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Voloxidation of the UO_2 Axial Blankets from Irradiated $(U,Pu)O_2$ Fuel Rods

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CONSOLIDATED FUEL REPROCESSING PROGRAM

VOLOXIDATION OF THE UO_2 AXIAL BLANKETS FROM IRRADIATED $(U,Pu)O_2$ FUEL RODS

J. H. Goode
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Chemical Technology Division

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ABSTRACT

Hot-cell experiments are being conducted to determine the effects of high-temperature oxidation (voloxidation) on the release of tritium and other gaseous fission products from the highly irradiated $(U,Pu)O_2$ and UO_2 of advanced power reactor fuel rods and on the subsequent dissolution of the uranium and plutonium oxides in HNO_3. Such a procedure might be an effective method for isolating fission product tritium before it can be combined and diluted by the aqueous streams of the processing plant. Two earlier reports in this series summarized experiments with the $(U,Pu)O_2$ from two experimental fuel rods that had been irradiated to nominal burnups of 16.5 and 17.5 at. % in EBR-2. This document describes experiments on the voloxidation of the UO_2 axial blankets of the same rods.

The stainless-steel-clad rods were cut into short lengths with a hydraulic shear and divided into fractions. One fraction was dissolved directly in HNO_3, while the other fraction was dissolved after being tumbled and oxidized in air at temperatures of 480 and 600°C. The off-gas stream was analyzed for particulate, semivolatile, and gaseous fission products after each test. Multiple short leaches were performed on the fuels to determine the rate of dissolution before and after voloxidation.

The tests showed that oxidation in air at 480 and 600°C released 99.8% of the tritium contained in the UO_2 axial blankets of highly irradiated $(U,Pu)O_2$ fuel rods. In one experiment, as much as 20% of the tritium in the blanket was released during heatup to 600°C. The treatments also volatilized up to 22% of the ^{14}C, 28% of the ^{85}Kr, and 7% of the ^{129}I from the UO_2.

Less than 0.1% of the ^{106}Ru was found outside the voloxidizer chamber. However, up to 0.5% of the $^{134-137}Cs$ in the UO_2 was found in the off-gas system after voloxidation at 600°C, while only ∿0.2% of the cesium was released at 480°C. The voloxidation apparently had little effect on the solubility of the uranium or plutonium in HNO_3.

The results of these experiments suggest that the hot-cell voloxidation tests should be conducted with mixtures of the $(U,Pu)O_2$ core and the UO_2 blanket since such a mixture would be equivalent to shearing a complete fuel rod. The UO_2 in the axial blanket of these rods contained 96 to 97% of the total tritium remaining in the fuel rod after irradiation. The suggested experiments could thus demonstrate whether more than 90% of the contained tritium in the mixture would be released by voloxidation at a temperature lower than that required for the mixed-oxide core alone.

1. INTRODUCTION

The Nuclear Materials and Equipment Corporation (NUMEC) fabricated three fuel assemblies for irradiation testing in the Experimental Breeder Reactor No. 2 (EBR-2). Each 0.25-in.-OD stainless-steel-clad fuel rod in the multirod assemblies contained a 14-in. vertical stack of two types of experimental $(U,Pu)O_2$ pellets. These were topped by ∿6 in. (∿35 g) of UO_2 pellets which served as an axial blanket. The fabrication of the rods is fully described in a 1970 NUMEC report[1] and is briefly summarized in two earlier reports from this series.[2,3] The two ORNL technical memoranda described the equipment and experimental procedures used with the $(U,Pu)O_2$ portions of two of the rods.

This document describes two tests in which the effects of voloxidation on the UO_2 blankets from the same rods, Nos. B-7 and C-13, were examined. Those rods had been irradiated to nominal peak burnups (for the fuel) of 16.5 and 17.5 at. %, respectively.

The earlier work on the mixed-oxide fuel indicated that the residual amount of tritium in the core fuel was very low. Thus, the UO_2 in the blanket contained ∿96 to 97% of all the tritium in the rod. It might be possible to release >90% of the tritium from a mixture of the core and blanket at a temperature lower than the ∿600°C required to oxidize the $(U,Pu)O_2$ at a reasonable rate.[3] The lower temperature (∿480°C) would reduce the volatility of semivolatile nuclides (e.g., iodine and cesium), would require less power to heat the voloxidizer, and could possibly increase the HNO_3 solubility of the $(U,Pu)O_2$ over that attained from voloxidation at 600 to 650°C. Lesser amounts of ^{14}C, ^{85}Kr, and ^{129}I might be released from the fuel.

2. EXPERIMENTAL

2.1 Fuel Specimens

The UO_2 axial blanket sections of rods B-7 and C-13 were each cut with a single-rod hydraulic shear into eleven 0.5-in.-long segments. Previously, the remaining portions of the rods had been sheared to include a small amount of the core [$(U,Pu)O_2$] with the UO_2 blanket; the net effect was to add a small amount of enriched uranium, plutonium, and fission products to the UO_2. The tritium balance should not have been significantly affected.

Four segments were chosen at random from each bottle of sheared UO_2 and dissolved in FBR-5A and FBR-6A experiments to determine the fission product inventories before voloxidation. The remaining seven segments from each rod were oxidized in FBR-5B and FBR-6B experiments and then dissolved in HNO_3. The UO_2 from rod B-7 was oxidized at 600°C, the apparent optimum temperature for the oxidation of $(U,Pu)O_2$ fuel,[4] while the UO_2 from rod C-13 was oxidized at 480°C, the apparent optimum temperature for oxidation of UO_2 to U_3O_8.[5]

2.2 Procedures

Voloxidation was conducted in a rotating stainless steel chamber that was equipped with sintered stainless steel filters (35-μm porosity) for the gas inlet and outlet. A thin, removable stainless steel liner covered about one-sixth of the voloxidizer interior and was used to measure the internal deposition of semivolatile fission products. A stainless steel tube was inserted inside the hollow gas exit shaft of the voloxidizer for deposition of other semivolatiles in the off-gas cooling zone. Outside the voloxidizer, heated tubing carried the off-gas to a heated filter pack containing filters and charcoal beds to trap particles and ^{129}I; this was followed by a HEPA filter, silica gel beds for sorption of tritiated water vapor, a multichannel analyzer (MCA) for gamma spectroscopy(^{85}Kr release rate), and a special plastic bag to collect one-tenth of the total off-gas flow for a cumulative measurement of ^{14}C and ^{85}Kr contents. A more detailed discussion of the equipment has been reported.[2,3]

A summary of the conditions for the four experiments is given below.

Table 1. Experimental tests with axial blanket UO_2

Run No.	5A	5B	6A	6B
Rod No.	B-7	B-7	C-13	C-13
No. of segments	4	7	4	7
Total wt, g[a]	13.4	29.6	14.1	29.7
Approximate cladding wt, g	3.0	5.8	3.1	5.9
Voloxidation temp., °C	None	600	None	480
Voloxidation atmosphere	None	Air	None	Air
Voloxidation rotation, rpm	None	12	None	12
Airflow, cm^3/min	None	300	None	300

[a]As sheared; handling losses due to sieving, weighing, etc., appear in subsequent tables.

Dissolutions were conducted in Pyrex glassware; three successive 2-hr leaches in 8 M, 3 M, and 8 M HNO_3 at 92 to 95°C were used to determine the HNO_3 solubility of the fuel. The insoluble residues were dried, weighed, and fused in Na_2CO_3 for analysis.

3. RESULTS AND DISCUSSION

3.1 Shearing

The single-rod hydraulic shear was used to cut each 0.25-in.-OD stainless-steel-clad rod into 0.5-in.-long segments for voloxidation and dissolution studies. A compilation of shearing data, showing the amounts of fuel released from each rod section, was previously reported.[3] Shear forces required to cut through the UO_2 blanket segments were in the range of 350 ± 50 kg per blade pass. Release of the axial blanket UO_2 from rod B-7 during shearing averaged ∿0.4 g (or 1.1%) per

cut and totaled ∿12%. Release of the blanket segment of UO_2 from the slightly higher burnup C-13 rod averaged 0.7 g (or 1.9%) per cut and totaled ∿21% of the blanket UO_2.

Four 0.5-in.-long segments of clad UO_2 were selected at random from each rod for dissolution in HNO_3 to provide a basis for comparison with voloxidized fuel samples. The remaining axial blanket fuel from rods B-7 and C-13 was used in experiments FBR-5 and FBR-6, respectively.

3.2 Voloxidation

Operation of the voloxidizer for UO_2 blanket experiments was similar to previous runs with NUMEC mixed-oxide fuels.[2,3] The UO_2 was oxidized at two temperatures, 480 and 600°C, to compare tritium evolution characteristics and the releases of semivolatiles. Deposition samples were obtained from inside the voloxidizer and from the off-gas system to measure the extent of fission product "plateout." Off-gases were monitored for gaseous radionuclide concentrations and continuously analyzed for O_2 content. Each run was continued beyond the point at which O_2 consumption had ended and the ^{85}Kr content in the off-gas had returned to system background levels. The size range of the voloxidized product from each run was determined by sieve analysis prior to dissolution.

Run identification and voloxidation conditions are listed in the following table for reference in the following sections.

Run no.	Rod no.	Charged to voloxidizer		Voloxidation conditions			
		Fuel wt[a] (g)	No. of clad pieces[b]	Time (hr)	Temp (°C)	Atmos	Rotation (rpm)
FBR-5	B-7	23.6	7	2.2	600	Air[c]	12
FBR-6	C-13	23.7	7	2.1	480	Air[c]	12

[a]Weight of oxide and fission products (only).
[b]Each piece was ∿0.5 in. long.
[c]Flow at 300 cm^3/min.

3.2.1 Material balances and weight gains during oxidation

Material balances calculated for the voloxidations are shown in Table 2. The theoretical weight gain for complete conversion of the UO_2 to U_3O_8 is ∿3.95%; however, the product yields from runs at both temperatures indicated a considerably smaller gain. As in earlier runs,[2,3] slight recovery and handling losses (<1%) and weighing errors associated with determining small differences in large quantities were factors which affected conversions estimated by this method. However, in each experiment the measured differences between the O_2 concentrations of the inlet and off-gas streams allowed the cumulative moles of O_2 consumed to be calculated. Good conversion was verified in both runs. The totals, based on O_2 use, indicated the maximum conversion of UO_2 to U_3O_8 to be 103.5% and 100.9% for runs FBR-5 and FBR-6, respectively, with an estimated error of ± 3% in the instruments. X-ray diffraction patterns from samples of the voloxidizer product in other experiments using irradiated UO_2 identified the converted material as U_3O_8-α.[6]

3.2.2 Comminution of fuel during voloxidation

Size distribution for the unclad fuel charged into and recovered from the voloxidizer during each experiment is listed in Table 3. Powdering and release of the U_3O_8 from the sheared cladding appeared to be equally effective during voloxidation at either temperature. In each case, >90% of the oxide was dislodged from the cladding by the oxidation; >93% of these fines were <44 μm in size. Voloxidation at 600 and 650°C had released only 60 to 80% of the $(U,Pu)O_2$ from 0.5-in.-long pieces sheared from the same NUMEC rods. In those runs, the dislodged fuel was still in fairly large pieces (+ 44 μm).[2,3]

3.2.3 Gaseous release profiles

Curves for the concentration of tritium and krypton in the off-gas during the FBR-5 and FBR-6 experiments are plotted as a function of run time in Figs. 1 and 2, respectively, and are related to the corresponding O_2 content of the voloxidizer off-gas. The krypton concentrations are instantaneous sample values; the tritium concentrations were averaged over 15-min collection periods. The cumulative O_2 consumption and fission gas release profiles (as percentages of amounts initially in the fuel) for these runs are shown in Figs. 3 and 4.

Table 2. Material balances on voloxidation of NUMEC axial blanket UO_2

	Run FBR-5 (600°C, air)	Run FBR-6 (480°C, air)
Input weight, g		
Total	29.4	29.6
Cladding	5.8	5.9
Fuel[a]	23.6	23.7
UO_2[b]	23.5	23.6
Output weight, g		
Total	29.7[c]	30.0[c]
Cladding	5.8	5.9
Fuel[a]	23.9	24.1
Theoretical weight gain, g[d]	0.93	0.93
Actual weight gain, g	0.3	0.4
Weight gain, %	1.28	1.70
Conversion, % (calc.)[e]	103.5	100.9

[a]Includes weight of UO_2 plus weight of fission products.
[b]Weight UO_2 = 0.995 x (total fuel weight), at ∿0.5 at % burnup.
[c]Some product unrecovered due to handling losses.
[d]Based on 3.95% weight gain of UO_2 for complete conversion to U_3O_8.
[e]Calculated from moles of O_2 consumed.

Table 3. Release of NUMEC blanket UO_2 from 0.5-in.-long stainless steel-sheared hulls by voloxidation

	Run FBR-5 Rod B-7 600°C		Run FBR-6 Rod C-13 480°C	
	In	Out	In	Out
Unclad oxide, g	3.78	21.8	7.30	22.5
Percentage of total oxide	16.0	91.2	30.8	93.4
Percentage of unclad oxide particles				
+500 μm	50.0	2.3	58.1	4.0
+150 μm	31.5	1.4	24.1	1.4
-150 μm	18.5	96.3[a]	17.8	94.6[a]

[a]More than 93% of the voloxidized fuel fines were sized <44 μm.

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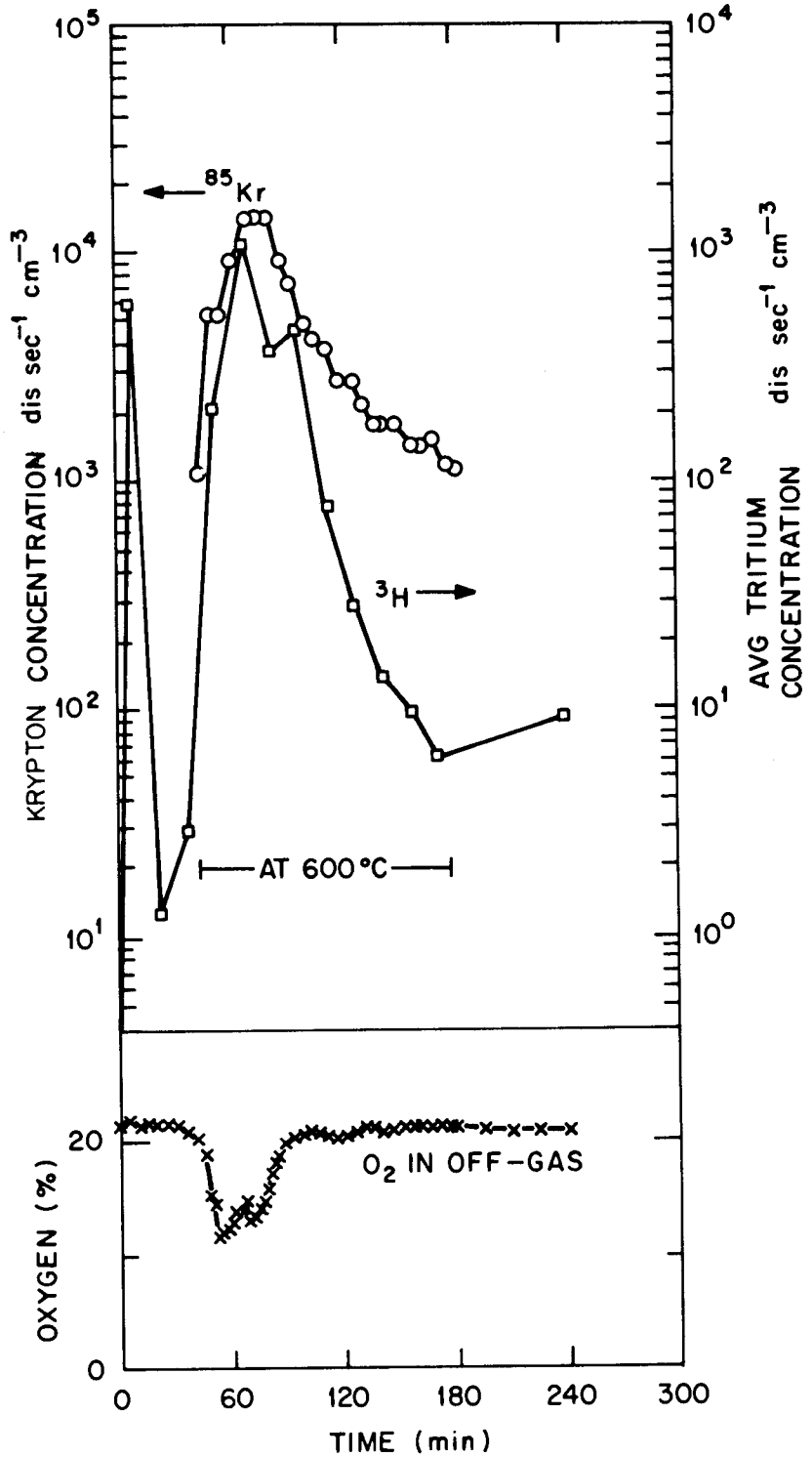

Fig. 1. Average tritium and krypton concentrations in off-gas (Run FBR-5B)

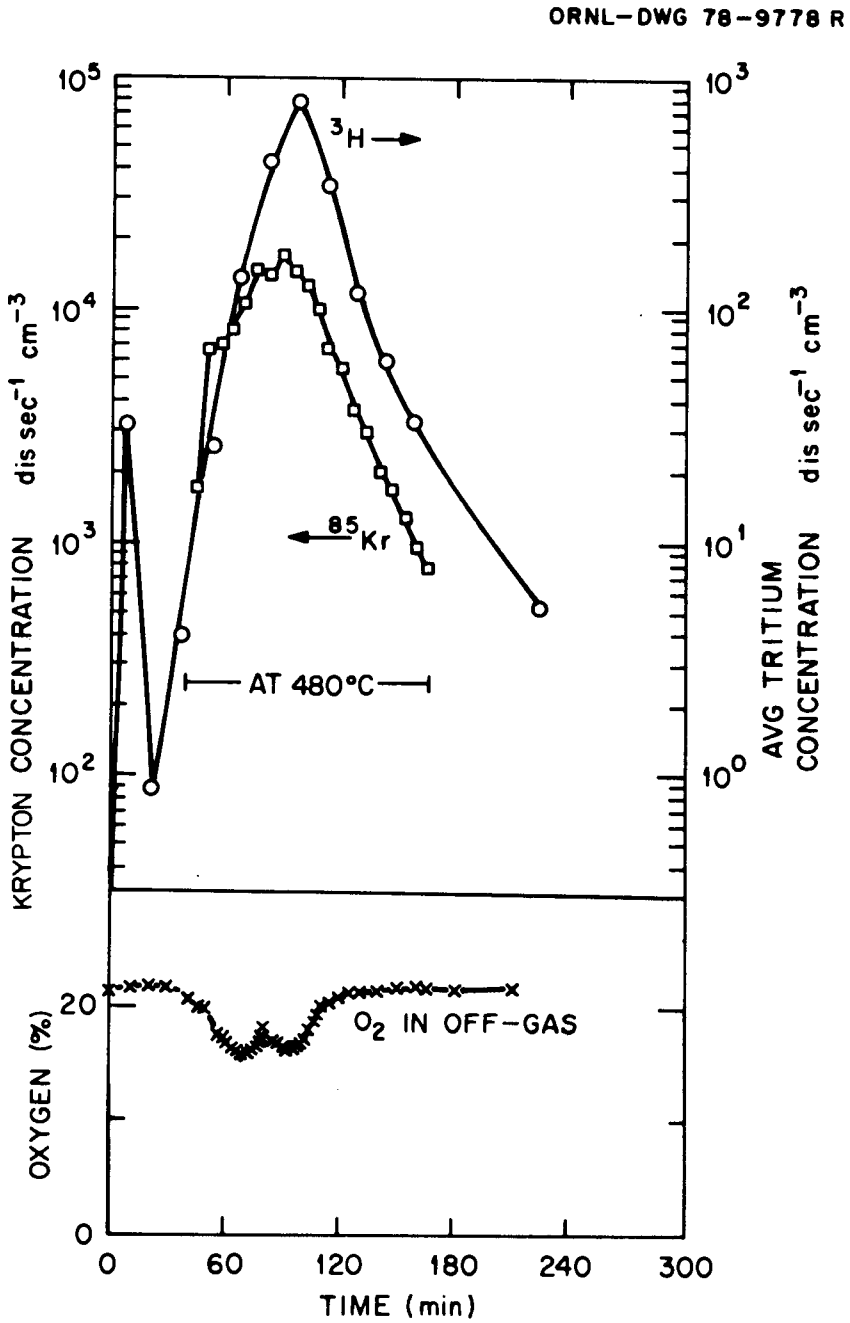

Fig. 2. Average tritium and krypton concentrations in off-gas (Run FBR-6).

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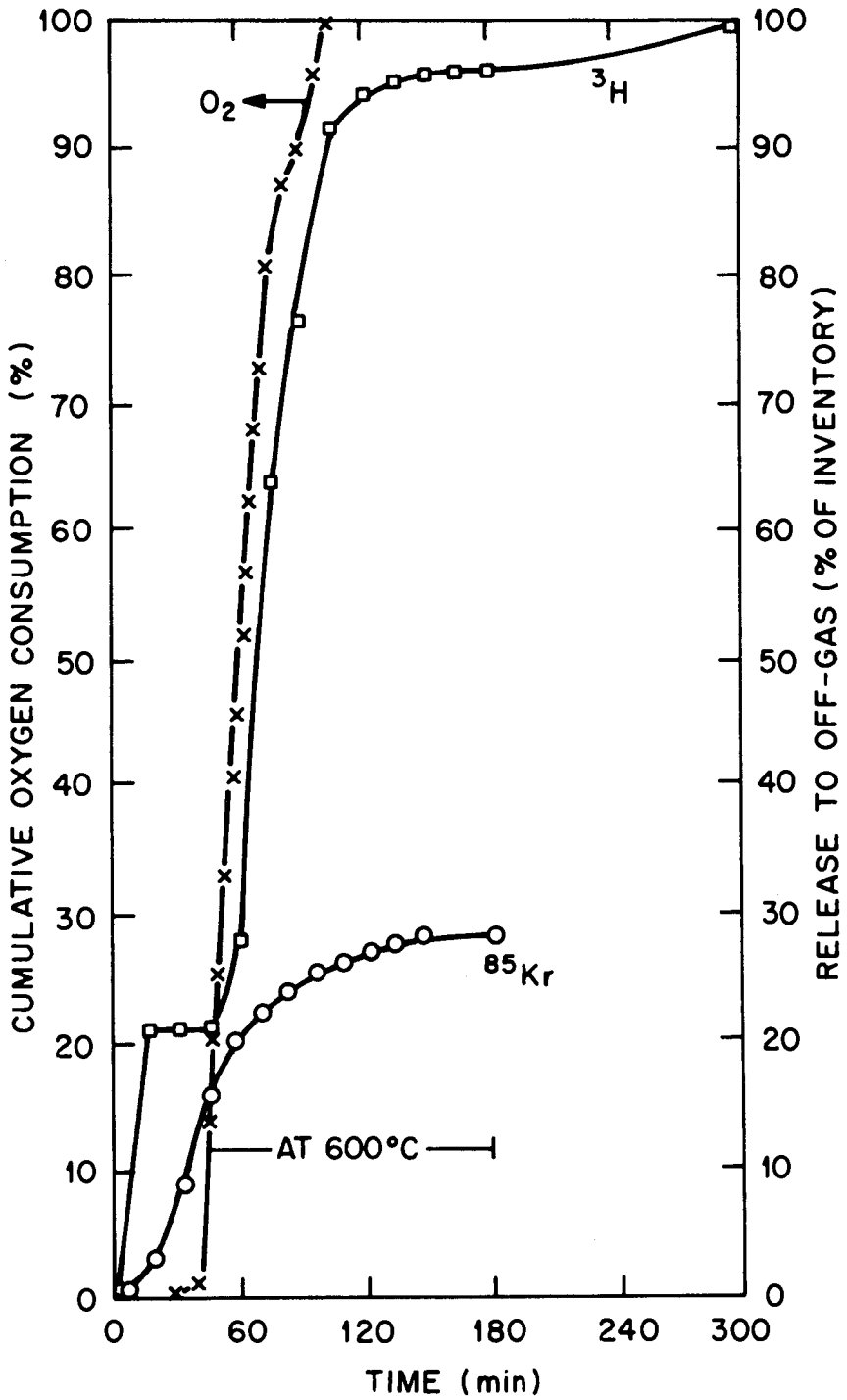


Fig. 3. Cumulative oxygen consumption and gaseous fission product release profiles (Run FBR-5).

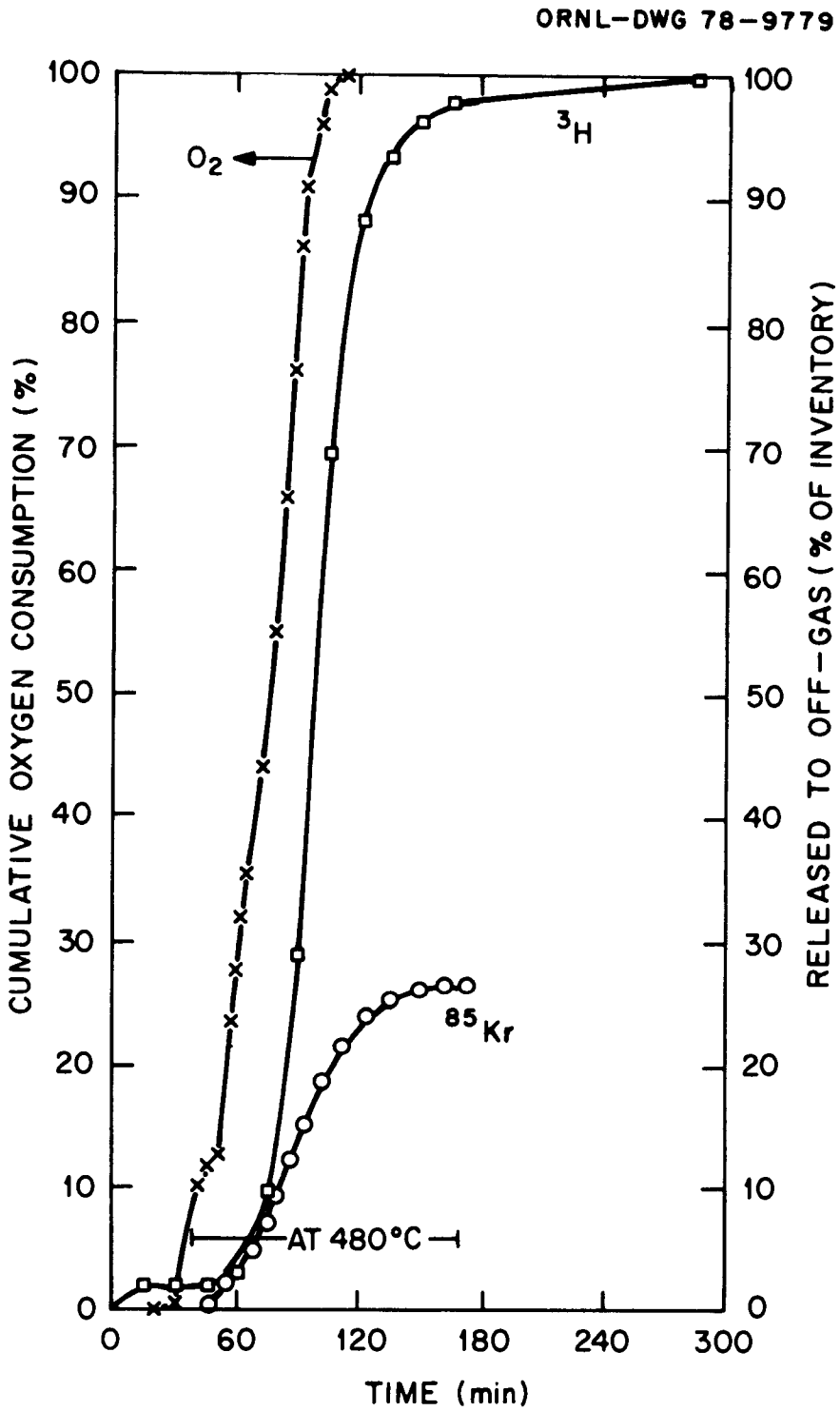


Fig. 4. Cumulative oxygen consumption and gaseous fission product release profiles (Run FBR-6).

The rate of tritium release from the UO_2 blanket was slightly faster at the higher voloxidation temperature. The evolution curve for voloxidation at 480°C (Fig. 4) indicates an apparent time lag of ∿30 min between O_2 consumption and tritium release. Similar curves for the 600°C run (Fig. 3) indicate a smaller time differential. Such a temperature effect could be related to the oxide conversion rate since the O_2 consumption at 600°C reached completion in ∿40% less time.

In both experiments, an initial sharp peak in the tritium concentration of the off-gas appeared during the beginning heatup period. Such a peak was not evident in previous voloxidations of NUMEC mixed oxides or other UO_2-type fuels but could imply that the tritium (present as ^3H_2O) on exposed surfaces was released as the fuel was heated. In the case of the FBR-5 experiment, >20% of the tritium in the fuel was evolved during the first 15 min of heating at a rate of ∿20°C/min. No additional release was measured until the temperature had reached 600°C and the fuel had begun to use O_2 at a significant rate.

Two hours of voloxidation at either temperature was sufficient to remove >96% of the tritium from the UO_2. An additional 2 to 4% of the released tritium, apparently sorbed on the piping, was recovered on the silica gel traps during air purges of the system following each run. Water and HNO_3 rinses of the heated off-gas line after each run and purge indicated that <0.1% of the total tritium had remained sorbed on system surfaces.

Peaks in the off-gas ^{85}Kr concentrations generally coincided with regions of maximum O_2 consumption (valleys in the O_2 concentration curves, Figs. 1 and 2), except during the first part of the 600°C experiment. Apparently, 14% of the total ^{85}Kr inventory in the blanket fuel was released during heatup to voloxidation temperature. No increase in off-gas ^{85}Kr concentration was measured during heatup for the 480°C run. In both runs, most of the krypton was released during the first 60 min at temperature. The remaining time was required for total system sweepout and gas collection.

3.2.4 Rate of O_2 consumption

Combined profiles for O_2 consumption and gaseous fission product release during the FBR-5 and FBR-6 voloxidation experiments were shown in Figs. 3 and 4. During the heatup period for each run, O_2 consumption

was apparently minimal until the temperature of the charge reached ∿480°C, when utilization of O_2 from the feed stream commenced. The initial utilization rate was more rapid in the 600°C run; consumption reached a maximum within 30 min after the voloxidation temperature had been attained. At the point of peak consumption in the 600°C run, ∿40% of the input O_2 was being consumed in a slightly sharper spike. During the 480°C run, the usage rate peaked with nearly 30% of the O_2 in the feed airstream being consumed. In both cases, there were variations (shown as double valleys in Figs. 1 and 2) in the O_2 utilization rate. A similar phenomenon was noted during voloxidations made in air with light water reactor fuel.[7] This apparent two-step oxidation may correspond to a slower usage due to a rate-limiting step, such as an intermediate phase change to U_4O_9.[6] In addition, the size ranges of a mixture of unclad fuel fragments and clad fuel pieces could also exhibit a rate-determining effect on O_2 consumption.

3.2.5 Fission product contents of UO_2 blanket

The inventory of fission products in NUMEC axial blanket UO_2 was determined by the dissolution of voloxidized and unvoloxidized fuel samples and from the collected voloxidizer and dissolution off-gases. The average fission product contents of the entire 6-in. UO_2 blanket from rods B-7 and C-13 are summarized in Table 4 as mean values from several experimental determinations. Most noticeable is the smaller quantity of tritium in the higher burnup rod (C-13) and the variations in the amounts of the volatile ^{134}Cs and ^{137}Cs. The differences in the cesium content, which were noted in gamma scans of the fuel rods made before the rods were sheared (Fig. 5), represent real axial variations. The difference in tritium content (30%) is likely due to a higher internal temperature during irradiation of C-13 which may have permitted more tritium to escape through the stainless steel cladding.

The burnup of the blanket UO_2, based on the ^{144}Ce contents, was ∿0.5%.

3.2.6 Release of gaseous fission products

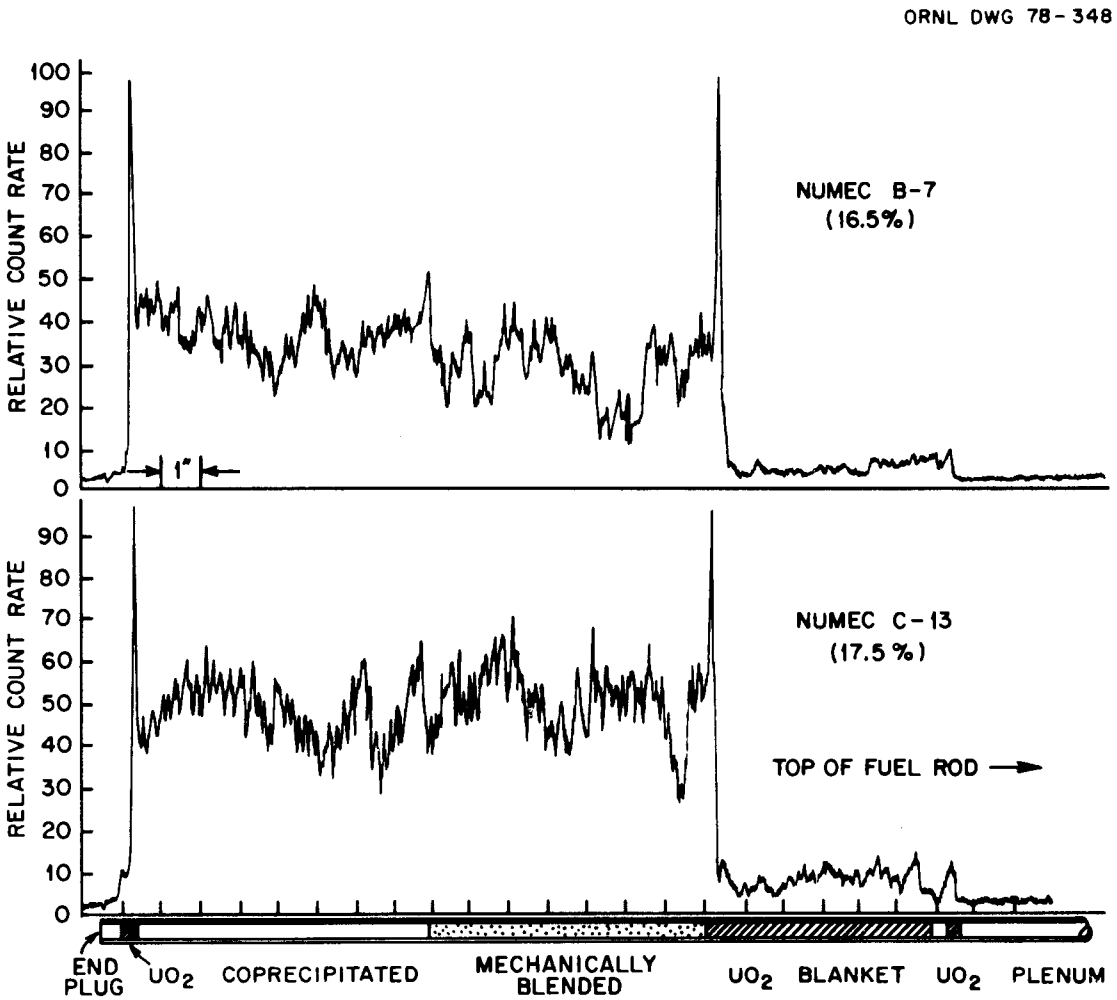
The releases of gaseous fission products from NUMEC blanket fuel were determined from samples of collected voloxidizer off-gas and from residual amounts in the voloxidized oxide. These are presented in Table 5 as percentages of the total fuel inventories listed in Table 4.

Table 4. Average fission product content of UO_2 blankets

Nuclide	Rod B-7 blanket[a]	Rod C-13 blanket[a]
U + Pu, g	29.49	29.95
^{3}H, dis $sec^{-1}g^{-1}$	6.35×10^{5}	4.50×10^{5}
^{14}C, dis $sec^{-1}g^{-1}$	1.84×10^{4}	3.52×10^{4}
^{85}Kr, dis $sec^{-1}g^{-1}$	2.31×10^{7}	3.21×10^{7}
^{106}Ru, dis $sec^{-1}g^{-1}$	$<1.2 \times 10^{8}$	$<1.4 \times 10^{8}$
^{125}Sb, dis $sec^{-1}g^{-1}$	$<1.3 \times 10^{7}$	$<2.3 \times 10^{7}$
^{129}I, μg/g	342[b]	342[b]
^{134}Cs, dis $sec^{-1}g^{-1}$	2.90×10^{8}	2.84×10^{8}
^{137}Cs, dis $sec^{-1}g^{-1}$	1.95×10^{9}	1.00×10^{9}
^{144}Ce, dis $sec^{-1}g^{-1}$	2.20×10^{8}	2.20×10^{8}

[a]Totals from two experiments each (5A + 5B and 6A + 6B), that is, complete blanket column.

[b]Assumed content from rod C-13 as best value.



INTEGRAL GAMMA SCANS OF NUMEC FUEL RODS
(>0.5 MeV)

Fig. 5. Integral gamma scans of NUMEC fuel rods B-7 and C-13.

Table 5. Release of gaseous radionuclides during voloxidation of NUMEC axial blanket UO_2

Run no.	Rod no.	Volox. temp	Released to voloxidizer off-gas (% of total fuel inventory)		
			$^{3}H^{a}$	$^{14}C^{a}$	$^{85}Kr^{a,b}$
FBR-5	B-7	600°C	99.8	22.3	28.1
FBR-6	C-13	480°C	99.8	11.3	26.4

[a]Based on residual content of voloxidized oxide.
[b]Determined from collected voloxidizer off-gas.

Release of ^{14}C and ^{85}Kr from the UO_2 blanket material was moderate. Apparently, the voloxidation temperature did not significantly affect the total release of either isotope. Although the percentage release of ^{14}C in FBR-6 was less, it should be noted that there was more ^{14}C in that fuel (rod C-13).

Total tritium releases were high (>99%) and did not appear to depend on the voloxidation temperature. In both experiments, the amount of tritium recovered from voloxidizer off-gas on adsorption traps was essentially 100% of the amounts listed in Table 4, thus confirming the percent releases obtained from residual tritium levels measured in the voloxidized oxide.

3.2.7 Fission product distribution during voloxidation

The inventories of selected fission products contained by axial blanket segments of NUMEC fuel rods were listed in Table 4. Recoveries (as percentages of those amounts) found on voloxidizer system surfaces and traps following voloxidations at 480 and 600°C are shown in Table 6.

In most cases, recovery totals for deposited and entrained fission products within the voloxidizer system were ∿1.0% or less of the total inventories for each. Except for ^{129}I, most of the fission product activity was found on stainless steel sheet samples located along the voloxidizer's inner walls. From the percentage distributions listed in Table 6, there appeared to be more materials left on the voloxidizer walls after the 480°C run than after the 600°C run. An increase in fission product

Table 6. Selected fission product recoveries from the voloxidizer and off-gas system following oxidation of NUMEC blanket UO_2

Nuclide	Run no.	Rod no.	Volox. temp (°C)	Distribution (% of total fuel inventory)	
				Voloxidizer walls	Off-gas system
^{106}Ru	FBR-5	B-7	600	0.19	0.07
	FBR-6	C-13	480	0.45	< 0.01
^{125}Sb	FBR-5	B-7	600	0.16	a
	FBR-6	C-13	480	0.34	a
^{129}I	FBR-5	B-7	600	0.18	6.60
	FBR-6	C-13	480	1.00	2.19
^{134}Cs	FBR-5	B-7	600	0.86	0.16
	FBR-6	C-13	480	1.00	0.02
^{137}Cs	FBR-5	B-7	600	0.66	0.47
	FBR-6	C-13	480	1.02	0.02
^{144}Ce	FBR-5	B-7	600	0.20	0.06
	FBR-6	C-13	480	0.59	0.03

[a]Not detected.

volatilization at the lower temperature might seem somewhat surprising, but such a result could reflect the dominating influence of other factors. For example, the results of isotopic analyses and Pu/(U + Pu) ratios in dissolver solutions indicate that the voloxidized blanket material probably contained some $(U,Pu)O_2$ (see Sect. 2.1). The presence of higher burnup mixed oxide could have thus increased the quantities of fission products that were exposed to the voloxidizer walls.

Release of ^{129}I from the NUMEC UO_2 blanket was apparently dependent on the oxidation temperature (i.e., the higher the temperature, the greater the amount volatilized); more ^{129}I was recovered in the off-gas system (on beds of charcoal at 125°C) following the 600°C run. Correspondingly, less iodine (<0.2% of the total inventory) was found on stainless steel sheet specimens located inside the voloxidizer during the same experiment. This pattern was similar to that seen during voloxidations of mixed-oxide core fuel from the same rods.[2,3] However,

there were significant differences in the total quantities of iodine volatilized from the two different fuel types. Up to 80% of the ^{129}I inventory in the mixed oxide was released during voloxidation at 650°C, and as much as 45% was released from the same fuel during oxidation at 600°C. Only ∿7% of the ^{129}I was volatilized from the UO_2 during voloxidation at 600°C and ∿3% at 480°C.

Less than 0.1% of the total ^{106}Ru and ^{144}Ce and <0.5% of the ^{137}Cs in the blanket fuel was found on samples in the off-gas system following each voloxidation. Generally, the largest quantities of fission product activity that passed the 35-μm pore size gas exit of the voloxidizer were found following the 600°C experiment and were located on stainless steel tubing insert specimens. An unusually large amount of cesium was found on off-gas system samples after one run (see Sect. 3.2.8). Ruthenium and cesium deposition from the off-gas onto cooling surfaces is shown in Fig. 6. The profiles for ^{106}Ru and ^{137}Cs indicate that up to an order of magnitude or more of activity was deposited on the tubing during the higher-temperature run. Increased cesium deposition at sample positions of ∿450°C and <150°C was also observed during some of the mixed-oxide voloxidations[2] and could signify temperature regions where enhanced collection of volatilized cesium might exist.

3.2.8 Revolatilization of cesium during voloxidation

In two preceding experiments (runs FBR-3 and FBR-4), the voloxidizer unit had been used for oxidizing coprecipitated $(U,Pu)O_2$. The total cesium content and the isotopic ratio of $^{137}Cs/^{134}Cs$ in the mixed oxide from the core differs considerably from that of the blanket (Table 7). The cesium isotopic ratios determined for both the $(U,Pu)O_2$ and the UO_2 and for the nuclides recovered from samples in contact with the voloxidizer walls were representative of the fuels (UO_2) that had been voloxidized. However, the $^{137}Cs/^{134}Cs$ ratios on the deposition specimens and the filter traps (outside the voloxidation chamber) used during the blanket experiments indicated contamination from the mixed oxide of the core. Since only the off-gas system samples appear to have been affected, it is possible that the source of contamination could have been residual cesium from previous runs. Earlier results[7] had indicated

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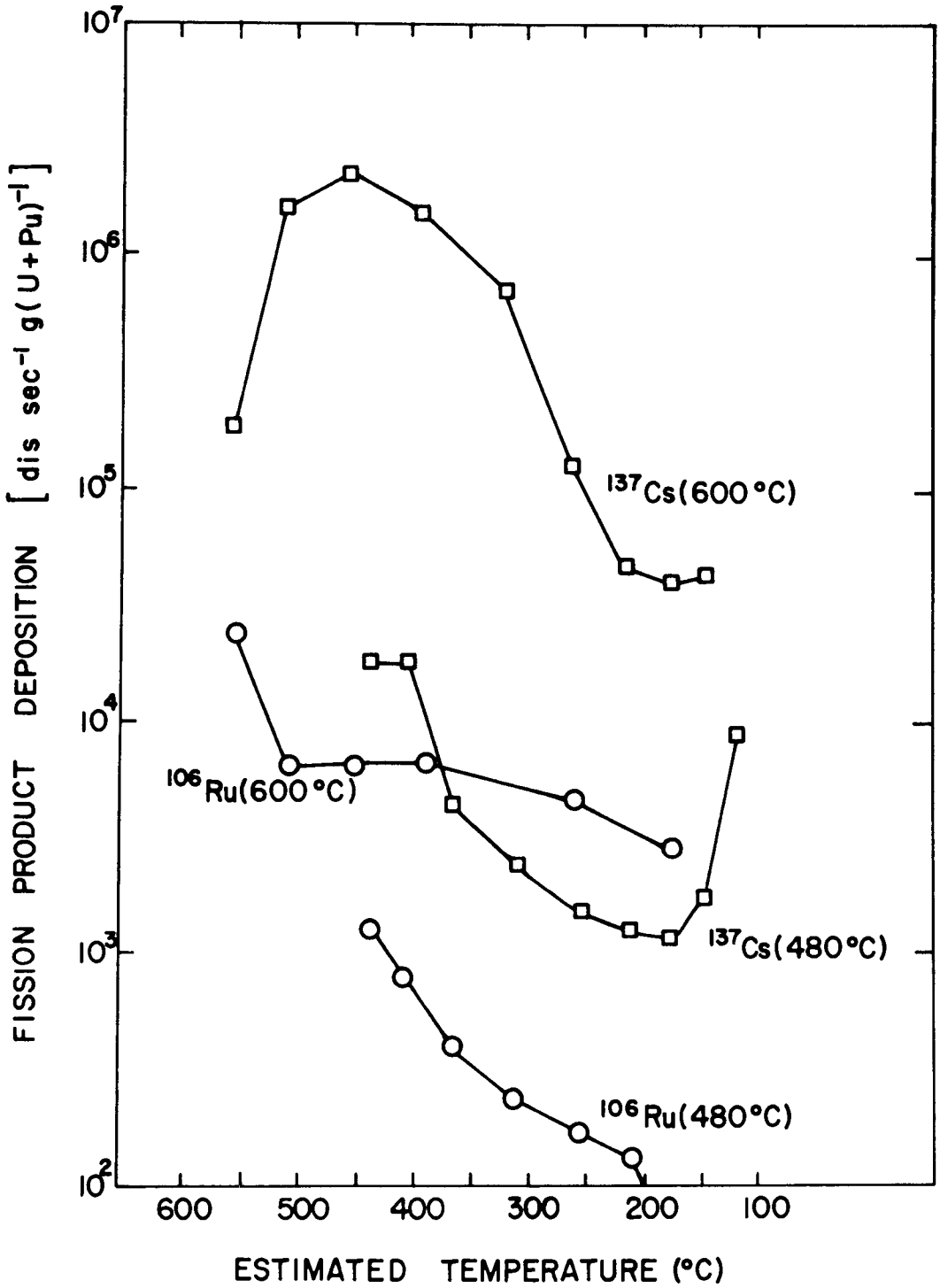

Fig. 6. Fission product deposition for voloxidation off-gas during voloxidation of NUMEC blanket fuel.

Table 7. Cesium ratios in the voloxidizer system following voloxidation of NUMEC fuels

Run no.	Rod no.	Fuel type	Activity location ($^{137}Cs/^{134}Cs$)			
			Fuel	Voloxidizer walls	Off-gas deposition specimens	Off-gas filter traps
FBR-4	C-13	$(U,Pu)O_2$	30.3	25.6	30.3	32.2
FBR-5	B-7	Blanket UO_2	6.76	5.13	28.6	28.8
FBR-6	C-13	Blanket UO_2	3.52	3.16	28.6	25.0

that ultrasonic cleaning of the voloxidizer between runs was mostly used to remove loose fuel dust and fission products but was apparently ineffective in removing plated materials. Reheating the system during subsequent experiments may have revolatilized some of the contaminants, which then "plated out" or became entrained on samples downstream from the voloxidizer.

3.3 Dissolution

3.3.1 Material balances

The material balances for the four dissolution experiments are listed in Table 8; the recoveries were 100.0 ± 0.19%.

3.3.2 Dissolution of uranium and plutonium

The amounts of uranium and plutonium remaining undissolved after each leach in HNO_3 are shown in Table 9. The results indicated that the voloxidized U_3O_8 (runs 5B and 6B) was apparently more soluble than the unvoloxidized controls (runs 5A and 6A); that is, up to 0.1% of the uranium and 0.6% of the plutonium in the control samples remained after three HNO_3 leaches, which is unusual.

Examination of the analyses showed that the "insoluble" plutonium was associated only with the dissolved cladding solution (dilute aqua regia); hence, the apparent loss may have been due to accidental contamination of the cladding by less than 1 mg of plutonium.

Table 8. Material balances for dissolutions

	Run no.			
	5A	5B	6A	6B
Input:				
Total weight, g	13.4	29.6	14.10	29.70
Output:				
UO_2, g	10.36	22.32	10.89	22.91
PuO_2, g	0.19	0.62	0.16	0.96
Leached cladding, g	3.00	5.80	3.10	5.90
Insoluble residue, g	0.06	0.07	0.02	0.14
Total, g	13.61	28.81	14.17	29.91
Recovery, %	101.5	97.3	100.5	100.7
Ratio Pu/(U + Pu)	0.018	0.026	0.015	0.040

Table 9. Uranium and plutonium undissolved after leaching in HNO_3

Leach no.[a]	Undissolved (% of total)							
	Run 5A		Run 5B		Run 6A		Run 6B	
	U	Pu	U	Pu	U	Pu	U	Pu
DS-1	0.15	0.64	<0.01	0.14	0.12	0.18	0.05	0.02
DS-2	0.11	0.60	<0.01	0.11	0.08	0.13	<0.01	0.02
DS-3	0.10	0.56	<0.01	0.05	0.07	0.13	<0.01	0.02

[a]DS-1, 8 M HNO_3, 92-95°C, 2 hr; DS-2, 3 M HNO_3, 92-95°C, 2 hr; DS-3, 8 M HNO_3, 92-95°C, 2 hr.

The mass spectrometric isotopic analyses (Table 10) indicated that when dissolved the seven voloxidized segments (5B and 6B) contained ∿9.5% ^{235}U, rather than being depleted to <0.7% ^{235}U after irradiation. This quantity is equivalent to between one and two $(U,Pu)O_2$ pellets mixed with the UO_2 blanket pellets. The ratios of Pu/(U + Pu) in Table 8 also indicate that the voloxidized segments contained more plutonium (2.6% and 4.0%) than the unvoloxidized samples (1.8% and 1.5%) and that much of the plutonium probably came from the $(U,Pu)O_2$ pellets mixed with the UO_2. These results thus reinforce the idea of contamination of the cladding, since the plutonium in mechanically blended $(U,Pu)O_2$ would have been less soluble than that formed by irradiation in the UO_2. The earlier dissolution tests with the pure mechanically blended fuel from these rods showed that up to 0.17% of the uranium and 0.13% of the plutonium remained after three similar HNO_3 leaches.[2]

Table 10. Mass spectrometric (isotopic) analyses of first leach solutions

Nuclide	Run no.			
	5A	5B	6A	6B
^{234}U	0.029	0.071	0.006	0.069
^{235}U	4.099	9.700	0.763	9.425
^{236}U	0.153	0.350	0.034	0.403
^{238}U	95.220	89.880	99.197	90.104
^{238}Pu	0.049	0.024	0.027	0.048
^{239}Pu	94.75	92.980	97.10	92.797
^{240}Pu	4.919	6.665	2.751	6.808
^{241}Pu	0.273	0.309	0.115	0.355
^{242}Pu	0.013	0.022	0.008	0.423

The rate of dissolution of the voloxidized U_3O_8 from the blanket of rod B-7 was monitored by periodically removing samples from the dissolver. The curves in Fig. 7 illustrate the rates of dissolution during the first 2 hr for both the uranium and plutonium. The data suggest a very rapid dissolution of the fines (40 to 70% in 2 min) and then a slower dissolution of larger particles for ∿1.5 hr, followed by the final dissolution of the resulting smaller particles.

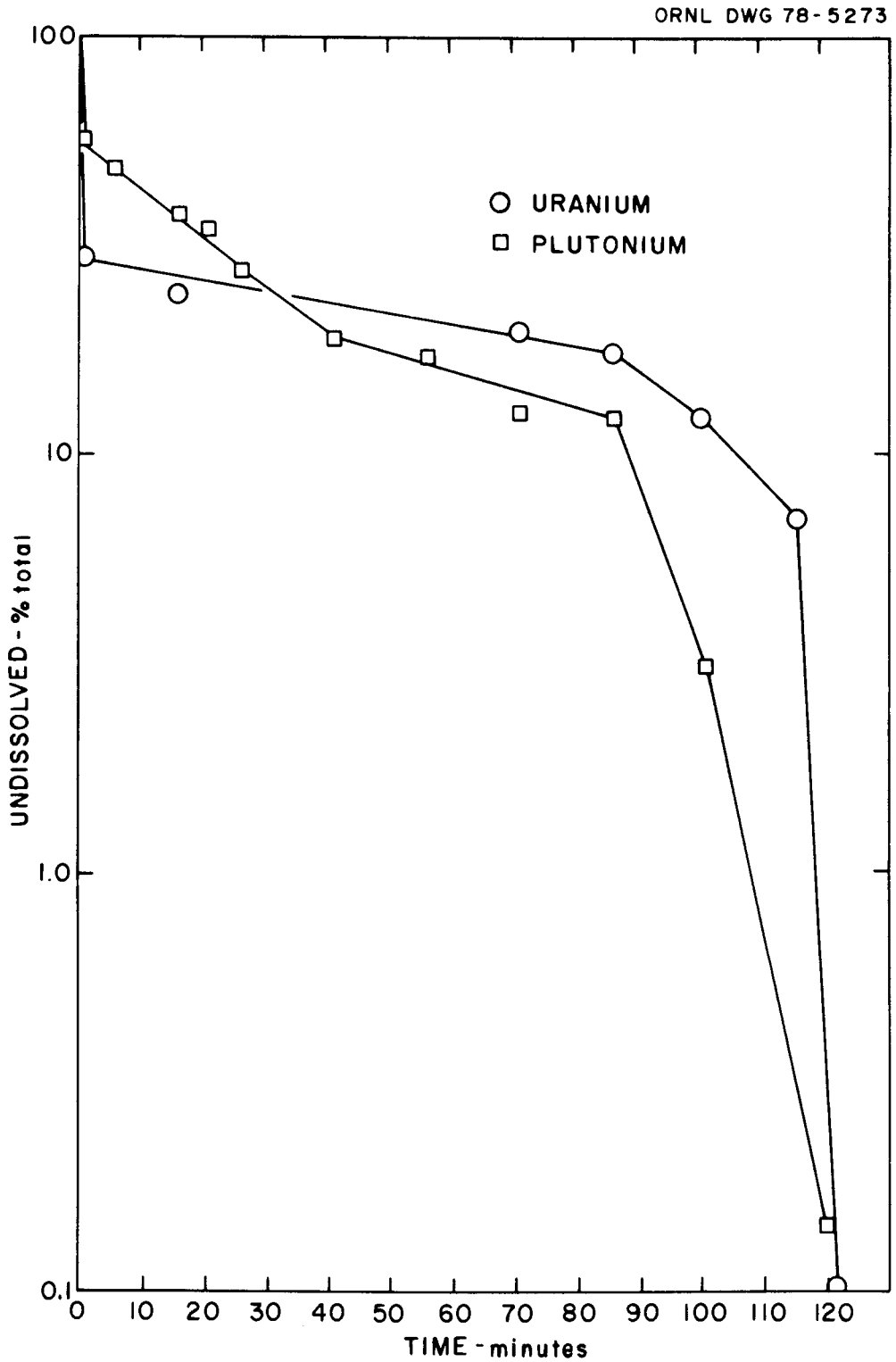

Fig. 7. Dissolution of uranium and plutonium in voloxidized U_3O_8 (Run FBR-5B).

3.3.3 Solubility of stainless steel cladding in HNO_3

The Type 316 stainless steel cladding of the blanket was partially dissolved during the three 2-hr leaches in 8 M, 3 M, and 8 M HNO_3. The quantity compares closely with that dissolved during the leaching of the fuel segments:

Time period	HNO_3 conc., M	Cladding dissolved (% of total present)		
		B-7 blanket	C-13 blanket	Fuel
1st leach	8	0.78	0.43	0.47
2nd leach	3	0.05	0.09	0.12
3rd leach	8	0.13	0.17	0.18

One can estimate that up to 1% of the cladding can be dissolved during 6 hr of leaching in HNO_3; most dissolves during the initial 2-hr period in 8 M HNO_3.

4. CONCLUSIONS

1. Voloxidation of the UO_2 axial blanket of a $(U,Pu)O_2$ fuel rod released 99.8% of the tritium from the oxide at both 480 and 600°C; the lower temperature might therefore be used for tritium removal from the mixed core [$(U,Pu)O_2$] and the blanket [UO_2].
2. Up to 22% of the ^{14}C, 28% of the ^{85}Kr, and 7% of the ^{129}I were also released by the voloxidation. Oxidation at 480°C apparently deposited more fission products on the interior walls of the unit, while 600°C enabled the semivolatiles to enter into the off-gas system.
3. From 40 to 70% of the voloxidized blanket U_3O_8 dissolved in 8 M HNO_3 within 2 min of the first leach and >99% within 2 hr.
4. Additional tests should be conducted with actual mixtures of the UO_2 axial blanket and the $(U,Pu)O_2$ mixed-oxide core of a simulated advanced reactor fuel rod in order to determine the optimal temperature for fission product removal.

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