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DEMONSTRATION OF THE ZIRFLEX AND SULFEX DECLADDING PROCESSES AND A MODIFIED PUREX SOLVENT EXTRACTION PROCESS, USING IRRADIATED ZIRCALOY-2 AND STAINLESS-STEEL-CLAD URANIA SPECIMENS

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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The Zirflex and Sulfex processes for chemical decladding Zircaloy or stainless-steel-clad UO_2 power reactor fuels were successfully demonstrated at irradiation levels as high as 28,200 Mwd/ton.

The Zircaloy jackets were dissolved in boiling 6 $\underline{M}$ NH_4F--1 $\underline{M}$ NH_4NO_3, and the stainless steel jackets were dissolved in refluxing 4 $\underline{M}$ H_2SO_4. Both processes gave average soluble losses of uranium and plutonium to the decladding reagents of about 0.05%. Centrifugation or filtration of the highly radioactive decladding waste solutions was required to recover UO_2 fines produced by fracture of the UO_2. The fines were recycled and dissolved with the UO_2 cores in boiling 4 $\underline{M}$ HNO_3 solution. About 5 to 6 hr were required for complete dissolution of the UO_2 core to produce terminal concentrations of 100 g of uranium per liter and 3 $\underline{M}$ HNO_3.

The core solution was a suitable solvent extraction feed after clarification and adjustment of plutonium valence with sodium nitrite. One cycle of the modified Purex process, in "Mini" mixer-settlers, using 100-g-uranium-per-liter feed solutions, gave losses of uranium and plutonium to the raffinate of less than 0.1%, and gross gamma decontamination factors of about 1.5×10^4 for the uranium product and about 5×10^3 for the plutonium product.

High purity $\underline{n}$-dodecane diluent for the 30% TBP solvent retarded the formation of nonremovable uranium-retaining degradation products in the solvent by factors of up to 20,

compared to Amsco-diluted TBP as measured by the uranium content of the washed solvent after six simulated cycles through the modified Purex process. The feed solutions were prepared from fuel specimens irradiated to 13,000 Mwd/ton and cooled about 1 year.

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1. INTRODUCTION

The design and construction of the first commercial power reactors in the United States was accompanied by laboratory studies on methods for reprocessing the spent fuel elements in order to produce feed solutions compatible with the nitric acid--tributyl phosphate solvent extraction systems used in USAEC reprocessing facilities. The subject of this report is the work done at Oak Ridge National Laboratory, which was concentrated on the chemical removal of zirconium alloy or stainless steel claddings from ceramic fuels, such as UO_2 and ThO_2-UO_2, which were to be used in the Shippingport Pressurized Water Reactor (PWR), the Yankee Atomic Electric Company reactor, the Consolidated Edison reactor, and others. Described also is the preparation of feed solutions and their subsequent use in a modified Purex solvent extraction system for the recovery of the uranium and plutonium.

1.1 Zirflex Process for Dissolving Zirconium or Zircaloy-2 Jackets

The Zirflex process, proposed by Hanford and others,[1-8] uses a boiling aqueous solution of ammonium fluoride and ammonium nitrate to dissolve zirconium or the high-zirconium alloys, such as Zircaloy-2. The reaction of zirconium with aqueous ammonium fluoride takes place with the evolution of hydrogen and ammonia gas:

$$Zr + 6\ NH_4F \longrightarrow (NH_4)_2ZrF_6 + 2\ H_2 + 4\ NH_3\ .$$

The addition of ammonium nitrate depresses hydrogen evolution and aids in the dissolution of the 1.5% tin present in Zircaloy-2. The modified reaction, used in these experiments, is as follows:

$$Zr + 6\ NH_4F + 0.5\ NH_4NO_3 \longrightarrow (NH_4)_2ZrF_6 + 5\ NH_3 + 1.5\ H_2O\ .$$

Average dissolution rates for unoxidized Zircaloy-2 are 10 to 15 mils/hr using a dissolvent consisting of 5.5 $\underline{M}$ NH_4F--0.5 $\underline{M}$ NH_4NO_3 at an F/Zr ratio of 7, and three- to fivefold less with Zircaloy-2 that had been exposed to high temperature air or water. Ammonia produced during the dissolution must be removed from the dissolvent to prevent a reduction in the dissolution rate and to prevent precipitation of the zirconium through an increase in the pH of the decladding solution. A high boilup rate with a high temperature in the condenser, or a steam sparge without reflux, effectively removed the ammonia.[7]

1.1.1 Solubility of UO_2 or UO_2-ThO_2 in the Zirflex process.

The uranium in the fuel element cores, sintered UO_2 or ThO_2-UO_2, is relatively insoluble in the fluoride decladding solution, giving losses proportional to the solubility of U(IV). The solubility of uranium decreases as the fluoride is complexed with uranium and as the ~~solution cools. The precipitated UF_4 can be removed and returned to~~ the dissolver to be dissolved with the core material. Oxidation of U(IV) to U(VI), with the resulting higher losses due to the greater solubility of uranyl fluoride, must be prevented during decladding. Hanford recommends that air sparging and similar procedures should be avoided.[7]

1.1.2 Corrosion of containers by Zirflex solutions.

Preliminary corrosion data showed that the Zirflex dissolvent corrodes stainless steel only slightly, permitting the use of a stainless steel dissolver and head-end system. Hanford found an average corrosion rate of 4.3 mils/month in cyclic decladding-core dissolution tests[7] for a type 309 stainless steel dissolver.

1.2 Sulfex Process for Dissolving Stainless Steel Jackets

Previous work at ORNL on the development of the Sulfex process, which uses boiling sulfuric acid to remove the stainless steel cladding from UO_2 or ThO_2-UO_2 ceramic cores, is described in refs 9 to 29. References 30 to 32 include processes for uranium and plutonium recovery from the sulfuric acid decladding wastes. Selected portions of the Sulfex studies at other sites are included in refs 33 to 35.

1.2.1 Dissolution rate for type 304L stainless steel jackets.

The dissolution rate of unirradiated 304L stainless steel in a 200% excess of boiling 4 M H_2SO_4 was about 2 mg $cm^{-2}min^{-1}$, which required about 4 to 5 hours for complete dissolution of the cladding.[16] Fisher at Hanford reported rates of 1 to 2 mg $cm^{-2}min^{-1}$ for type 304L stainless steel dissolving in refluxing 4 M sulfuric acid, which correspond to uniform penetration rates of 4 to 5 mils/hr, while on a pilot-plant scale the penetration rate was between 3 to 4 mils/hr in a recirculating dissolver.[34]

1.2.2 Solubility of UO_2 in the Sulfex decladding process.

Previous work showed losses of uranium and plutonium from sintered UO_2 pellets (93 to 95% of theoretical density) to the decladding solution ranged from 0.004 to 0.005% from unirradiated pellets[16,34] to 0.05 to 0.06% from pellets irradiated to 1440 Mwd/ton.[16] Tons means metric tons of uranium throughout this report. Swanson, at Hanford, reported dissolution rates for irradiated UO_2 in boiling 4 M H_2SO_4 of 0.02% per hour, which was decreased by the presence of the dissolving stainless steel and increased by the presence of ferric iron and air.[35]

1.3 Previous Applications of the Zirflex and Sulfex Processes

In 1959 the Zirflex and Sulfex processes were tested at Oak Ridge at irradiation levels of less than 1500 Mwd/ton. These initial tests on prototype PWR and YAEC fuels showed promise as decladding methods, but losses of uranium and plutonium to the decladding solutions appeared to increase in proportion to the irradiation level of the fuel specimens.[16] In 1961 a comprehensive program of flowsheet testing was proposed to the Savannah River Laboratories,[36] and, with their support, hot-cell tests were made to determine whether losses of uranium and plutonium would continue to increase at higher irradiation levels or whether other factors would adversely influence the performance of the Zirflex or Sulfex processes. In addition, the highly-irradiated UO_2 cores were dissolved in nitric acid, and the resulting feed solutions were put through one cycle of a modified Purex solvent extraction process suggested by the Savannah River Laboratory. Progress reports in this series are given in refs 37 to 40.

1.4 Acknowledgments

The authors wish to acknowledge the technical assistance of B. Lopez-Perez of the Spanish Junta de Energia Nuclear, who supervised part of the hot-cell operation performed by technicians L. A. Byrd, R. C. Shipwash, and G. E. Woodall. J. W. Ullmann was assisted by E. J. Frederick, C. W. Schersten, and G. A. West in the design and supervision of fabrication of prototype fuel specimens, arrangements for irradiations, and shipping of the specimens to Oak Ridge from Chalk River, the National Reactor Testing Station, and other sites. The wide variety of chemical ~~and radiochemical analyses were performed by the Analytical Chemistry~~ Division groups of C. E. Lamb, E. I. Wyatt, and J. H. Cooper, and W. R. Musick. Valuable assistance in radiation control was given by Health Physics personnel, J. Burden, R. B. Malcolm, B. T. Walters, and J. A. Westbrook during the receipt and transfer of fuel specimens and analytical samples during the hot cell program.

2. DESCRIPTION OF THE ZIRFLEX AND SULFEX FLOWSHEETS

2.1 Zirflex Decladding Process and Preparation of Solvent Extraction Feed

Figure 1 shows the Zirflex flowsheet used in the demonstration of the process on a Zircaloy-clad UO_2 specimen irradiated in the NRX to 16,800 Mwd/ton. The irradiated specimen was placed into a horizontal Pyrex glass dissolver in contact with a welded Ni-o-nel corrosion specimen, a volume of 6 $\underline{M}$ NH_4F--1 $\underline{M}$ NH_4NO_3 sufficient to give a F/Zr mole ratio 7 in the terminal decladding solution was added, and the solution heated to boiling. Makeup water was continuously added to

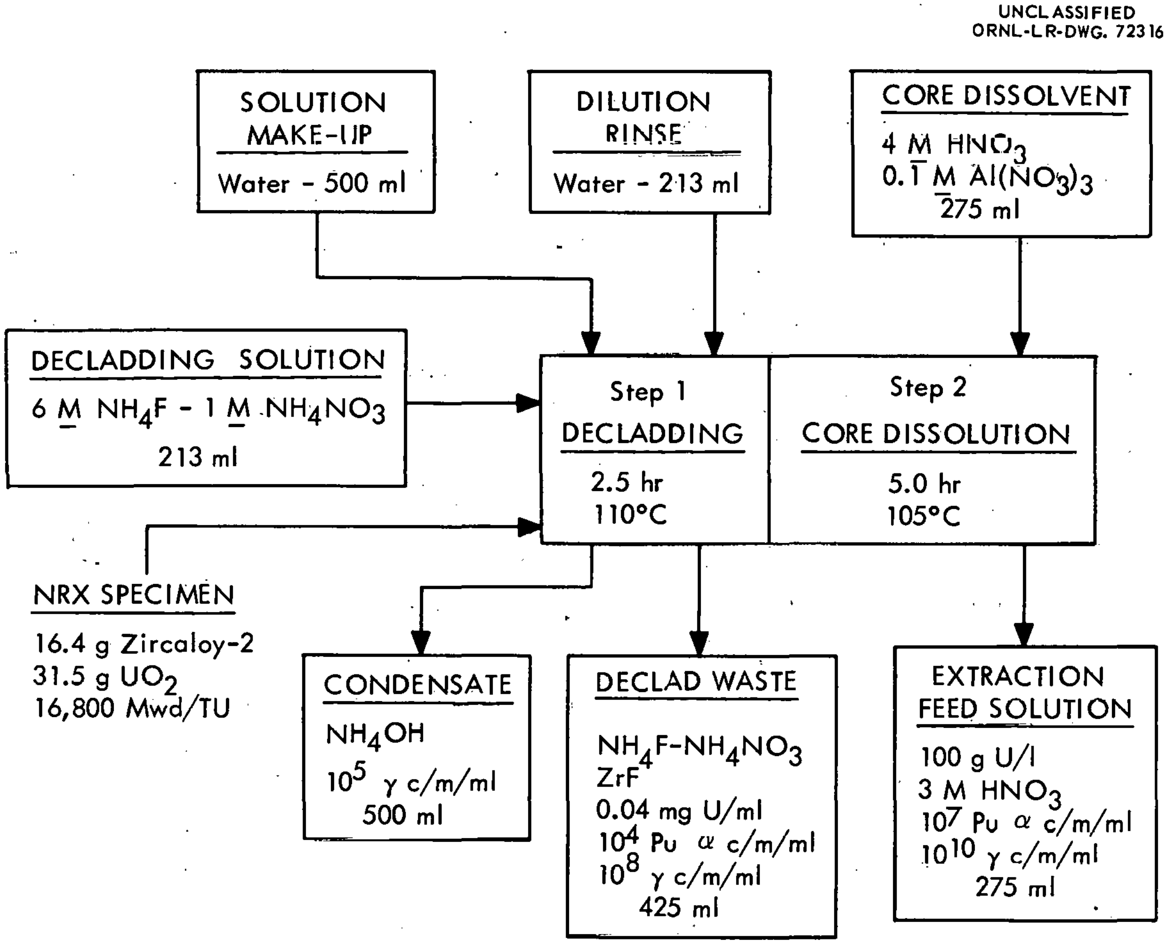

Fig. 1. Zirflex decladding and feed preparation.

the dissolver at the same rate as the steam and ammonia vapors were withdrawn through a downdraft condenser into a collection vessel. At the end of the reaction (2 to 3 hr), the decladding solution was withdrawn by vacuum, and the end-plug heel and UO_2 pellets were washed with an equal volume of water. The wash water was then used to dilute the decladding solution prior to filtration in order to make a stable decladding waste containing about 0.4 M zirconium (Fig. 2). The off-gas from the decladding reaction was passed through two caustic scrubbers prior to discharge to the off-gas system.

Following decladding and washing, the UO_2 core and fines retained on the filter were transferred to a 2-liter flask, along with the Ni-o-nel corrosion specimen, for dissolution of the UO_2 in dilute nitric acid containing a small amount of aluminum to complex any fluoride carried over on the pellets.

In order to produce directly a solvent extraction feed suitable for use in a modified Purex process flowsheet, 4 M HNO_3 was used as the core dissolvent. A uranium concentration in the feed of 100 g/liter was chosen in order to limit the concentration of U^{235} and thus allow processing in existing large process vessels of a Purex plant. The nitric acid concentration (4 M) was chosen to give a feed acidity of 3 M.

2.2 Sulfex Decladding Process and Preparation of Solvent Extraction Feed

Figure 3 shows the Sulfex flowsheet used in the hot-cell studies. A molecular weight of stainless steel of 55 and an acid consumption of 2 moles per mole of stainless steel was assumed. An excess of sulfuric acid was added to the dissolver, then the irradiated specimen and Ni-o-nel corrosion specimen were inserted, the dissolver closed, off-gas adjusted, and the heat turned on. If the decladding reaction had not begun after 1 hr of boiling, the passive fuel specimen was touched with iron wire to start the dissolution of the stainless steel. After the reaction ceased, the decladding solution was withdrawn by vacuum and the pellets washed with water. The decladding solution was diluted to prevent precipitation in experiments where solubility of stainless steel components

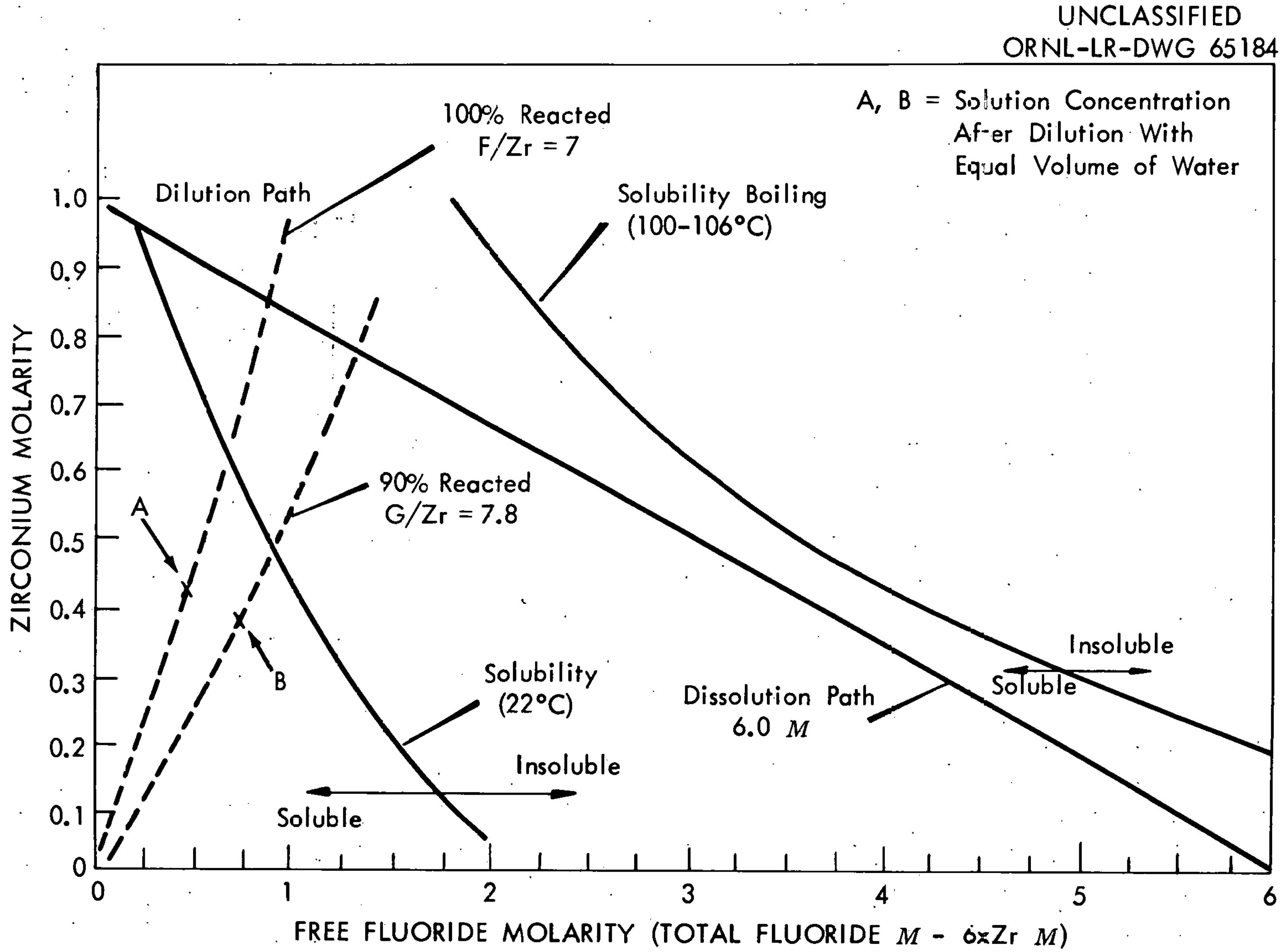

Fig. 2. Solubility of zirconium in ammonium fluoride solutions (adapted from Fig. 1, HW-65979).

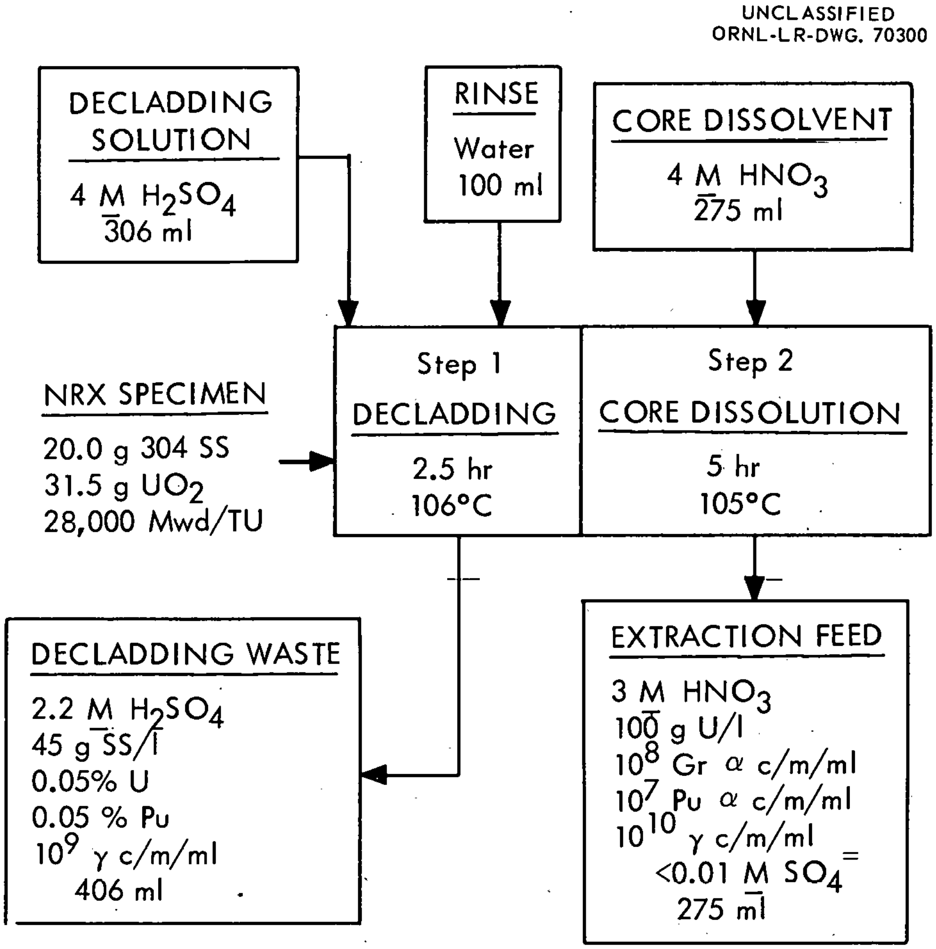

Fig. 3. Sulfex decladding and feed preparation.

in sulfuric acid had been exceeded. The decladding solution was finally filtered and sampled for analysis.

The UO_2 core was dissolved in the same manner as after the Zirflex head-end process. The pellets and fines were boiled in 4 M HNO_3 to produce a raw feed solution 3 M in HNO_3 and containing 100 g of uranium per liter.

2.3 Modified Purex Solvent Extraction Process

Figure 4 presents the Modified Purex flowsheet used in the process demonstration at high irradiation levels. The solvent extraction feed solution was made by dissolving the UO_2 core to produce a solution 3 M in HNO_3 containing 100 g of uranium per liter. The solution was then made 0.05 M in $NaNO_2$ to adjust the valence of the plutonium to the more extractable Pu(IV) state and was fed by displacement with Amsco 125-82 from a stainless steel tank to a 16-stage KAPL "Mini" mixer-settler used as the A-bank extraction-scrub contactor. The feed point of the contactor was adjustable to give combinations of 5 extraction--11 scrub or 7 extraction--9 scrub stages. The 30% TBP solvent was contacted countercurrently with the feed and 3 M HNO_3 aqueous scrub streams, and then cascaded to the 16-stage B-bank, or plutonium partitioning contactor. The feed point of the partitioning bank was also moveable to give either 7 scrub--9 partitioning or 5 scrub--11 partitioning stages. In the B-bank the plutonium was reduced to Pu(III) by the ferrous ion in the nitric acid-ferrous sulfamate partitioning solution (BX) and collected as the aqueous plutonium product, which was scrubbed free of uranium by the countercurrent 30% TBP solvent (BS) stream. The solvent bearing the uranium was then cascaded to an 8-stage stripping contactor where the uranium was stripped from the solvent by 0.02 M HNO_3. The waste solvent (CW) was discharged directly to the radioactive waste tank farm on a once-through basis. Periodic flowing stream samples were taken using master-slave manipulators and polyethylene sample bottles.

Previous experience with the "Mini" mixer-settler showed a 50% stage efficiency with similar flowsheets and, consequently, operation using 7 extraction--9 scrub stages was equivalent to operation with

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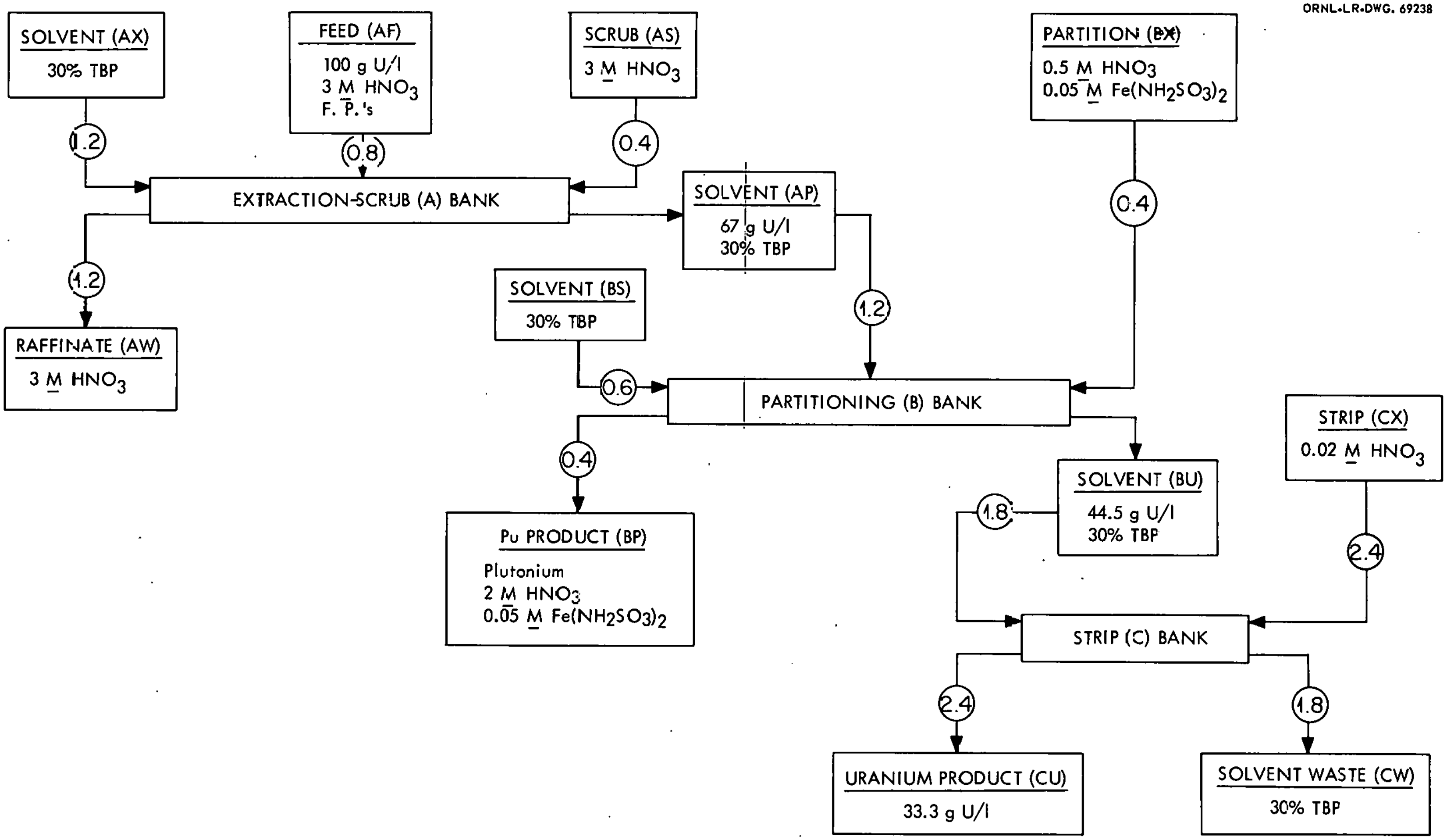

Fig. 4. Flowsheet for modified Purex solvent extraction (flows in ml/minute).

3.5 theoretical extraction stages and 4.5 theoretical scrub stages. The 8-stage stripping contactor had the equivalent of 4 theoretical stripping stages.

3. EXPERIMENTAL

3.1 Experimental Equipment Used in the Zirflex-Sulfex Studies

Figure 5 shows the hot-cell equipment as it was installed at the beginning of the Zirflex-Sulfex program. The round-bottom, 2-liter dissolver, heating mantle, and condenser are at the left on a Lab jack; the horizontal decladding dissolver and heater are at the right rear, with the Sulfex reflux condenser in place. The Zirflex downdraft condenser, condensate catch tank, and water-addition vessel are in standby position. The large cardboard tubes at the top of the rack lead to waste cans. Standard KAPL "Mini" mixer-settlers, drive motors, and catch vessels are shown mounted on a metal support frame at the left rear.

The horizontal decladding vessel was a very satisfactory design for ease of handling and replacement. Two sizes of horizontal dissolver (60-mm and 90-mm-OD Pyrex glass) permitted different volumes of decladding solutions and numbers of specimens to be processed without difficulty. The rachet-operated Lab jacks were also satisfactory for remote adjustment of vessel elevation, and the use of standard glass and Neoprene O-ring joints with metal clamps permitted easy replacement of equipment pieces.

3.2 History of the Fuel Specimens

3.2.1 <u>Fabrication of the specimens used in the Zirflex decladding experiments</u>.

Zirflex specimens for the irradiation program were of 3 main types: actual Westinghouse PWR blanket rods; 3-in.-long Zircaloy-2-clad PWR pellets encapsulated at ORNL; and 4.5-in.-long Zircaloy-2-clad 3.91%-enriched sintered UO_2 pellets encapsulated at ORNL. Density of the PWR UO_2 pellets was 93 to 95% of theoretical (10.95 g/cm^3), and the density of the enriched pellets was 96%.

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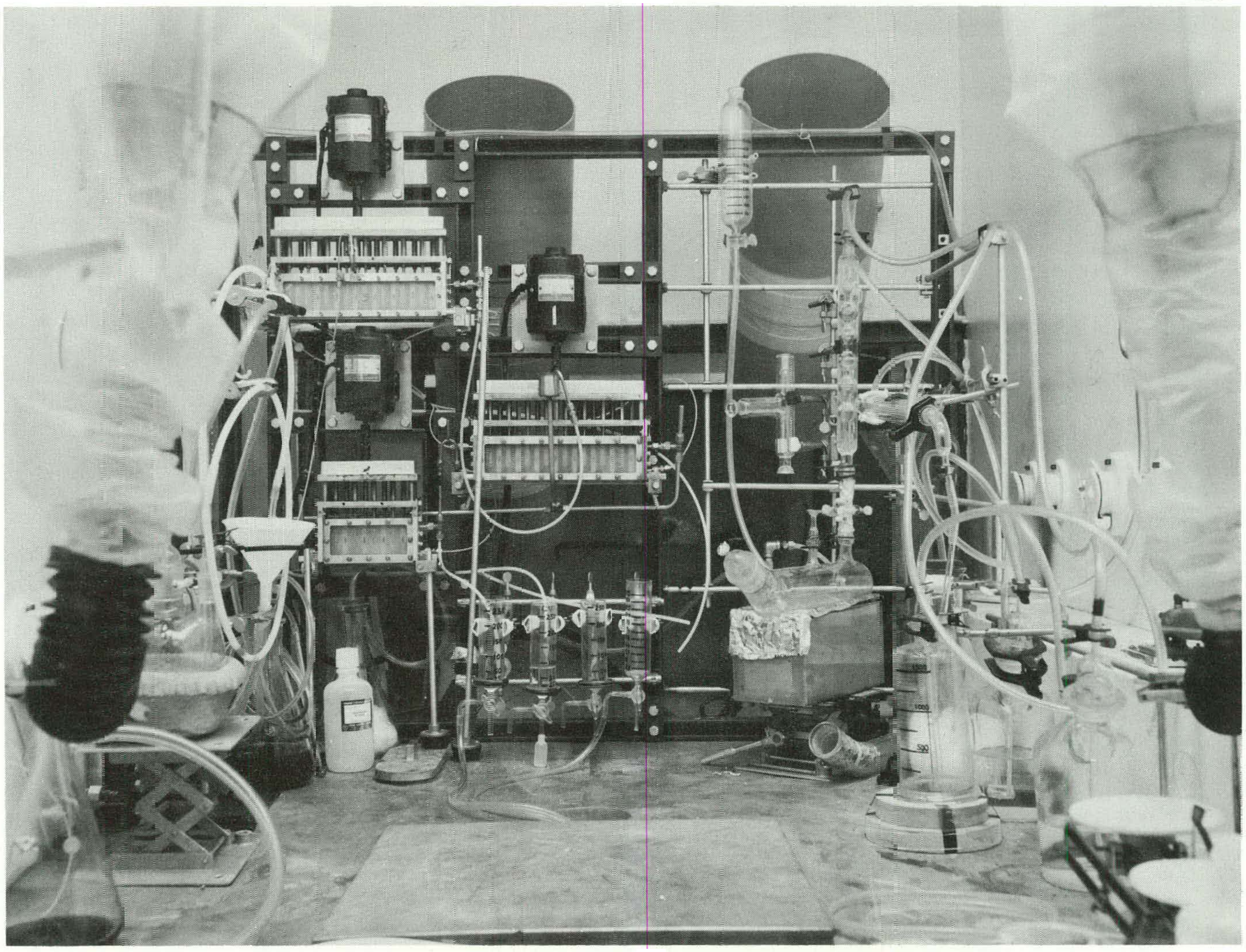

Fig. 5. Assembled equipment for Zirflex-Sulfex-Purex hot cell experiments.

The PWR blanket prototype fuel specimens (Fig. 6) were 10.25-in.-long x 0.413-in.-OD., had a 0.027-in. Zircaloy-2 cladding, and contained 26 UO_2 pellets of natural enrichment. The specimens were manufactured by the Westinghouse Electric Corporation Atomic Power Division according to WEC Dwg. 400C155, "PWR Core 1-Blanket, Fuel Rod Assembly," and corrosion tested, "Pentrex" tested, helium leak-tested, and certified reactor grade.[41,42]

The UO_2 pellets used to fabricate the irradiation specimens were presumed to have been manufactured by Westinghouse according to the procedures described in the book, The Shippingport Pressurized Water Reactor:[43] "There were four steps in the fuel component manufacturing process: agglomeration, compaction, sintering, and grinding.

"Agglomeration converted "as-received" nonflowing UO_2 powder into free-flowing granules. ("As-received" UO_2 refers to the powdered raw material produced by the Mallinkrodt Chemical Works by the hydrogen reduction of UO_3 obtained from mineral sources.) The brown-colored UO_2 powder had an apparent density of 3.0 g/cm^3, contained greater than 50 wt % fines (through -325-mesh particles), and consequently was not free flowing. In the agglomeration step the very small particles were bound together by a water-soluble organic binder, polyvinyl alcohol (PVA). Sterotex, a hydrogenated vegetable oil product, was then blended into the batch to provide lubricity and increase compactability. After blending, the granular UO_2 was ready for charging to the compacting press.

"...The pressure used was 125 tons/in^2. and resulted in a green (or "as-pressed") density of 73 to 74% of theoretical. The pressed compact, 0.4 in. diameter by 0.4 in. long had good green strength and could withstand reasonable handling ... .

"... As a preliminary step before sintering, the compacts were preheated in a separate furnace to remove the volatile hydrocarbons introduced by the organic binder (PVA) and the lubricant (Sterotex)... The production sintering process converted the 73 to 74% theoretical density compacts to 93 to 95% sintered pellets by applying a temperature of 1675°C for a period of eight hours.

"Grinding was the final step used to obtain precise dimensions... .

"...the sintered and ground pellets were checked for corrosion resistance in 750°F steam at 2000 psig for 20 hours. Not a single corrosion failure, as evidenced by physical change, was found among the 166,000 pellets tested during the entire manufacturing period. These 166,000 pellets amounted to a 4% random sample of the total fuel component production."

An earlier Westinghouse document further discusses the manufacture of the UO_3, UO_2, compaction tests, density, sintering tests, etc., on the raw materials.[44]

Recent density determinations on the PWR UO_2 pellets at ORNL, using the mercury displacement method, gave an average density for 19 pellets of 10.36 g/cm^3, or 94.7% of theoretical and within the PWR specifications of 93 to 95%. The densities ranged from 10.29 to 10.46 g/cm^3 by this method.

The 3-in. ORNL-clad specimens (Fig. 7) were fabricated in the ORNL "hot shop" in April 1958, using reject reactor grade PWR UO_2 pellets, received under IC-1597 via the Savannah River Plant on December 19, 1957, and Zircaloy-2 tubing, having a 30-mil wall, and bar stock.[45] The pellets were centerless ground at the Y-12 Plant at Oak Ridge to 0.357- to 0.359-in. OD and had odd lengths up to 0.375-in. long. After one end plug had been Heliarc welded onto the Zircaloy tubing in a dry box, the box was evacuated, backfilled with helium, and the pellets loaded into the specimen. The final end plug was then welded in the inert atmosphere. The welds were then dye checked and the specimens autoclaved for 24 hr at 300°C and 1250 psig, including 300 psig of oxygen overpressure, to test for leakage. Appendix A summarizes fabrication data for the ORNL 3-in. PWR specimens.

The other irradiation specimens used in the Zirflex experiments (Figs. 8 and 9) were made according to ORNL-LR-Dwg C-21345 from Zircaloy-2 tubing and bar stock, and the UO_2 pellets were made under specifications outlined in the proposal for PRFR irradiations in the Chalk River NRX reactor.[46] The Mark I irradiation specimens were 4.5-in.-long x 0.3125-in.

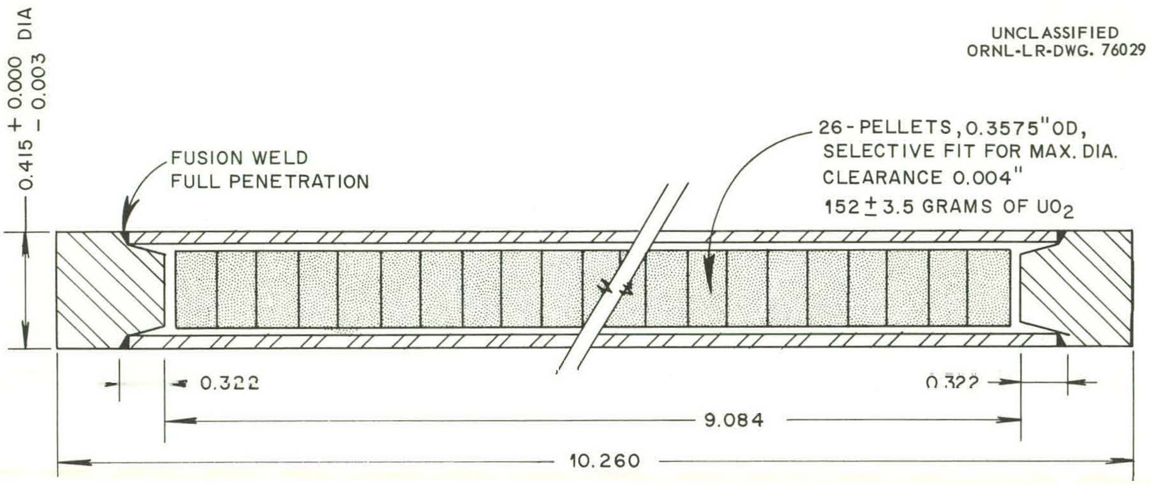

Fig. 6. PWR Core 1-blanket fuel rod assembly. (Zircaloy-2 clad, natural enrichment UO_2 pellets.)

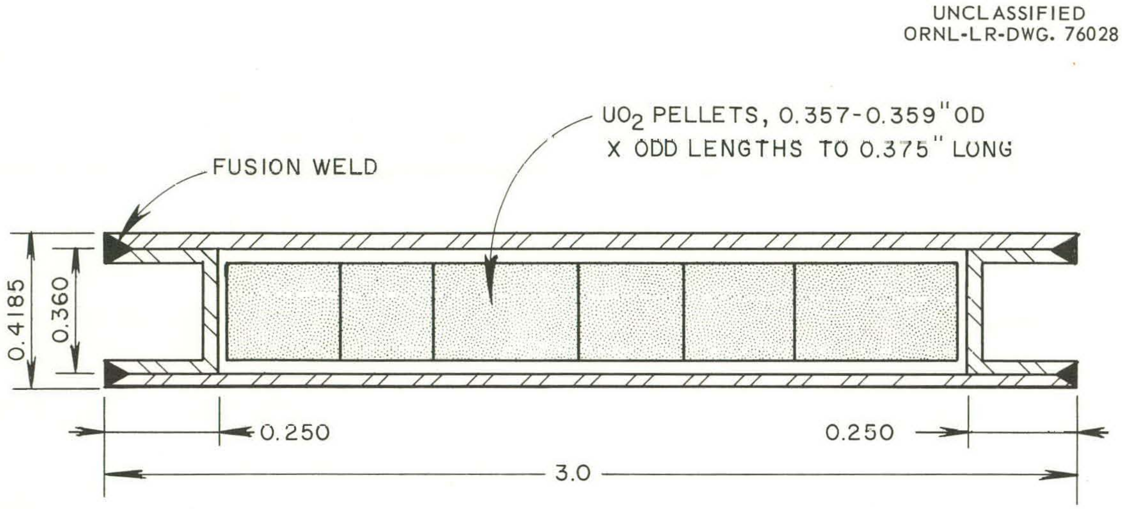

Fig. 7. ORNL 3-in. PWR irradiation specimen (Zircaloy-2 clad, natural enrichment UO_2 pellets.)

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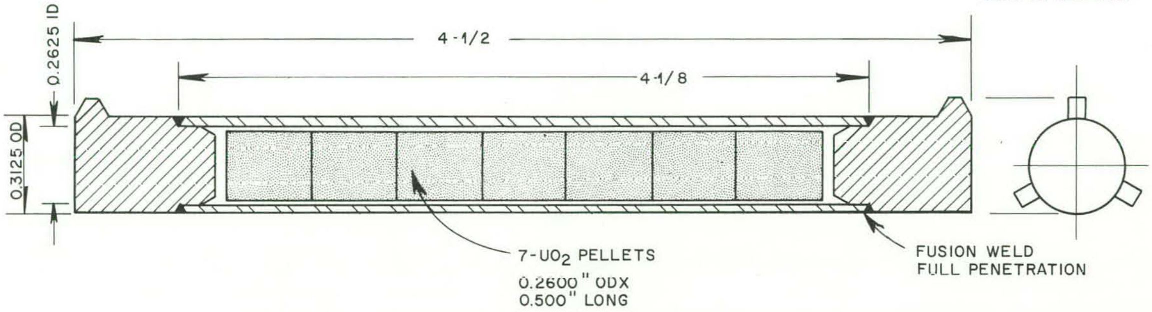

Fig. 8. ORNL Mark I irradiation specimen (Zircaloy-2clad, 3.91% enriched UO_2 pellets.)

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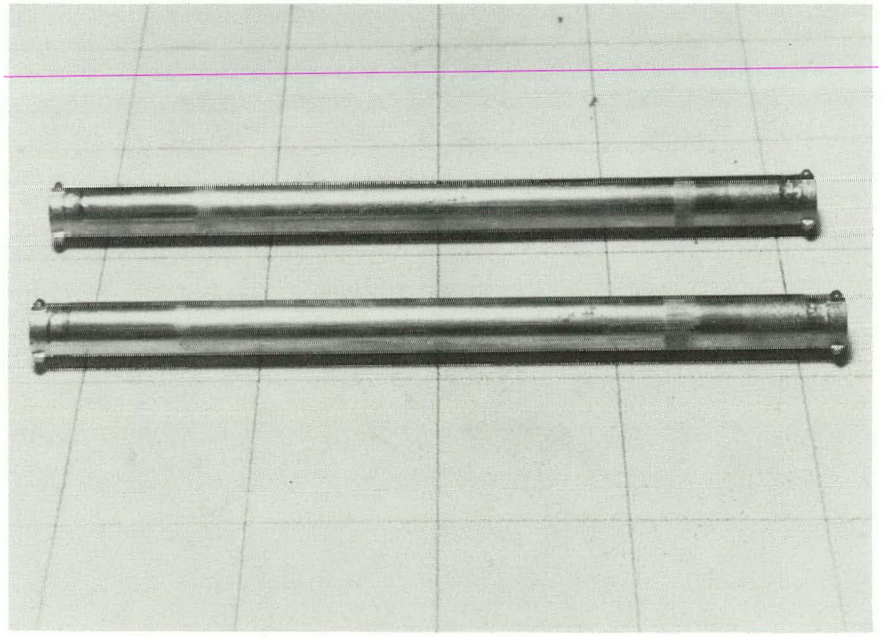

Fig. 9. Unirradiated Zircaloy-clad Mark I irradiation specimens. (Background is 1-inch grid.)

in OD and were filled with seven uranium dioxide pellets manufactured by the Nuclear Material and Controls Corp., whose quality control report listed the following impurities in the 3.91% enriched uranium dioxide:[47]

Fe	- 55 ppm	Mo	- 4 ppm	Si	- 50 ppm
B	- 0.2	Sn	- 4	Ni	- 25
Cd	- 0.2	Cu	- 5	F	- 1
Na	- 10	Pb	- 2	V	- 5
Mg	- 10	Cr	- 5	Ag	- 1

The report also stated the density of the lot of pellets to be 95.9% of theoretical, exceeding the specifications of 94 ± 1%. The ORNL Inspection Engineering Department, reporting on a 10% sampling (306 pellets) of the entire lot, determined that 278 exceeded specifications, 27 met, and only 1 was below specification density. Of the 278 pellets exceeding specification, 184 were greater than 95.7% of theoretical.[48] The ORNL Analytical Chemistry Division reported the O:U ratio of two random pellets to be 2.025 and 2.017. Each pellet had been inspected by the vendor as to diameter (0.2600 ± 0.0005-in.), length (0.500 ± 0.005 in.), and other dimensions. The pellets were inserted into the Zircaloy-2 shell assembly and placed in a helium atmosphere. The final end cap was welded into place without removing the specimen from the helium atmosphere. Each assembly was then tested with dye penetrant, x-ray radiography, helium-leak tested, glycol-vacuum tested, and finally pickled, weighed, and then autoclaved in water for 24 hr at 300°C and 1250 psi, and reweighed. Any rod that gained more than 0.004 g was rejected. Clearance between the UO_2 pellets and the 0.025-in. Zircaloy-2 of the tubing was 0.00125 in.

3.2.2 Irradiation history of the Zirflex specimens.

The first Zirflex experiments (HZ 1-4) were made to test the equipment and process with long-decayed PWR blanket rods of low irradiation level. Irradiation had been requested in the ETR at neutron fluxes of less than 2×10^{14}.[49] It was calculated that each rod would develop 8.05×10^{3} watts at a neutron flux of 1×10^{14} and 1.23×10^{4} at a flux of 2×10^{14}, giving metal-wall temperatures of 180°F and 210°F, respectively, using a saturation temperature at 32.2 psia of 255°F.[50]

The specimens were irradiated in positions I-3-NE and I-3-SW of the ETR arranged in two vertical rows of three rods each as ORNL experiments 43-6 and 43-7. The experiments were inserted on 10/27/58 for cycle 8, removed on 11/19/58, stayed out during cycle 9, were reinserted for cycle 10 on 12/8/58, but received on irradiation after 12/29/59, and were discharged on 1/5/59 because of a suspected fission product leak in one of the experiments.[51,52] The peak unperturbed neutron flux during the 1.5 cycles (43 days) of irradiation was about 1.5×10^{14}, giving an estimated peak 400 Mwd/ton.[53]

Four additional prototype PWR blanket rods were processed during runs HZ-16, -17, -21, and -22. They had been irradiated in the MTR or ETR to nominal levels of 5000, 10,000, and 11,000 Mwd/ton at unperturbed neutron fluxes ranging from 1.1 to 3.0×10^{14}. Two of the ORNL 3-in. specimens, irradiated to a nominal 12,000 Mwd/ton in the ETR at fluxes up to 3.3×10^{14} were processed in run HZ-18.[54] Figure 10 shows one of the specimens after irradiation.

The other Zirflex tests were made with 4.5-in. specimens irradiated in the NRX reactor at Chalk River. Twelve specimens from the region of highest flux were chosen for experiments HZ-5 through 15, and 4 from a lower flux region for HZ-19 and 20. ORNL holder 2, containing 20 ThO_2 and 100 UO_2 fuel specimens, each clad in Zircaloy-2, was inserted in position M-12 in the NRX reactor on 2/25/60, was irradiated for 327 full power days at peak neutron fluxes varying between 3.9×10^{13} to 5.6×10^{13}, and was discharged on 4/3/61. The average irradiation was calculated to be 17,610 Mwd/ton, and the peak irradiation was calculated to be 20,600 Mwd/ton.[54] The surface temperature of the specimens was calculated to be between 207 and 214°F.[47] Appendix B summarizes the complete irradiation history of holder 2.

Table 1 summarizes the fabrication and irradiation histories of the Zirflex test specimens. Included are the results of the isotopic analyses of the uranium before and after irradiation and the total burnup in megawatt days per metric ton, as calculated from the radiochemical analysis for the Cs^{137} content of the core solutions of approximately 100-g batches of uranium, that is, 1 PWR blanket rod or 4 NRX specimens.

Table 1. Irradiation Summary of Zirflex Process Test Specimens: Zircaloy-2-clad Sintered UC_2 Pellets

All specimens unbonded, helium filled, exposed to reactor cooling water WAPD PWR specimens 10.25 x 0.413 in. OD, ORNL-NRX specimens 4.5 x 0.3125 in. OD, other ORNL specimens 3 x 0.420 in. OD

Expt. No.	Irrad. No.	Specimen No.	Mfr.	Specimen Wt (g)	UO_2 Pellets		Enrichment (% U^{235})		Reactor	Date In	Date Out	Reactor Position	Peak Unpert. Flux Range	Irrad. (Mwd/TU)	Reactor Cycles	Average Power (Kw/KgU)
					Wt (g)	Theor. Den.	Start	End								
HZ-						%							$\times 10^{14}$			
1	43-7	ZDP-2412	WAPD	199.5	152 ± 3	93-95	0.71	unk.	ETR	10/27/58	1/ 5/59	I-3-SW	1.80	412	2	9.6
2	43-6	IDY-0018	WAPD	202.0	152 ± 3	93-95	0.71	unk.	ETR	10/27/58	1/ 5/59	I-3-NE	1.10	216	2	5.0
3	43-6	ZED-0931	WAPD	199.5	152 ± 3	93-95	0.71	unk.	ETR	10/27/58	1/ 5/59	I-3-NE	1.10	262	2	6.1
4	43-6	QEB-2904	WAPD	199.9	152 ± 3	93-95	0.71	unk.	ETR	10/27/58	1/ 5/59	I-3-NE	1.10	182	2	4.2
5	NRX-2	X-33	ORNL	47.0	31.25	96	3.91	1.70	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	16,800	22	51.4
6	NRX-2	X-13	ORNL	47.0	31.25	96	3.91	1.70	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	16,800	22	51.4
7	NRX-2	X-12	ORNL	47.3	31.25	96	3.91	1.70	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	16,800	22	51.4
8	NRX-2	X-9	ORNL	47.0	31.25	96	3.91	1.70	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	16,800	22	51.4
9	NRX-2	X-116	ORNL	47.0	31.25	96	3.91	1.66	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	17,700	22	54.2
10	NRX-2	X-60	ORNL	47.0	31.25	96	3.91	1.66	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	17,700	22	54.2
11	NRX-2	X-90	ORNL	46.8	31.25	96	3.91	1.66	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	17,700	22	54.2
12	NRX-2	X-36	ORNL	47.0	31.25	96	3.91	1.66	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	17,700	22	54.2
13	NRX-2	X-11	ORNL	46.7	31.25	96	3.91	1.68	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	17,400	22	53.3
14	NRX-2	X-115	ORNL	47.3	31.25	96	3.91	1.68	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	17,400	22	53.3
15	NRX-2	X-57,X-86	ORNL	94.4	62.50	96	3.91	1.68	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	17,400	22	53.3
16	43-10	RDR-1015	WAPD	201.2	152 ± 3	93-95	0.71	0.20	MTR	4/6/59	3/28/60	I-52-SE	3.00	8,950	17	27.9
17	43-38	ECJ-1237	WAPD	--	152 ± 3	93-95	0.71	0.14	ETR	12/22/59	6/ 5/61	GEH-18-IE4	1.5-2.6	13,100	13	25.3
18	43-34-35	23,29	ORNL	108.6	76.9	93-95	0.71	0.18	ETR	11/30/59	6/ 5/61	GEH-18-IE2	1.5-3.3	13,700	14	24.4
19	NRX-2	X-76,X-22	ORNL	93.8	62.50	96	3.91	2.46	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	14,600	22	45.8
20	NRX-2	X-10,X-40	ORNL	94.0	62.50	96	3.91	2.46	NRX	2/25/60	4/ 3/61	M-12	0.39-0.56	14,600	22	45.8
21	43-14	KDA-1660	WAPD	199.4	152 ± 3	93-95	0.71	0.24	ETR	4/23/59	4/17/61	I-3-NE	1.1-1.5	7,100	21	10.7
22	43-14	ZCQ-4176	WAPD	198.8	152 ± 3	93-95	0.71	0.30	ETR	4/23/59	4/17/61	I-3-NE	1.1-1.5	6,150	21	9.3

Figure 11 shows a 4.5-in.-long, Zircaloy-2-clad specimen after irradiation in the NRX reactor to 16,800 Mwd/ton. The unirradiated specimen was a continuous irridescent-gold to violet color, due to autoclaving, whereas the irradiated specimen was striped, corresponding to the location of the pellets.

3.2.3 Fabrication of the specimens used in the Sulfex decladding experiments.

Sulfex irradiation specimens were also of three major types: prototype Yankee Atomic Electric Company irradiation test specimens, 5.1-in. long x 0.342-in. in OD, obtained from the Westinghouse Atomic Power Department; two varieties of ORNL stainless-steel-clad PWR UO_2 pellets, about 3-in. long; and ORNL stainless-steel-clad, 96% density, 3.91% enriched UO_2 of the same dimensions as the Zirflex NRX specimens. Densities of the UO_2 pellets were 93 ± 1.5% for the WCAP Yankee specimens, 93 to 95% for the PWR UO_2, and 96% for the special pellets.

Fabrication of WCAP Specimens -- the WCAP specimens used in experiments HS-4 and HS-5 (Fig. 12) were made at the Blairsville Metals Plant and at the Atomic Fuel Plant at Cheswick, Pa., of the Westinghouse Atomic Power Department, as a part of the Yankee Atomic Electric Company research and development program.[55] Fabrication procedures for WCAP specimens were as follows.[56]

(1) Pelletization of UO_2 powders. Eighteen UO_2 pellets were required for each three-tube assembly. The raw material was enriched UO_2 powder purchased from the Mallinkrodt Chemical Company. The powders were pressed into pellets, nominally 0.300 in. diameter by 0.600 in. long, then prefired at 800°C for 2 hr to remove volatiles, followed by a 2 sinter at 1550°C to achieve interparticle bonding. The sintering was done in a dissociated-ammonia atmosphere. The pellets were finally centerless ground to various diameters after sintering to provide a varied pellet-tube clearance in the test specimens. Density of each group of pellets was 93 ± 1.5% of theoretical.

(2) Loading and Welding Tubes. All tubes were measured for size and examined for discontinuities with an eddy-current tester, cleaned

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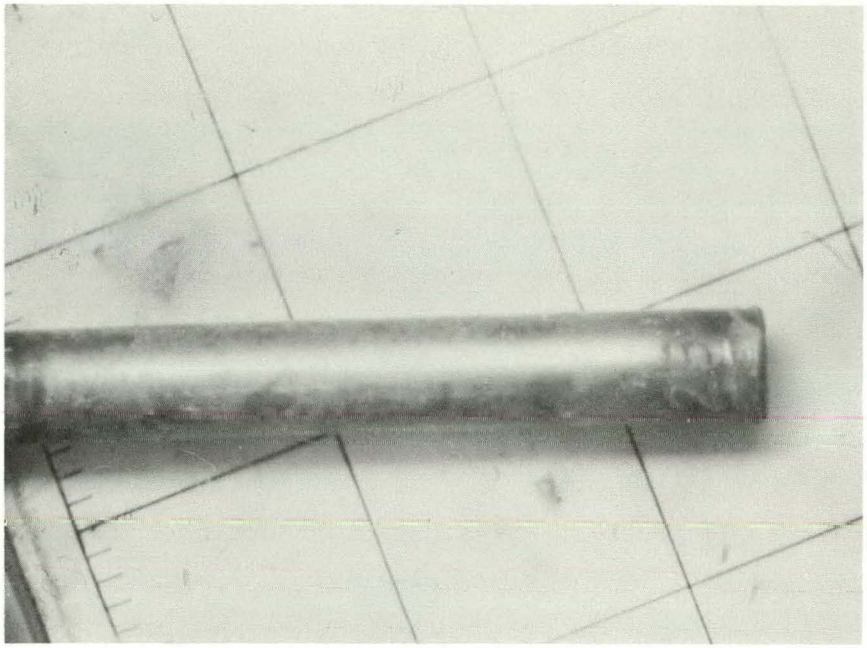

Fig. 10. ORNL 3-in. PWR specimen irradiated in ETR to 13,700 Mwd/ton. (Background 1-inch grid.)

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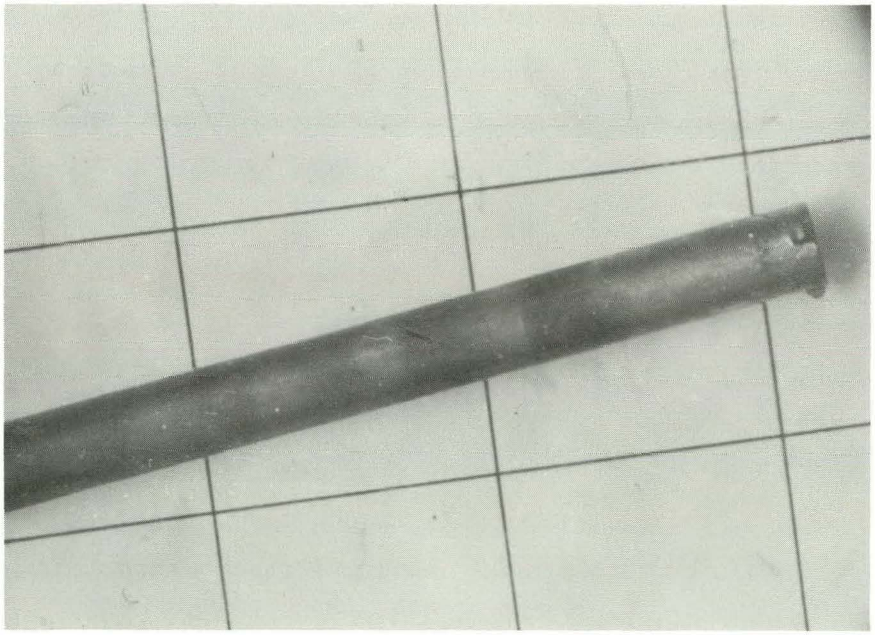

Fig. 11. Zircaloy-2 clad Mark I irradiation specimen after irradiation in MRX reactor to 16,800 Mwd/ton. (Background is 1-in. grid.)

with acetone, one end plug Heliarc-welded in place, transferred to a weld box for evacuation, back-filled with helium, and the other end plug pressed in. The final welds were inspected by helium-leak testing and radiography.

(3) Brazing. Nicrobraze No. 50 (11 to 15% Cr, 9 to 11% P, balance Ni) mixed with Acroiloid cement was used as brazing compound to attach ferrules to form a three-tube assembly. Brazing was done at 1825°F in a dry hydrogen atmosphere for 15 min.

(4) Autoclave Test. The brazed bundles were subjected to an autoclave test in degassed, demineralized water at 600°F and 1600 psi for 48 hr, followed by weighing and other examinations.

WCAP 1-3 (HS-4). Tubes G-6, G-8, J-10. The object of the irradiation was to proof test maximum pellet-to-tube cold clearance for Yankee fuel elements (0.0050 in.). The type 316 stainless steel cladding was 0.021-in. thick and was 0.342-in. in outer diameter. The enrichment of the UO_2 pellets was 2.7%, and the weight of the UO_2 per tube was 39.7541 to 40.0413 g.[56]

WCAP 2-1 (HS-5). Tubes A-1, A-3, A-7. The object of this irradiation was to determine the effect of pellet-to-tube clearances (0.0075, 0.0050, 0.0025 in.) on the center temperatures of UO_2 pellets. The cladding thickness and diameter were the same as in WCAP 1-3. The weight of UO_2 per tube was 38.4952-39.5194 and was enriched to 5.4%.[56]

ORNL-NRX No. 1 Specimens. The specimens used in experiments HS-6 through HS-13 (Fig. 13) were similar to the Zirflex specimens and were fabricated according to ORNL-LR-Dwg C-21345 from 0.025-in.-wall stainless steel tubing, type 304 bar stock, and special UO_2 pellets, made under specifications outlined in the proposal for PRFR irradiations in the NRX reactor.[46] The Mark I irradiation specimens were 4.5 in. long x 0.3125 in. in outer diameter and were filled with seven uranium dioxide pellets, weighing 31 to 32 g, of 3.91% enrichment and 95.9% theoretical density, manufactured by Nuclear Material and Controls Corp. (Numec). Total weight of each specimen was about 51 to 52 grams.

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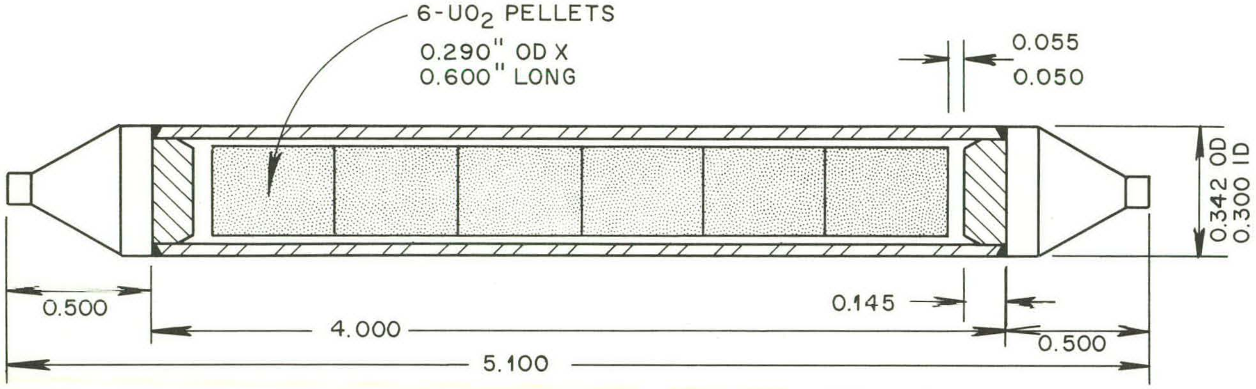

Fig. 12. WCAP-1 and -2 radiation test-tube assembly (Type 316 stainless steel-clad, 2.7 or 5.4% enriched UO_2 pellets.)

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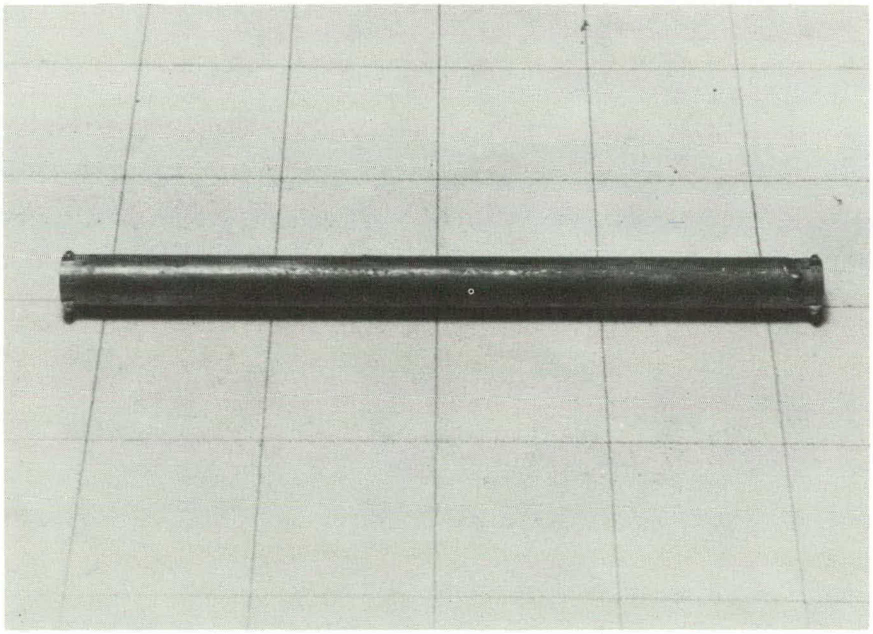

Fig. 13. Unirradiated stainless-steel clad Mark I irradiation specimen. (Background is 1-inch grid.)

ORNL-WAPD Specimens. Two series of 3-in.-long specimens (Figs. 14 and 15) were fabricated at ORNL from stainless steel tubing and WAPD-PWR reject UO_2 pellets acquired under IC-1597 from Savannah River. The UO_2 pellets were centerless-ground at the Y-12 Plant to 0.365 in. OD, and six or seven pellets were loaded into each stainless steel tube and the tube welded closed at one end in a dry box. After evacuation of the box and back filling with helium, the final weld was made to seal the other end. The welds were dye checked, and the specimens then autoclaved to test for leakage. Appendix C tabulates fabrication data on these ORNL specimens.[45,57]

3.2.4 Irradiation history of the Sulfex specimens

WCAP 1-3 (HS-4). The experiment was irradiated in MTR position A-28-NW at a point 18.5 to 24.5 in. below the top reflector, which had measured thermal neutron fluxes of 1.24×10^{13} at the top of the capsule to 0.95×10^{13} at the bottom. The specimens were inserted for cycle 93 in September 1957 and discharged at cycle 96 shutdown on 12/9/57, having accumulated an unperturbed time-integrated flux (nvt) of 2.07×10^{20}. Cobalt-aluminum flux monitor measurement of thermal neutron exposure (nvt) showed 4.91×10^{19} at the top of the capsule and 3.76×10^{19} at the bottom. The burnup of the capsule was calculated by WAPD to be 1981 Mwd/ton.[56] Figure 16 shows one end of the irradiated specimen prior to decladding; note the cut ferrules that formed the three-tube assembly.

WCAP 2-1 (HS-5). The capsule was irradiated in MTR position A-20-NE at a point 17.0-23.5 in. below the top reflector, which had a measured thermal neutron fluxes of 0.63×10^{13} at the top to 0.85×10^{13} at the bottom of the capsule. The specimens were inserted for cycle 94 and discharged at cycle 96 on 12/9/57, having accumulated an unperturbed nvt of 0.62×10^{20}. Cobalt-aluminum flux monitor measurements of thermal neutron exposure (nvt) showed 1.74×10^{19} at the top and 2.33×10^{19} at the bottom of the capsule. WAPD calculated the burnup of the capsule to be 1,066 Mwd/ton.[56]

Capsules WCAP 1-3 and 2-1 were located at about the peak flux position in the experimental channels and thus delivered the peak design heat flux at the cladding surface of 450,000 Btu $hr^{-1}ft^{-2}$.

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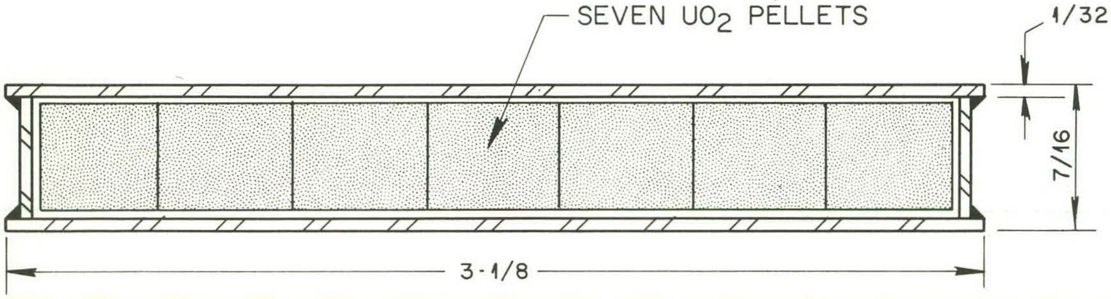

Fig. 14. ORNL Series I stainless steel-clad irradiation specimen.

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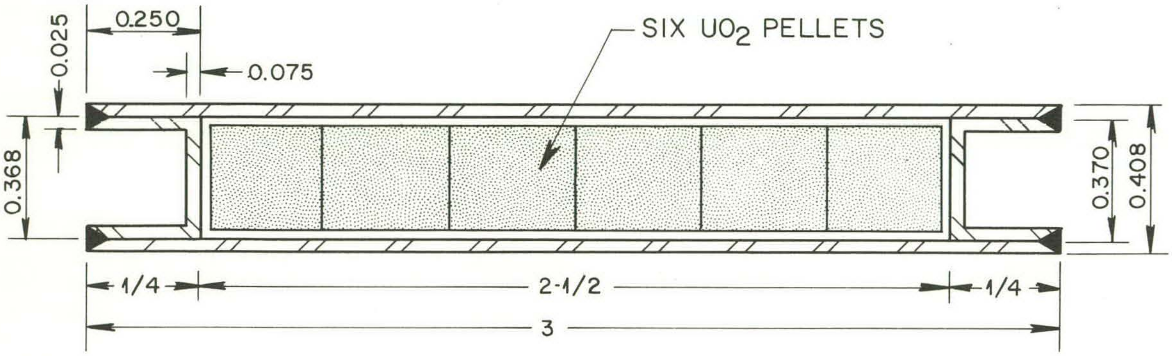

Fig. 15. ORNL Series II stainless steel-clad irradiation specimen.

ORNL-NRX (HS 6-13). Holder 1, containing 60 UO_2 and 60 ThO_2-UO_2 specimens and a total of 3165 g U + Th, was inserted into position J-21 of the NRX reactor on 2/25/60 and was moved to L-15 on 3/22/60. The holder was irradiated for 505 full-power days at unperturbed peak neutron fluxes ranging from 4.3 to 5.6 x 10^{13} and was discharged on 11/20/61. The average irradiation, calculated from measured water temperatures at the exit of the holder, was 22,910 Mwd/ton, and the peak exposure was 25,600 Mwd/ton.[54] Appendix B gives a detailed history of holder No. 1.

Figure 17 shows 4.5-in.-long stainless-steel-clad specimens after irradiation in the NRX reactor. Note the heavy scale deposits on the pins that had been irradiated to 22,800 Mwd/ton.

ORNL-WAPD Specimens (HS-14 to -22). Table 2 summarizes the irradiation histories of the 3-in. specimens made at ORNL as well as those of the other Sulfex specimens. The 3-in. specimens were irradiated in the ETR or MTR at neutron fluxes up to 3.3 x 10^{14} to nominal irradiation levels of 8500 to 11,000 Mwd/ton.[54] Actual total burnups were calculated from Cs^{137} analyses to range from 7900 to 20,400 Mwd/ton. Figures 18 and 19 show 3-in. specimens from MTR-ETR irradiations of 9700 to 12,900 Mwd/ton.

3.3 Description of the Zirflex Decladding Experiments

3.3.1 Procedures

The volume of 6 M NH_4F--1 M NH_4NO_3 was chosen to give an F/Zr mole ratio of 7 in the final decladding solution if all the Zircaloy were dissolved (See Fig. 1). During decladding, makeup water was continuously added to the boiling solution at the same rate as the steam and ammonia vapors were removed through a downdraft condenser. Two 1 M NaOH scrubbers were used to treat the off-gas.

The final decladding solution was diluted with an equal volume of water to prevent the precipitation of ammonium fluozirconate on cooling to room temperature and then was allowed to cool to decrease the solubility of UF_4 and thus reduce uranium losses. The cold, diluted decladding solution was withdrawn from the dissolver, vacuum filtered through No. 2

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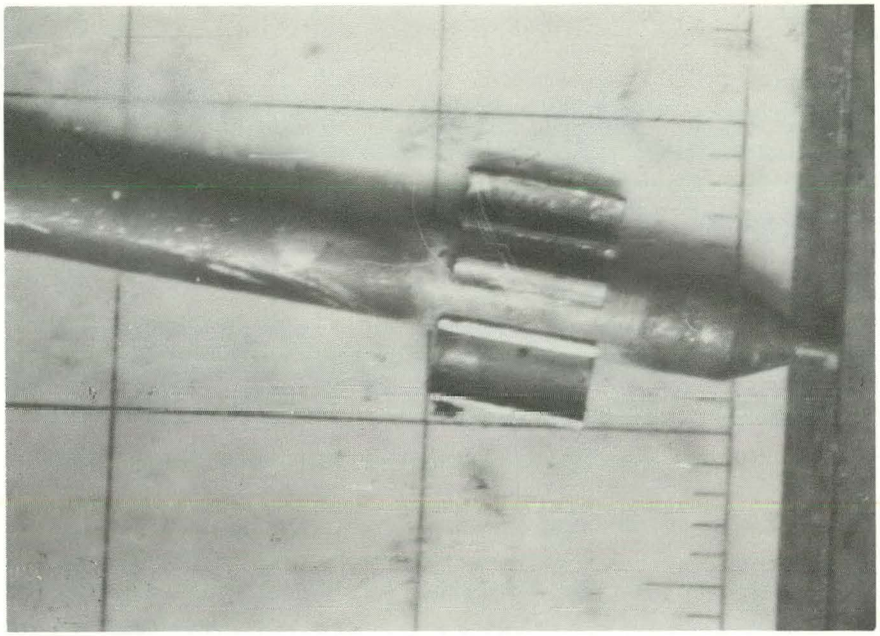

Fig. 16. One end of WCAP 1-3 after irradiation to 1545 Mwd/ton in the MTR. (Background is 1-inch grid.)

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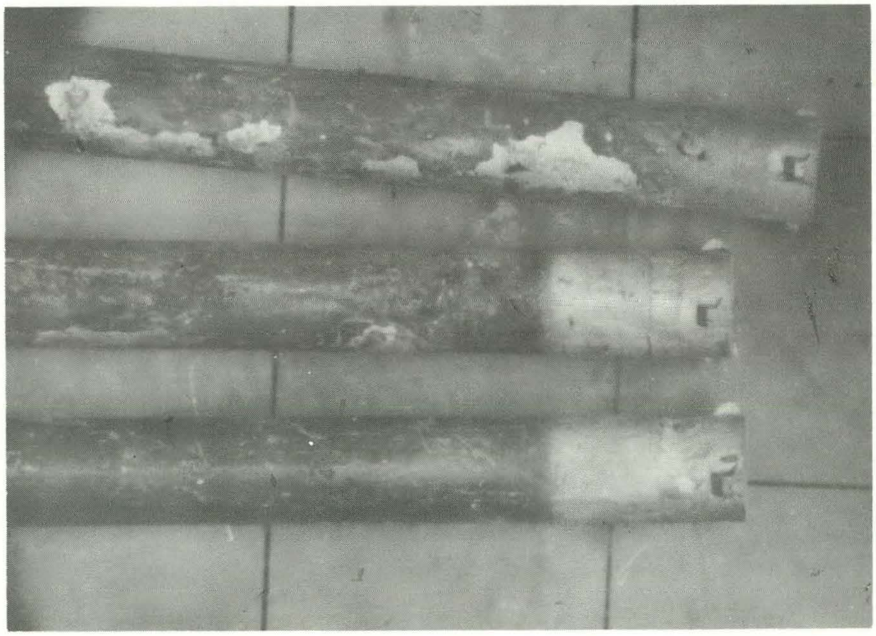

Fig. 17. Stainless steel-clad Mark I specimens irradiated to 22,800 Mwd/ton in the NTX reactor. (Background is 1-inch grid.)

Table 2 . Irradiation Summary of Sulfex-Process Test Specimens: Stainless-steel-clad Sintered UO_2 Pellets

All specimens unbonded, helium filled, exposed to reactor cooling water. WCAP-YAEC specimens 4.8 x 0.342 in. OD
ORNL-NRX Specimens 4.5 x 0.3125 in. OD; other ORNL specimens 3 x 0.438 in. OD and 3 x 0.408 in. OD

Expt. No. -HS-	Irrad. No.	Spec. No.	Spec. Mfr.	Spec. Wt (g)	Type of SS	UO_2 Pellets Wt (g)	UO_2 Pellets Theor. Den. %	Enrichment (% U^{235}) Start	Enrichment (% U^{235}) End	Reactor	Date In	Date Out	Reactor Position	Peak Unper. Flux Range x 10^{14}	Irrad. (Mwd/T)	Reactor Cycles	Average Power (Kw/KgU)
4	1-3	--	WCAP	63.5	316	39.7	93 ± 1.5	2.7	--	MTR	9/19/57	12/ 9/57	A-28-NW	0.095-0.124	1,545	4	--
5	2-1	--	WCAP	64.0	316	39.5	93 ± 1.5	5.4	5.4	MTR	10/10/57	12/ 9/57	A-20-NE	0.051-0.085	2,790	3	--
6	NRX-1	U-273	ORNL	52.0	304	31.25	96	3.91	1.27	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	22,800	31	45.2
7	NRX-1	U-391	ORNL	52.0	304	31.25	96	3.91	1.27	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	22,800	31	45.2
8	NRX-1	U-278	ORNL	52.2	304	31.25	96	3.91	1.27	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	22,800	31	45.2
9	NRX-1	U-336	ORNL	52.0	304	31.25	96	3.91	1.27	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	22,800	31	45.2
10	NRX-1	U-270	ORNL	51.4	304	31.25	96	3.91	1.24	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	28,200	31	55.8
11	NRX-1	U-252	ORNL	51.0	304	31.25	96	3.91	1.24	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	28,200	31	55.8
12	NRX-1	U-402	ORNL	51.2	304	31.25	96	3.91	1.24	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	28,200	31	55.8
13	NRX-1	U-341	ORNL	51.7	304	31.25	96	3.91	1.24	NRX	2/25/60	11/20/61	J-21, L-15	0.43 -0.56	28,200	31	55.8
14	43-18	2 each	ORNL	106	304L	81	93-95	0.72	0.17	MTR	10/12/59	1/29/62	A-38-SE,L-56	1.7 -3.2	20,400	39	28.1
15	43-18	2 each	ORNL	106	304L	81	93-95	0.72	0.17	MTR	10/12/59	1/29/62	A-38-SE,L-56	1.7 -3.2	20,400	39	28.1
16	43-24-28	13, 17	ORNL	106	304L	82	93-95	0.72	0.15	ETR	10/19/59	5/29/61	GEH-18-IE6	1.6 -3.1	9,700	17	16.8
17	43-30	19	ORNL	53	304L	41	93-95	0.72	0.15	ETR	11/22/59	5/29/61	GEH-18-IE4	2.3	9,700	17	16.8
18	43-29	18	ORNL	53	304L	41	93-95	0.72	0.10	MTR	12/14/59	7/ 5/61	L-56-CT	1.5 -2.5	12,900	28	23.7
19	43-25-31	14, 20	ORNL	105	304L	82	93-95	0.72	0.10	ETR	10/19/59	7/10/61	GEH-18-IE6	2.5 -3.3	12,900	18	20.3
20	43-10	12, 18	ORNL	128.8	304L	84.0	93-95	0.72	0.19	MTR	4/ 6/59	3/28/60	L-52-SE	3.0	7,900	17	24.6
21	43-10	5, 15	ORNL	128.0	304L	85.0	93-95	0.72	0.19	MTR	4/ 6/59	3/28/60	L-52-SE	3.0	7,900	17	24.6
22	43-10	4, 6	ORNL	129.8	304L	86.9	93-95	0.72	0.19	MTR	4/ 6/59	3/28/60	L-52-SE	3.0	7,900	17	24.6

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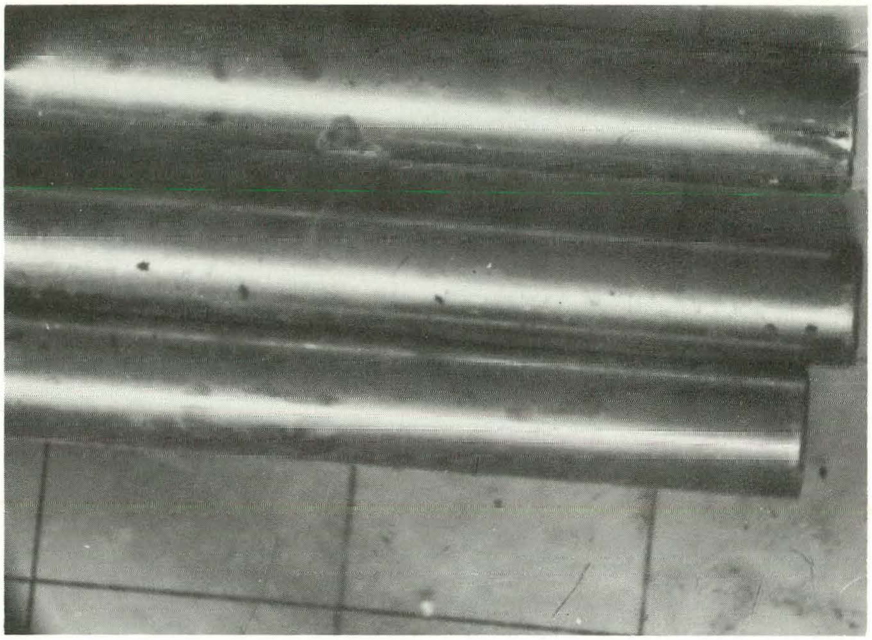

Fig. 18. ORNL 3-in. stainless-steel-clad specimens irradiated to 7900 Mwd/ton in MTR. (Background is 1-inch grid.)

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Fig. 19. ORNL 3-in. stainless-steel clad specimen irradiated to 12,900 Mwd/ton in ETR. (Background is 1-inch grid.)

filter paper on a Büchner funnel, sampled, and discarded. The UO_2 pellets were washed twice and finally refluxed with water to remove residual fluoride. The pellets, Zircaloy scrap (if any), and residual water were transferred from the dissolver to the filter, the solids photographed, and then placed in the core dissolver along with residues from the filter paper. The Zircaloy scrap and end caps were retained and not returned to the decladding dissolver.

The UO_2 cores were dissolved in 4 $\underline{M}$ HNO_3--0.1 $\underline{M}$ $Al(NO_3)_3$ to make a solvent extraction feed (100 g of uranium per liter), which was stored in polyethylene bottles until enough was on hand to make a solvent extraction run.

3.3.2 Results

Table 3 presents a complete summary of the Zirflex decladding experiments.

Zircaloy Heel. -- The actual weight of end-plug heel was measured in the first three experiments only and amounted to an average of 12% of the total Zircaloy in the PWR specimens. The end plugs were not passive, however, and had been attacked by the decladding solution. Figure 20 shows a partially dissolved end plug from an unirradiated PWR specimen; other photographs in Sec 3.4 and 3.5 show the end plugs among the washed UO_2 pellets. The heel was not allowed to build up during the series of experiments but was removed after each core dissolution for ease of operation.

Passivity of Zircaloy. -- Twenty-six irradiated specimens were dissolved in the Zirflex series, and only 1 of the 26 appeared to be partially passive. Figure 21 shows NRX specimen X-33 as it appeared after a nominal 2-hr decladding period. About half of the Zircaloy had been dissolved, apparently by an undercutting attack from one end, and an additional 3.0 hr was required to dissolve the remaining 8 g of cladding. The remaining specimens dissolved by general surface attack.

Losses of Uranium and Plutonium. -- 1. Length of Decladding Time. In general, about 2.5 to 3.0 hr were required to dissolve the cladding,

Table 3. Zirflex Decladding of Irradiated Zircaloy-Clad UO_2 Pellets in 6 $\underline{M}$ NH_4F-1 $\underline{M}$ NH_4NO_3

Run No. HZ-	Irrad. Level (Mwd/T)	Decay Period, (mo)	Spec. Wt. (g)	Approx. Wt of Zr-2, (g)	Vol. Declad Sol'n. (ml)	Total Time (hr)	Purge Gas[a] Used	Soluble Loss[b] (%)		Activity of Declad Sol'n.[b,c] (counts min^{-1} ml^{-1})			Condensate	
								U	Pu	Gross β	Gross γ	Gross α	Rate (ml/hr)	γ Activity (counts min^{-1} ml^{-1})
1	412	35	199.5	46	580	2.0	None							
2	216	35	202.0	46	580	2.1	None	0.04	0.37	8.2×10^{4}	2.8×10^{5}			3.0×10^{3}
3	262	35	199.5	46	580	2.5	None	0.01	0.03	6.7×10^{4}	1.2×10^{5}			1.1×10^{3}
4	182	35	199.9	46	580	1.5	None	0.001	0.006		1.4×10^{5}			4.3×10^{5}
5	16,800	8	47.0	16	213	2.0	None	0.08	0.01	3.96×10^{7}	2.41×10^{8}	5.1×10^{3}	200	6.8×10^{4}
6	16,800	8	47.0	16	213	10.0	None	0.03	0.02	4.15×10^{7}	2.30×10^{8}	2.0×10^{4}	165	1.3×10^{5}
7	16,800	8	47.3	16	213	8.0	None	0.07	0.02	3.99×10^{7}	3.02×10^{8}	6.2×10^{3}	156	3.8×10^{4}
8	16,800	8	47.0	16	213	6.0	None	0.04		3.61×10^{7}	2.66×10^{8}		225	2.9×10^{4}
9	17,700	8	47.0	16	213	4.0	None	0.05	0.04	4.27×10^{7}	3.41×10^{8}	1.4×10^{4}	325	2.2×10^{6}
10	17,700	8	47.0	16	213	3.0	None	0.06	0.02	4.10×10^{7}	3.10×10^{8}	1.7×10^{4}	220	1.8×10^{5}
11	17,700	8	46.8	16	213	3.0	N_2	0.04	0.01	4.18×10^{7}	2.86×10^{8}	7.0×10^{3}	367	9.5×10^{4}
12	17,700	8	47.0	16	213	3.0	N_2	0.04	0.03		3.18×10^{8}		333	1.1×10^{5}
13	17,400	9	46.7	16	213	3.5	Air	0.07	0.05	1.94×10^{7}	2.93×10^{8}		357	7.3×10^{6}
14	17,400	9	47.3	16	213	4.1	Air	0.09	0.01	4.88×10^{7}	3.72×10^{8}		375	3.6×10^{5}
15	17,400	9	94.4	32	426	3.0	Air	0.08	0.01	3.33×10^{7}	3.45×10^{8}		483	1.1×10^{5}
16	8,950	22	201.2	46	580	3.0	None	0.04	0.01	1.2×10^{7}	8.6×10^{7}		330	
17	13,100	7		46	580	2.5	None	0.28	0.08	1.2×10^{8}	5.9×10^{8}		250	
18	13,700	7	108.6	32	415	3.3	None	0.11	0.08				250	
19	14,600	9	93.8	32	426	3.5	None	0.04	0.06	1.5×10^{7}	8.9×10^{7}	1.2×10^{6}	390	
20	14,600	9	94.0	32	426	2.5	None	0.09	0.08	1.5×10^{7}	1.0×10^{8}	3.4×10^{5}	450	
21	7,100	10	199.4	46	580	2.5	None	0.05	0.04	2.3×10^{7}	1.4×10^{8}		400	
22	6,150	10	198.8	46	580	2.5	None	0.04	0.08	1.9×10^{7}	1.0×10^{8}		240	

[a] Purge gas: "None" means steam-ammonia atmosphere.

[b] Activity counted in diluted decladding solution.

[c] Counting efficiency: β, 10%; γ, 20%; α, 50%.

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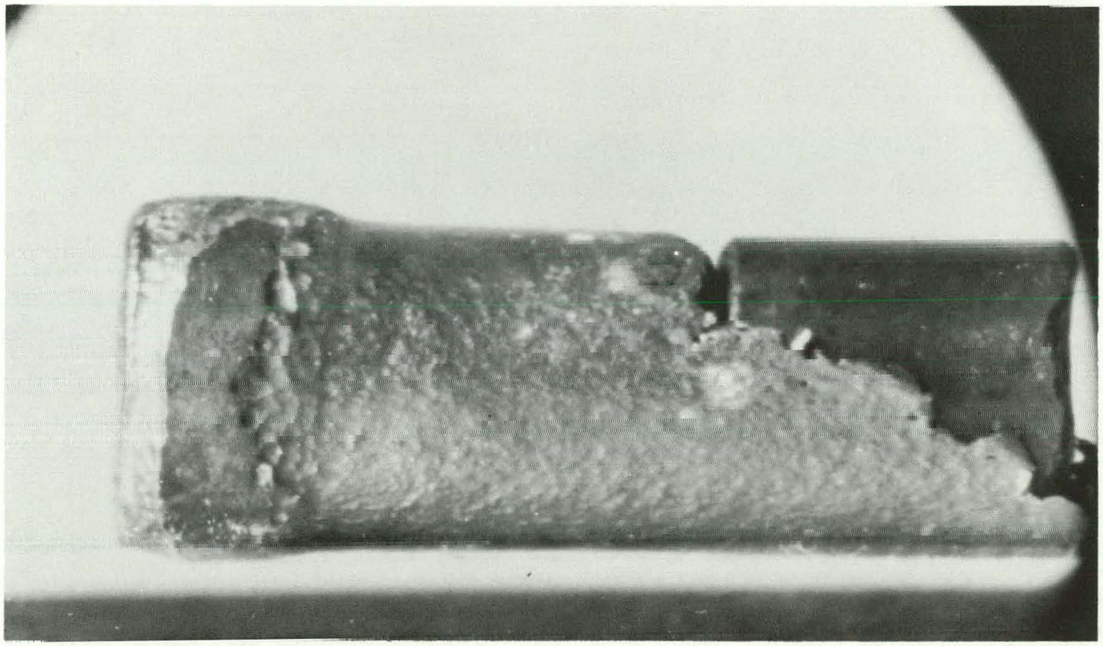

Fig. 20. Partially-dissolved unirradiated Zircaloy-2-clad PWR blanket specimen (X).

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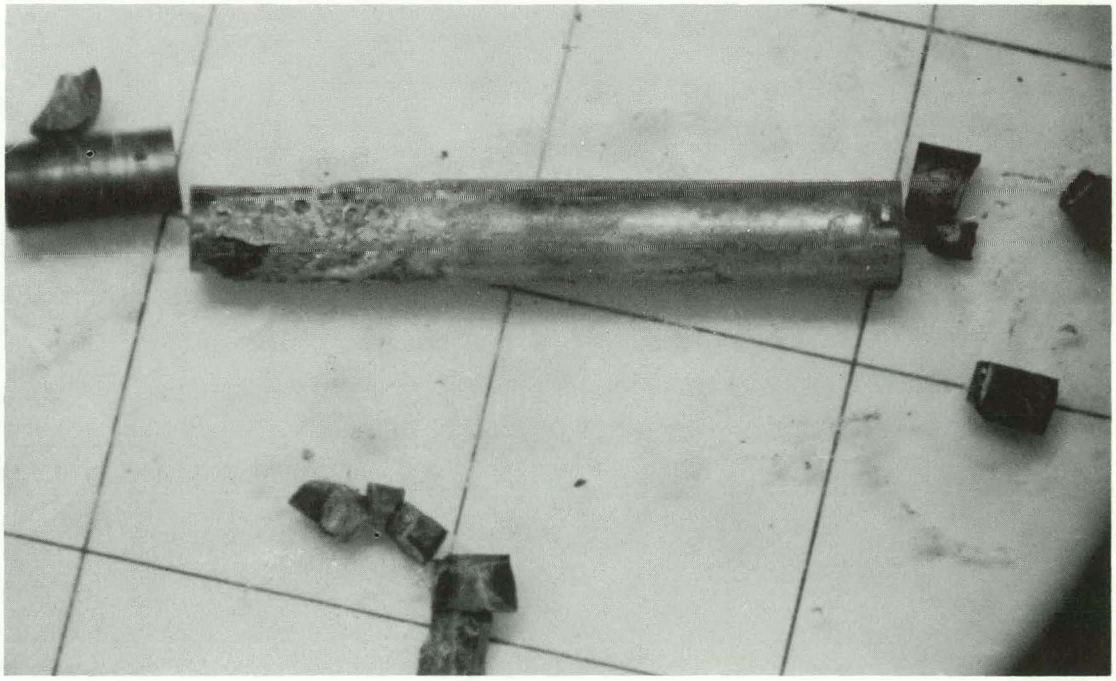

Fig. 21. Partially-dissolved Zircaloy-2-clad Mark I specimen irradiated in NTX to 16,800 Mwd/ton. (Background is 1-inch grid.)

leaving an end-plug heel. The exposed UO_2 pellets were refluxed in the decladding solution for up to 10 hr to determine whether losses of uranium or plutonium would increase with length of exposure. The results of experiments HZ-6 to -10 (Table 3) showed little effect on losses due to increasing the time of UO_2 exposure to the refluxing NH_4F--NH_4NO_3 solution.

2. Effect of Purge Gas. The soluble uranium losses to the decladding solution (Table 3) ranged from 0.03 to 0.09%, and the plutonium losses from 0.01 to 0.04%. The use of a nitrogen purge gas in the decladding vessel in addition to the normal steam-ammonia atmosphere had little or no effect on losses of uranium and plutonium. The use of an air purge, in runs HZ 13 to 15, however, apparently increased the soluble uranium losses by a factor of about 1.5 to 2, although it is possible that this small change was the result of variations in the precision of the uranium analyses. Average values for six experiments using no purge gas, two experiments using nitrogen, and three using an air purge, gave plutonium losses of 0.02%. The uranium losses were calculated to be 0.04% using nitrogen, 0.05% using no purge gas, and 0.08% using air, based upon uranium analyses of 0.03 mg/ml, 0.03 mg/ml, and 0.05 mg/ml, respectively, in the filtered, diluted decladding solutions.

It can be seen from the solubility curves for U(VI) and U(VI) in Zirflex solutions (Fig. 22) at boiling point and at room temperature, that for a free-fluoride molarity between 0.5 and 0.9, uranium losses should lie between 0.02 and 0.08 g/liter if conditions are controlled such that the U(IV) valence state is maintained.[6] The fact that the losses did fall in this range for every experiment is strong evidence that the uranium was present in the tetravalent state, and that solubility limits controlled the loss. It is possible that the slight increase in losses when a purge of air was used is due to the somewhat more oxidizing atmosphere, producing some U(VI). A similar argument could be used to explain the slight drop in losses when nitrogen was used as a purge gas. However, neither of these changes is considered significant.

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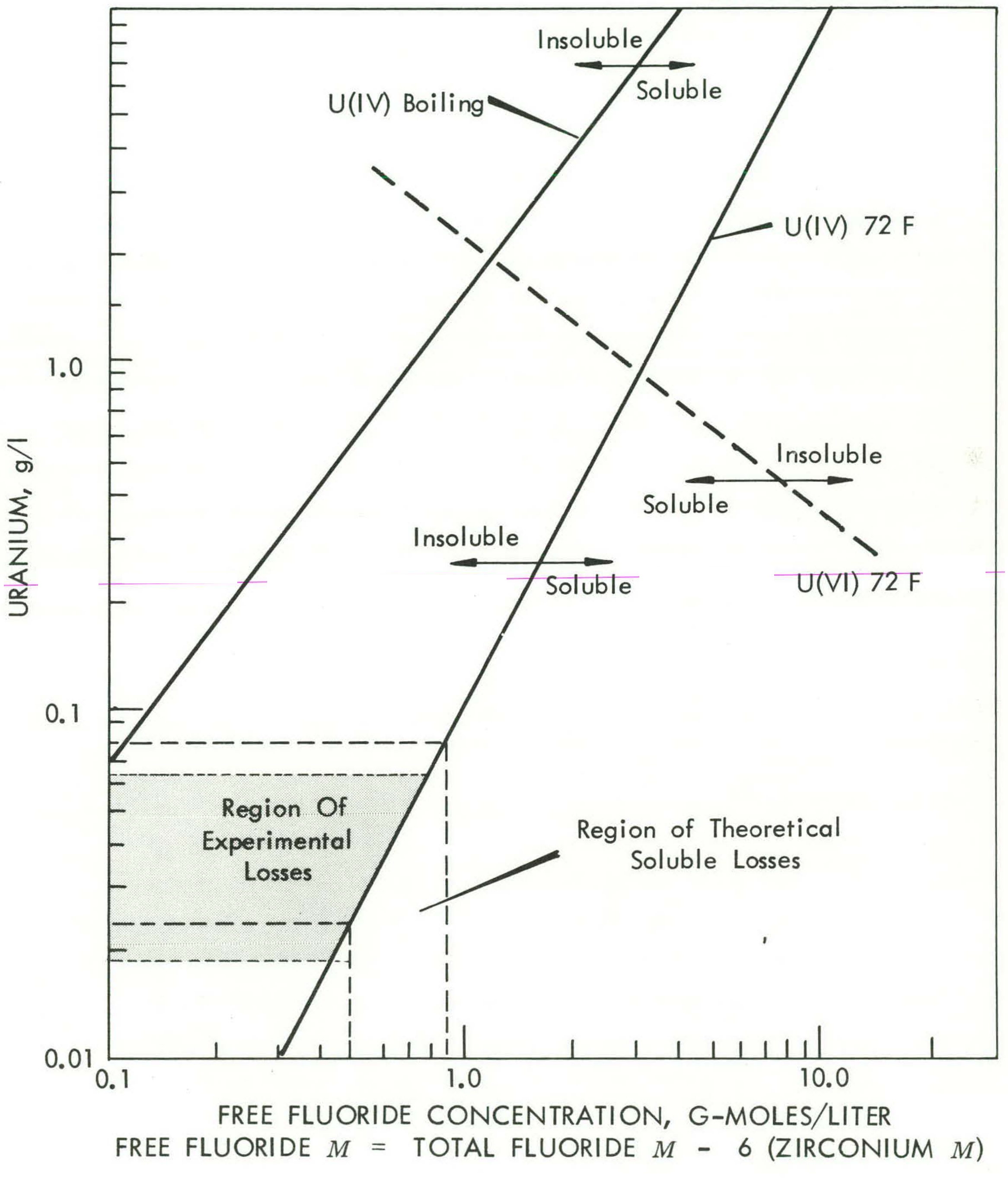

Fig. 22. Solubility of uranium in zirflex solutions (adapted from Fig. 9, HW-65979).

Decladding Solution Radioactivity. -- Gross gamma activity in the decladding solution of the high burnup specimens (2-3 x 10^8 gross gamma counts $\text{min}^{-1}\text{ml}^{-1}$) was several orders of magnitude greater than that in the low-burnup, long-decayed pins, making it a high activity waste stream.

Gamma scan indicated that 1 to 2% of the activity was contributed by ruthenium and cesium, while the remainder was due to zirconium-niobium activities. The bulk of this zirconium-niobium activity was apparently due to activation of the Zircaloy cladding. This was verified by the fact that the ratio of zirconium-niobium gamma activity to total-rare-earth beta activity was 0.37 in the core solution but was 280 in the decladding solution. The gamma activity (3 x 10^8 counts $\text{min}^{-1}\text{ml}^{-1}$) was equivalent to 0.73% of the gamma activity in the core solution.

Gross alpha activity in the decladding solutions was essentially no greater than the plutonium alpha activity in the same sample, indicating low solubility of the transplutonium elements.

Condensate Radioactivity. -- Analysis of the steam-ammonia condensates showed the radioactive contamination was principally due to entrained zirconium-niobium activities, with only slight traces of other fission products present. Adequate de-entrainment devices should minimize this source of contamination. The two caustic scrubbers following the condensate catch vessel picked up little contamination. The gross β and γ activities of the scrubber solutions were 10^3 to 10^4 counts $\text{min}^{-1}\text{ml}^{-1}$, again due to entrained zirconium-niobium.

Decladding Residues. -- A light-gray residue (0.63 g) filtered from the decanted decladding solution of PWR rod RDR-1015 in run HZ-16 was analyzed chemically, spectrographically, and radiochemically. The residue contained about 2 wt % uranium, 0.02 wt % plutonium (i.e. 0.2 mg of plutonium per gram of solids), and had a "specific" gamma activity of around 2.5 x 10^{12} dis $\text{min}^{-1}\text{g}^{-1}$ principally cerium, ruthenium, and zirconium-niobium. A nitric-hydrochloric acid--insoluble residue from the analytical preparation consisted of calcium and zirconium oxides or fluorides plus traces of corrosion products. The soluble material was primarily calcium and silica, with small amounts of lead, uranium, plutonium, and fission products present. Figure 23 shows a typical decladding residue from the 10.26-in. WAPD-PWR rod from run HZ-17, weighing about 0.2 g.

3.4 Description of the Sulfex Decladding Experiments

3.4.1 Experimental results

Decladding Rate. -- The average dissolution rate of a WCAP specimen in a 300% excess of 4 $\underline{M}$ H_2SO_4 during run HS-4 was 1.99 mg $cm^{-2}min^{-1}$. About 50% of the stainless steel was in solution at the end of 2.75 hr, which included part of the end plugs and most of the 21-mil cladding, since the dissolution rate is equivalent to a uniform penetration rate of 5.0 mils/hr. The uranium concentration in the decladding solution after 2.25 hr was 0.004 mg/ml, indicating that the cladding had not been penetrated. The sample taken at 4.75 hr contained 0.17 mg of uranium per milliliter, indicating that penetration had occurred at about 3.6 hr, based on a 5.0-mils/hr rate.

Dissolution rates for the remaining specimens are listed in Table 4 and shown in Figs. 24-26 as a function of reaction time and dissolved iron.

Uranium and Plutonium Losses. -- Tests with irradiated specimens showed normal losses of about 0.05% of uranium and plutonium with the Sulfex system (Table 4). Occasional high losses were encountered. The erratic results cannot be explained except through cross contamination of samples with core solution. Run HS-14, in particular, suggests that this mechanism because of an unusually high gamma count was found in the decladding solution. Runs 5-7, using 6 $\underline{M}$ H_2SO_4 as the decladding reagent, show consistently higher uranium losses than the 4 $\underline{M}$ H_2SO_4.

Figure 27 shows the dissolution of uranium in spent Sulfex decladding solutions as a function of time and oxidizing environment. Unirradiated NRX specimens were declad in 4 $\underline{M}$ H_2SO_4 in the laboratory, using similar equipment, and then refluxed in the spent decladding solutions. In the control experiment the dissolver was closed as in the hot-cell tests.

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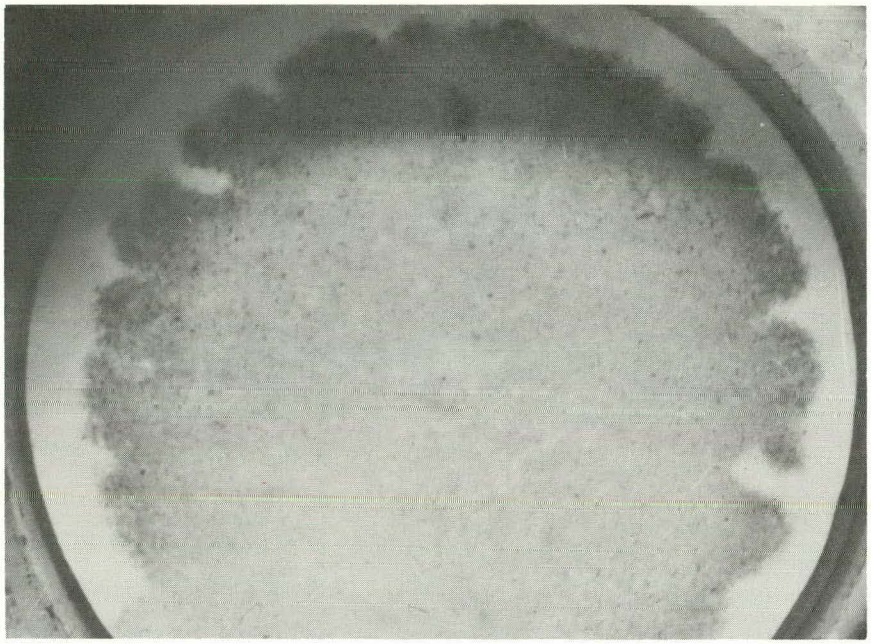

Fig. 23. Residue (0.2 g) from Zirflex decladding of PWR blanket rod on 3-in. filter.

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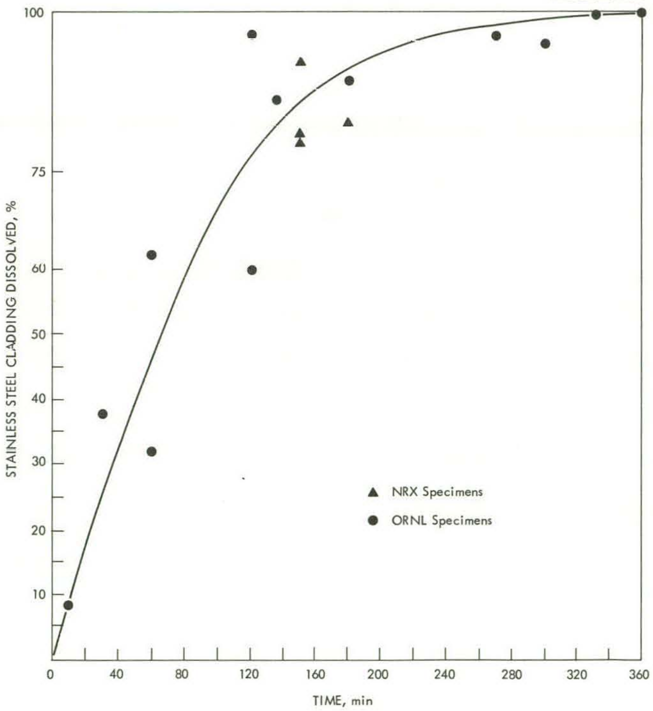

Fig. 24. Dissolution of stainless steel in boiling sulfuric acid.

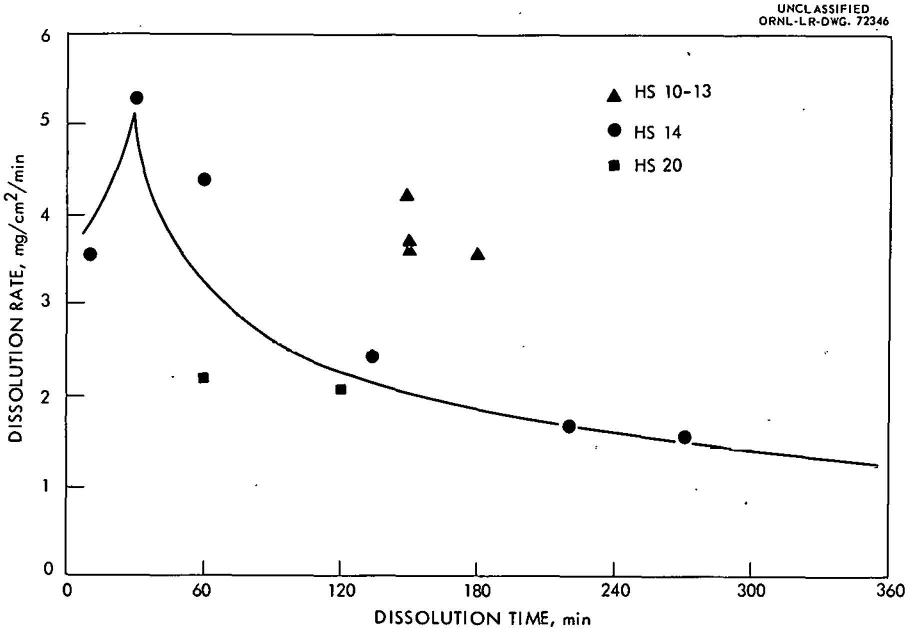

Fig. 25. Stainless steel dissolution rate vs dissolved iron concentration (runs HS 10-20).

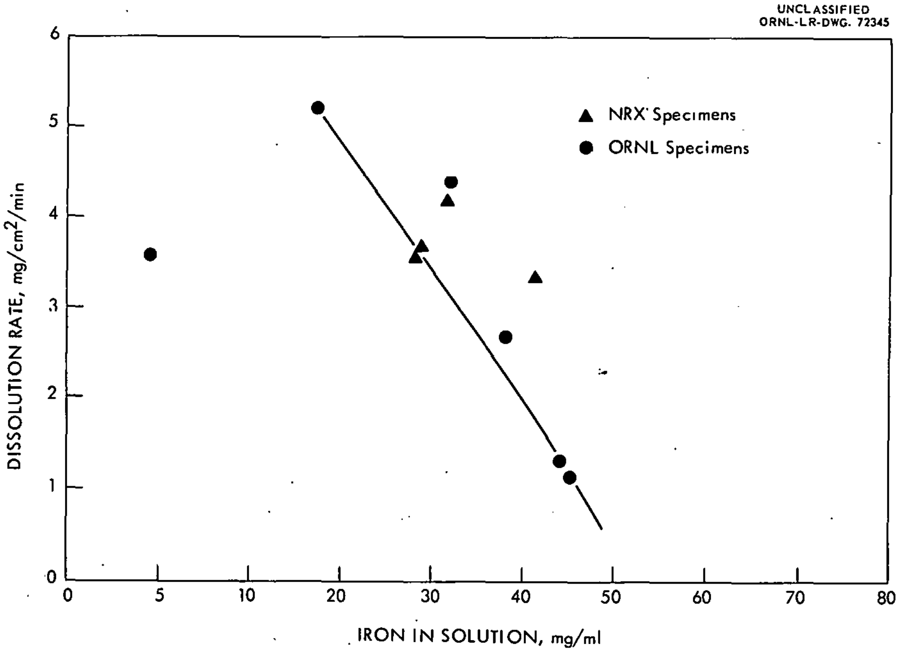

Fig. 26. Dissolution rate of stainless steel cladding in 4 M H_2SO_4 as function of time.

Table 4. Sulfex Decladding of Irradiated Stainless-Steel-Clad UO_2 in Boiling Sulfuric Acid

Run No. HS	Irrad. Level (Mwd/T)	Decay Period (mo)	Spmn. Type[a]	Total Weight (g)	Approx. Wt.SSt. (g)	Declad Sol'n-H_2SO_4			Total Time (hr)	Declad Rate mg$(cm^2)^{-1}$-min^{-1}	Soluble Loss (%)		Activity of Declad Sol'n (counts min^{-1} ml^{-1})			Terminal Sol'n Conc.			Purge Gas Used
						Vol. (ml)	Conc. (M)	Excess (%)			U	Pu	Gross β x 10^8	Gross γ x 10^9	Gross α x 10^5	Vol. (ml)	H^+ (N)	Fe (mg/ml)	
4	1,545	51.	W	63.5	23.8	470	4	300	4.75	1.99	0.20	0.12	0.72	0.43		450	3.75	30.4	None
5	2,790	51.	W	64.0	24.5	240	6	200	3.0	3.65	0.23	0.12	0.39	0.21		570	3.75	31.9	None
6	22,800	4.	N	52.0	20.5	208	6	200	2.0	3.60	0.77	0.17	4.38	2.55		410	4.10	22.5	N_2
7	22,800	4.	N	52.0	20.5	204	6	200	2.1	3.46	0.89	0.03	3.53	2.41		410	4.14	24.1	N_2
8	22,800	4.	N	52.2	20.5	408	4	300	2.2	3.95	0.08	0.04	4.36	3.19	0.69	400	3.85	30.0	N_2
9	22,800	4.	N	52.0	20.5	306	4	200	2.2	3.95	0.06	0.04	4.81	2.90	0.58	408	4.81	29.2	N_2
10	28,200	4.	N	51.4	20.5	306	4	200	2.5	3.63	0.08	0.01		5.45		408	4.31	27.9	N_2
11	28,200	4.	N	51.0	20.5	306	4	200	2.5	3.69	0.03	0.01		2.70		408	4.68	28.6	None
12	28,200	4.	N	51.2	20.5	306	4	200	2.5	4.22	0.08	0.05		4.30		400	4.47	32.2	None
13	28,200	4.	N	51.7	20.5	306	4	200	3.0	3.52	0.05	0.00		3.00		408	4.25	29.0	None
14	20,400	2.5	P	106.0	25.0	375	4	200	3.7	2.70	0.18	0.32		17.20		500	3.06	29.8	None
15	20,400	2.5	P	106.0	25.0	375	4	200	4.5		0.03	0.03	10.4	6.35		500	3.28	33.9	None
16	9,700	10	P	106.0	24.0	375	4	200	6.0		0.08	0.29	14.3	4.85		400	4.43	44.7	None
17	9,700	10	P	53.0	12.0	188	4	200	5.5		0.03	0.07	5.78	4.29	3.51	200	4.76	43.9	None
18	12,900	9.5	P	53.0	12.0	188	4	200	2.0	3.38	0.05	0.22	6.89	4.61		200	4.81	41.7	None
19	12,900	9.5	P	105.0	23.0	375	4	200	5.0		0.02	0.10	5.61	4.74		400	5.46	41.6	None
20	7,900	24	P	128.8	44.8	375	4	200	11.5	2.10	0.23	0.46		4.53		400	3.95	42.6	None
21	7,900	24	P	128.0	43.0	500	4	300	5.7		0.05	0.11	7.43	5.86	7.35	500	3.77	51.2	None
22	7,900	24	P	129.8	42.9	500	4	300	6.5		0.05	0.11		4.67		500	3.15	46.9	None

[a] W = 93 ± 1.5% density UO_2 pellets in WCAP specimens manufactured and irradiated in MTR in 1957 by Westinghouse for Yankee development program. Run 4 UO_2 enriched to 2.7%, Run 5 enriched to 5.4% U-235.

N = 96% density UO_2 pellets, enriched to 3.91% U-235, manufactured by Numec and clad by ORNL. Irradiated in NRX in 1960-61.

P = 93-95% density UO_2 pellets manufactured by WAPD for PWR blanket, natural enrichment, and clad by ORNL. Irradiated in MTR and ETR from 1959-1962.

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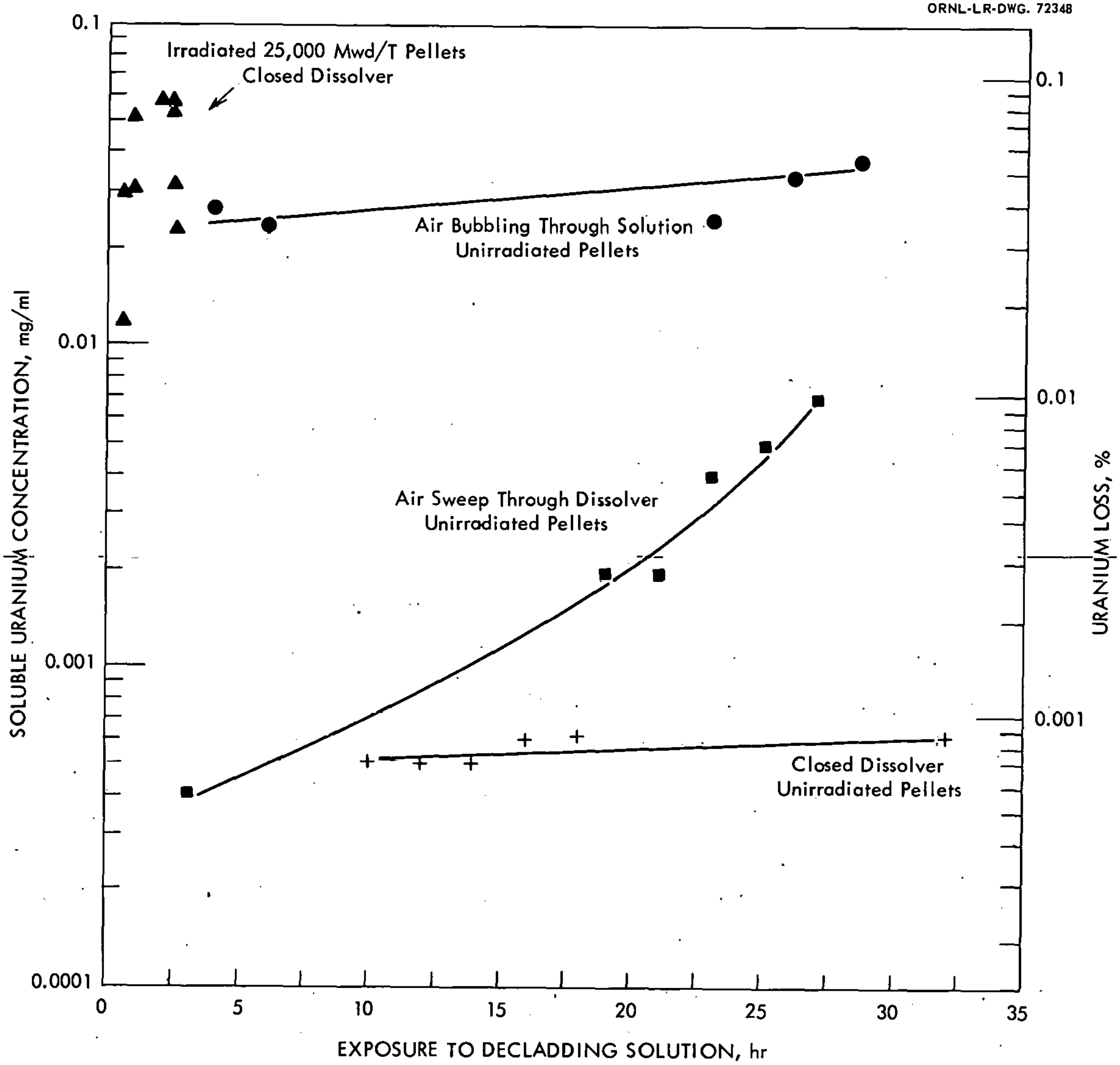

Fig. 27. Solubility of high density UO_2 in spent Sulfex decladding solution (2.5 $\underline{M}$ H_2SO_4-1 $\underline{M}$ SS $(SO_4)_2$).

In the second test an air sweep was passed across the top of the refluxing solution. In the third, air was bubbled through the acid during the decladding and refluxing steps. These experiments confirmed earlier data on the increase in UO_2 dissolution rate due to air oxidation.[16] Uranium losses of the 25,000 Mwd/ton NRX specimens were a hundred times greater than those for the unirradiated control samples and are shown as a scatter of points in Fig. 27. A 0.05% loss, however, also occurred at 1440 Mwd/ton,[16] and it was concluded that losses did not change appreciably at irradiations greater than 1000 Mwd/ton.[16]

Decladding Residues. -- The removal of stainless-steel cladding leaves metallic end plugs, pieces of undissolved cladding, undissolved scale, plus fragments and fines of UO_2 from the fractured core material. These solids must be removed from the decladding solution prior to its disposal. Figures 28a and b show a typical residue from the decladding of 2 NRX specimens in 6 $\underline{M}$ H_2SO_4 for about 2 hr; note the undissolved end plug and weld material as well as the fines in Fig. 28b. Table 5 summarizes the size distribution of the residues from decladding experiments. The table lists the initial weight of the irradiated specimens and the weight of each that had been dissolved and that which remained. Particle size was measured with U.S. Standard sieves. From 0.5 to 2.5% of the total weight of each specimen was present as fines smaller than 10 mesh (2000 μ), with 0.2 to 0.4% smaller than 100 mesh (149 μ).

Chemical and spectrographic analyses were made of the fines from four of the decladding runs. The fines are variable in composition and contained up to 6% uranium along with silica, stainless steel, and fission products (Table 6). Most of the material would be soluble in nitric acid during the core dissolution step if it were not removed with the decladding solution.

Passivation. -- Passivity of the stainless-steel cladding occurred randomly and was not predictable (Table 7). Of the ORNL series-2 specimens, 3 out of 4 irradiated together as experiment 43-18 were passive, and 3 out of 6 irradiated as 43-10, from series 1, were passive to either

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(a)

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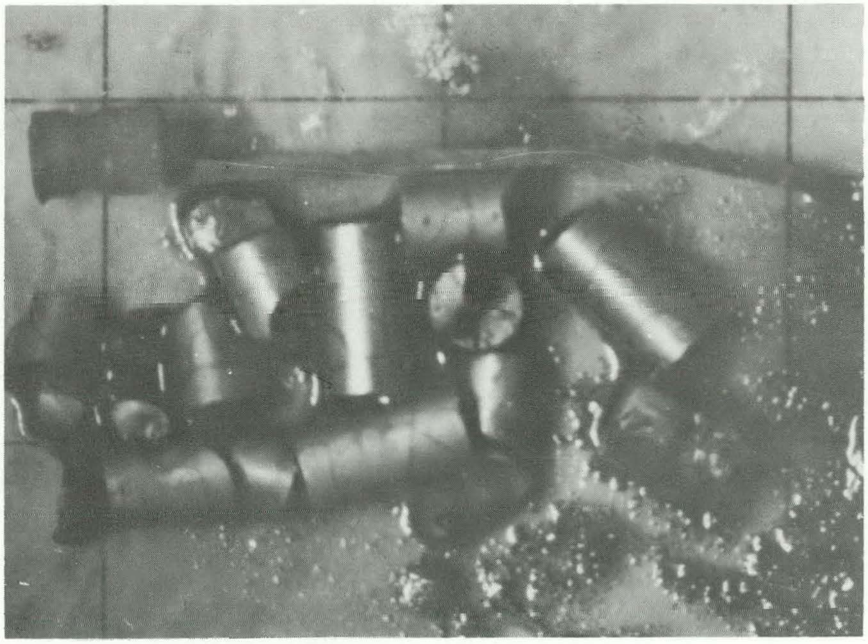

(b)

Fig. 28. Sulfex decladding residues from Mark I specimens irradiated to 22,800 Mwd/ton (Background is 1-in. grid).

Table 5. Size Distribution of Solid Residues from Sulfex Decladding Experiments

Run No.	Type Specimen	Irrad. (Mwd/ton)	Specimen wt. (g)	Spec. Dist. after Decladding[a] (%) Soluble SS	+10 mesh	-10 mesh	-10 +100 mesh	-100 mesh
6	NRX	22,800	52.0	27.0	bal	2.3	---	---
7	NRX	22,800	52.2	27.2	bal	1.9	---	---
8	NRX	22,800	52.0	23.2	bal	1.5	---	---
10	NRX	28,200	51.4	22.2	bal	2.3	---	---
11	NRX	28,200	52.0	22.2	bal	2.3	---	---
15	ORNL	20,400	105.6	22.8	bal	1.4	---	---
16	ORNL	9,700	105.1	22.8	76.7	0.5	---	---
17	ORNL	9,700	53.2	25.8	73.9	0.5	---	---
18	ORNL	12,900	52.5	21.6	76.3	---	1.0	0.4
19	ORNL	12,900	104.8	20.2	78.8	---	0.7	0.3

[a] U.S. Std. sieves...+10 mesh includes end plugs and SS scrap plus UO_2.

Table 6. Analyses of Fines from Sulfex Decladding of Irradiated Stainless-Steel-Clad UO_2

Run No.	Irrad. (Mwd/ton)	U (mg/g)	Counts $min^{-1}g^{-1}$ Pu α	Gross γ	γ Scan, F.P.	Spect. Analysis VS-Strong	Mod-Weak
7	22,800	1.2	$5.6x10^5$	$6.1x10^9$	Ru, Zr-Nb, Cs	--	--
16	9,700	60.7	$2.7x10^7$	$6.9x10^{11}$	Ru, Zr-Nb	Nb, Pd, Si	SS, Mo
19	12,900	59.7	$4.6x10^7$	$2.4x10^{11}$	Ru, Zr-Nb	Nb, Pd, Si	SS
22	7,900	9.8	$4.8x10^6$	$5.8x10^9$	Ru, Zr-Nb, Cs	Pd, Mo	Si, Nb, SS

Table 7. Passivation of Sulfex Specimens

Source of Specimen	Type of SS Cladding	Number of Specimens	Number of Passive Specimens
WCAP	316	2	0
ORNL series 1	304L	6	3
ORNL series 2	304L + 347	10	4
ORNL-NRX	304	14	14

4 or 6 M decladding solution, and required initiation of the reaction with iron wire. The WCAP specimens were not passive in this series of experiments, although one of two pins from the same lot of irradiated specimens that had been declad in the earlier ORNL Sulfex work in 1959 was passive. The 1959 experiments also involved 11 ORNL-manufactured stainless-steel-clad specimens from series 1, irradiated in the LITR and the MTR, of which 10 were passive and required initiation of the reaction with iron wire or other means. The preponderance of active WCAP specimens is probably due to the Nicrobraze alloy that holds the ferrules to the specimens and which begins to dissolve first and thus destroys the passive coating on the pin. These results confirm earlier results with brazed fuel assemblies in nitrate-free systems.[17]

3.5 UO_2 Core Fragmentation

Fragmentation of the irradiated UO_2 pellets is one of the major problems associated with the chemical reprocessing of Zircaloy- or stainless-steel-clad power reactor fuels. A multipurpose reprocessing plant must be equipped to handle a variety of fuels from a number of reactors. Specifications for the density of the UO_2 could vary from swaged UO_2, having a density of 75 to 85% of theoretical, to high-grade sintered pellets having a density of about 96% or greater.

High levels of irradiation, in terms of megawatt days per ton of uranium, and a large number of thermal cycles in the reactor had a pronounced effect on the fragmentation of the WCAP and PWR UO_2 pellets used in these experiments. These pellets, of 93 to 95% density, were more fractured as the irradiation level increased. Six irradiated UO_2 cores were wet-sieved through U.S. Standard sieves during the series of experiments. The results of the sieving experiments are listed in Table 8 and show that at irradiation levels of 10 to 20,000 Mwd/ton, about 1.5% of the UO_2 was smaller than 10 mesh (2000 μ). Figures 29 to 35 illustrate this effect. Consequently, the large number of fines produced will necessitate a centrifuge as a major item of equipment in the plant. This centrifuge will serve to remove the UO_2 and other fines

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Fig. 29. UO_2 pellets from HZ-22 on 1-in. grid. WAPD-PWR rod irradiated to 6150 Mwd/ton U.

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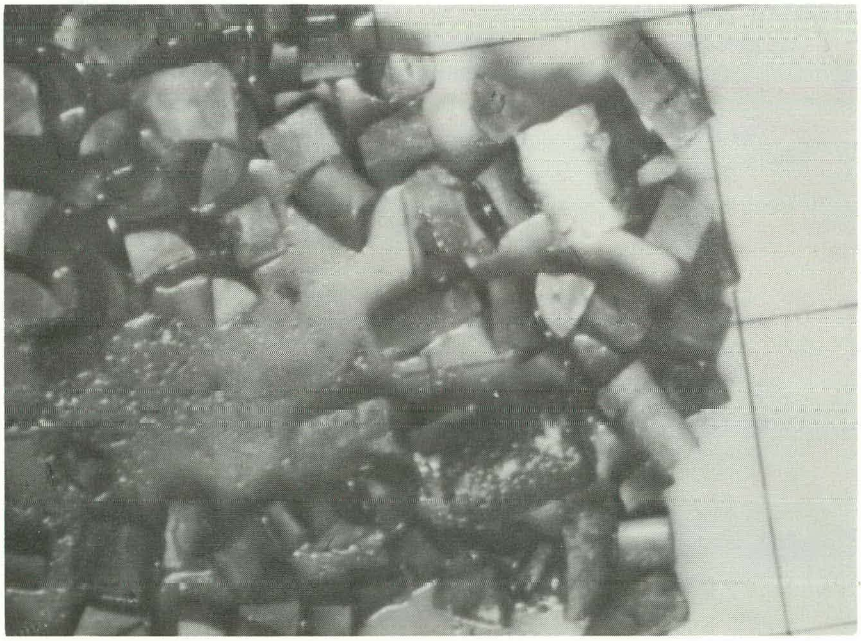

Fig. 30. UO_2 pellets from HZ-21 on 1-in. grid. WAPD-PWR rod irradiated to 7100 Mwd/ton U.

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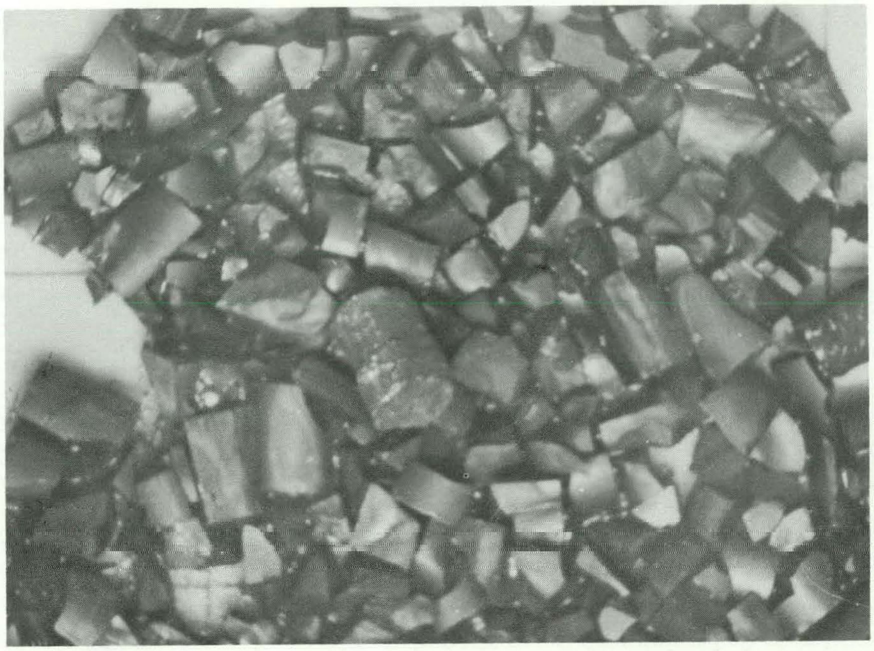

Fig. 31. UO$_2$ pellets from HZ-16 on 1-in. grid. WAPD-PWR rod irradiated to 8950 Mwd/ton U.

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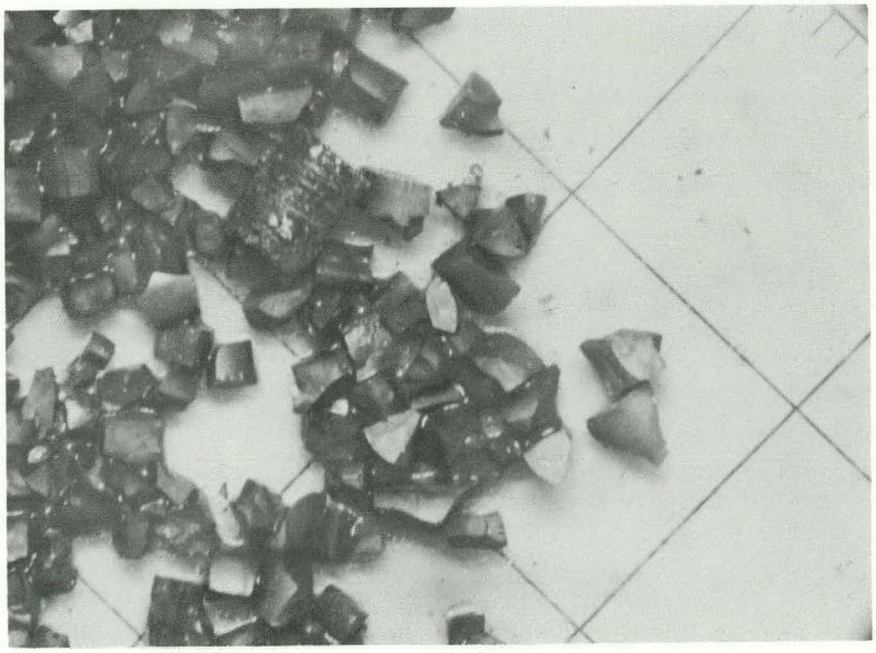

Fig. 32. UO$_2$ pellets from HZ-17 on 1-in. grid. WAPD-PWR rod irradiated to 13,100 Mwd/ton U.

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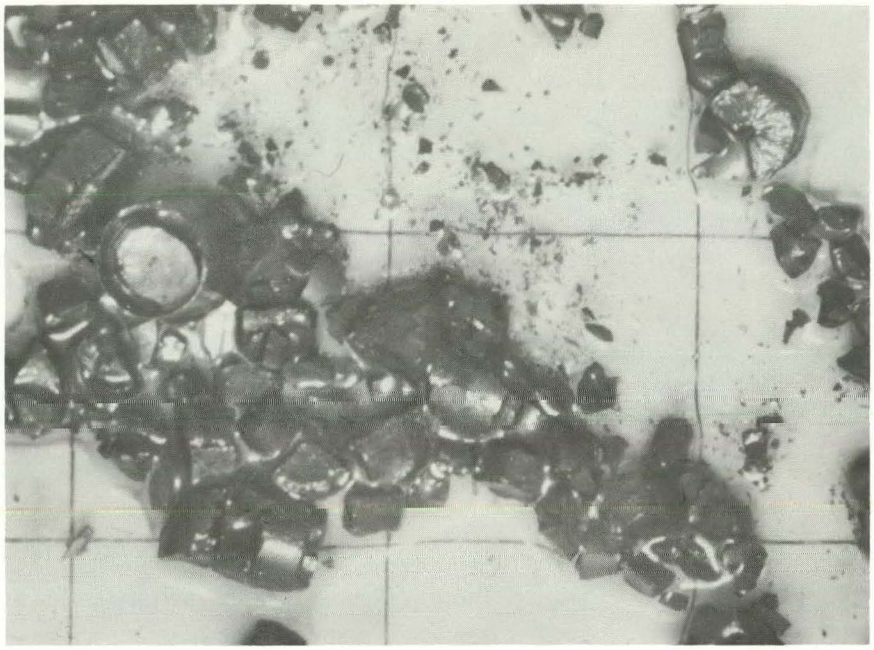

Fig. 33. UO_2 pellets from HZ-18 on 1-in. grid. WAPD-PWR pellets clad at ORNL, irradiated to 13,700 Mwd/ton U.

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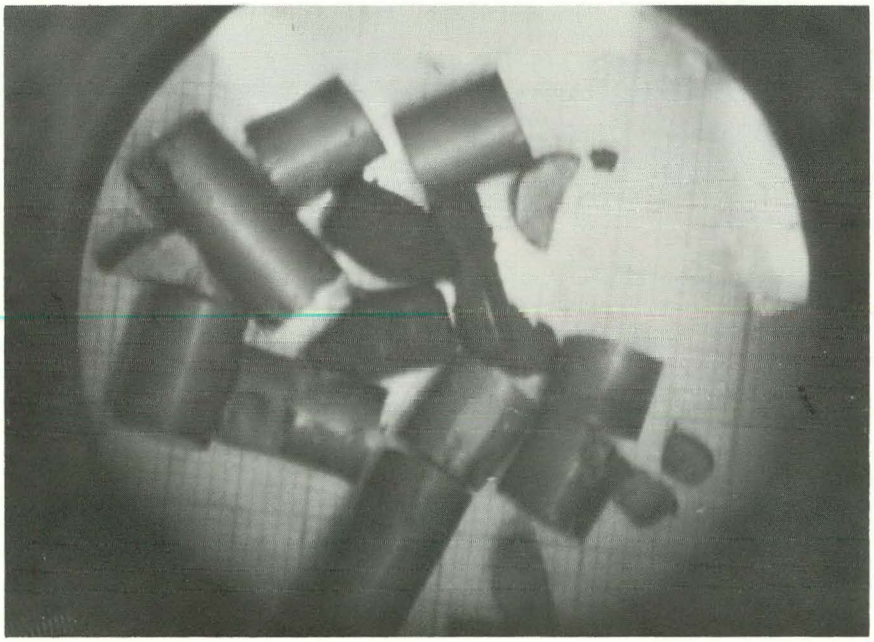

Fig. 34. WCAP 93 ± 1.5% density UO_2 irradiated to 1545 Mwd/ton. (Background is 1 cm grid with 1 mm subdivisions.)

Table 8. Particle-Size Measurements of Irradiated UO_2

Irradiation Level (Mwd/ton)	Size Distribution (wt %)				
	+10 Mesh	-10 Mesh to +50 Mesh	-50 Mesh	-10 Mesh to +100 Mesh	-100 Mesh
262	99.7	0.2	0.1	---	---
9,700	98.8	1.0	0.2	---	---
12,900	98.5	---	---	1.0	0.5
20,400	98.6	---	---	1.4	---

from the decladding solution prior to discharge of the solution to waste, and to recycle them back to the dissolver for the core-dissolution step.

In contrast to the large amount of fines produced in the 93 to 95%-density pellets, the special 96%-density pellets used in the NRX irradiations produced few fines at much higher burnups (Figs. 36 to 38). Note the great number of cracked, but still intact, pellets in the photographs. The pellets appear to be whole when declad, but bumping during boiling and handling break them into small pieces. The greater number of intact pellets in the NRX specimens over those in the PWR specimens may be due to the higher density of the UO_2, the smaller diameter of the pellets, and/or the better heat transfer in the NRX specimens because of the expansion of the pellets against the jacket due to the original 0.001-in. clearance, versus the up-to-0.004-in. clearance in the PWR pins.

3.6 Core Dissolution

Dissolution of the irradiated UO_2 is required to prepare solvent extraction feed for the modified Purex process used to recover the uranium and plutonium. The solvent extraction flowsheet specifies a feed 3 $\underline{M}$ in HNO_3 containing 100 g of uranium per liter; therefore, a relatively low acid concentration was needed to produce a feed solution needing no further adjustment. The first dissolutions were made with 5 $\underline{M}$ HNO_3 as the dissolvent.

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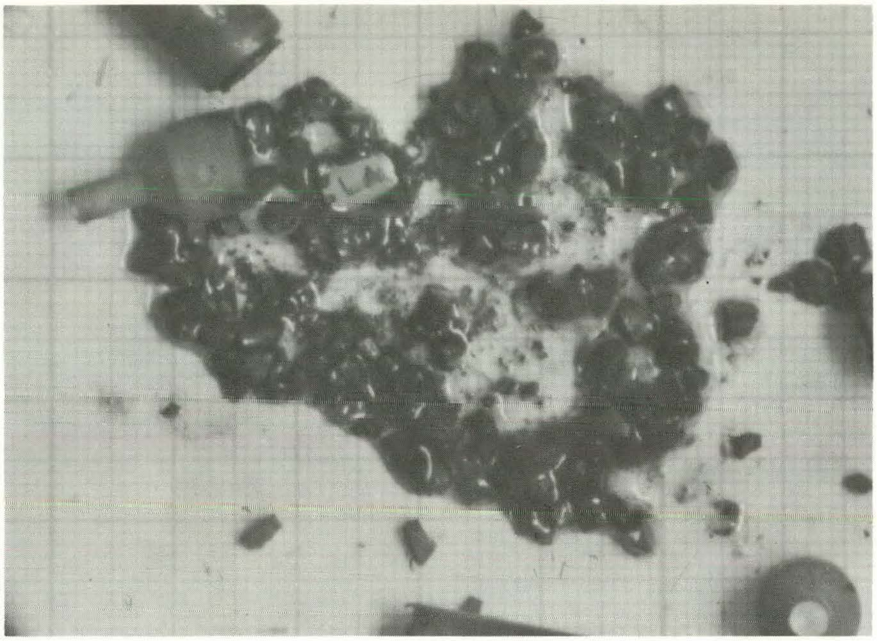

Fig. 35. WCAP 93 ± 1.5% density UO_2 irradiated to 32,000 Mwd/ton. (Background is 1 cm grid with 1 mm subdivisions.)

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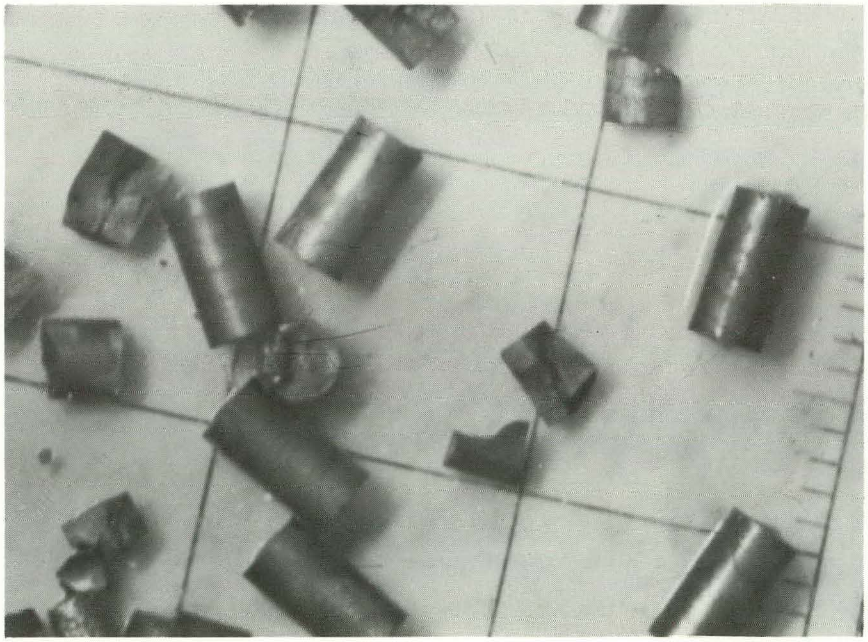

Fig. 36. UO_2 pellets from HZ-19 on 1-in. grid. Numec (NRX) pellets irradiated to 14,600 Mwd/ton U.

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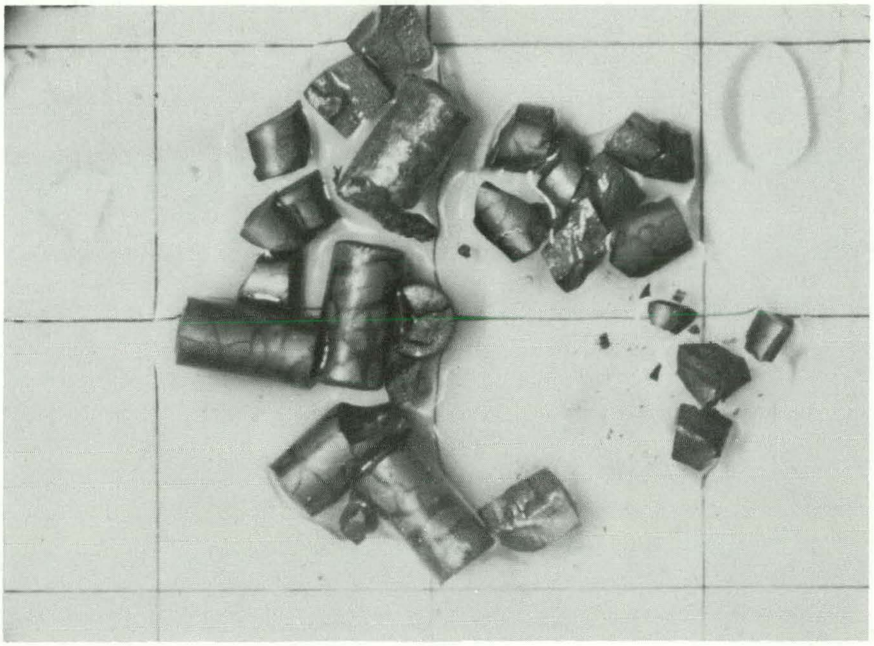

Fig. 37. UO_2 pellets from HZ-6 on 1-in. grid. Numec pellets irradiated to 16,800 Mwd/ton in NRX reactor.

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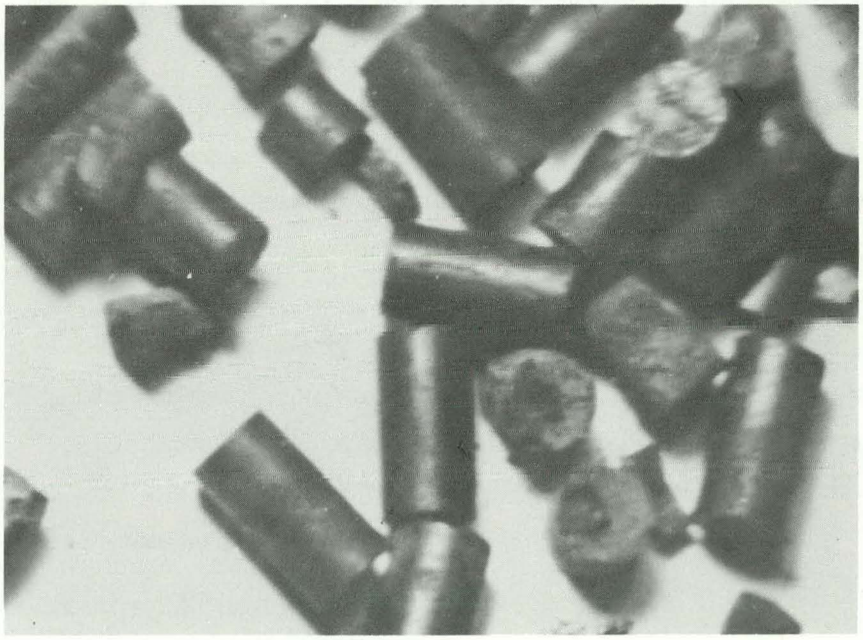


Fig. 38. UO_2 pellets from HS 23-24 in 3-in. pan. Numec pellets irradiated to 25,000 Mwd/ton in NRX reactor.

3.6.1 Dissolution of low-density (93 to 95%) WAPD-PWR or WCAP pellets.

Four successive core dissolutions were made of the PWR UO_2 pellets from runs HZ-1 through -4 in 5 M HNO_3. Dissolution was complete in about 1 hr, yielding solvent extraction feed solutions of about 100 g of uranium per liter, with acidities between 4.08 to 4.43 M HNO_3 (Table 9). Acid consumption was lower than expected with 5 M HNO_3, as compared to 10 M HNO_3, and resulted in a 1 M excess over the desired flowsheet value of 3 M.

Small amounts of undissolved residues found on the paper after filtration of the feed were analyzed spectrographically and did not contain uranium or plutonium but consisted of calcium, iron, chromium, and tin compounds. The calcium was from the water, the iron and chromium from a stainless steel screen in the core dissolver, and the tin from the Zircaloy-2.

Burnup analyses, by the Cs^{137} method, (Appendix D) indicated the four specimens had been irradiated to levels between 182 and 412 Mwd/ton. Fission product carryover to the off-gas scrubbers was negligible, with less than 0.001% of the gross gamma activity in the NaOH solutions. Almost no zirconium-niobium was present because of the long decay time.

Figure 39 shows the rates of dissolution of unirradiated and irradiated low-density PWR UO_2 in boiling 4 M HNO_3. The dissolution rate of cores irradiated up to about 6000 Mwd/ton was faster than that of unirradiated pellets because of the increased surface area due to fragmentation during irradiation. Dissolution was practically complete in 1 hr. The initial dissolution rate was faster for pellets irradiated to greater than 9000 Mwd/ton than for unirradiated pellets due to fragmentation, but then decreased as if a refractory material had been encountered. However, about 98 to 99% of the uranium was in solution at the end of 3 hr, and 2-3 hr of additional reflux was necessary for complete dissolution.

Table 10 lists the amount of uranium in solution at various times during the dissolution of irradiated PWR and WCAP UO_2 in boiling 4 M HNO_3 to a terminal uranium concentration of about 100 g/liter. Material

Table 9. Dissolution of Irradiated UO_2 in Boiling 4 M Nitric Acid-Modified Purex Process Feed Preparation

					Core Solution Analysis								Undissolved Residue				
									Radiochemical Analysis (counts min^{-1} ml^{-1})								
Run No.	Irrad. Level (Mwd/T)	Initial Enrich. (%U^{235})	Decay Per. (Mos)	Diss. Time (hr)	HNO_3 Conc. (M)	U Conc. (mg/ml)	$SO_4^{=}$ Conc. (mg/ml)	F^- Conc. (mg/ml)	Gross α	Pu α	Gross β	Gross γ	Residue Wt. (g)	U Content (mg/g)	Pu Content	Gross γ Activity (counts $min^{-1}g^{-1}$)	Spectro. Analysis
HZ-4	182	0.72	35	2	4.43	97		.0.01	1.51×10^{6}	1.44×10^{6}	8.47×10^{7}	2.90×10^{7}					Ca,Cr,Fe,Sn
HZ-2	216	0.72	35	2	4.12	109		0.01	1.60×10^{6}	1.55×10^{6}	9.37×10^{7}	3.27×10^{7}					Ca,Cr,Fe,Sn
HZ-3	262	0.72	35	2	4.39	100		0.01	1.96×10^{6}	1.82×10^{6}	1.08×10^{8}	3.75×10^{7}					Ca,Cr,Fe
HZ-1	412	0.72	35	2	4.08	95		0.01		2.82×10^{6}	1.50×10^{8}	6.50×10^{7}	0 1				Ca
HS-4	1,545	5.4	51	6	3.33	115			5.17×10^{6}	2.98×10^{6}	5.38×10^{8}	3.00×10^{8}					
HS-5	2,790	2.7	52	5	3.25	107	0.01		3.46×10^{6}	1.25×10^{6}	8.45×10^{8}	4.22×10^{8}	1 5	175	0.25	3.2×10^{10}	
HZ-22	6,150	0.72	10	3	2.73	111			7.95×10^{7}	4.20×10^{7}	7.38×10^{9}	4.03×10^{9}					
HZ-21	7,100	0.72	10	3	4.44	88			1.48×10^{8}	4.20×10^{7}	6.66×10^{9}	4.09×10^{9}					
HS 20-22	7,900	0.72	24	6	2.73	102	0.2		8.46×10^{7}	5.32×10^{7}	3.94×10^{9}	2.45×10^{9}	0.7	38	0.4	1.5×10^{10}	Co,Cr,SSt
HZ-16	8,950	0.72	22	5	2.73	103			7.59×10^{7}	4.09×10^{7}	4.71×10^{9}	2.87×10^{9}	0.9				
HS 16-17	9,700	0.72	10	6	3.27	113	1.1		2.74×10^{8}	4.62×10^{7}	1.03×10^{10}	4.29×10^{9}					
HS 18-19	12,900	0.72	9.5	6	2.78	101	1.0		3.29×10^{8}	3.48×10^{7}	1.24×10^{10}	8.62×10^{9}					
HZ-17	13,100	0.72	7	4	2.94	88			3.59×10^{8}	6.58×10^{7}	1.37×10^{10}	1.05×10^{10}	0.3				
HZ-18	13,700	0.72	7	4	3.79	101			5.59×10^{8}	9.21×10^{7}	1.58×10^{10}	1.18×10^{10}					
HZ 19-20	14,600	3.91	9	5	302	106			3.32×10^{7}	2.50×10^{7}	2.15×10^{10}	1.13×10^{10}	0.7				
HZ 5-8	16,800	3.91	8	3	3.74	106			7.49×10^{8}	4.74×10^{7}	3.57×10^{10}	1.97×10^{10}				8.1×10^{10}	U,Al,Zr,Mo,Ni
HZ 13-15	17,400	3.91	9	5	3.24	99			6.79×10^{7}	4.05×10^{7}	2.79×10^{10}	1.32×10^{10}	0.7	91	0.3	7.4×10^{11}	
HZ 9-12	17,700	3.91	8	3	3.37	95			6.69×10^{7}	2.85×10^{7}	2.81×10^{10}	1.56×10^{10}					Zr,Ni,Fe,Mo,Pd
HS 14-15	20,400	0.72	.2.5	6	2.40	120	1.0		3.44×10^{9}	1.21×10^{8}	6.23×10^{10}	8.45×10^{10}	1 5				U,Zr
HS 6-9	22,800	3.91	4	6	3.09	112	2.5		2.40×10^{8}	6.25×10^{7}	5.07×10^{10}	5.05×10^{10}	1.1				
HS-3	27,300	5.4	13	5	3.86	129			1.57×10^{8}	8.25×10^{7}	2.28×10^{10}	1.06×10^{10}	0.6	130	0.5	1.22×10^{9}	
HS 10-13	28,200	3.91	4	6	2.88	102	1.0		2.32×10^{8}	5.89×10^{7}	5.09×10^{10}	4.83×10^{10}	1 3	123	1.3	1.47×10^{12}	Ca,Mo,Zr-Nb

Table 10. Percentage of Low-Density UO_2 Dissolved in Boiling 4 M HNO_3 as a Function of Time

Approx. 113 g of UO_2 per liter of acid

Time (min)	Uranium in Solution (%)			
	1,545 Mwd/ton	7,980 Mwd/ton	8,130 Mwd/ton	27,300 Mwd/ton
10	55.6	--	--	--
15	--	56.2	80.6	--
20	79.6	--	--	--
30	--	69.6	97.9	89.7
40	99.4	--	--	--
60	--	84.9	97.9	98.7
120	--	94.5	100.0	--
300	100.0	100.0	--	100.0

balances on the plutonium alpha, gross beta, and gross gamma activity of the dissolvent showed comparable dissolution rates.

Table 9 summarizes analytical data on the dissolved core materials. Analyses of the black residues from each dissolution, which contained up to 0.25% of the total uranium, indicated that the solids were undissolved UO_2, fission products, and stainless-steel oxides in the case of Sulfex residues. A second dissolution in 4 M HNO_3 dissolved almost all of the uranium, plutonium, and fission products, leaving a gray-white powder of nitric acid-insoluble oxides, sulfates, or fluorides.

3.6.2 Dissolution of high-density (96%) Numec pellets

Figure 40 shows the rates of dissolution of irradiated and unirradiated UO_2 pellets of higher density. The same effect of an increased dissolution rate due to fragmentation after irradiation is seen as in the lower-density pellets. Complete dissolution of the uranium required about 5 hr vs 6 to 7 for unirradiated pellets. The fission products, as measured by the gamma activity of the solution, dissolved slower but were almost all in solution after the 5-hr dissolution period.

The UO_2 pellets from Zirflex decladding experiments HZ 5-8 (16,800 Mwd/ton) were combined for a core dissolution experiment. Since the

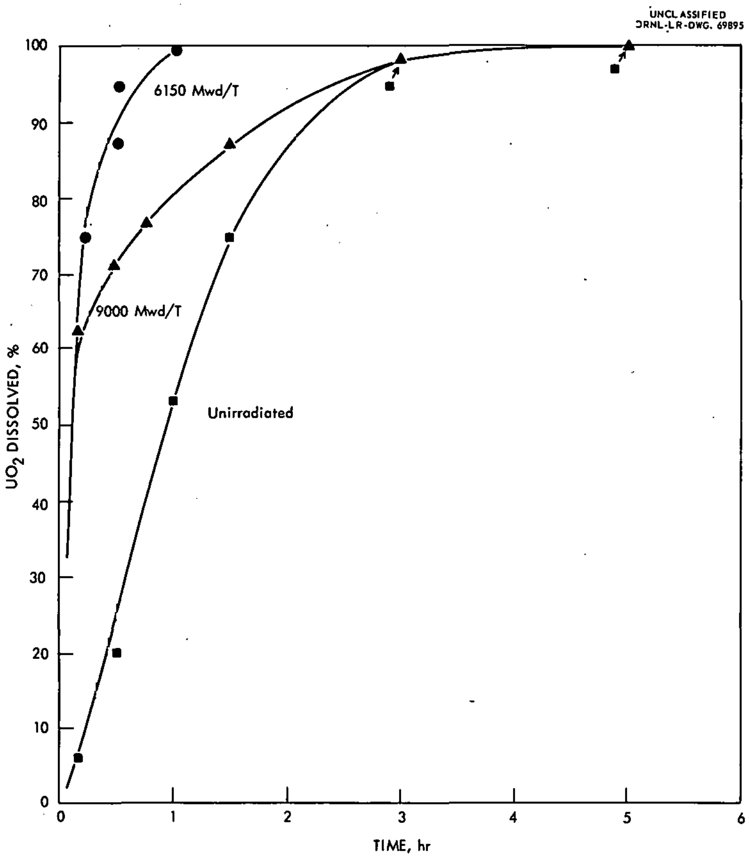


Fig. 39. Dissolution rates of unirradiated and irradiated WAPD-PWR UO_2 pellets in boiling 4 M HNO_3.

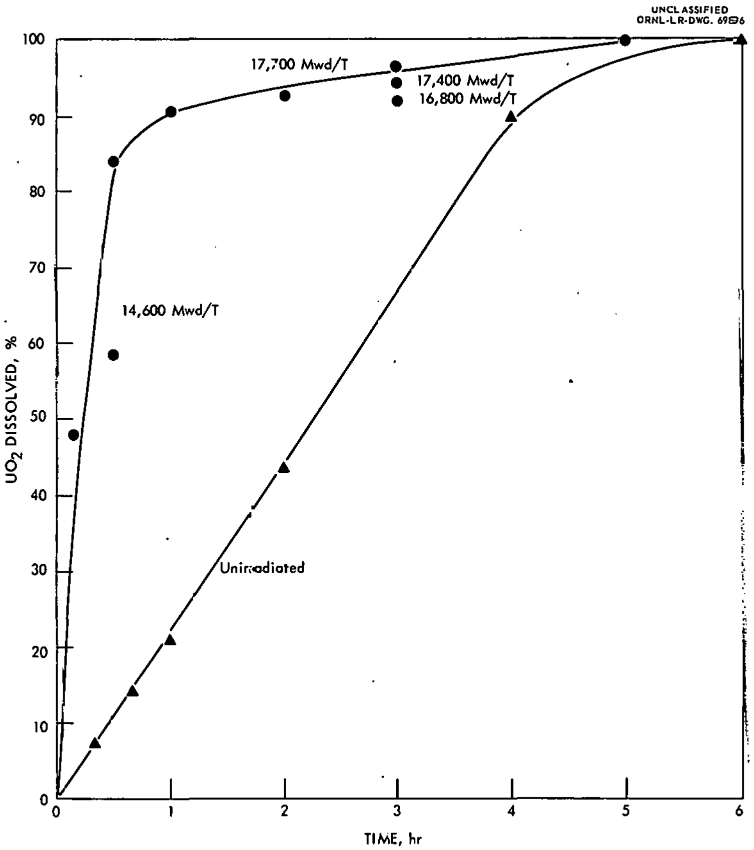


Fig. 40. Dissolution rates of unirradiated and irradiated Numec UO_2 pellets in boiling 4 M HNO_3.

5 M HNO_3 core dissolvent, used for the low-burnup PWR specimens, produced a 4 M HNO_3 feed, boiling 4 M HNO_3--0.1 M $Al(NO_3)_3$ was used as the dissolvent. The reaction was continued for 3 hr, at which time it appeared to stop. Filtration of the feed solution, which contained 106 g of uranium per liter, gave a thin layer of black solids on the filter paper which contained up to 4 or 5% of the uranium in the pellets. Spectrographic analysis of the undissolved black residue is shown in Table 11, and it is evident that the major portion of the residue was undissolved UO_2.

The filtered core solution was muddy green, which appeared black through the windows of the cell. A very small amount of solid was centrifuged from the core solution; spectrographic analyses of the solids and supernatant appear in Table 11 and indicated that the solids were small particles of UO_2 that had passed through the No. 2 filter paper. Table 12 presents a detailed analysis of the core solution.

Using Cs^{137} activity as a standard, Ullmann calculated[54] that the NRX Zirflex specimens from Holder 2 had been irradiated in a pseudo-flux of 1.75×10^{13} neutrons $cm^{-2}sec^{-1}$, and with this assumption he calculated the concentration of the total strontium and molybdenum produced. His values of 5.1 μg/ml for strontium and 16.5 μg/ml for molybdenum compared very well with the spectroscopic analysis in Table 5 of 2 to 10 μg/ml for strontium and about 25 μg/ml for molybdenum, indicating that all the fission products were in solution.

The core pellets of the second 4 NRX (HS 9-12) pins were refluxed for 3 hr in 1100 ml of 4 M HNO_3--0.1 M $Al(NO_3)_3$, and the solution was filtered through No. 2 paper. The spectrographic analysis of the core solution is shown in Table 11; other analyses of the core solution are shown in Table 9.

The filter paper, containing the undissolved residue from the dissolution, was returned to the dissolver with 500 ml 4 M HNO_3--0.1 M $Al(NO_3)_3$, refluxed for another 3 hr and filtered. This solution contained 0.51 mg U/ml, 2.55×10^6 Pu α counts $min^{-1}ml^{-1}$, 3.68×10^9 Gr β counts $min^{-1}ml^{-1}$, 2.48×10^9 Gr γ counts $min^{-1}ml^{-1}$, and 7.12×10^6 Gr α

Table 11. Spectrographic Analysis of 16,800-17,700 Mwd/ton UO_2 Dissolutions

VS = very strong; S = strong; M = moderate; W = weak; VW = very weak; T = trace; FT = faint trace; -- = sought not found; numerals = μg/ml.

	HZ 5-8 Core Dissolution			HZ 9-12 Dissolution	
Element	Filter Cake	Sol'n Solids	Sol'n Supernate	Core Solution	Final Residue
Ag	FT	FT	--	--	T
Al	S	T	VS	100-500	VW
Ba				25	--
Be		--	T	--	T
Ca	W	T	W	25-100	W
Cd	W			--	--
Ce		?	VW	100-250	--
Cr	T			2	W
Cu				2	FT
Dy				--	
~~Eu~~				--	
Fe	W	VW	M	10	M
La	W	?	T	50-100	--
Mg	W				T
Mn				--	VW
Mo	M	W	M	25	M
Nb	T			--	--
Nd	M	?		100	
Ni				5	S
Rh				<50	
Si	FT			--	--
Sa	W			--	W
Sr	W	?	VW	2-10	
Ti	T			--	T
U	VS	S		VS	T
Y	W			10-20	
Zr	M	M	M	5	VS

Table 12. Analysis of 16,800 Mwd/ton UO_2 Core Solution (HZ 5-8)
Alpha activity counted at 52% geometry; β at 10% geometry; and γ at 20% geometry.

U - 106 mg/ml

H^+ 3.74 M

Gr α - 7.49×10^7 counts $min^{-1}ml^{-1}$ (39.6% 5.15-Mev α; 17.6% 5.50-Mev α; 39.9% 6.11-Mev α).

Pu α - 4.74×10^7 counts $min^{-1}ml^{-1}$ (77.0% 5.15-Mev α; 22.1% 5.50-Mev α; 0% 6.11-Mev α).

Gr β - 3.57×10^{10} counts $min^{-1}ml^{-1}$

TRE β - 2.37×10^{10} counts $min^{-1}ml^{-1}$

Gr γ - 1.92×10^{10} counts $min^{-1}ml^{-1}$

Zr-Nb γ - 3.69×10^{10} counts $min^{-1}ml^{-1}$

Ru γ - 2.08×10^9 counts $min^{-1}ml^{-1}$

Cs^{137} γ - 1.22×10^{10} dis $min^{-1}ml^{-1}$

counts $min^{-1}ml^{-1}$ after filtration. A few tenths of a gram of black solids, removed from the solution by the second filtration, were boiled for 3 hr in 475 ml of 4 M HNO_3--0.05 M KF solution, cooled, and refiltered. The final light-gray undissolved residue was analyzed spectrographically (Table 11), and appeared to be mainly ZrO_2 and corrosion products along with a trace of uranium. The filtrate contained 0.25 mg U/ml, 7.34×10^8 Gr β counts $min^{-1}ml^{-1}$, 5.21×10^9 Gr γ counts $min^{-1}ml^{-1}$, 1.48×10^5 Gr α counts $min^{-1}ml^{-1}$, and 5.60×10^4 Pu α counts $min^{-1}ml^{-1}$. Radiochemical analyses showed that 99% of the gamma activity in the final filtrate was due to zirconium-niobium, confirming the spectrographic analysis above.

Table 13 presents alpha pulse analyses of the core solutions from the Sulfex experiments. These data are presented to show the buildup and burnout of transuranium elements at the high irradiation levels of these specimens and to give a complete picture of the problems associated with the processing of power reactor fuels.

The alpha activity of the core solution from HZ 5-8, based on pulse analysis of the gross alpha counting plate, the plutonium (TTA) counting

Table 13. Alpha Pulse Analyses of Dissolved UO_2 from Sulfex Decladding Experiments
Approximately 100 g U/liter, 3 M HNO_3

Run No.	Irrad. (Mwd/ton)	Uranium-235 Enrichment(%)		Gross α (% Distribution)[b]					Plutonium α (% Distribution)[b]		
		Start	End	c/m/ml	5.15 Mev	5.50 Mev	5.80 Mev	6.10 Mev	c/m/ml	5.15 Mev	5.50 Mev
1	7,980[a]	5.4	4.4	2.80×10^7	67.1	20.6	--	12.2	2.60×10^7	--	--
2	8,130[a]	5.4	3.4	8.37×10^7	35	26	--	35	4.88×10^7	--	--
3	27,300	5.4	2.7	1.57×10^8	--	--	--	--	8.25×10^7	--	--
4	1,545[a]	2.7	--	5.17×10^6	--	--	--	--	2.98×10^6	--	--
5	2,790[a]	5.4	5.4	3.48×10^6	--	--	--	--	1.25×10^6	--	--
6-9	22,800	3.9	1.3	2.40×10^8	15.1	8.9	--	66.8	6.25×10^7	57.7	33.5
10-13	28,200	3.9	1.2	2.32×10^8	17.8	9.4	--	72.8	5.89×10^7	65.9	34.1
14-15	20,400	0.7	--	3.44×10^9	2.8	3.0	16.2	78.0	1.21×10^8	59.9	40.1
16-17	9,700	0.7	0.2	2.74×10^8	23.7	9.7	4.5	62.0	4.62×10^7	76.9	23.1
18-19	12,900	0.7	0.1	3.29×10^8	18.2	8.8	4.4	68.6	3.48×10^7	71.9	28.1
20-22	7,900	0.7	0.2	8.46×10^7	51.6	25.8	4.7	17.8	5.32×10^7	79.9	20.1

[a] By KAPL.

[b] 5.15 Mev due to Pu^{239} and Pu^{240}; 5.50 Mev due to Pu^{238} and Am^{241}; 5.80 Mev due to Cm^{244}; and 6.10 Mev due to Cm^{242}.

plate, and the effluent from a plutonium-retaining anion exchange column, is as follows:

$Pu^{239} + Pu^{240}$ α	2.96×10^7 counts $min^{-1} ml^{-1}$
Am^{242} α	0.27×10^7 counts $min^{-1} ml^{-1}$
Cm^{242} α	2.98×10^7 counts $min^{-1} ml^{-1}$
Total α	7.26×10^7 counts $min^{-1} ml^{-1}$ vs 7.49×10^7 Gr α counts $min^{-1} ml^{-1}$.

3.7 Solvent Extraction of the Dissolved UO_2 Core Solutions

The core solutions prepared as described in Sec 3.5 and in Table 9 were combined and adjusted to make solvent extraction feed solutions having the compositions shown in Table 14. The feeds were treated with additives in certain cases in an attempt to suppress the extraction of zirconium-niobium and then processed through the "Mini" mixer-settlers according to the Fig.-4 flowsheet described in Sec 2.3. Table 15 summarizes the results of the solvent extraction tests, which were generally as expected.

3.7.1 General Results

A control run of 30-hr duration, using long-decayed feed from experiments HZ 1-4, gave a loss of plutonium to the aqueous raffinate of about the same order (0.5%) as in run 2, primarily due to the ommision of sodium nitrite from the feed. Uranium extraction was good, with 7 stages giving a loss of 0.004% vs 0.07% with 5 stages as in run 2. Since the uranium product of run 1 contained 0.77% of the plutonium, the number of partitioning stages in the B bank was increased from 9 in run 1 to 11 in run 2. This change reduced the plutonium loss to 0.03% but increased the uranium content of the plutonium product from 0.0001 to 0.005 mg/ml. The stripped solvent in the control run retained 2.2% of the uranium because of the lack of stages in the strip bank -- 8 mechanical stages, having 50% efficiency, vs 11 theoretical stages required to give 0.01% loss.

Run 2, the first "hot" run using feed at 17,200 Mwd/ton, was operated for 32 hr to determine steady-state conditions. Samples taken at 12, 24, and 30 hr after startup showed that equilibrium had been

Table 14. Feed Solution Analysis for Modified Purex Process Solvent Extraction Runs

Run No.	Irrad. Level[a] (Mwd/T)	Decay Period[b] (mo)	Free Acid (M)	Uranium Conc. (mg/ml)	Radiochemical Analysis (counts min^{-1} ml^{-1})								Feed Solution Mixture (See Table 9)
					Gr α x 10^7	Pu α x 10^7	Gr β x 10^{10}	TRE β x 10^{10}	Gr γ x 10^{10}	Zr-Nb γ x 10^9	Ru γ x 10^9	Cs γ x 10^9	
2	17,200	8.0	3.4	96.4	7.1	4.2	3.2	2.0	1.5	11.3	1.5		50% HZ 5-8 + 50% HZ 9-12
3	17,400	8.0	2.7	90.9	6.9	3.9	2.5	1.7	1.1	4.3	1.3	4.1	30% Run 2 feed + 70% HZ 13-15
4	12,260	8.0	3.0	95.8	4.8	2.8	1.7	1.4	1.1	5.8	0.6	3.0	30% HZ 3 + 70% Run 3 feed
5	14,000	8.0	3.2	89.8	16.0	2.8	1.6	1.2	1.1	6.2	1.4	2.5	55% HZ 19-20 + 37% HZ 17 + 8% $H_2C_2O_4$
7	28,200	4.0	2.7	96.1	23.4	5.9	5.1	3.4	4.5	32.6	4.3	6.8	HS 10-13
8	20,400	2.5	3.3	107.2	253.	12.3	6.2	3.5	7.1	59.5	12.6	4.3	HS 14-15
9	13,100	2.5	3.1	107.0	123.	8.5	2.7	1.7	2.3	17.2	5.4	2.4	39% HS 16-17 + 43% HS 18-19 + 18% Run 8 feed
10	13,100	2.5	3.2	108.0	85.3	7.8	2.2	1.2	2.1	12.0	3.9	2.1	Same as Run 9
11	7,900	24.0	2.7	102.0	8.7	5.6	0.4		0.2		0.6	1.5	HS 20-22
12	7,900	24.0	3.1	94.4	8.0	5.6	0.4			0.7	0.5	1.5	90% HS 20-22 + 10% oxime
13	7,900	24.0	3.3	92.4	6.7	5.5	0.4		0.2	0.4	0.5	1.5	90% HS 20-22 + 10% oxime

[a] Irradiation level average value of mixture of core solutions (Table 9).

[b] Period of shortest-decayed feed solution in mixture (Table 9).

[c] Counting efficiencies: β-10%, γ-20%, α-52%.

Table 15. Summary of Modified Purex Process Solvent Extraction Runs at High Irradiation Levels

"Mini" mixer-settlers; Run 2 used 5 extraction and 11 scrub stages; all other runs used 7 extraction, 5 scrub stages in A-bank; 5 scrub, 11 partition stages in B-bank; and 8 strip stages in C-bank

Run No.	Run Length (hr)	TBP Diluent	Irrad. Level[a] (Mwd/T)	Decay Period[b] (mo)	Feed Treatment[c]	Losses (%)					Decontamination Factors								Remarks
						AW		BP	CW		Feed to Uranium Product				Feed to Plutonium Product				
						U	Pu	U	U	Pu	Gr β $\times 10^4$	Gr γ $\times 10^4$	Ru γ $\times 10^3$	Zr-Nb γ $\times 10^3$	Gr β $\times 10^3$	Gr γ $\times 10^3$	Ru γ $\times 10^3$	Zr-Nb γ $\times 10^3$	
2	32	Amsco	17,200	8.0	None	0.07	0.53	0.0003	2.2	0.01	8.1	2.1	5.9	32.0	0.98	20.0	5.0	9.8	11 Scrub stages
3	15	Amsco	17,400	8.0	None	0.004	4.0	0.009	7.0	0.01	0.7	0.14		1.3	1.3	2.2		2.6	9 Scrub stages
4	15	Amsco	12,260	8.0	0.1 M diacetyl monoxime	0.006	0.32	0.015	0.42	0.01	1.6	0.33		0.4		5.2		1.3	
5	15	Amsco	14,000	8.0	0.05 M oxalic acid	0.001	0.06	0.014	2.2	0.03	7.0	2.3	5.8	17.0	12.0	3.0	0.6	0.6	
7	15	Dodecane	28,200	4.0	None	0.001	0.20	0.001	0.15	0.02	5.4	1.9	4.6	21.0	12.0	7.8	18.0	14.0	
8	15	Adakane	20,400	2.5	0.05 M $NaNO_2$	0.006	0.12	0.048	1.96	0.04	2.1	1.2	13.0	14.0	0.72	1.1	0.6	2.0	
9	15	Adakane	13,100	2.5	0.05 M $NaNO_2$	0.008	0.07	0.002	0.37		2.7	1.3	34.0	11.0	17.0	4.6			
10	15	Adakane	13,100	2.5	0.05 M $NaNO_2$, 0.1 M H_2SO_4	0.012	0.09	0.001	0.23		2.1	0.71	24.0	4.6	46.0	15.0			
11	6	Adakane	7,900	24.0	0.05 M $NaNO_2$	0.006	0.001				0.3	0.09							No Scrub Flow
12	12	Adakane	7,900	24.0	0.05 M $NaNO_2$, 0.1 M diacetyl monoxime	0.14	0.001	0.004	0.06		0.1	0.09	0.6	0.08	0.42	0.35			No Scrub Flow
13	11	Adakane	7,900	24.0	0.05 M $NaNO_2$, 0.04 M 3-oximino, 2-4 pentane dione	0.037	0.096	0.006	0.02	0.02	0.2	0.2	1.4	0.69	0.24	0.55			

[a] Average value from mixture of core solutions (See Table 9).

[b] Period of shortest-decayed feed solution (See Table 14).

[c] H_2SO_4 and $NaNO_2$ added to feed at ambient temperature, other additives digested 2 hr at 80-85°C.

reached at the 12-hr sampling time in all three contactors. Decontamination from fission products was about 10 times better than in run 3, where 9 scrub stages were used. Black solids accumulated at the interfaces of the extraction stages after about 12 hr of operation but did not affect the mixer-settler performance. Spectrographic analysis of the black interface "crud" showed it to be primarily calcium and aluminum compounds containing 0.7 wt % uranium, 5×10^6 plutonium α, 4×10^9 Gross β, and 2.6×10^9 Gross γ counts $min^{-1}g^{-1}$, with the gamma activity due to zirconium-niobium, ruthenium, and cesium.

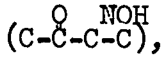
The addition of sodium nitrite to the feed improved plutonium extraction. Radiolytic nitrite formation did not appear sufficient for plutonium-valence adjustment.

Shorter decay times, 75 days in run 8 vs 15 months in run 7, did not materially affect operation or decontamination.

The presence of 0.1 M sulfate in the feed of run 10, simulating accidental carryover of Sulfex decladding reagent, had little effect on uranium and plutonium losses to the raffinate but decreased the decontamination from zirconium-niobium by a factor of about 2 over run 9, the basis for comparison.

Alpha pulse analysis of the aqueous raffinates of runs 2 to 5 indicated about 2% of the gross α activity was due to Pu^{239} and Pu^{240} (5.15 Mev), about 10% had a 5.50-Mev energy and was due to Pu^{238} and Am^{241}, while about 85%, having a 6.11-Mev energy, was due to Cm^{242}. Pulse analysis of the plutonium α activity in the AP, BP, and CU as well as the AF, showed about 75% was Pu^{240} and 25% was Pu^{238}. Pulse analysis of the gross α activity in the stripped organic waste stream showed that 84% was due to Cm^{242} and only 9% due to plutonium; thus the "loss" figures quoted in Table 15 for plutonium to the CW stream are high by a factor of about 10.

3.7.2 Effect of feed additives

In tracer experiments Blake[58] showed that the addition of oximinoketone compounds to solvent extraction feeds might improve decontamination from ruthenium and zirconium-niobium by complexing fission products in the aqueous phase and reducing their extractability. The feed solutions in runs 4, 5, 12, and 13 were digested for 2 hr at 80 to 85°C after the addition of about 10 vol % of diacetyl monoxime  $(\mathrm{C}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{NOH}}{\mathrm{C}}-\mathrm{C})$, 10 vol % 3-oximino-2, 4-pentanedione, or a smaller amount of oxalic acid, a principal degradation product of the oximes, which may have been responsible for the improved decontamination.

The addition of 0.05 M oxalic acid to the feed had a greater effect on decontamination in run 5 than the oxime in run 4. Diacetyl monoxime, however, improved plutonium extraction over that from untreated feed, and in addition aided in partitioning the plutonium in the B bank. The plutonium product in run 4 was bright blue, as opposed to a brownish-violet in the other runs.

The additive tests, however, were not conclusive since nearly equal decontamination from fission products was obtained in runs not containing oximes. Runs 11-15, expected to be a series of rechecks of additive tests using portions of a single batch of feed, took place at the time that radiation damage finally took its toll of the polyethylene tubing and Teflon valve seats. Six months in a radiation field of 600 to 1000 r/hr embrittled and cracked the tubing carrying the aqueous scrub to the A bank, causing no scrub flow in the bank and giving gamma decontamination factors for the uranium, from the AF to the AP, of about 900 for runs 11 and 12. The poor decontamination in run 13 was due to the maloperation during runs 11 and 12, which upset the equilibria of all three mixer-settler banks. Run 14, using oxalic acid, was not completed because of leakage of liquid through an embrittled Teflon seat on a valve on the feed displacement tank.

3.7.3 Solvent degradation during processing of highly irradiated fuels.

The effect of radiation damage to a 30% TBP solvent upon recycle during the processing of highly irradiated fuels by the modified Purex process was also investigated. Three sets of batch equilibrations were made to simulate operation of the modified Purex flowsheet in the "Mini" mixer-settlers through six complete cycles of extraction, scrubbing, and stripping, followed by two sodium carbonate and one nitric acid washes for solvent cleanup prior to recycle. Feed solutions, made from UO_2 irradiated to 8950 to 27,300 Mwd/ton, contained about 100 g of uranium per liter, 10^8 Gross α, 10^7 Pu α, 10^{10} Gross γ, and 10^{10} Gross β counts $min^{-1}ml^{-1}$ and exposed the solvent to energies of about 0.14 whr/liter per cycle.

Two different solvents made with purified TBP diluted with Amsco 125-82, a branched-chain hydrocarbon containing about 7% unsaturates and manufactured by the polymerization of butenes and pentenes, were degraded. Uranium-complexing agents were formed that could not be removed from the organic phase by the carbonate and acid washes. After six cycles, the cleaned solvent retained between 0.5 and 1.8 g of uranium per liter. TBP diluted with n-dodecane or its commercial equivalent, Adakane-12, did not exhibit the same degradation, and after six cycles retained only 0.09 g of uranium per liter. A six-cycle control test in similar equipment using unirradiated feed solutions and the Adakane diluent ~~for TBP gave a uranium retention of 0.06 g of uranium per liter.~~ Plutonium retention by the washed Amsco-TBP solvent increased eightfold (to 0.02% loss) after 6 cycles, whereas that of the Adakane-TBP actually decreased by a factor of 2 at the end of 6 cycles. Fission product retention by the washed solvent was erratic, and no conclusions could be drawn.

These tests on solvent degradation indicated that high-quality diluent for the TBP solvent is an essential requirement for radiochemical processing at power reactor irradiation levels.

3.8 Corrosion Data

Rough tests of Ni-o-nel as a material of construction for the Zirflex-Sulfex-core dissolution vessel were made during the hot-cell tests. During the Zirflex tests the Ni-o-nel corrosion specimen accumulated 46.75 hr totally immersed in boiling Zirflex decladding solution (6 M NH_4F--1 M NH_4NO_3) while in contact with the Zircaloy-clad specimens, plus 14.5 hr in the boiling core dissolvent (4 M HNO_3), for a total of 61.25 hr. The total weight loss was 0.1916 g, equivalent to 2.8 mils/month, which may be a satisfactory corrosion rate.

Weight gains during the Sulfex program prevented the collection of accurate data on the behavior of the specimen. No severe localized corrosion was noted, however.

4. CONCLUSIONS

4.1 Zirflex Decladding Process

The Zirflex process for the removal of Zircaloy-cladding from UO_2 cores was successfully demonstrated on a laboratory scale with prototype specimens irradiated up to 17,700 Mwd/ton of uranium. About 2 to 3 hr was required to dissolve the Zircaloy cladding in boiling 6 $\underline{M}$ NH_4F--1 $\underline{M}$ NH_4NO_3, leaving an end-plug heel. The losses of uranium and plutonium to the decladding solution averaged about 0.05%, within their limits of solubility in the spent decladding solution at room temperature. Continuous removal of the steam and ammonia vapor off-gas to prevent an increase in pH of the dissolvent, followed by dilution with an equal volume of water to about 0.4 $\underline{M}$ zirconium, gave a stable, decladding waste containing about 10^9 dis $min^{-1}ml^{-1}$, due to zirconium-niobium activity induced in the Zircaloy cladding during irradiation. The diluted waste solution required centrifugation to recover UO_2 fines and other solids for recycle to the dissolver for the core-dissolution step.

4.2 Sulfex Decladding Process

Dissolution of the stainless steel cladding of sintered UO_2 pellets was successfully demonstrated on prototype power reactor fuel specimens at irradiation levels up to 28,200 Mwd/ton. The stainless steel cladding dissolved over a 2 to 3 hr period in a 200% excess of boiling 4 $\underline{M}$ H_2SO_4, after initiation of the reaction with iron wire, at rates of 2 to 4 mg $cm^{-2}min^{-1}$. Losses of soluble uranium and plutonium to the decladding reagent were about 0.05% at irradiation levels greater than 1000 Mwd/ton. Clarification of the decladding solution was required to recover UO_2

fines produced by the fracture of the core pellets. Gross gamma activity of the stable decladding solutions was 10^9-10^{10} dis $min^{-1}ml^{-1}$, due mainly to Co^{60}.

4.3 Core Dissolution

The UO_2 core pellets, irradiated up to 28,200 Mwd/ton, required 5 to 6 hr for complete dissolution in boiling 4 M HNO_3 to terminal concentrations of 100 g per liter for the uranium and 3 M for the HNO_3, which was suitable for direct use as a solvent extraction feed after clarification. A very small amount of highly radioactive insoluble oxides or fluorides of the cladding material was centrifuged from the solvent extraction feed solution. Uranium and plutonium loss to these solids were less than 0.1%.

4.4 Modified Purex Solvent Extraction Process

The recovery of the uranium and plutonium from highly irradiated prototype power-reactor fuel specimens was successfully demonstrated using one cycle of a modified Purex solvent extraction flowsheet in "Mini" mixer-settlers. Losses of uranium and plutonium to the raffinate were 0.001 to 0.04% and 0.001 to 0.12%, respectively, under normal flowsheet conditions using about 3.5 theoretical extraction stages. About 4.5 theoretical scrubbing stages gave an average gross γ decontamination factor for the uranium of about 1.5×10^4, and 5.5×10^3 for the plutonium product. The presence of 0.1 M sulfate in the feed had little effect on flowsheet performance.

Recycle of the 30% TBP solvent through six simulated cycles of the flowsheet, using an average 13,000 Mwd/ton feed solution, including sodium carbonate and nitric acid washes for solvent recovery, showed that solvent diluted with a branched-chain hydrocarbon, Amsco 125-82, was degraded more than solvent diluted with a high-purity n-dodecane or its commercial equivalent. After six cycles and a total calculated irradiation dose of 0.14 watt-hr/liter the Amsco solvent retained between 0.5 to 1.8 g of uranium per liter after solvent recovery, compared with 0.09 g per liter for the n-dodecane-diluted TBP. Plutonium and ruthenium were not significant for either solvent, i.e. less than 0.02%.

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APPENDIX A

Fabrication History of Zirflex Test Specimens
3" PWR Blanket Fuel Pins Fabricated in ORNL Hot Shop[45]
(April 15, 1958)

Irrad. No. 43-	Pin No.	Total wt (g)	UO_2, (g)	Status on August 1962
20	3	54.3320	37.1151	In MTR; 32,000 Mwd/ton
20	8	54.2993	36.8210	In MTR; 32,000 Mwd/ton
20	9	52.6481	35.2632	In MTR; 32,000 Mwd/ton
20	11	54.0943	36.5387	In MTR; 32,000 Mwd/ton
20	12	54.5704	37.0985	In MTR; 32,000 Mwd/ton
20	16	55.5818	40.0741	In MTR; 32,000 Mwd/ton
32	20	52.2811	35.3617	In MTR; 54,000 Mwd/ton
33	22	53.6132	36.2310	In MTR; 58,000 Mwd/ton
34	23	55.3391	40.5608	Used in HZ-18
35	29	53.3292	36.4137	Used in HZ-18
36	30	56.1644	41.3769	In ETR; 22,000 Mwd/ton
37	32	53.2314	35.9431	In ETR; 22,000 Mwd/ton

Notes:

1. Specimens autoclaved 24 hr at 300°C and 1250 psig, including oxygen overpressure.
2. Total weights given after autoclaving test.
3. Specimens filled with UO_2 and welded in helium-atmosphere glove box.
4. UO_2 pellets PWR reactor-grade rejects received under IC-1597 via SRP on 12/19/57. Density 93 to 95% of theoretical. Pellets centerless ground at Y-12 to 0.357-0.359 in. OD x odd lengths to 0.375 in.

APPENDIX B.

Irradiation History of NRX Holders 1 and 2

		Holder 1 (3165 g U + Th)			Holder 2 (3264 g U + Th)		
Date	Full Power Days	Peak Flux x 10^{13}	kw[a]	kwd	Peak Flux x 10^{13}	kw[a]	kwd
2/25-3/1/60	4.49	5.0	160	718	5.0	172	772
3/1-3/13	12.45	5.0	152	1890	5.5	184	2290
3/14-3/20	5.86	4.5	132	774	5.5	180	1055
3/25-4/9	15.08	5.5	152	2290	5.5	180	2710
4/10-5/1	21.14	5.6	164	3470	5.5	180	3810
5/6-5/29	23.42	5.6	168	3760	5.6	192	4500
6/2-7/3	29.15	5.5	164	4780	5.0	172	5020
7/6-7/24	16.66	5.5	168	2800	5.5	188	3130
7/29-8/21	23.25	5.5	168	3910	5.5	188	4370
8/27-9/18	20.25	5.5	168	3400	5.4	192	3890
9/23-10/16	21.30	5.2	160	3408	5.6	200	4260
10/20-11/20	30.90	5.2	160	4940	5.0	180	5560
11/25-11/30	2.65	4.7	144	380	4.8	172	455
11/30-12/14	13.40	4.7	144	1930	4.4	160	2140
12/15-12/18	3.00	4.9	152	455	4.3	156	465
12/22-1/3/61	7.20	4.7	144	1037	4.3	156	1133
1/4-1/23	17.10	4.7	144	2463	4.5	164	2804
1/26-1/31	4.90	4.6	140	686	4.1	148	725
2/1-2/18	17.90	4.8	147	2631	4.5	164	2935
2/19-2/26	6.90	4.5	139	959	4.1	141	973
3/2-3/26	24.00	4.3	134	3216	4.1	151	3624
3/27-4/3	6.00	4.3	134	804	3.9	143	858
4/6-4/13	4.20	4.3	134	563	(327 days)		57482
4/14-4/24	8.60	4.3	134	1152			
4/27-5/29	31.64	5.5	122	3860	Avg	17610	Mwd/ton
6/2-6/26	23.29	5.5	124	2888	Peak	20600	Mwd/ton
6/29-7/24	18.62	5.5	117	2178			
7/28-8/21	20.38	5.6	126	2568			
8/21-9/18	23.14	5.6	122	2818			
9/19-10/23	26.97	5.6	121	3263			
10/23-11/20	21.70	5.6	117	2539			
		(505 days)		72520			
		Avg	22910	Mwd/ton			
		Peak	25600	Mwd/ton			

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[a] Measured value from water temperature at exit of holder.

APPENDIX C.

Fabrication Data for 3" ORNL Stainless Steel-Clad UO_2 Irradiation Specimens[45,57]

Series 1.

Specimen Number	Wt UO_2, grams	Wt UO_2 + SS, grams	Wt After Autocl. and Buffing-g.	Irrad. No.	Remarks
1	44.0009	65.7605	65.7276	LITR	3-1/8" x 7/16" dia x 1/32" wall
2	43.3675	65.0738	65.0186	LITR	304L SS tubing and bar stock
					end caps.
3	43.5045	65.4165	64.4004	LITR	Autoclaved 105 hr at 300°C,1600
4	44.2768	65.8040	65.7558	43-10	psig.
5	43.1625	64.1544	64.1055	43-10	
6	43.8048	65.3974	65.3603	43-10	
7	41.7086	63.4415	63.3961	43-3	3-1/8" x 7/16" dia x 1/32" wall
8	41.8165	62.8946	62.8622	43-3	304 ELC SS tubing, 304L barstock
9	41.7565	63.2924	63.2686	43-3	end caps.
10	41.7235	63.2904	63.2594	43-3	
11	41.5353	62.5224	62.4994	43-3	Autoclaved 4 days at 300°C, 1600
12	42.1880	63.2655	63.2436	43-10	psig., including 350 psig. oxygen
13	41.9413	63.2832	63.2359	43-3	overpressure.
14	41.1595	62.2934	62.2664	43-3	
15	41.8610	63.3921	63.3537	43-10	
16	42.0379	63.4203	63.3966	43-3	
17	41.2339	62.9158	62.8757	43-3	
18	41.8021	63.8726	63.8430	43-10	
19	41.6842	62.9783	62.9574	43-3	

Series 2.

Specimen Number	Wt UO_2, grams	Wt UO_2 + SS, grams	Wt After Autocl. and Buffing-g.	Irrad. No.	Remarks
1	40.3759		52.9473	43-18	3" x 0.408" OD x 0.019" wall
2	39.8366		52.5309	43-18	type 304L SS tubing and type 347
3	40.3431		52.7261	43-18	SS end plugs.
4	40.2594		52.6204	43-18	
5	40.2644		53.1994	43-18	
6	40.5772		53.2894	43-18	Autoclaved 24 hr at 300°C, 1250
7	40.2301		52.8735	43-18	psig., including 300 psig.
8	40.1028		52.8169	43-18	
9	40.1000		52.4935	43-18	
10	40.5948		53.0459	43-18	
11	40.9166		53.4373	43-22	
12	39.9806		52.4368	43-23	
13	40.1686		52.4451	43-24	
14	41.1757		53.5157	43-25	
15	40.0386		52.5054	43-26	
16	40.4411		52.3015	43-27	
17	40.1783		52.6636	43-28	
18	40.4661		52.5395	43-29	
19	40.2102		53.2314	43-30	
20	40.5656		51.3452	43-31	

APPENDIX D

Revised Method for Burnup Calculations from Cs^{137} Analysis

$$\lambda = \frac{0.693}{(29.2\ y)(365\ d)(24\ h)(60\ m)} = 4.51 \times 10^{-8}$$

$Y = 6.15\%$

$t =$ time from date of mid-irradiation to date of analysis in minutes

$$(1)\quad \frac{Cs^{137}\ d/m/ml}{mg\ U/ml} \times \frac{1}{\lambda Y} \times \frac{238}{6.02 \times 10^{20}} = \text{fissions/atom U}$$

$$(2)\quad \frac{Cs^{137}\ d/m}{mg\ U} \times \frac{1}{\lambda Y} \times \frac{238}{6.02 \times 10^{20}} \times \frac{100}{e^{-\lambda t}} = \%\ \text{U atoms fissioned}$$

$$(3)\quad \frac{Cs^{137}\ d/m}{mg\ U} \times \frac{1}{\lambda Y} \times \frac{238}{6.02 \times 10^{20}} \times \frac{100}{e^{-\lambda t}} \times 9.65 \times 10^{5} = \text{Mwd/TU charged}$$

$$(4)\quad e^{-\lambda t} \simeq 1 - \lambda t$$

$$(5)\quad \frac{Cs^{137}\ d/m}{mg\ U} \times \frac{1}{4.51 \times 10^{-8} \times 6.15 \times 10^{-2}} \times \frac{238}{6.02 \times 10^{20}} \times \frac{100}{1-\lambda t}$$

$$\times\ 9.65 \times 10^{5} = \frac{1.38 \times 10^{-4}}{(1-\lambda t)} \times \frac{Cs^{137}\ d/m}{mg\ U}$$

$$(6)\quad \text{Mwd/TU charged} = \frac{1.38 \times 10^{-4}}{(1-\lambda t)} \times \frac{Cs^{137}\ d/m}{mg\ U}$$

For example, in run HZ-22, WAPD-PWR pin No. ZCQ-4176 was inserted into the MTR on 4/23/59 and was discharged on 4/3/61, making the date of mid-irradiation 5/1/60. The core solution sample was analyzed on 2/27/62, or 22 months (1.02×10^{6}) from the date of mid-irradiation. The uranium analysis of the sample was 109 mg/ml and the Cs^{137} analysis was 4.62×10^{9} dis $min^{-1} ml^{-1}$.

On the basis of these results:

$$\lambda t = 4.51 \times 10^{-8} \times 1.02 \times 10^{6} = 4.60 \times 10^{-2}$$

$$1 - \lambda t = 0.954\ .$$

$$\frac{Cs^{137}\ d/m}{mg\ U} = \frac{4.62 \times 10^{9}}{1.09 \times 10^{2}} = 4.24 \times 10^{7}$$

Substituting in equation (6):

$$\frac{1.38 \times 10^{-4}}{0.954} \times 4.24 \times 10^{7} = \underline{6.15 \times 10^{3}\ \text{Mwd/TU charged}}\ .$$

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