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HEAD-END REPROCESSING STUDIES WITH H. B. ROBINSON-2 FUEL

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HEAD-END REPROCESSING STUDIES WITH

H. B. ROBINSON-2 FUEL

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ABSTRACT

A series of exploratory hot-cell tests was made to determine the effects of voloxidation on tritium, fission product removal, and on subsequent steps of the light water reactor fuel cycle. The 100-g scale experiments indicated that >99% of the tritium, 50% of the ^{14}C , 6% of the ^{85}Kr , and smaller amounts of other elements were volatilized and collected when the UO_2 was roasted in air at 480°C for ~ 4 hr. There was little effect on the solubility of the uranium and plutonium in HNO_3 . The experiments indicated that the first 2-hr leach usually dissolved >99.9% of the uranium and plutonium, and varying amounts of fission products, in voloxidized or unvoloxidized fuel. Two additional HNO_3 leaches on the unvoloxidized fuel dissolved all but 0.004% of the plutonium; the additional leaches on the voloxidized material left $\sim 0.02\%$ of the plutonium.

1. SUMMARY AND CONCLUSIONS

One proposal for the retention of tritium within a light water reactor fuel processing plant is the application of voloxidation; that is, the sheared fuel is roasted in air or oxygen to convert the solid UO_2 to powdered U_3O_8 and oxidize the tritium to HTO . The tritiated water vapor can be carried in the gas stream to scrubbers or absorbents where it may be immobilized. This would permit the tritium to be separated before the fuel is dissolved into the aqueous system of the plant. A series of exploratory hot-cell tests was conducted on a 100-g scale to determine the effectiveness of voloxidation in removing

tritium from Zircaloy-clad UO_2 and its effect on subsequent processing steps. Three-year-decayed 31,000-MWd/ton burnup UO_2 fuel from the Carolina Power and Light Company's H.B. Robinson-2 Reactor was used for these baseline tests under reference conditions of 12-rpm rotation, 480°C , and using air as the oxidant.

The exploratory tests indicated that tritium was essentially quantitatively removed from the UO_2 fuel; however, only 60 to 70% of the tritium released from the UO_2 was accounted for by leaching silica gel or molecular sieve absorbents located outside the hot cell. The Zircaloy cladding contained a large fraction of the total tritium, but did not appear to be affected by the voloxidation. Up to 6% of the ^{85}Kr in the fuel, 1% of the ^{129}I , and $\sim 50\%$ of the ^{14}C were volatilized after ~ 3 to 4 hr of roasting. The stainless steel voloxidizer walls were coated with small quantities ($\sim 10^{-2}\%$) of ^{106}Ru , ^{125}Sb , $^{134-137}\text{Cs}$, ^{144}Ce , and ^{154}Eu ; however, only about 0.22% of the ^{129}I in the fuel was deposited on the walls. Smaller amounts of solid fission products ($\sim 10^{-3}\%$) passed a 35- μm pore size, sintered metal filter at the gas exit of the voloxidizer.

The voloxidation had little effect on the solubility of the U_3O_8 and/or PuO_2 in 7 M HNO_3 in the temperature range 92 to 95°C . Recoveries were $>99.97\%$ after 2 hr of leaching. The weight of the HNO_3 insoluble residue, however, increased from ~ 0.2 to ~ 0.6 wt % of the UO_2 . This fission product residue was composed primarily of ruthenium, palladium, rhodium, molybdenum, technetium, and small amounts of zirconium.

The preliminary hot-cell tests using the fuel from one commercial light water reactor indicated that voloxidation under one set of conditions resulted in the removal and retention of essentially all of the tritium and about one-half of the ^{14}C from the fuel before it was dissolved in HNO_3 . These promising results suggest that hot-cell work should be continued to determine the optimum conditions for the removal of these long-lived fission products from irradiated fuel. Future experiments are being planned to test the effects of sheared length, time, temperature, oxygen content, speed of rotation, and other variables on the release of volatile fission products and on the dissolution of the fuel in HNO_3 .

2. INTRODUCTION

The Oak Ridge National Laboratory is conducting flowsheet studies for the Alternative Fuel Cycle Technologies Program under the organizational lead of the Savannah River Operations Office (SRO) of the Department of Energy and the DuPont Savannah River Laboratory (SRL). One of these tasks, Voloxidation and Dissolution, includes the testing of steps for the proposed reprocessing flowsheets with irradiated fuels from typical commercial power reactors. A number of dissolution, solution stability, and solvent extraction tests have been reported by Campbell at ORNL¹⁻⁵ and by researchers at SRL.⁶⁻⁸ This document describes hot-cell experiments using irradiated UO_2 from the Carolina Power and Light Company's H. B. Robinson-2 Reactor, located in Hartsville, South Carolina. These baseline (reference conditions) tests involved shearing segments of the long fuel rods into 1-in. pieces, subjecting some of the fuel segments to voloxidation at 480°C ,* and then dissolving the oxidized or unoxidized uranium oxides in simmering HNO_3 to compare the effects of the voloxidation treatment. Future tests will include parametric studies of loading, cladding length, time, temperature, and atmosphere during voloxidation on the removal of tritium and on the subsequent processing steps, dissolution, and feed treatment.

Early data on the release of fission products upon oxidation of irradiated UO_2 and $(\text{U,Pu})\text{O}_2$ were summarized in a 1973 ORNL report.⁹ In general, it was found that >90% of the fission product tritium was volatilized when UO_2 was oxidized to U_3O_8 ; however, recovery of the tritium from the off-gas stream was not a primary objective of the earlier hot-cell tests.

*Voloxidation - a conceptual treatment of irradiated reactor fuel for the volatilization, collection, and retention of fission product tritium before the fuel is dissolved in HNO_3 . Baseline experiments consisted of tumbling the Zircaloy-clad UO_2 in a flowing stream of air at 480°C (the apparent optimum temperature) to oxidize the UO_2 to U_3O_8 ; this releases tritium as HTO or T_2O to the gas stream, along with varying amounts of certain other fission products.

3. EXPERIMENTAL

3.1 Reactor Fuel

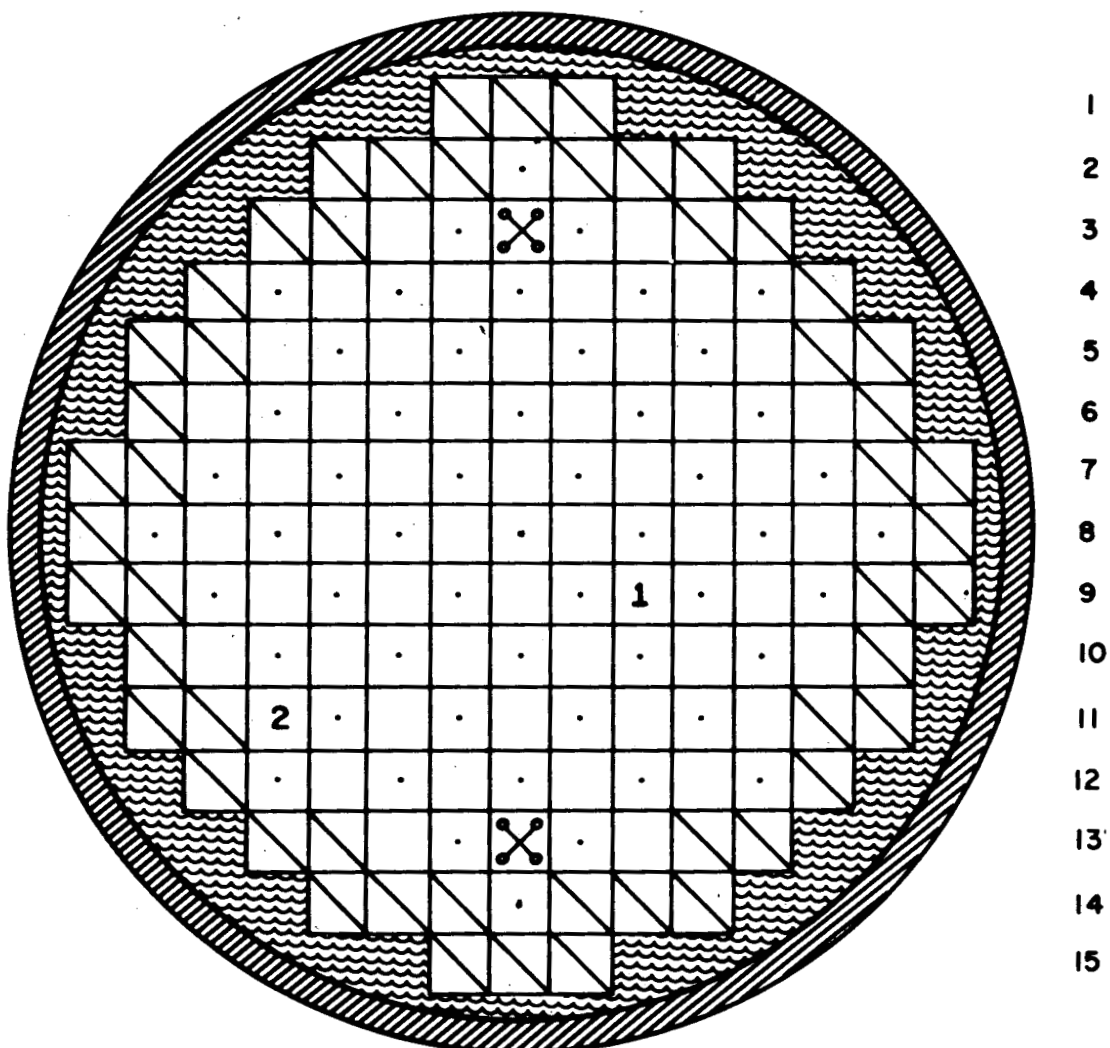
The Carolina Power and Light Company H. B. Robinson-2 Reactor is a 665-MW(e) pressurized water reactor (PWR) located in Hartsville, South Carolina. The core consists of 157 assemblies (Fig. 1), each containing 204 UO_2 -filled fuel rods (Fig. 2). The rods are about 152 in. long and have a 144-in.-long active section stacked with 0.367-in. OD by 0.600-in.-long sintered UO_2 pellets, which are slightly enriched in ^{235}U , and a 6.83-in. gas plenum. The 0.024-in.-thick Zircaloy-4* cladding has an 0.422-in. OD. Assembly B05 was loaded into the first core of H.B. Robinson-2 in 1971 and was irradiated through two cycles in positions F-9 and M-11 (Fig. 1) to a peak burnup of $\sim 31,000$ MWd/ton and an average burnup of $\sim 28,000$ MWd/ton. The average power was ~ 7 kW/ft at beginning of life (BOL) and ~ 5.3 kW/ft at end of life (EOL). The assembly was discharged on May 6, 1974, at the end of Cycle 2. Rod No. G-10 was located near the center of Assembly B05 (solid dot on Fig. 2); its approximate axial power profile after the second cycle is shown in Fig. 3.¹⁰ The segments used in these baseline tests (Nos. 5 and 6) were located just above the center of the rod.

3.2 Equipment

Figure 4 shows the hand-operated, single-rod hydraulic shear. A 2-in.-diam hydraulic piston drives a hardened steel blade vertically through fuel rod segments 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 (Hastings-Raydist mass flow meters) and humidified by bubbling through water before they are introduced into the cell. The gases entering and exiting a rotating stainless steel voloxidizer pass through 35- μm sintered metal filters and then into a calibrated cooling zone on the shaft of the voloxidizer, which contains inserts for measuring the deposition of volatile fission products. The gases then pass through a heated filter pack for removal

*1.2-1.7 wt % Sn, 0.18-0.24 wt % Fe, 0.07-0.13 wt % Cr, 70 ppm maximum Ni, balance Zr.

ORNL DWG. 77-1244 RI



R P N M L K J H G F E D C B A

CORE ARRANGEMENT-H.B.ROBINSON-2 REACTOR

SHOWING LOCATION OF ASSEMBLY B05
DURING FIRST (1) AND SECOND (2) CYCLES





-  PRIMARY-SECONDARY SOURCE ASSEMBLY
-  REGION 1 (enrichment 1.85%) 53 ASSEMBLIES
-  REGION 2 (enrichment 2.55%) 52 ASSEMBLIES
-  REGION 3 (enrichment 3.10%) 52 ASSEMBLIES

Fig. 1. Core arrangement - H. B. Robinson-2 Reactor.

ORNL DWG 77-1246

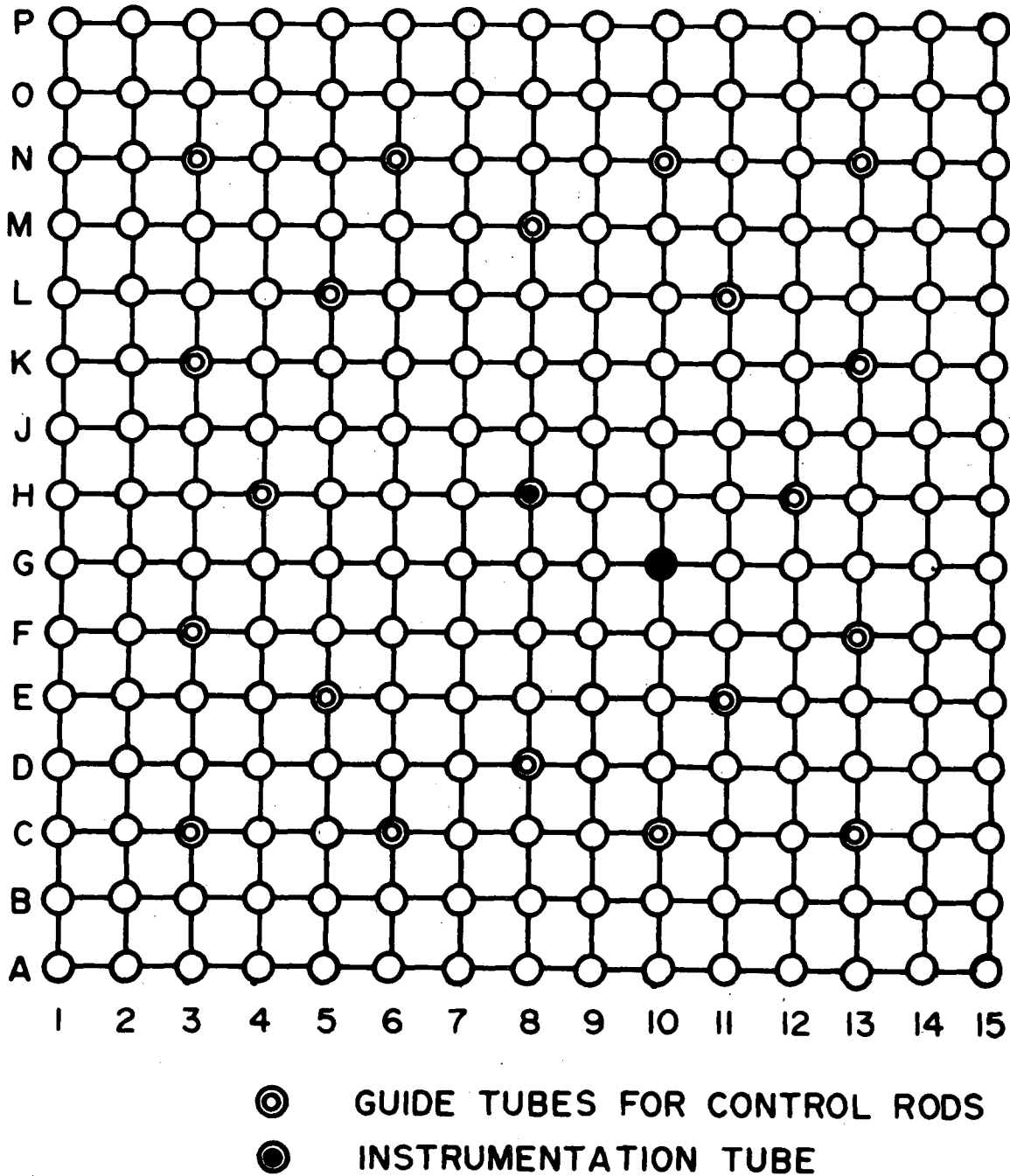


Fig. 2. Schematic of fuel rod array in H. B. Robinson-2 Assembly B05.

ORNL DWG 77-1245A

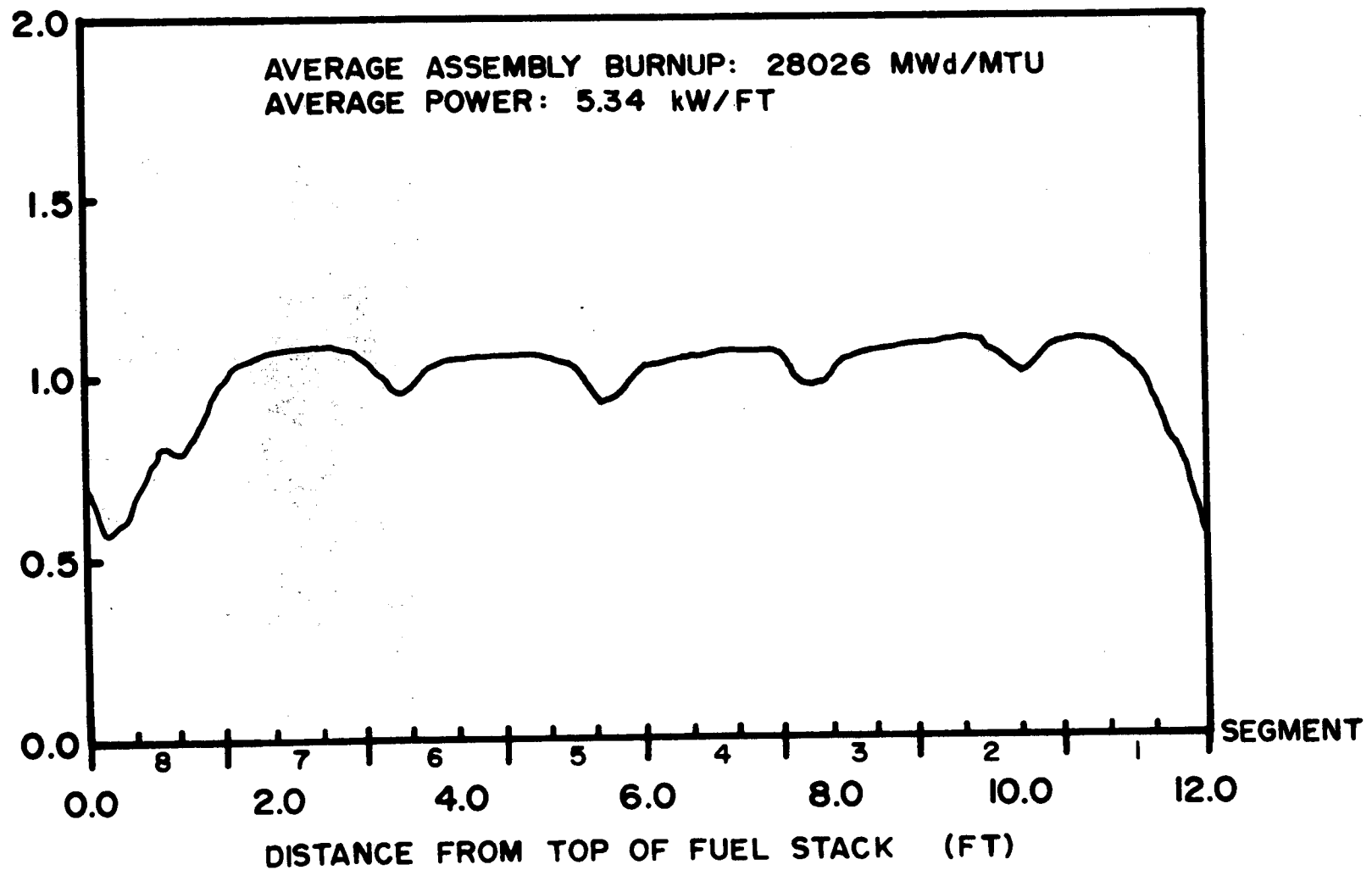


Fig. 3. Carolina Power and Light H. B. Robinson-2 Reactor,
axial power profile, Cycle 2, Assembly B05.

ORNL PHOTO 0979-76

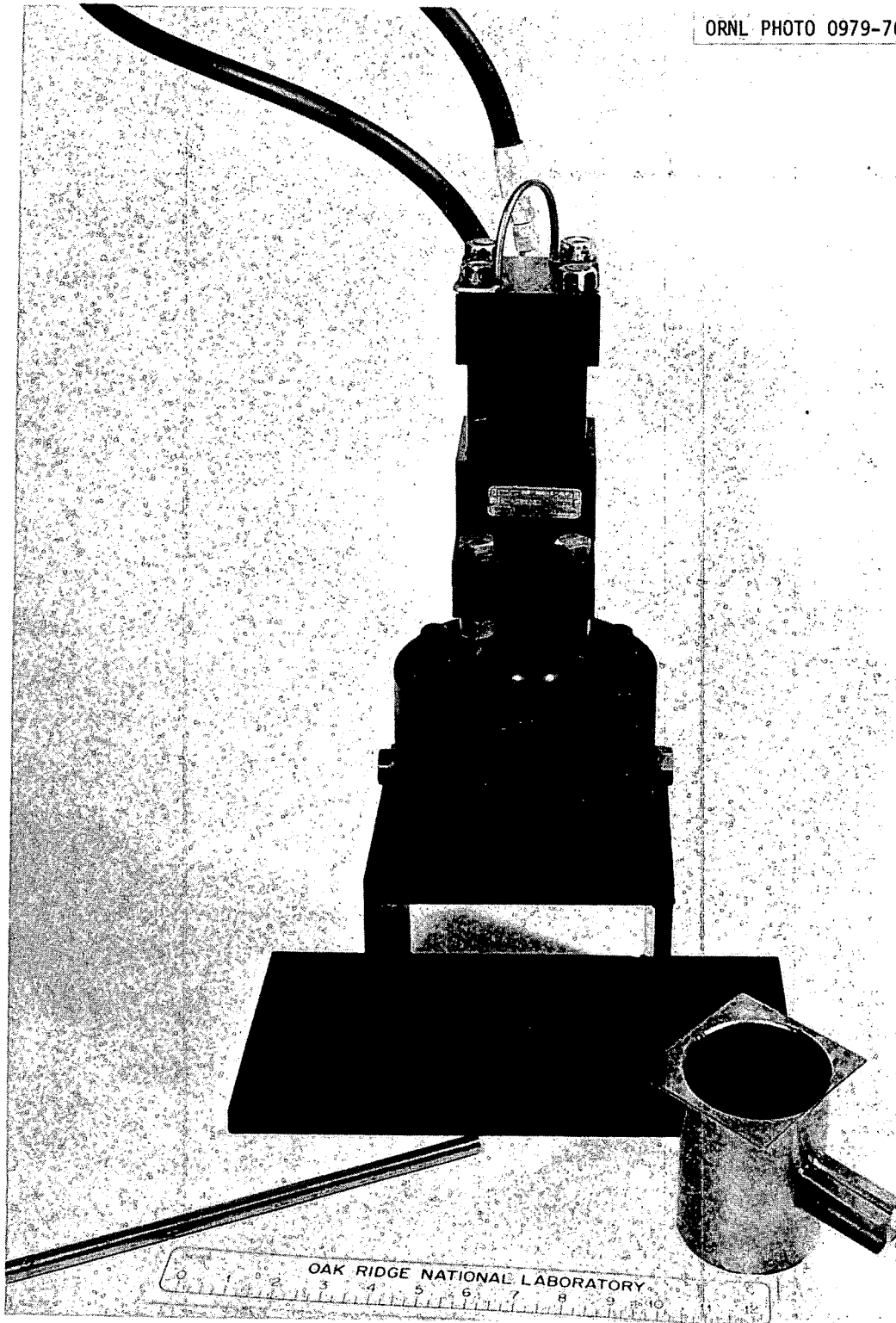


Fig. 4. Single-pin hydraulic shear.

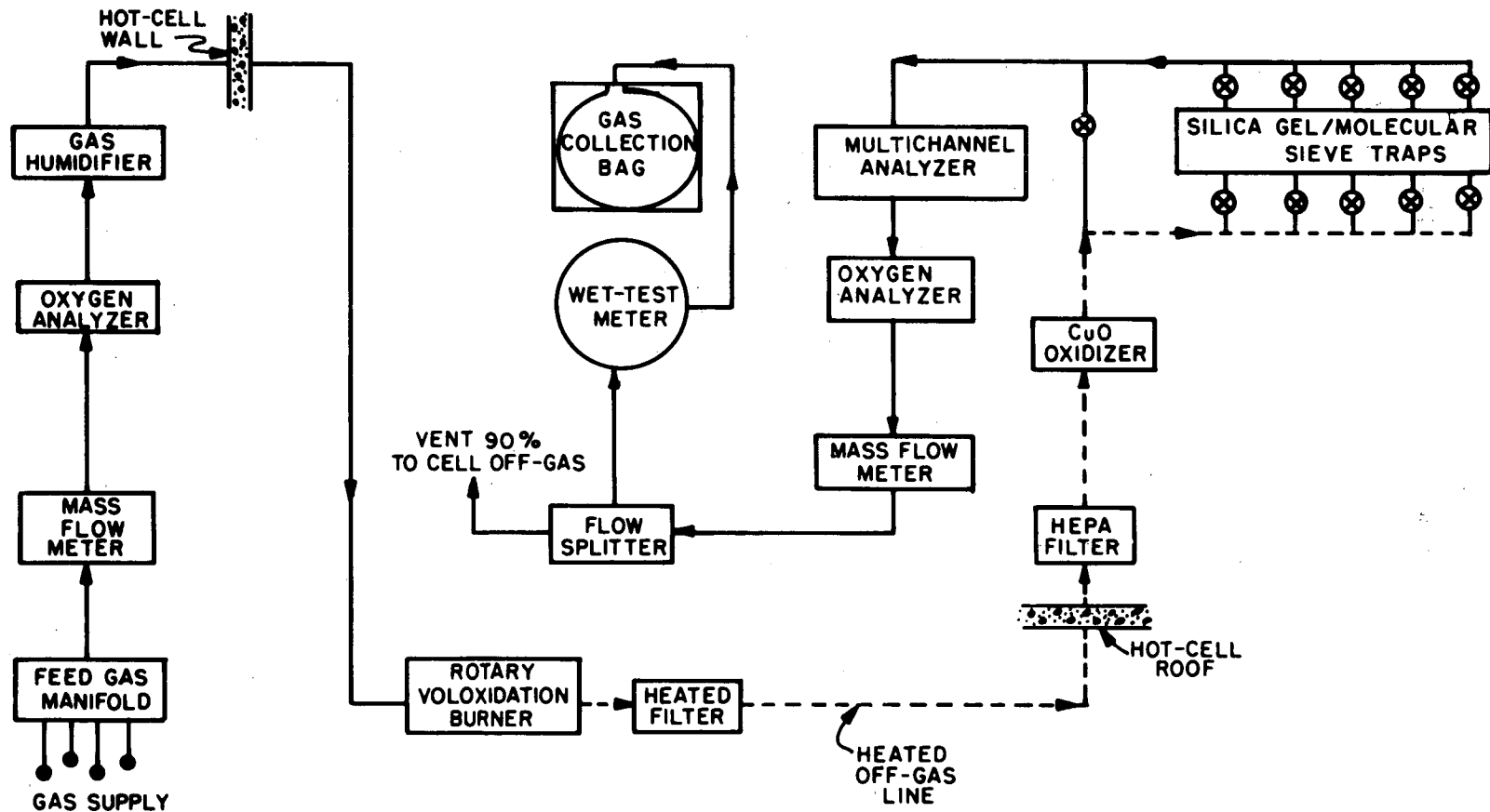


Fig. 5. Schematic diagram of hot-cell voloxidation equipment.

of particulates and exit 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 (if any) to HTO and $^{14}\text{CO}_2$, and then pass to silica gel and Type 4A molecular sieve traps for capture of the tritiated water. The oxygen content of the exit gas is continuously measured (International Biophysics Corporation differential oxygen meter) for comparison with the incoming oxygen content (air), and the ^{85}Kr content is monitored with a multichannel gamma spectrometer (MCA). Finally, 10% of the flow is collected as a composite sample for ^{14}C and ^{85}Kr assay.

Figure 6 is a photograph of the feed gas manifold; Fig. 7 gives a general view of the cell interior; Fig. 8 shows the penthouse area tritium traps and associated equipment; and Fig. 9 shows the ^{85}Kr analyzer, exit gas manifold, and collection system. The disassembled rotary voloxidizer and fission product deposition inserts are shown in Fig. 10, whereas Fig. 11 indicates how the vertical, heated filter pack assembly (r) is connected between the voloxidizer (e) and the heated off-gas line. The dissolution experiments were conducted with the apparatus that is depicted schematically 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 fitted with fritted glass gas dispersion tubes. A 600°C copper oxide bed is used to convert elemental tritium to HTO before it reaches the second trap and scrubber. The filtered gas stream is passed through a MCA to determine the rate of ^{85}Kr evolution. Cessation of the ^{85}Kr evolution is used to indicate completion of the dissolution. The off-gas is collected for sampling in a special plastic bag. There is a holdup of $\sim 1800 \text{ cm}^3$ (a delay of $\sim 27 \text{ min}$) between the dissolver and the MCA.



Fig. 6. Feed gas manifold and controls.

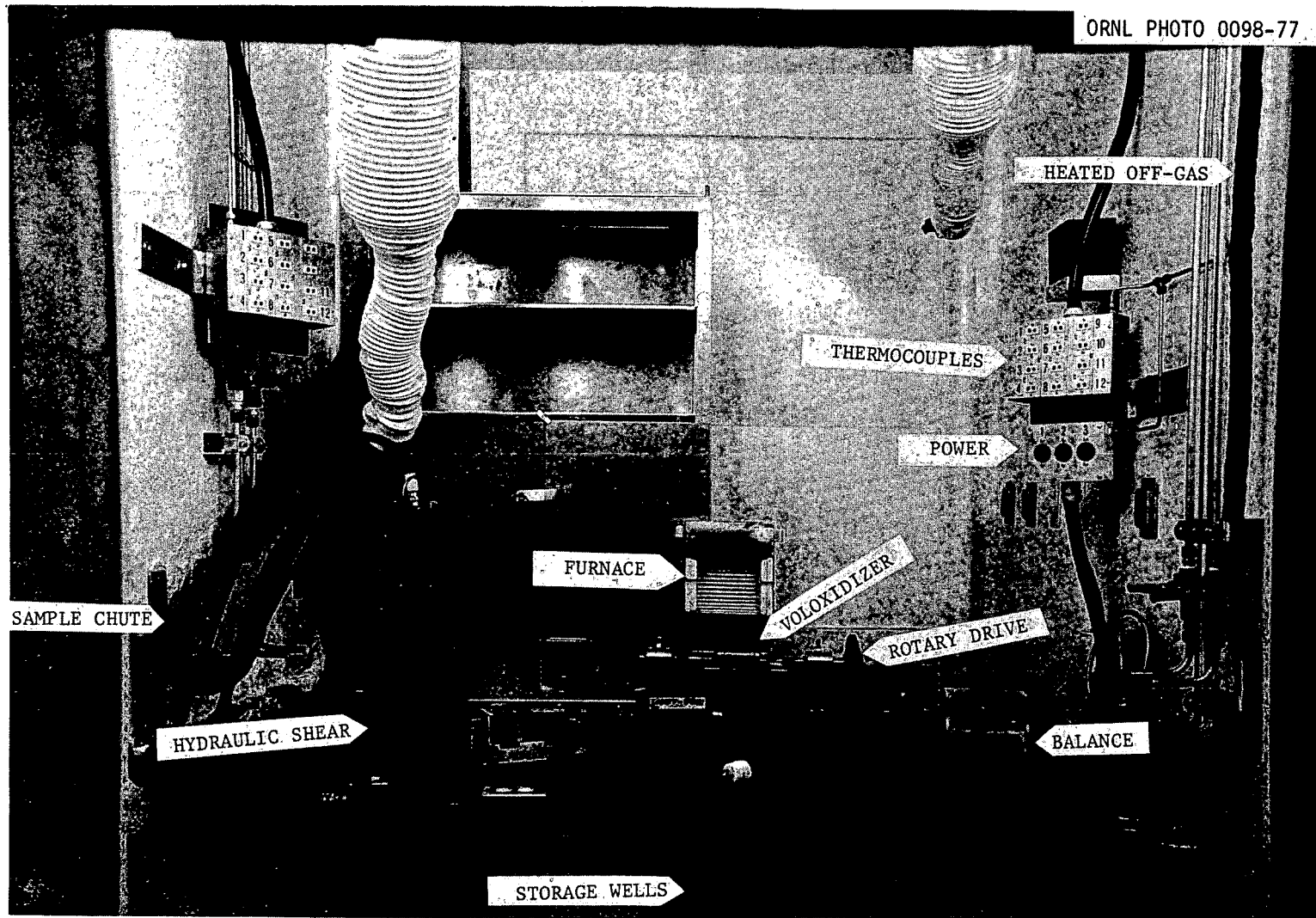


Fig. 7. General view of hot-cell interior.

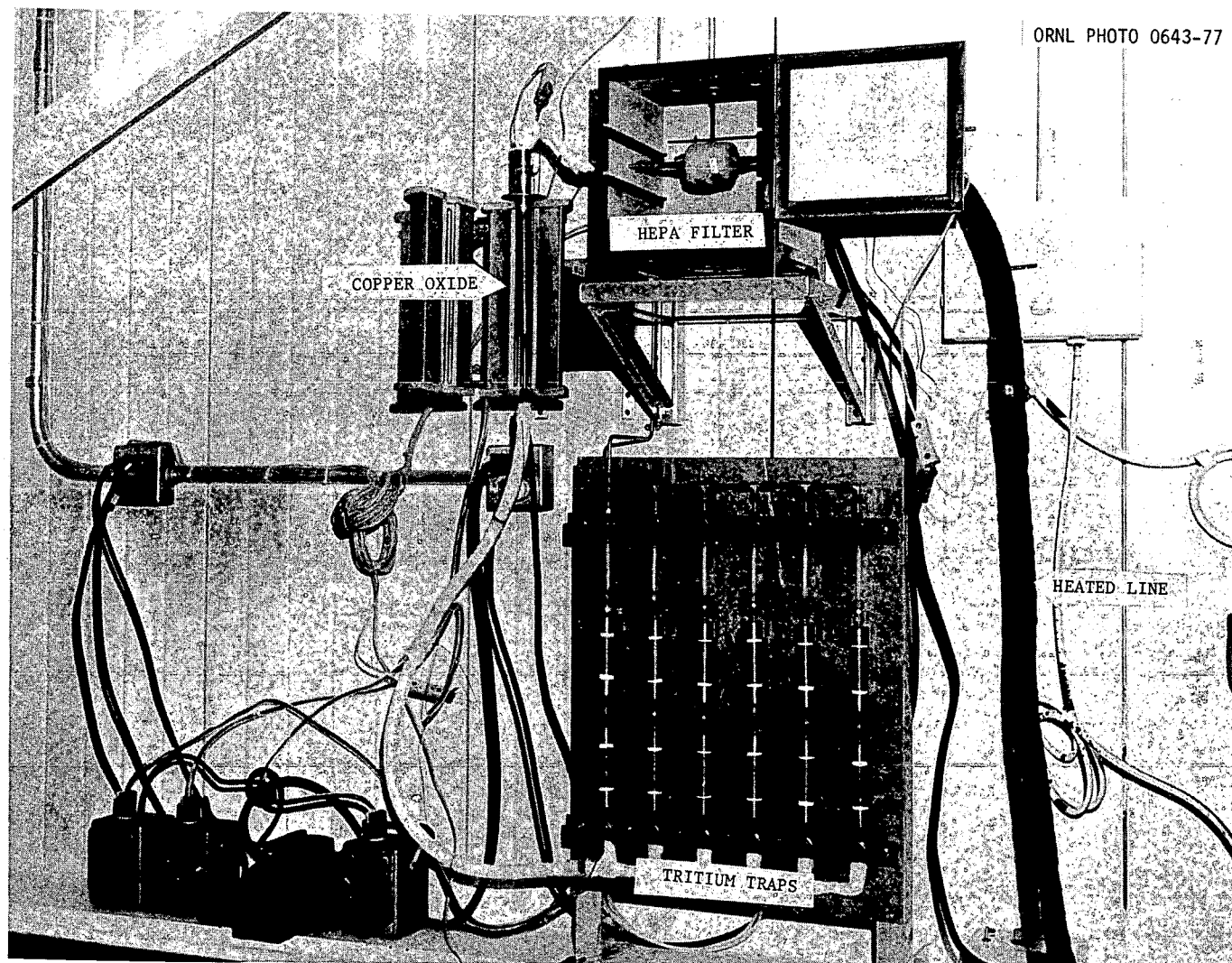


Fig. 8. Tritium traps and associated equipment.

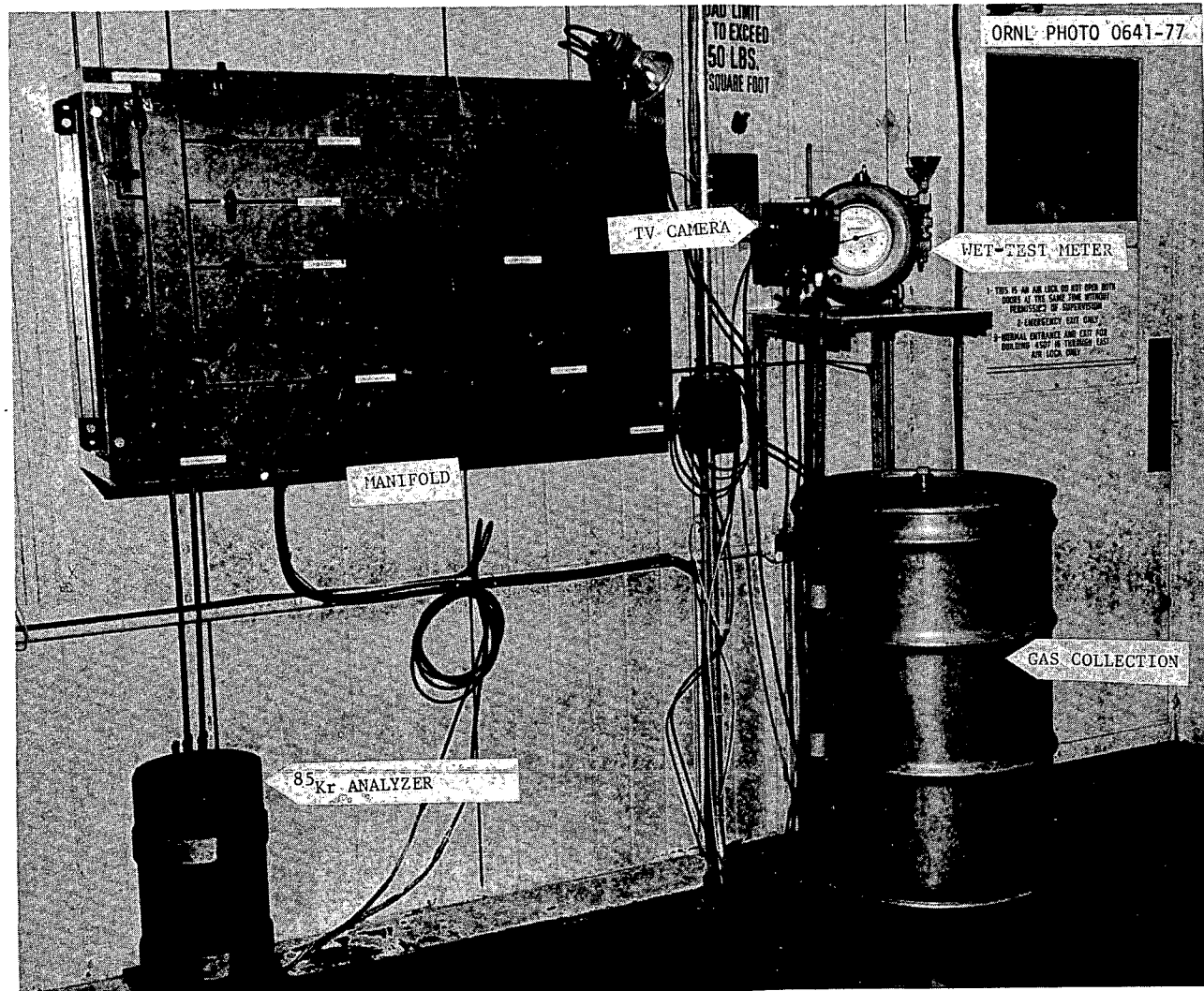


Fig. 9. Krypton analyzer and exit gas manifold.

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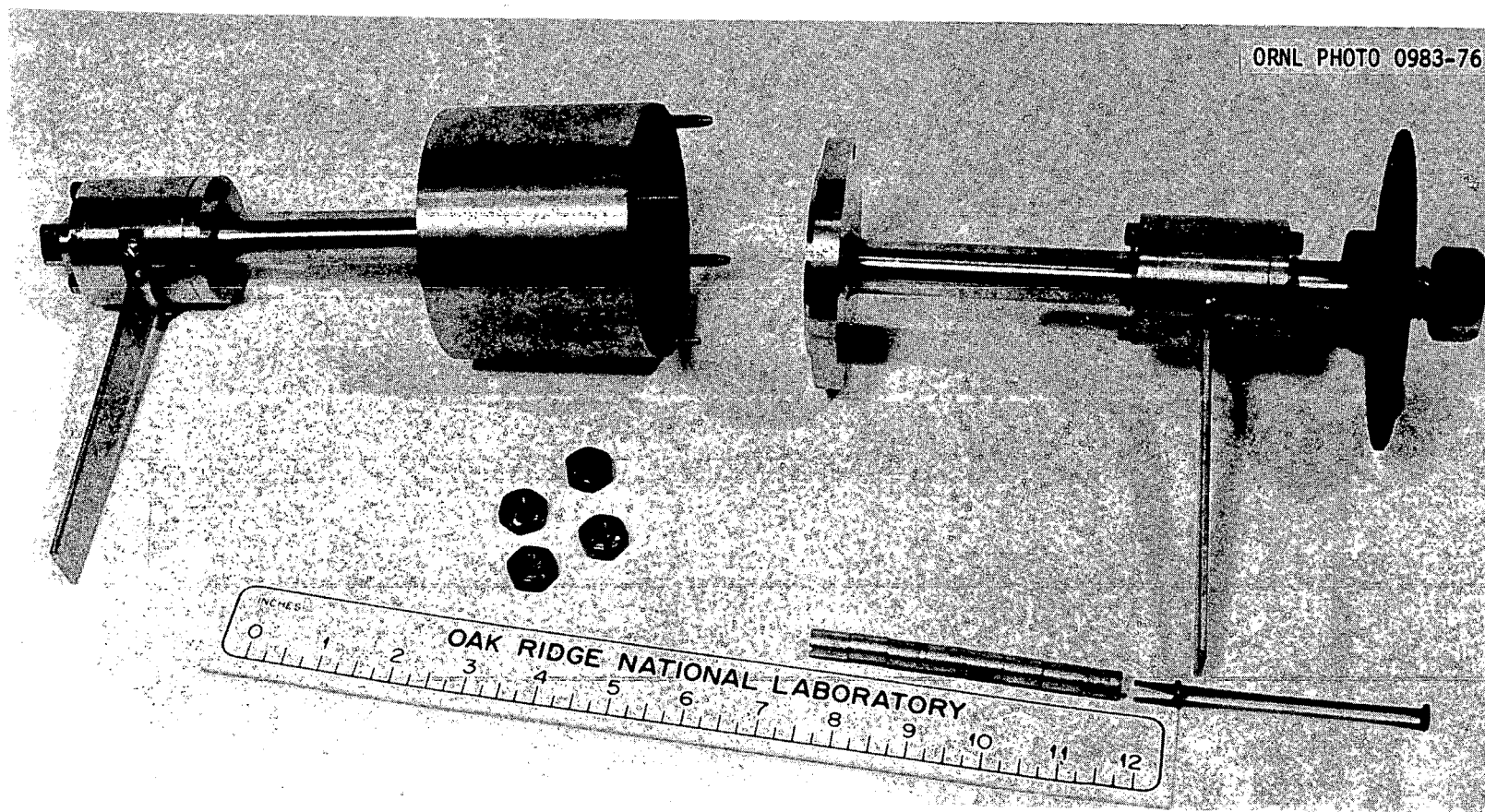


Fig. 10. Rotary voloxidizer and deposition inserts.

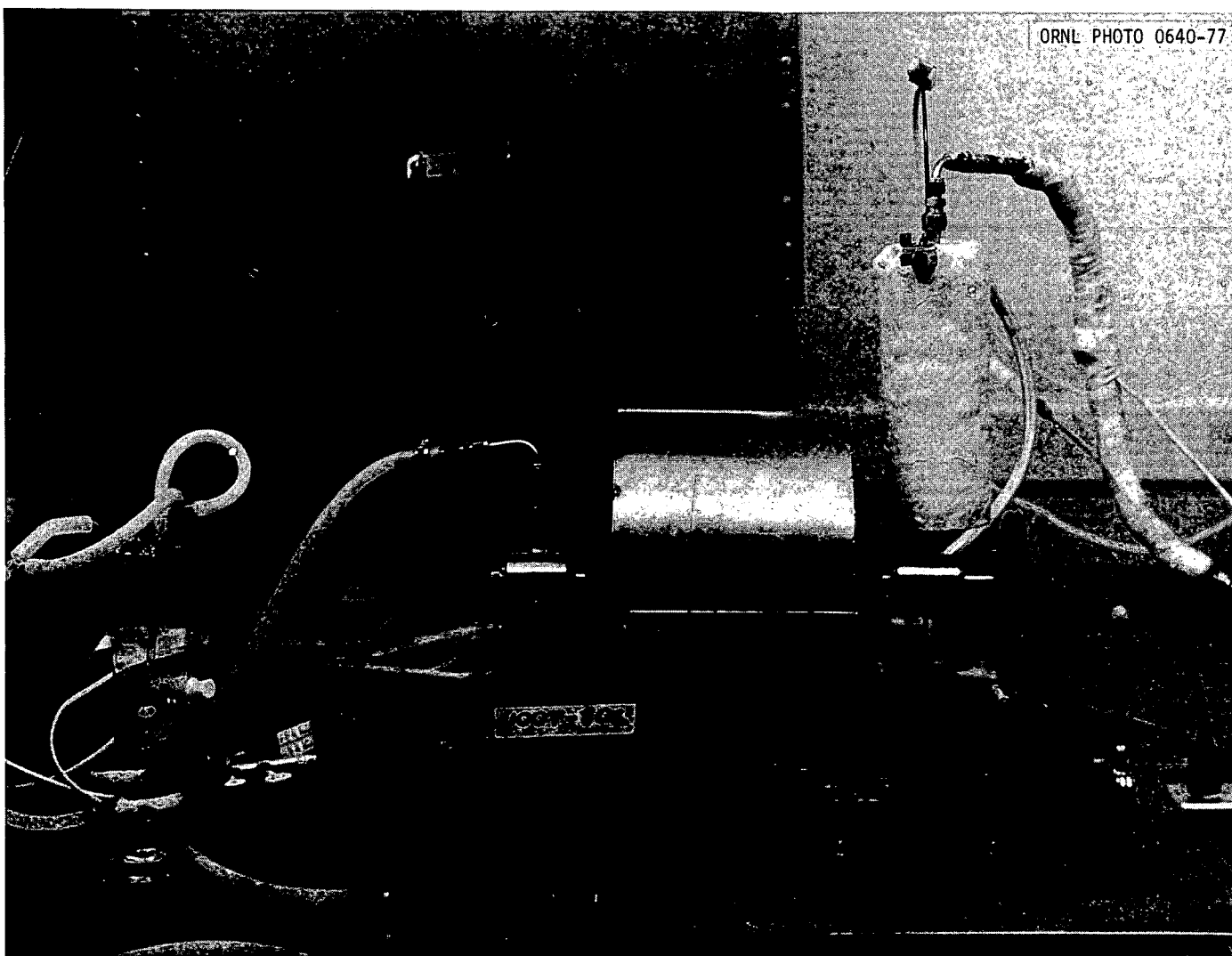


Fig. 11. Heated filter pack assembly.

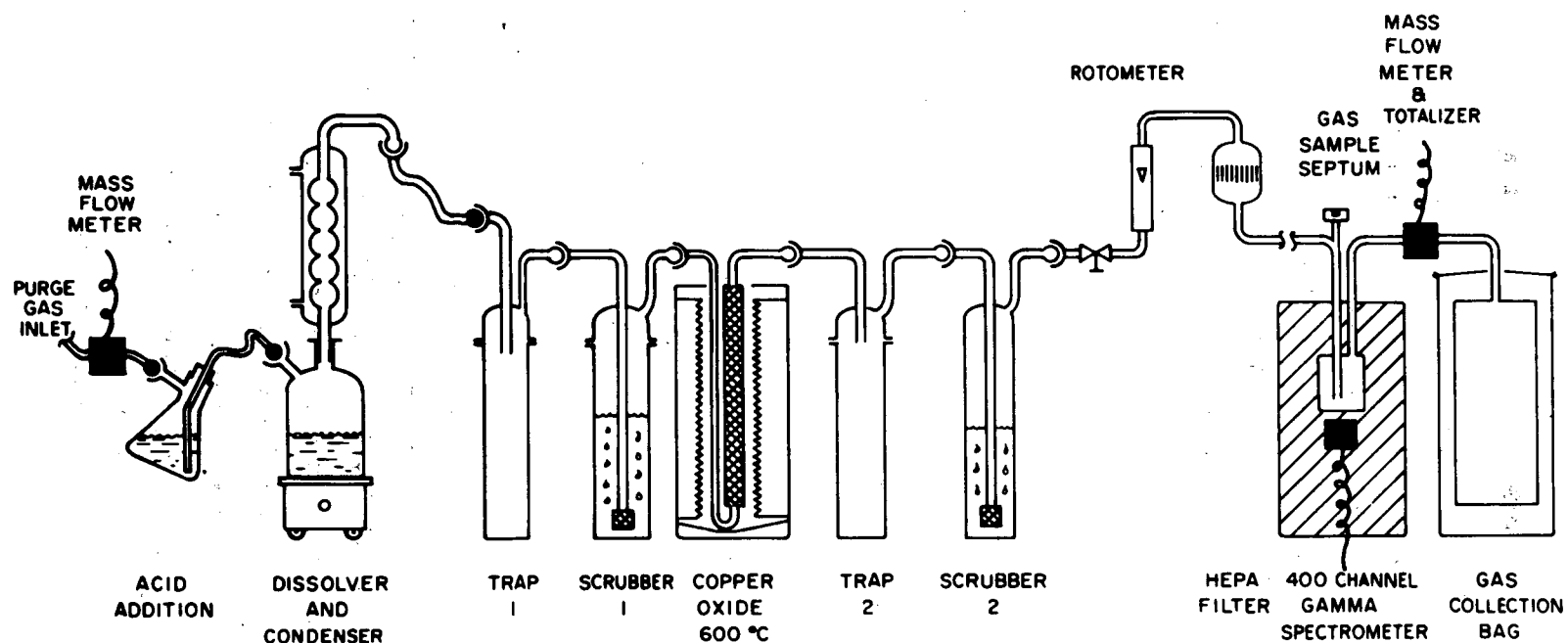


Fig. 12. Schematic diagram of dissolution equipment.

4. RESULTS

4.1 General

Figure 13 is a tabular summary of the operations and materials involved in the baseline experiments with segments 5 and 6 from Rod G-10 of H. B. Robinson-2 Assembly B05. Note that the 34 cuts produced 613.7 g of clad segments and 108.4 g of dislodged oxide. The products of each voloxidation were subdivided into smaller batches for dissolution; one batch of U_3O_8 and cladding (LWR-2B) was reserved and held for future use.

4.2 Shearing

4.2.1 Shearing procedure

The single-pin hydraulic shear was used to prepare cut fuel pieces and loose oxide fines from segments 5 and 6 of H. B. Robinson Rod G-10, Assembly B05, for head-end reprocessing studies at baseline (reference) operating conditions. The unused portion of sheared fuel from these segments provided an inventory for future studies.

Each rod segment, measuring 18 in. long, was manually fed into the shear chamber and positioned so that 1.0-in.-long pieces were obtained with each blade pass. The shear was operated with a hand pump located at the front cell face; shear force per square inch on the 2-in.-diam hydraulic cylinder was indicated on a gage at the pump. An in-cell intercom system provided an audible check on the completion of cutting action as each piece of fuel fell into the beaker beneath the shearing chamber. Since previous studies using an apparatus outfitted with a purging system showed essentially zero releases, collection and monitoring of off-gases from the shearing operation were not undertaken.

Sheared fuel from the two rod segments was mixed together and then separated into two portions: one containing 1.0-in.-long Zircaloy-4 clad pieces of UO_2 and the other containing loose fuel fragments and fines dislodged from the hulls. Four random samples of clad UO_2 were selected from the first portion for HNO_3 dissolution to determine the initial fission product and heavy metal content of the fuel. The dislodged oxide fines were given a screen-size analysis prior to their use in the voloxidation studies.

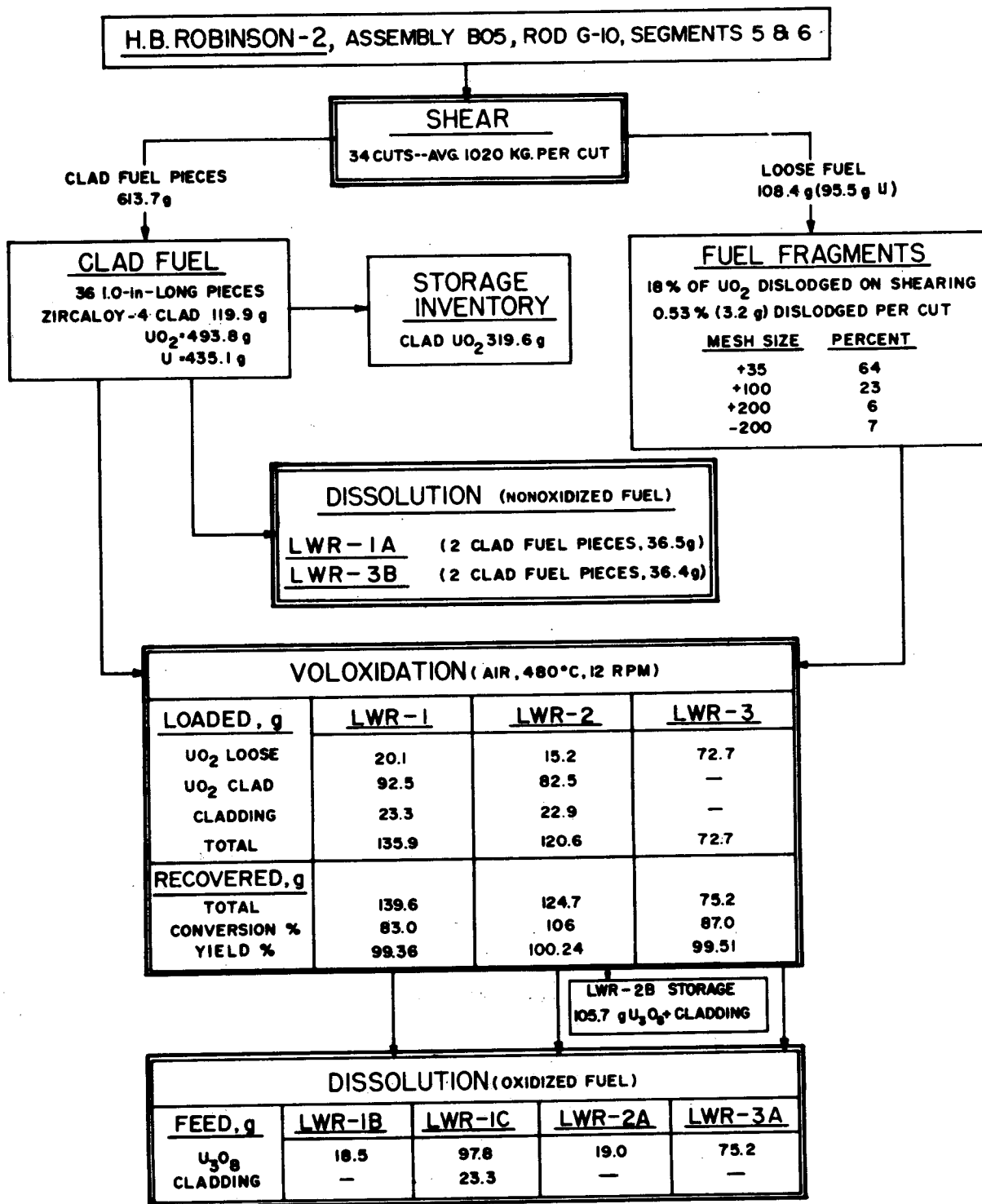


Fig. 13. Generalized flowsheet of hot-cell operations.

4.2.2 Shearing results

A total of 34 cuts was made on the two segments using shear forces consistently within the 925- to 1065-kg range; the average force to cut the 0.422-in. OD (0.024-in. clad thickness) fuel was 1020 kg [this is approximately three times the force necessary to shear 0.25-in.-diam stainless steel clad (0.015-in. thickness) UO_2 blanket material from irradiated fast reactor fuel rods].¹¹ Deformation of the ends of the cut pieces was minimal, with no evidence of significant pillowing or closure (see Fig. 14). No Zircaloy fragments and <0.3 g of zirconium fines (~ 0.01 g per cut) were found in the loose oxide material.

A total of 602 g of UO_2 was contained in the two segments from Rod G-10. During the shearing process, 108.4 g (18% of the total) was dislodged from the hulls. Release of fuel from the cladding, with each shear cut averaged 3.2 g, or $\sim 0.53\%$ of inventory.

Additional Robinson fuel rod segments, each measuring ~ 18 in. long and containing ~ 310 g of fuel, were cut to varying lengths to supply clad and unclad fuel samples for future reprocessing studies. A compilation of data taken on the amounts of fuel dislodged by shearing is shown in Table 1. Examination of the data indicated that the fraction of the fuel inventory released per cut times the length between cuts remained close to a value of 2.51×10^{-3} .

As part of the baseline experiments with H. B. Robinson fuel, fines released from shearing segments 5 and 6 of Rod G-10 were characterized according to screen size distribution. The analysis was as follows:

Mesh	Size (μm)	Weight (g)	Percent
+ 35	500	69.9	64
+100	149	25.0	23
+200	74	6.5	6
-200		<u>7.3</u>	<u>7</u>
	Total	108.7 ^a	100

^aSlight variations in weight are due to cumulative differences in weighings (0.28%).

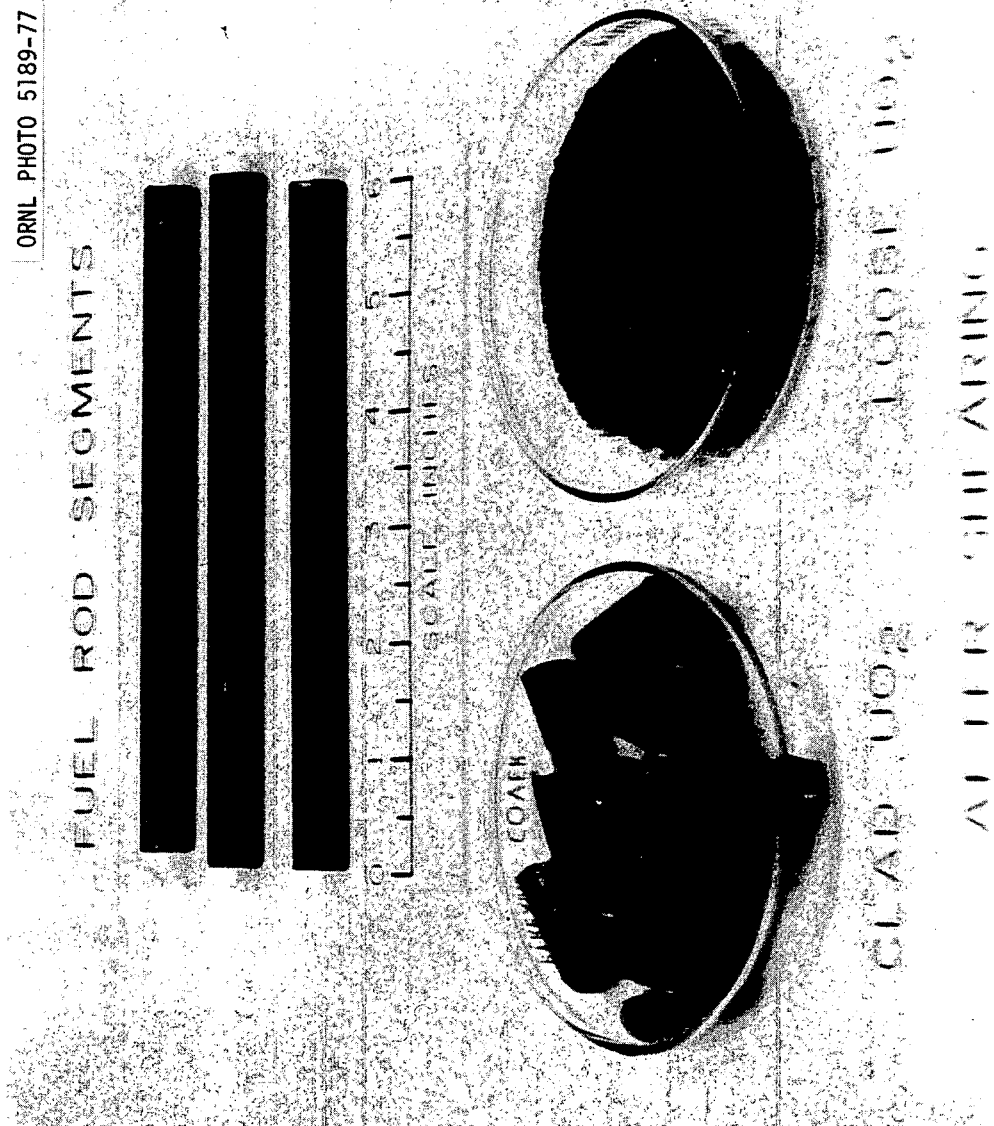


Fig. 14. Sheared H. B. Robinson fuel segments and loose fines.

Table 1. Effects of cut length on release of UO_2 from cladding during shearing of 31,000-MWd/ton fuel rods from the H. B. Robinson-2 Reactor

Approx. cut length (in.)	Av. no. of cuts	Av. release per cut (g)	Av. wt. of UO_2 released (g)	Percent of total UO_2	Percent release calculated ^a	No. of segments sheared ^b
0.25	70	4.38	306.3	97.8	100.5	4
0.375	47	4.38	206.0	66.4	67.0	1
0.5	35	5.21	182.2	57.8	50.2	1
1.0	17	3.26	55.5	18.2	25.1	3
1.5	11	5.55	61.0	18.6	16.7	1
2.0	8	4.53	36.2	11.7	12.6	6
2.75	6	4.38	26.3	8.4	9.1	1
4.5	3 ^c	2.07	6.2	2.0	-	1

^aCalculated by formula $P(\%) \times L \text{ (in.)} = 25.1 \text{ in.}$, where P is percent of fuel inventory released per cut and L is cut length.

^bEach rod segment is ~18 in. long.

^cCut with tubing cutter; all other cuts made with single-pin fuel shear.

4.3 Voloxidation

4.3.1 Voloxidation procedures

The sheared fuel was used in three voloxidation experiments. For Runs 1 and 2, the rotary voloxidizer was loaded with a mixture of loose UO_2 and UO_2 clad in 1-in. hulls (seven clad pieces in each run). The ratio of loose fuel to clad fuel in each experiment was similar to the amount dislodged from the hulls during shearing. Conditions for the two replicate runs were: time, 4.0 to 4.5 hr; temperature, 480°C ; atmosphere, air fed at 200 to $300\text{ cm}^3/\text{min}$ (STP); and agitation, rotation at 12 rpm. For Run 3 the voloxidizer was charged with unclad oxide fragments only, and all conditions remained the same except the time at temperature was shortened to 3.0 hr.

During each run, the system was monitored for redistribution of particulates and semivolatile species. Sampling was performed in the following manner:

1. A brass sheet specimen covering approximately one-sixth of the voloxidizer's inner surface area was placed in contact with the voloxidizer wall to check for fission product deposition and scouring by hulls. This specimen remained inside the voloxidizer for all three runs to permit a cumulative measurement.
2. A $35\text{-}\mu\text{m}$ pore size, sintered metal frit in the exit end (cooling zone) of the voloxidizer was followed by stainless steel deposition tubing inserts and steel wool packing (Fig. 10).
3. A heated filter pack at 125°C containing metal frits, graded filter papers, and charcoal granules was located in-line immediately after the rotary exit seal. It is shown (standing vertically) in the assembled system in Fig. 11.
4. A heated HEPA filter was placed in the off-gas line outside the cell for secondary particulate removal (Fig. 8).

The deposition tubing and steel wool inserts, the filter pack inserts, and the HEPA filter were removed from the system following each run.

Once the fuel was loaded, the voloxidizer was sealed and connected to the gas flow system, and the entire assembly was tested for air tightness at 6-psi gauge pressure. After its integrity was verified, heat was

applied slowly over a 30- to 45-min period until the temperature reached 480°C, where it was maintained for the duration of the oxidation. During the heat-up period and for the length of the voloxidation, air was admitted to the system at a rate of 200 to 300 cc/min (STP) and the voloxidizer was rotated moderately at 12 rpm. To ensure completeness of reaction under these conditions, each voloxidation was continued beyond the point at which oxygen consumption had ended and the ^{85}Kr concentration in the off-gas had returned to near background levels.

During each experiment, the voloxidation off-gases were sent to the sampling area above the cell via a heated line, where they were sequentially trapped for $^3\text{H}_2\text{O}$ content using silica gel and Type 4A molecular sieves. The off-gases were continuously analyzed for ^{85}Kr and O_2 content and were collected for cumulative measurements on ^{85}Kr and ^{14}C release. Following each run, the cooling voloxidizer received a 2- to 3-hr air purge to sweep any remaining off-gases from the system.

Generally, the same operational and sampling procedures were followed for all three experiments; however, some system improvements were made prior to the second and third runs. During the LWR-2 voloxidation, a HEPA filter was not used because of earlier difficulties in keeping it properly heated. We found that inadequate heating of the filter had actually affected measurement of the tritium release rate in the first experiment. For the LWR-3 experiment, another model HEPA filter was inserted and used successfully. A gas sampling port was installed at the inlet of the flow-through sensor of the multichannel analyzer (see Fig. 12). It was used during the LWR-3 run to extract flowing stream gas samples from the off-gas line at the same time the gas was being counted for ^{85}Kr . We also found that the mass flow metering system, including the flow totalizer and calibrated flow splitter, was sufficient to monitor gas flow volumes during the first two experiments; therefore, the wet-test meter was eliminated from the system for the third experiment.

4.3.2 Oxygen consumption

The rate of oxygen consumption during each voloxidation of H. B. Robinson fuel was obtained by measuring the concentration of oxygen in the off-gas and calculating the difference from the inlet gas concentration (air, 20.9%) over successive time periods. Reaction of the UO_2 began as the temperature passed 400°C. During all these runs, a

temporary reduction in the rate of oxygen consumption was noted (see Fig. 15). This apparent two-step oxidation was more sharply defined with unclad UO_2 fragments (run LWR-3). In each case, the phenomenon occurred at ~40 to 50% of the total oxygen usage. This could correspond to a slower usage due to a rate-limiting step, such as an intermediate phase change to U_4O_9 . In addition, if small oxide fines are converted appreciably faster than the larger (>1 mm) UO_2 lumps, then as-sheared particle size of the loose fuel fragments may also have a rate-determining effect on oxygen consumption. Another factor is the presence of clad fuel. In runs LWR-1 and LWR-2, where sheared 1-in. pieces of fuel were voloxidized, access to the UO_2 was limited, thereby slowing the conversion process. Cladding effects on the utilization rate can also be seen in cumulative oxygen consumption curves indicating the percentage of total O_2 consumed (Fig. 16). Oxygen usage was completed after 2 hr of voloxidation at 480°C for unclad UO_2 ; however, during experiments with clad fuel pieces, it took nearly twice as long for the oxidation to be completed.

An estimate of the oxide conversion may be obtained by the weight gain of the UO_2 feed. Theoretical weight gain for complete conversion of UO_2 to U_3O_8 is 3.95% of initial weight. Material balances are presented in Table 2. Recoveries of voloxidized product indicated yields of >99% in each experiment. Estimated conversions from the weight gains were 83.1, 106.0, and 87.1% for LWR-1, LWR-2, and LWR-3, respectively. Errors include weight losses due to unrecovered oxide, weighing errors, and oxidation of the Zircaloy (if any).

Cumulative oxygen usage may also be used to estimate the oxide conversion. Calculated moles of oxygen consumed based on totalized gas flows and averaged O_2 concentrations showed conversions of 112, 115, and 80% when compared with the theoretical amounts for LWR-1, LWR-2, and LWR-3, respectively. Instrument calibration and flow measurement errors are the most probable cause for the relatively widespread values.*

*Improved flow instrumentation and computational methods, including the use of a Hewlett-Packard 3050B Data Acquisition System, now give more accurate estimates of oxide conversion based on cumulative oxygen usage.

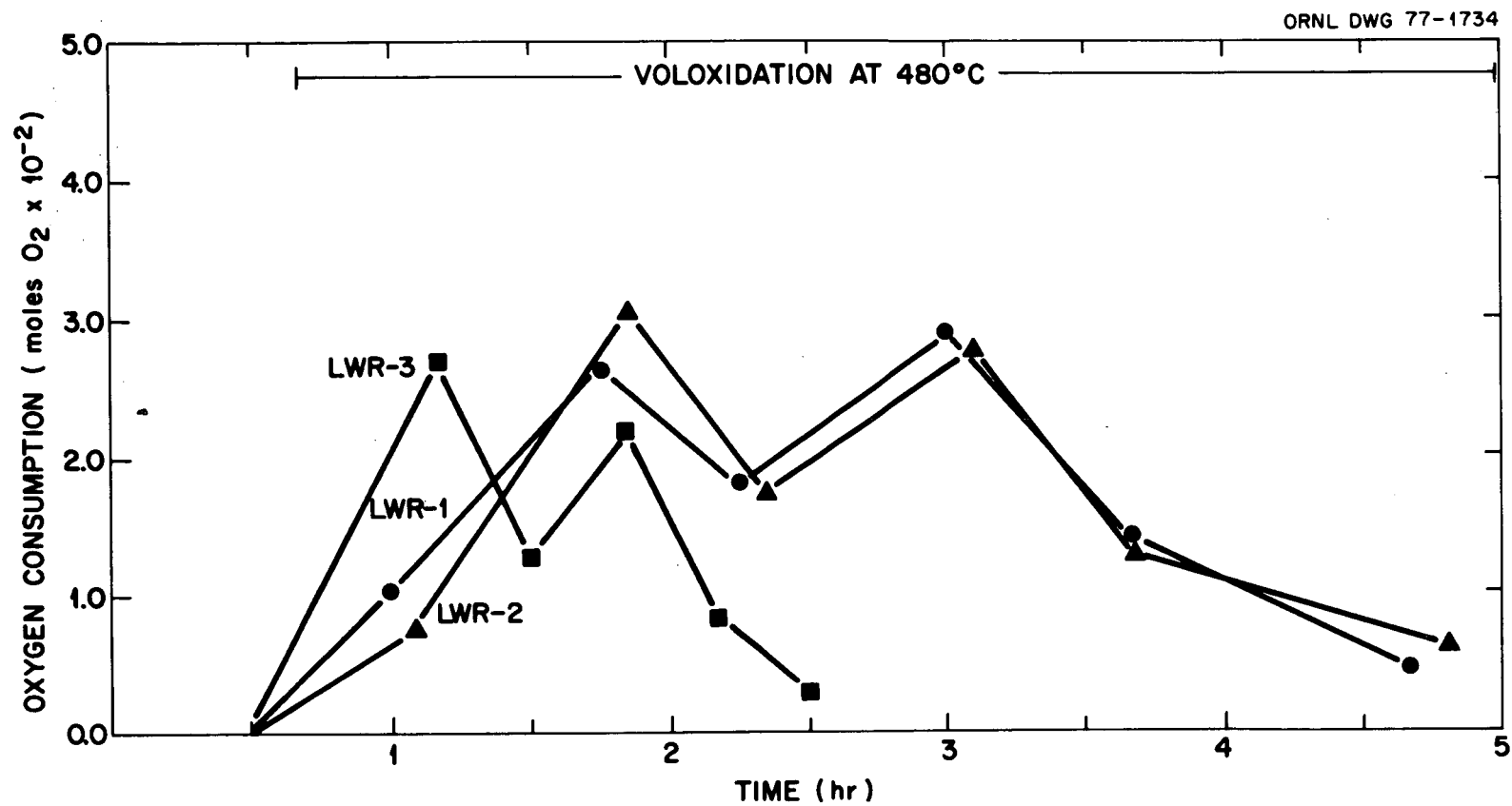


Fig. 15. Oxygen consumption during voloxidation in air at 480°C.

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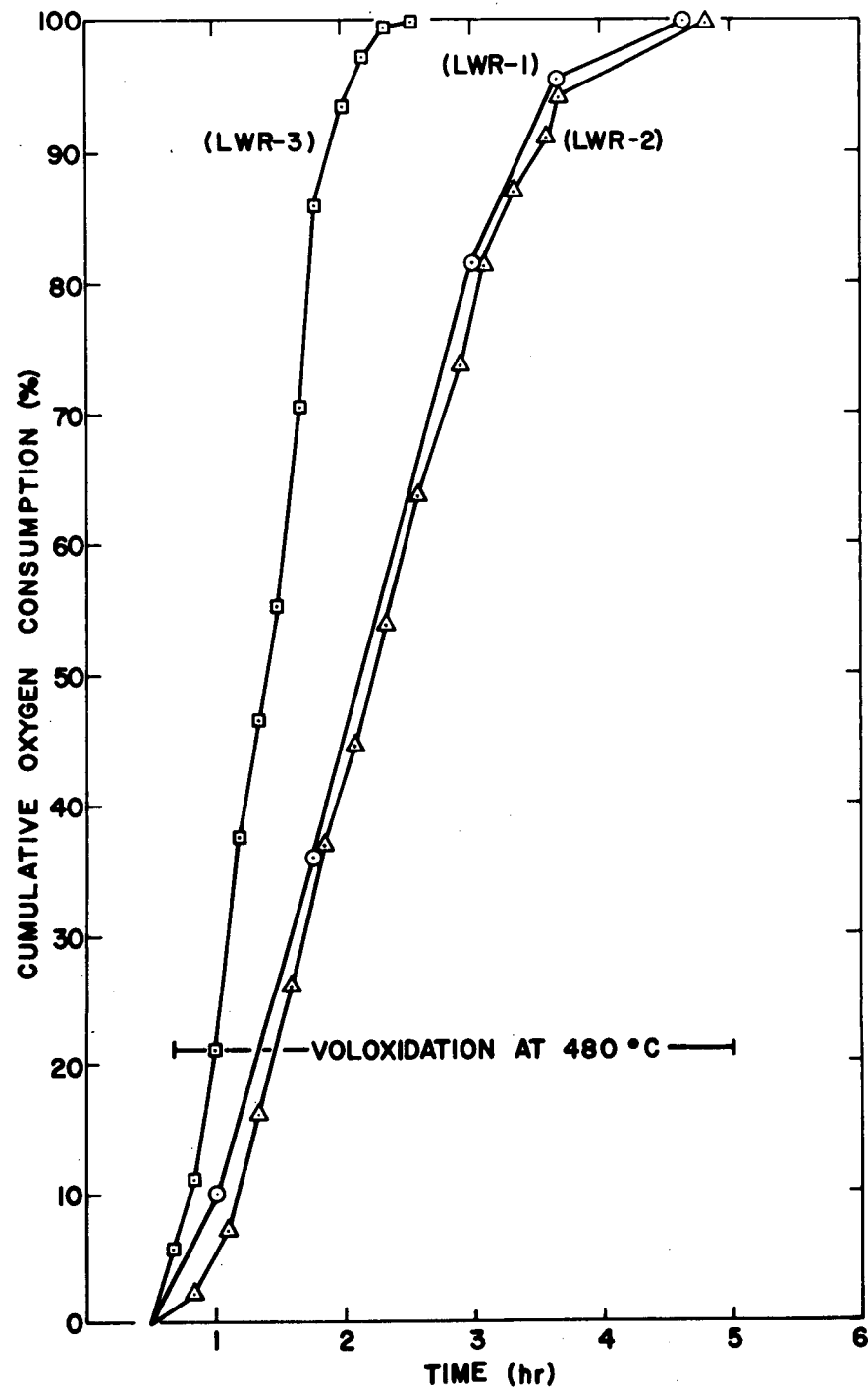


Fig. 16. Cumulative oxygen consumption during voloxidation in air at 480°C.

Table 2. Material balance on voloxidation of UO_2 , 31,000 MWd/ton
(H. B. Robinson-2 Reactor, Rod G-10, Assembly B05)

	Run No.		
	LWR-1	LWR-2	LWR-3
Inputs (g)			
UO_2 (clad)	92.5	82.5	-
UO_2 (fines)	20.1	15.2	72.7
Cladding	23.3	22.9	-
Total	135.9	120.6	72.7
Outputs (g)			
U_3O_8^a	116.3	101.8	75.2
Cladding	23.3	22.9	-
Total	139.6	124.7	75.2
Weight gain (g)	3.7	4.1	2.5
Yield (%) ^b	99.36	100.24	99.51
Oxide conversion (%) ^c	83.1	106.0	87.1

^aIncludes unconverted UO_2 if present.

^bBased on 3.95% increase in oxide weight as 100% theoretical yield.

^cMeasured from weight gain of recovered product; assuming no zirconium oxidation and no loss of powders.

The voloxidation was completed in all of the runs with nearly all (>99%) of the oxide being released from the hulls as fine powder (Fig. 17). This gives further indication of the completeness of conversion. Pulverization was also very effective, with >99% of the powder in the <44- μ m fraction.

4.3.3 Fission gas evolution

The gaseous release data obtained from these experiments were derived from comparisons between the total amount of a fission product present in the fuel, determined by the dissolution of the fuel, and the measured amounts of radionuclide activity present in known volumes of off-gas collected over specified time intervals. Tritium was collected as $^3\text{H}_2\text{O}$ on silica gel and Type 4A molecular sieve traps, which were subsequently leached in 50 ml of water for analytical sampling. Analysis for tritium in dissolver solutions of voloxidizer product showed tritium removal from the oxide to be essentially complete. The krypton (^{85}Kr) content in the off-gas was continuously counted using an on-line MCA set for 10-min accumulation periods. Gamma spectrometry on flowing stream samples (~7 ml) of voloxidizer off-gas also give instantaneous measurements on ^{85}Kr concentration.

Tritium and krypton evolution rate curves are related to the voloxidation process (i.e., the rate of depletion of oxygen concentration in the voloxidizer off-gas as a function of run time). These are shown for the LWR-1 and LWR-2 voloxidations of Zircaloy-clad fuel in Figs. 18 and 19, respectively, and for the LWR-3 voloxidation of unclad oxide in Fig. 20. A tritium release rate curve for LWR-1 was not obtained due to an apparent condensation of $^3\text{H}_2\text{O}$ vapor in an inadequately heated HEPA filter downstream from the voloxidizer; this problem was eliminated during later runs.

The double-peaking effect observed for oxygen consumption during voloxidation is also visible to some degree for the release of ^{85}Kr into the off-gas stream, as measured by the MCA. During the unclad fuel experiment, the double peaks for oxygen utilization and ^{85}Kr release were again present, but the ~20-min time lag by the ^{85}Kr peaks behind the O_2 peaks was not seen. It should be noted that the ^{85}Kr evolution rate curve in Fig. 20 is a display of flowing stream gas sample concentrations (the accumulation-count delay from the MCA is not a factor).

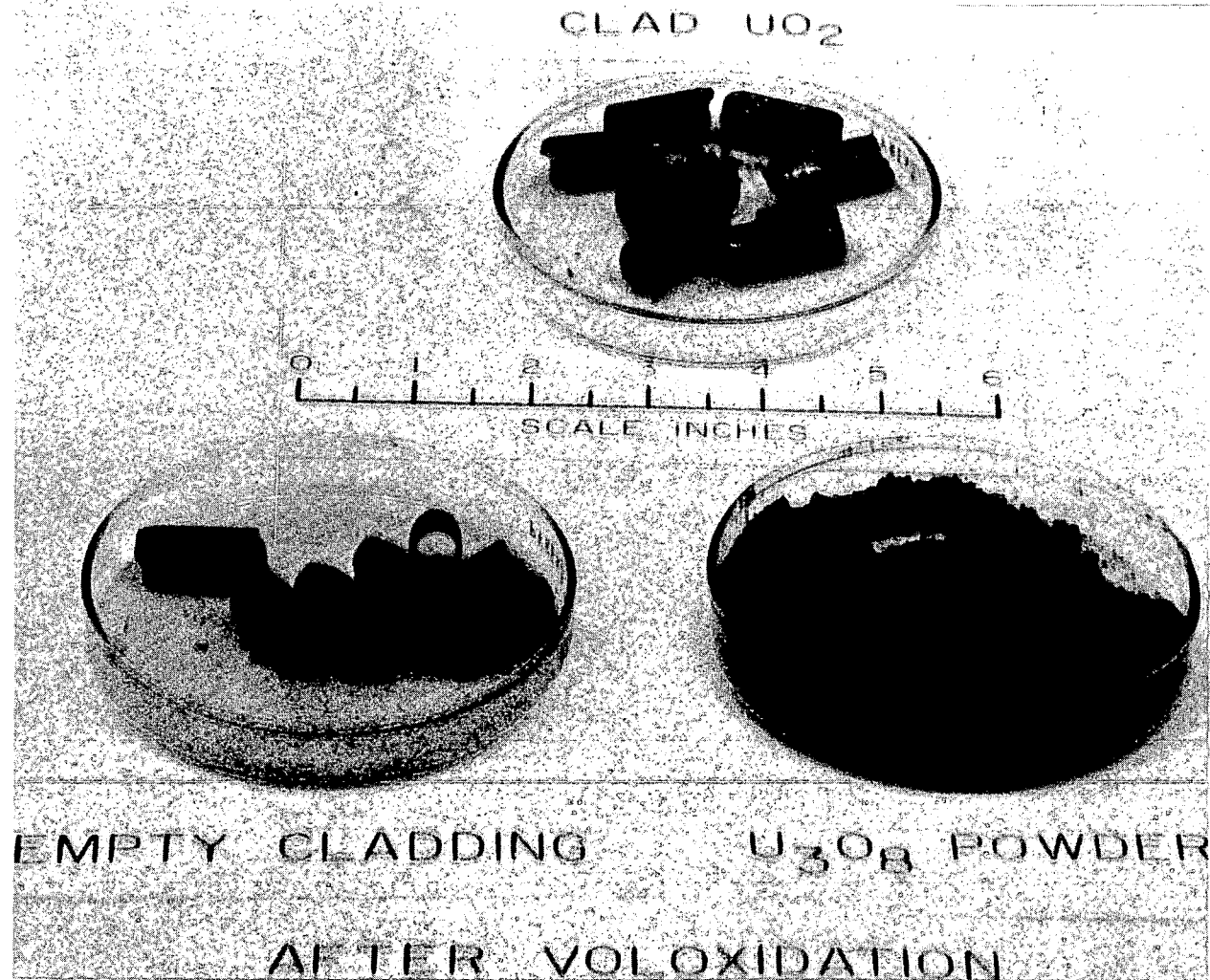


Fig. 17. Voloxidized U_3O_8 and cladding.

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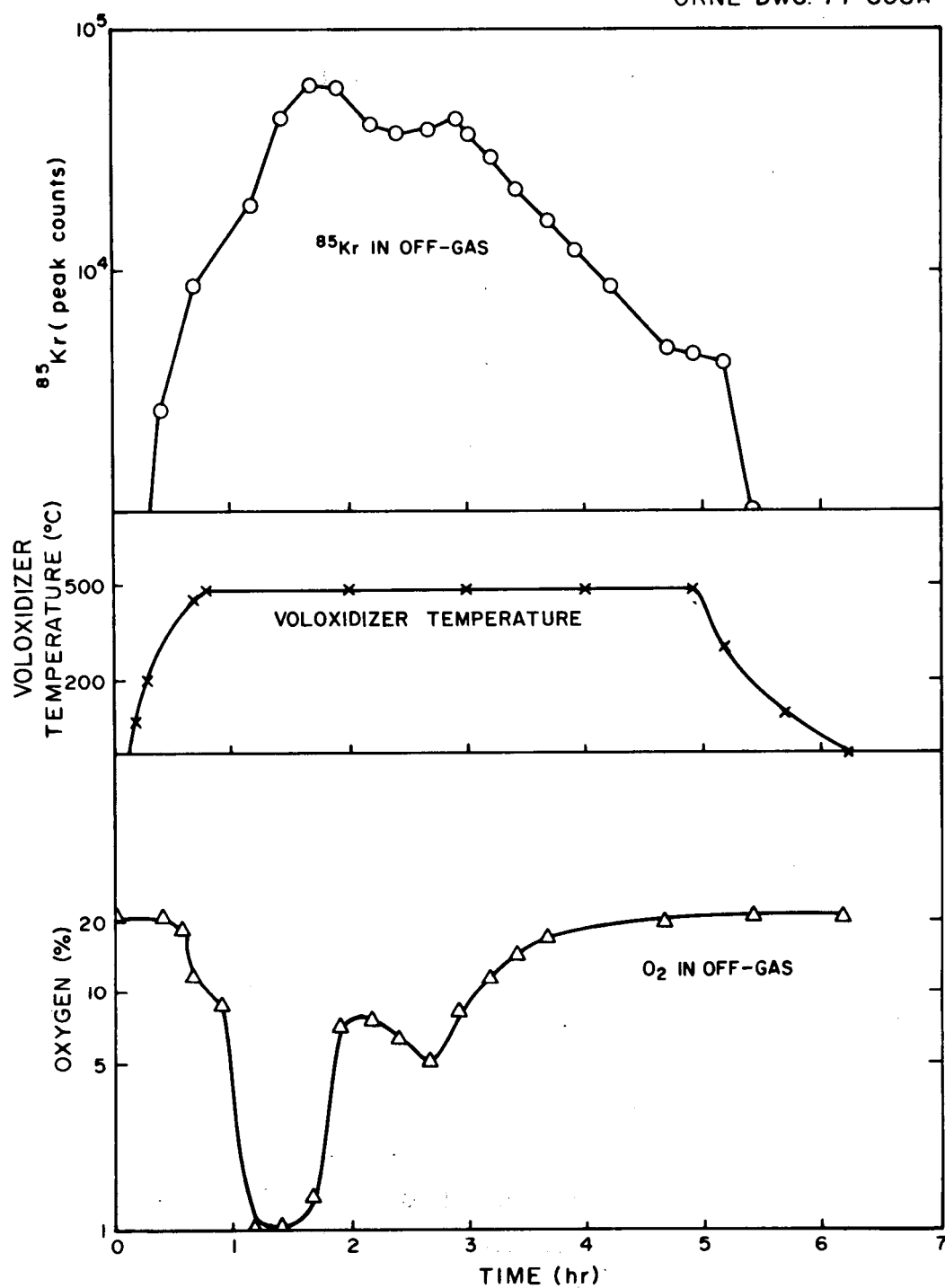


Fig. 18. Release of ^{85}Kr and oxygen consumption - Run LWR-1.

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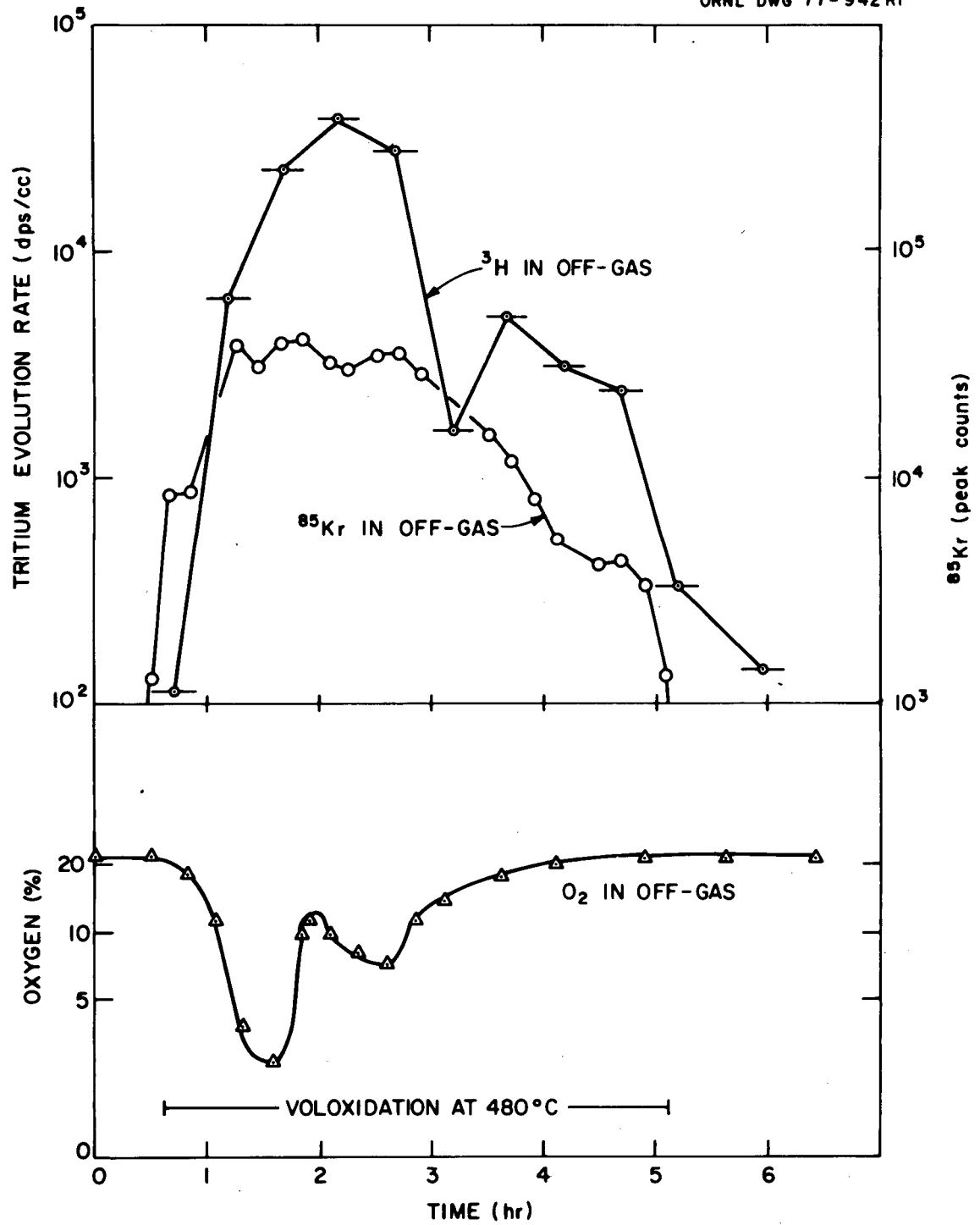


Fig. 19. Release of tritium, ^{85}Kr , and oxygen consumption - Run LWR-2.

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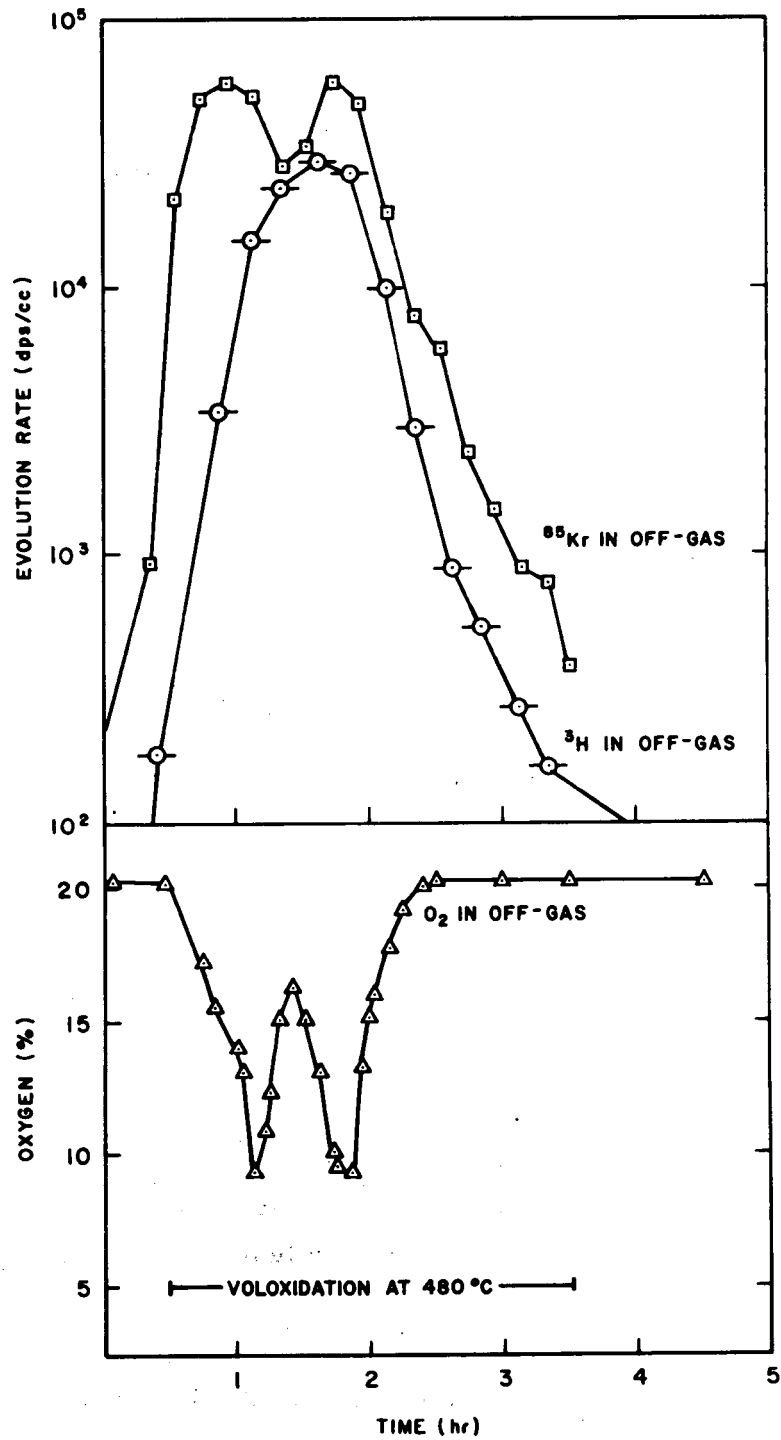


Fig. 20. Release of tritium, ^{85}Kr , and oxygen consumption - Run LWR-3.

A similar double-release pattern for tritium is evident from the evolution rate data obtained during the run with clad fuel, shown in Fig. 19. However, during the voloxidation of unclad UO_2 fragments, no such double-peaking effect for tritium concentrations measured in the off-gas was observed (see Fig. 20). In both cases, there was a delay of at least 45 min between the time of peak oxygen utilization and the peak in tritium evolution. This is attributed to a holdup of HTO on the surfaces, even though they are heated to $>100^\circ\text{C}$.

Krypton and tritium release profiles (percentages of amounts initially in the fuel) are shown for runs LWR-2 and LWR-3 in Figs. 21 and 22, respectively. Accumulations during the initial 30 min at 480°C were low, $<2\%$ for ^{85}Kr and $\leq 10\%$ for ^3H . Evolution of krypton during the clad fuel run (LWR-2) did not significantly decrease until the voloxidizer charge had been at temperature for 2.5 hr. During the voloxidation of unclad fuel (LWR-3), the release of ^{85}Kr was nearly finished after only 1.5 hr at temperature. In both cases, the utilization of oxygen had reached ~ 80 to 90% completion.

The delayed-release patterns (double peaking) during the LWR-2 run caused the tritium evolution to occur over the full 4.5-hr voloxidation of clad UO_2 ; however, a 3.0-hr voloxidation treatment was sufficient to remove the tritium from unclad UO_2 fragments. Tritium recovery from in-line surfaces and adsorption media was on the order of 65 to 70% of the amount found in dissolution of unvoloxidized oxide. Analyses for tritium in dissolver solutions of voloxidizer product showed tritium removal from the oxide to be ~ 97 to $\sim 100\%$.*

In addition to rate of release measurements for ^3H and ^{85}Kr , cumulative gas samples were taken from collected voloxidizer off-gas for readings on the total amount of ^{14}C evolved. Gaseous release totals for the three experiments were as follows:

*Tritium content of the cladding was essentially unaffected by voloxidation, see Sect. 4.4.5.

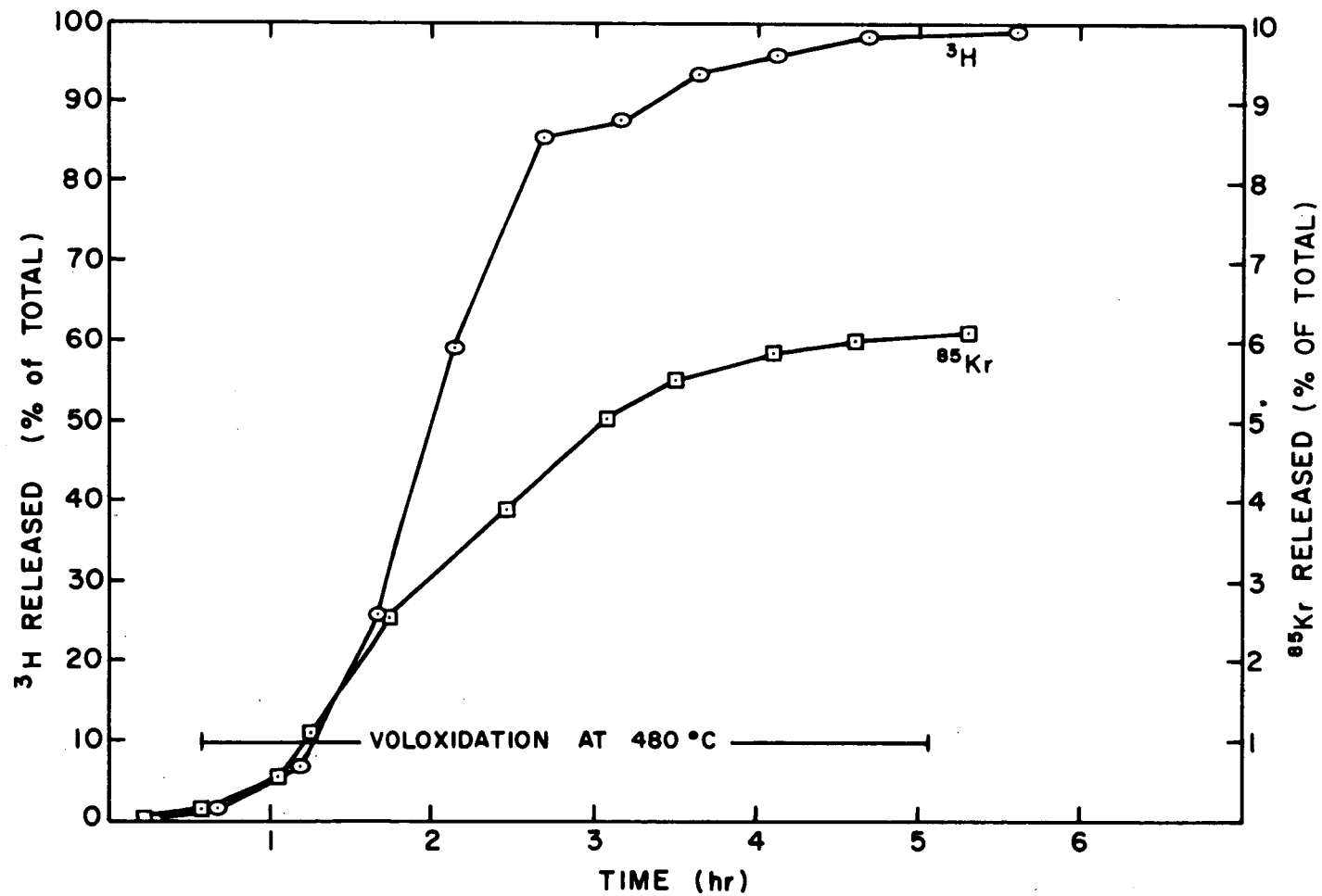


Fig. 21. Release profile of tritium and krypton - Run LWR-2.

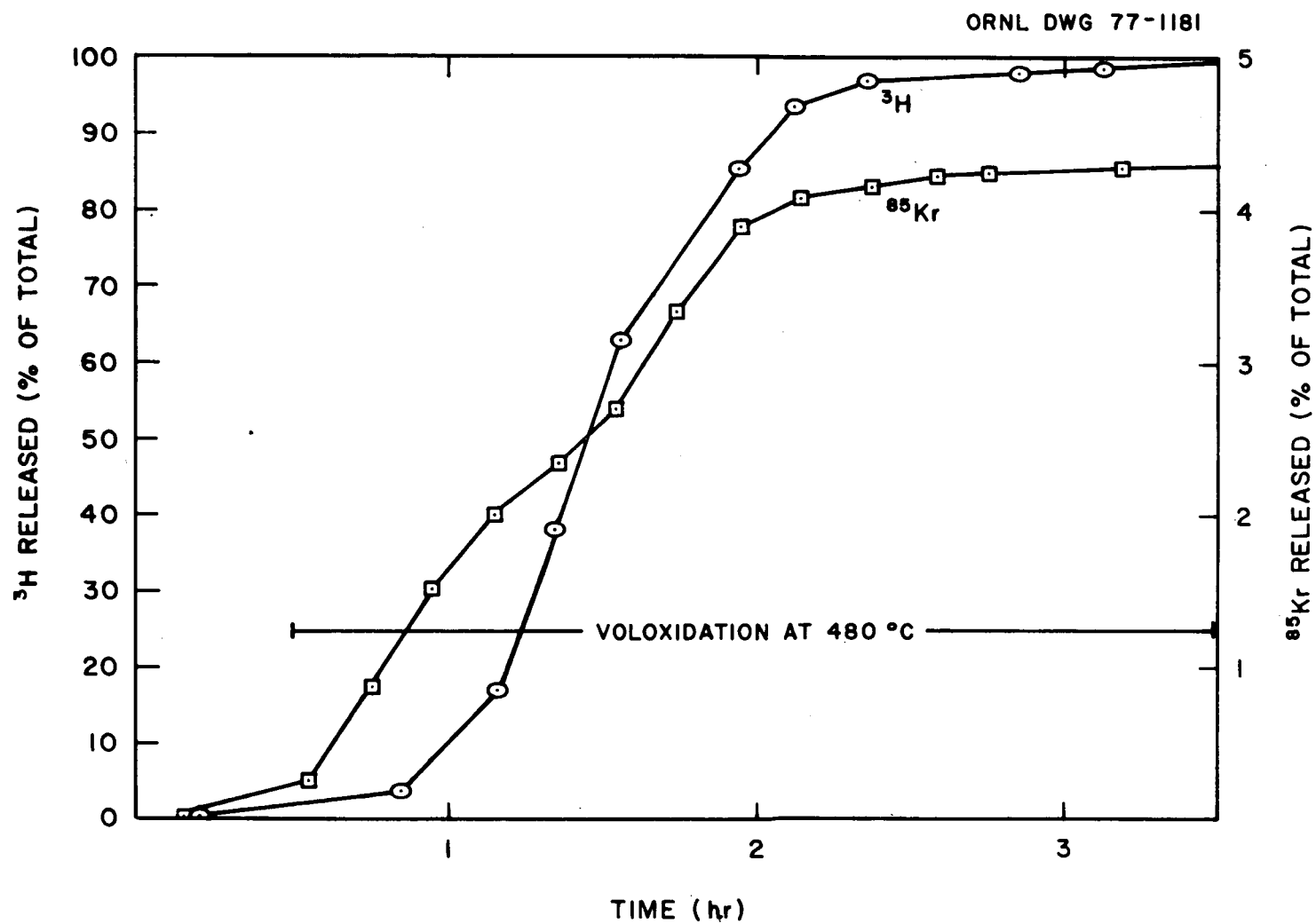


Fig. 22. Release profiles for krypton and tritium - Run LWR-3.

Run No.	Released to voloxidizer off-gas (% initially in UO ₂)		
	³ H ^a	¹⁴ C ^b	⁸⁵ Kr ^c
LWR-1	97.2	32.0 ^d	6.5
LWR-2	99.89	52.0	6.07
LWR-3	>99.99	~100.0	4.3

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

^bBased on residual ¹⁴C levels from dissolution of voloxidized oxide.

^cBased on ⁸⁵Kr release from dissolution of voloxidized fuel.

^dPartial loss of sample.

Sampling and analysis problems experienced with initial gas bag samples caused lower-than-expected values for the cumulative release of ¹⁴C during the LWR-1 run. Residual levels of ¹⁴C present in oxidized fuel from the replicate experiment indicate that a voloxidation release on the order of 50% might be expected from 1.0-in.-long pieces of Zircaloy-clad UO₂. Release of ¹⁴C from unclad fuel fragments was found to be essentially complete during the LWR-3 voloxidation experiment. The characteristically low releases of ⁸⁵Kr during these runs are in general agreement with the values anticipated from earlier voloxidation tests with LWR fuels.⁹

4.3.4 Fission product distribution

Following each voloxidation of clad and unclad H. B. Robinson fuel, deposition and filter trap samples were collected (for gamma spectrometry) from areas downstream of the voloxidizer. Following the LWR-3 run, the brass sheet specimen that had remained in contact with the inner walls of the voloxidizer during all three runs was also analyzed to indicate cumulative fission product deposition (or plateout) on the voloxidizer's inner surfaces. The accumulated amounts of each fission product on the sheet were adjusted by the ratio of the areas in order to estimate (on a per-gram-of-uranium basis) the deposition over the total surface area of the voloxidizer during each experiment.

Fission product recoveries from the voloxidizer walls and voloxidizer off-gas system are listed in Table 3 as percentages of the total fuel inventories for each run. During the experiments with clad fuel, only

Table 3. Selected fission product recoveries from the voloxidizer and off-gas system following voloxidation of 31,000-MWd/ton H. B. Robinson fuel in air at 480°C

Nuclide	Fuel inventory ^a [dis sec ⁻¹ (g U ⁻¹)]	LWR run No. ^b	Distribution (% of fuel inventory)	
			Burner walls ^c	Off-gas system
¹⁰⁶ Ru	2.42E09	1	7.20E-03	7.93E-05
		2	7.15E-03	5.83E-05
		3	7.15E-03	2.38E-03
¹²⁵ Sb	9.36E07	1	2.61E-02	5.22E-05
		2	2.60E-02	8.12E-05
		3	2.61E-02	1.08E-03
¹²⁹ I	152 ^d	1	0.22	0.657
		2	0.22	0.039 ^e
		3	0.22	1.08
¹³⁴ Cs	1.77E09	1	1.69E-02	7.63E-05
		2	1.69E-02	5.88E-05
		3	1.69E-02	2.01E-04 ^f
¹³⁷ Cs	3.21E09	1	2.06E-02	7.82E-05
		2	2.06E-02	6.11E-05
		3	2.06E-02	2.03E-03 ^f
¹⁴⁴ Ce	2.54E09	1	1.36E-02	6.18E-05
		2	1.36E-02	4.84E-05
		3	1.36E-02	6.18E-05

^aDetermined from dissolution of unvoloxidized fuel.

^bRuns 1 and 2 with Zircaloy-clad pieces; run 3 with unclad fuel.

^cCalculated as prorated averages based on analysis of one cumulative sample.

^dμg (g)⁻¹; average value from dissolutions by D. O. Campbell (ref. 4).

^eRecovered from charcoal papers; charcoal beds at 125°C used during LWR-1 and LWR-3.

^fCross contamination from other experiment; see text.

small quantities (~ 0.01 to 0.03% of the total) of ^{106}Ru , ^{125}Sb , $^{134-137}\text{Cs}$, and ^{144}Ce appeared to have coated the voloxidizer's inner surfaces, with $<0.0001\%$ of the total inventory of each being transferred to downstream locations. Slightly larger amounts of fission products were found in the off-gas system after voloxidation of unclad UO_2 . Activation analyses on leaches from the sheet specimen insert and on beds of charcoal from the heated off-gas filter trap showed that $\sim 1\%$ of the total ^{129}I was removed from the fuel by rotary voloxidation at 480°C . However, most of the volatilized iodine passed through the $35\text{-}\mu\text{m}$ sintered steel filter and into the off-gas system. The apparent low value for ^{129}I recovery downstream from the voloxidizer during the second experiment is most likely due to ineffective adsorption by charcoal-impregnated filter papers.

Gamma spectrometry performed on tubing samples taken from the off-gas line following the LWR-3 voloxidation of unclad fuel showed an increased percentage of downstream ^{106}Ru , ^{125}Sb , and $^{134-137}\text{Cs}$ deposition. This may have been due in part to the release of residual contamination from a voloxidation at 650°C of fast, irradiated $(\text{U,Pu})\text{O}_2$ made between LWR-2 and LWR-3.* Deposited cesium levels at this location were particularly high; $^{137}\text{Cs}/^{134}\text{Cs}$ ratios were similar to those found during the fast fuel run (FBR-1, 21.7; LWR-3, 18.4) and were an order of magnitude larger than those seen in the LWR-1 and LWR-2 voloxidations (LWR-1, 1.86; LWR-2, 1.88).

Ultrasonic cleaning of the voloxidizer between runs was effective in removing loose dust and fission products from the walls and the sintered-metal, exit-gas filter, but was not effective in removing plated materials. Heating the system during the LWR-3 experiment may have revolatilized some of the contaminants, which subsequently "plated out" on the tubular deposition inserts downstream from the voloxidizer. It is likely that effects of cladding (or absence of cladding) on particulate and semivolatile fission product distribution during this voloxidation run may have been partially obscured; however, the effects of surface contamination and revolatilization are continuing to be studied as a separate area of interest.

*The brass sheet specimen used during the LWR series was not inside the voloxidizer during the $(\text{U,Pu})\text{O}_2$ voloxidation; hence, it was not contaminated.

The distributions of fission products recovered from the off-gas system following each voloxidation are shown in Tables 4, 5, and 6. Most of the fission products that passed a 35- μm pore size, sintered steel filter at the gas exit of the voloxidizer deposited from the rapidly cooling gas onto tubing insert specimens. (The exception was ^{129}I , which was adsorbed on beds of charcoal heated to 125°C.) Pre-run calibrations of the voloxidizer indicated that deposition temperatures in this region could be estimated with reasonable accuracy. One display of data for the voloxidizer under operation at 500°C shows the relatively narrow distribution of off-gas temperatures over a wide range of flow rates (Fig. 23). Profiles for measured fission product levels as a function of temperature are shown for the voloxidations performed on clad UO_2 in Figs. 24 and 25 and on unclad UO_2 in Fig. 26. Steel wool packing in some of the tubing segments enhanced fission product collection by a factor of 10, perhaps signifying the utility of an extended surface or the presence of particles in the gas. For the first two runs, the relative depositions of ^{106}Ru , ^{137}Cs , and ^{144}Ce did not vary greatly as the off-gas cooled from $\sim 400^\circ\text{C}$ down to $\sim 100^\circ\text{C}$; this suggests particulate matter. However, for the third run, at temperatures $< 350^\circ\text{C}$, ruthenium deposition was greater than that for cesium, a reversal of the pattern noted in the clad fuel runs and further indication of the likelihood of revolatilized fission products from the $(\text{U,Pu})\text{O}_2$ voloxidation.*

Most of the entrained activity in the graded-filter system was associated with particulates sized between 5 and 10 μm . Only traces of activity (mostly ^{106}Ru and ^{137}Cs) were found in the heated off-gas line or in the secondary particulate HEPA filters.

4.4 Dissolution

4.4.1 General

Dissolution of unvoloxidized or voloxidized fuel is necessary in order to determine the amounts of tritium, ^{14}C , krypton, iodine, or other fission products that remain in the fuel after the head-end treatments and to determine whether the solubility of the UO_2 is affected. Two experiments to determine the starting inventory were conducted with unvoloxidized Zircaloy-clad UO_2 from the same segment of Robinson fuel

*Separate voloxidizers are now currently in use for different fuel types to prevent cross contamination.

Table 4. Distribution of selected fission products remaining in the voloxidizer off-gas system following voloxidation of Zircaloy-clad H. B. Robinson fuel in air at 480°C (LWR-1)

Nuclide	System distribution (% of total released from voloxidizer)				Total found in off-gas system [dis sec ⁻¹ g (U) ⁻¹]
	Deposition specimens	Graded filters ≤ 10 μm	Charcoal	HEPA filter	
¹⁰⁶ Ru	73.92	24.57	1.30	0.21	1.92E03
¹²⁵ Sb	95.30	a	4.70	b	4.89E01
¹²⁹ I	0.90	22.55	76.55	b	0.998 ^c
¹³⁴ Cs	70.93	28.75	0.20	0.13	1.35E03
¹³⁷ Cs	71.67	27.75	0.43	0.14	2.51E03
¹⁴⁴ Ce	74.74	22.21	3.04	b	1.57E03

^aBelow limits of detection.

^bTrace quantities.

^cμg (g)⁻¹.

Table 5. Distribution of selected fission products remaining in the voloxidizer off-gas system following voloxidation of Zircaloy-clad H. B. Robinson fuel in air at 480°C (LWR-2)

Nuclide	System distribution (% of total released from voloxidizer)			Total found in off-gas system [dis sec ⁻¹ g (U) ⁻¹]
	Deposition specimens	Graded filters ≤ 10 μm	Charcoal ^a	
¹⁰⁶ Ru	87.26	5.24	7.50	1.41E03
¹²⁵ Sb	90.92	3.87	5.21	7.60E01
¹²⁹ I	57.63	b	42.37	0.059 ^c
¹³⁴ Cs	85.49	5.95	8.56	1.04E03
¹³⁷ Cs	85.16	6.22	8.62	1.96E03
¹⁴⁴ Ce	87.26	5.66	7.08	1.23E06
Gross γ	86.45	5.63	7.92	1.00E03 ^d

^aCharcoal papers; charcoal beds used during LWR-1 and LWR-3.

^bUndetected.

^cμg (g)⁻¹.

^dCounts sec⁻¹ g⁻¹.

Table 6. Distribution of selected fission products remaining in the voloxidizer off-gas system following voloxidation of unclad H. B. Robinson fuel in air at 480°C (LWR-3)

Nuclide	System distribution (% of total released from voloxidizer)				Total found in off-gas system [dis sec ⁻¹ g (U) ⁻¹]
	Deposition specimens	Graded filters ≤ 10 μm	Charcoal	HEPA filter	
¹⁰⁶ Ru	99.86	0.03	0.07	0.04	5.76E04
¹²⁵ Sb	99.39	0.17	0.23	0.20	1.01E03
¹²⁹ I	5.75	a	94.25	a	1.634 ^b
¹³⁴ Cs	98.54	0.39	0.50	0.57	3.55E03
¹³⁷ Cs	99.59	0.11	0.19	0.11	6.52E04
¹⁴⁴ Ce	96.16	1.10	1.14	1.60	1.57E03
Gross γ	99.60	0.12	0.19	0.09	1.77E04 ^c

^aUndetected.

^bμg (g)⁻¹.

^cCounts sec⁻¹ g⁻¹.

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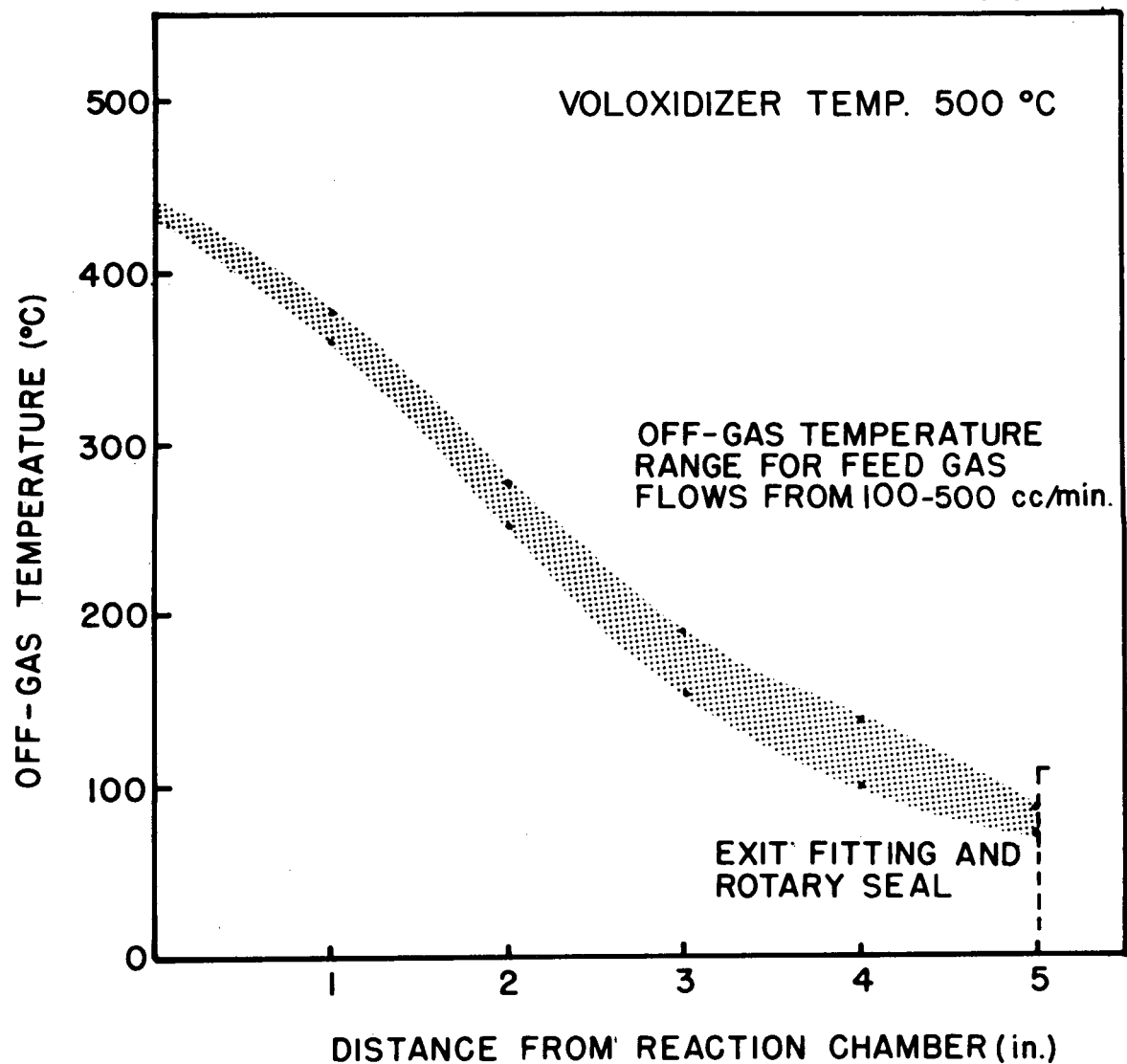


Fig. 23. Temperature of voloxidizer off-gas as a function of distance from the reaction chamber.

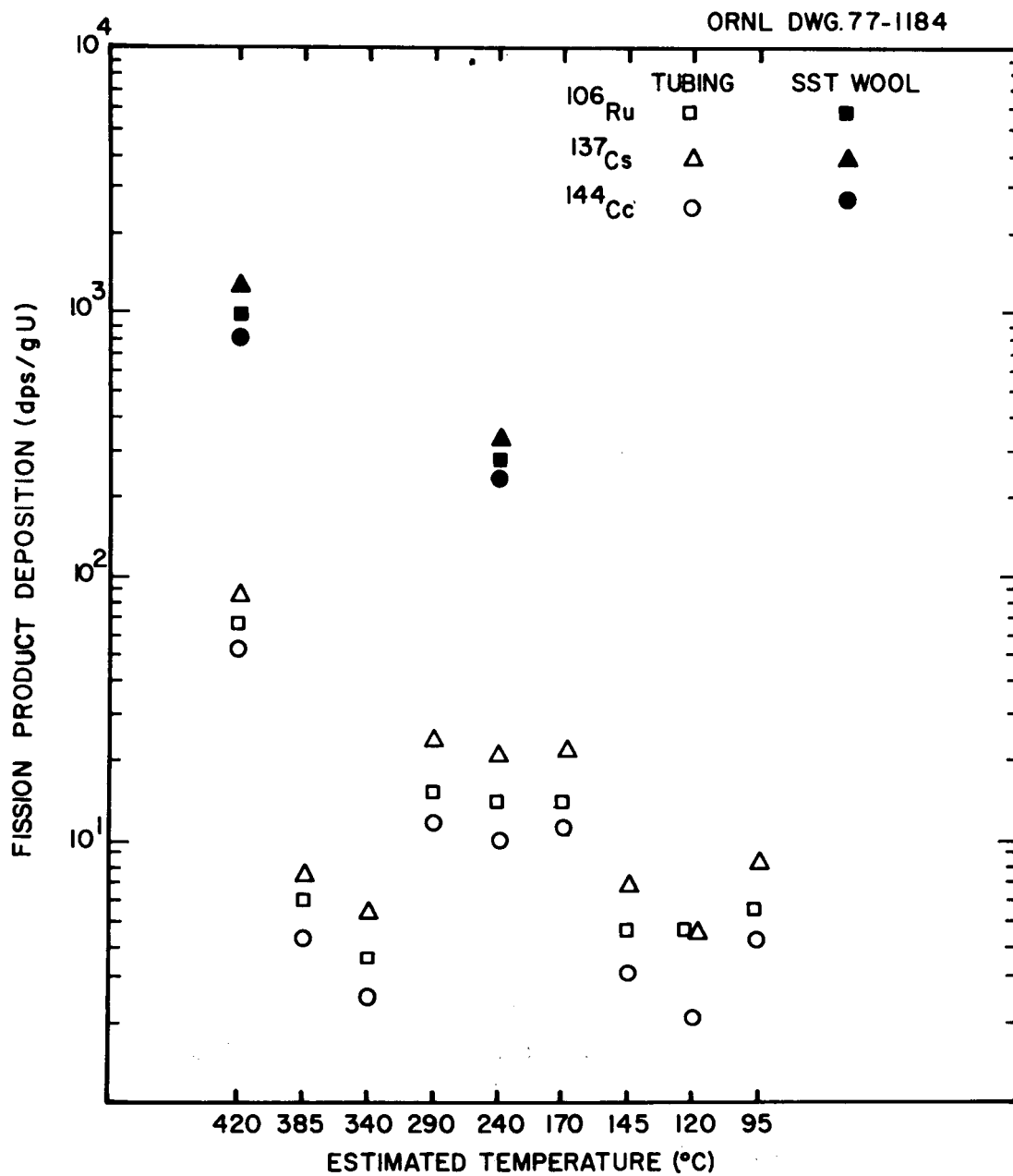


Fig. 24. Fission product deposition from voloxidizer off-gas (Run LWR-1).

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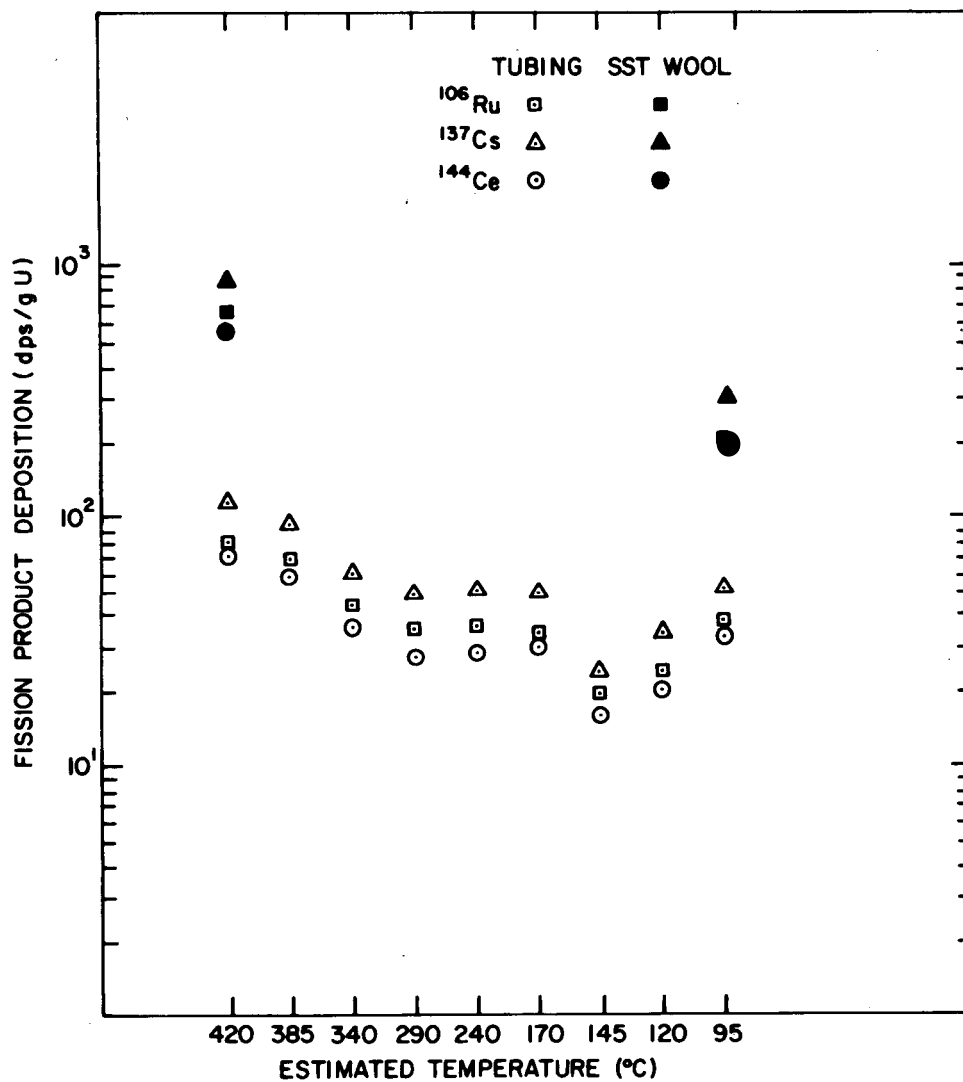


Fig. 25. Fission product deposition from voloxidizer off-gas (Run LWR-2).

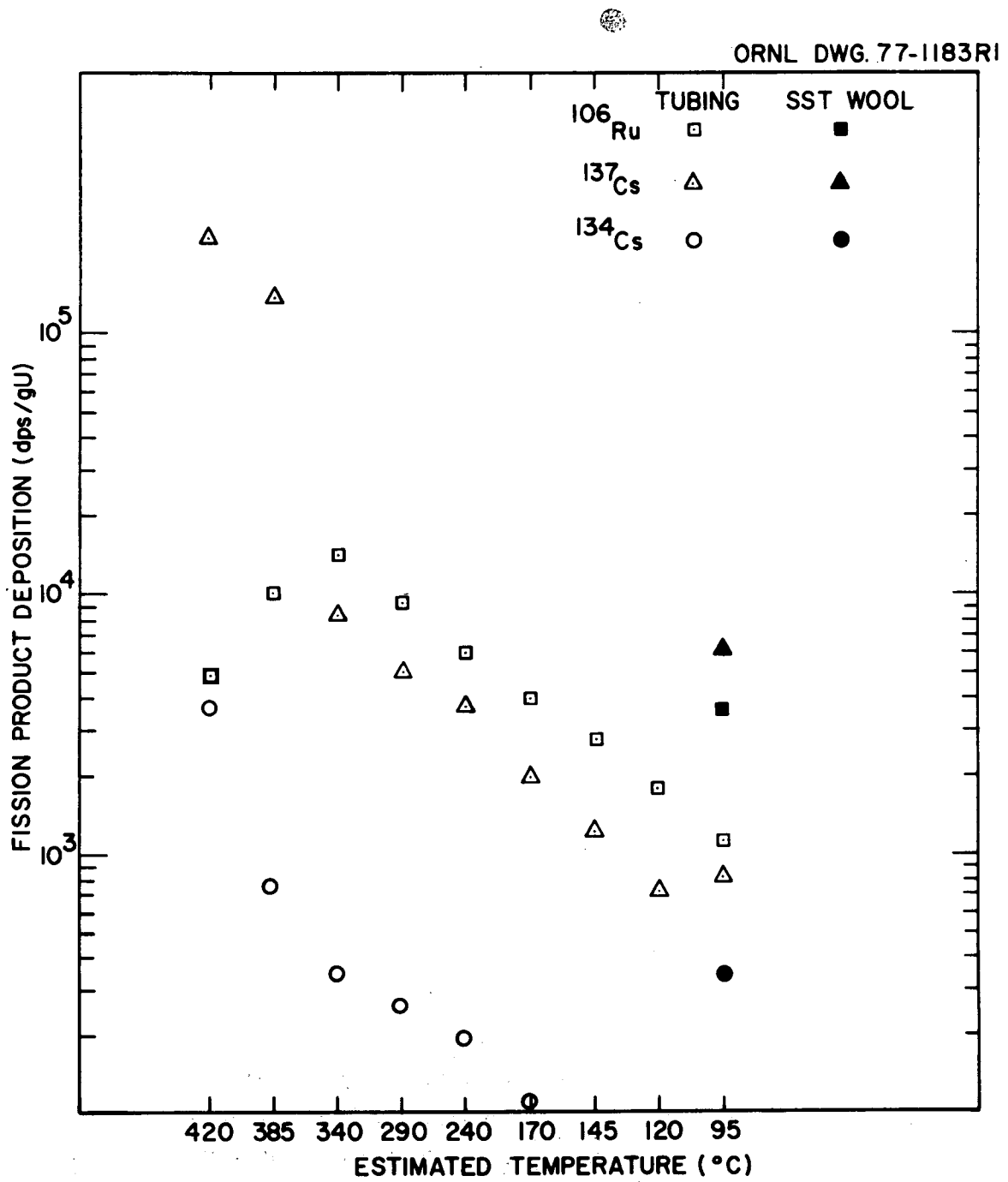


Fig. 26. Fission product deposition from voloxidizer off-gas (Run LWR-3).

Rod G-10 as that used in the voloxidation tests. Four dissolutions were made with voloxidized material:

Dissolution experiment	Fuel from voloxidation No.	Dissolution procedure	
		Complete	Partial
1A	None		x
1B	1		x
1C	1	x	
2A	2		x
3A	3		x
3B	None	x	

The complete dissolution procedure simulated the operation of a continuous, countercurrent leacher or dissolver:

Leach 1. 2-hr, 7 M HNO_3 , 92 to 95°C. Represents contact of fuel and cladding with fresh dissolvent.

Leach 2. 2-hr, 3 M HNO_3 , 92 to 95°C. Represents contact of fuel, cladding, and residue with spent dissolvent.

Leach 3. 2-hr, 7 M HNO_3 , 92 to 95°C. Additional contact of fuel, cladding, and residue with fresh dissolvent.

Leach 4. 2-hr, 8 M HNO_3 --0.05 M KF, 92 to 95°C. Extra leach with stronger reagent for material balance purposes (not part of the normal dissolution flowsheet).

The partial procedure consisted of only the first leach to determine the amounts of tritium, krypton, and iodine in the fuel. Each leach solution was centrifuged, and the supernatant liquids and insoluble residues were submitted for ionic and radiochemical analysis. Off-gases were passed through traps and scrubbers and finally collected for determination of the fission product content. Leached Zircaloy cladding was dissolved in 6 M NH_4F --1 M NH_4NO_3 or in 10 M HF--0.05 M HNO_3 to determine the amounts of residual uranium, plutonium, and fission products.

These procedures enabled us to accomplish the following objectives:

1. Compare the effect of voloxidation on the rate of dissolution and the solubility of the uranium, plutonium, and fission products.

2. Determine the amounts of $^3\text{H}_2$, ^{14}C , ^{85}Kr , ^{129}I , etc., in the fuel before and after voloxidation.
3. Characterize the volatility of fission products during dissolution. This was done by rinsing lines and traps and by absorbing fission products in scrubbers.
4. Characterize the leached cladding.
5. Characterize the insoluble residues from the dissolutions.

Material balances were calculated from the sums of each analysis. Sources of error in the material balances could be due to variations in weights (± 0.1 g) of starting and voloxidized products, uranium and plutonium analyses ($\pm 5\%$), and volumes of leach solutions (± 1 to 2 ml). Plutonium weights were calculated from the plutonium alpha activity per milliliter of solution (thenoyltrifluoroacetone extraction method) and a calculated specific activity for the plutonium [α counts min^{-1} (mg Pu) $^{-1}$] based on its isotopic composition. For example, in Run LWR-1:

$$\begin{aligned}
 &^{238}\text{Pu} \ 1.66\% \times 1.97 \times 10^{10} \text{ counts min}^{-1} \text{ mg}^{-1} \\
 &= 3.27 \times 10^8 \text{ counts min}^{-1} \text{ (mg Pu)}^{-1} \\
 &^{239}\text{Pu} \ 54.62\% \times 6.95 \times 10^7 \text{ counts min}^{-1} \text{ mg}^{-1} \\
 &= 3.80 \times 10^7 \text{ counts min}^{-1} \text{ (mg Pu)}^{-1} \\
 &^{240}\text{Pu} \ 26.18\% \times 2.70 \times 10^8 \text{ counts min}^{-1} \text{ mg}^{-1} \\
 &= 7.07 \times 10^7 \text{ counts min}^{-1} \text{ (mg Pu)}^{-1} \\
 &^{242}\text{Pu} \ 5.85\% \times 4.41 \times 10^6 \text{ counts min}^{-1} \text{ mg}^{-1} \\
 &= 2.58 \times 10^5 \text{ counts min}^{-1} \text{ (mg Pu)}^{-1} \\
 &\text{Total} = 4.36 \times 10^8 \text{ counts min}^{-1} \text{ (mg Pu)}^{-1}
 \end{aligned}$$

Fission product weights in the irradiated UO_2 were calculated using the average values derived from spark source mass spectrometry (SSMS) analysis of the first-leach solutions and the dissolution residues.

4.4.2 Material balances

Material balances for this first series of dissolution experiments are given in Table 7. The initial weights of UO_2 or U_3O_8 include the fission products and plutonium formed during irradiation. Recoveries were generally within the limits of experimental error and satisfactorily accounted for the material. Note that voloxidation increased the amount of insoluble residue from ~ 0.2 wt % in runs -1A and -3B (unvoloxidized) to ~ 0.6 wt % in runs -1B, -1C, -2A, and -3A (voloxidized). Voloxidation

Table 7. Overall material balances on dissolution of unvoloxidized UO_2 or voloxidized U_3O_8

Voloxidation Run No.	None	-1	-1	-2	-3	None
Dissolution Run No.	-1A	-1B	-1C	-2A	-3A	-3B
Inputs (g)						
U_3O_8^a	0.00	18.50	97.80	19.00	75.20	0.00
UO_2 , equivalent ^b	29.75	17.81	94.18	18.29	72.42	29.60
Cladding	<u>6.75</u>	<u>0.00</u>	<u>23.30</u>	<u>0.19</u>	<u>0.00</u>	<u>6.80</u>
Total, as UO_2	36.50	17.81	117.48	18.48	72.42	36.40
Outputs (g)						
UO_2	29.20	17.53	92.33	18.36	72.87	28.41
PuO_2	0.25	0.14	0.82	0.16	0.50	0.26
Residue	0.05	0.11	0.42	0.11	0.53	0.06
Cladding	6.75	0.00	23.30	0.19	0.00	6.80
Fission products	<u>0.53</u>	<u>0.32</u>	<u>1.68</u>	<u>0.33</u>	<u>1.33</u>	<u>0.52</u>
Total, as UO_2	36.78	18.10	118.57	19.15	75.22	36.05
Recovery (%)	100.8	101.7	100.9	104.6	103.9	99.0
Residue (wt % of fuel)	0.18	0.60	0.45	0.57	0.72	0.20

^aIncludes plutonium and other fission products.

^b $\text{UO}_2 = \text{U}_3\text{O}_8 \times 0.963$.

also appeared to increase the small amount of undissolved uranium and plutonium reporting to the residue by about the same factor (Table 8).

4.4.3 Isotopic analyses of fuel

The postirradiation uranium and plutonium isotopic analyses for two of the first-leach (most concentrated) solutions are given in Table 9. The calculated specific activity of the plutonium in each sample, derived from the isotopic analysis, is also listed; it was used to calculate the weight of plutonium in each sample.

Alpha energy (pulse height) analysis of the gross alpha and plutonium alpha samples from first-leach solutions indicated the presence of other transuranium elements (Table 10). For example, radiochemical and alpha pulse height analyses indicated that the first-leach solution from run LWR-3B contained the following nuclides:

Nuclide	Concentration (mg/ml)	Concentration (g/g of U)	ORIGEN (g/g of U)	Experimental ORIGEN
Uranium	307.9	1.00	1.00	
Plutonium	2.85	9.02×10^{-3}	9.57×10^{-3}	0.94
^{241}Am	4.33×10^{-2}	1.37×10^{-4}	2.21×10^{-4}	0.62
^{242}Cm	3.83×10^{-5}	1.21×10^{-7}	1.05×10^{-7}	1.15
^{244}Cm	7.21×10^{-3}	2.28×10^{-5}	5.64×10^{-5}	0.40

Agreement between calculated and experimental values was good for plutonium, but the higher actinide values once again indicated the need for certain refinements in the ORIGEN calculation.¹⁰

Alpha pulse height data on samples of the insoluble dissolution residues from several experiments (Table 11) indicated the residue contained less curium than the leach solutions [i.e., $\sim 1.4 \times 10^6$ alpha counts min^{-1} (mg U) $^{-1}$ compared with $\sim 3.3 \times 10^6$ alpha counts min^{-1} (mg U) $^{-1}$].

4.4.4 Uranium and plutonium contamination of cladding

More uranium and plutonium were found associated with the leached cladding segments when the cladding was dissolved in 6 M NH_4F --1.0 M NH_4NO_3 (Zirflex reagent) than when it was dissolved in 10 M HF --0.05 M HNO_3 (Table 12). Additional tests are indicated, since the 2.05×10^5 plutonium counts min^{-1} (g Zr-4) $^{-1}$ in run LWR-1A is equivalent to

Table 8. Uranium and plutonium dissolved in successive leaches

Leach no.	HNO ₃ (M) ³	KF (M)	Time (hr)	Amount dissolved each leach (% of total)											
				Run 1A ^a		Run 1B		Run 1C		Run 2A		Run 3A		Run 3B ^a	
				U	Pu	U	Pu	U	Pu	U	Pu	U	Pu	U	Pu
1	7	0	2	99.99	99.99	99.98	99.96	99.93	99.72 ^b	99.99	99.97	99.98	99.97	99.76 ^b	99.97
2	3	0	2	c	-	-	-	0.05	0.14	-	-	-	-	0.02	0.02
3	7	0	2	-	-	-	-	0.001	0.02	-	-	-	-	<0.01	0.01
4	8	0.05	2	-	-	-	-	0.001	0.003	-	-	-	-	-	-
Residue	-	-	-	0.001	0.004	0.010	0.038	0.004	0.009	0.012	0.017	0.018	0.026	0.144 ^b	0.004

^aNot oxidized before dissolution.

^bThese values can be rejected on a statistical basis, particularly the uranium in the residue of Run 3B.

^cNo leach performed.

Table 9. Isotopic analyses of first leach solutions from Rod G-10, Assembly B05, H. B. Robinson-2 Reactor (at. %) ^a

Mass	As fabricated	Run LWR-1	Run LWR-2
Uranium isotopes			
²³³ _U		<0.001	<0.001
²³⁴ _U	0.023	0.013	0.015
²³⁵ _U	2.56	0.629	0.628
²³⁶ _U		0.354	0.354
²³⁸ _U	97.42	99.00	99.00
Plutonium isotopes			
²³⁸ _{Pu}		1.66	1.63
²³⁹ _{Pu}		54.62	55.00
²⁴⁰ _{Pu}		26.18	26.20
²⁴¹ _{Pu}		11.69	11.30
²⁴² _{Pu}		5.85	5.87
²⁴⁴ _{Pu}		<0.001	<0.001

^aSpecific activities of plutonium for Runs LWR-1 and LWR-2 are 4.36×10^8 and 4.30×10^8 alpha counts min⁻¹ (mg Pu)⁻¹, respectively.

Table 10. Alpha energy analyses of first leach solutions^a

Run No.	U mg/ml	Pu α (cts min ⁻¹ ml ⁻¹)	5.15 MeV, %	5.50 MeV, %	Gr α (cts min ⁻¹ ml ⁻¹)	5.15 MeV, %	5.50 MeV, %	5.80 MeV, %	6.11 MeV, %
1A	316.6	1.17 x 10 ⁹	23.2	68.8	2.34 x 10 ⁹	12	38	26	19
1B	157.6	5.64 x 10 ⁸	24.4	69.6	1.13 x 10 ⁹	14	43	28	9
1C	316.1	1.22 x 10 ⁹			2.35 x 10 ⁹				
2A	319.7	1.23 x 10 ⁹			2.42 x 10 ⁹				
3A	273.7	8.01 x 10 ⁸	30	70	1.99 x 10 ⁹	14	49	30	8
3B	307.9	1.24 x 10 ⁹	<u>26</u>	<u>74</u>	2.29 x 10 ⁹	<u>17</u>	<u>46</u>	<u>30</u>	<u>6</u>
		Average	26	71	Average	14	44	29	11

^a5.15 MeV α - ²³⁹Pu + ²⁴⁰Pu.
5.50 MeV α - ²³⁸Pu + ²⁴¹Am.
5.80 MeV α - ²⁴³⁻²⁴⁴Cm.
6.11 MeV α - ²⁴²Cm.

Table 11. Alpha energy analyses of insoluble residues^a

Run No.	U mg/g	Pu α (cts min ⁻¹ ml ⁻¹)	5.15 MeV, %	5.50 MeV, %	Gr α (cts min ⁻¹ ml ⁻¹)	5.15 MeV, %	5.50 MeV, %	5.80 MeV, %	6.11 MeV, %
1A	48.54	6.71 x 10 ⁷			3.16 x 10 ⁸	12.3	58.5	19.2	5.3
1B	14.97	1.97 x 10 ⁸			9.37 x 10 ⁸	18.0	62.7	12.7	3.5
1C	6.69	6.98 x 10 ⁷			ND ^b				
2A	18.30	1.13 x 10 ⁸			1.48 x 10 ⁹	22.3	61.4	12.6	3.7
3A	21.67	9.19 x 10 ⁷	26.7	73.8	1.59 x 10 ⁹	19.6	61.0	15.2	4.0
3B	630	6.34 x 10 ⁷	<u>32.0</u>	<u>68.0</u>	1.86 x 10 ⁸	<u>13.5</u>	<u>57.6</u>	<u>23.9</u>	<u>5.0</u>
		Average	30	70	Average	17.1	60.4	16.9	4.3

^a 5.15 MeV α - ²³⁹Pu + ²⁴⁰Pu.
5.50 MeV α - ²³⁸Pu + ²⁴¹Am.
5.80 MeV α - ²⁴³⁻²⁴⁴Cm.
6.11 MeV α - ²⁴²Cm.

^bND = not determined.

$\sim 92 \mu\text{Ci/kg}$ Zr-4, or about ten times the limit of $10 \mu\text{Ci/kg}$ for consideration for disposal as alpha-free waste. These values [$10^5 \text{ counts min}^{-1} (\text{g Zr-4})^{-1}$] are typical of earlier unpublished hot-cell results on leaching irradiated PWR-1 blanket rods. In the earlier tests, contamination was suspected because when segments of the leached PWR-1 cladding were removed from the cell, washed, and dissolved in a laboratory hood (to minimize cross contamination), we found only ~ 10 to $16 \mu\text{Ci/kg}$ Zircaloy. Larger-scale tests in batch or continuous countercurrent leaches are needed to determine the lower limits of alpha contamination (see below for beta-gamma contamination).

4.4.5 Tritium in cladding

The amounts of tritium found in the fuel solutions consistently showed only 50 to 60% of the total estimated by ORIGEN; it was suspected that the remainder was in the Zircaloy cladding. We therefore installed a 600°C copper oxide unit, two traps, and two scrubbers in the off-gas lines and dissolved leached cladding segments from Runs 1A, 1C, and other sheared segments in $6 \text{ M NH}_4\text{F} - 1 \text{ M NH}_4\text{NO}_3$ (Zirflex solution). All of the solutions, including the Zirflex reagent, scrubbers, and trap rinsings, were analyzed for tritium. We found that substantial amounts of tritium had been fixed in the cladding and had been scrubbed from the off-gas stream after the copper oxide unit:

Run No.	$\text{dis sec}^{-1} (\text{g Zr-4})^{-1}$
1A	3.18×10^7
1C	2.25×10^7
Batch 2	2.18×10^7
Batch 3	2.69×10^7
Average	2.58×10^7

This is equivalent to $\sim 40\%$ of the tritium formed in Rod G-10 of Assembly B05.

Table 12. Effect of dissolvent on the amount of uranium and plutonium found in or on leached cladding

Run No.	Uranium [mg (g Zr-4) ⁻¹]		Plutonium [alpha counts min ⁻¹ (g Zr-4) ⁻¹]	
	10 M HF--0.05 M HNO ₃ dissolvent	6 M NH ₄ F--1 M NH ₄ NO ₃ dissolvent	10 M HF--0.05 M HNO ₃ dissolvent	6 M NH ₄ F--1 M NH ₄ NO ₄ dissolvent
1A	0.006	0.071	4.00 x 10 ⁴	2.05 x 10 ⁵
1Ca	0.003	0.095	4.18 x 10 ⁴	7.60 x 10 ⁵
1Cb	0.015		5.00 x 10 ⁴	

4.4.6 Fission product distribution during dissolution

Fission products in the segments of Rod G-10 were determined by summing the radiochemical analyses and/or gamma spectroscopy results on solutions, solids, and gases produced by each experiment. For comparison, the estimated concentrations of the fission products were calculated by Beatty, Campbell, and Croff in August 1976, using the ORIGEN computer code¹² and some generalized irradiation conditions. The estimated quantities of fission products [$\text{dis sec}^{-1} (\text{g U})^{-1}$ or $\mu\text{g} (\text{g U})^{-1}$] are compared with the experimentally determined values in Table 13. Many agreed quite well, while others did not. One analytical problem area was the purification of ^{99}Tc in the presence of larger quantities of ^{106}Ru . The calculated yield for ^{134}Cs isotope may be incorrect since the ^{137}Cs value was in close agreement; similarly, the calculated yield of ^{106}Ru may be too high. Relatively small amounts of ^{125}Sb were masked by other fission products in gamma spectroscopy. We were not able to account for ^{129}I in our system in amounts close to those of Campbell at ORNL⁵ and Harmon at SRL⁶ (i.e., 152 and 165 $\mu\text{g } ^{129}\text{I}$ per gram of uranium, respectively). In that run, $\sim 1.3 \mu\text{g}$ per gram of uranium was recovered from the voloxidizer walls and $\sim 79 \mu\text{g}$ per gram of uranium from the dissolver solution that had not been sparged, purged, or agitated during the dissolution. This indicated that the ^{129}I deposited onto the equipment before it could be recovered.

The overall recoveries of heavy metals and fission products in the fuel and cladding, on a run-by-run basis, are given in Table 14. The experimental values show little differences between the voloxidized and unvoloxidized fuel, except for tritium and ruthenium. The tritium listed includes that collected during voloxidation, during dissolution, and retained in the cladding; recovery in the voloxidation experiments was 79.4% of that found in nonvoloxidized fuel.

The distribution of fission products within the dissolution apparatus (Fig. 12) is shown in Tables 15 through 19. The location of the nuclide in the tables refers to the solution or solid in which the material was found. They include:

DS-1 - clarified first-leach solution (7 M HNO_3 start) after simmering 2 hr at 92 to 95°C.

Table 13. Comparison of "best" experimental totals with ORIGEN-predicted totals for fission products in H. B. Robinson UO_2 and cladding

Nuclide	Calculated ^a [dis sec ⁻¹ (g U) ⁻¹]	Experimental mean		Experimental Calculated
		[dis sec ⁻¹ (g U) ⁻¹]	No. of values	
³ H ₂	1.76 x 10 ⁷	1.79 x 10 ⁷	5	1.02
¹⁴ C	1.97 x 10 ⁴	2.05 x 10 ⁴	2	1.04
⁸⁵ Kr	2.66 x 10 ⁸	3.56 x 10 ⁸	3	1.34
⁹⁹ Tc	710 µg/g	371 µg/g	1	0.52
¹⁰⁶ Ru	3.08 x 10 ⁹	2.30 x 10 ⁹	5	0.75
¹²⁵ Sb	1.92 x 10 ⁸	9.69 x 10 ⁷	3	0.50
¹²⁹ I	187 µg/g	8.0 µg/g	1	0.43
¹³⁴ Cs	3.10 x 10 ⁹	1.72 x 10 ⁹	4	0.55
¹³⁷ Cs	3.62 x 10 ⁹	3.32 x 10 ⁹	4	0.92
¹⁴⁴ Ce	3.13 x 10 ⁹	2.54 x 10 ⁹	9	0.81

^aORIGEN run of Aug. 26, 1976. Decayed to Apr. 1, 1977 (1060 days from discharge).

Table 14. Overall recoveries of heavy* metals and fission products from H. B. Robinson
UO₂ fuel and Zircaloy-4 cladding

Nuclide	Run No.				
	1A ^a	3B ^a	1BC ^b	2A ^c	3A ^c
Uranium (g)	25.73	25.03	96.79	16.17	64.20
Plutonium (g)	0.22	0.23	0.89	0.14	0.44
Gross α ^d	7.25×10^9	7.44×10^9	7.25×10^9	7.35×10^9	7.29×10^9
³ H ₂ ^e	1.80×10^7	1.79×10^7	1.55×10^7	1.41×10^7	1.31×10^7
¹⁴ C ^e	1.15×10^4	2.03×10^4	2.07×10^4	1.61×10^4	1.69×10^4
⁸⁵ Kr ^e	3.23×10^8	3.88×10^8	Lost	3.33×10^8	f
⁹⁹ Tc (μg/g of U)	104.5	f	371.0	f	f
¹⁰⁶ Ru ^e	2.52×10^9	2.07×10^9	2.24×10^9	2.03×10^9	2.59×10^9
¹²⁵ Sb ^e	Low	9.60×10^7	9.16×10^7	6.44×10^7	1.03×10^8
¹²⁹ I (μg/g of U)	13	22	59	79	80
¹³⁴ Cs ^e	1.77×10^9	1.34×10^9	1.71×10^9	1.78×10^9	1.62×10^9
¹³⁷ Cs ^e	3.50×10^9	2.55×10^9	3.29×10^9	3.38×10^9	3.12×10^9
¹⁴⁴ Ce ^e	2.64×10^9	1.98×10^9	2.42×10^9	2.65×10^9	2.46×10^9

^aNot voloxidized.

^bVoloxidized; materials in dissolutions -1B and -1C calculated as one batch.

^cVoloxidized.

^dAlpha counts min⁻¹ (g U)⁻¹].

^e[dis sec (g U)⁻¹].

^fNot analyzed.

Table 15. Distribution of selected nuclides during the dissolution of H. B. Robinson-2 fuel in HNO₃
(Run LWR-1A: two-piece, unvoloxidized, clad UO₂; total 36.50 g)

Location ^a	Nuclide (%)											
	Uranium	Plutonium	³ H ₂ O	¹⁴ C	⁸⁵ Kr	⁹⁹ Tc	¹⁰⁶ Ru	¹²⁵ Sb	¹²⁹ I	¹³⁴ Cs	¹³⁷ Cs	¹⁴⁴ Ce
DS-1	98.44	98.85	52.91	99.26	N.A. ^b	4.65	72.00	≤ ^c	4.59	96.63	96.96	97.35
DS-1 rinse	1.55	1.14	0.63	0.73	N.A.	N.A.	1.03	≤	N.A.	1.20	1.21	1.20
T-1 rinse	0.002	0.003	0.037	N.A.	N.A.	N.A.	0.002	≤	0.27	0.003	0.003	<0.003
S-1	N.A.	N.A.	0.064	<0.001	N.A.	N.A.	0.006	≤	94.79	<0.007	<0.001	<0.001
T-2 rinse	N.A.	N.A.	0.036	N.A.	N.A.	N.A.	0.001	≤	≤	<0.001	<0.001	<0.001
S-2	N.A.	N.A.	0.009	<0.001	N.A.	N.A.	0.001	≤	≤	<0.001	<0.001	<0.001
DS-2	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit
DS-3	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit
DS-4	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit	Omit
Residue	0.001	0.004	N.A.	Omit	Omit	95.35	26.69	≤	N.A.	2.00	1.63	<0.001
Cladding	<0.001	<0.001	45.74	N.A.	N.A.	N.A.	0.27	≤	N.A.	0.17	0.19	0.23
Off-gas bag	d	-	-	N.A.	100.0	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Total (mg)	25,729.3	217.7	-	-	-	-	-	-	-	-	-	-
Total ^e	-	-	4.69 ₈ x 10 ⁸	2.97 ₅ x 10 ⁵	8.31 ₉ x 10 ⁹	2712 ^f	6.53 ₁₀ x 10 ¹⁰	-	326 ^f	4.74 ₁₀ x 10 ¹⁰	9.08 ₁₀ x 10 ¹⁰	8.68 ₁₀ x 10 ¹⁰
Total [dis sec ⁻¹ (gU) ⁻¹]	-	-	1.80 ₇ x 10 ⁷	1.15 ₄ x 10 ⁴	3.23 ₈ x 10 ⁸	104.5 ^g	2.52 ₉ x 10 ⁹	-	13 ^g	1.77 ₉ x 10 ⁹	3.50 ₉ x 10 ⁹	2.64 ₉ x 10 ⁹

^aSee text for description.

^bN.A. - not analyzed for nuclide.

^c< - below limits of detection by gamma spectroscopy.

^dMeans not applicable or not used (-).

^eDisintegrations per second as of Apr. 1, 1977.

^fμg.

^gg.μg (gU-Pu)⁻¹.

Table 16. Distribution of selected nuclides during the dissolution of H. B. Robinson-2 fuel in HNO₃
(Run LWR-3B: two-piece, unvoloxized, clad UO₂; total 36.40 g)

Location ^a	Nuclide (%)											
	Uranium	Plutonium	³ H ₂ O	¹⁴ C	⁸⁵ Kr	⁹⁹ Tc	¹⁰⁶ Ru	¹²⁵ Sb	¹²⁹ I	¹³⁴ Cs	¹³⁷ Cs	¹⁴⁴ Ce
DS-1	98.40	98.98	59.99	13.26	- ^b	91.2	52.64	81.94	11.97	99.97	99.69	99.97
DS-1 rinse	1.36	0.99	0.68	0.13	-	8.8	11.35	6.87	0.78	<0.001	<0.001	<0.001
T-1 rinse	N.A. ^c	N.A.	N.A.	< ^d	-	N.A.	0.001	0.001	2.77	<0.001	<0.001	<0.001
S-1	N.A.	N.A.	N.A.	86.72	-	N.A.	<0.001		85.26	<0.001	<0.001	<0.001
T-2 rinse	-	-	-	-	-	-	-	-	-	-	-	-
S-2	-	-	-	-	-	-	-	-	-	-	-	-
DS-2	0.06	0.023	0.006	N.A.	-	N.A.	0.033	0.283	N.A.	0.027	0.027	0.027
DS-3	0.04	0.006	0.010	N.A.	-	-	3.64	2.45	N.A.	<0.001	<0.001	<0.001
DS-4	-	-	-	-	-	-	-	-	-	-	-	-
Residue	0.14	0.004	N.A.	N.A.	-	N.A.	32.36	8.37	N.A.	<0.001	0.26	<0.001
Cladding	-	-	38.97	-	-	N.A.	-	-	-	-	-	-
Off-gas bag	-	-	-	-	100.00	N.A.	-	-	-	-	-	-
Total (mg)	25,032.0	230.4	-	-	-	-	-	-	-	-	-	-
Total ^e	-	-	4.50 _{x10⁸}	5.12 _{x10⁵}	9.77 _{x10⁹}	1697 ^f	5.22 _{x10¹⁰}	2.42 _{x10⁹}	552.4 ^f	3.38 _{x10¹⁰}	6.43 _{x10¹⁰}	4.99 _{x10¹⁰}
Total [dis sec ⁻¹ -(gU) ⁻¹]	-	-	1.79 _{x10⁷}	2.03 _{x10⁴}	3.88 _{x10⁸}	67.2 ^g	2.07 _{x10⁹}	9.80 _{x10⁷}	21.9 ^g	1.34 _{x10⁹}	2.55 _{x10⁹}	1.98 _{x10⁹}

^aSee text for description.

^b(-) means not applicable or not used.

^cN.A. - not analyzed for nuclide.

^d< - below limits of detection by gamma spectroscopy, not applicable or not used.

^eDisintegrations per second as of Apr. 1, 1977.

^fμg.

^gg.μg(gU-Pu)⁻¹.

Table 17. Distribution of selected nuclides during the dissolution of H. B. Robinson-2 fuel in HNO_3
(Run LWR-1BC: 139.6 g U_3O_8 and cladding from voloxidation LWR-1)

Location ^a	Nuclide (%)											
	Uranium	Plutonium	$^3\text{H}_2\text{O}$	^{14}C	^{85}Kr	^{99}Tc	^{106}Ru	^{125}Sb	^{129}I	^{134}Cs	^{137}Cs	^{144}Ce
DS-1	98.91	98.79	2.26	1.07	^b	85.36	14.86	\leq^c	19.78	99.88	98.69	99.99
DS-1 rinse	1.03	1.04	0.03	<0.01	-	0.20	0.13	\leq	0.003	\leq	1.02	\leq
T-1 rinse	0.002	<0.001	0.003	N.A. ^d	-	-	<0.001	\leq	0.15	\leq	\leq	\leq
S-1	<0.001	<0.001	<0.001	73.12	-	-	0.003	\leq	78.34	\leq	\leq	\leq
T-2 rinse	-	-	\leq	-	-	-	<0.001	\leq	-	\leq	\leq	\leq
S-2	-	-	\leq	3.27	-	-	0.002	\leq	-	\leq	\leq	\leq
DS-2	0.04	0.012	<0.001	N.A.	-	N.A.	0.48	0.44	N.A.	\leq	0.054	\leq
DS-3	0.001	0.019	N.A.	N.A.	-	N.A.	0.71	3.10	N.A.	\leq	\leq	\leq
DS-4	<0.001	0.002	N.A.	N.A.	-	N.A.	0.24	0.19	N.A.	\leq	\leq	\leq
Residue	0.005	0.014	-	N.A.	-	14.44	83.43	82.79	N.A.	\leq	0.12	\leq
Cladding	0.002	0.005	41.12	N.A.	-	N.A.	0.12	13.41	-	0.12	0.12	\leq
Off-gas bag	-	-	-	-	Lost	-	-	-	-	-	-	-
Total (mg)	96,792.2	849.8	-	-	-	-	-	-	-	-	-	-
Total ^e	-	-	1.28_9 $\times 10^9$	2.02_6 $\times 10^6$	-	7521^f	2.19_{11} $\times 10^{11}$	8.94_9 $\times 10^9$	5729^f	1.67_{11} $\times 10^{11}$	3.21_{11} $\times 10^{11}$	2.36_{11} $\times 10^{11}$
Total[dis/sec ⁻¹ - (g U) ⁻¹	-	-	1.55_7 $\times 10^7$	2.07_4 $\times 10^4$	-	77^g	2.29 $\times 10$	9.16_7 $\times 10^7$	58.6^g	1.71_9 $\times 10^9$	3.24_9 $\times 10^9$	2.42_9 $\times 10^9$

^a See text for description.

^b (-) means not applicable or not used.

^c \leq - below limit of detection by gamma spectroscopy.

^d N.A. - not analyzed for nuclide.

^e Disintegrations per second as of Apr. 1, 1977; includes releases during voloxidation.

^f μg .

^g $\mu\text{g}(\text{g U-Pu})^{-1}$.

Table 18. Distribution of selected nuclides during the dissolution of H. B. Robinson-2 fuel in HNO_3
(Run LWR-2A: 19.0 g U_3O_8 without cladding from voloxidation LWR-2)

Location ^a	Nuclides (%)											
	Uranium	Plutonium	$^3\text{H}_2\text{O}$	^{14}C	^{85}Kr	^{99}Tc	^{106}Ru	^{125}Sb	^{129}I	^{134}Cs	^{137}Cs	^{144}Ce
DS-1	97.85	98.16	0.079	0.001	-b	N.A. ^c	18.54	d	1.48	98.02	98.07	98.15
DS-1 rinse	2.14	1.81	<0.001	0.001	-	N.A.	0.36	≤	≤	1.88	1.85	1.84
T-1 rinse	N.A.	N.A.	<0.001	N.A.	-	N.A.	<0.001	<0.001	0.48	<0.001	0.001	<0.001
S-1	N.A.	N.A.	<0.001	0.011	-	N.A.	<0.001	<0.001	13.15	≤	<0.001	≤
T-2 rinse	-	-	-	-	-	-	-	-	-	-	-	-
S-2	-	-	-	-	-	-	-	-	-	-	-	-
DS-2	-	-	-	-	-	-	-	-	-	-	-	-
DS-3	-	-	-	-	-	-	-	-	-	-	-	-
DS-4	-	-	-	-	-	-	-	-	-	-	-	-
Residue	0.012	0.019	N.A.	N.A.	-	N.A.	81.13	<90	-	≤	0.008	≤
Cladding	-	-	(47.87) ^e	-	-	-	-	-	-	-	-	-
Off-gas bag	-	-	-	-	94.13	-	-	-	-	-	-	-
Total (mg)	16,173.6	144.1	-	-	-	-	-	-	-	-	-	-
Total ^f	-	-	2.30×10^8	1.39×10^6	2.86×10^{10}	-	3.31×10^{10}	1.05×10^9	1291^g	2.90×10^{10}	5.51×10^{10}	4.32×10^{10}
Total [dis sec ⁻¹ (g U) ⁻¹]	-	-	1.41×10^7	1.61×10^4	3.33×10^8	-	2.03×10^9	6.44×10^7	79.1^h	1.78×10^9	3.38×10^9	2.65×10^9

^aSee text for description.

^b(-) means not applicable or not used.

^cN.A. - not analyzed for nuclide.

^d< - below the limits of detection by gamma spectroscopy.

^e() - calculated value from other runs.

^fDisintegrations per second as of Apr. 1, 1977; includes releases during voloxidation.

^gμg.

^hμg(gU-Pu)⁻¹.

Table 19. Distribution of selected nuclides during the dissolution of H. B. Robinson-2 fuel in HNO_3
(Run LWR-3A: 75.2 g U_3O_8 from voloxidized, unclad UO_2 in LWR-3)

Location ^a	Nuclide (%)											
	Uranium	Plutonium	$^3\text{H}_2\text{O}$	^{14}C	^{85}Kr	^{99}Tc	^{106}Ru	^{125}Sb	^{129}I	^{134}Cs	^{137}Cs	^{144}Ce
DS-1	98.05	98.12	0.002	<0.001	- b	-	13.20	≤ ^c	52.17 ^d	98.17	98.16	98.23
DS-1 rinse	1.93	1.86	<0.001	<0.001	-	-	0.36	≤	1.41	1.86	1.82	1.75
T-1 rinse	-	-	-	-	-	-	-	-	-	-	-	-
S-1	-	-	-	-	-	-	-	-	-	-	-	-
T-2 rinse	-	-	-	-	-	-	-	-	-	-	-	-
S-2	-	-	-	-	-	-	-	-	-	-	-	-
DS-2	-	-	-	-	-	-	-	-	-	-	-	-
DS-3	-	-	-	-	-	-	-	-	-	-	-	-
DS-4	-	-	-	-	-	-	-	-	-	-	-	-
Residue	0.018	0.026	N.A. ^e	N.A.	-	N.A.	86.78	>90	N.A.	≤	≤	≤
Cladding	-	-	(49.61)	-	-	-	-	-	-	-	-	-
Off-gas bag	-	-	-	-	-	-	-	-	-	-	-	-
Total (mg)	64,201.3	436.3	-	-	-	-	-	-	-	-	-	-
Total ^f	-	-	8.49 ₈ x 10 ⁸	1.09 ₆ x 10 ⁶	-	-	1.67 ₁₁ x 10 ¹¹	6.66 ₉ x 10 ⁹	6016 ^g	1.05 ₁₁ x 10 ¹¹	2.02 ₁₁ x 10 ¹¹	1.59 ₁₁ x 10 ¹¹
Total [dis sec ⁻¹ (g U) ⁻¹]	-	-	1.31 ₇ x 10 ⁷	1.69 ₄ x 10 ⁴	-	-	2.59 ₉ x 10 ⁹	1.03 ₈ x 10 ⁸	80 ^h	1.62 ₉ x 10 ⁹	3.12 ₉ x 10 ⁹	2.46 ₉ x 10 ⁹

^aSee text for description.

^b(-) means not applicable or not used.

^c≤ - below limits of detection by gamma spectroscopy.

^dNo purge of dissolver-reflux only.

^eN.A. - not analyzed for nuclide.

^fDisintegrations per second as of Apr. 1, 1979; includes releases during voloxidation.

^gμg.

^hμg(gU-Pu)⁻¹.

DS-1 rinse - clarified 3 M HNO_3 used to rinse dissolver, cladding, and insoluble residue after first leach.

T-1 rinse - 3 M HNO_3 rinse of reflux condenser, connecting tubing, and empty spray trap located between dissolver and scrubber.

S-1 - 3 M NaOH from first off-gas scrubber.

T-2 - 3 M HNO_3 rinse of second empty spray trap located after 600°C copper oxide unit.

S-2 - 3 M NaOH from second off-gas scrubber.

DS-2 - clarified second-leach solution (3 M HNO_3).

DS-3 - clarified third-leach solution (7 M HNO_3).

DS-4 - clarified fourth-leach solution (8 M HNO_3 --0.05 M KF).

Residue - undissolved solids remaining after leaching.

Cladding - clarified solution of Zircaloy in HF -- HNO_3 or NH_4F -- NH_4NO_3 .

Off-gas bag - cumulative volume of dissolution off-gases and purge air.

The data indicate that most of the tritium in the fuel remained in the feed solutions, except for small amounts of condensate or spray that were carried to the first trap or scrubber. The ^{14}C in the fuel (except in Run 1A) also reported to the first scrubber, thus confirming Campbell's results.⁴ The ^{129}I (except in Run 3A) was also removed during dissolution by purging the oxides of nitrogen out of the dissolver to the first scrubber. Only trace quantities of other fission products were volatilized during dissolution, but additional amounts of the partially soluble ruthenium and antimony were dissolved by the third and fourth leaches with fresh 7 M HNO_3 . The amount of ruthenium in the insoluble residue increased by voloxidation from ~30% of the total in the fuel to >80% of the total.

The release of ^{85}Kr to the off-gas during dissolution in 7 M HNO_3 is shown in Figs. 27 and 28. Dissolution began almost at once as the ambient temperature HNO_3 was added to the dissolver. The apparent delay in the release was due to an 1800-cm^3 , or ~27-min, holdup between the dissolver and the multichannel ^{85}Kr analyzer atop the hot cells.

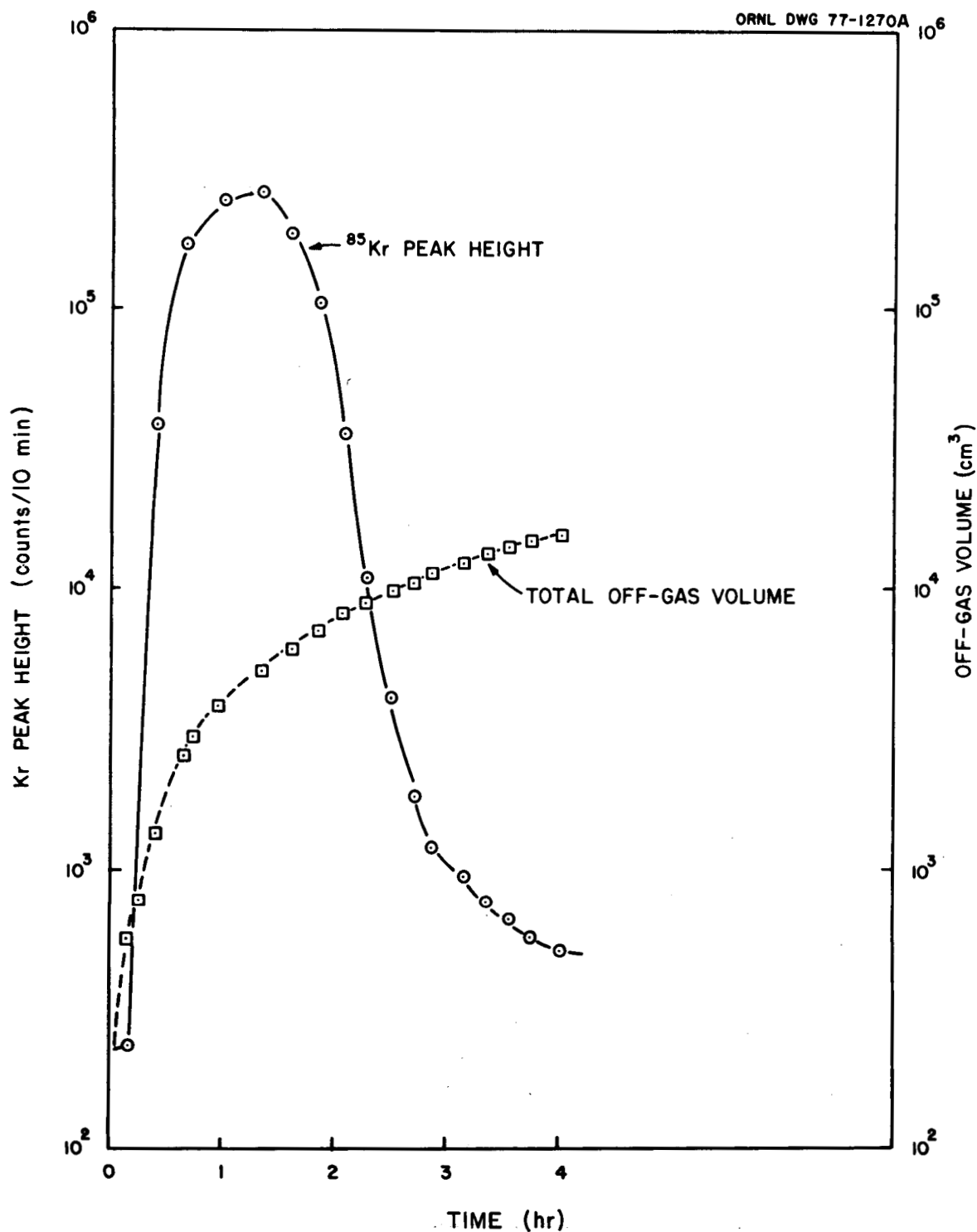


Fig. 27. Release of krypton during dissolution of 1-in. clad segments of UO_2 in HNO_3 .

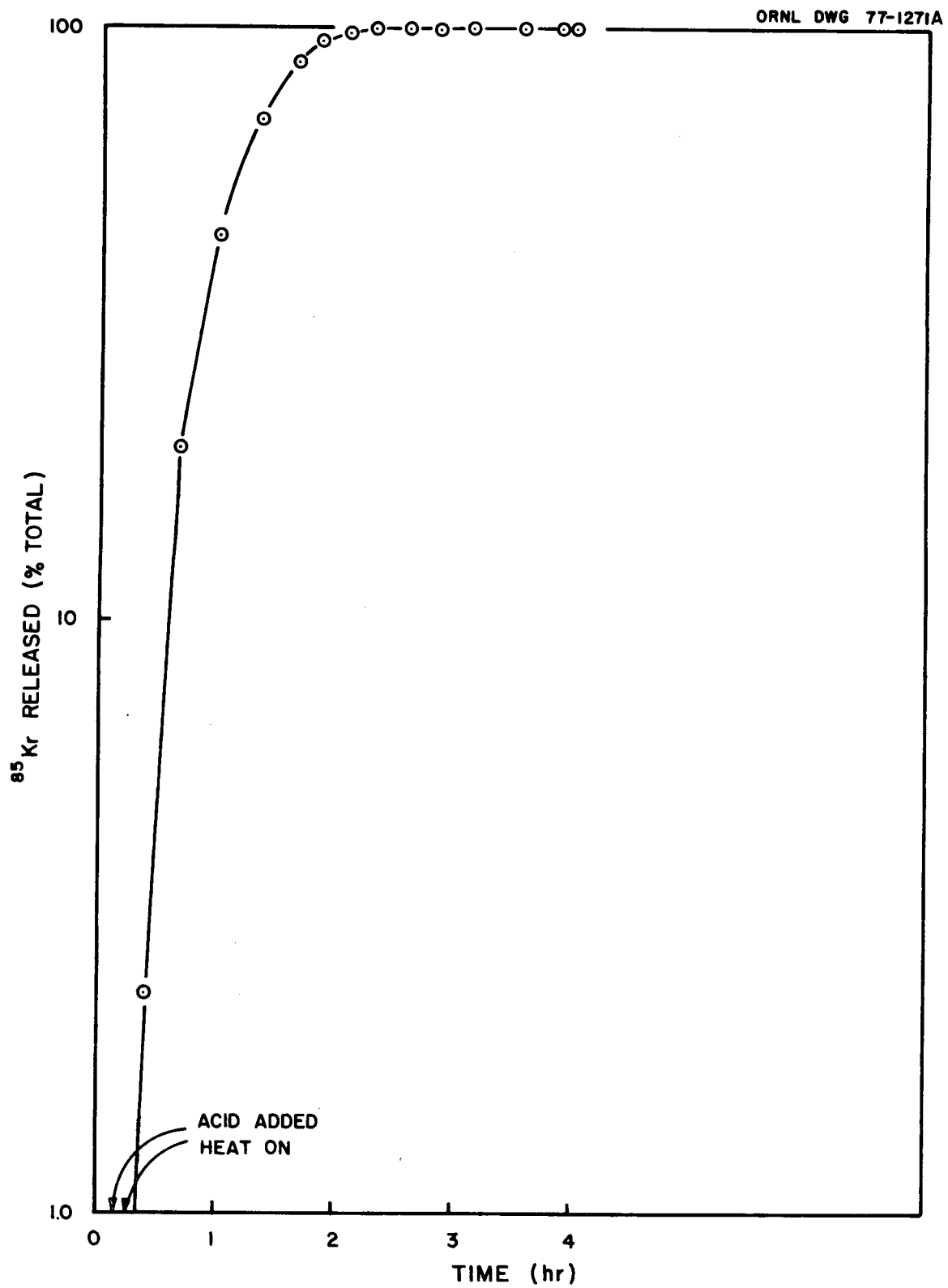


Fig. 28. Cumulative release of krypton during dissolution of UO_2 in HNO_3 .

4.4.7 Fission product content of first-leach solutions

Analyses of the first-leach solutions (i.e., dissolver product) from the dissolution experiments are summarized in Table 20. Examination of the data suggests several preliminary observations: (1) the cladding may hinder the volatilization of tritium and ^{14}C from the fuel (e.g., Runs 1BC and 2A with cladding vs Run 3A without); (2) the residual ^{14}C is released to the off-gas when the fuel is dissolved; (3) the effect of voloxidation on ^{99}Tc has not been resolved by radiochemical analysis; (4) ruthenium and antimony solubility decreases after voloxidation; (5) voloxidation at 480°C has essentially no effect on cesium and cerium solubility.

Elemental analyses of nonvoloxidized (Run 1A) and voloxidized (Run 1B) leach solutions as determined by SSMS are given in Table 21. Although the plutonium concentration of ~ 4.2 g per liter in Run LWR-1A does not agree with radiochemical analysis, the concentration in Run 1B is approximately correct (~ 1.3 g per liter). Wet chemical analysis (Table 20) gave a concentration ratio between runs of 2:1 for uranium plus plutonium. The SSMS analysis for the fission products indicates approximately the correct ratio of 2:1 for the soluble elements and also shows the decrease in solubility of ruthenium, rhodium, and others. Although samarium and gadolinium appear to be less soluble after voloxidation, these elements were not major components in SSMS examination of the residue, nor were they found in emission spectroscopy analysis of the residues.

4.4.8 Fission products in dissolution residues

The composition of the dissolution residue has been fairly well established as a mixture of molybdenum, technetium, the noble metals, and small amounts of zirconium.⁴ Analyses by SSMS and emission spectroscopy (ES) of the residues from four of these runs, LWR-1A, LWR-1B, LWR-1C, and LWR-3A, were in fair agreement:

Table 20. Analyses of first-leach solutions (dissolver product) from Rod G-10, Assembly B05, H. B. Robinson-2 Reactor

Analysis	Run No.				
	1A ^a	3B ^a	1BC ^b	2A ^b	3A ^c
H ⁺ (M)	4.53	N.A. ^d	5.04	4.58	5.42
Uranium (g/liter)	316.60	307.90	272.0	319.70	273.70
Plutonium (g/liter)	2.69	2.85	2.39	2.86	1.86
Pu α ^e	3.70 x 10 ⁹	4.03 x 10 ⁹	3.78 x 10 ⁹	3.85 x 10 ⁹	2.9 x 10 ⁹
Gross α ^e	7.39 x 10 ⁹	7.44 x 10 ⁹	7.33 x 10 ⁹	7.57 x 10 ⁹	7.2 x 10 ⁹
²⁴¹ Am α ^e		5.14 x 10 ⁸			
²⁴²⁻²⁴⁴ Cm α ^e		2.74 x 10 ⁹			
³ H ₂ [dis sec ⁻¹ (gU) ⁻¹] ^f	9.79 x 10 ⁶	1.07 x 10 ⁷	8.19 x 10 ⁴	1.12 x 10 ⁴	2.29 x 10 ²
¹⁴ C [dis sec ⁻¹ (gU) ⁻¹]	1.14 x 10 ⁴	2.69 x 10 ³	7.90	≤ ^g	≤
⁹⁹ Tc [dis sec ⁻¹ (gU) ⁻¹]	4.85	6.73 x 10 ¹	18.24	N.A.	2.27
¹⁰⁶ Ru [dis sec ⁻¹ (gU) ⁻¹]	1.81 x 10 ⁹	1.32 x 10 ⁹	3.37 x 10 ⁸	3.84 x 10 ⁸	3.50 x 10 ⁸
¹²⁵ Sb [dis sec ⁻¹ (gU) ⁻¹]	≤	8.53 x 10 ⁷	≤	≤	≤
¹²⁹ I [dis sec ⁻¹ (gU) ⁻¹]	0.58	2.79	11.59	1.19	7.86 x 10 ¹
¹³⁴ Cs [dis sec ⁻¹ (gU) ⁻¹]	1.77 x 10 ⁹	1.34 x 10 ⁹	1.71 x 10 ⁹	1.77 x 10 ⁹	1.62 x 10 ⁹
¹³⁷ Cs [dis sec ⁻¹ (gU) ⁻¹]	3.39 x 10 ⁹	2.54 x 10 ⁹	3.29 x 10 ⁹	3.37 x 10 ⁹	3.12 x 10 ⁹
¹⁴⁴ Ce [dis sec ⁻¹ (gU) ⁰¹]	2.57 x 10 ⁹	1.98 x 10 ⁹	2.42 x 10 ⁹	2.66 x 10 ⁹	2.46 x 10 ⁹

^aNot oxidized, clad fuel.

^bClad fuel voloxidized, 480°C, 4 hr.

^cUnclad fuel voloxidized, 480°C, 4 hr.

^dN.A. - not analyzed.

^e[counts min⁻¹ (g U)⁻¹].

^f~1060-days decay from discharge.

^g< - below the limits of detection.

Table 21. Spark source mass spectrometric analysis of first leach solutions

	Run		Ratio ^a 1A/1B
	LWR-1A	LWR-1B	
Mass equivalent (µg/ml)			
235	3000	1000	3.0
236	1500	500	3.0
237	200	40	5.0
238	Major	Major	-
239	3000	900	3.3
240	1200	400	3.0
241	700	200	3.5
242	300	80	3.8
243	50	10	5.0
Element			
Cs	900	500	1.8
Nd	900	400	2.3
Pd	800	250	3.2
Mo	600	200	3.0
Ru	500	20	25.0
Sm	350	80	4.4
Zr	350	130	2.7
Ce	300	100	3.0
Ba	300	200	1.5
Tc	300	40	7.5
Gd	200	10	20.0
Pr	150	70	2.1
Ca	150	50	3.0
Rh	150	15	10.0
Rb	150	70	2.1
Tc	150	40	3.8

^a $\frac{1A(U)}{1B(U)} = 2.01.$

Element	Residue composition, wt %				
	LWR-1A	LWR-1B	LWR-1C		LWR-3A
	SSMS	SSMS	SSMS	ES	ES
Tc	~2.0	2.0	3.0	8.0	2.5
Pd	6.0	7.0	10.0	10.0	12.5
Ru	35.0	40.0	30.0	45.0	55.0
Rh	0.25	0.20	1.0	5.0	13.5
Mo	15.0	13.0	10.0	30.0	10.0
Zr	6.0	5.0	<1.0	1.0	2.0
Sr	<1.0	1.0	<1.0	-	-

Calculations based on the ^{106}Ru radiochemical analyses for each of the residues, the specific activity of ^{106}Ru (2.95×10^{-4} g/Ci), and on the isotopic fraction of ^{106}Ru to total ruthenium (0.01031) indicated a slightly lower, but similar, ruthenium content of ~24 wt % in each of the residues.

Run No.	Total $^{106}\text{Ru}^a$ (dis sec $^{-1}$)	Calc. ruthenium wt. (mg)	Residue wt. (mg)	Ruthenium in residue (%)
LWR-1A	1.74×10^{10}	13.5	53.0	25.5
LWR-1BC	1.62×10^{11}	125.2	527.5	23.7
LWR-2A	2.69×10^{10}	20.8	106.4	19.5
LWR-3A	1.67×10^{11}	129.1	530.0	24.4
LWR-3B	2.01×10^{10}	15.5	57.2	27.2

^aTotal ^{106}Ru in residue only.

Voloxidation thus appeared to make more of the fission products insoluble; for example, ruthenium in the residue increased from 27 to 83% of the total ruthenium, thus contributing to the overall increase in weight (Table 7). The oxidation had little effect on the cesium and rare earths; data for technetium are incomplete.

Run No.	Oxidized at 480°C	% of total isotope found in residue			
		^{99}Tc	^{106}Ru	^{137}Cs	^{144}Ce
LWR-1A	No	95.4	26.8	1.6	<1.0
LWR-1B	Yes	9.8	83.6	<1.0	<1.0
LWR-1C	Yes	29.9	83.8	<1.0	<1.0
LWR-2A	Yes	a	81.1	<1.0	<1.0
LWR-3B	Yes	a	86.8	<1.0	<1.0

^aAnalyses inconclusive.

4.4.9 Fission products in cladding

Segments of leached cladding were dissolved in 10 M HF--0.05 HNO₃ or in 6 M NH₄F--1 M NH₄NO₃ to determine the residual uranium and plutonium (reported above) and fission products. We found, using the two reagents, little difference in the amounts of radionuclides, except for the effect of additional leaching.

Run No.	Nuclide, dis sec ⁻¹ (g Zr-4) ⁻¹					
	^{106}Ru		^{125}Sb		^{137}Cs	
	10 M HF	Zirflex	10 M HF	Zirflex	10 M HF	Zirflex
LWR-1A ^a	1.62×10^7	2.59×10^7	6.64×10^7	6.18×10^7	2.56×10^7	1.19×10^7
LWR-1C ^b	1.19×10^7	9.19×10^6	5.15×10^7	5.13×10^7	1.72×10^7	7.53×10^6

^aOne 2-hr leach, 8 M HNO₃.

^bThree 2-hr leaches as per procedures.

Using the values for residual fission products from Run LWR-1C (above), the weights of cladding, and the weights of the uranium in the fuel rods charged to the dissolver, we calculated the levels of contamination on the leached cladding to be:

Nuclide	dis sec ⁻¹ (g U) ⁻¹	Ci/MTU ^a	Ci/MT Zr-4
¹⁰⁶ Ru	3.12 x 10 ⁶	84	294
¹²⁵ Sb	1.46 x 10 ⁷	395	1383
¹³⁴ Cs	2.38 x 10 ⁶	64	224
¹³⁷ Cs	4.88 x 10 ⁶	132	462
¹⁴⁴ Ce	Very low	Very low	Low

^aMTU - metric tons of uranium.

Based on the weight of leached Zircaloy-4 alone, the amounts associated with waste cladding would be 3.5 times greater. The contamination levels agree closely with those reported by Campbell.⁴

5. ACKNOWLEDGMENTS

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7. APPENDIX

Table 1. H. B. Robinson-2 Reactor core mechanical design parameters
(all dimensions are for cold conditions)^a

<u>Active portion of the core</u>	
Equivalent diameter, in.	119.7
Active fuel height, in.	144.0
Length-to-diameter ratio	1.2
Total cross section area, ft ²	78.1
<u>Fuel assemblies</u>	
Number	157
Rod array	15 x 15
Rods per assembly	204 ^b
Overall dimension, in.	8.426 x 8.426
Fuel weight (as UO ₂), lb	176,200
Rod pitch, in.	0.553
Total weight, lb	226,200
Number of grids per assembly	7
Guide thimble ID, in. (above dashpot)	0.512
(at dashpot)	0.455
<u>Fuel rods</u>	
Number	32,028
Outside diameter, in.	0.422
Diametral gap, in.	0.0065
Clad thickness, in.	0.0243
Clad material	Zircaloy-4
Overall length, in.	152.360
Plenum length, in.	6.83
<u>Fuel pellets</u>	
Material	UO ₂ sintered
Density (% of theoretical)	
Region 1	94 (10.3 g/cc)
Region 2	92 (10.08 g/cc)
Region 3	91 (9.97 g/cc)
Fuel enrichments, wt %	
Region 1	1.85
Region 2	2.55
Region 3	3.10
Diameter, in.	0.3669
Length, in.	0.600

^aData taken from P. E. MacDonald, Aerojet Nuclear Company, personal communication to A. P. Malinauskas, ORNL (July 30, 1975).

^bTwenty-one rods are omitted, twenty to provide passage for control rods and one to contain in-core instrumentation.

Table 2. H. B. Robinson-2 Reactor, Assembly B05, power history^a

Date	Power			
	Average (kw/ft)	Peak (kw/ft)	EFPD ^b (kw/ft)	Burnup (MWd/MTU) ^c
Cycle I				
Oct. 1971	6.984	9.526	95.574	3738.414
Nov. 1971	6.968	9.659	119.979	4690.838
Dec. 1971	7.103	9.952	149.677	5872.262
Jan. 1972	7.241	9.564	177.194	6988.207
Feb. 1972	7.294	9.487	205.307	8136.586
Mar. 1972	6.975	8.703	235.551	9318.067
Apr. 1972	6.984	8.912	265.175	10476.822
May 1972	6.850	8.711	270.689	10688.366
June 1972	6.850	8.711	289.456	11408.360
July 1972	6.907	8.626	312.617	12304.323
Aug. 1972	6.580	8.267	341.243	13359.268
Sept. 1972	6.491	7.817	369.039	14369.771
Oct. 1972	6.544	8.384	398.627	15454.203
Nov. 1972	6.329	8.330	423.646	16341.049
Dec. 1972	6.230	8.228	443.9	17047.761
Jan. 1973	6.514	8.189	460.4	17649.731
Feb. 1973	6.659	8.503	475.7	18220.347
Mar. 1973	6.111	8.036	487.167	18612.816
Cycle II				
May 1973	5.412	6.976	6.477	18809.141
June 1973	5.136	6.565	25.432	19354.386
July 1973	5.576	7.332	58.801	20396.486
Aug. 1973	5.619	7.447	87.589	21302.456
Sept. 1973	5.448	7.052	116.562	22186.500
Oct. 1973	5.263	6.922	145.215	23031.092
Nov. 1973	5.322	6.678	166.160	23655.400
Dec. 1973	5.356	6.774	192.626	24449.312
Jan. 1974	5.384	6.783	221.157	25309.643
Feb. 1974	5.365	6.736	247.853	26111.799
Mar. 1974	5.349	6.681	278.105	27018.065
Apr. 1974	5.349	6.68	307.254	27891.366
May 1974	5.336	6.453	311.759	28026.
Total			799	

^aData taken from P. E. MacDonald, Aerojet Nuclear Company, personal communication to A. P. Malinauskas, ORNL (July 30, 1975).

^bEffective full power days.

^cTotal burnup (average) - 28026 MWd/MTU; total burnup [peak 3 ft (3 to 6 ft from bottom)] - 31363.9 MWd/MTU; discharged May 6, 1974.

Table 3. Assembly B05, average exposure and heat ratings during irradiation^a

Assembly average exposure (MWd/MTU)	Average (kw/ft)
Cycle 1	
3,595	7.03
6,886	7.24
10,532	6.85
13,191	6.58
16,205	6.33
18,515	6.11
Cycle 2	
18,713	6.01
22,119	5.45
25,276	5.38
27,007	5.35
28,026	5.34

^aThe axial flux shape measurements are from the center of Assembly B05 during Cycle 1. The Cycle 2 axial flux shapes are the weighted average of measurements taken in two immediately adjacent assemblies. (Data taken from P. E. MacDonald, Aerojet Nuclear Company, personal communication to A. P. Malinauskas, ORNL, July 30, 1975.)

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