fuels

Run No.	Input total (g)	Output total (g)	Weight gain (g)	Yield[a] (%)	Oxide conversion (%) Measured[a]	Oxide conversion (%) Calculated[b]
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-15	115.8[c]	119.1[c]	3.3	99.8	92.9	127.0
LWR-16	102.1	105.9	3.8	99.9	96.2	124.9
LWR-17	152.2[c]	156.8[c]	4.6	99.8	94.7	107.2
LWR-18	100.2	103.8	3.6	99.7	92.6	127.7
LWR-19	196.1[c]	201.6[c]	5.5	99.7	92.9	97.0

[a] Based on 3.95% increase in UO_2 weight (excluding fission products and insolubles) for 100% theoretical yield.

[b] Determined from oxygen consumption measurements.

[c] Totals include cladding weight: LWR-2, 22.9 g; LWR-15, 23.3 g; LWR-17, 26.4 g; and LWR-19, 43.4 g.

explained by handling losses on the order of 0.2 wt %. Measured oxide conversions for the PWR runs tended to be slightly greater than those for the BWR runs (95.4% vs 92.8%); however, the difference is probably insignificant since each 0.1% weight loss is equivalent to ∿2.5% conversion.

Calculated conversions based on the amount of oxygen consumed were generally higher; an average conversion value of 111.3% was obtained for the same experiments. This was probably due to small errors in on-line flow rate and concentration measurements introduced over the run; however, one cannot completely exclude other oxygen sinks (Zircaloy cladding, fission products, etc.).

3.2.3 Fuel comminution

Size distributions for the unclad fuel charged to and recovered from the voloxidizer during the comparison experiments are listed in Table 5. In the earlier Robinson experiments[2] (LWR-1 to -15), it was shown that oxidation of the fuel resulted in essentially complete pulverization of the oxide, regardless of whether the UO_2 feed was in cladding or not. The same results were observed in the tests with Oconee (LWR-16 and -17) and Dresden (LWR-18 and -19) fuels. Less than 0.2% of the fuel remained associated with the cladding following each 4-h voloxidation. Although the Robinson voloxidized products were not sized in fractions <44 μm, more detailed sieve analyses on the products from the other UO_2 fuels showed that >99% was sized smaller than 20 μm. Several hours of sieving were required to attain constant weight values in the smallest size fractions. This might indicate some tendency for the very fine powders to agglomerate or stick together lightly. Agglomerated particles consisting of crystallites sized between 2 and 5 μm are visible in scanning electron microscope photographs taken of the voloxidized Oconee fuel (Fig. 1).

3.2.4 Fission product contents of power reactor fuels

The inventory of fission products in the fuels from the H. B. Robinson-2, Oconee-1, and Dresden-3 reactors was determined by the dissolution of unvoloxidized and voloxidized segments and fragments of fuel and by analyzing the solutions, insoluble residues, and gas streams. The best values for the fission-product content are listed in Table 6;

Table 5. Fuel comminution during voloxidation

Mesh size	Opening (µm)	Size distribution (% of fuel remaining on indicated screen)							
		Unoxidized feed[a]			Voloxidized product				
		Robinson	Oconee	Dresden	LWR-2[b]	LWR-3	LWR-15[b]	LWR-16	LWR-18
14	1400		62.3	56.8					
18	1000		6.5	8.2					
20	840		3.6	4.6					
35	500	64.3	8.9	10.3					
50	300		6.1	6.6					
100	150	23.0	5.5	5.4				0.1	0.2
200	75	6.0	3.3	3.0					
	<75	6.7							
325	44		1.5	1.1	0.2	0.1	0.4	0.1	
	<44				99.8	99.9	99.6		
400	38		0.5	0.7					
635	20		0.7	1.3					
	<20		1.1	2.0				99.8	99.8

[a] Unclad UO_2 in approximate 100-g sized batches for runs LWR-3, -16, and -18.

[b] LWR-19 feed was in 2-in.-long clad pieces; feed for the other runs was in 1-in.-long pieces except for LWR-17, where 56% of the fuel had become dislodged from the cladding prior to being voloxidized.

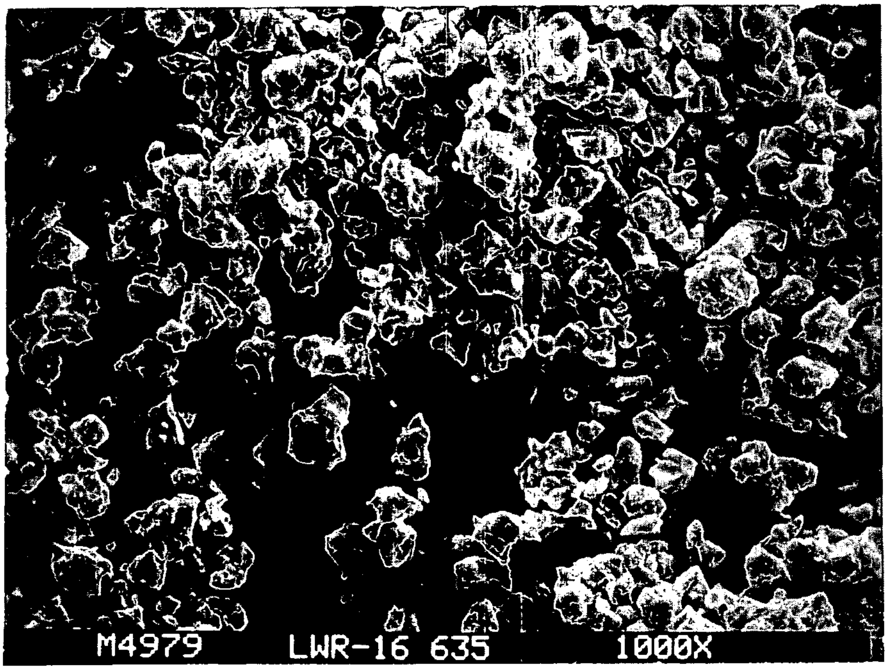

Fig. 1. Agglomerated fuel particles in Oconee voloxidizer product (1 cm = 10 μm).

Table 6. Experimental and calculated fission-product contents of light water reactor fuels (calculated values in parentheses)

	dis s^{-1} g(U + Pu)$^{-1}$								
	^{3}H	^{14}C	^{85}Kr	^{106}Ru	^{125}Sb	^{129}I[a]	^{134}Cs	^{137}Cs	^{144}Ce
H. B. Robinson-2	1.02 E+07	2.15 E+04	3.44 E+08	2.37 E+09	9.87 E+07	157	1.76 E+09	3.30 E+09	2.55 E+09
	(1.76 E+07)[b]	(1.97 E+04)	(2.66 E+08)	(3.08 E+09)	(10.9 E+07)	(187)	(3.10 E+09)	(3.62 E+09)	(3.13 E+09)
Oconee-1	0.83 E+07	1.54 E+04[b]	2.18 E+08	1.66 E+09	9.73 E+07	188	1.15 E+09	2.55 E+09	2.36 E+09
	(0.99 E+07)	(1.54 E+04)	(1.57 E+08)	(1.68 E+09)	(16.5 E+07)	(108)	(0.86 E+09)	(2.03 E+09)	(1.83 E+09)
Dresden-3)	0.25 E+07	1.48 E+04	1.46 E+08	0.56 E+09	5.83 E+07	217	0.51 E+09	1.98 E+09	0.59 E+09
	c	c	c	c	c	c	c	c	c

[a] μg/g (U + Pu).

[b] ORIGEN calculated.

[c] Not calculated.

these concentrations form the basis of the calculated releases of fission products. The estimated fission-product concentrations calculated by the ORIGEN code are also tabulated.

3.2.5 Release of gaseous fission products

A comparison was made of ^3H recoveries during voloxidation and dissolution experiments with UO_2 fuel from the following three reactors: H. B. Robinson-2 (PWR), Oconee-1 (PWR), and Dresden-3 (BWR). Shown in Table 7 are the ^3H contents of the voloxidizer off-gas and the dissolver solutions from voloxidized and unvoloxidized fuels. The ^3H decontamination factors (DFs) and the percent removal for each reaction condition were also calculated. The data are complete for the tests with the Oconee and Dresden fuels; selected conditions from the H. B. Robinson experimental series[2] are presented for comparison.

The ^3H released from the UO_2 during voloxidation was collected and measured on silica gel traps located in the voloxidizer off-gas system. Improvements made to the sampling system over a period of time apparently had a favorable effect on ^3H material balances. Recoveries ranged from $\sim$70% of the ^3H inventory for the H. B. Robinson UO_2 up to $\sim$ 92% of the ^3H contained by the Dresden UO_2. However, even during the earlier Robinson fuel experiments, the highest ^3H concentrations found in voloxidized fuel (U_3O_8) were on the order of 1.0×10^4 dis s^{-1} g $(U+Pu)^{-1}$, which indicated total releases of 99.8% or better during the voloxidation step. Evidently, neither the presence of cladding nor the use of pure oxygen rather than air as the oxidant had a major effect on the total amounts of ^3H released, but both do have a major effect on the release rate. In fact, during the clad fuel experiments, ^3H concentrations in the dissolver solutions were slightly lower. These results indicate that 3 to 4 h of voloxidation in air at 480°C, with agitation, should be sufficient to quantitatively remove the ^3H from unclad UO_2 fuel. At least 4 h at temperature might be required for clad fuel segments (in 1- or 2-in. lengths). Less time would be required in a pure oxygen atmosphere.

Gaseous fission-product releases from the UO_2 during voloxidation are presented in Table 8 as percentages of the total measured fuel contents. Tritium release fractions were obtained by differences in the

Table 7. Distribution of ^{3}H during voloxidation of light water reactor fuel

Fuel	Conditions	^{3}H recovered [dis s^{-1} $g(U + Pu)^{-1}$]			^{3}H removed by voloxidation	
		Voloxidizer off-gas	Dissolver	Total	DF for ^{3}H[a]	% of total ^{3}H
H. B. Robinson-2 (PWR) 28,000 MWd/ton[b]	Unclad					
	480°C, air	7.20 E+06	1.10 E+04	7.21 E+06	656	99.8
	Unoxidized		1.04 E+07	1.04 E+07		
	Clad[c]					
	480°C, air	6.70 E+06	<1.0 E+04	6.71 E+06	>671	>99.9
	480°C, O_2	6.70 E+06	∿1.03 E+03	6.70 E+06	6700	>99.9
Oconee-1 (PWR) 18,000 MWd/ton[b]	Unclad					
	480°C, air	5.60 E+06	5.80 E+03	5.61 E+06	967	99.9
	Unoxidized		8.33 E+06	8.33 E+06		
	Clad[c]					
	480°C, air	6.70 E+06	1.10 E+03	6.70 E+06	6090	>99.9
Dresden-3 (BWR) 13,900 MWd/ton[b]	Unclad					
	480°C, air	2.20 E+06	5.0 E+02	2.20 E+06	4400	>99.9
	Unoxidized		2.50 E+06	2.50 E+06		
	Clad[d]					
	480°C, air	2.30 E+06	2.02 E+02	2.30 E+06	11,500	>99.9

[a] DF = the ratio of ^{3}H in the voloxidizer feed to the amount of ^{3}H contained in the voloxidizer product.

[b] Average burnup.

[c] 1-in.-long pieces.

[d] 2-in.-long pieces.

Table 8. Gaseous release totals during voloxidation

		Gaseous radionuclide release from UO_2					
		$^{3}H^{a}$		$^{14}C^{b}$		$^{85}Kr^{b}$	
		dis $s^{-1}g(U + Pu)^{-1}$	% of inventory	dis $s^{-1}g(U + Pu)^{-1}$	% of inventory	dis $s^{-1}g\ (U + Pu)^{-1}$	% of inventory
H. B. Robinson-2							
LWR-2	1-in. clad	∿1.02 E+07	99.9	1.12 E+04	52.0[a]	2.10 E+07	6.1
LWR-3	Unclad	∿1.02 E+07	>99.9	1.74 E+04	81.0[a]	1.48 E+07	4.3
LWR-15[c]	1-in. clad	∿1.02 E+07	>99.9	2.45 E+03	11.4	1.86 E+07	5.4
Oconee-1							
LWR-16	Unclad	8.32 E+06	99.9	1.74 E+03	11.3	1.30 E+07	6.0
LWR-17	1-in. clad + unclad	∿8.33 E+06	>99.9	9.12 E+02	5.9	1.29 E+07	5.9
Dresden-3							
LWR-18	Unclad	∿2.47 E+06	>99.9	2.58 E+03	17.4	6.67 E+06	4.6
LWR-19	2-in. clad	∿2.47 E+06	>99.9	3.69 E+03	24.9	6.78 E+06	4.6

[a] Based on residual content of voloxidized oxide.

[b] Determined from collected voloxidizer off-gas.

[c] Pure oxygen purge at 0.75 moles/h.

dissolver solutions with or without prior voloxidation. As stated above, the recoveries of ^3H in the voloxidation tests generally ranged from 70 to 90% of the total amount that was found by dissolving the untreated fuel.

Krypton releases were typically low, ranging from 4.3 to 6.1% of the amounts in the fuel. The quantities of ^{85}Kr released during voloxidation of the PWR fuels were two to three times the amounts released during oxidation of the BWR fuel. The presence of cladding apparently had little effect on the krypton release totals. Although the largest ^{85}Kr release was from 1-in. clad segments of the Robinson fuel, run LWR-2 was also the longest in duration (4.5 h at temperature).

Releases of ^{14}C from the UO_2 fuels during voloxidation were quite variable, ranging from ∿6 to 81% of the fuel inventory values. Much of the scatter in the ^{14}C release totals can be attributed to difficulties with recovery and analysis of the gaseous carbon, particularly during the earlier (H. B. Robinson fuel) runs. An ∿5% CO_2 carrier was used in the voloxidizer purge gas,* and improved analytical techniques were adopted for the experiments with Oconee and Dresden fuel. The results are still somewhat varied; however, the LWR-17 might be excluded along with the earliest Robinson runs since it used a smaller amount (2% CO_2) of carrier gas. Hence, the releases of ^{14}C to the voloxidizer off-gas range from ∿11 to 25% of the fuel contents, and apparently the greatest ^{14}C recoveries [up to 3.69 E+03 dis $s^{-1}g(U + Pu)^{-1}$] occurred during voloxidation of the Dresden (BWR) fuel. Additional experiments would be needed to verify this.

3.2.6 Release of ^3H from Zircaloy cladding

The total amount of ^3H contained in the UO_2 from the two PWR fuels was greater than that contained by the lower burnup BWR fuel (Table 9) by a factor of 3 to 4. In fact, determinations of the ^3H content in the Zircaloy cladding indicated that ∿40% of the total ^3H generated by

---

*The use of CO_2 in the purge gas affected the mass flow rate measurements during these runs and caused slight errors in the oxygen consumption calculations. These errors were compensated for after each experiment. In subsequent runs, the CO_2 carrier gas was added separately to the off-gas collection bag (prior to sampling), and the gas flow measurements were not affected.

Table 9. Removal of ^{3}H from UO_2 fuel and Zircaloy cladding during voloxidation

Fuel	Burnup (MWd/ton)	Linear heat rating (kW/ft)	Weight per inch	^{3}H contents		Removed by voloxidation		
				By weight	dis s^{-1} in.$^{-1}$	Percent of total	dis s^{-1} in.$^{-1}$	Percent of total
Robinson (PWR)	28,000	∿5.5	3.31 g Zr	2.85 E+07 dis s^{-1} g(Zr)$^{-1}$	9.43 E+07	38.4	1.09 E+05	0.045
			14.86 g(U+Pu)	1.02 E+07 dis s^{-1} g(U+Pu)$^{-1}$	1.52 E+08	61.6	∿1.52 E+08	∿61.6
					2.43 E+08			
Oconee (PWR)	23,000	∿5.5	3.61 g Zr	2.25 E+07 dis s^{-1} g(Zr)$^{-1}$	8.12 E+07	40.7	6.79 E+04	0.034
			14.21 g(U+Pu)	8.33 E+06 dis s^{-1} g(U+Pu)$^{-1}$	1.18 E+08	59.3	∿1.18 E+08	∿59.3
					1.99 E+08			
Dresden (BWR)	18,000	∿13.4	5.82 g Zr	1.37 E+07 dis s^{-1} g(Zr)$^{-1}$	7.97 E+07	56.4	a	a
			24.92 g(U+Pu)	2.47 E+06 dis s^{-1} g(U+Pu)$^{-1}$	6.16 E+07	43.6	∿6.16 E+07	∿43.6
					1.41 E+08			

[a] Not determined.

fission in the PWRs was contained in the cladding, while as much as 56% of the total generated ^{3}H was located in the cladding from the BWR fuel rod. This variation is probably due to the linear heat ratings of the two types of reactors — ∿5.5 kW/ft for the PWRs and ∿13.4 kW/ft for the Dresden-3 reactor.

The quantities of ^{3}H released from the Zircaloy cladding were measured during voloxidation of fuel hull segments from the two PWRs. Cladding specimens from the Oconee-1 and the H. B. Robinson-2 reactors were first leached in HNO_3 to remove adherent UO_2 and then oxidized. Voloxidations of the cladding segments were conducted under the same conditions (6 h at 480°C in air) as those used for the oxidation of the unclad or clad UO_2 samples.

In each case, the ^{3}H evolved from the cladding was <0.05% of the total ^{3}H recovered when clad UO_2 was voloxidized. Off-gas concentration curves indicated that ∿75% of the evolved ^{3}H was released during the initial heatup and first hour at temperature. The recovery of ^{85}Kr from the Oconee cladding amounted to ∿1.5% of the amount found when clad Oconee fuel was voloxidized. Oxygen consumption peaks indicated that up to a maximum of 50% of the oxygen in the air feed-gas was being consumed within about a 30-min period during each run. The measured weight gains of Zircaloy-4 cladding were ∿0.5%. Calculated weight gains based on oxygen consumption were slightly higher at ∿1.0%.

3.2.7 Off-gas concentration profiles

The concentration profiles and consumption-release curves for voloxidations of unclad fuel fragments from each reactor — Robinson (LWR-3), Oconee (LWR-16), and Dresden (LWR-18) — are shown in Figs. 2-7, respectively. Each set of curves shows a general close correspondence between oxygen utilization rates and the release rates to the gas from the UO_2. The sharp spikes at 15-min intervals in the oxygen and ^{85}Kr off-gas curves during runs LWR-16 and LWR-18 resulted from the sequential additions of the air contained in the ^{3}H traps to the oxygen-depleted off-gas as the traps were sequentially switched on-line. The computerized data scans at 2-min intervals picked up the momentary concentration changes. These concentration changes could not be obtained during the LWR-3 experiment when samples were taken manually and less frequently.

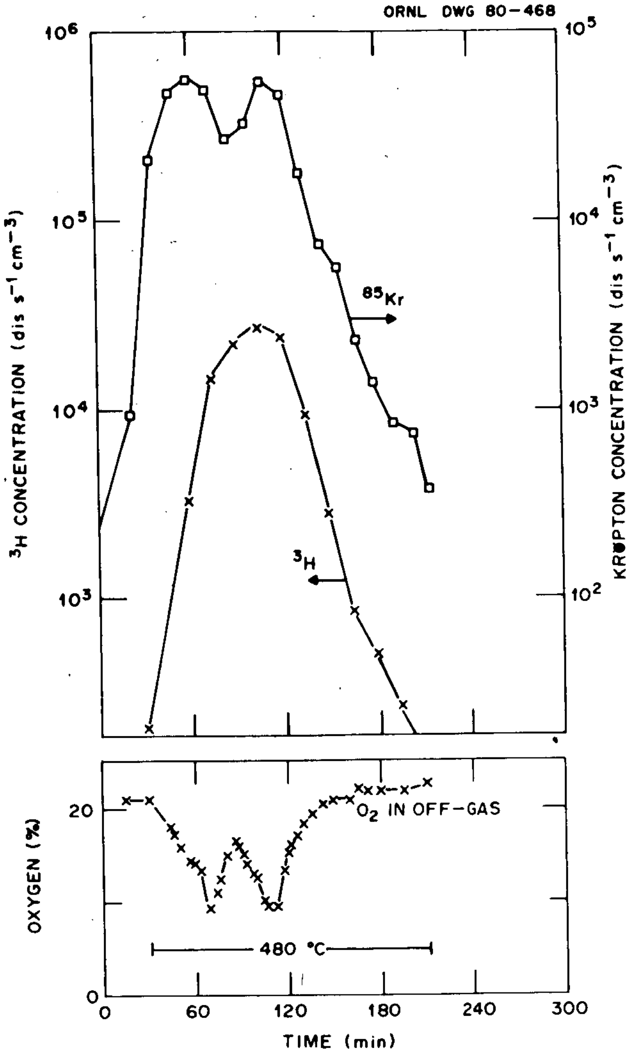

Fig. 2. Off-gas concentration profiles during voloxidation of unclad H. B. Robinson-2 UO_2 (LWR-3).

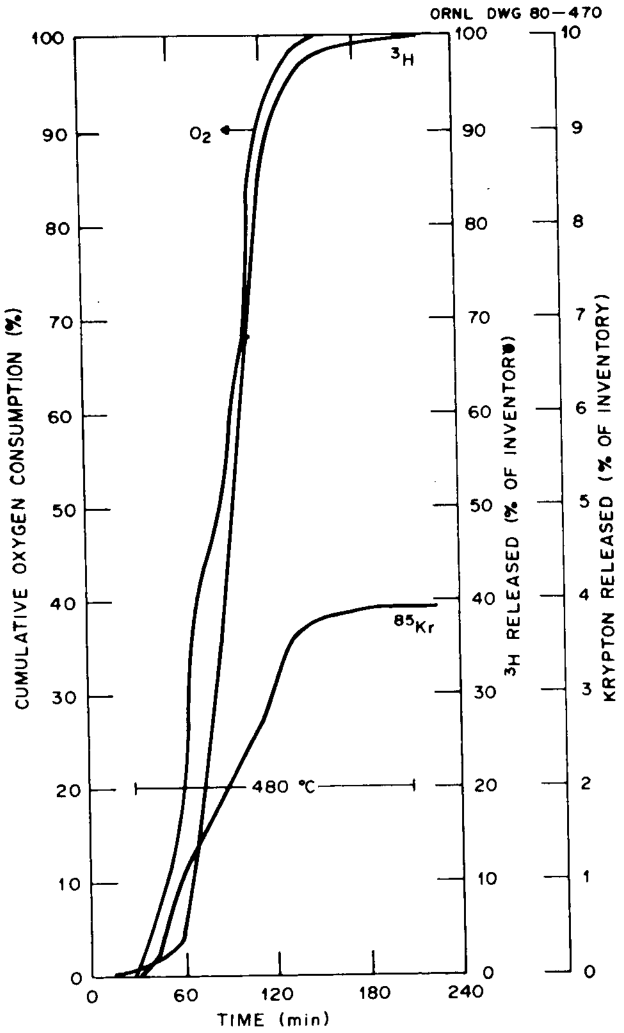

Fig. 3. Gaseous release and oxygen consumption during voloxidation (LWR-3).

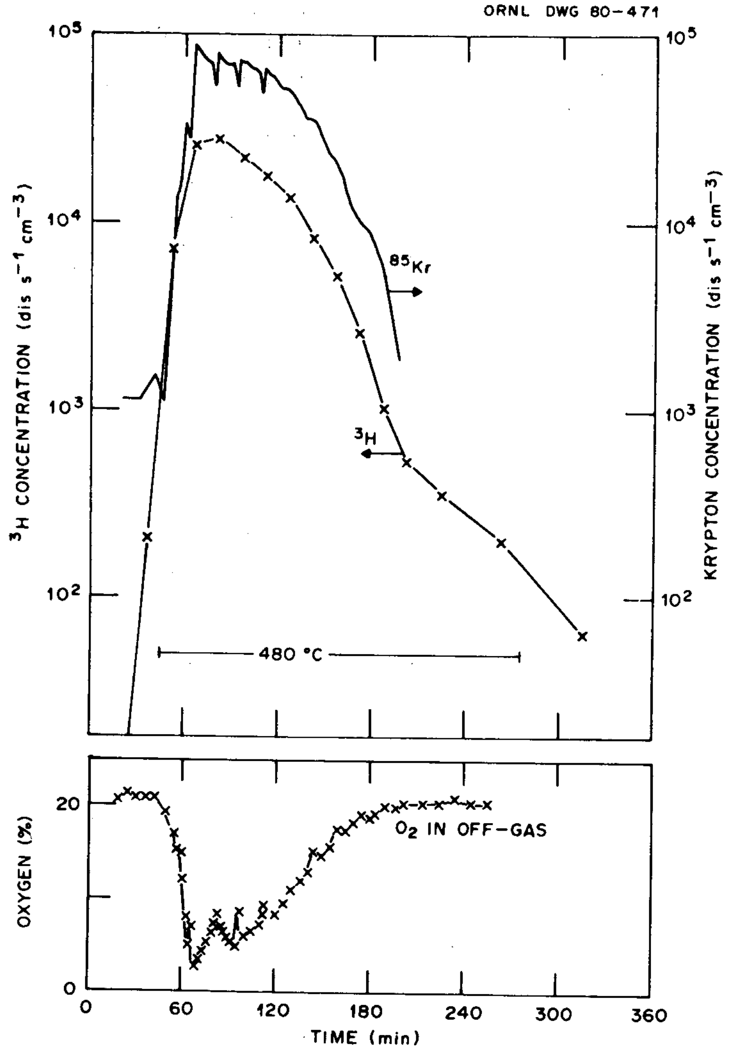

Fig. 4. Off-gas concentration profiles during voloxidation of unclad Oconee-1 UO_2 (LWR-16).

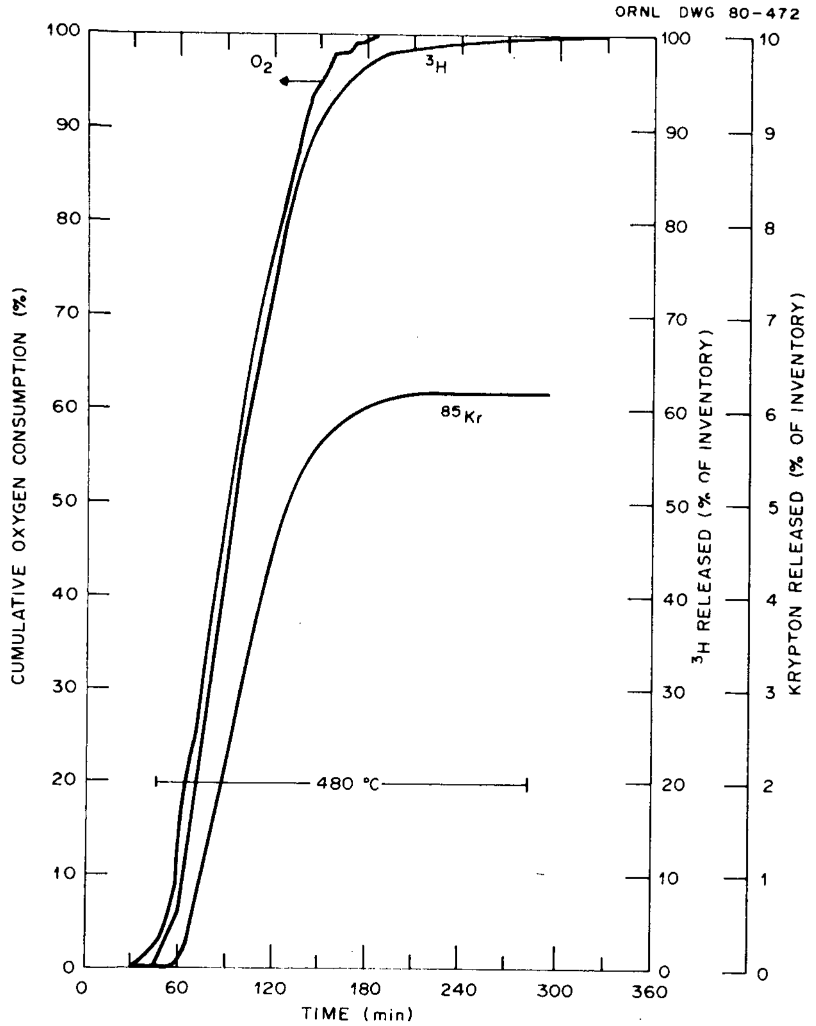

Fig. 5. Gaseous release and oxygen consumption during voloxidation (LWR-16).

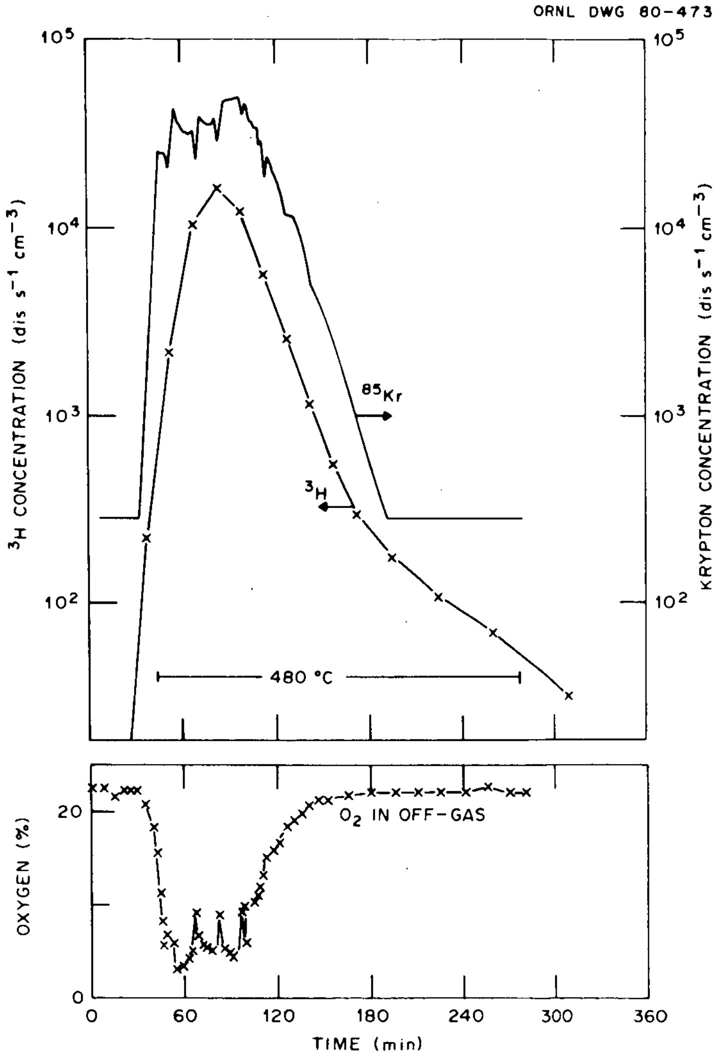

Fig. 6. Off-gas concentration profiles during voloxidation of unclad Dresden-3 UO_2 (LWR-18).

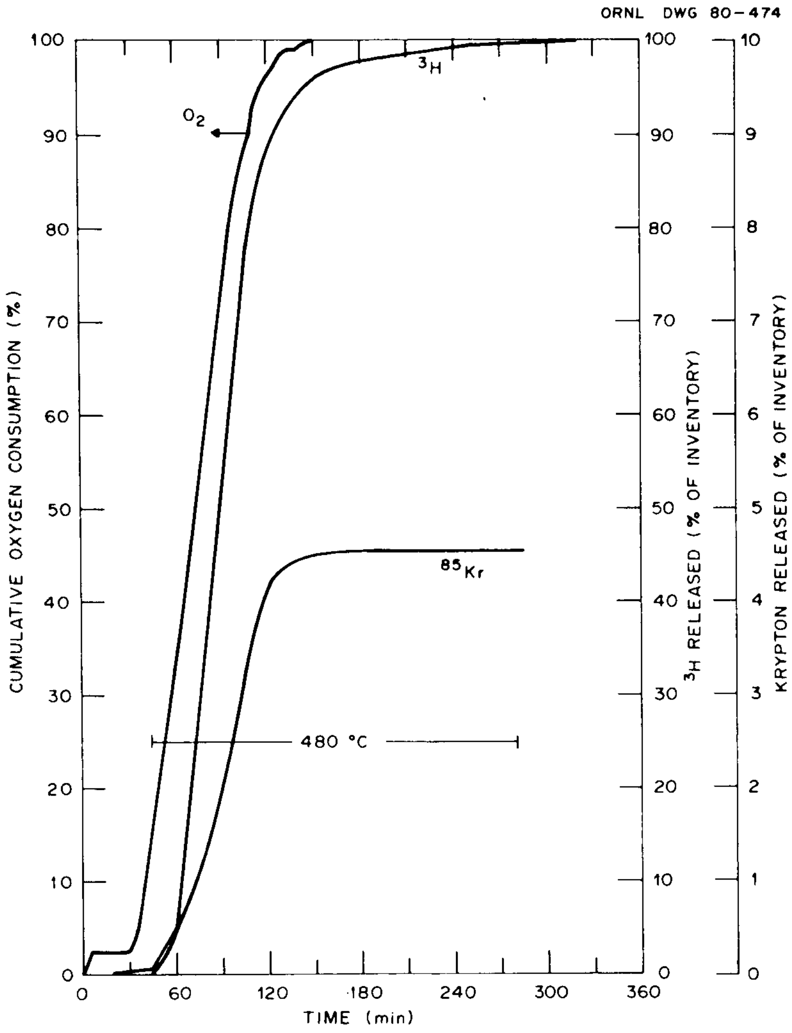

Fig. 7. Gaseous release and oxygen consumption during voloxidation (LWR-18).

The collection of ^{3}H on the traps paralleled the utilization of oxygen and the release of ^{85}Kr but lagged behind in the later stages of each experiment, indicating either a slower release rate or a slower transport through the heated lines. The experiments using air (oxygen rates of 0.1 to 0.15 moles/h) showed indications of double-peaked oxygen consumption patterns. This was especially the case during the voloxidation of the H. B. Robinson fuel, when there was a very pronounced corresponding double-peaked release of ^{85}Kr (Fig. 2). This phenomenon is thought to be related to the two-stage oxidation of UO_2 to U_4O_9, and then U_3O_8, which apparently occurs during oxidation in air under these conditions.[2]

No double-peaked consumption or release pattern was seen during the oxidation of unclad Robinson fuel in pure oxygen (feed rate = 0.75 moles O_2/h). The oxygen utilization and gaseous releases were characterized by very sharp spikes (Fig. 8). A second spike in the ^{3}H release was observed during the LWR-15 experiment when clad fuel was oxidized. As seen in Table 10, 100% utilization of the oxygen was attained during the LWR-15 run, and oxygen consumption was completed within an hour after start-up. In each of the air runs, no more than 70 to 85% of the oxygen in the feed gas was utilized at the time of peak consumption, and oxygen consumption occurred over a 2- to 4-h period, depending on whether cladding was present.

The ^{3}H and krypton peak heights (maximum concentrations in the off-gas) were related to the rate of oxygen consumption: the off-gas concentrations were several times greater in the pure oxygen experiment than they were during the air experiments (see Table 10). A comparison of the ^{3}H release profiles from the three fuels, shown in Fig. 9, indicates that the relative peak heights are in about the same ratio as the initial ^{3}H contents of the fuels. The profile for the Oconee fuel was extended 30 to 40 min beyond that of the other fuels, suggesting that ^{3}H release from that fuel was somewhat inhibited (>99.9% release was attained within 4 h). The presence of cladding was definitely an inhibiting factor on the ^{3}H releases, as shown in Fig. 10 (Oconee), Fig. 11 (Dresden), and Fig. 9 (Robinson). Release profiles for ^{3}H were extended from 30 min to 60 min when the fuel was clad in 1- and 2-in. long pieces. However, even for the

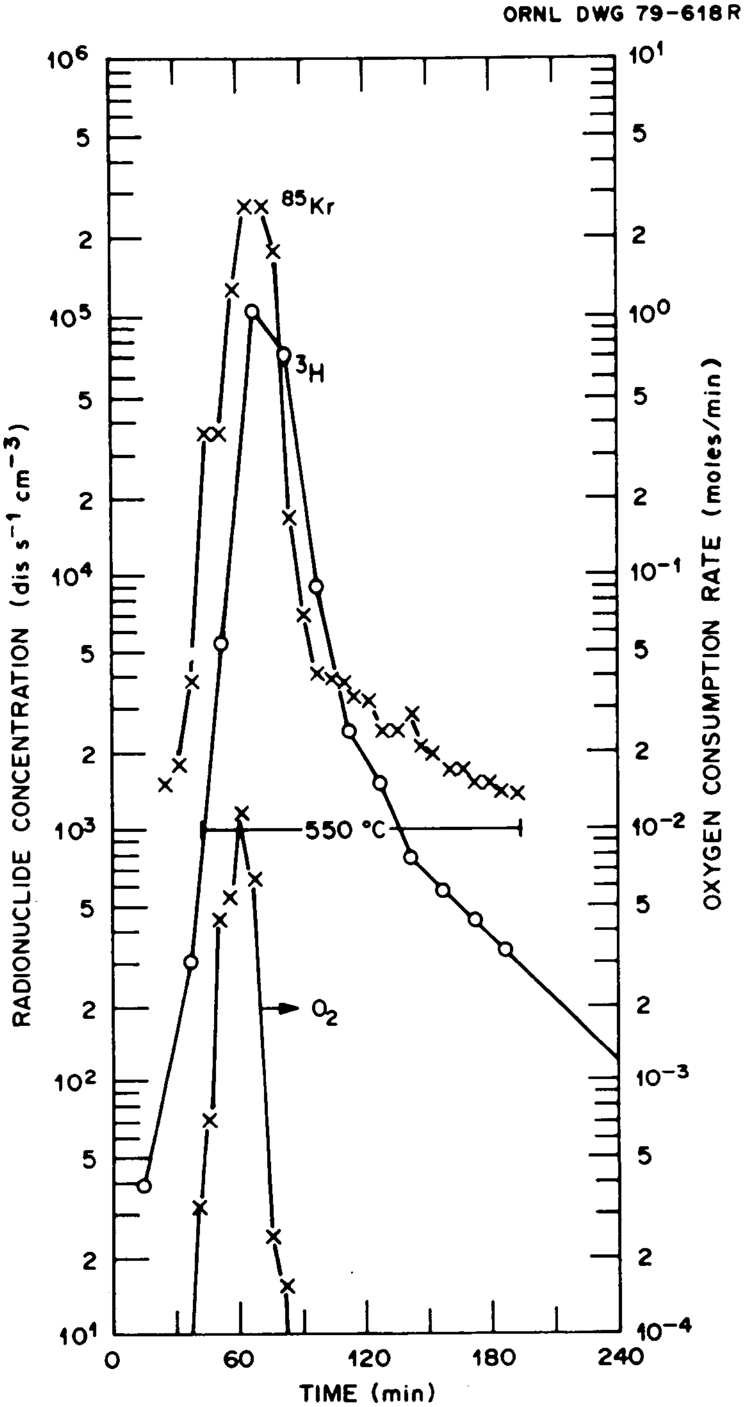

Fig. 8. Typical off-gas concentration profiles during voloxidation of unclad UO_2 in oxygen.

Table 10. Gaseous release and oxygen consumption during voloxidation

Fuel	Run No.	Conditions		Oxygen util. peak rate (moles/h)	Max. conc. of ^{85}Kr in off-gas (dis s^{-1} cm^{-3})	Max. conc. of ^{3}H in off-gas (dis s^{-1} cm^{-3})	Time[a] (min)				
		Cladding length	O_2 feed rate (moles/h)				Cumulative O_2		^{3}H release		
							50%	100%	50%	90%	99%
Robinson	LWR-2	1 in.	0.1	0.07	5.55 E+04	4.07 E+04	135	290	120	200	280
	LWR-3	Unclad	0.15	0.07	5.66 E+04	2.95 E+04	85	140	95	125	180
	LWR-15	1 in.	0.75	0.75[b]	3.06 E+05	9.98 E+04	46	60	66	74	170
Oconee	LWR-16	Unclad	0.15	0.125	8.70 E+04	2.79 E+04	92	189	96	149	230
	LWR-17	1 in. + unclad	0.15	0.12	7.81 E+05	3.14 E+04	88	205	107	160	240
Dresden	LWR-18	Unclad	0.15	0.13	4.96 E+04	1.56 E+04	73	165	88	126	225
	LWR-19	2 in.	0.15	0.12	5.57 E+04	1.49 E+04	99	180	108	158	260

[a] All times include an approximate 40-min heatup to operating temperature of 480°C.

[b] At maximum utilization, output flow from voloxidizer was equal to 0.

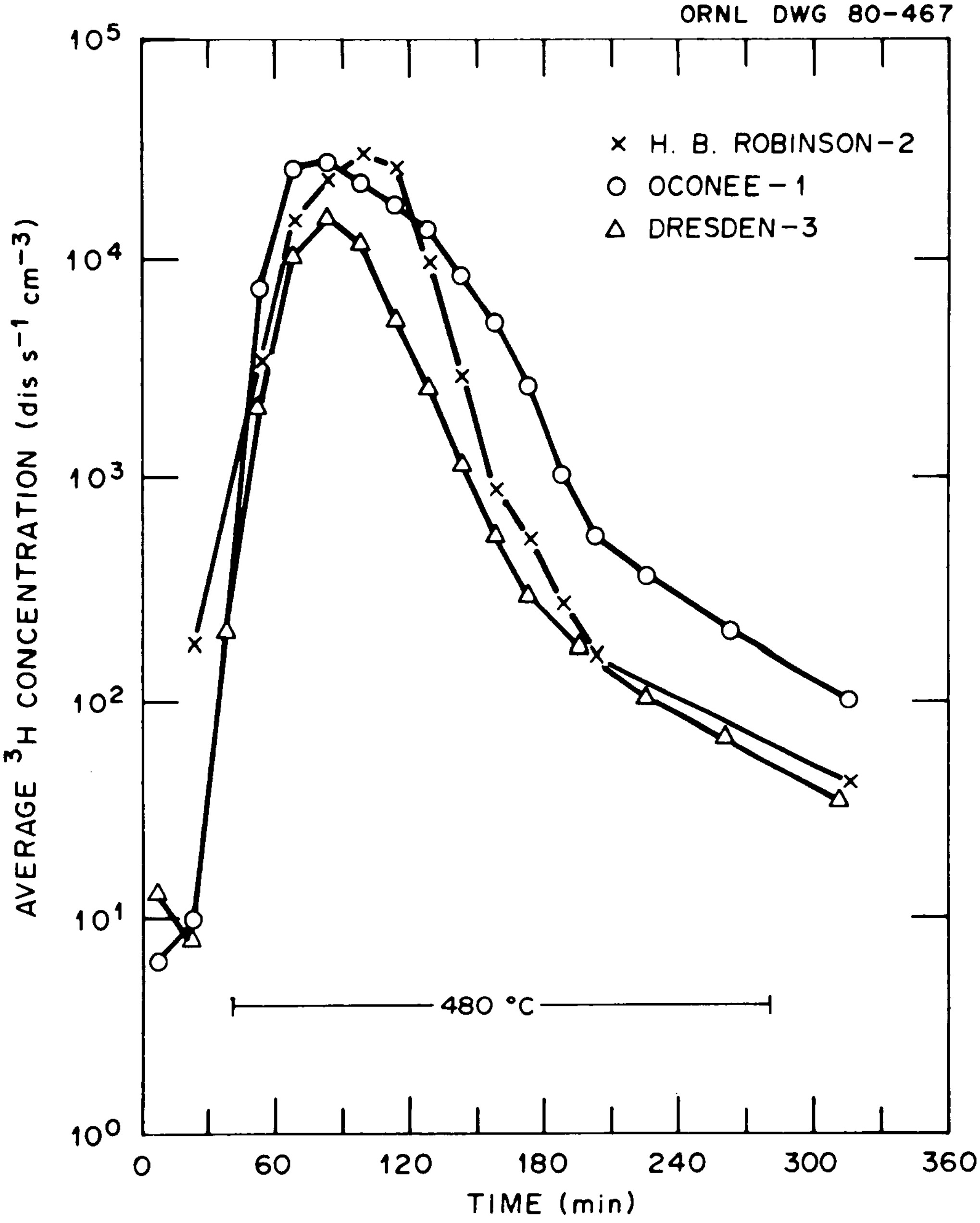

Fig. 9. Off-gas ^{3}H concentration profiles during voloxidation of power reactor fuels.

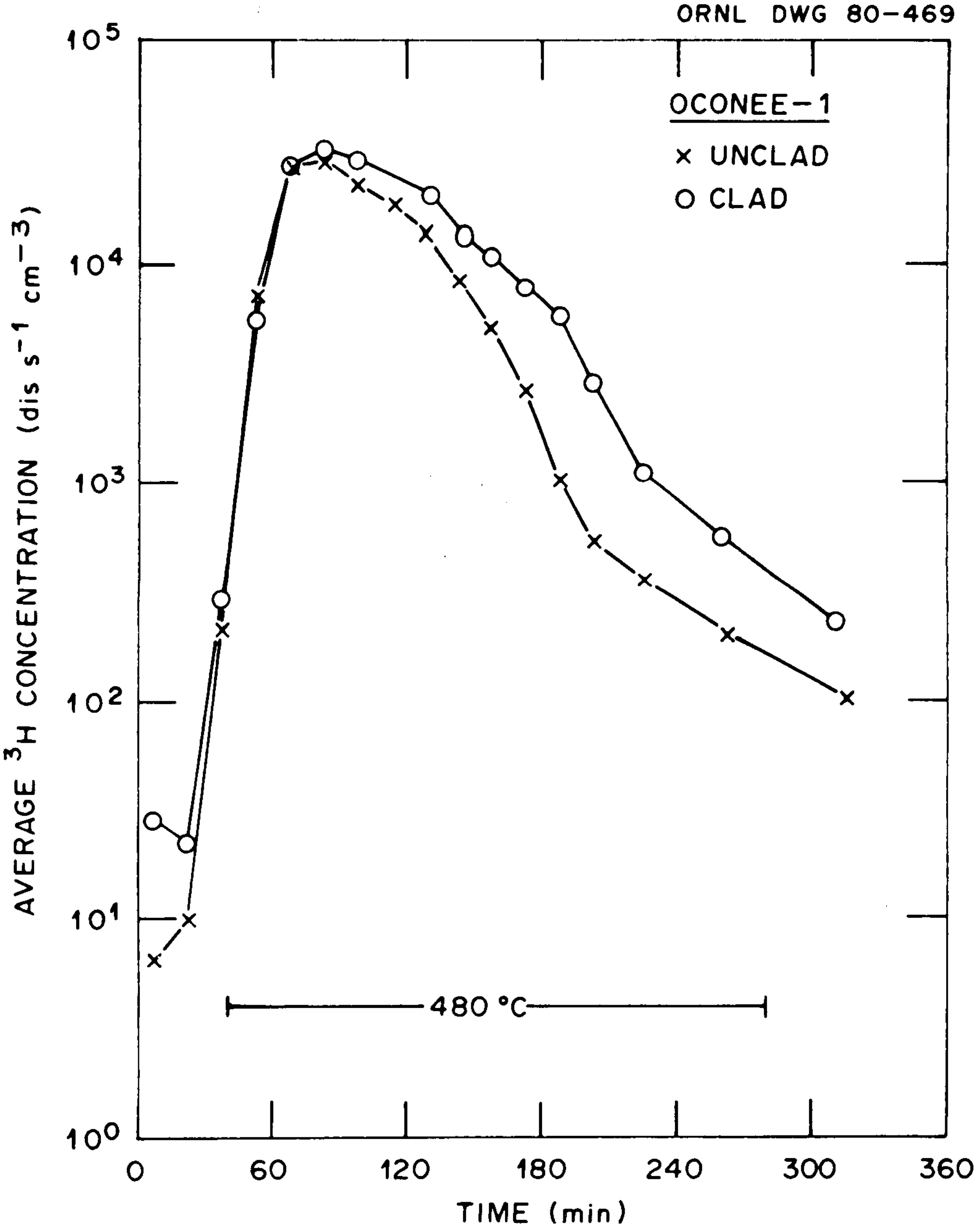

Fig. 10. Off-gas ^{3}H concentration profiles during voloxidation of Oconee-1 fuel.

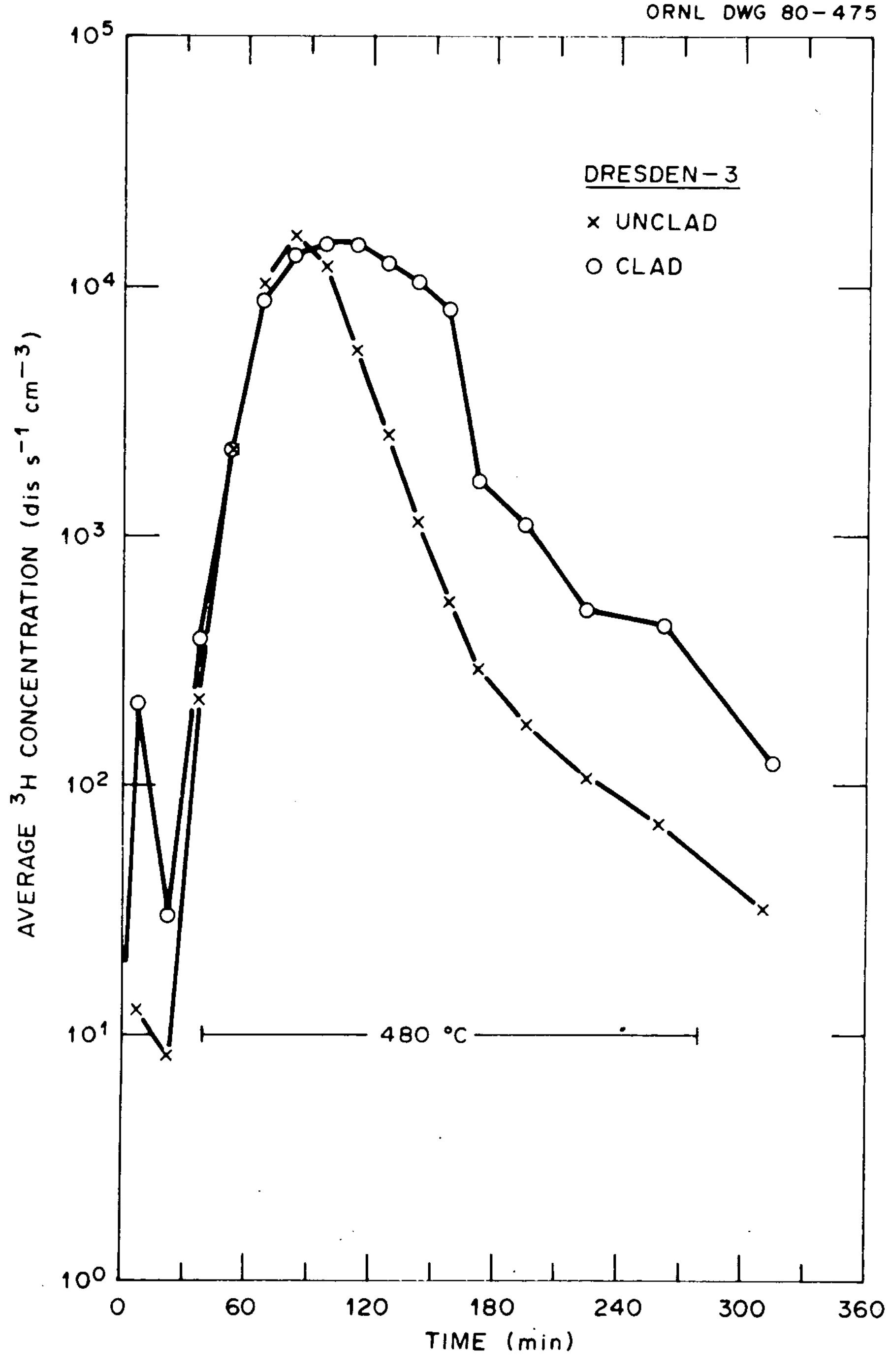

Fig. 11. Off-gas ^{3}H concentration profiles during voloxidation of Dresden-3 fuel.

Dresden fuel (with 2-in. cladding, the most severe cladding case), the time required to reach 99% release of the ^3H from the UO_2 was only ∿35 min longer than when no cladding was present (see Table 10). The longest time required to achieve 99% release occurred with the 1-in. clad Robinson UO_2 (280 min); however, the lower purge rate (0.1 moles O_2/h) during that run (LWR-2) also slowed the transport of ^3H through the off-gas system.

3.2.8 Fission-product distribution

The amounts of fission products remaining on the voloxidizer walls and on samples located in the off-gas system were determined following the comparative voloxidation tests. After each experiment, the samples (or HNO_3 leaches of the samples) were analyzed by gamma spectrometry; selected samples underwent activation analysis to determine the presence of ^{129}I. The deposition and entrainment samples for the clad Oconee-1 fuel run (LWR-17) were not analyzed immediately but were reused during the clad Dresden-3 fuel voloxidation (LWR-19) before being analyzed. Selected fission product recoveries are shown in Table 11 as percentages of the inventories listed in Table 6.

Generally, 0.1 to 0.2% of the total ^{106}Ru, ^{125}Sb, $^{134-137}Cs$, and ^{144}Ce was released from the fuel and was found in the system after voloxidation in air or oxygen. Apparently, there was greater fission-product volatility from the Oconee fuel, particularly with regard to the amounts recovered from inside the voloxidizer. In at least one case (Robinson, LWR-15), the leach solution for the voloxidizer sheet sample was probably contaminated by fuel. Perhaps some fuel dust remained on the sample prior to leaching. Brushing or ultrasonic washing of the sheets usually provides adequate pre-cleaning.

With the exceptions of ^{129}I 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 from the off-gas system were mostly <0.001% of the amounts in the fuel (Sect. 3.2.9).

Recoveries of volatilized iodine were usually on the order of 1 to 5% of the total fuel inventories (highest for the Dresden fuel), nearly all of which was located on downstream charcoal beds heated to 125°C (Table 12). The charcoal filter papers used in LWR-2 were not as effective at iodine retention as the charcoal beds. Most of the other

Table 11. Recoveries of selected fission products from the voloxidizer walls and the off-gas system

Nuclide	Fuel	Run No.	Conditions[a]	Distribution (% of inventory in UO_2)		Total recovered [dis s^{-1} g(U+Pu)$^{-1}$]
				Voloxidizer walls	Off-gas system	
			Unclad			
^{106}Ru	Robinson	LWR-3	Air	0.007	0.003	2.30 E+05
	Oconee	LWR-16	Air	0.089	0.026	1.90 E+06
	Dresden	LWR-18	Air	0.029	0.037	3.67 E+05
			Clad			
	Robinson	LWR-2	Air	0.007	<0.001	1.61 E+05
	Robinson	LWR-15	O_2	0.038[b]	0.080	2.71 E+06
	Dresden	LWR-19[c]	Air	0.066	0.087	8.48 E+05
			Unclad			
^{125}Sb	Robinson	LWR-3	Air	0.025	0.001	2.52 E+04
	Oconee	LWR-16	Air	0.197	d	1.91 E+05
	Dresden	LWR-18	Air	0.070	d	4.07 E+04
			Clad			
	Robinson	LWR-2	Air	0.026	<0.001	2.52 E+04
	Robinson	LWR-15	O_2	0.119[b]	<0.001	1.15 E+05
	Dresden	LWR-19[c]	Air	0.128	d	7.47 E+04
			Unclad			
^{129}I	Robinson	LWR-3	Air	0.22	1.08	1.98[e]
	Oconee	LWR-16	Air	0.147	1.08	2.30[e]
	Dresden	LWR-18	Air	0.044	4.56	10.0[e]
			Clad			
	Robinson	LWR-2	Air	0.22	0.04[f]	0.40[e]
	Robinson	LWR-15	O_2	21.2[b]	1.17	34.0[e]
	Dresden	LWR-19[c]	Air	0.086	0.60	1.48[e]
			Unclad			
^{134}Cs	Robinson	LWR-3	Air	0.017	<0.001	3.10 E+05
	Oconee	LWR-16	Air	0.160	d	1.85 E+06
	Dresden	LWR-18	Air	0.034	d	1.72 E+05
			Clad			
	Robinson	LWR-2	Air	0.017	<0.001	3.10 E+05
	Robinson	LWR-15	O_2	0.246[b]	<0.001	4.23 E+06
	Dresden	LWR-19[c]	Air	0.097	d	4.91 E+05
			Unclad			
^{137}Cs	Robinson	LWR-3	Air	0.021	0.002	7.64 E+05
	Oconee	LWR-16	Air	0.165	d	4.21 E+06
	Dresden	LWR-18	Air	0.039	d	7.77 E+05
			Clad			
	Robinson	LWR-2	Air	0.021	<0.001	6.97 E+05
	Robinson	LWR-15	O_2	0.323[b]	<0.001	1.07 E+07
	Dresden	LWR-19[c]	Air	0.100	d	1.98 E+06
			Unclad			
^{144}Ce	Robinson	LWR-3	Air	0.014	<0.001	3.56 E+05
	Oconee	LWR-16	Air	0.154	d	3.65 E+06
	Dresden	LWR-18	Air	0.033	g	1.92 E+05
			Clad			
	Robinson	LWR-2	Air	0.014	<0.001	3.56 E+05
	Robinson	LWR-15	O_2	0.233[b]	<0.001	5.92 E+06
	Dresden	LWR-19[c]	Air	0.116	d	6.76 E+05

[a] All run at 480°C.

[b] These results appear to be in error (see text).

[c] LWR-19 deposition and entrainment specimens were also in-line during the LWR-17 run with Oconee fuel.

[d] Trace quantities.

[e] μg/g (U+Pu).

[f] Charcoal paper used instead of charcoal bed.

[g] Not detected.

Table 12. Distribution of selected fission products in the voloxidizer off-gas system

Nuclide	Run No.	System distribution (% of total released from voloxidation)					Total found in off-gas system [dis s^{-1} $g(U+Pu)^{-1}$]
		Deposition tubing	Graded filter papers		Charcoal[a] bed	HEPA filter	
			≥5 µm	0.3 µm			
^{106}Ru	LWR-3	99.86	0.03	0.01	0.07	0.04	5.76 E+04
	LWR-16	99.87	0.07	0.03	0.02	0.01	4.27 E+05
	LWR-18	98.71	1.24	0.05	0.01	b	2.08 E+05
	LWR-2	87.23	5.23	b	7.54	b	1.41 E+03
	LWR-15	99.96	0.02	0.01	c	c	1.83 E+06
	LWR-19[d]	99.99	0.01	c	c	c	4.82 E+05
^{129}I	LWR-3	5.75	b	b	94.25	b	1.63[e]
	LWR-16	f	f	f	100.0	f	2.03[e]
	LWR-18	f	f	f	100.0	f	9.90[e]
	LWR-2	57.6	b	b	42.4	b	0.06[e]
	LWR-15	f	f	f	100.0	f	1.78[e]
	LWR-19[d]	f	f	f	100.0	f	1.29[e]
^{137}Cs	LWR-3	99.59	0.10	0.01	0.19	0.11	6.52 E+04
	LWR-16	86.25	10.98	0.96	0.40	1.41	3.61 E+02
	LWR-18	98.49	0.87	0.15	0.19	0.30	7.74 E+02
	LWR-2	82.48	7.38	b	10.15	b	1.66 E+03
	LWR-15	96.83	1.03	0.27	1.45	0.42	3.59 E+02
	LWR-19[d]	85.02	8.18	1.99	2.21	2.59	4.14 E+02

[a] LWR-2 used charcoal papers.

[b] Not detected.

[c] Trace quantities.

[d] Sample specimens used for two runs.

[e] µg/g(U + Pu).

[f] No analysis.

fission products reporting to the off-gas system were deposited on tubing specimens immediately beyond the exit-gas frit.

As seen in the earlier experiments with Robinson fuel,[2] during the voloxidations of Oconee and Dresden fuel, the ruthenium released from the UO_2 evidently acted somewhat differently from the 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 volatilized ruthenium was retained on tubing specimens, where surface temperatures ranged from above 400°C down to ∿100°C (Fig. 12). Higher temperatures and higher oxygen purge rates tended to increase the ruthenium volatility and deposition. During voloxidations at 480°C in air, more ^{106}Ru was recovered on specimens when the Oconee fuel was voloxidized than when the Dresden or Robinson fuels were voloxidized. An increase in voloxidation temperature to 550°C increased the ^{106}Ru deposition from the Robinson fuel by an order of magnitude. Voloxidation in pure oxygen (LWR-15) further increased the amount of volatilized ruthenium deposited in the off-gas train. This could indicate that oxidation to the more volatile RuO_4 was occurring under the more severe oxidizing conditions. An alternate explanation could be the gradual accumulation of fission products in the voloxidizer, leading to higher releases to the off-gas system.

3.2.9 Actinide and fission-product accumulation

The cumulative amounts of plated-out and entrapped species recovered from inside the voloxidizer after each experiment (or series of experiments) are shown in Fig. 13 as a function of the total amounts of fuel processed. The greatest buildup of fission products and heavy-metal oxides occurred during voloxidations of H. B. Robinson UO_2 in pure oxygen and at higher (550°C) temperatures. Those experiments were run during the initial throughput of 800 g (U + Pu). Subsequent voloxidations of Robinson, Oconee, and Dresden UO_2 in air added significantly less to the accumulation totals. After 41 h of operation and a throughput of 1270 g, the total actinide recoveries were on the order of 10 g/m^2 inside the voloxidizer (inside surface area = 0.037 m^2), which amounts to ∿0.03% of the cumulative amount processed.

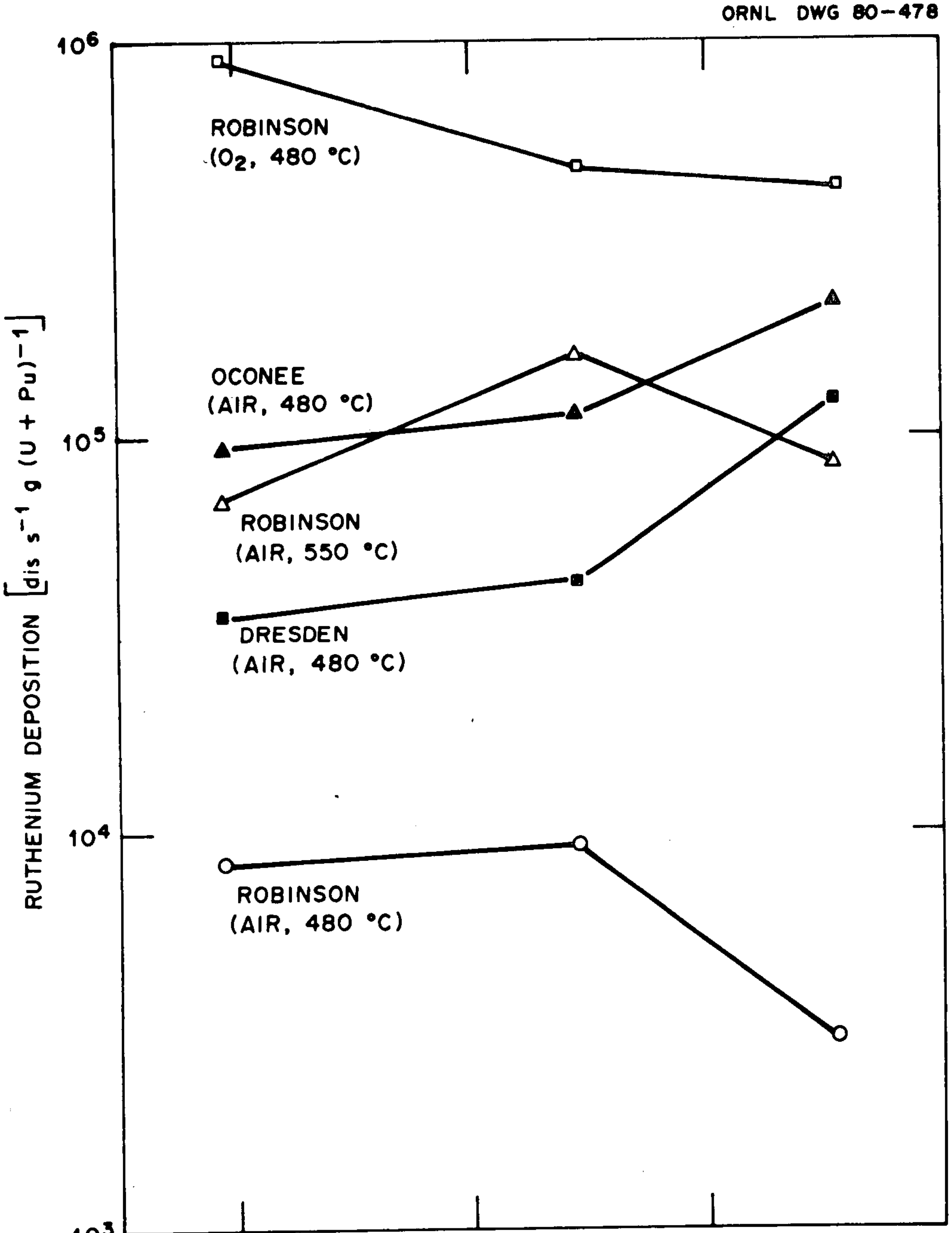

Fig. 12. Deposition of ruthenium from off-gas as a function of tubing temperature.

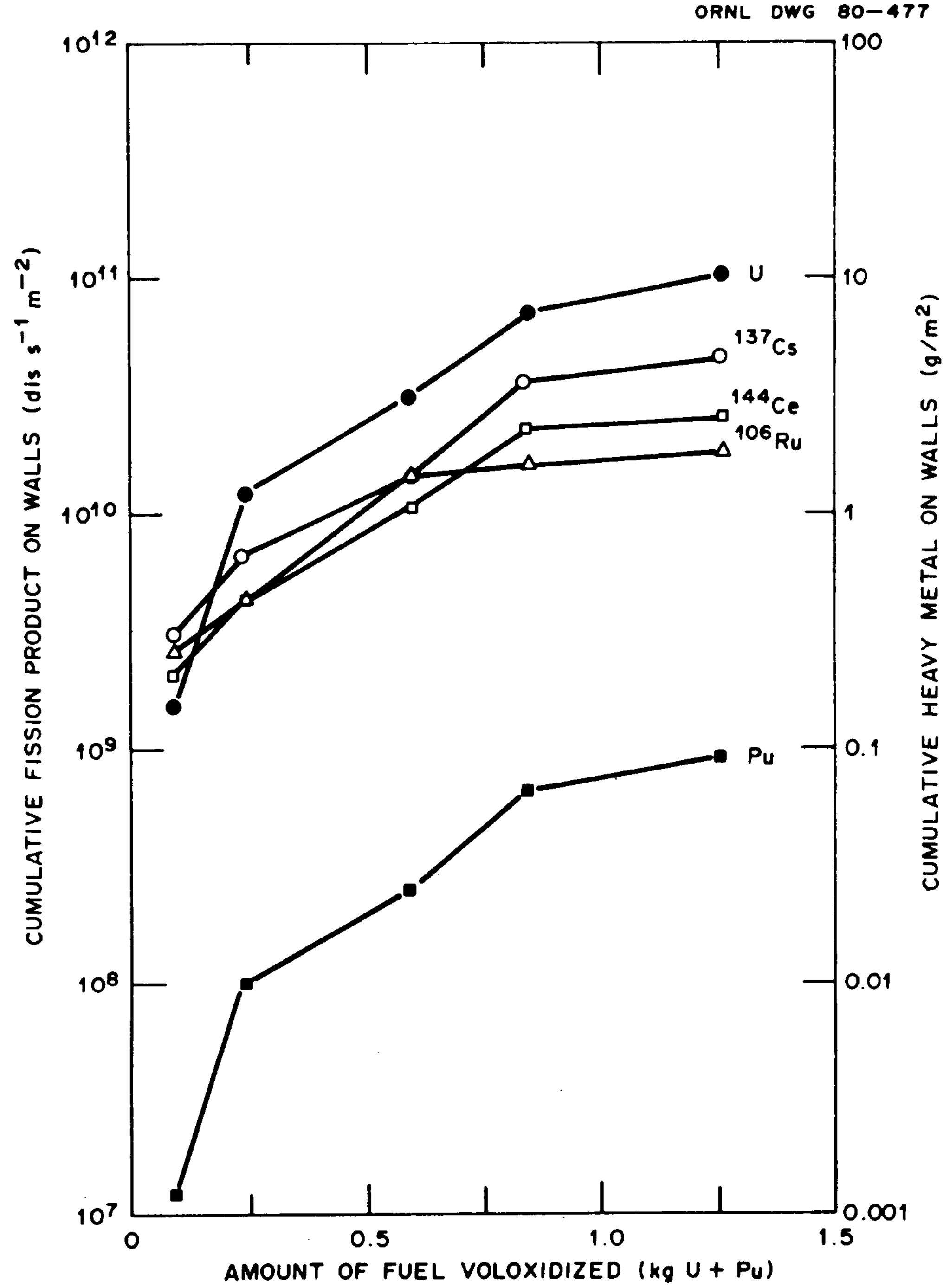

Fig. 13. Deposition of heavy metals and fission products on voloxidizer walls.

Fission-product deposition was also minimal, particularly during the period when air-purged voloxidations were being run. The flatter slope for ^{106}Ru deposition is an indication that the ruthenium had a greater tendency to be volatilized to the off-gas system. Generally, the concentrations of fission products on the walls are in the same ratio as they are in the LWR fuels, although there appears to be some enrichment with respect to the ^{137}Cs concentration.

3.3 Dissolution

3.3.1 Material balances

Material balances and the experimental conditions for the dissolution of the Dresden, Oconee, and Robinson fuels are shown in Tables 13-15, respectively. The dissolvent used was 7 M HNO_3, a period of 2 h was allowed for each leach, and the solutions were held just at the boiling temperature. Multiple leaches of the insoluble residues were made in most cases; some of the earlier dissolutions, however, had only one leach, made solely to determine the residual tritium-to-fuel ratio. The material balances ranged from 98.8 to 104.8%, and averaged 102%.

3.3.2 Insoluble residues

The quantities of HNO_3-insoluble fission product residues increased, as expected, with increasing burnup and voloxidation (Table 16). Voloxidation increased the total weight of residue over unvoloxidized fuel by factors of >2. The weight gain was primarily due to the greater insolubility of Ru, Rh, Pd, Mo, and Tc.

3.3.3 Dissolution of PuO_2

The overall solubility of the PuO_2 in the three fuels was not affected by the voloxidation, although the rate of dissolution of a small amount may be slowed. The dissolutions of plutonium in oxidized and unoxidized Robinson, Dresden, and Oconee fuels in successive leaches are summarized in Table 17. Tables 18 and 19 typically summarize the dissolution of the other nuclides.

The rate of dissolution of the fuels is rapid and essentially complete within a few hours; >99% dissolved in <30 min, as determined by the rate of ^{85}Kr evolution during the first leach and by the plutonium analyses of the second and third leach solutions (Fig. 14).

Table 13. Summary of Dresden-3 dissolutions[a]

Voloxidation	None	480°C	480°C
Run No.	18A	18B	19A[b]
Starting wt, g	30.0	30.0[c]	30.0
First leach: vol, ml	133	132	135
U dissolved, %	99.99	99.93	99.99
Pu dissolved, %	99.97	99.84	99.72
Second leach: vol, ml	30	30	-
U dissolved, %	0.001	0.070	-
Pu dissolved, %	0.012	0.131	-
Third leach: vol, ml	30	30	-
U dissolved, %	<0.001	0.001	-
Pu dissolved, %	0.005	0.003	-
Residue: wt, g	0.0078	0.0670	0.1223
U undissolved, %	<0.001	0.002	0.01
Pu undissolved, %	0.016	0.025	0.28
Recovery:			
UO_2, g	29.86	28.82	28.14
PuO_2, g	0.20	0.17	0.17
Residue, g	0.0078	0.0670	0.1223
Soluble fission product, g	0.75	0.72	0.50
Total, g	30.82	29.78	28.93
% starting wt	103	103	101
Total (U+Pu), g	26.45	25.54	24.95
Total Pu/(U+Pu) ratio	0.0062	0.0060	0.0060
Wt R-1, % $(U,Pu)O_2$ dissolved	0.026	0.128	0.432
Average wt residue, %	0.026	0.280	

---

[a] Procedure: 7 M HNO_3, 2 h, boiling for each leach shown (- indicates that leach was omitted).

[b] Voloxidized with cladding present; dissolved separately.

[c] U_3O_8; UO_2 ∿28.89 g.

Table 14. Summary of Oconee-1 dissolutions[a]

Voloxidation	None	480°C	480°C	480°C
Run No.	16A	16B	17A	17B[b]
Starting wt, g	20.6	29.9[c]	30.1	26.6[d]
First leach: vol., ml	61	134	134	100
U dissolved, %	99.99	99.91	99.92	∿99
Pu dissolved, %	99.89	99.81	99.80	∿99
Second leach: vol, ml	30	30	30	-
U dissolved, %	0.005	0.085	0.074	-
Pu dissolved, %	0.055	0.165	0.172	-
Third leach: vol., ml	30	30	30	-
U dissolved, %	<0.001	<0.001	<0.001	-
Pu dissolved, %	0.009	0.004	0.005	-
Residue, wt, g	0.0349	0.1053	0.1102	-
U undissolved, %	<0.001	0.003	0.004	-
Pu undissolved, %	0.049	0.022	0.026	-
Recovery, UO_2, g	19.76	29.12	28.79	0.16
PuO_2, g	0.15	0.22	0.22	0.01
Residue, g	0.0349	0.1053	0.1102	-
Soluble fission product, g	0.50	0.74	0.73	-
Total, g	20.44	30.19	29.85	0.17
% starting wt	99.2	104.8	103.0	
Total (U+Pu), g	17.53	25.86	25.56	
Total Pu/(U+Pu) ratio	0.0074	0.0077	0.0076	
Wt R-1, % $(U,Pu)O_2$ dissolved	0.175	0.359	0.380	
Average wt residue, %	0.175	0.370		

[a] Procedure: 7 $\underline{M}$ HNO_3, 2h, boiling for each leach shown (- indicates that leach was omitted).

[b] Voloxidized with cladding present; dissolved separately.

[c] U_3O_8; $UO_2 = 0.963\ U_3O_8$.

[d] Eight 1-in. pieces of cladding.

Table 15. Dissolution of selected H. B. Robinson-2 samples[a]

Voloxidation	None	480°C	480°C	480°C
Starting wt, g	29.6	19.0[b]	75.2[b]	250[b]
Run No.	3B	2A	3A	15A
1st leach: vol, ml	80	50	230	100
U dissolved, %	99.76[c]	99.99	99.98	99.95
Pu dissolved, %	99.97	99.97	99.97	99.85
2nd leach: vol., ml	50			30
U dissolved, %	0.02			0.04
Pu dissolved, %	0.02			0.13
3rd leach: vol., ml	50			
U dissolved, %	<0.01			
Pu dissolved, %	0.01			
Residue: wt, g	0.0572	0.1064	0.5300	0.1111
U undissolved, %	0.144[c]	0.012	0.018	0.007
Pu undissolved, %	0.004	0.017	0.026	0.013
Recovery: UO_2, g	28.41	18.36	72.87	23.28
PuO_2, g	0.26	0.16	0.50	0.19
Residue, g	0.0572	0.1064	0.5300	0.1111
Soluble fission product, g	0.52	0.33	1.31	0.42
% starting wt	98.8	104	104	99.8
Total (U+Pu), g	25.26	16.31	64.64	20.32
Total Pu/(U+Pu) ratio	0.0091	0.0086	0.0068	0.0084
Wt R-1, % $(U,Pu)O_2$ dissolved	0.200	0.575	0.722	0.473
Average wt residue, %	0.200		0.590	

[a] Procedure: 7 M HNO_3, 2 h, boiling for each leach shown (- indicates that leach was omitted).

[b] U_3O_8; $UO_2 = 0.963\ U_3O_8$.

[c] These values rejected on statistical basis.

Table 16. Nitric acid-insoluble residue

	Dresden-3	Oconee-1	Robinson-2	Difference due to burnup
Reactor burnup, MWd/ton	18,000	23,000	31,000	13,000[a]
Oxidized, wt % $(U,Pu)O_2$ dissolved	0.280	0.370	0.590	0.310
Not oxidized, wt % $(U,Pu)O_2$ dissolved	0.026	0.175	0.200	0.174
Difference due to oxidation, wt % $(U,Pu)O_2$ dissolved	0.254	0.195	0.390	0.242 (av)

[a] 31,000 - 18,000 MWd/ton.

Table 17. Plutonium in insoluble residue

	Dresden-3	Oconee-1	Robinson-2	Difference due to burnup
Reactor burnup, MWd/ton	18,000	23,000	31,000	
Oxidized, % of total	0.025[a]	0.024	0.019	
Not oxidized, % of total	0.016	0.049	0.004	0
Difference due to oxidation, % of total	0.009	0.0	0.015	

[a] One experimental value of 0.28% was discarded.

Table 18. Distribution of selected nuclides during dissolution of oxidized Dresden-3 fuel (Run No. LWR-18B: 30.0 g U_3O_8)

Location[a]	Volume	% found								
		U	Pu	^{3}H	^{85}Kr	^{106}Ru	^{125}Sb	^{134}Cs	^{137}Cs	^{144}Ce
DS-1	132 mℓ	99.93	99.84	99.99		76.9	58.3	99.94	99.92	99.95
DS-2	29.5 mℓ	0.07	0.13	b		1.2	3.5	0.04	0.05	0.05
DS-3	25.0 mℓ	0.01	0.01			1.0	1.8	c		c
Residue	0.0670 g	0.01	0.03			20.8	36.6	0.02	0.02	c
Scrubber	500 mℓ			0.01		c	c	c	c	c
Gas bag	12 ℓ				99.9	c				
Total, mg		25,388.9	153							
Total, dis/s				1.27E+04	3.76E+09	3.77E+09	4.46E+08	1.10E+10	5.02E+10	1.29E+10
Total, dis s^{-1} $g(U)^{-1}$				4.96E+02	1.47E+08	1.48E+08	1.75E+07	4.31E+08	1.97E+09	5.05E+08

[a] See text for description.

[b] Blank indicates no analysis.

[c] Below limits of detection by gamma spectroscopy.

Table 19. Distribution of selected nuclides during dissolution of unvoloxidized Oconee-1 fuel (Run No. LWR-16A: 20.6 g UO_2)

Location[a]	Volume	% found									
		U	Pu	^{3}H	^{14}C	^{85}Kr	^{106}Ru	^{125}Sb	^{134}Cs	^{137}Cs	^{144}Ce
DS-1	61 mℓ	99.99	99.99	99.90	b		71.21	92.42	>99.9	>99.9	>99.9
DS-2	30 mℓ	0.01	0.06				12.42	4.24	c	c	c
DS-3	30 mℓ	<0.01	<0.01				7.07	1.21	c	c	c
Residue	0.0349 g	<0.01	0.05				9.29	2.21	c	c	c
Scrubber	504 mℓ			0.10			c	c	c	c	c
Gas bag	12 ℓ				99.9	99.9	c	c	c	c	c
Total, mg		17,404	134								
Total, dis/s				1.46E+08	8.25E+04	3.70E+09	2.91E+10	1.47E+09	1.92E+10	4.33E+10	4.00E+10
Total, dis s^{-1} $g(U)^{-1}$				8.33E+06	4.71E+03	2.11E+08	1.66E+09	8.36E+07	1.09E+09	2.47E+09	2.28E+09

[a] See text for description.

[b] Blank indicates no analysis.

[c] Below limits of detection by gamma spectroscopy.

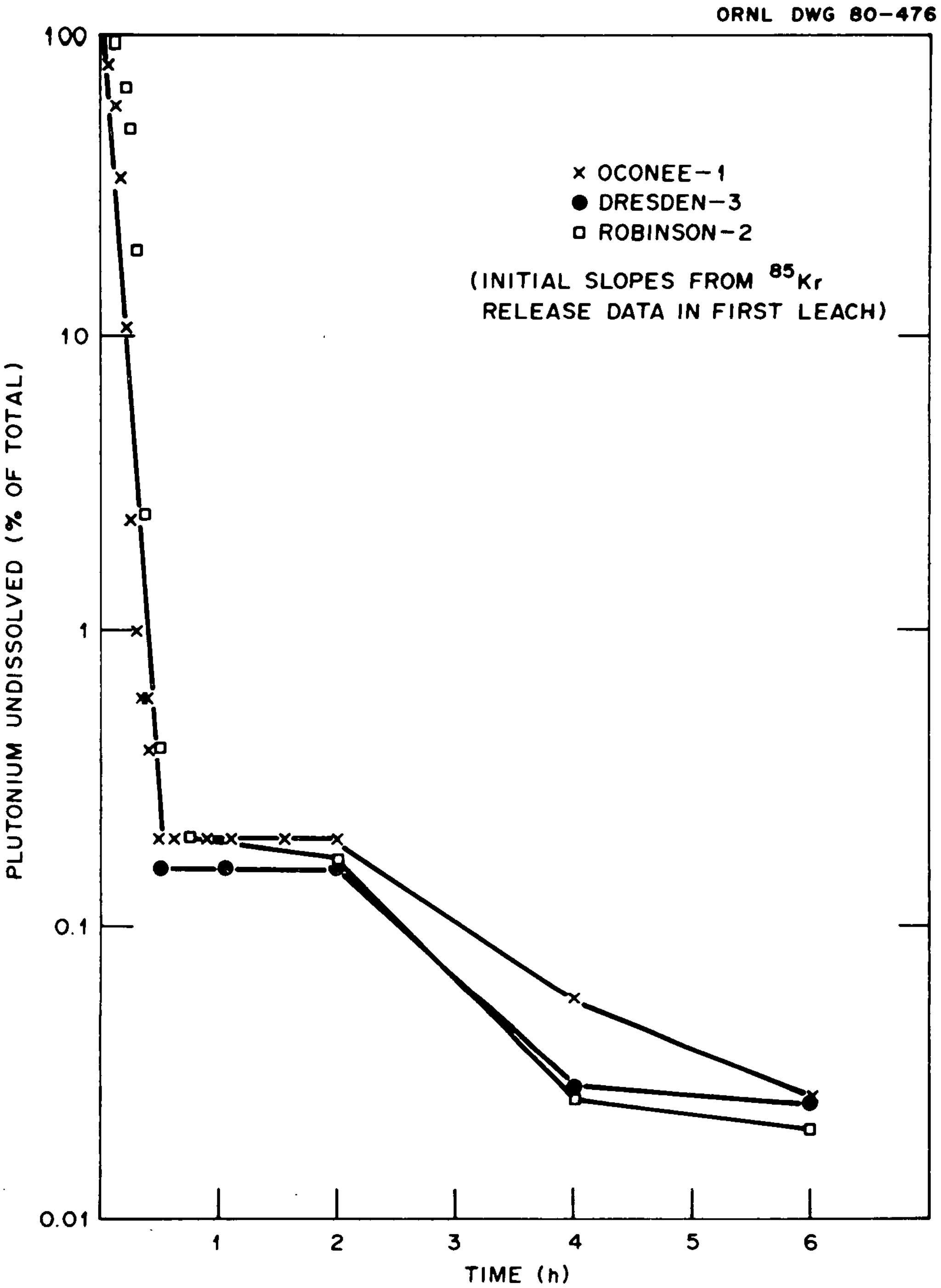

Fig. 14. Dissolution of PuO_2 from oxidized LWR UO_2 fuels.

3.3.4 Isotopic analyses of fuel solutions

Mass spectrometric analyses of the uranium and plutonium isotopic composition are reported in Table 20.

3.3.5 Tritium in cladding

The ^3H content of the Zircaloy cladding was determined by dissolving leached segments of the Zircaloy in Zirflex reagent[6] (6 $\underline{M}$ NH_4F-1 $\underline{M}$ NH_4NO_2) and passing the off-gases (a mixture of ammonia and hydrogen) through a hot CuO trap and absorbing the ammonia and tritiated water in first a dilute acid and then a basic scrubber. The distribution of ^3H found was ∿4% in the Zirflex solution, ∿95% in the acidic scrubber, and 1% in the basic scrubber (Table 21). The analyses indicated (Table 22) that the BWR cladding, which operated at a higher power level and higher temperatures than the PWR, contained a significantly greater fraction (64%) of the ^3H generated in the fuel from the PWR cladding (40%).

The ^{14}C content of the cladding was also measured in the Zirflex solution and the two scrubbers. Essentially all of the ^{14}C found was in the NaOH solution (Table 23).

4. ACKNOWLEDGMENTS

We wish to acknowledge the work of the able Chemical Technology Division technicians, O. L. Kirkland, J. R. Travis, and C. S. Webster, who performed the hot-cell manipulations. The ORNL Analytical Chemistry Division service groups, under the direction of W. H. Christie, W. R. Laing, H. A. Parker, J. C. Price, J. R. Sites, J. R. Stokely, and R. L. Walker, performed the myriad analyses required for the material balances. Mr. Tom Emswiler, at Battelle-Columbus Laboratory, Mr. Vic Storhok, at INEL, and Mr. Mike Rigdon and Mr. Mike Montgomery, at Babcock and Wilcox-Lynchburg, shipped the irradiated fuel rods to ORNL. The HRLEL group, under the supervision of E. M. King and R. L. Lines, cut the long rods into shorter lengths.

Table 20. Isotopic analyses of irradiated UO_2 (wt %)

	H. B. Robinson-2 EOC-3[a]		Oconee-1 EOC-2[a]		Dresden-3 EOC-3[a]
	Calculated	Found	Calculated	Found	Found
MWd/ton[b]	31,000		23,680		17,800
^{233}U	<0.001	0.001	0.001	0.001	c
^{234}U	0.013	0.014	0.012	0.011	c
^{235}U	0.607	0.628	0.786	0.739	c
^{236}U	0.349	0.354	0.232	0.253	c
^{238}U	99.03	99.00	99.08	98.997	c
^{238}Pu	1.30	1.65	0.789	0.854	0.777
^{239}Pu	56.91	54.81	63.363	63.747	66.447
^{240}Pu	24.10	26.19	20.343	22.883	22.226
^{241}Pu	12.23	11.50	11.949	9.202	8.176
^{242}Pu	5.46	5.86	3.556	3.264	2.373

[a] EOC = end of cycle.

[b] Peak burnup of fuel rod.

[c] Not determined.

Table 21. Distribution of ^3H during Zirflex dissolution of Zircaloy cladding

Reactor	^3H found (% of total)		
	Dissolution solution	HNO_3 scrubber[a]	NaOH solution
Dresden	4.2	94.8	0.9
Oconee	3.6	95.6	0.8
Robinson	3.4	94.7	2.0

[a] Preceded by hot CuO.

Table 22. Tritium content of fuel and Zircaloy cladding

	Dresden-3	Oconee-1	Robinson-2
Fuel, dis $s^{-1}g(U)^{-1}$	2.47 E+06 (36%)	8.33 E+06 (61%)	3.87 E+07 (60%)
Cladding, dis $s^{-1}g(Zr)^{-1}$	1.32 E+07 (64%)	2.25 E+07 (39%)	2.58 E+07 (40%)

Table 23. Distribution of ^{14}C during Zirflex dissolution of Zircaloy cladding

Reactor	^{14}C found (% of total released)		
	Dissolution solution	HNO_3 scrubber[a]	NaOH solution
Dresden-3	<5	<11	>84
Oconee-1	<3	<8	>89
Robinson-2	<1	<1	>98

[a] Preceded by hot CuO.

5. CONCLUSIONS

1. The release of ^{3}H during the voloxidation of the UO_2 fuel from two PWR reactors and one BWR reactor was essentially quantitative (i.e., >99.9% over 4 h using oxygen feed rates in the range of 0.1 to 0.75 moles/h).
2. During voloxidation at 480°C in air, from 2 to 3 h was required to complete the oxidation of unclad UO_2, and from 3 to 4 h was required when using 1- or 2-in.-long segments of clad UO_2. During oxidation of clad UO_2 at a temperature of 480°C in pure oxygen, the reaction was complete in 1 to 1.5 h.
3. The release of ^{85}Kr in the three fuels was $\sim$4 to 6% of inventory.
4. A temporary reduction in the rate of oxygen consumption (and ^{85}Kr release) at low purge rates was seen during voloxidation of each LWR fuel. This phenomenon was most pronounced with the H. B. Robinson UO_2 and is apparently related to the formation of U_4O_9 as an intermediate product.
5. The weight gains and oxygen consumption during voloxidation indicated good conversions to U_3O_8 in each case. The fuel was dislodged from the cladding; the oxide product was a fine powder (more than 99% was <20 μm).
6. Fission-product volatilization during oxidation in air or oxygen at 480°C was not extensive for any of the UO_2 fuels. Generally, less than 0.1 to 0.2% of the inventories of ruthenium, cesium, and cerium was deposited on the interior surfaces of the equipment. Except for ^{106}Ru and ^{129}I, quantities reporting to the off-gas system were minimal (<0.001% of the fuel inventories). Up to $\sim$0.1% of the total ^{106}Ru was recovered on surfaces in the voloxidizer off-gas system, which suggests that ruthenium may have a higher volatility, particularly under more severe oxidizing conditions.
7. The amount of actinide accumulated in the voloxidizer was $\sim$0.03% of the cumulative amount processed [1270 g (U+Pu)] after 41 h of operation.
8. The voloxidation of the three different UO_2 fuels did not significantly affect the solubility of the uranium and plutonium in 7 M HNO_3 but did

create a fission-product residue that was two to three times more acid-insoluble. About 0.02 to 0.03% of the plutonium was not dissolved by three 2-h leaches in boiling 7 M HNO_3.

6. REFERENCES

1. J. H. Goode and R. G. Stacy, Head-end Reprocessing Studies with H. B. Robinson-2 Fuel, ORNL/TM-6037 (June 1978).

2. J. H. Goode, R. G. Stacy, and V. C. A. Vaughen, Head-end Reprocessing Studies with the H. B. Robinson-2 Fuel. II. Parametric Voloxidation Studies, ORNL/TM-6888 (in preparation).

3. V. Pasupathi et al., Determination and Microscopic Study of Incipient Defects in Irradiated Power Reactor Fuel Rods, EPRI-NP-812 (July 1978).

4. R. G. Stacy and J. H. Goode, Shearing of Irradiated Reactor Fuels, ORNL/TM-6835 (in preparation).

5. W. Davis, Jr., G. A. West, and R. G. Stacy, Oxide Particle Size Distribution from Shearing Irradiated and Unirradiated LWR Fuels in Zircaloy and Stainless Steel Cladding: Significance for Risk Assessment, NUREG/CR-0868, ORNL/NUREG-60, Interim Report (October 1979).

6. J. L. Swanson, The Zirflex Process, in Progress in Nuclear Energy, Process Chemistry, Series III, pp. 289-303, Vol. 3, Pergamon Press, Oxford, 1961.

ORNL/TM-7103
Dist. Category UC-86
(Applied)

Internal Distribution

1. W. J. Armento
2. S. M. Babcock
3. J. O. Blomeke
4. E. C. Bradley
5-7. W. D. Burch
8. J. A. Carter
9. E. D. Collins
10. R. M. Counce
11. D. J. Crouse
12. M. J. Feldman
13-17. J. H. Goode
18. J. C. Griess
19. W. S. Groenier
20. G. L. Haag
21. D. C. Hampson
22. W. D. Holland
23. S. I. Hurrell
24. R. T. Jubin
25. L. J. King
26. J. Q. Kirkman
27. C. E. Lamb
28. R. E. Leuze
29. B. E. Lewis
30. J. C. Mailen
31. A. P. Malinauskas
32. J. L. Marley
33. J. R. Merriman
34. A. D. Mitchell
35. R. E. Norman
36. E. D. North
37-40. R. H. Powell
41. G. W. Renfro
42. J. H. Shaffer
43-47. D. P. Stevens
48. B. B. Spencer
49-53. R. G. Stacy
54. J. R. Stokely
55. D. W. Swindle
56. O. K. Tallent
57. J. E. Van Cleve, Jr.
58-60. V. C. A. Vaughen
61. J. E. Vath
62. B. L. Vondra
63. T. D. Welch
64. M. E. Whatley
65. R. G. Wymer
66. O. O. Yarbro
67. S. Beard (consultant)
68. L. Burris, Jr. (consultant)
69. G. R. Choppin (consultant)
70. L. J. Colby, Jr. (consultant)
71. W. H. Corcoran (consultant)
72. W. H. Lewis (consultant)
73. M. J. Szulinski (consultant)
74. A. K. Williams (consultant)
75-76. Central Research Library
77. Y-12 Technical Library-
Document Reference Section
78-82. Laboratory Records
83. Laboratory Records, RC
84. ORNL Patent Section

External Distribution

85-86. W. W. Ballard, Chief, Nuclear Fuel Cycles Programs Branch, Division of Nuclear Power Development, DOE, Washington, DC 20545

87. Office of Assistant Manager, Energy Research and Development DOE-ORO, Oak Ridge, Tennessee 37830

88-176. Given distribution as shown in TID-4500 under UC-86, Consolidated Fuel Reprocessing category (Applied)

☆U.S. GOVERNMENT PRINTING OFFICE: 1980-640-245/093