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Head-end Processing Studies with Mechanically Blended (U,Pu)O₂ Reactor Fuels

J. H. Goode
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CHEMICAL TECHNOLOGY DIVISION

HEAD-END PROCESSING STUDIES WITH MECHANICALLY BLENDED (U,Pu)O₂ REACTOR
FUELS

J. H. Goode
R. G. Stacy

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HEAD-END PROCESSING STUDIES WITH MECHANICALLY BLENDED (U,Pu)₂ REACTOR FUELS

J. H. Goode
R. G. Stacy

ABSTRACT

Scouting studies were made of the effects of fabrication, irradiation, and voloxidation on the release of fission products and on the nitric acid solubility of three prototype specimens of mechanically blended (U_{0.8}Pu_{0.2})₂O₂ reactor fuels (the specimens were not typical of present-day reactor-grade mixed oxide). Up to 96% of the fission product tritium, 53% of the krypton, 81% of the ¹⁴C, 95% of the ¹²⁹I, and 5% of the cesium contained in two mixed-oxide specimens obtained from the Nuclear Materials Equipment Corporation were volatilized after voloxidation in air for 4 hr at 650°C. The voloxidation, however, increased the amount of plutonium that would not dissolve in nitric acid from 0.02% to ~2%. A stronger, secondary dissolvent, containing fluoride, was necessary in order to dissolve the remaining plutonium in the NUMEC fuels, leaving an insoluble residue of noble metal fission products--ruthenium, molybdenum, technetium, palladium, rhodium, and corrosion products. A fluoride-containing secondary dissolvent might not be necessary if the mixed oxide is manufactured as a true solid solution. The studies also indicated that the lower-temperature UO₂ axial blanket of the NUMEC rods contained up to 100 times more tritium per gram of fuel than in the higher-temperature (U,Pu)₂O₂ core.

Irradiation to 10.7 at. % in the Experimental Breeder Reactor-2 did not render the plutonia in a vibratorily compacted (U_{0.8}Pu_{0.2})₂O₂ fuel rod that had been fabricated at Argonne National Laboratory completely soluble in nitric acid; 3.75% of the plutonium remained after three 2-hr leaches in 8 M HNO₃. Since the fuel contained discrete PuO₂ particles prior to irradiation, it may be concluded that long-term irradiations at high linear heat ratings cannot be relied upon to eliminate the use of a fluoride-containing secondary dissolvent to dissolve all of the plutonium.

1. INTRODUCTION

The Chemical Technology Division at the Oak Ridge National Laboratory has been studying the effects of fabrication, irradiation, and certain head-end reprocessing steps on the solubility of mixed uranium and plutonium oxides in nitric acid. This work is being

conducted to determine the potential problem areas of a reprocessing flowsheet. Earlier work indicated that up to 35 wt % PuO_2 in UO_2 would dissolve in nitric acid, without the use of a corrosive fluoride catalyst, if the PuO_2 and UO_2 were in a solid solution.¹

Irradiated prototype and experimental fuel rods, obtained from a number of sources in the United States, were utilized in the hot cell for these scouting studies. The studies involved the following principal, presolvent extraction steps of the flowsheet: (1) shearing the fuel rods into short lengths, (2) dissolving the pellets in nitric acid, (3) adjusting the concentrations and/or valence of the nitric acid, uranium, and plutonium, and (4) determining the amounts and characteristics of the material that did not dissolve in nitric acid. Another step, voloxidation -- that is, oxidation of the fuel at elevated temperatures -- was also tested as a method for removing radioactive tritium from the fuel and concentrating it before it was dissolved in nitric acid. The removal of the tritium prior to its introduction into the aqueous system of the processing plant could thus reduce the amount released to the environment as condensates, low-level wastes, and so forth.

This report summarizes the dissolution studies conducted on two types of mechanically mixed 20% PuO_2 --80% UO_2 fuels. One type used was a vibratorily compacted fuel rod that had been fabricated by Argonne National Laboratory (ANL) and irradiated to a nominal burnup of 10.7 at % in the Experimental Breeder Reactor-2 (EBR-2). The other experiments were carried out to determine the effect of voloxidation on both the solubility and the release of fission products from two experimental rods that had been fabricated by the Nuclear Materials and Equipment Corporation (NUMEC). The NUMEC specimens, irradiated in the fast flux of the EBR-2 to burnups of 16.5 and 17.5 at. %, each contained two kinds of $(\text{U,Pu})\text{O}_2$ pellets (mechanically blended and coprecipitated fuels) and a UO_2 blanket stacked axially in a common tube. (Unfortunately, this method of assembly was later found to have an influence on the results of the experiments.)

2. EXPERIMENTAL

2.1 Fabrication and Irradiation of Samples

2.1.1 Vibratorily compacted (U,Pu)O₂

Vibratory compaction is a method of loading fuel rods with powdered uranium and plutonium oxides. Weighed portions of -325 mesh particles of UO₂ (enriched to 93% ²³⁵U) and PuO₂ were ball-milled together and then heated to 1200°C under very high pressure in a sealed tube to form an intimate mixture (Dynapak). The resulting product was ground and then compacted into fuel rods by vibratory techniques (Vipac).² Experimental fuel rod ASOV-14, containing (U_{0.8}Pu_{0.2})O₂, was fabricated by ANL and irradiated in three subassemblies (S/A) in EBR-2 to a nominal peak burnup of 10.7 at. % (Fig. 1). The irradiation history of Rod ASOV-14 is shown in Table 1.

Table 1. Brief irradiation history of ANL fuel rod ASOV-14 in EBR-2^a

Subassembly	Date in reactor	Date out reactor	MWd	Peak burnup, at. %
X072	12-13-69	9-14-70	9,251	3.8
X113	4-22-71	9-22-72	13,516	7.7
X176	12-10-72	9-22-73	<u>9,132</u>	10.7
			31,899	

^aL. A. Niemark, Argonne National Laboratory, personal communication to J. H. Goode, October 1976.

This rod was chosen for a dissolution experiment since an early post-irradiation examination at ANL showed a large amount of unrestructured fuel in the cooler portion of the rod near the cladding;² unrestructured, mechanically blended fuel generally contains nitric acid-insoluble, plutonium-rich particles.¹ In addition, these particles were desired for another hot-cell program.

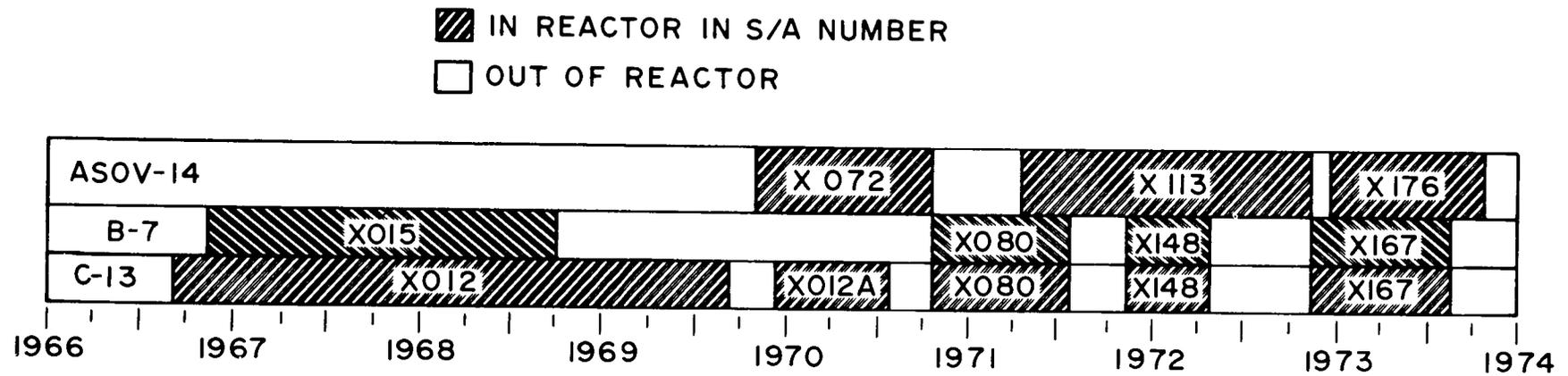


Fig. 1. Irradiation history of ANL ASOV-14, NUMEC B-7, and NUMEC C-13 capsules in EBR-2 reactor.

2.1.2 NUMEC (U,Pu)O₂ fuel rods

The fabrication of a series of sodium-encapsulated, replicate fuel rods (each containing the two types of fuel) to be irradiated in EBR-2 to three different burnup levels is described in a 1970 NUMEC document.³ Each of the three reactor subassemblies contained a variety of fuel types which differed in fabrication method, oxygen-to-metal(O:M) ratio, density, and so forth. Series A (one group of 11 rods) and Series B (several other rods) were discharged at burnups of ~33,000 and 57,000 MWd/ton, respectively. The remaining Series B and C rods were irradiated to burnups which greatly exceeded the original design level of 100,000 MWd/ton.

We chose NUMEC specimens B-7 and C-13, rods with different burnups that contained coprecipitated and mechanically blended (U,Pu)O₂ from the same pellet batches, for these tests. Each rod also contained an axial UO₂ pellet blanket atop the stack of mixed-oxide pellets (Table 2). Mechanical blending refers to the physical mixing of the proper proportions of UO₂ (enriched to 93% ²³⁵U) and PuO₂ powders by grinding in a ball mill for an extended period. The powder is then pressed into pellets, which are sintered at high temperatures in a reducing atmosphere. The coprecipitated (U,Pu)O₂ and the UO₂ blanket portions of each rod were examined in other experiments and will be reported in future documents.

Rod No. B-7 was inserted into EBR-2 in S/A X015 on November 15, 1966, for irradiation to a nominal burnup of 60,000 MWd/ton. The sodium-encapsulated rod was actually irradiated at 14 kW/ft in S/A X015, X080, X148, and X167 to a burnup of 16.5 at %; it was discharged in July 1973. Rod C-13 was inserted into EBR-2 on August 10, 1966, as a part of S/A X012, and was irradiated to a peak burnup of 17.5 at % in Subassemblies X012A, X080, X148, and X167. The rod was also discharged on July 13, 1973, and shipped to ORNL in 1975 (Fig. 1).

2.2 Postirradiation Examinations

2.2.1 Argonne National Laboratory Rod ASOV-14

No examination of this rod was made; the fueled portion was cut (not sheared) into segments measuring ~1 in. long for the dissolution

Table 2. Fabrication data for NUMEC fuel rods

	Lower fuel		Upper fuel		Axial blanket	
	B-7	C-13	B-7	C-13	B-7	C-13
Type of fuel	CP ^a	CP	MB ^b	MB	UO ₂	UO ₂
Weight, g	41.23	40.83	39.43	38.43	35.20	34.90
Length, in.	7.38	7.21	6.95	6.96	5.64	5.64
Density, %	82.80	83.79	85.44	83.17	89	89
Smear density, %	91.90	82.87	83.04	80.84	-	-
O:M ratio	2.003	2.003	1.992	1.992	2.0	2.0
NUMEC fabrication batch No.	4	4	15	15	29	29

^aCoprecipitated (CP).

^bMechanically blended (MB).

experiment (Fig. 2). The upper photo (2a) shows the 11 segments that were dissolved, whereas the lower photo (2b) shows the end of a segment with a center void and fission-product deposits visible in the cracks.

2.2.2 NUMEC Rods B-7 and C-13

These rods were gamma-scanned at the ORNL High Radiation Level Examination Laboratory (HRLEL) for fission product distribution, punctured to determine the volume and composition of the released fission gases in the plenum, and then cut into convenient lengths for transfer to the Chemical Technology Division hot cells.

Figure 3 shows the fuel and blanket locations and differential gamma scans (0.55 to 0.75 MeV) of the rods made at ORNL in December 1976. The scans showed redistribution of cesium; in addition to the usual high peaks at the ends of the fuel column at the UO₂ blanket pellets, the other peaks observed along the column were primarily due to ¹³⁷Cs. The valleys on the scans, however, indicated the presence of other fission and activation products, ¹⁰⁶Ru, ¹⁴⁴Ce, and ⁶⁰Co, along with ¹³⁴⁻¹³⁷Cs (i.e., the spectrum of more "normal" fuel and cladding, unmasked by the redistributed cesium).

The plenums were punctured in December 1976, and the released gases were analyzed by mass spectrometry (Table 3). The mass distribution of the xenon and krypton isotopes present in the gas are listed in Table 4. The total amount of ⁸⁵Kr released from the plenum of rod B-7 was 7.683×10^{10} dis/sec; this is equivalent to ~95% of the total amount of ⁸⁵Kr in the rod ($\sim 4.50 \times 10^9$ dis/sec was recovered from the dissolution). A total of 1.14×10^{11} dis/sec of ⁸⁵Kr was released when the plenum of C-13 was punctured; this is equivalent to ~93% of the total amount of ⁸⁵Kr in the rod.

2.3 Equipment

The hand-operated, single-rod hydraulic shear is shown in Fig. 4. A 2-in.-diam hydraulic piston drives a hardened steel blade vertically through fuel rod segments which are positioned horizontally through holes in the side of the cutting chamber; the cut segments (up to 3 in. long) fall into the cup below. Figure 5 is a schematic flow chart for the hot-cell voloxidation equipment. Feed gases are metered

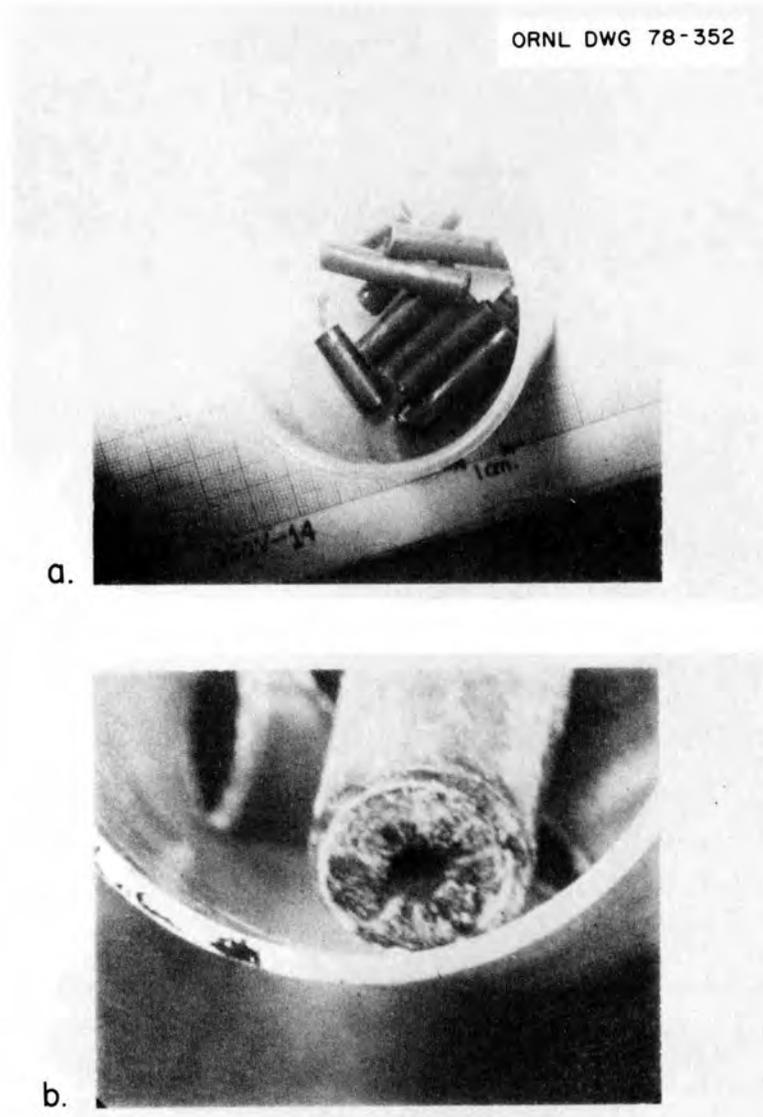


Fig. 2. Segments of ASOV-14 fuel rod (a) as cut, (b) close-up showing center void and fission product deposits on cracks.

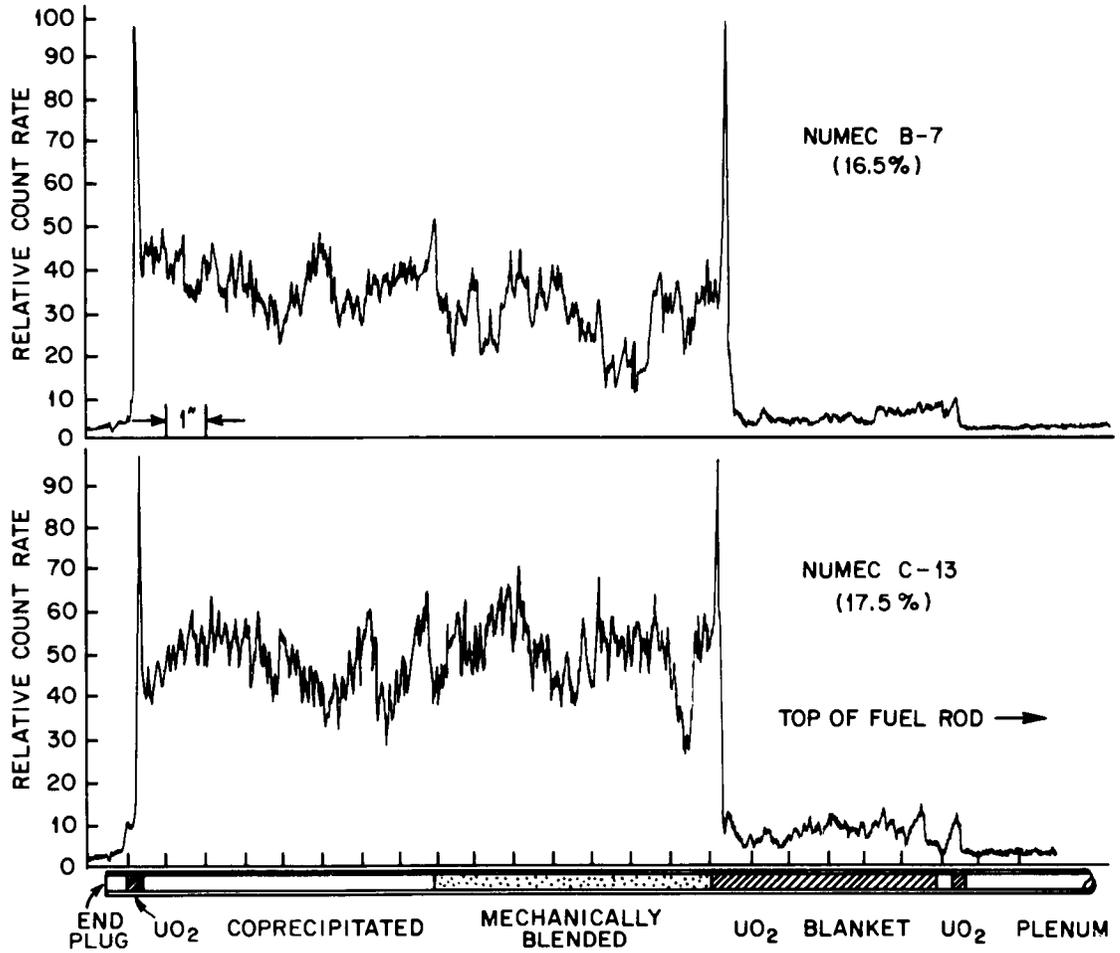


Fig. 3. Integral gamma scans of NUMEC fuel rods (>0.5 MeV).

Table 3. Mass spectrometer analysis of fission gases in plenum of
NUMEC rods B-7 and C-13

Gas released	Rod no..	
	B-7	C-13
Gas volume, cm ³ (STP)	204.34	239.62
Void volume, cm ³ (STP)	16.73	11.54
H ₂ , % of total	<0.01	0.02
He, % of total	8.80	7.76
H ₂ O, % of total	0.05	0.05
N ₂ + CO, % of total	0.02	0.12
O ₂ , % of total	<0.01	0.02
Ar, % of total	0.01	0.06
CO ₂ , % of total	<0.01	<0.01
Kr, % of total	12.00	11.70
Xe, % of total	79.20	80.27

Table 4. Isotopic analysis of xenon and krypton (%) in fission gases of NUMEC rods B-7 and C-13

Isotope	Rod no.	
	B-7	C-13
^{78}Kr	0.01	0.01
^{80}Kr	0.01	0.01
^{82}Kr	0.03	0.05
^{83}Kr	15.91	15.66
^{84}Kr	28.61	28.59
^{85}Kr	4.95	4.72
^{86}Kr	50.50	50.97
^{128}Xe	0.01	0.01
^{130}Xe	0.05	0.05
^{131}Xe	14.57	14.33
^{132}Xe	22.70	22.78
^{134}Xe	34.04	34.17
^{136}Xe	28.63	28.66

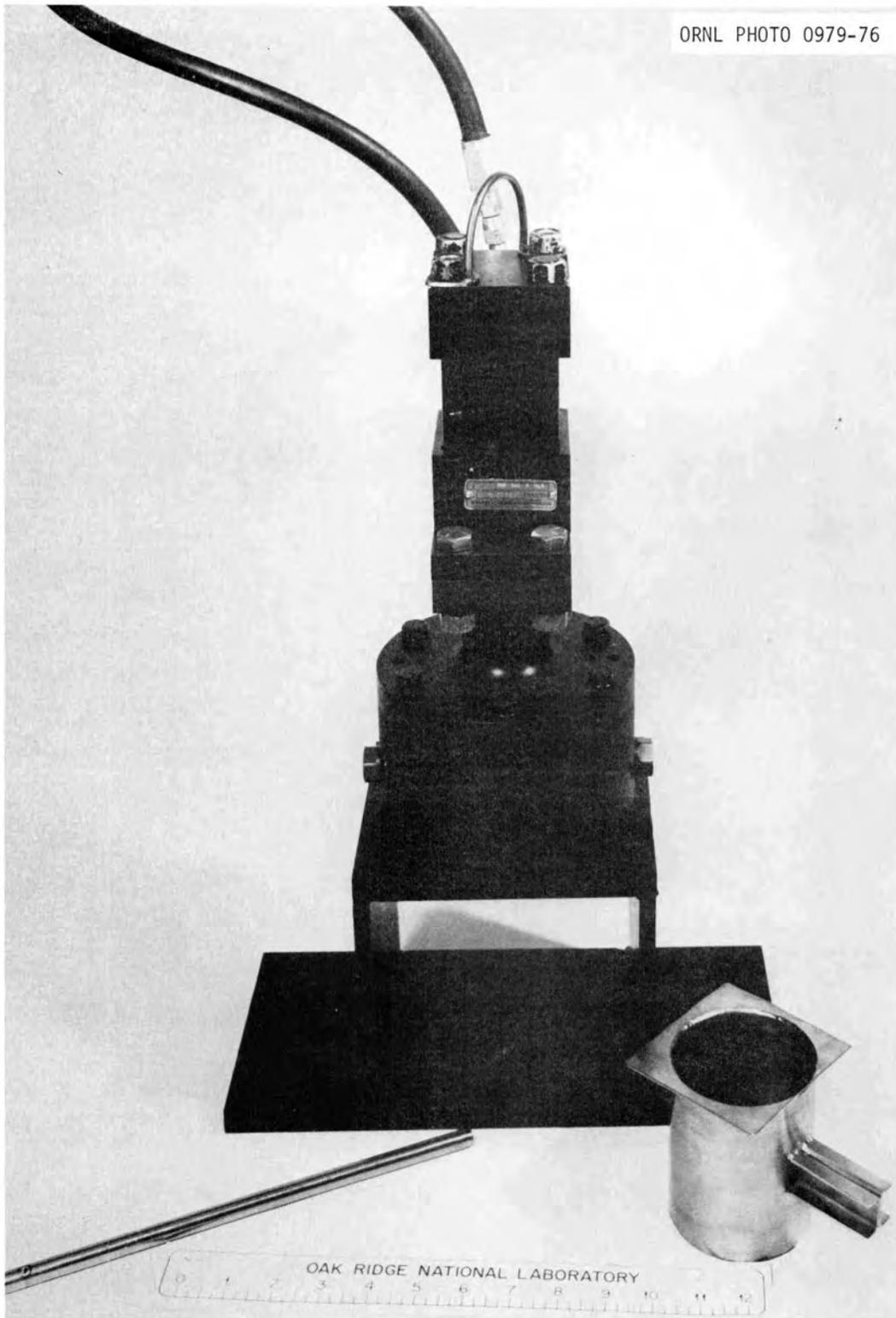


Fig. 4. Single-rod hydraulic shear.

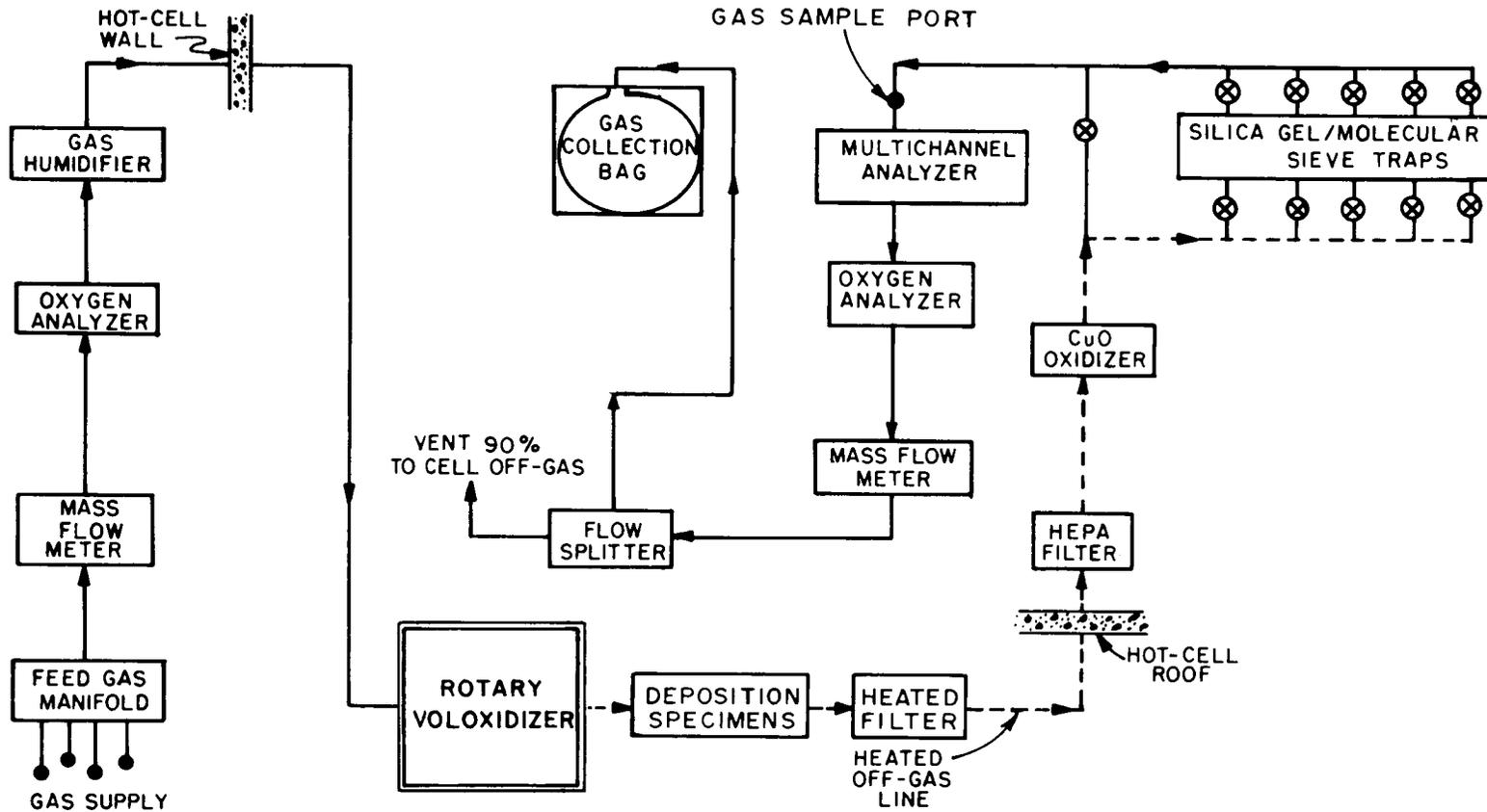


Fig. 5. Schematic flow chart of hot-cell voloxidation equipment.

(Hastings-Raydist mass flow meters) and humidified by bubbling them through water before they are introduced into the cell (Fig. 6). The gases pass through 35- μm sintered-metal filters on the inlet and exit of a rotating stainless steel voloxidizer. The gases are then cooled in a calibrated cooling zone in the shaft of the voloxidizer. This shaft is hollow and contains inserts for measuring the deposition of volatile fission products (Fig. 7). The gases then pass through a heated filter pack (Fig. 8) for removal of particulates and out of the cell via a heated line to the Penthouse area above the cell roof. Here the gases are filtered again, oxidized in a 600°C copper oxide unit to convert elemental tritium and ^{14}C to HTO and $^{14}\text{CO}_2$, respectively, and then passed through silica gel and Type 4A molecular sieve traps for capture (Fig. 9). The oxygen content of the exit gas is then continuously measured (International Biophysics Corporation differential oxygen meter) for comparison with the incoming oxygen content (air), and the ^{85}Kr content is monitored in a multichannel gamma spectrometer (Fig. 10). Finally, 10% of the flow is collected as a composite sample for the ^{14}C and ^{85}Kr assay. (Figure 11 is a general view of the cell interior.)

A schematic diagram of the primary dissolution glassware and equipment is shown in Fig. 12. A metered flow of air (60 to 70 cm^3/min) is used to transfer dissolution-leaching acid into a Pyrex dissolver fitted with a reflux condenser and is then used to carry the off-gases through empty condensate traps and 3 M NaOH scrubbers containing fritted-glass gas dispersion tubes. A 600°C copper oxide oxidizer in the cell is used to convert elemental tritium to HTO before it reaches the second trap and scrubber. After HEPA filtration, the gas stream is passed out of the cell and into a multichannel gamma spectrometer to determine the rate of ^{85}Kr evolution. The cessation of ^{85}Kr evolution is used to indicate the completion of fuel dissolution. The off-gas is collected for sampling in a special plastic bag. There was a holdup of $\sim 1800 \text{ cm}^3$ (delay of ~ 27 min) between the dissolver and the multichannel analyzer.



Fig. 6. Feed gas manifold outside the hot cell.

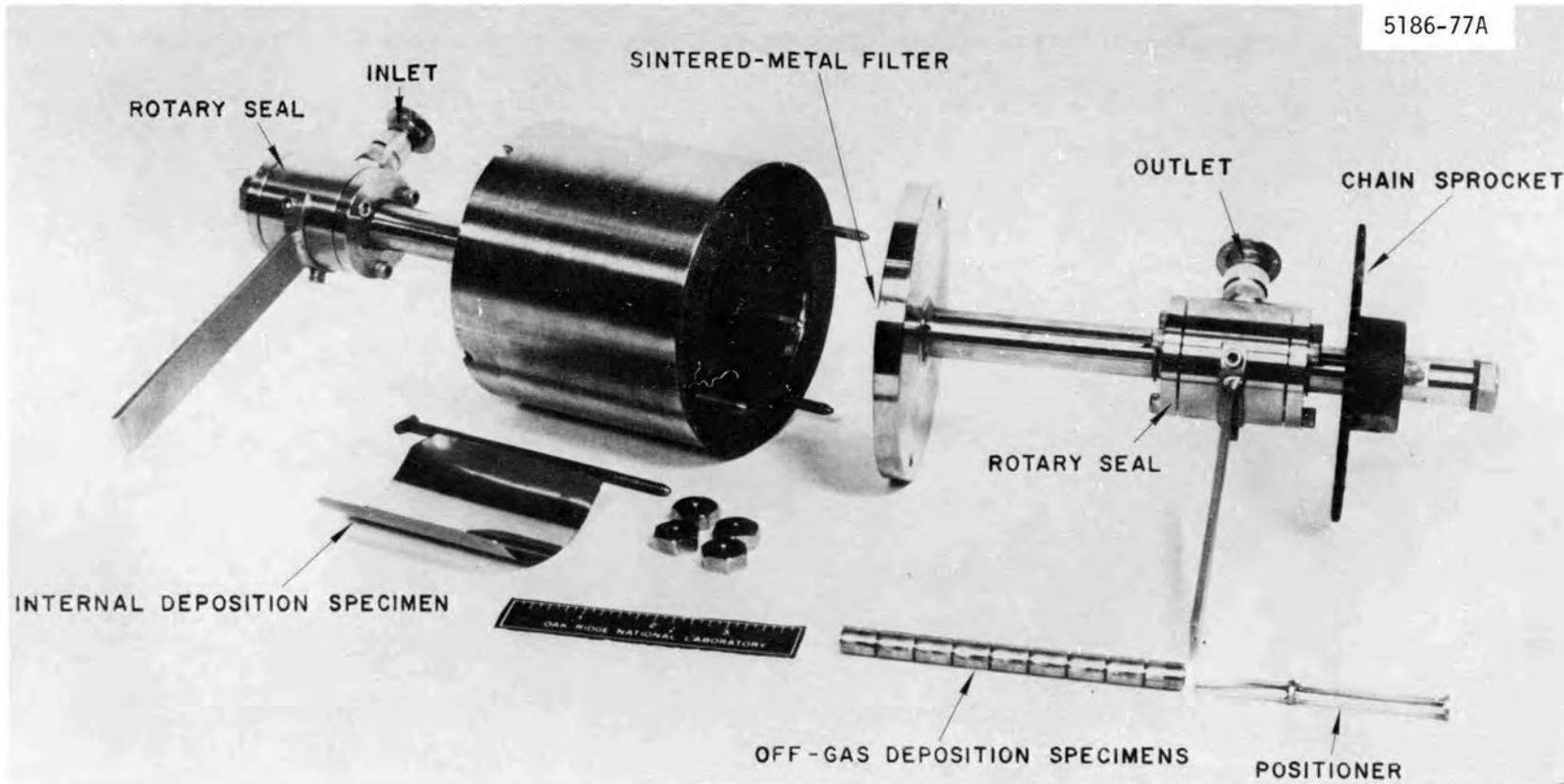


Fig. 7. Disassembled voloxidizer.

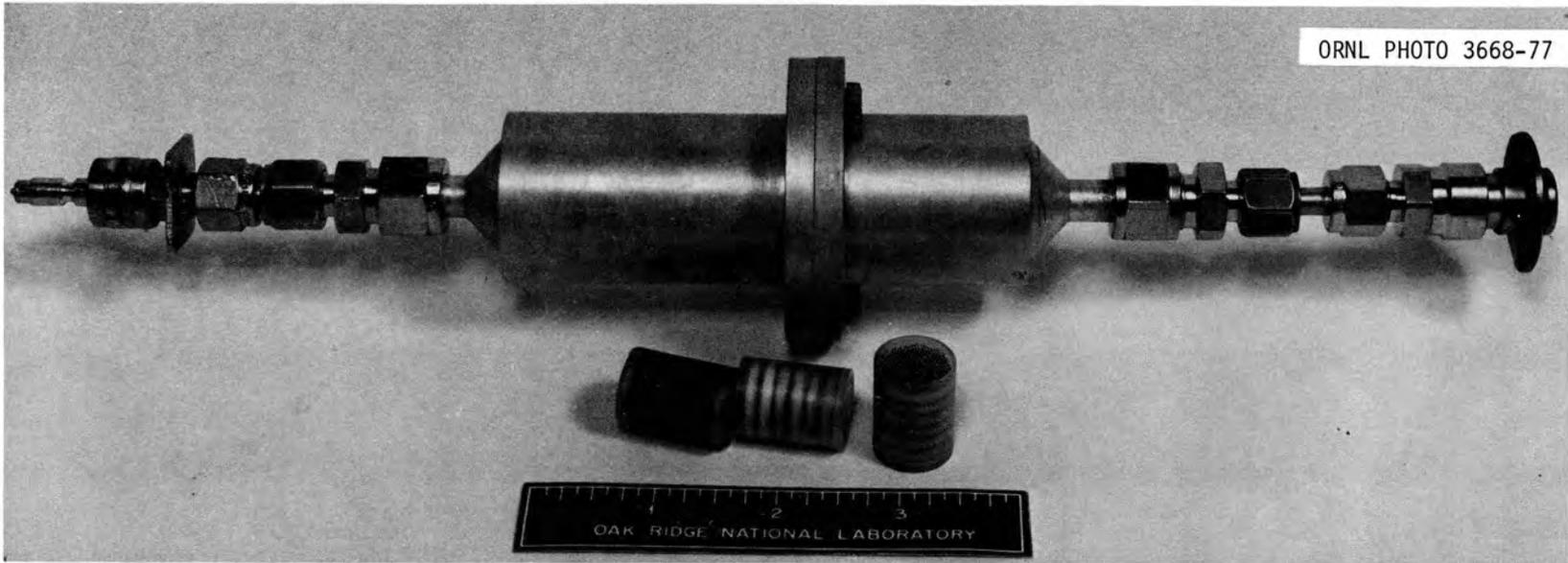


Fig. 8. Heated filter pack assembly.

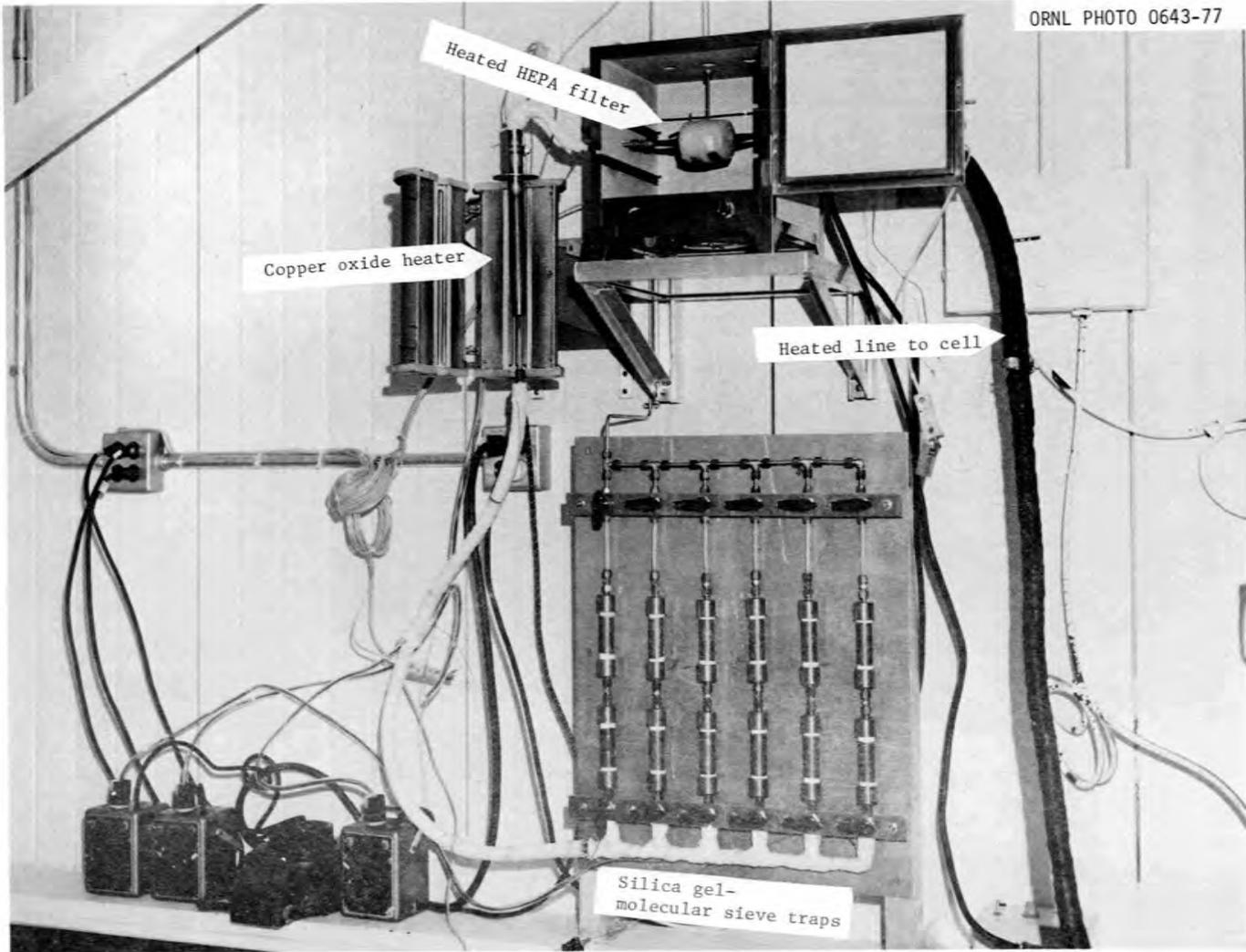


Fig. 9. Tritium traps and associated equipment.

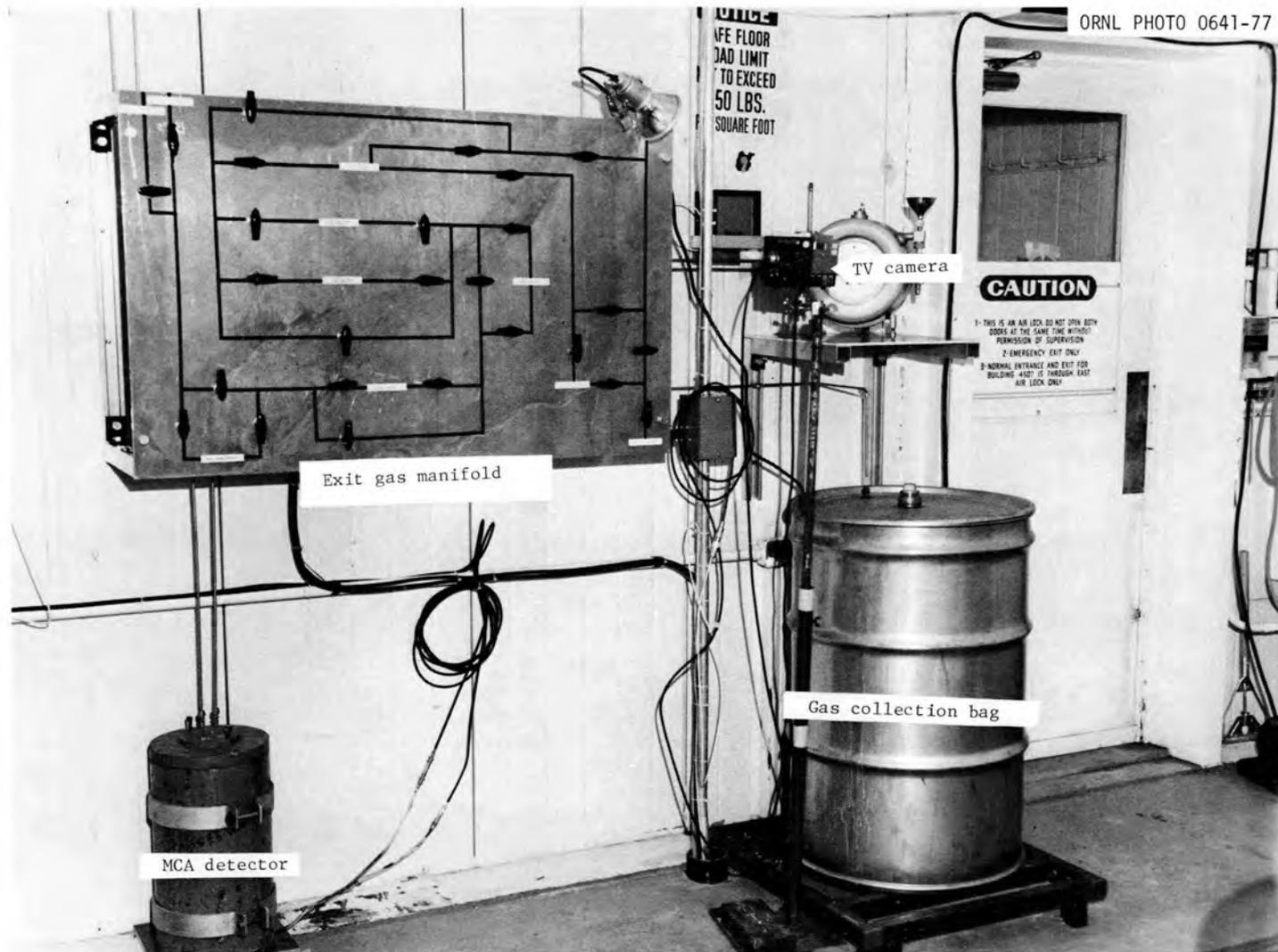


Fig. 10. Krypton-85 analyzer and exit-gas collection system.

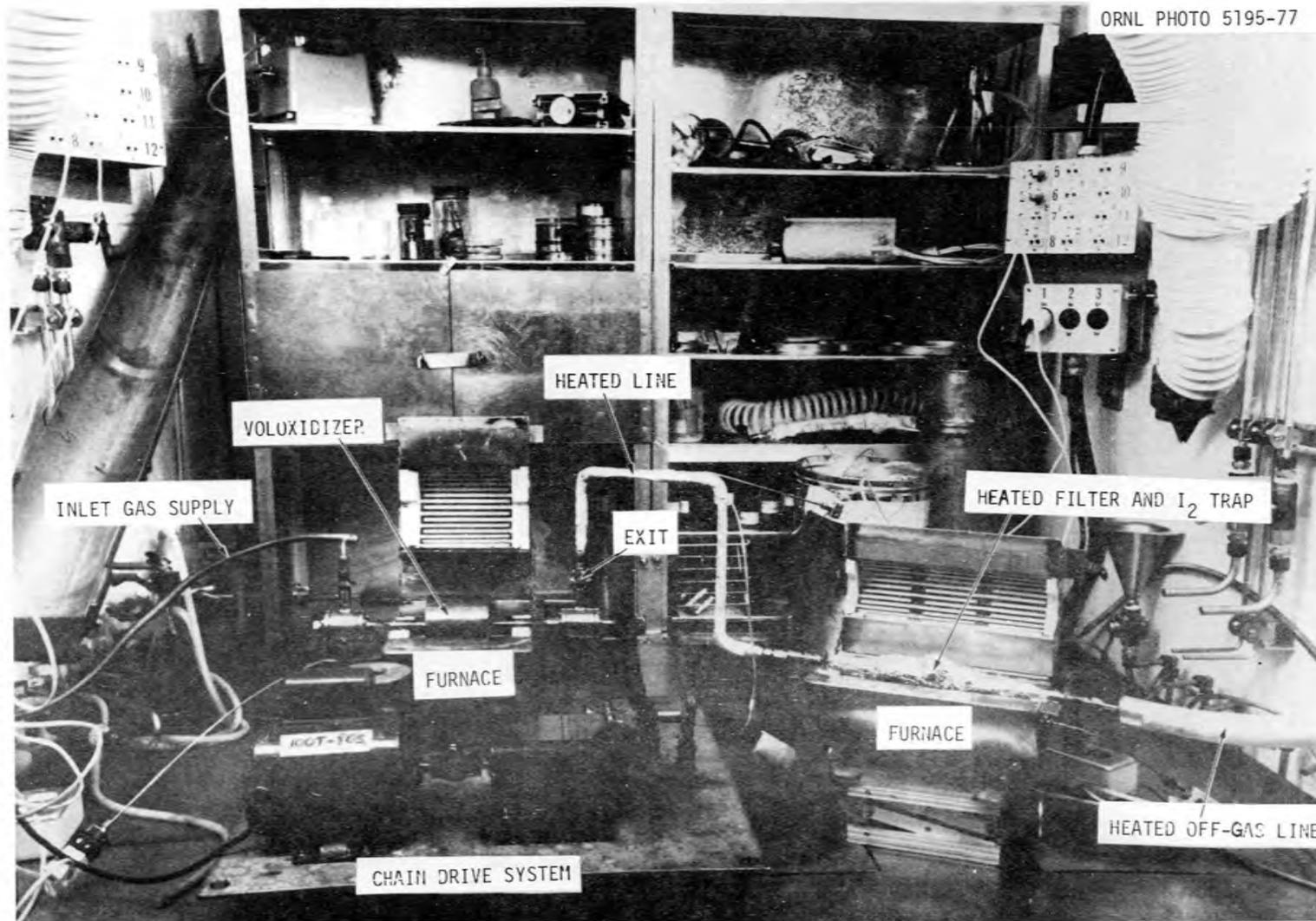


Fig. 11. General view of hot-cell interior.

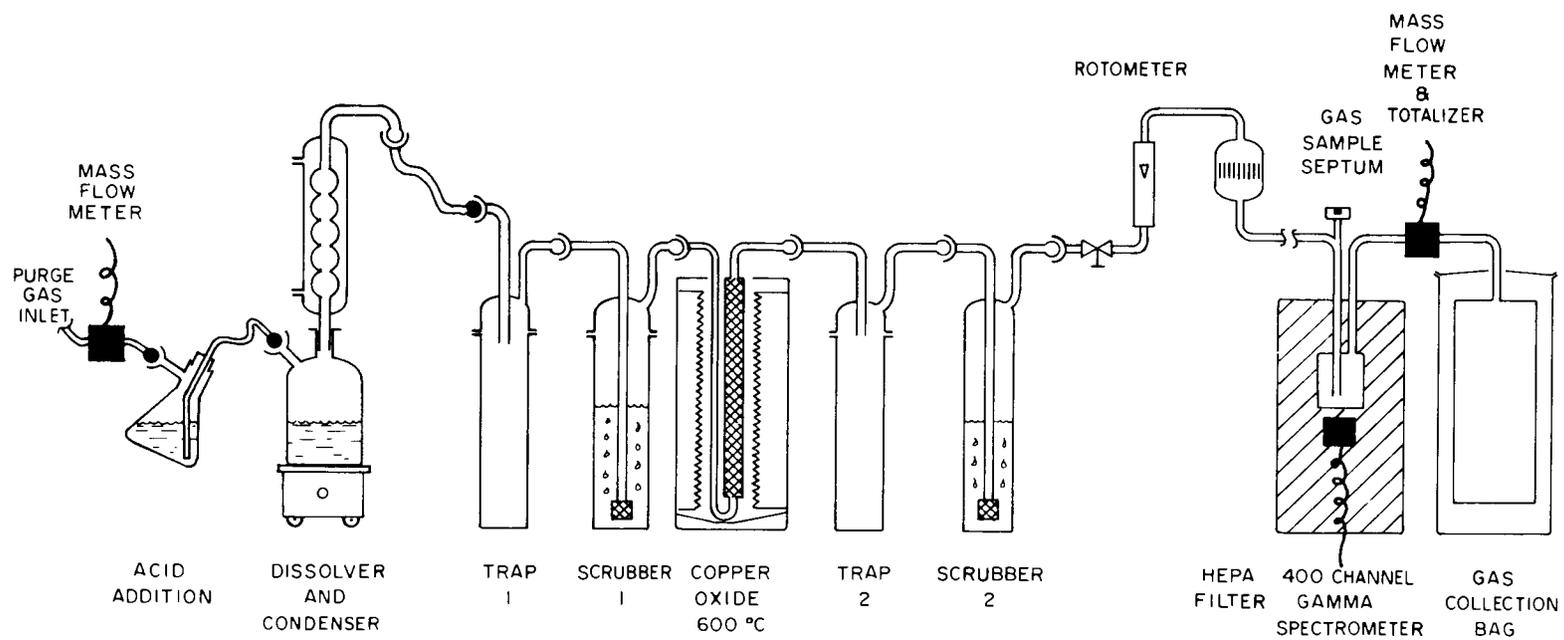


Fig. 12. Schematic diagram of dissolution apparatus.

3. RESULTS AND DISCUSSION

3.1 Shearing NUMEC Rods

The single-rod hydraulic shear was used to cut the two rods into 0.5-in.-long segments for the voloxidation and dissolution studies. The following cutting forces were measured for each section of the rod:

Type of pellet	Average force per cut (kg)	
	Rod B-7	Rod C-13
Coprecipitated	215	212
Mechanically blended	167	167
UO ₂ axial blanket	379	292

The forces appear to relate almost linearly to the preirradiation smear densities of the three types of pellets within the Type 316L stainless steel-clad rod having an outside diameter of 0.252 in. and a wall 0.015 in. thick (i.e., 82.5%, 80.8%, and ~89%, respectively). Deformation to the ends of the cut pieces was moderate. A large number of the rods had jagged and uneven edges, but there was no evidence of significant pillowing (closure) on the ends.

About 10% of the mechanically blended fuel was dislodged from the cladding by the shearing. Sieve analysis of the 3.6 and 4.4 g of loose oxide gave the following size distribution.

Mesh size	Opening (μm)	Rod B-7		Rod C-13	
		Weight (g)	Percent total	Weight (g)	Percent total
+ 35	+500	1.96	54	2.8	64
+100	+149	0.92	26	1.0	23
-100	-149	<u>0.72</u>	<u>20</u>	<u>0.6</u>	<u>13</u>
Total		3.60	100	4.4	100

The release from the cladding averaged ~0.35 g per cut of the shear.

Two 0.5-in.-long segments of the stainless steel-clad, mechanically blended (U,Pu)O₂ were selected at random from each rod for dissolution in nitric acid to provide baseline information for comparison with voloxidized fuel in other experiments. The remaining mechanically blended fuel from rods B-7 and C-13 was used in voloxidation runs FBR-1 and FBR-2, respectively. [The sheared segments of coprecipitated (U,Pu)O₂ and UO₂ blanket materials were stored for subsequent studies with those types of fuels.]

3.2 Voloxidation of NUMEC Fuel

3.2.1 Voloxidation - general

The voloxidation apparatus and gas flow system used during these studies were described above. Operation and sampling procedures were chosen to identify gaseous release totals and release rates, fission product distribution, and oxygen consumption during batch voloxidation experiments.

Once the fuel was loaded, the voloxidizer was sealed and connected to the gas flow system, and the entire assembly was tested for leak tightness with air at a gauge pressure of 6 psi. After its integrity was verified, the temperature was slowly increased over a 30- to 45-min period until the voloxidizer reached 650°C, where it was maintained for the duration of the oxidation. During the heat-up period and for the length of the experiment, air was admitted to the system at a rate of 200 to 300 cm³/min (STP), and the voloxidizer was rotated at 12 rpm. To ensure completeness of reaction at these conditions, each voloxidation was continued beyond the point at which oxygen consumption had ended and the ⁸⁵Kr concentration in the off-gas had returned to near the system background levels. Following each run, the voloxidizer received a 2-hr purge during cooling to sweep any of the remaining off-gases from the system.

Sampling of the system for particulates and semivolatile species was conducted in the following sequence:

1. Sheet specimens and coupons were located inside the voloxidizer to check for fission product deposition and scouring by the cladding.

2. A sintered-metal filter with a pore size of 35 μm in the exit end of the voloxidizer was followed by stainless steel deposition tubing inserts and steel wool packing within the hollow shaft of the voloxidizer.
3. The deposition tube was followed by a heated filter pack (at 125°C) that contained sintered-metal filters, graded filter papers, and charcoal granules.
4. A heated HEPA filter located outside the cell provided secondary removal of particulates from the stream prior to passage of the gas through beds of hot copper oxide and silica gel, which had been inserted for final oxidation and removal of tritium, respectively.

The rotary voloxidizer was charged for run FBR-1 with 40.4 g of sheared, mechanically blended (U,Pu) O_2 from NUMEC rod B-7 (11 clad pieces containing 28.1 g of fuel and 3.6 g of loose fuel fines). For run FBR-2, the voloxidizer was loaded with 40.2 g of sheared fuel and cladding from Rod C-13 (ten clad pieces containing 27.1 g of fuel and 4.4 g of loose fuel fines). Experimental conditions are given in the following table.

Table 5. Experimental conditions for runs FBR-1 and FBR-2

Run no.	Rod no.	Burnup (at. %)	Fuel charged to voloxidizer ^a (g)	Voloxidation conditions			
				Time (hr)	Temp. (°C)	Atmos. ^b	Rotation (rpm)
FBR-1	B-7	16.5	31.7	3.2	650	Air	12
FBR-2	C-13	17.5	31.5	4.1	650	Air	12

^aFuel weight includes (U,Pu) O_2 and fission products only.
^bFlow at 200 to 300 cm^3/min .

3.2.2 Oxygen consumption

The high burnup (~17 at. %) attained by the NUMEC rods makes it necessary to account for the approximate weight of the fission products when calculating the amounts of heavy-metal oxide contained in each

voloxidizer charge and product. ORIGEN calculations for the irradiation of this fuel yielded:

reactor input, 1000 kg U + Pu [1136.4 kg (U,Pu)O₂]
reactor output, 15.4 kg Xe + Kr (~95% released during irradiation),
113.2 kg fission product oxides,
1007.8 kg (U,Pu)O₂ [886.8 kg U + Pu],
1136.4 kg total.

Based on these totals,^{*} material balances for voloxidations of the mixed-oxide portions of both fuel rods were calculated and are shown in Table 6.

The theoretical weight gain for the conversion of the UO₂ in the (U_{0.865}Pu_{0.135})O₂ (post-irradiation) to U₃O₈ is ~3.22%.^{*} Measured weight gains on the voloxidized products were somewhat less, which indicated slight handling losses (~1%); hence, an estimate of the amount converted by this method could not be made. The actual conversion of UO₂ to U₃O₈ was probably somewhat closer to the theoretical amount, considering the recovery losses and weighing inaccuracies on such small quantities. It was possible to measure differences between the oxygen concentrations of the inlet and off-gas streams for the two experiments, and the calculated moles of oxygen consumed verified good conversion. The totals, based on oxygen use, indicated maximum conversions of 100% and 92% for runs FBR-1 and FBR-2, respectively.

During the heat-up period in both experiments, oxygen consumption began when the temperature of the charge reached ~400°C and was nearly finished after 0.5 hr. Maximum consumption took place within 15 min after the voloxidation temperature reached 650°C. At the point of peak consumption, close to 90% of the oxygen in the feed air stream was being consumed. (Combined profiles for oxygen consumption and gaseous fission product release are presented in Sect. 3.2.3.)

Sieve analyses were performed on the loose oxide charged to and recovered from the voloxidizer during each run. The results, given in Table 7, indicated that voloxidation of the mechanically blended

^{*}See Appendix.

Table 6. Material balances on the voloxidation of NUMEC mechanically blended (U,Pu)O₂

	Run FBR-1, rod B-7	Run FBR-2, rod C-13
Input weight, g		
Total	40.40	40.20
Cladding	<u>8.65</u>	<u>8.74</u>
Fuel ^a	31.75	31.46
(U,Pu)O ₂ ^b	28.56	28.30
Output weight, g		
Total	40.90	40.70
Cladding	<u>8.65</u>	<u>8.74</u>
Fuel	32.25	31.96
Theoretical weight gain, g ^c	0.92	0.91
Actual weight gain, g	0.5	0.5
Conversion (calc.), % ^d	~100.0	92.0

^aIncludes weight of (U,Pu)O₂ + weight of fission products.

^bWeight of (U,Pu)O₂ = 0.8984 x (total fuel weight).

^cBased on 3.22% weight gain of (U,Pu)O₂ for full conversion of UO₂ to U₃O₈.

^dCalculated from moles of oxygen consumed.

Table 7. Release of NUMEC mechanically blended (U,Pu)O₂ from 0.5-in.-long, stainless steel-clad segments by voloxidation in air at 650°C

	Run FBR-1, rod B-7		Run FBR-2, rod C-13	
	In	Out	In	Out
Loose oxide, g	3.6	19.0	4.2	20.6
% of total oxide	11.3	58.9	13.4	64.5
Loose oxide particles, μm	+500 (54) ^a	-	+500 (63)	-
	+149 (26)	+149 (44)	+149 (23)	+149 (67)
	-149 (20)	+ 44 (21)	-149 (14)	+ 44 (15)
	-	- 44 (35)	-	- 44 (18)

^aNumbers in parentheses () indicate the percentage of the designated size of loose oxide particles.

(U,Pu)O₂ in air at 650°C increased the amounts of loose fuel to ~60 to 65% of the total, nearly a fivefold increase in the amount initially dislodged by shearing. Comminution of fuel from rod B-7 was more complete than that from rod C-13. A graphic display of the size distributions of unclad fuel from the two rods (shown in Fig. 13) also illustrates the differences in fuel comminution following each processing step.

3.2.3 Gaseous fission product release

Tritium and krypton evolution curves (as concentrations in the off-gas) were derived from measured amounts of radionuclide activity present in known volumes of off-gas that were collected over specified time intervals. These curves are plotted as a function of voloxidation run time in Figs. 14 and 15 for runs FBR-1 and FBR-2, respectively, and are related to the corresponding oxygen content of the voloxidizer off-gas. The cumulative oxygen consumption and fission gas release profiles (percentages of amounts initially in the fuel) are shown for each run in Figs. 16 and 17. In all graphs, the time of 0.0 hr represents the start of the heat-up period.

The tritium traps were not replaced soon enough during the first run to adequately describe the early part of the tritium release curve. Measurements on the first trap indicated that ~28% of the total tritium in the fuel was evolved during the heat-up (as compared with ~5% of the total krypton released during the same period). In both experiments, most of the tritium and krypton evolved was measured during the first hour at temperature, with the evolution rates diminishing rapidly thereafter. In the FBR-1 experiment, close to 93% of the tritium was released while the fuel was at temperature. Another 3% was released during the cooling period, bringing the total tritium release up to 96%.

A double peak (or delayed-) release pattern for tritium was observed during voloxidation of both NUMEC rods. There was a delay of at least 30 min between the point of peak oxygen consumption and the final peak in tritium evolution. This is partially attributed to the holdup of HTO on the surfaces, even though they were heated to >100°C. Tritium evolution was essentially completed after 1.5 hr at temperature,

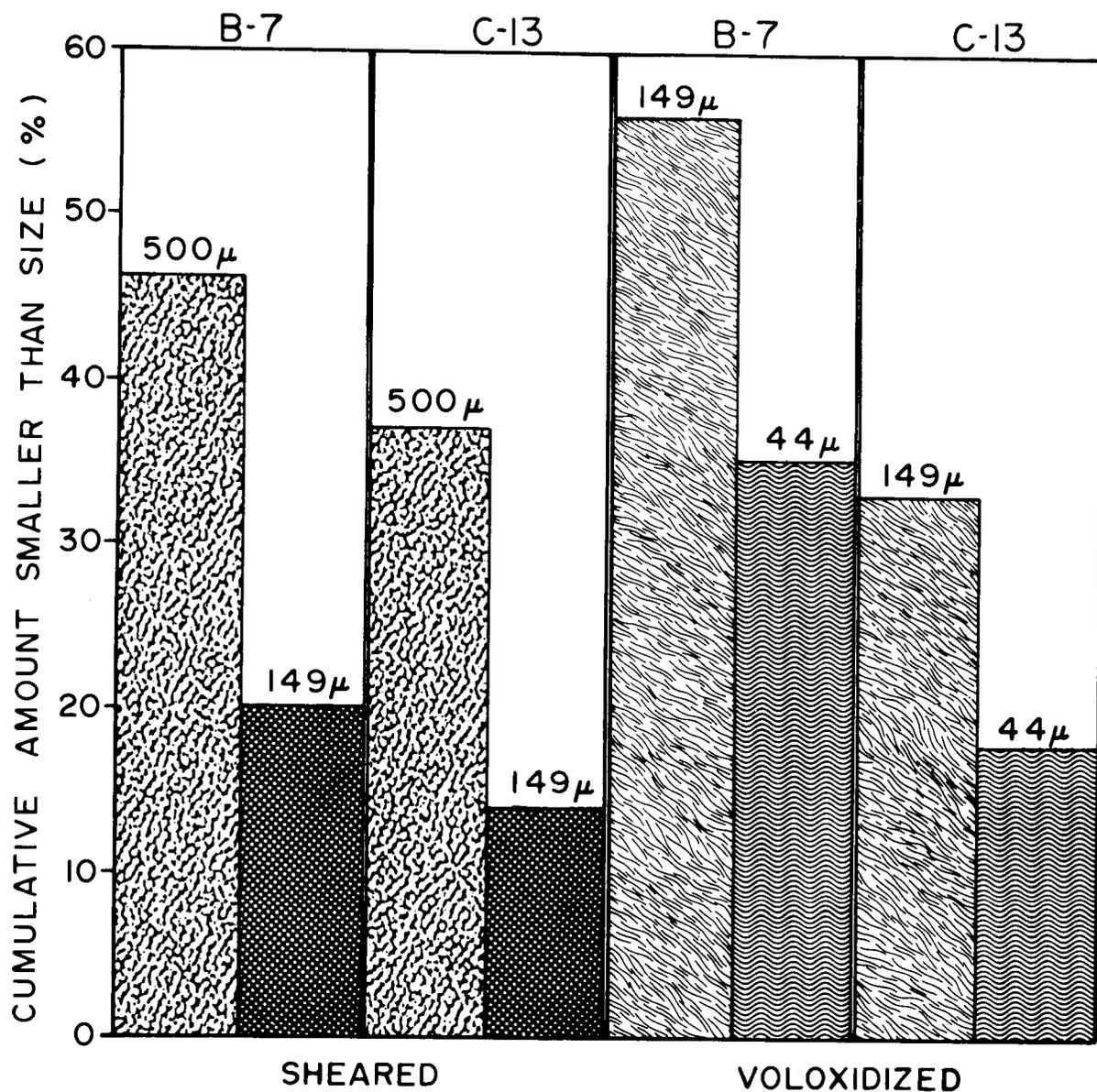


Fig. 13. Size distribution of unclad, mechanically blended (U,Pu)O₂.

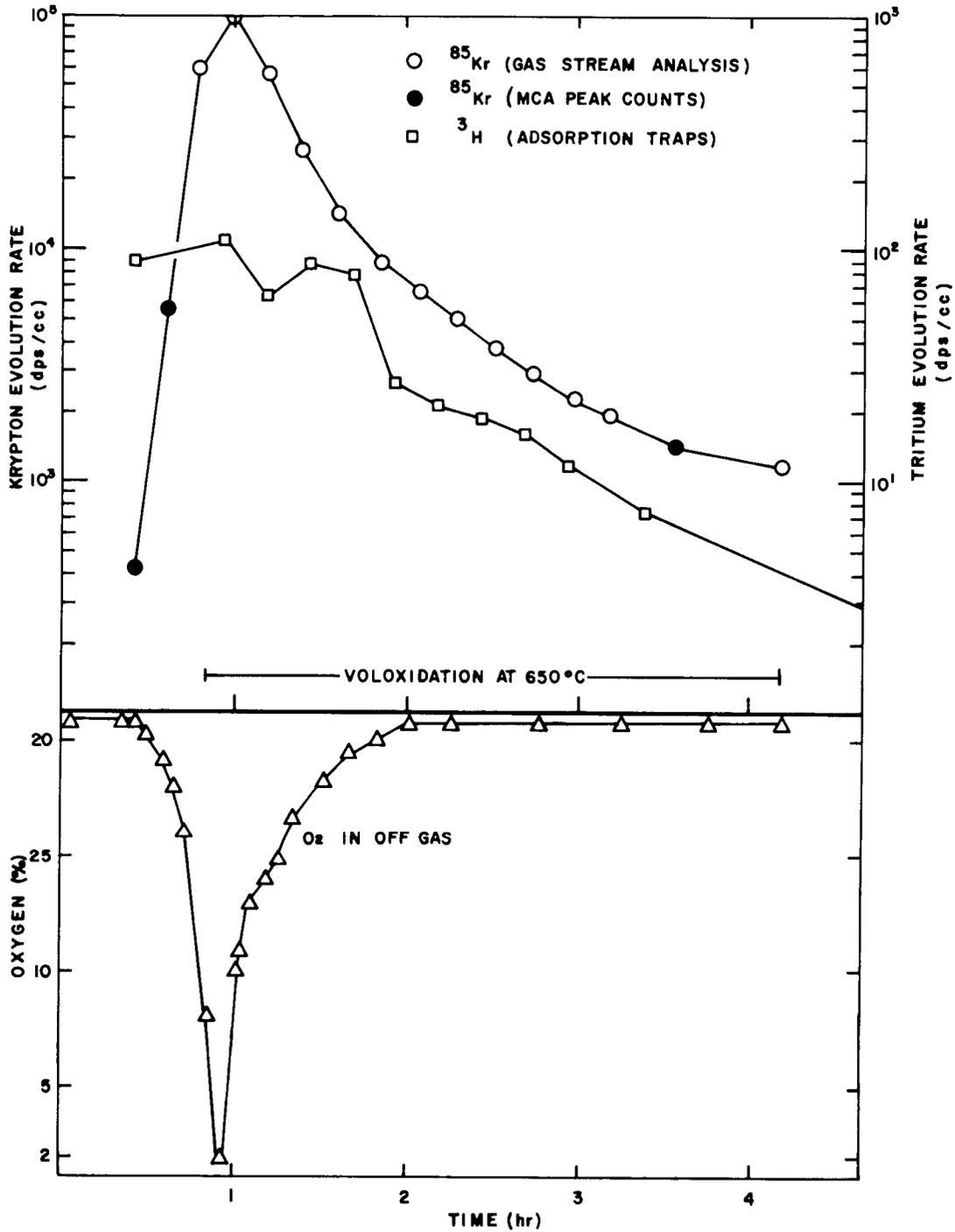


Fig. 14. Tritium and krypton evolution and oxygen consumption during voloxidation of NUMEC B-7 (U,Pu)O₂ in air at 650°C (run FBR-1).

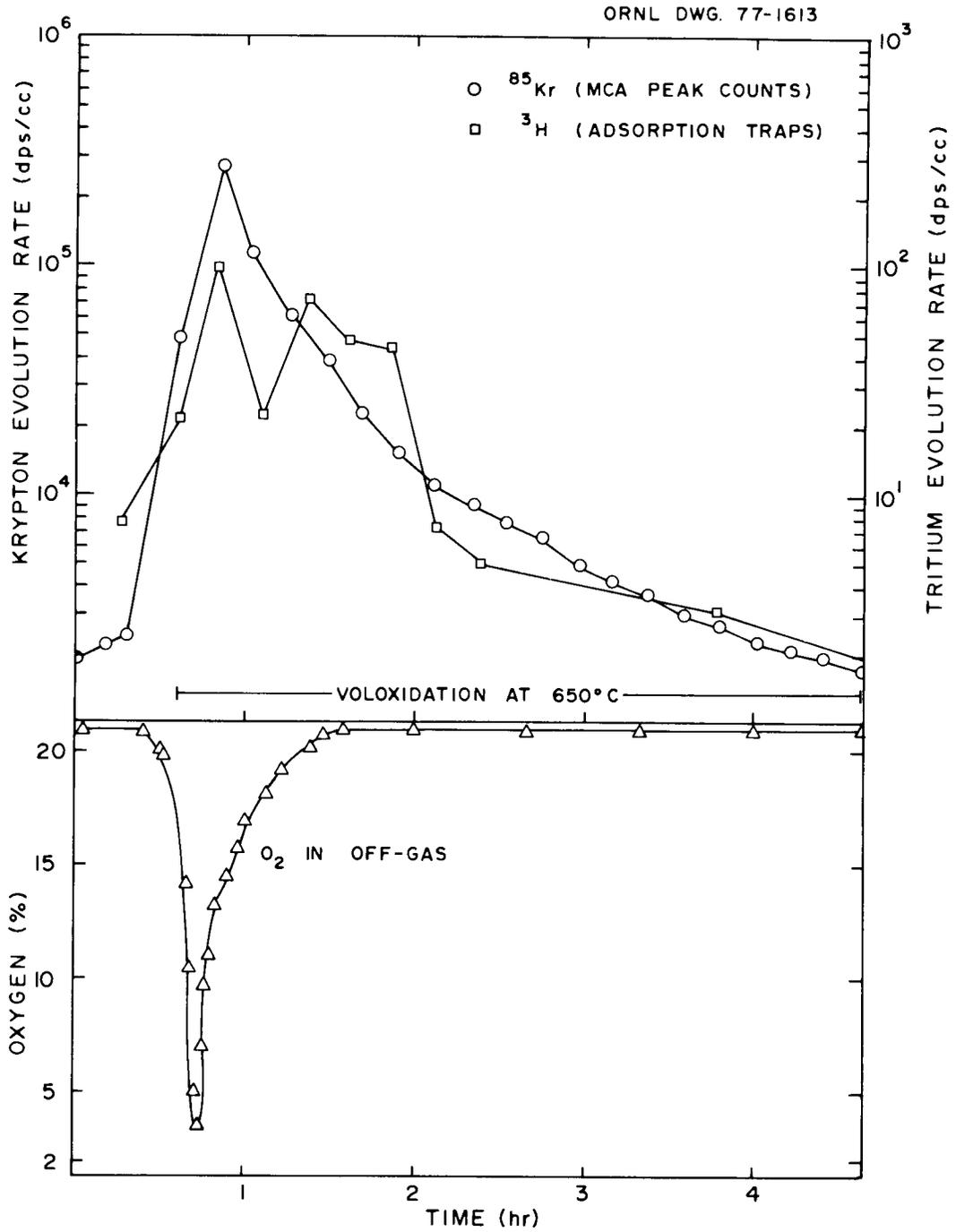


Fig. 15. Tritium and krypton evolution and oxygen consumption during voloxidation of NUMEC (U,Pu)O₂ in air at 650°C (run FBR-2).

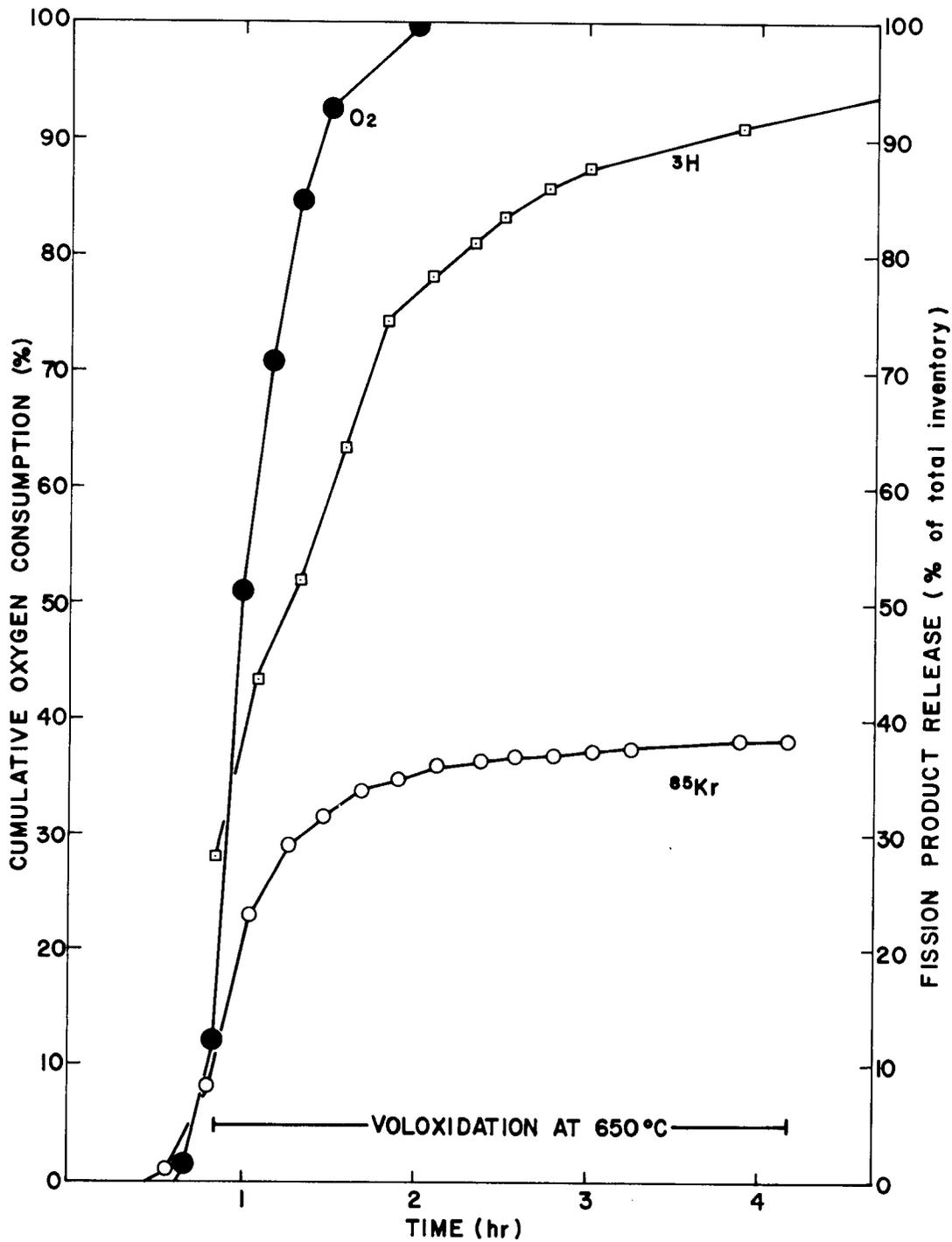


Fig. 16. Release of tritium and krypton and cumulative oxygen consumption during vooxidation of NUMEC B-7 (U,Pu)O₂ in air at 650°C (run FBR-1).

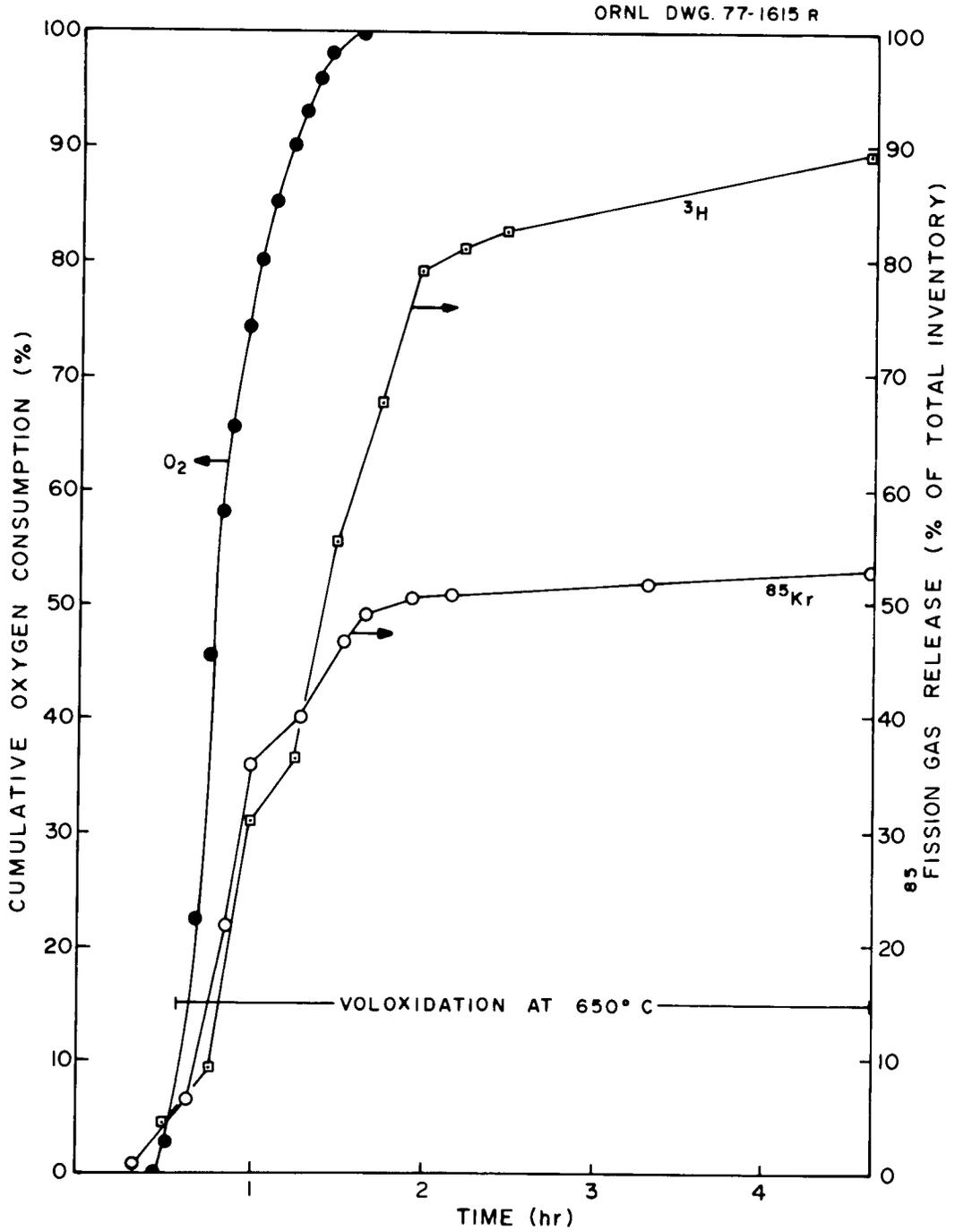


Fig. 17. Release of ^{85}Kr and cumulative oxygen consumption during voloxidation of NUMEC C-13 (U,Pu) O_2 in air at 650°C (run FBR-2).

although small amounts ($<5.0 \text{ dis sec}^{-1} \text{ ml}^{-1}$) continued to be absorbed from the gas from the remainder of the voloxidation and during the final air purge. Water rinses of the heated off-gas line after the second run showed tritium concentrations of $\sim 3 \times 10^2 \text{ dis sec}^{-1} \text{ g (U + Pu)}^{-1}$ voloxidized. This indicates that $<0.2\%$ of the total tritium had not been recovered from the silica gel traps during both runs.

Three hours of voloxidation in air at 650°C released nearly 38% of the krypton in the fuel from rod B-7. Under the same conditions, $\sim 52\%$ of the krypton in fuel from rod C-13 was released. Measurements of krypton concentration changes obtained from flowing stream gas samples corresponded closely with those taken from multichannel analyzer counts and indicated no apparent time lag between the peak in krypton release and the period of increased oxygen utilization.

In addition to release rate measurements for tritium and krypton, gas samples were taken from collected voloxidizer off-gas to determine the total amount of carbon-14 that was evolved.

The inventory of gaseous fission products contained by the NUMEC mixed oxide was determined by the dissolution of voloxidized and nonvoloxidized fuel samples and from the collected voloxidizer off-gases. The results are shown in Table 8 for each rod as "best" values from several experimental determinations. The voloxidations performed on the mechanically blended portions of each rod resulted in the release of appreciable amounts of the ^3H , ^{14}C , and ^{85}Kr contained in the fuel. These releases are presented in Table 9, as percentages of the total fuel inventories given in Table 8.

The tritium release totals are somewhat tentative at this time, since both samples that were given the voloxidation treatment appeared to contain more tritium than those that were not voloxidized. There is evidence, however, (see Sect. 3.3.5) which indicates that this may be due to contamination of the voloxidation samples by the axial blanket UO_2 during shearing and sample preparation. This would have caused the calculated tritium releases during voloxidation to appear smaller than they actually were.

Table 8. Gaseous radionuclide inventories found in NUMEC (U,Pu)O₂

Rod no.	Gaseous fission product content [dis sec ⁻¹ g (U + Pu) ⁻¹]		
	³ H	¹⁴ C	⁸⁵ Kr
B-7	1.01 x 10 ⁵	4.52 x 10 ⁴	5.58 x 10 ⁷
C-13	1.51 x 10 ⁵	4.41 x 10 ⁴	8.88 x 10 ⁷

Table 9. Release of gaseous radionuclides during voloxidation of NUMEC mechanically blended (U,Pu)O₂ in air at 650°C

Run no.	Rod no.	Released to voloxidizer off-gas (% of total fuel inventory)		
		³ H ^a	¹⁴ C ^a	⁸⁵ Kr ^b
FBR-1	B-7	95.91	87.26	38.17
FBR-2	C-13	91.46	66.44	52.59

^aBased on residual levels determined from the dissolution of voloxidized oxide.

^bDetermined from collected voloxidizer off-gas.

3.2.4 Fission product distribution

Following each voloxidation, the deposition and filter trap samples were collected for gamma spectrometric analyses. A brass sheet specimen that had remained in contact with the inner walls of the voloxidizer during both runs was also analyzed in order to provide an estimate of the amounts of fission products that were deposited (or plated out) on the inner surfaces of the voloxidizer.

Fission product recoveries from the voloxidizer walls and off-gas system are listed in Table 10 as percentages of the total fuel inventories found for each NUMEC rod. Only small quantities (~0.1 to 0.2% of the total) of ^{106}Ru , ^{125}Sb , and ^{144}Ce appeared to have coated the inner surfaces of the voloxidizer with less than 0.1% of the total inventory of each being transferred to downstream locations. Cesium, however, was considerably more volatile, with as much as 6% of the ^{134}Cs and 4% of the total ^{137}Cs in the fuel being volatilized; 20 to 30% of the volatilized cesium was located outside the voloxidation chamber in the voloxidizer off-gas system. Activation analyses of the charcoal beds from the heated off-gas filter trap showed that from 75% to 81% of the recovered ^{129}I was removed from the fuel by rotary voloxidation at a temperature of 650°C and that only small amounts (<1.0% of the total) were deposited on the voloxidizer walls. Distributions of selected fission products recovered from the off-gas system following each experiment are shown in Tables 11 and 12. A complete set of gamma-scan analyses on samples from run FBR-1 was not obtained. Most of the fission products that passed the sintered-metal filter (35- μm pore size) at the gas exit of the voloxidizer were found on the deposition tubing insert specimens. (The exception was ^{129}I , which was adsorbed on charcoal beds heated to 125°C.)

Pre-run calibrations of the voloxidizer indicated that the deposition temperatures in the exit shaft could be estimated with reasonable accuracy. One display of such data for the voloxidizer under operation at 650°C shows the relatively narrow distribution of off-gas temperatures over a wide range of flow rates (Fig. 18).

Table 10. Fission product recoveries from the voloxidizer walls and off-gas system following oxidation of NUMEC mechanically blended (20% PuO₂--80% UO₂) in air at 650°C

Nuclide	Rod no.	Fuel inventory ^a [dis sec ⁻¹ g (U+Pu) ⁻¹]	Distribution (% of total fuel inventory)	
			Voloxidizer walls ^b	Off-gas system
¹⁰⁶ Ru	C-13	1.40 x 10 ⁹	0.07	0.05
¹²⁵ Sb	C-13	5.77 x 10 ⁸	0.11	0.08
¹²⁹ I	B-7	220 ^c	0.77	80.8
	C-13	220 ^d	0.80	75.7
¹³⁴ Cs	B-7	2.55 x 10 ⁸	4.35	1.61
	C-13	3.89 x 10 ⁸	2.96	1.48
¹³⁷ Cs	B-7	1.13 x 10 ¹⁰	2.88	0.66
	C-13	1.17 x 10 ¹⁰	2.88	1.26
¹⁴⁴ Ce	C-13	3.05 x 10 ⁹	0.19	0.05

^aDetermined from the dissolution of voloxidized and unvoloxidized fuel.

^bCalculated as prorated average based on the analysis of one cumulative sample.

^cµg/g.

^dAssumed content from rod B-7 as a best value.

Table 11. Distribution of selected fission products remaining in the voloxidizer off-gas system following oxidation of NUMEC B-7 mechanically blended 20% PuO₂--80% UO₂ in air at 650°C (run FBR-1)

Nuclide	System distribution (% of total released from voloxidizer)					Total found in off-gas system [dis sec ⁻¹ g (U + Pu) ⁻¹]
	Deposition tubing	Charcoal bed	Silver zeolite crystals	Graded filter (>5 μm)	Off-gas line ^a	
⁹⁰ Sr	86.4	0.49	0.29	12.9	ND ^b	999
¹²⁹ I	7.39	86.8	7.42	0.05	c	117.8 ^d
¹³⁴ Cs	92.2	3.76	2.73	1.07	0.24	9.11 x 10 ⁶
¹³⁷ Cs	92.4	3.75	2.58	1.05	0.25	1.97 x 10 ⁸

^aProrated average following two experiments.

^bNot determined.

^cTrace quantities.

^dμg/g.

Table 12. Distribution of selected fission products remaining in the voloxidizer off-gas system following oxidation of NUMEC C-13 mechanically blended 20% PuO₂--80% UO₂ in air at 650°C (run FBR-2)

Nuclide	System distribution (% of total released from voloxidizer)						Total found in off-gas system [dis sec ⁻¹ g (U + Pu) ⁻¹]
	Deposition tubing	Graded filter papers		Charcoal bed	Off-gas line ^a	HEPA filter	
		> 5 μm	0.3 μm				
Gross gamma	75.6	1.48	20.6	0.22	0.35	1.13	2.50 x 10 ^{7b}
¹⁰⁶ Ru	82.6	1.25	14.6	0.25	0.08	1.25	6.29 x 10 ⁵
¹²⁵ Sb	78.1	1.31	18.4	0.25	0.33	1.65	4.76 x 10 ⁵
¹²⁹ I	1.9	0.29	0.73	97.0	c	0.3	166.6 ^d
¹³⁴ Cs	81.1	1.41	15.5	0.40	0.40	1.21	5.74 x 10 ⁶
¹³⁷ Cs	81.4	1.36	15.5	0.34	0.35	1.08	1.48 x 10 ⁸
¹⁴⁴ Ce	74.2	1.79	21.6	0.41	0.41	1.66	1.41 x 10 ⁶
¹⁵⁴ Eu	91.7	0.70	6.8	0.13	0.18	0.41	5.82 x 10 ⁴

^aProrated average following two experiments.

^bCounts sec⁻¹g⁻¹.

^cTrace quantities.

^dμg/g.

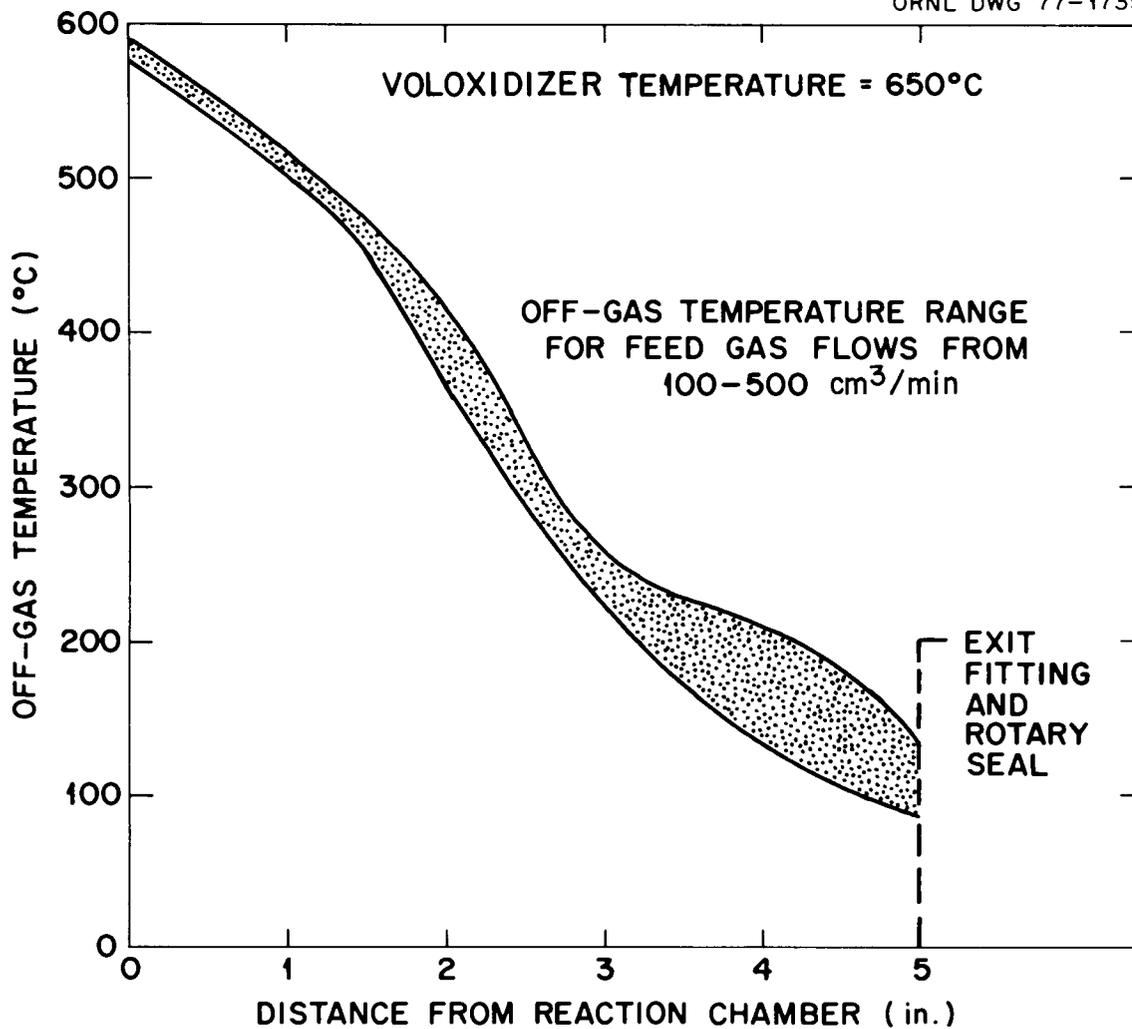


Fig. 18. Temperature of the voloxidizer off-gas as a function of distance from the reaction chamber.

Deposition profiles from the two experiments are shown in Fig. 19 for cesium, cerium, and ruthenium. Deposition on steel wool packing in the cool end of the tubing ($\sim 195^\circ\text{C}$) was increased by an order of magnitude or more, which could signify the trapping effect of an extended surface, or perhaps the presence of particles in the gas. The apparent shift in the ^{137}Cs pattern during run FBR-1 may have been due to a slightly increased flow velocity of the off-gas at this point. No submicron filter papers or HEPA filters were situated in the gas line for the FBR-1 experiment; consequently, system backpressures averaged 25% less than those in the second experiment. The flow velocity may have been slightly higher. Most of the entrained activity found on the graded filter papers was associated with particulates sized between 0.3 and 5 μm . Only trace quantities of radionuclides were found in the heated off-gas line or in a downstream HEPA filter.

3.3 Dissolution of NUMEC Fuel

3.3.1 Procedure

The leaching procedure was chosen to approximately simulate the operation of a continuous countercurrent dissolver; however, for the sake of simplicity during the analyses, no uranium, plutonium, or fission products were present in the leachants. In the experiments, the fuel segments were first leached in 8 M HNO_3 , then the cladding was removed from the insoluble fuel residue and washed, and each solid portion was treated in separate vessels for the rest of the experiment.

The leaching conditions for the fuel and cladding were:

1st leach - 8 M HNO_3 , 2 hr, 92-95°C (fuel plus cladding);

2nd leach - 3 M HNO_3 , 2 hr, 92-95°C (fuel residue and cladding separated);

3rd leach - 8 M HNO_3 , 2 hr, 92-95°C (fuel residue and cladding separated);

4th leach - 8 M HNO_3 --0.05 M KF, 2 hr, 92-95°C (residue only);

5th leach - 5 M HNO_3 --2 M HCl --0.05 M KF, 2 hr, 92-95°C (cladding only).

The final leaches, containing potassium fluoride, were for plutonium material balance purposes. The insoluble residues from the fuel and cladding were centrifuged, washed, dried, and weighed prior to analysis.

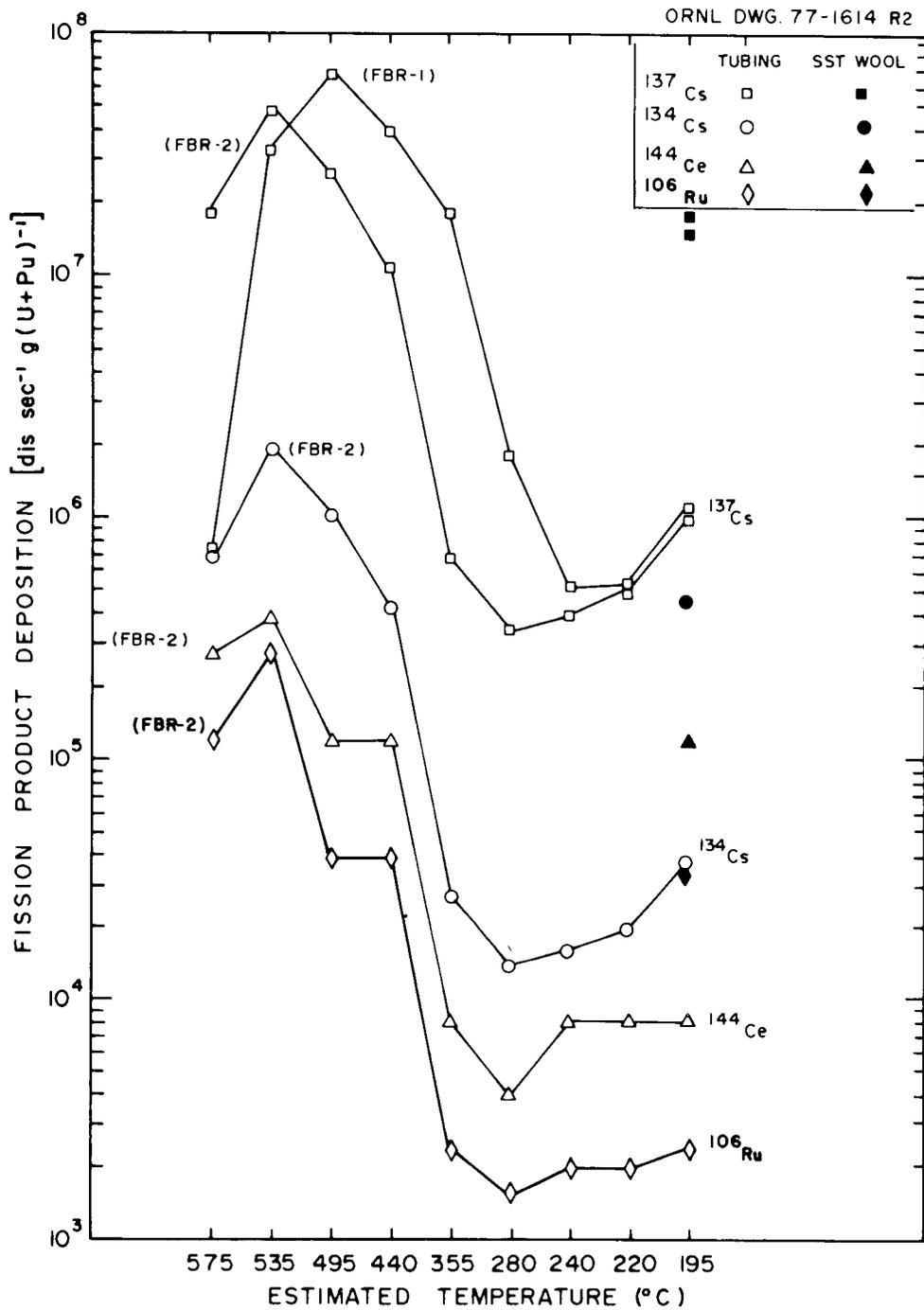


Fig. 19. Fission product deposition from voloxidizer off-gas during oxidation of NUMEC mechanically blended (U,Pu)₂O₃ at 650°C.

The off-gases from the first nitric acid leach were passed through a reflux condenser, an empty condensate trap, and bubbled through a fritted glass dispersion tube into a gas washing bottle filled with 3 M NaOH (Fig. 12). Each vessel and the connecting lines were rinsed and sampled for fission product activity.

3.3.2 Material balances

The overall material balances for the experiments varied within $\pm 3\%$ (Table 13). The weight of residue from the voloxidized fuel was $\sim 2\%$ of the analytical weight of $(U,Pu)O_2$, compared to $\sim 1\%$ from unvoloxidized fuel:

Run no.	Rod no.	Burnup (at. %)	Voloxidation	$(U,Pu)O_2$ by anal. (g)	Residue wt (g)	Residue % of fuel wt
-1A	B-7	16.5	No	4.32	0.0494	1.14
-1BC	B-7	16.5	Yes	30.10	0.5027	1.67
-2A	C-13	17.5	No	4.77	0.0552	1.16
-2B	C-13	17.5	Yes	28.82	0.5848	2.03

The slight differences in residue weights between the two fuels are due to the greater quantities of insoluble fission products in rod C-13.

3.3.3 Isotopic analyses

The uranium and plutonium isotopic analyses for the first-leach solutions are shown in Table 14. The analyses show the expected depletion of fissile isotopes with increasing burnup and the growth of the heavier nuclides. The plutonium isotopes contributed $\sim 88\%$ of the gross alpha activity, americium $\sim 11\%$, and curium $< 1\%$.

Table 13. Weight balances for dissolution experiments with NUMEC fuel rods

Expt. no.	Rod no.	Burnup (at %)	No. of pieces	Starting wt. (g)	Leached clad (g)	(U,Pu)O ₂ by anal. (g)	Residues ^a wt (g)	Soluble fission products ^b (g)	Total (g)	Diff. Variation (%)
-1A	B-7	16.5	2	5.9	1.41	4.32	0.05	0.21	6.00	+ 1.7
-1BC	B-7	16.5	11	40.9	8.50	30.10	1.76	1.36	41.72	+ 2.0
-2A	C-13	17.5	1	6.8	1.52	4.77	0.06	0.23	6.58	- 2.8
-2B	C-13	17.5	10	40.1	8.74	28.82	0.81	1.58	39.95	- 0.1

^aIncludes residue from cladding dissolution in addition to residue from HNO₃--KF leach of the fuel.
^bCalculated from spark source mass spectrometry analysis (SSMS).

Table 14. Uranium and plutonium isotopic analyses for the first leach solutions

Isotope	Preirradiation	Rod no.	
		B-7 (%)	C-13 (%)
^{233}U	a	0.001	0.001
^{234}U	a	0.672	0.674
^{235}U	92.05	89.32	88.42
^{236}U	a	3.01	3.45
^{238}U	a	7.01	7.47
^{238}Pu	a	0.030	0.029
^{239}Pu	93.44	91.15	90.67
^{240}Pu	6.06	8.41	8.91
^{241}Pu	0.49	0.37	0.41
^{242}Pu	0.02	0.03	0.03

^aNot reported, in ref. 3.

Plutonium material balances were calculated from the mass spectroscopic (isotopic) analysis of the plutonium in the first-leach solutions and the specific activity of each plutonium isotope. For example, in FBR-1A:

Isotope	Fraction	Specific activity (counts min ⁻¹ mg ⁻¹)	Fraction x specific activity (counts min ⁻¹ mg Pu ⁻¹)
^{238}Pu	0.00042	1.97×10^{10}	8.27×10^6
^{239}Pu	0.9113	6.95×10^7	6.33×10^7
^{240}Pu	0.0841	2.70×10^8	2.27×10^7
^{242}Pu	0.00031	4.41×10^6	1.37×10^3
			9.43×10^7

3.3.4 Uranium and plutonium recovery

It may be seen (Table 15) that 99.99% of the unvoloxidized plutonium and 99.98% of the uranium were soluble in nitric acid and that only a small amount was associated with the leached cladding. This may be compared with 99.82% plutonium dissolved after 6 hr in 6 M HNO_3 in a 1974 experiment with NUMEC Series A rods containing fuels from the same fabrication batches, but at a burnup of 33,000-MWd/ton.⁴

Voloxidation of the mechanically blended fuel, however, dramatically reduced the nitric acid solubility of both the uranium and plutonium, in addition to significantly increasing the amount of insoluble fission- and corrosion-product residue (Table 16 and Fig. 20). Note that up to 2.21% of the voloxidized plutonia did not dissolve in three nitric acid leaches, compared with \sim 0.02% from the unvoloxidized plutonia.

3.3.5 Fission product recoveries

The amounts of fission products associated with each gram of $(\text{U,Pu})\text{O}_2$ in rods B-7 and C-13 varied considerably. This was suggested by the large variations in the axial count rates shown in the integral gamma scans (Fig. 3). Tables 17 and 18 summarize the experimentally determined fission product inventory in the mechanically blended portions of the rods and the quantities calculated using the ORIGEN code.^{5,6}

The data generally indicate that most of the fission product recoveries from voloxidized samples were slightly higher than those from the unvoloxidized samples and both were slightly higher than the ORIGEN estimate of concentration (except for volatile nuclides such as tritium, krypton, and iodine). A comparison of the best experimental values and the calculated values is presented in Table 19. It is known that tritium passed through the stainless steel cladding into the reactor coolant and that krypton was recovered from the fission gases in the plenum of the rod. The iodine and technetium differences, however, are still under investigation. The variability in the concentration of ^{134}Cs particularly is probably due to its volatile precursor; ^{137}Cs is also volatile and condenses in the fuel cladding gap and at the cooler ends of a fuel rod.

Table 15. Leaching of unvoloxidized, stainless steel-clad, mechanically blended (U,Pu)O₂ from NUMEC rod B-7 (2-hr each, 92-95°C)

Leach no.	Dissolvent	Fuel fraction				Cladding fraction			
		Uranium		Plutonium		Uranium		Plutonium	
		mg	% total	mg	% total	mg	% total	mg	% total
1	8 M HNO ₃	3123.70	99.72	672.50	99.78	-	-	-	-
2	3 M HNO ₃	3.48	0.11	0.59	0.09	0.02	<0.001	0.002	<0.01
3	8 M HNO ₃	4.08	0.13	0.78	0.12	0.18	<0.01	0.04	<0.01
4	8 M HNO ₃ -- 0.05 M KF	0.60	0.02	0.01	<0.01	-	-	-	-
Cladding	5 M HNO ₃ -- 2 M HCl-- 0.05 M KF	-	-	-	-	0.29	<0.01	0.07	<0.01
Residue ^a		0.04	<0.01	<0.01	<0.01	0.07	<0.01	0.01	<0.01
Total		3132	88.87	677	99.99	0.56	0.02	0.13	0.01

^aResidue: undissolved by previous leaches. Determined by fusion and analysis.

Table 16. Leaching of irradiated, stainless steel-clad, mechanically blended 20% PuO₂--80% UO₂ from NUMEC rods B-7 and C-13 (2-hr, 92-95°C)

Leach	Dissolvent	Fuel not oxidized - % total dissolved				Fuel oxidized - % total dissolved			
		Rod B-7		Rod C-13		Rod B-7		Rod C-13	
		U	Pu	U	Pu	U	Pu	U	Pu
1	8 <u>M</u> HNO ₃	99.72	99.78	99.79	99.85	99.27	97.32	99.00	96.23
2	3 <u>M</u> HNO ₃	0.11	0.09	0.12	0.38	0.36	0.45	0.60	0.81
3	8 <u>M</u> HNO ₃	0.14	0.12	0.06	0.04	0.16	0.58	0.17	0.67
4	8 <u>M</u> HNO ₃ -- 0.05 <u>M</u> KF	0.02	<0.01	0.01	0.01	0.09	1.57	0.12	2.13
Cladding	5 <u>M</u> HNO ₃ -- 2 <u>M</u> HCl	0.01	0.01	<0.01	<0.01	0.06	0.02	0.09	0.02
Residue ^a	-	<0.01	<0.01	0.02	0.01	0.05	0.06	0.03	0.06

^aResidue: undissolved by previous leaches. Determined by fusion and analysis.

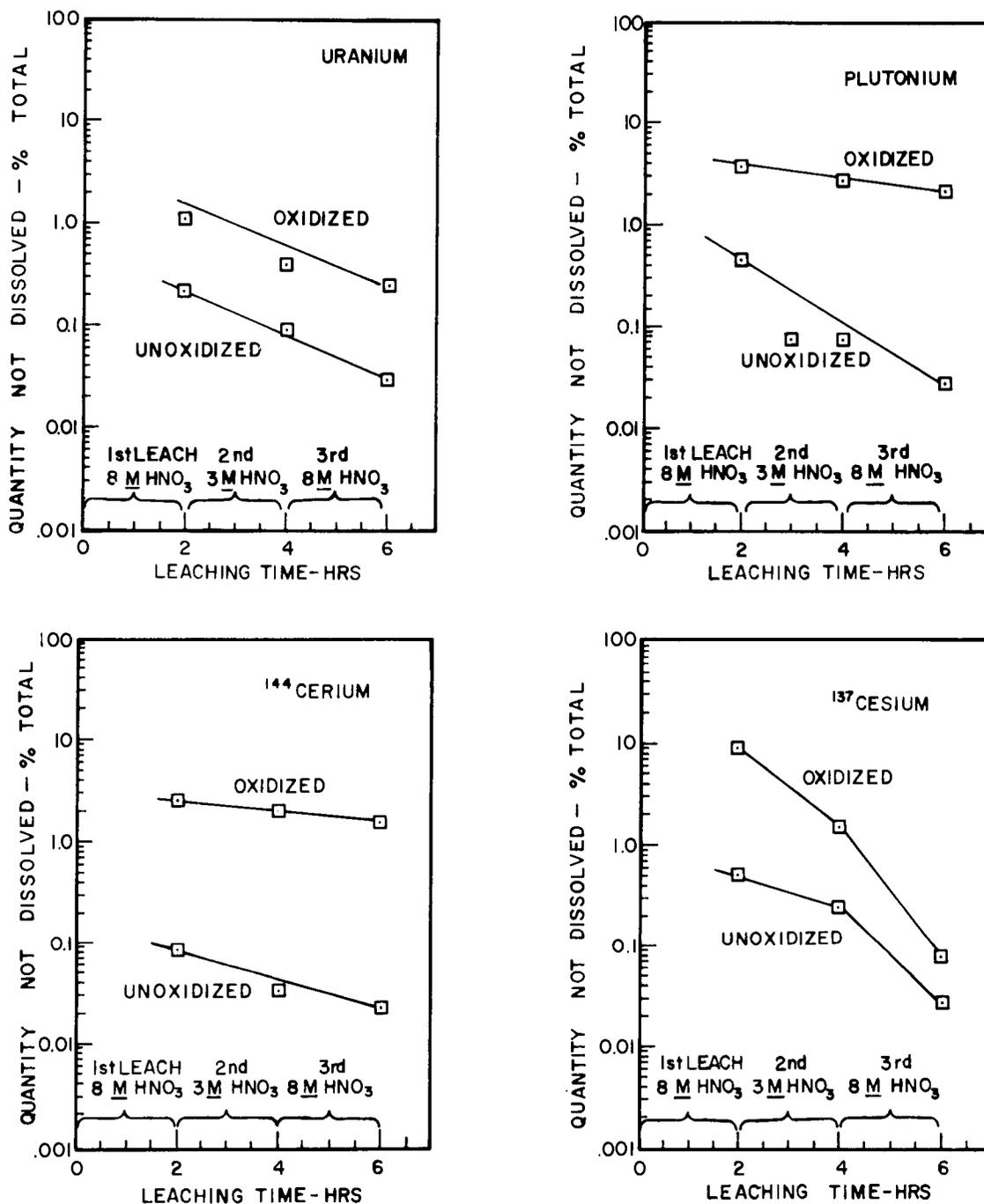


Fig. 20. Dissolution of NUMEC mechanically blended (U,Pu)O₂ and fission products in nitric acid.

Table 17. Fission product inventory found in (U,Pu)O₂ from NUMEC rod B-7 mechanically blended fuel (16.5% peak burnup)

Nuclide	ORIGEN calculated	Run 1A (not voloxidized)	Run 1BC (voloxidized)	"Best" value ORIGEN
³ H ₂ , dis sec ⁻¹ g ⁻¹	6.92 x 10 ⁷	5.93 x 10 ^{3^a}	1.01 x 10 ^{5^b}	8.57 x 10 ⁻⁵
¹⁴ C, dis sec ⁻¹ g ⁻¹	7.81 x 10 ^{4^c}	5.88 x 10 ⁴	3.25 x 10 ⁴	0.75
⁸⁵ Kr, dis sec ⁻¹ g ⁻¹	9.14 x 10 ⁸	5.58 x 10 ⁷	4.41 x 10 ⁷	0.06 ^d
⁹⁰ Sr, dis sec ⁻¹ g ⁻¹	9.03 x 10 ⁹	1.03 x 10 ¹⁰	ND ^e	1.14
⁹⁰ Tc, µg/g	2.69 x 10 ³	3.54 x 10 ²	ND ^e	0.13
¹⁰⁶ Ru, dis sec ⁻¹ g ⁻¹	1.23 x 10 ⁹	1.34 x 10 ⁹	1.71 x 10 ⁹	1.24
¹²⁵ Sb, dis sec ⁻¹ g ⁻¹	3.81 x 10 ⁸	4.06 x 10 ⁸	7.02 x 10 ⁸	1.07
¹²⁹ I, µg/g	6.86 x 10 ²	2.20 x 10 ²	1.86 x 10 ²	0.32
¹³⁴ Cs, dis sec ⁻¹ g ⁻¹	1.88 x 10 ⁸	2.87 x 10 ⁸	1.69 x 10 ⁸	1.21
¹³⁷ Cs, dis sec ⁻¹ g ⁻¹	9.66 x 10 ⁹	1.19 x 10 ¹⁰	1.06 x 10 ¹⁰	1.17
¹⁴⁴ Ce, dis sec ⁻¹ g ⁻¹	2.17 x 10 ⁹	3.13 x 10 ⁹	2.92 x 10 ⁹	1.39

^aMost tritium escapes from stainless steel cladding during irradiation.

^bSee text for comment.

^cBased on 570 ppm of nitrogen in mechanically blended fuel and no loss during irradiation.

^dRecovery from puncture gas plus fuel was 1.15 x 10⁹ dis sec⁻¹ g(U + Pu)⁻¹ or a ratio of 1.30.

^eNot determined.

Table 18. Fission product inventory found in (U,Pu)O₂ from NUMEC rod C-13 mechanically blended fuel (17.5% peak burnup)

Nuclide	ORIGEN calculated	Run 2A (not voloxidized)	Run 2B (voloxidized)	"Best" value ORIGEN
³ H ₂ , dis sec ⁻¹ g ⁻¹	8.03 x 10 ⁷	6.71 x 10 ³	7.32 x 10 ⁴	8.36 x 10 ^{-5^a}
¹⁴ C, dis sec ⁻¹ g ⁻¹	9.34 x 10 ^{4^b}	6.03 x 10 ⁴	3.79 x 10 ⁴	0.65
⁸⁵ Kr, dis sec ⁻¹ g ⁻¹	1.06 x 10 ⁹	8.88 x 10 ⁷	7.23 x 10 ⁷	0.08 ^c
⁹⁹ Tc, µg/g	3.17 x 10 ³	ND ^d	8.13 x 10 ²	0.26
¹⁰⁶ Ru, dis sec ⁻¹ g ⁻¹	1.20 x 10 ⁹	1.13 x 10 ⁹	1.31 x 10 ⁹	1.02
¹²⁵ Sb, dis sec ⁻¹ g ⁻¹	4.18 x 10 ⁸	6.42 x 10 ⁸	3.07 x 10 ⁸	1.14
¹²⁹ I, µg/g	8.09 x 10 ²	4.90 x 10 ¹	5.57 x 10 ¹	0.07
¹³⁴ Cs, dis sec ⁻¹ g ⁻¹	2.43 x 10 ⁸	5.51 x 10 ⁸	2.62 x 10 ⁸	1.08
¹³⁷ Cs, dis sec ⁻¹ g ⁻¹	1.29 x 10 ¹⁰	1.50 x 10 ¹⁰	7.53 x 10 ⁹	1.16
¹⁴⁴ Ce, dis sec ⁻¹ g ⁻¹	2.04 x 10 ⁹	2.84 x 10 ⁹	2.71 x 10 ⁹	1.36

^aMost tritium escapes through the hot stainless steel cladding during irradiation.

^bBased on 570 ppm of nitrogen in mechanically blended fuel and no loss during irradiation.

^cRecovery from puncture gas plus fuel was 1.72 x 10⁹ dis sec⁻¹ g (U + Pu)⁻¹,

^dNot determined.

Table 19. Comparison of calculated and experimental inventories of fission products in two NUMEC rods

Nuclide	Calculated		C-13 B-7	Experimental values ^a		C-13 B-7
	Rod B-7	Rod C-13		Rod B-7	Rod C-13	
³ H ₂ , dis sec ⁻¹ g ⁻¹	6.92 x 10 ⁷	8.03 x 10 ⁷	1.16	5.93 x 10 ³	6.71 x 10 ³	1.13
¹⁴ C, dis sec ⁻¹ g ⁻¹	7.81 x 10 ⁹	9.34 x 10 ⁴	1.20	5.88 x 10 ⁴	6.03 x 10 ⁴	1.03
⁸⁵ Kr, dis sec ⁻¹ g ⁻¹	9.14 x 10 ⁸	1.06 x 10 ⁹	1.16	1.15 x 10 ⁹	1.72 x 10 ⁹	1.50
⁹⁹ Tc, µg/g	2.69 x 10 ³	3.17 x 10 ³	1.18	3.54 x 10 ²	8.13 x 10 ²	2.30
¹⁰⁶ Ru, dis sec ⁻¹ g ⁻¹	1.20 x 10 ⁹	1.23 x 10 ⁹	1.03	1.53 x 10 ⁹	1.22 x 10 ⁹	0.80
¹²⁵ Sb, dis sec ⁻¹ g ⁻¹	3.81 x 10 ⁸	4.18 x 10 ⁸	1.10	4.06 x 10 ⁸	4.75 x 10 ⁸	1.17
¹²⁹ I, µg/g	6.86 x 10 ²	8.09 x 10 ²	1.18	2.20 x 10 ²	5.57 x 10 ¹	0.25
¹³⁴ Cs, dis sec ⁻¹ g ⁻¹	1.88 x 10 ⁸	2.43 x 10 ⁸	1.29	2.28 x 10 ⁸	2.62 x 10 ⁸	1.15
¹³⁷ Cs, dis sec ⁻¹ g ⁻¹	9.66 x 10 ⁹	1.29 x 10 ¹⁰	1.36	1.13 x 10 ¹⁰	1.50 x 10 ¹⁰	1.33
¹⁴⁴ Ce, dis sec ⁻¹ g ⁻¹	2.17 x 10 ⁹	2.04 x 10 ⁹	0.94	3.03 x 10 ⁹	2.78 x 10 ⁹	0.92

^aAverage or best value from Tables 17 and 18 used.

The analyses from both rods showed that more tritium was present in the voloxidized (U,Pu)O₂ than in the unvoloxidized material (e.g., 10⁵ vs 10³ dis sec⁻¹ g (U + Pu)⁻¹ in rod B-7 and 10⁴ vs 10³ in rod C-13). This is contrary to all prior experience and suggests that some portion of UO₂ from the adjacent upper axial blanket may have been included with the top of the (U,Pu)O₂ fuel column during shearing (Fig. 3). The UO₂ blankets, which operate at lower internal temperatures, were found to contain tritium concentrations up to 100 times greater than those of the (U,Pu)O₂ fuel.

Rod no.	HTO [dis sec ⁻¹ g (U + Pu) ⁻¹]	
	(U, Pu)O ₂ fuel	UO ₂ blanket
B-7	5.93 x 10 ³	4.67 x 10 ⁵
C-13	6.71 x 10 ³	3.88 x 10 ⁵

For the complete rods, the UO₂ blankets thus contained 34 and 25 times more total tritium than the (U,Pu)O₂ in rods B-8 and C-13, respectively.

The inclusion of blanket UO₂ with the mixed oxide was also suggested by isotopic analyses of the uranium in the unvoloxidized and voloxidized fuel from rod C-13; the voloxidized material contained ~0.80% more ²³⁸U and 0.95% less ²³⁵U than the unvoloxidized fuel.

Another reason for the variability of the fission product content of the fuel is the variation in the fission rate along the height of the EBR-2 core. For example, we took two random segments from the bottles of sheared, mechanically blended fuel for the unvoloxidized (i.e., control) experiments; isotopic and radiochemical analyses indicated that these segments had experienced higher burnup and perhaps higher temperatures as well. This could be explained by axial variations in the fission rate and subsequent different local burnups in EBR-2 (Fig. 21). If we assumed that the two 0.5-in. segments used in FBR-1A came from the lower inch of the mechanically blended fuel (nearer the center of the EBR-2 core), then the local-to-average fission rate was ~1.08; the remaining mechanically blended fuel, used in FBR-1B and 1C, had a local-to-average fission rate of ~0.91. An indicated ratio of 0.84

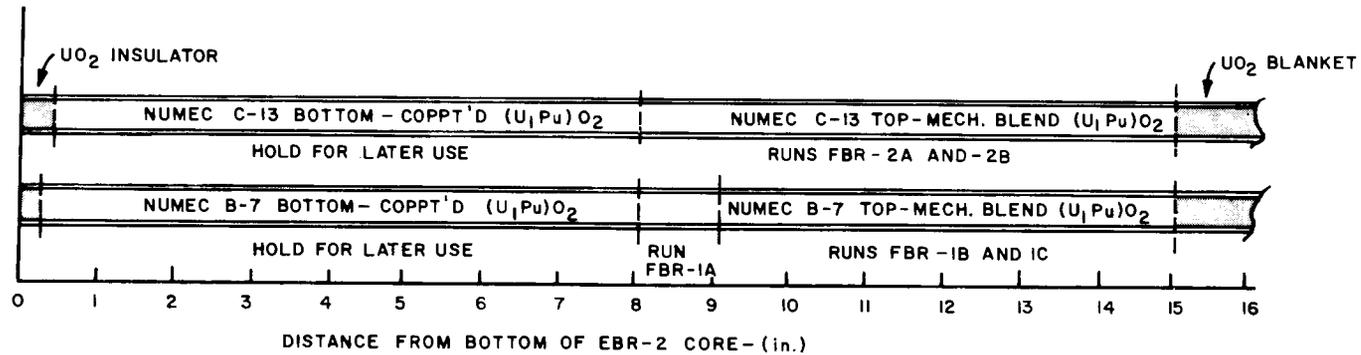
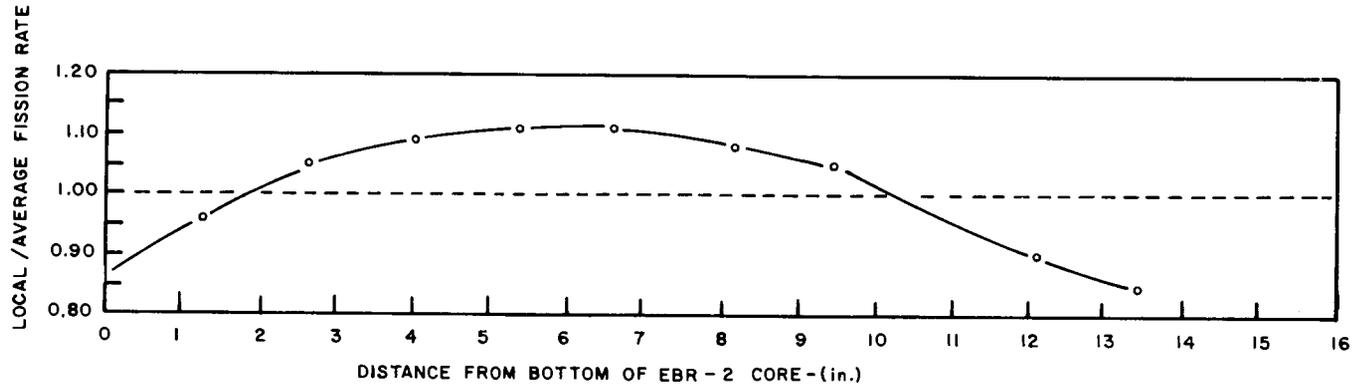


Fig. 21. Axial variation of fission rate in the core of EBR-2.

between the two samples is thus obtained (between -1A and -1BC). The ratios of various fission products in each run (krypton, iodine, cesium, and cerium) were found to have similar values (Table 18). In addition, tritium differences may also be due to the higher temperature at the center location. Finally, the fuel segments used in experiment -1A also had 1.04 times less plutonium than did the fuel used in experiment -1BC.

We therefore concluded that the control samples were not random with respect to the average flux and that the flux or fission rate variations in the core of the EBR-2 make detailed fission product characterization in these experiments most difficult. It would be better to homogenize the entire rod for such a test.

3.3.6 Volatility of fission products during dissolution

Dissolution of the fuel in nitric acid released the contained ^{85}Kr in essentially one "burst," as measured on the multichannel gamma spectrometer in the off-gas system (Fig. 22). The quantities of other fission products found in the dissolver and residue, the reflux condenser and condensate trap, and the first sodium hydroxide scrubber are summarized in Table 20. It may be seen that essentially all but the ^{14}C , ^{85}Kr , and ^{129}I remain in the dissolver or residue.

The quantities of fission products released by the dissolution of the voloxidized fuel are shown in Table 21. They were similar to the results from unvoloxidized fuel (Table 20) in that most of the nuclides, except for ^3H and ^{14}C , remained in the dissolver solution.

3.3.7 Cladding solubility

The various leach solutions were analyzed for their iron content to determine the amount of Type 316 stainless steel that had dissolved in the various reagents. Pure nitric acid dissolved ~1% of the cladding during the 2-hr leaches at 92 to 95°C, but the addition of 0.05 M KF to 8 M HNO_3 made a much more corrosive dissolvent (Table 22).

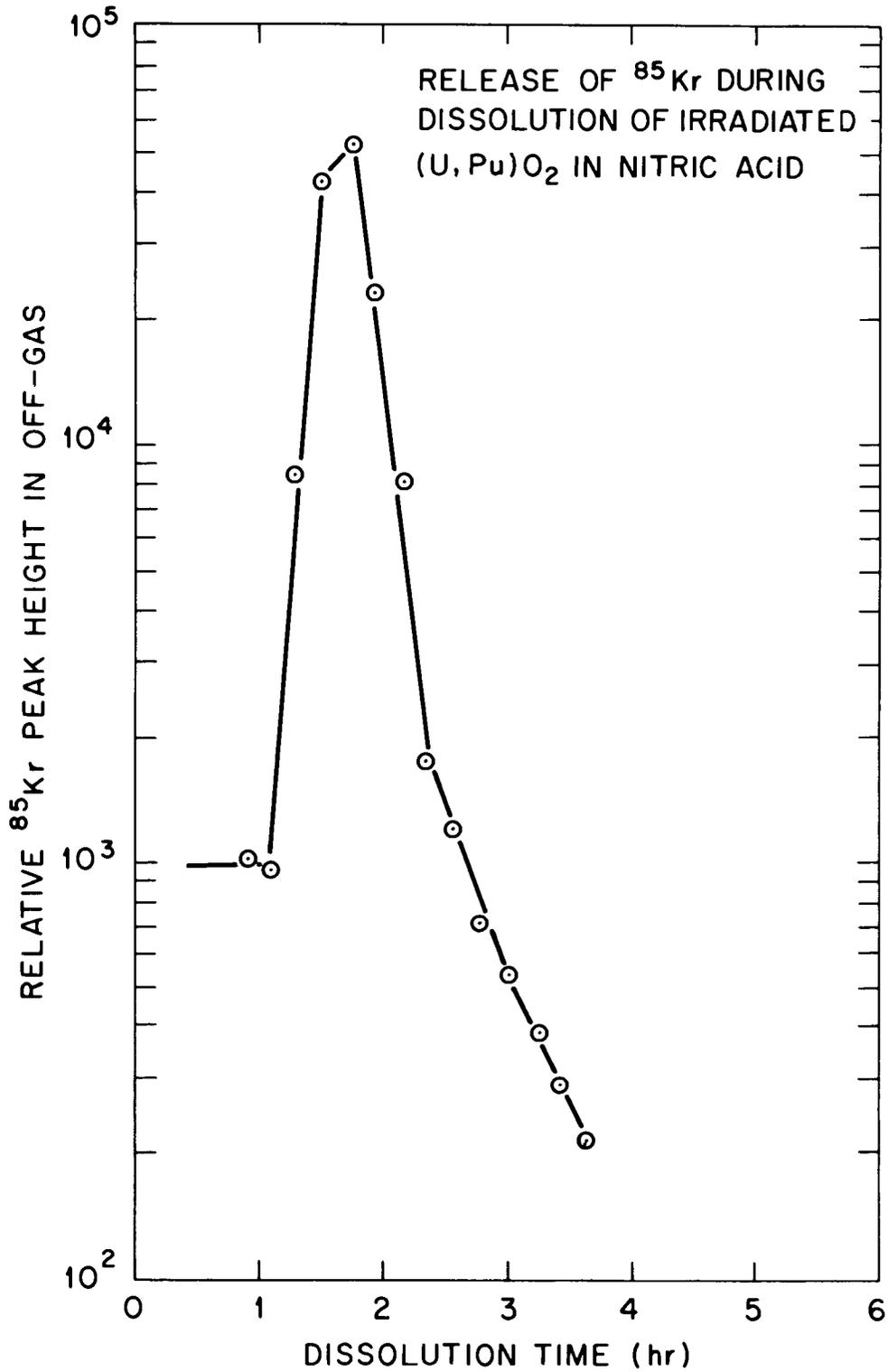


Fig. 22. Release of ^{85}Kr during dissolution of irradiated $(\text{U}, \text{Pu})\text{O}_2$ in nitric acid.

Table 20 . Release of selected fission products during the dissolution of unvoloxidized (U,Pu)O₂ in 8 M HNO₃

Nuclide	Total found [dis sec ⁻¹ g (U + Pu) ⁻¹]	Amount found - % of total		
		Dissolver and residue	Condenser and cond. traps	NaOH scrubber
Gross gamma	2.47 x 10 ^{9^a}	99.99	0.004	< 0.001
³ H ₂ O	5.93 x 10 ³	92.58	6.59	< 0.001
¹⁴ C	5.33 x 10 ⁴	3.06	< 0.01	96.94
⁸⁵ Kr	5.38 x 10 ⁷	-	-	-
¹⁰⁶ Ru	1.34 x 10 ⁹	99.99	0.003	0.001
¹²⁵ Sb	4.06 x 10 ⁸	99.99	0.004	0.001
¹²⁹ I	220.4 ^b	2.87	0.03	93.97
¹³⁷ Cs	1.19 x 10 ¹⁰	99.99	0.004	<0.001
¹⁴⁴ Ce	3.13 x 10 ⁹	99.99	0.003	<0.001

^aCounts sec⁻¹g⁻¹.
^bμg/g.

Table 21. Volatility of selected fission products during the dissolution of
voloxidized (U,Pu)O₂ in 8 M HNO₃

Nuclide	Total found [dis sec ⁻¹ g (U + Pu) ⁻¹]	Amount found - % total		
		Dissolver and residue	Condenser and trap	NaOH scrubber
Gross gamma	2.25 x 10 ⁹ ^a	~99.99	0.005	<0.001
³ H ₂ O	4.11 x 10 ³	70.01	3.70	23.11
¹⁴ C	5.77 x 10 ³	22.90	<0.01	77.19
⁸⁵ Kr	4.41 x 10 ⁷	-	-	-
¹⁰⁶ Ru	2.91 x 10 ⁹	>99.99	<0.001	<0.001
¹²⁵ Sb	7.01 x 10 ⁸	>99.99	<0.001	<0.001
¹²⁹ I	167.5 ^b	5.4	3.6	90.8
¹³⁷ Cs	1.04 x 10 ¹⁰	>99.99	0.006	<0.001
¹⁴⁴ Ce	2.92 x 10 ⁹	>99.99	0.006	<0.001

^aCounts sec⁻¹g⁻¹.

^bμg/g.

Table 22. Dissolution of Type 316 stainless steel during leaching of (U,Pu)O₂ in nitric acid

Leach no.	Reagent	Iron (mg/ml)	Stainless steel	
			(g)	(% total dissolved)
1	8 <u>M</u> HNO ₃	0.28	0.040	0.47
2	3 <u>M</u> HNO ₃	0.22	0.010	0.12
3	8 <u>M</u> HNO ₃	0.34	0.015	0.18
4	8 <u>M</u> HNO ₃ -- 0.05 <u>M</u> KF	5.11	0.304	3.58

3.4 Dissolution of Vibratorily Compacted Fuel

3.4.1 Procedure

The experimental procedure involved leaching 1-in. segments of the clad fuel for 2 hr in simmering 8 M HNO₃, separating the solution, and then washing the residue with 3 M HNO₃. A sample of the once-leached, insoluble residue was submitted for scanning electron microscopic examination.

The residue was leached again with 8 M HNO₃ for 2 hr, and then the insoluble residue and cladding were separated. The leached cladding was rinsed and dissolved in boiling 5 M HNO₃--2 M HCl. A portion of the remaining insoluble fuel residue was leached once in boiling 8 M HNO₃--0.05 M KF and twice in 12 M HCl to test the effectiveness of stronger reagents for dissolving the heavy metals, fission products, etc. The remaining solids were fused in sodium carbonate to complete the run.

3.4.2 Material balance and recovery of uranium and plutonium

An overall material balance, based on experimental weights, showed good recovery from the original 11 fuel segments (110.49 g):

Leaching cladding	34.47 g
UO ₂ recovered	52.86 g
PuO ₂ recovered	<u>10.87 g</u>
Total	98.20 g

This recovery indicates that some 12.29 g of fission products were present (i.e., 16.2% of the weight of UO₂, PuO₂, and fission products released from the cladding). The burnup of the specimen was apparently higher than the nominal 10.7 at. % (see Sect. 3.4.4).

The quantities remaining undissolved after each leach are shown in Table 23.

The two 2-hr leaches with 8 M HNO₃ dissolved 99.14% of the urania and 96.06% of the plutonia, which is fairly typical for nonhomogeneous, mechanically blended mixed-oxide fuels. The HNO₃--KF mixture dissolved all the fissile material except 0.01% of the uranium and 0.07% of the plutonium; the 12 M HCl dissolved essentially all of the remaining residue.

Table 23. Quantities of undissolved materials after leaching irradiated Vipac (U,Pu)O₂

Dissolvent	Weight undissolved		Uranium		Plutonium	
	grams	% total	grams	% total	grams	% total
Start	64.786	100.0	46.570	100.0	9.589	100.0
1st 8 <u>M</u> HNO ₃	1.817	2.80	0.883	1.90	0.596	6.22
2nd 8 <u>M</u> HNO ₃	1.203	1.86	0.398	0.86	0.376	3.92
8 <u>M</u> HNO ₃ --0.05 <u>M</u> KF	0.570	0.88	0.006	0.01	0.006	0.07
12 <u>M</u> HCl	0.598 ^a	0.92	0.001	<0.01	<0.001	<0.01

^aPossibly due to differences in drying residues.

It may also be seen that two 2-hr leaches with 8 M HNO₃, followed by rinsing the cladding and solids with dilute (3 M) HNO₃, were sufficient to dissolve the low-plutonia, high-urania [Pu/(U + Pu) = 0.167] mixed oxide that was in solid solution. The insoluble residues had Pu/(U + Pu) ratios of 0.403, 0.486, and 0.507 after the first and second nitric acid leaches and the HNO₃--KF leach, respectively. These results confirm other results which indicated that even irradiation to >100,000 MWd/ton at high linear heat ratings (12 to 15 kW/ft) will not render "poor" fuel soluble in nitric acid,¹ and that a secondary dissolvent will be required.

3.4.3 Isotopic analysis of irradiated fuel

Table 24 lists the pre- and postirradiation isotopic analyses of the uranium and plutonium.

3.4.4 Dissolver solution stability

Analyses of the clarified (centrifuged) first nitric acid leach of the mixed-oxide fuel rod are summarized in Table 25. The burnup of the specimen, based upon the total amount of ¹⁴⁴Ce in the solution, was calculated to be 16 wt %, thus confirming the value determined by weight.

The first-leach solution from ASOV-14 was recentrifuged after 4 days and again after 19 days (from the original clarification). Table 26 summarizes chemical and SSMS analyses of the two solids which were centrifuged from the solution, washed, dried, and weighed. It may be seen that the 19.4 mg of solids [equivalent to ~300 g per metric ton of (U,Pu)O₂] that precipitated after the first 4 days was different from that removed after another 15 days of aging. The first solids were richer in uranium than the secondary solids [Pu/(U + Pu) = 0.06 vs 0.25] and contained a smaller amount of noble metals. The second batch of precipitated solids contained greater amounts of barium, cesium, tellurium, noble metals, and inert materials, which are not listed. Further investigation of this phenomenon is planned. Campbell has discussed the appearance of black solids in previously clarified LWR dissolver solutions.⁷ Those solids, originally thought to have been unusually fine dissolution residues that were not removed by centrifugation, were found to appear at the rate of 20 to 25 g per day per metric ton of uranium (MTU) until ~350 g/MTU had been produced; the rate of formation then

Table 24. Isotopic analyses of uranium and plutonium before and after irradiation of ASOV-14 in EBR-2

Mass	Uranium (at. %)		Mass	Plutonium (at. %)	
	Before	After		Before	After
^{233}U	-	≤ 0.002	^{238}Pu	-	0.035
^{234}U	1.06	0.901	^{239}Pu	90.21	89.01
^{235}U	93.00	84.14	^{240}Pu	8.27	10.32
^{236}U	0.80	2.30	^{241}Pu	0.78	0.58
^{238}U	5.13	12.66	^{242}Pu	0.04	0.06

Table 25. Analysis of clarified ASOV-14 dissolver solution

Component	Concentration	Component	Concentration
HNO ₃	4.84 M	¹⁰⁶ Ru	2.38 x 10 ⁷ dis sec ⁻¹ ml ⁻¹
Uranium	195.9 mg/ml	¹²⁵ Sb	2.71 x 10 ⁷ dis sec ⁻¹ ml ⁻¹
Plutonium	39.2 mg/ml	¹²⁹ I	21.8 µg/ml
Plutonium alpha	3.72 x 10 ⁹ counts min ⁻¹ ml ⁻¹	¹³⁴ Cs	8.09 x 10 ⁷ dis sec ⁻¹ ml ⁻¹
Gross alpha	4.88 x 10 ⁹ counts min ⁻¹ ml ⁻¹	¹³⁷ Cs	1.92 x 10 ⁹ dis sec ⁻¹ ml ⁻¹
Americium alpha	7.54 x 10 ⁸ ^a counts min ⁻¹ ml ⁻¹	¹⁴⁴ Ce	1.38 x 10 ⁹ dis sec ⁻¹ ml ⁻¹
³ H	2.28 x 10 ⁴ dis sec ⁻¹ ml ⁻¹	¹⁵⁴ Eu	6.16 x 10 ⁷ dis sec ⁻¹ ml ⁻¹
⁹⁰ Sr	2.24 x 10 ⁹ dis sec ⁻¹ ml ⁻¹	Mo	500 µg/ml
⁹⁹ Tc	233.6 µg/ml	Zr	1000 µg/ml
		Fe	2000 µg/ml

^aAlpha energy: 4.78 MeV α(²³³U), 0.22%; 5.15 MeV α(²³⁹Pu, ²⁴⁰Pu), 78.5%; 5.50 MeV α(²³⁹Pu, ²⁴¹Am), 20.1%; 5.80 MeV α(²⁴⁴Cm), 0.03%; 6.11 MeV α(²⁴²Cm), 1.2%.

Table 26. Precipitates from the clarified dissolver solution

Sample no.	7D1-S2	7D1-S3 ^a
Days after first clarification	4	19
Weight, mg	19.4	17.2
Uranium, mg	16.1	1.2
Plutonium, mg	1.0	0.4
Pu/(U + Pu) ratio	0.06	0.25
Ba, µg/g	50,000	600,000
Cs, µg/g	20,000	300,000
Te, µg/g	<5,000	50,000
Pd, µg/g	3,000	30,000
Rh, µg/g	10,000	≤15,000
Ru, µg/g	30,000	80,000
Tc, µg/g	3,000	<2,000
Mo, µg/g	10,000	20,000
Zr, µg/g	<1,000	2,000
Fe, µg/g	50,000	300,000

^aOther inert elements not listed.

decreased. Campbell's preliminary analyses showed them to be distinctly different from the dissolution residues; typical emission spectrographic analyses indicated the presence of 3 to 4 wt % Pd, 5 to 10 wt % Ru, 8 to 14 wt % Rh, 1 to 6 wt % Mo, 0.2 to 6 wt % Zr, plus other elements.

Material balances on some of the radioactive fission products reaffirmed earlier results that indicated very little ruthenium would dissolve (Table 27). Antimony and technetium were distributed between the residues and the leaches.

3.4.5 Volatile fission products

Volatile fission product concentrations were measured in the first nitric acid leach (dissolver solution), in a condensate vapor trap, and in two successive sodium hydroxide scrubbers (Table 28). The results reaffirm those in the experiment with NUMEC fuel; that is, essentially all fission products except ^{14}C , ^{85}Kr , and ^{129}I remain in the dissolver.

3.4.6 Dissolution residue characterization

The final residues from the leachings of the Vipac mixed-oxide fuel amounted to $\sim 0.92\%$ of the initial fuel weight. The scanning electron microscope (Fig. 23) showed images of very small particles ($\leq 2\text{-}\mu\text{m}$ diam) and x-ray dispersion lines for molybdenum, technetium, barium, cesium, and cerium. Emission spectroscopy indicated that the major constituents were molybdenum, ruthenium, technetium, rhodium, and palladium. Spark source mass spectrometry and semiquantitative emission spectroscopy data on three residue samples from rod ASOV-14 indicated quite similar compositions for the noble metal fission products (Table 29). Table 30 compares our results with those of others using electron microprobe analyses of noble metal inclusions in irradiated $(\text{U,Pu})\text{O}_2$ fuel specimens. The results are quite similar; some variation would be due to the numerous chemical treatments our dissolution residues received. Optical microscopic examination showed discrete reddish-orange particles on a black matrix.

Table 27. Solubility of selected fission products

Fission product	Predicted total ^a	Total found	Total insoluble	Insoluble, % total found
⁹⁹ Tc, mg	136.4	86.7 ^b	33.2	38.30
¹⁰⁶ Ru, dis/sec	1.50 x 10 ¹¹	1.01 x 10 ¹¹	9.45 x 10 ¹⁰	93.56
¹²⁵ Sb, dis/sec	3.63 x 10 ¹⁰	1.63 x 10 ¹⁰	8.95 x 10 ⁹	54.83
¹³⁷ Cs, dis/sec	6.01 x 10 ¹¹	5.46 x 10 ¹¹	2.54 x 10 ⁹	0.47
¹⁴⁴ Ce, dis/sec	6.67 x 10 ¹¹	3.29 x 10 ¹¹	3.74 x 10 ⁹	1.14

^a Approximations predicted by ORIGEN; exact irradiation conditions uncertain.

^b Since intermediate leaches were not analyzed for ⁹⁹Tc, the total found is probably low.

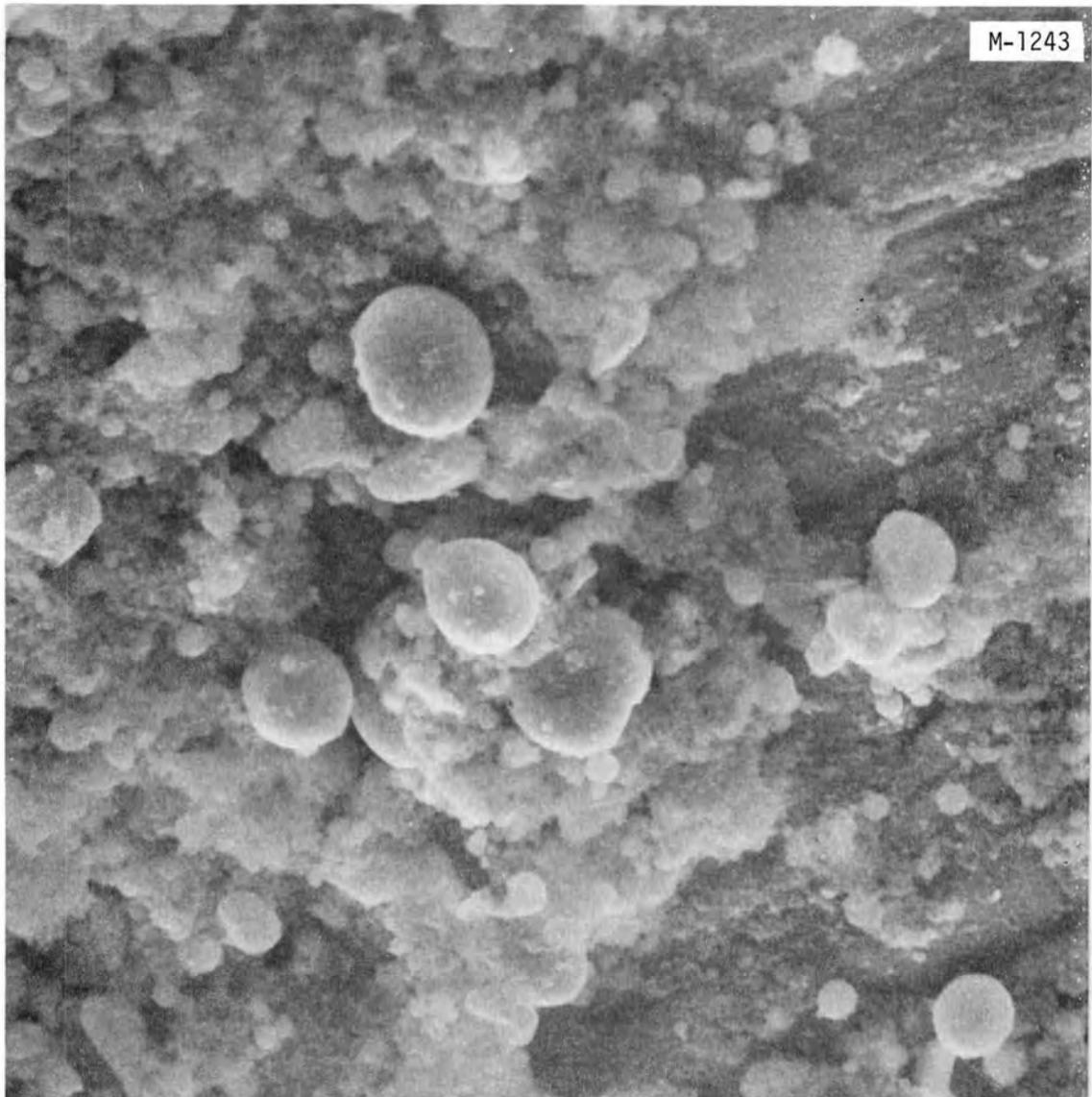
Table 28. Distribution of volatile fission products during dissolution of (U,Pu)O₂ rod ASOV-14 (10.7% burnup)

Fission product	Total found		% of total found in			
	dis sec ⁻¹	% ORIGEN ^a	Dissolver solution	Vapor trap	Scrubber 1	Scrubber 2
³ H ₂ O	6.03 x 10 ⁶	0.15	86.62	12.89	0.07	0.42
¹²⁹ I	1.62 x 10 ⁴ ^b	30.0	30.81	0.41	69.93	0.85
¹⁴ C	1.40 x 10 ⁶	34.0	NA ^c	Trace	100.0	Trace
¹⁰⁶ Ru	1.01 x 10 ¹¹	67.0	6.43	0.003	0.012	<0.001

^aApproximations only (uncertain irradiation conditions).

^bμg.

^cNot analyzed, but presumed small in highly acidic solution.



—→ | | ←—
1 μ m

Fig. 23. Scanning electron microscope view of residue from the dissolution of $(U,Pu)O_2$.

Table 29. Composition of residue after leaching with HNO_3 , $\text{HNO}_3\text{--KF}$, and HCl acids^a

Residue no.	7D1-S1	7D2-S1	7D4-7
Final residue weight, g	0.0822	0.3695	0.0718
Weight of noble metals in final residue, g	0.0388	0.1375	0.0177
Composition, % of noble metal weight			
Palladium	9	2	8
Rhodium	2	2	4
Ruthenium	63	54	61
Technetium	11	19	8
Molybdenum	15	34	20

^aComposition without presence of Fe, Cr, Ni, Mn, Al, Si, and other materials introduced during sample fusion and dissolution.

Table 30. Comparison of dissolution residue with noble metal inclusions in irradiated mixed-oxide fuels

	Particle or inclusion (wt %)					
	This work	Ewart ^a	Sauvage ^b	Johnson ^c	Bramman ^d	O'Boyle ^e
Palladium	2-9	5	-	2-7	2	2
Rhodium	2-3	11	3.3	8-16	7	13
Ruthenium	54-63	37	34.4	30-51	32	49
Technetium	8-19	10	16.7	12-20	15	17
Molybdenum	15-23	38	45.6	22-51	41	20

^aF. T. Ewart, Electron Probe Analysis of Mixed Oxide Fuels from Experimental SP-993, AERE-R-7322 (May 1973).

^bR. Sauvage, Redistribution During Irradiation of Constituents and Fission Products in Aluminum-Plutonium Mixed Oxide Fuel, CEA-R-4649 (January 1975).

^cC. E. Johnson, "Chemistry of Irradiated Fast Reactor Fuels and Materials," in Chemical Engineering Division Annual Report - 1970, ANL-7775 (April 1971).

^dJ. I. Bramman et al., "Metallic Fission Product Inclusions in Irradiated Oxide Fuels," J. Nucl. Mater. 25, 201-15 (1968).

^eD. R. O'Boyle et al., Trans. Am. Nucl. Soc. 11, 101 (1968).

Brown et al.,² at ANL, in their postirradiation examination of sibling rods ASOV-5 and ASOV-6, at 2.7 at. % burnup, commented on the metallic-appearing inclusions (of up to 6- μ m diam) in the columnar and equiaxed grain regions of those rods. The inclusions consisted mainly of ruthenium, molybdenum, and technetium, with small amounts of rhodium and palladium. They noted that the ruthenium and molybdenum content varied with radial location; the ruthenium decreased and the molybdenum increased radially from the central void (i.e., down the thermal gradient). The Ru-Mo-Tc inclusions were heavily concentrated at the junctures between long and short columnar grains and between the columnar and equiaxed grains. The suggested variations in the composition of the inclusions may be attributed to the radial changes in the oxidation state of the fuel^{8,9} due to irradiation.

3.4.7 Leached cladding characterization

The stainless steel cladding of rod ASOV-14 was dissolved in dilute aqua regia (5 M HNO₃--2 M HCl), after previously undergoing the first fuel dissolution in 8 M HNO₃, two rinses in boiling 3 M HNO₃, and four rinses in cold 3 M HNO₃. We obtained 0.41 g (~1%) of the insoluble residue from the original 34.47 g of cladding. The residue contained 0.0004 g of uranium and 0.0001 g of plutonium; the 750 ml of aqua regia solution contained 0.0015 g of uranium and 0.0001 g of plutonium. These totals are equivalent to 0.004% of the uranium in the rod and 0.002% of the plutonium. (Further tests are necessary to establish the variability of these quantities and to set limits on the possibility of cross-contamination of the leached cladding during handling in the hot cell.)

The only detectable fission product associated with the cladding was ¹³⁷Cs. Approximately 0.023% of the total ¹³⁷Cs was found in the aqua regia solution ($\sim 1.6 \times 10^5$ dis sec⁻¹ ml⁻¹). The activation products ⁵⁴Mn and ⁶⁰Co were higher than the ¹³⁷Cs by factors of 46 and 41, respectively. More molybdenum was present in solution than could have come from Type 304 stainless steel cladding (0.02 wt %); fission product molybdenum may have been associated with the cesium.

4. SUMMARY AND CONCLUSIONS

Exploratory tests were made of the effects of fabrication, irradiation, and voloxidation on the release of fission products and on the nitric acid solubility of mechanically blended (U,Pu) O_2 reactor fuels. The three experimental, mechanically blended stainless steel-clad specimens had been irradiated in the EBR-2 at a burnup of from 10.7 to 17.5 at. % and had decayed \sim 3 years before testing. The tests consisted of gamma scanning, fission gas puncture, cutting the rods into short lengths, voloxidation, and dissolution in nitric and other acids. The distribution of selected fission products and the uranium and plutonium was followed throughout the experiments.

A dissolution experiment was conducted using vibratorily compacted Dynapak (U $_{0.8}$ Pu $_{0.2}$) O_2 from an ANL irradiation experiment to provide a plutonium-rich residue for the testing of reagents to dissolve plutonia. We found that irradiation in the EBR-2 to a nominal 10.7 at. % at linear heat ratings of >12 kW/ft did not render the plutonium in the fuel soluble in nitric acid through formation of a solid solution with UO_2 . Three 2-hr leaches in 8 M HNO_3 left 3.75% of the original plutonium undissolved. A residue of noble metal fission products, consisting of major proportions of ruthenium, molybdenum, and technetium, and smaller proportions of palladium and rhodium, also remained after dissolution. The source of the residue was most likely the nitric acid-resistant fission product inclusions collected in the grain boundaries of the oxide fuel.

The NUMEC fuel specimens were used in two other experiments on the effect of voloxidation of irradiated, mechanically blended (U $_{0.8}$ Pu $_{0.2}$) O_2 in air at 650°C. The tests indicated that up to 96% of the tritium, 87% of the ^{14}C , and 53% of the ^{85}Kr were volatilized. With the exception of cesium, only small quantities of fission products ($\leq 0.2\%$ of the total) coated the inner surfaces of the voloxidizer, $<0.1\%$ of the total ^{106}Ru and ^{144}Ce was transferred to downstream locations. Up to 3 to 4% of the total ^{137}Cs was volatilized in a 3- to 4-hr voloxidation period. As much as 30% of the volatilized cesium passed through a sintered-metal filter with a pore size of 35 μm into the off-gas system, where it was deposited on the tubing walls at temperatures between 350 to 550°C. Up to 81% of the ^{129}I also passed into the off-gas system and was adsorbed on activated

charcoal. The voloxidation also increased the amount of plutonium that would not dissolve in nitric acid, without the use of fluorides, from 0.025% to ~2%. Dissolution of a UO_2 axial blanket from the same rods at a lower operating temperature showed concentrations of up to 100 times more tritium in the UO_2 than in the higher-temperature (U,Pu) O_2 core.

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6. APPENDIX

From the ORIGEN calculations for the irradiation of NUMEC (U,Pu)O₂ to an approximate burnup of 17 at. %, the reactor output, based on a 1000-kg input of uranium and plutonium [1136.4 kg (U,Pu)O₂], was listed in Sect. 3.2.2. Puncture gas analyses have indicated that all of these outputs, except for ~5% of the total krypton and xenon, was released from the fuel during irradiation (Sect. 2.2.2). The adjusted totals would then be representative of the fuel contents fed to the voloxidizer.

Voloxidizer feed:	0.77 kg Xe + Kr (the ~5% remaining in the fuel),
	113.2 kg fission product oxides,
	<u>1007.8</u> kg (U,Pu)O ₂ [886.8 kg U + Pu],
	1121.77 kg total fuel, excluding cladding.

Thus, the weight of (U,Pu)O₂ would amount to 89.84% of the total fuel weight (not including cladding) entering the voloxidizer.

According to analyzed values for uranium and plutonium, the ratio of plutonium to uranium in the fuel is:

$$\text{Pu/U} + \text{Pu} = 0.185.$$

Then, for Pu = 1,

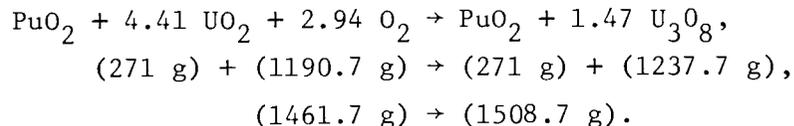
$$1/\text{U} + 1 = 0.815,$$

$$1 = 0.185 \text{ U} + 0.185$$

$$0.815 = 0.185 \text{ U},$$

$$\text{U} = 4.41.$$

Based on 1 mole of PuO₂ for the oxidation of the (U,Pu)O₂ fuel, the stoichiometric equation would be



Thus, the weight increase of 47 g represents a 3.22% increase in the weight of the (U,Pu)O₂ for full conversion of the UO₂ to U₃O₈.

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