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Hot Cell Demonstration of Zirflex and Sulfex Processes: Report Number 1.

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ABSTRACT

Four runs have been conducted in the Zirflex-Sulfex headend hot cell equipment. Prototype PWR blanket rods, Zircaloy-2 clad UO_2 , irradiated from 159 to 356 Mwd/Ton and decayed 2 years, were declad in boiling 6 M NH_4F -1 M NH_4NO_3 , terminating with a F/Zr mol ratio of 7 in the spent decladding solution. Average decladding time was 1.5 hr, leaving end cap residues of about 5 g per pin. At the end of the decladding maximum loss of uranium and plutonium to the decladding solution was 0.04 and 0.37%, respectively. The core pellets were largely shattered with less than 0.5 wt % smaller than 10 mesh. Core dissolution was complete in 5 M HNO_3 in about 40 minutes, yielding a solvent extraction feed containing 4 M HNO_3 and 100 g U/l. Solid residue from the decladding and core dissolution was less than 0.001% of the initial weight, and consisted of traces of Ca, Fe, Cr, and Sn; uranium and plutonium were not detected.

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1.0 INTRODUCTION

The comprehensive hot cell evaluation and demonstration program for the Zirflex and Sulfex decladding processes, which was planned as an adjunct to the program of the Savannah River Laboratory and outlined in ORNL-CF-61-5-37⁽¹⁾, was begun during the latter part of November, 1961. The object of the program is to determine whether effects of irradiation level adversely influence the performance of the Zirflex or Sulfex flowsheets for decladding prototype Zircaloy-2 and stainless steel-clad uranium dioxide fuel specimens or solvent extraction by a modified Purex process.

During the month of November and early December, a total of 4 long-decayed prototype PWR blanket rods of low irradiation level (less than 400 Mwd/T) were declad, the cores dissolved, and a solvent extraction run made in "Mini" mixer-settlers. These runs served mainly to test the equipment and operations in the hot cell prior to tests with the highly-irradiated NRX specimens during the month of December. Because of the long decay period of about 2 years, fission product analyses were of little interest, but the analyses for uranium and plutonium losses were of value to the program.

2.0 ZIRFLEX PROCESS

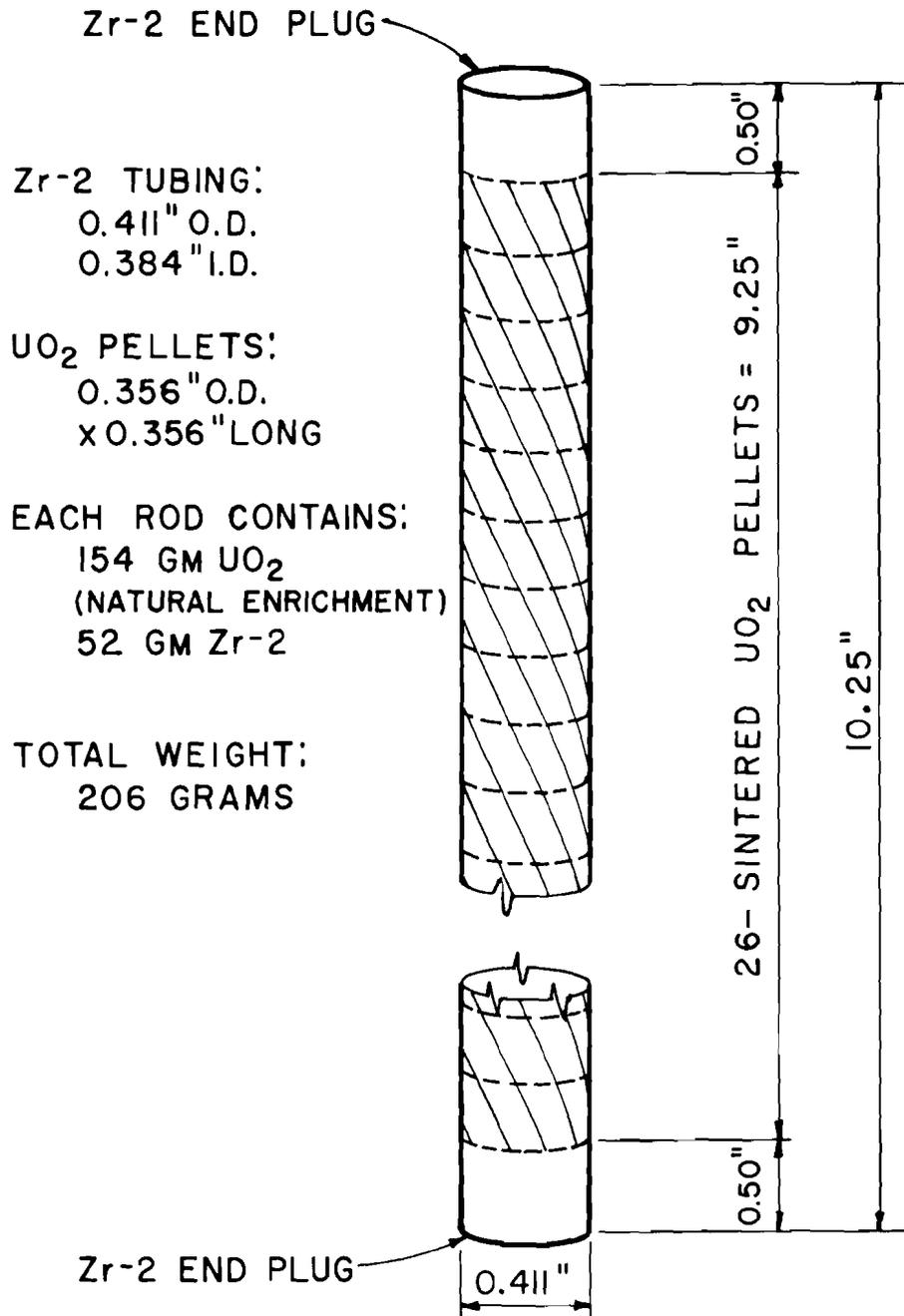
2.1 Procedures

The Zirflex process was developed at ORNL and Hanford as a method for removing zirconium or Zircaloy cladding from uranium dioxide fuels of the PWR blanket type. Numerous references on the process are available and will not be summarized here. The flowsheet conditions used in these experiments were those described in CF-61-5-37⁽¹⁾, which assumed that the volume of $6 \text{ M NH}_4 \text{ F} - 1 \text{ M NH}_4 \text{ NO}_3$ was chosen to give a F/Zr mol ratio of 7 in the final decladding solution if 90% of the Zircaloy was dissolved. Makeup water was continuously added to the boiling solution during decladding at the same rate as the steam and ammonia vapors were removed through a down-draft condenser. Two 1 M NaOH scrubbers were used to treat the off-gas before discharge to the plant vessel off-gas system. No purge gas was used in this series of experiments.

The final decladding solution was diluted with an equal volume of water to prevent precipitation of ammonium fluozirconate at ambient temperatures, and allowed to cool to decrease the solubility of UF_4 and reduce soluble losses. The cold, diluted decladding solution was withdrawn from the dissolver, vacuum-filtered through No. 2 filter paper on a Buchner funnel, sampled, and discarded. The UO_2 pellets were washed twice and finally refluxed with water to remove residual fluoride from their surfaces. 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 5 M HNO_3 to make a solvent extraction feed of 100 g U/l, which was stored in polyethylene bottles until enough was on hand to make a solvent extraction run.

2.2 Fuel Specimen History

The first series of Zirflex experiments was made with PWR blanket prototype fuel specimens 10.25" long, 0.411" diameter, with a 0.0135" Zr-2 cladding, containing 26 UO_2 pellets (natural enrichment) weighing 152.5 ± 3.5 g and 52 g Zr-2 as cladding and end plugs. The specimens, (Fig. 1) 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, helium leak tested, "Pentrex" tested, and certified reactor grade^(2,3). Fuel pellet density was estimated to be 10.27 g/cc (93.5%) by E. J. Frederick, whereas actually they turned out to be about 96% of theoretical. In order to prevent localized boiling at the metal wall of the specimens, Frederick requested irradiation at fluxes less than 2×10^{14} n/cm²/sec⁽⁴⁾. He calculated each rod would develop 8.05×10^3 watts at 1×10^{14} and 1.23×10^4 watts at 2×10^{14} n/cm²/sec., giving metal wall temperatures of 180°F and 210°F, respectively, using a saturation temperature at 32.2 psia of 255°F⁽⁵⁾. The specimens were irradiated in position I-3-NW of the ETR arranged in 2 vertical rows of 3 rods each as ORNL experiments 43-6 and 43-7⁽⁶⁾. The experiments were inserted on 10/27/58 for cycle 8, removed on 11/19/58, stayed out during cycle 9, were



PWR Zr-2 CLAD UO₂ PELLET POWER REACTOR
BLANKET FUEL ROD

Fig. 1.

reinserted for cycle 10 on 12/8/58, but received no irradiation after 12/29/59, and were discharged on 1/5/59 because of a suspected fission product leak in one of the experiments⁽⁶⁾. The peak flux during the 1.5 cycles (43 days) of irradiation was about 1.5×10^{14} (7), giving an estimated peak 400 Mwd/T.

2.3 Decladding

Run HZ-1. Because of difficulties with leaky fittings on the decladding dissolver condenser, no samples were taken during the decladding of pin number ZDP-2412 from ORNL 43-7. Decladding was completed in less than 2 hours without passivation or precipitation of ammonium fluozirconate. The fractured pellets were washed, photographed, and stored under water in a closed bottle until a series of core dissolutions was made. A total of 4.1 g of undissolved end caps remained after the decladding.

Run HZ-2. Run HZ-2, made with pin IDY-0018 from ORNL 43-6, was terminated after 2.1 hours leaving a total of 7.3 g of Zircaloy end caps undissolved. Examination after one hour of boiling showed blackening and pitting, but penetration had not occurred. The pellets were again fractured with a few small fragments present. No rare earth, zirconium-niobium, or ruthenium activities were found in the decladding solution. Gamma spectrometer analysis indicated only the presence of Sb^{125} , a long-lived fission product, which was also found in the condensate and caustic scrubbers. Activity levels were 2×10^5 Gr γ c/m/ml (equivalent to 0.66% of the total gross γ activity in the pellets) in the decladding solution and up to 3×10^3 Gr γ c/m/ml in the condensate and scrubber solutions (0.005% of the total gross γ activity). Soluble uranium and plutonium losses to the decladding solution were 0.04% and 0.37%, respectively.

Figure 2 shows the condition of the core pellets, as photographed in a 1-inch square grid, with essentially no fines present. This is typical of the condition of the cores of 3 of the fuel specimens.

Run HZ-3. Run HZ-3 was made with pin ZED-0931 from ORNL 43-6. Decladding appeared complete in 1.5 hours, but the pellets were digested at the boiling point for an additional 1 hour as make-up water was added and condensate collected. A considerable number of UO_2 fines were found with the fractured

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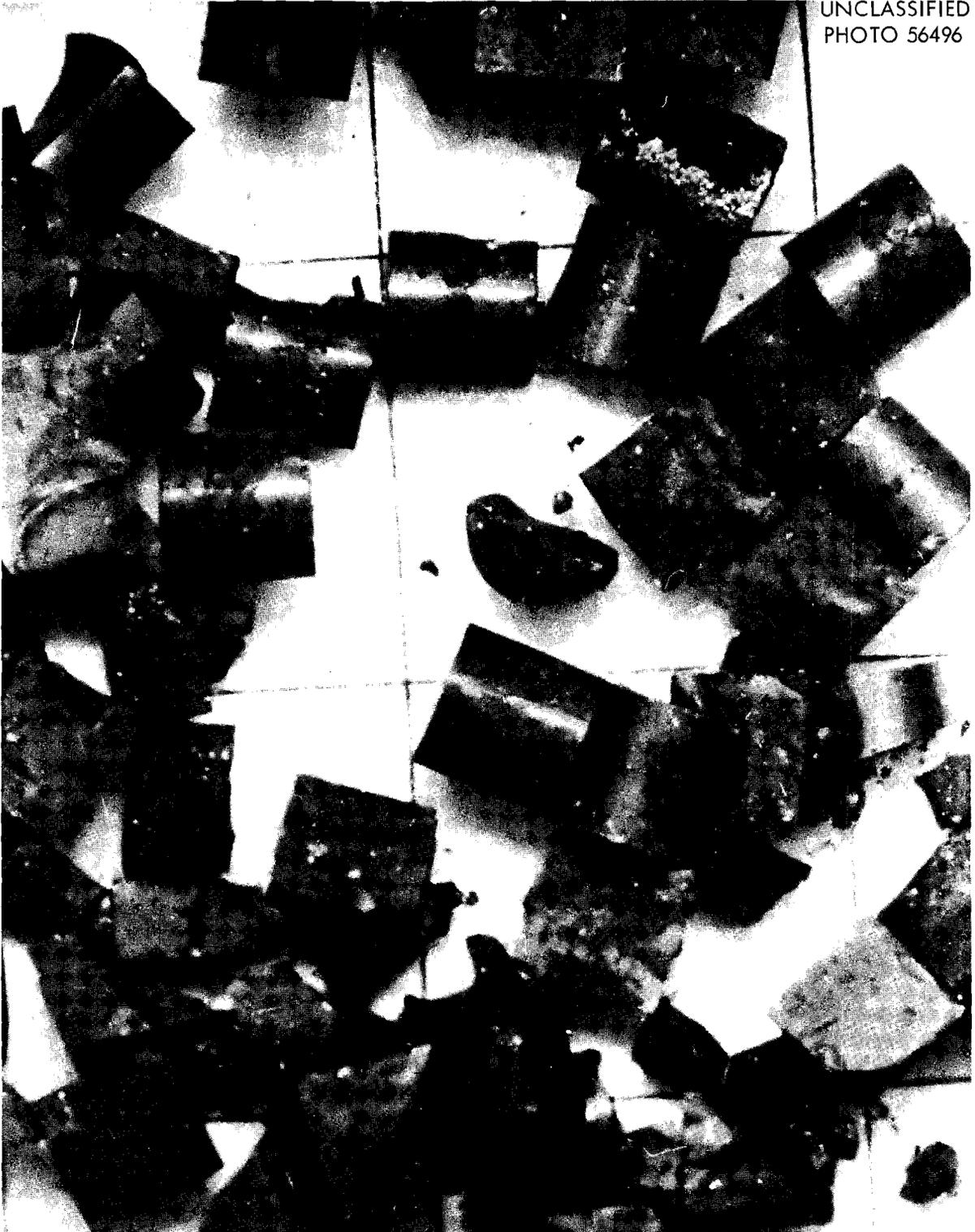


Fig. 2. UO_2 Pellets from Run HZ-2 on a 1- Inch Grid. Irradiated to 191 Mwd/T Uranium.

pellets of this pin (Fig. 3). Size distribution of the core material was 99.7 wt % larger than 10 mesh, 0.2 wt % - 10 + 50 mesh, and about 0.1 wt % smaller than 50 mesh.

Fission product activity in the decladding solution and the condensate was about 0.3% of the total gross γ activity, while the scrubbers contained less than 0.005%. Losses of soluble uranium and plutonium were 0.015% and 0.03%, respectively, to the decladding solution. Analysis of 2 successive cold water washes and one wash in which the pellets were boiled with water for 10 minutes indicated that the washes removed essentially no uranium, plutonium, or fission product activity from the exposed core.

Although inspection of the fuel specimen with binoculars at the ETR in 1959 showed no visible cracking or corrosion that could account for the fission product leak that caused removal of the experiment from the ETR⁽⁸⁾, it is believed that the greater number of fines found in this specimen might be due to a leak in view of the fact that the pellets of the other specimens in 43-6 and 43-7 were intact or in large pieces.

Run HZ-4. This run, using pin QEB-2904 from ETR 43-6, was made under essentially the same conditions as the previous runs in this series except that the decladding solution was withdrawn at the end of 1.5 hours, when the reaction had stopped, and the pellets were refluxed with water prior to washes with cold water. Uranium losses of 0.001% were considerably lower than in Runs 2 and 3, and may be due to the shorter exposure time of the pellets to the decladding solution. The plutonium loss was 0.006%.

2.4 Core Dissolution

Four successive core dissolutions in 5 M HNO_3 were made of the UO_2 pellets from Runs HZ-1 through 4. Dissolution was completed in about 0.75 hours, yielding solvent extraction feed solutions of about 100 g U/l with acidities between 4.08 to 4.43 M HNO_3 . Acid consumption was lower using the 5 M HNO_3 than with a 10 M dissolvent, resulting in a 1 M excess over the desired flowsheet value of 3 M. Very small amounts of undissolved residues found on the paper after filtration of the feed did not contain uranium or plutonium, but consisted of calcium, iron, chromium, and tin

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Fig. 3. UO_2 Pellets from Run HZ-3 on a 1-Inch Grid. Irradiated to 217 Mwd/T Uranium.

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. Burnup analyses, by the Cs¹³⁷ method, indicated the 4 specimens had been irradiated to levels between 159 and 356 Mwd/T. Fission product carry-over to the off-gas scrubbers was negligible, with less than 0.001% of the gross γ activity in the sodium hydroxide solutions. Essentially no Zr-Nb was present in the core solution because of long decay of the pins. Table 1 summarizes the 4 runs.

Table 1. Summary of Zirflex Experiments on Low Burn-up PWR Rods

Run No.	HZ-1	HZ-2	HZ-3	HZ-4
Irradiation Cladding Temp. *	ETR 43-7 195°F	ETR 43-6 195°F	ETR 43-6 195°F	ETR 43-6 195°F
Pin Number	ZDP-2412	IDY-0018	ZED-0931	QEB-2904
Burn-up Irrad. Rate	356 Mwd/T 8.3 Mw/T	191 Mwd/T 4.4 Mw/T	217 Mwd/T 5.1 Mw/T	159 Mwd/T 3.7 Mw/T
Appearance	Bright	Tarnished	Tarnished	Discolored
Rod Weight	199.5 g	202.0 g	199.5 g	199.9 g
Declad Time	ca. 2 hr	ca. 1.5 hr	1.5 hr	1.5 hr
Total Time	ca. 2 hr	2.1 hr	2.5 hr	1.5 hr
Pellet Cond'n	fractured	fractured, few fines	fractured, many fines	fractured
Zr-2 Scrap	4.1 g	7.3 g	5.9 g	not deter.
Sol. U Loss	not deter.	0.037%	0.015%	0.001%
Sol. Pu Loss	not deter.	0.37%	0.03%	0.006%

* Calculated temperature during irradiation-water cooled

3.0 SOLVENT EXTRACTION BY MODIFIED PUREX PROCESS

One cycle of a modified Purex solvent extraction flowsheet was made with the feed solutions prepared from the cores of the PWR rods declad by the Zirflex process. Because of the unexpected high (4 M) terminal acidity of the feed solutions, the feed was diluted to 3 M HNO₃ with water and the flow

ratios adjusted to give an AP stream of the proper concentration. The solvent was calcium hydroxide-treated TBP diluted to 30 volume per cent with as-recieved Amsco 125-82. It was used on a once-through basis, being discarded directly down the hot drain with no provisions for recycle. The "Mini" mixer-settlers were arranged with 7 extraction and 9 scrub stages in the A Bank, 7 scrub and 9 partitioning stages in the B Bank, and 8 strip stages in the C Bank. Actual process conditions were as follows:

AF(1.1 ml/min) = 69.8 mg U/ml, 3.23 M HNO₃, 0.045 mg Pu/ml, 1.17 x 10⁸
Gr β c/m/ml, 3.32 x 10⁷ Gr γ c/m/ml.
AS(0.4 ml/min) : 3 M HNO₃
AX(1.2 ml/min) : 30% TBP
BS(0.65 ml/min) : 30% TBP
BX(0.40 ml/min) : 0.5 M HNO₃, 0.05 M Fe(NH₂SO₃)₂
CX(2.3 ml/min) : 0.02 M HNO₃

Results of the 30 hour test run of the modified Purex flowsheet using the above conditions gave uranium and plutonium losses to the raffinate of 0.004% and 0.53%, respectively. The plutonium loss was primarily due to omission of sodium nitrite from the feed. The BP, which contained 0.145 mg Pu/ml and less than 0.0001 mg U/ml, showed Gr β and Gr γ decontamination factors of 2.3 x 10⁴ and 2.3 x 10³, respectively. The uranium product, having β and γ D.F.'s of 6.75 x 10⁴ and 7.5 x 10³, contained 0.77% of the plutonium due to lack of partitioning stages. The stripped solvent retained 2.2% of the uranium and less than 0.1% of the plutonium because of the lack of stages in the "Mini" strip bank, i.e. 8 mechanical stages vs 11 theoretical stages. Analysis of the A Bank indicated that the 7 mechanical extraction stages were equivalent to 3.5 theoretical stages.

4.0 WORK IN PROGRESS

As of December 31, 1961, 8 of the NRX 20,000 Mwd/T pins had been declad and core dissolutions of the pellets from the pins completed. It appears that the pellets had been fractured but were essentially intact

(i.e. had not fallen apart) when declad. The soluble uranium losses to the 8 decladding solutions ranged from 0.03% to 0.08% and the plutonium losses from 0.01% to 0.04%. Gross gamma activity of the decladding solutions averaged around 3×10^8 c/m/ml, principally Zr-Nb with about 1-2% contributed by Ru and Cs. Rare earths accounted for about 3% of the 4×10^7 gross beta c/m/ml in the decladding solutions.

Decladding experiments are continuing with nitrogen and air atmospheres being introduced into the decladding vessel to determine their effect during operation.

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