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HOT CELL DEMONSTRATION OF ZIRFLEX AND SULFEX PROCESSES: REPORT NO. 3

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ABSTRACT

Hot cell demonstration of the Zirflex decladding process coupled with a modified Purex solvent extraction process was completed using specimens of Zircaloy-clad UO_2 irradiated to levels of 6150-14,600 Mwd/TU. Soluble losses of uranium and plutonium to the decladding solutions were about 0.05%. Centrifugation of the decladding solution is probably necessary to remove up to 1% of the UO_2 present as fines resulting from the fracture of low (93-95%) density pellets; high (96%) density pellets produced few fines. Approximately 5 hours was required to dissolve the UO_2 core material (14,000 Mwd/TU) in 4 M HNO_3 versus 6-7 hours for unirradiated pellets to produce a solvent extraction feed of 100 g U/l and 3 M HNO_3 . Gamma decontamination factors for uranium in the Purex CU stream and plutonium in the BP stream were increased by factors of 2-10 from the normal 1.3×10^3 and 2.1×10^3 , respectively, by pretreatment of the solvent extraction feed with diacetyl monoxime or its degradation product, oxalic acid. Preliminary data indicate radiation damage degrades the solvent, 30% TBP diluted with Amsco 125-82, upon one pass through the mixer-settler banks with feed solutions irradiated to levels greater than 12,000 Mwd/T causing a decrease in Zr "Z" test by a factor of 15.

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1.0 INTRODUCTION

Hot cell experiments were continued on the demonstration of the Zirflex headend process and on a modified Purex solvent extraction process using highly irradiated fuel specimens of Zircaloy-2-clad uranium dioxide. Previous work included decladding of long-decayed prototype PWR blanket rods irradiated to a peak of 412^* Mwd/T, dissolution of the core material, and the subsequent solvent extraction of the resulting feed solution ⁽¹⁾. Following these equipment tests 12 Zircaloy-clad UO_2 pins, irradiated to a nominal 20,000 Mwd/T in the NRX reactor and decayed about 9 months, were declad and the core materials dissolved. These tests indicated that losses of uranium and plutonium to the decladding solution were apparently due solely to solubility in the $NH_4F-NH_4NO_3$ reagent. Dissolution of 99.5% of the UO_2 core material in 4 M HNO_3 required about 5 hours versus 7 hours for unirradiated UO_2 from the same batch ⁽²⁾.

In order to complete the demonstration of the Zirflex process over an intermediate range of irradiation levels, additional NRX specimens from a lower flux position in the same 20,000 Mwd/T holder were declad along with PWR blanket rods irradiated to between 6150 and 13,700 Mwd/T. Solvent extraction runs were made with the 20,000 Mwd/T feed solutions.

2.0 EXPERIMENTAL

2.1 Fuel Specimen History

Seven additional decladding runs were made using 3-10.26" WAPD PWR blanket rods ⁽¹⁾, 4-4.5" NRX pins ⁽²⁾, and 2-3" pins made from centerless-ground WAPD reject pellets clad in Zr-2 at ORNL ⁽³⁾. Density of the WAPD-PWR UO_2 pellets was 93-95% of theoretical and that of the specially prepared NRX pellets was 96%. The PWR blanket pins were irradiated in the ETR or MTR to nominal burnups of 5000, 10,000, and 11,000 Mwd/T, the 2-3" ORNL pins in the ETR to a nominal 12,000 Mwd/T, and the NRX pins to an estimated 17,000 Mwd/T. Decay periods were from 7-23 months for the 10.26" PWR pins, 7 months for the 3" PWR pins, and about 9 months for the 4.5" NRX pins. Table 1 summarizes the histories of the irradiated specimens.

* See section 2.3.3.



Fig. 1 and 2 show the condition of the specimens from HZ-18 and HZ-20 prior to decladding.

2.2 Zirflex Decladding

Decladding conditions were the same as in the previous experiments in this series:

- (1) PWR rods were dissolved in 580 ml of 6 M NH_4F -1 M NH_4NO_3 per rod, the NRX pins were dissolved in 213 ml of 6 M NH_4F -1 M NH_4NO_3 per rod, and the 3" pins dissolved in 208 ml of 6 M NH_4F -1 M NH_4NO_3 per pin, which is equivalent to a F/Zr mol ratio of 7 in terminal decladding solution.
- (2) Water was continuously added to dissolver as steam and ammonia vapors were withdrawn and condensed.
- (3) Steam-ammonia atmosphere in the dissolver; no purge gas.
- (4) Specimens were declad in contact with Ni-o-nel corrosion specimen.
- (5) Decladding solution was diluted with an equal volume of water before filtration and sampling.

Table 2 summarizes the decladding experiments in this series, and shows, in general, the same results as obtained previously. The unusually high loss of 0.28% of the uranium to the decladding solution in Run HZ-17 cannot be explained, since the physical appearance of the UO_2 after decladding was no different than that of PWR rods of higher or lower irradiation levels (Figs. 3-8) and the chemical environment during decladding was also the same. Surface oxidation of the UO_2 during manufacture of the rods might possibly be the cause of the increased solubility of the uranium in the decladding solution. Gamma scanning and radiochemical analysis of the decladding solution indicated Zr-Nb activities contributed essentially all of the activity of waste solutions. Two to three hours is sufficient to remove the cladding, leaving an end cap heel in the dissolver. End caps are visible in Figs. 3-8.

The light gray residue (0.63 g) from the decladding of PWR rod RDR-1015 in Run HZ-16 was analyzed chemically, spectrographically, and radio-

Table 1. Irradiation History of Zirflex Fuel Specimens

Run No.	Pin No.	Fabricator	Irrad. No.	Reactor	First Inserted	Max. Thermal Flux	Date Discharged	Full Power Days	Irrad.* Mwd/T	Irrad. Rate, Mw/T
HZ-16	RDR-1015	WAPD**	43-10	MTR	4/6/59	3.0×10^{14}	3/28/60	224	8950	40.1
HZ-17	ECJ-1237	WAPD**	43-38	ETR	12/22/59	2.6×10^{14}	6/5/61	240	13,100	54.6
HZ-18	23	ORNL**	43-34	ETR	11/4/59	3.3×10^{14}	6/5/61	246	13,700	55.7
	29	ORNL**	43-35	ETR	11/4/59	3.3×10^{14}	6/5/61	246	13,700	55.7
HZ-19	X-22, X-76	ORNL***	No. 2	NRX	2/25/60	5.6×10^{13}	4/3/61	327	14,600	44.6
HZ-20	X-10, X-40	ORNL***	No. 2	NRX	2/25/60	5.6×10^{13}	4/3/61	327	14,600	44.6
HZ-21	KDA-1660	WAPD**	43-14	ETR	4/23/59	1.5×10^{14}	4/3/61	280	7100	25.3
HZ-22	ZCQ-4167	WAPD**	43-14	ETR	4/28/59	1.5×10^{14}	4/3/61	280	6150	21.9

* Based on Cs¹³⁷ analysis of core solution.

** Pellet density 93-95% of theoretical.

*** Pellet density 96% of theoretical.

Table 2. Decladding of Irradiated Zircaloy-2-clad UO₂ Pellets in 6 M NH₄F-1 M NH₄NO₃

Run No.	Irrad. Mwd/T	Total Rod wt, g	Approx. Zr-2 wt, g	Declad Sol'n Vol, ml	Declad Time, hrs	Cond. Rate, ml/hr	Soluble U Loss, ^(a)		Soluble Pu Loss, ^(a)		Decladding Solution Activity, ^(a)		
							mg/ml	%	c/m/ml	%	Gr β c/m/ml	Gr γ c/m/ml	Gr α c/m/ml
HZ-16	8950	201.2	45	580	3.0	330	0.052	0.044	5.48×10^3	0.011	1.2×10^8	8.6×10^7	--
HZ-17	13,100	--	45	580	2.5	250	0.332	0.28	6.15×10^3	0.079	1.2×10^8	5.9×10^7	--
HZ-18	13,700	99.3	32	415	3.3	250	0.138	0.11	9.16×10^3	0.076	--	--	--
HZ-19	14,600	93.8	33	426	3.5	390	0.026	0.043	1.1×10^4	0.065	1.5×10^7	8.9×10^7	1.2×10^6
HZ-20	14,600	94.0	33	426	2.5	450	0.053	0.088	1.3×10^4	0.076	1.5×10^7	1.0×10^8	3.4×10^5
HZ-21	7100	199.4	45	580	2.5	400	0.062	0.052	1.9×10^3	0.039	2.3×10^7	$14. \times 10^8$	--
HZ-22	6150	198.8	45	580	2.5	240	0.052	0.044	4.08×10^3	0.083	1.9×10^7	1.0×10^8	--

(a) In decladding solution diluted 1:1 with water.

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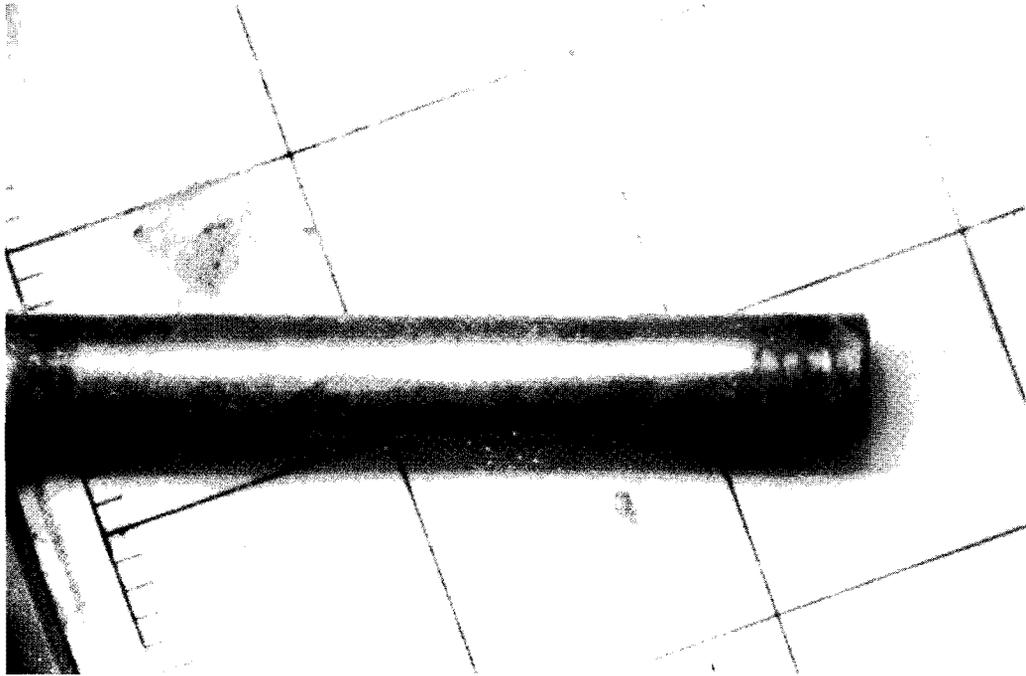


Fig. 1. ORNL Pin #23 (HZ-18) before decladding (13,700 Mwd/T U).

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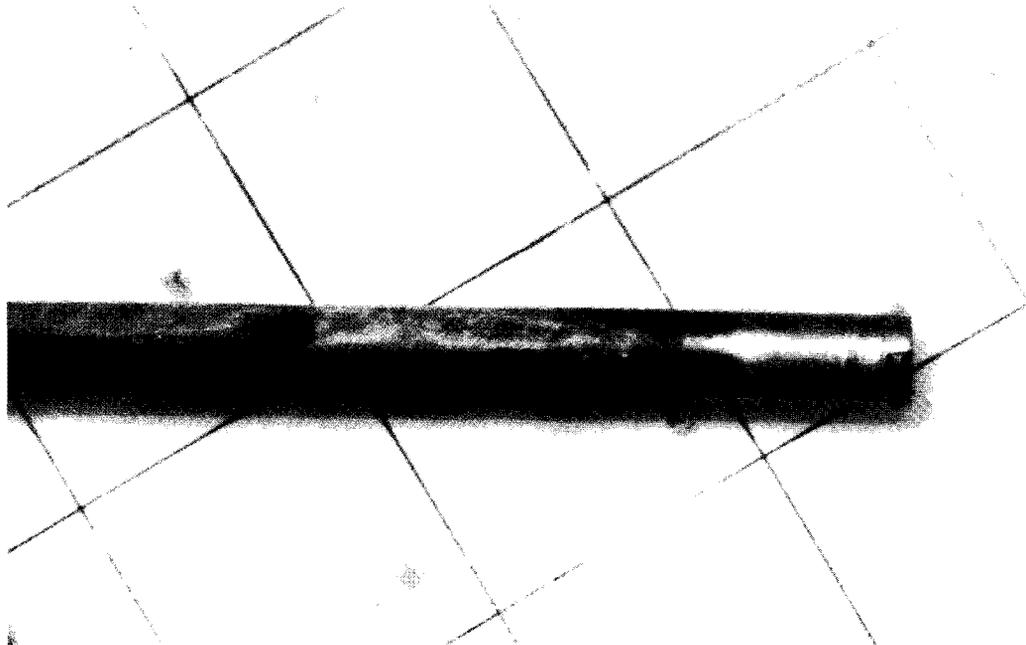


Fig. 2. Portion of NRX Pin #X-40 (HZ-20) before decladding (14,000 Mwd/T U).

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Fig. 3. UO_2 pellets from HZ-22 on 1" grid. WAPD-PWR rod irradiated to 6150 Mwd/T U.

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Fig. 4. UO_2 pellets from HZ-21 on 1" grid. WAPD-PWR rod irradiated to 7100 Mwd/T U.

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Fig. 5. UO_2 pellets from HZ-16 on 1" grid. WAPD-PWR rod irradiated to 8950 Mwd/T U.

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Fig. 6. UO_2 pellets from HZ-17 on 1" grid. WAPD-PWR rod irradiated to 13,100 Mwd/T U.

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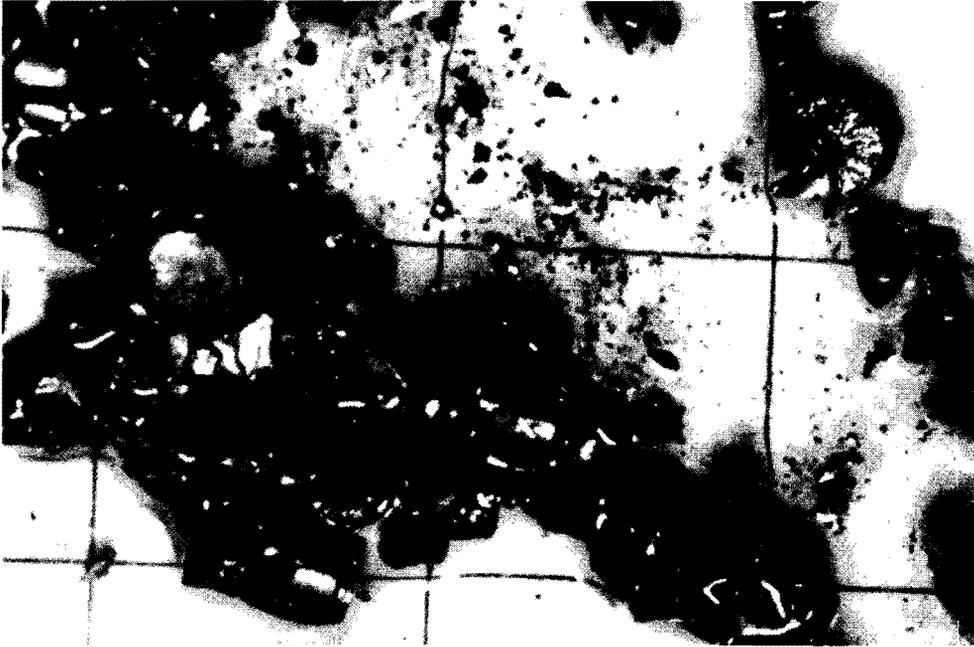


Fig. 7. UO₂ pellets from HZ-18 on 1" grid. WAPD-PWR pellets clad at ORNL, irradiated to 13,700 Mwd/T U.

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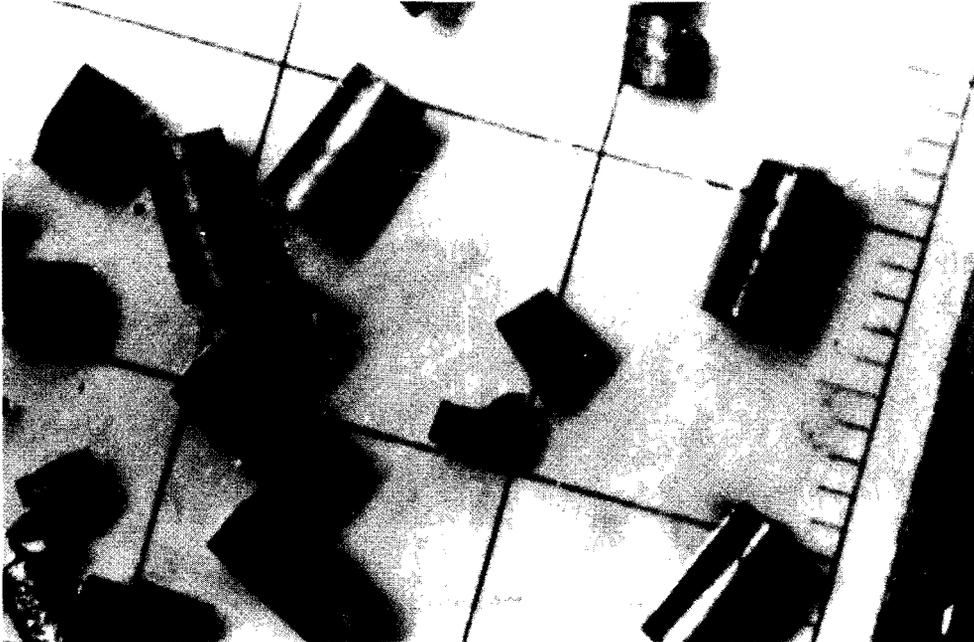


Fig. 8. UO₂ pellets from HZ-19 on 1" grid. Numec (NRX) pellets irradiated to 14,600 Mwd/T U.

chemically. A very small amount of insoluble residue from the analytical preparation appeared to be calcium and zirconium oxides or fluorides plus traces of corrosion products. The soluble material was primarily calcium and silica with smaller amounts of lead, uranium, plutonium, and fission products present. The original 0.63 g of decladding residue contained about 2 w/o uranium, 0.02 w/o plutonium (i.e. 0.2 mg Pu/g solids), and had a "specific" gamma activity of around 2.5×10^{12} d/m/gram, principally cerium, ruthenium, and zirconium-niobium. Figure 9 shows a typical decladding residue from a 10.26" WAPD-PWR rod from Run HZ-17, weighing about 0.2 grams; the UO_2 pellets from HZ-17 are shown in Fig. 6.

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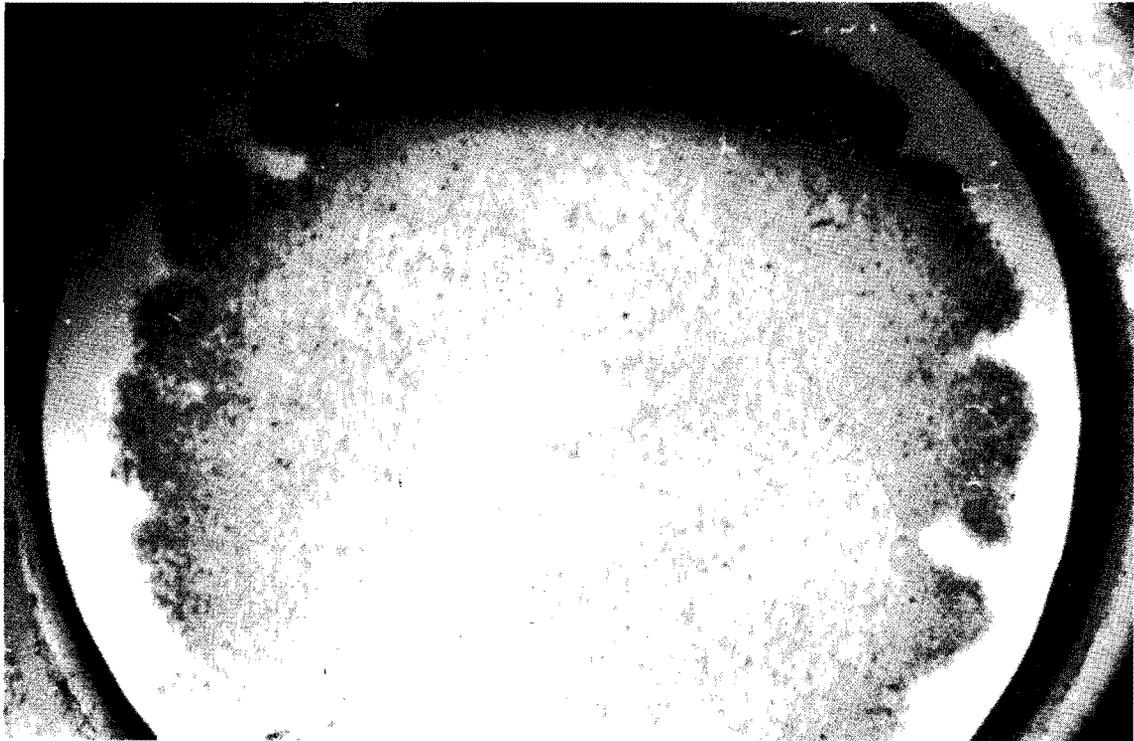


Fig. 9. Decladding residue from HZ-17 on 3" filter.

On the basis of the quantity of UO_2 fines from the low density (93-95%) PWR pellets, Figs. 3, 4, and 7, and the other solids in the decladding solution, the original SRP proposal for a centrifuge or other solids-separation system for treatment of the decladding and core solutions appears probably necessary.

2.3 Core Dissolution

2.3.1 Rates of Dissolution of UO_2 . Low Density (93-95%) WAPD-PWR Pellets. Fig. 10 shows the rates of dissolution of unirradiated and irradiated low density PWR UO_2 in boiling 4 M HNO_3 . It appears that lower levels of irradiation, i.e. about 6000 Mwd/T and lower, greatly increase the rate of dissolution of uranium (and fission products) over that of unirradiated pellets because of the increased surface due to fragmentation of the irradiated pellets. Dissolution is essentially complete in 1 hour. At higher irradiation levels, i.e. greater than 9000 Mwd/T, the rate of uranium dissolution is initially faster than that of unirradiated pellets due to a greater number of fragments, but decreases as if a refractory material had been encountered. Irradiation rate is probably the important factor, as the 9000 Mwd/T pellets were irradiated in a flux of 3×10^{14} n/cm²/sec at a rate of 40.1 Mw/T, while the 6150 Mwd/T pellets were irradiated in a flux of 1.5×10^{14} n/cm²/sec at a rate of 21.9 Mw/T. The higher center temperature of the pellets at the higher flux may have caused partial sintering. About 98-99% of the uranium is in solution at the end of 3 hours and 2-3 hours of additional reflux is necessary for complete dissolution. The fission products and plutonium, however, appeared to dissolve within 1-2 hours.

Unirradiated PWR pellets were completely dissolved in boiling 6 M HNO_3 in about 1.5 hours.

High Density (96%) Numec Pellets. Figure 11 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 requires about 5 hours versus 6-7 for unirradiated pellets. The fission products, as measured by the gamma activity of the solution,

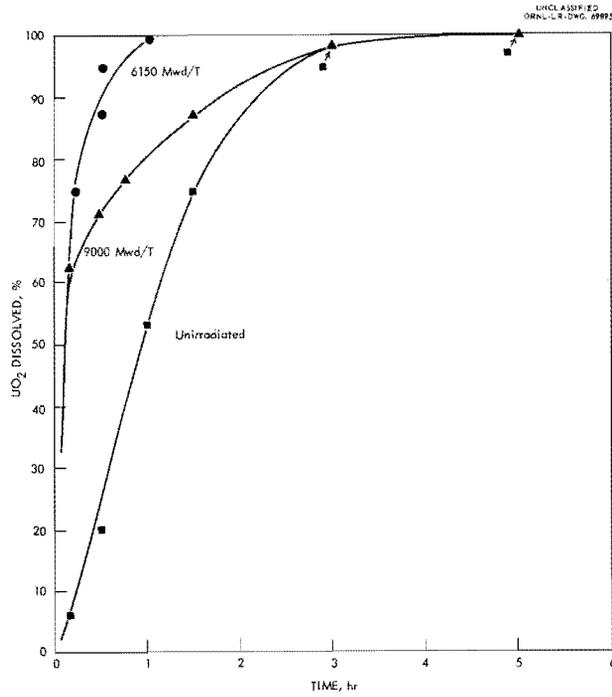


Fig. 10. Dissolution rates of unirradiated and irradiated WAPD-PWR UO_2 pellets in boiling 4 M HNO_3 .

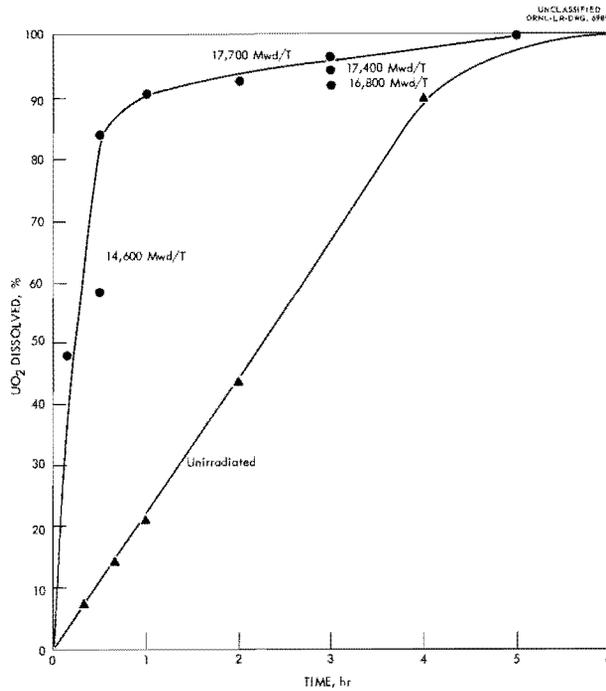


Fig. 11. Dissolution rates of unirradiated and irradiated Numec UO_2 pellets in boiling 4 M HNO_3 .

dissolve at a slower rate, but are essentially in solution after the 5 hour dissolution period.

2.3.2 Dissolution Residues. The undissolved residue from the cores of 4 NRX pins irradiated to greater than 15,000 Mwd/T after 5 hours of boiling in the core solvent-4 M HNO_3 , weighed approximately 0.5 g, or about 0.5% of the initial charge to the dissolver. Analysis indicated the material was 9% uranium by weight (x 0.03% of total uranium), and spectrographically the remainder was essentially all zirconium (oxide). Approximately 0.03% of the plutonium from the 4 pins was also in the residue, plus 2.6% of the total gross gamma core activity. These results indicate the presence of insoluble ZrO_2 which should probably be removed from the system prior to solvent extraction.

2.3.3 Irradiation Level Calculations. Previously reported values for the irradiation levels of the specimens dissolved during the Zirflex program appeared to be 10-20% low, particularly the NRX specimens whose peak and average burnup values had been calculated from an actual heat balance around the specimen holder in the NRX reactor. Mass spectrometer analysis of the uranium isotope composition of the NRX specimens after irradiation showed levels, due to U-235 burnup alone, about 10% greater than those calculated from the Cs^{137} content of the core solution. Plutonium burnout would also increase the irradiation level. The obvious sources of error in the burnup calculations appear to be loss of cesium during decladding through plating or exchange with the Pyrex glass equipment in the cell from the $\text{NH}_4\text{F-NH}_4\text{NO}_3$ solution, plating-out from the analytical dilutions prior to analysis, and thirdly, errors in the values of the Cs^{137} decay constant and yield.

It is possible that some of the cesium is lost by plating or exchange during decladding, since it is found in only small amounts (~3% of Gr γ activity) in the Zirflex reagent. Other investigators (7) have found considerable quantities of cesium present in Sulfex and Darex decladding solutions, and have suggested migration of the gaseous predecessors from the core to the cladding followed by decay to cesium. The Canadians have reported in TID-7610 on the problems of burnup analysis by the cesium method,

and have added "dead" cesium to their solutions to suppress the exchange reaction ⁽⁴⁾. Discussions with M. F. Osborn of the ORNL Solid State Division, J. W. Ullmann, Chemical Technology Division, and S. C. Furman, Manager of the Radioactive Materials Laboratory at GEVAL, led to revisions in the previous calculation method for burnup from Cs¹³⁷ analysis (see Appendix A). Using a yield of 6.15% and the unpublished GEVAL value of 29.2 years for the Cs¹³⁷ half-life, the burnups of the specimens in all of the Zirflex runs were recalculated and are shown in Table 3. The new values are in better agreement with the estimated burnup and mass spectrometer results.

Table 3. Variation in Irradiation Level of Zirflex Specimens According to Analytical Method.

Run No.	Estimated Peak Burnup, Mwd/T ^(a)	Earlier Reported Burnup, Mwd/T ^(b)	Recalculated Burnup, Mwd/T ^(c)	U ²³⁵ Burnup, Mwd/T ^(d)
HZ-1	400	356	412	--
HZ-2	400	191	216	--
HZ-3	400	217	262	--
HZ-4	400	159	182	--
HZ-5-8	20,000	15,100	16,800	16,500
HZ-9-12	20,000	15,750	17,700	16,750
HZ-13-15	20,000	--	17,400	16,600
HZ-16	11,000	--	8,950	--
HZ-17	10,000	--	13,100	--
HZ-18	10,000	--	13,700	--
HZ-19-20	20,000	--	14,600	--
HZ-21	5,000	--	7,100	--
HZ-22	5,000	--	6,150	--

(a) Estimated peak burnup calculated from reactor data.

(b) Earlier reported burnup calculated from Cs¹³⁷ analysis and on yield of 5.9%, half-life of 28.5 years, and 0.9116 Mwd/g U²³⁵ fissioned.

(c) Recalculated burnup based on Cs¹³⁷ analysis, yield of 6.15%, half-life of 29.2 years, and decay from date of mid-irradiation to date of analysis.

(d) U²³⁵ burnup based on consumption of U²³⁵ by mass analysis of uranium isotopes and 746 Mwd/kg U²³⁵ consumed. Plutonium burnup must be added to the uranium value.

2.4 Corrosion

The Ni-o-nel corrosion specimen has accumulated a total of 46.75 hours totally immersed in boiling Zirflex decladding solution, 6 M NH_4F -1 M NH_4NO_3 , during dissolution of the Zr-2 cladding, plus 14.5 hours in the boiling core dissolvent, 4 M HNO_3 , during dissolution of the UO_2 cores for a total of 61.25 hours. The total weight loss was 0.1916 grams, equivalent to 2.8 mils per month. Fig. 12 shows the inside of the V-shaped specimen which shows indications of localized attack at one end. This will be checked in subsequent experiments. Fig. 13 shows the outside of the specimen along the weld, where no localized corrosion is noted.

2.5 Solvent Extraction

Four additional first cycle Purex solvent extraction runs were made using core solutions from the highly-irradiated NRX specimens as feed. Fig. 14 shows the flowsheet conditions. In two of the runs additives were used in an attempt to retain more of the Zr-Nb activity in the aqueous waste stream. Uranium and plutonium decontamination factors and losses were determined for all runs, and the extent of uranium, plutonium, and fission products retention in the organic stream was measured. Stage efficiencies in the mini-mixer settlers were close to 50%. The compositions of the feed solution for the four runs are given in Table 4. Solvent was 30% TBP in Amsco 125-82.

2.5.1 Run HMS-2. Solvent Extraction Run Description. This run was continued for approximately 30 hours with flowing stream samples taken at 12, 24, and 30 hours after startup. The "A" bank had 5 mechanical extraction and 11 mechanical scrub stages, the "B" bank had 5 scrub and 11 partitioning stages, and the "C" bank 8 strip stages. Table 5 gives the decontamination factors at three sample times. It was noted that black solids accumulated at the interfaces of the extraction stages in the "A" bank after about 12 hours of operation, but this apparently did not affect the mixer-settler performance.

Run HMS-3. Run HMS-3 was continued for 14.5 hours with samples taken at 8.5 and 14.5 hours after startup. During this run, 7 extraction and 9 scrub stages were used in the "A" bank. The "B" bank operated as in run HMS-2 (Table 5).

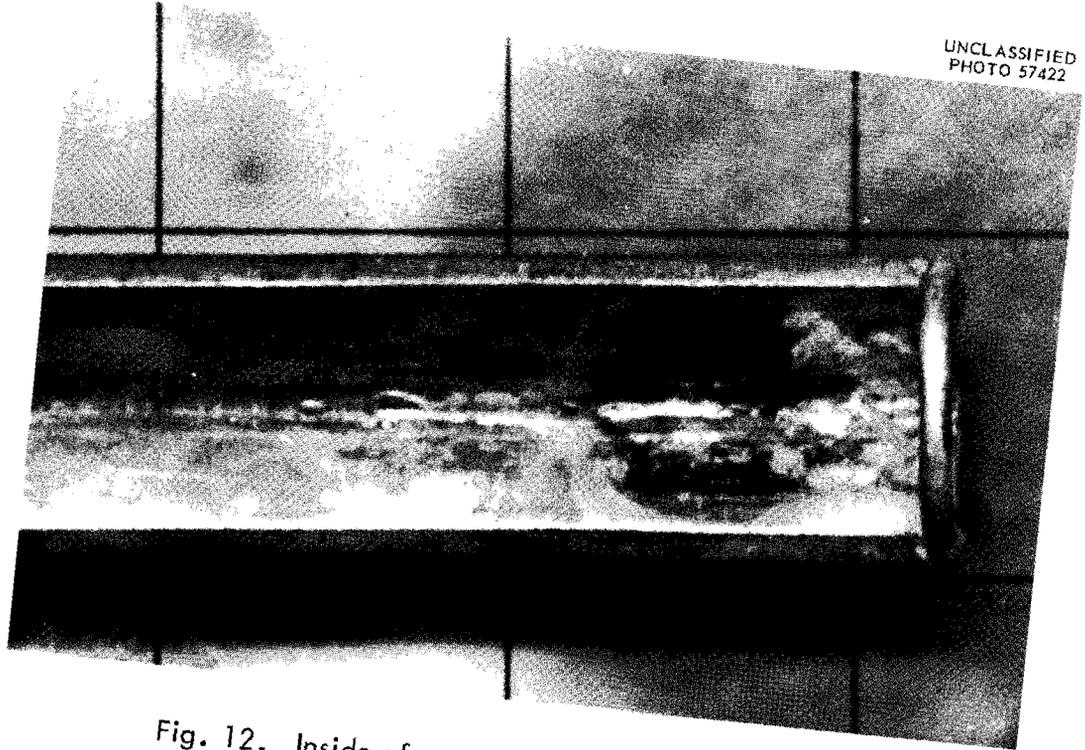


Fig. 12. Inside of corrosion specimen after HZ-22.

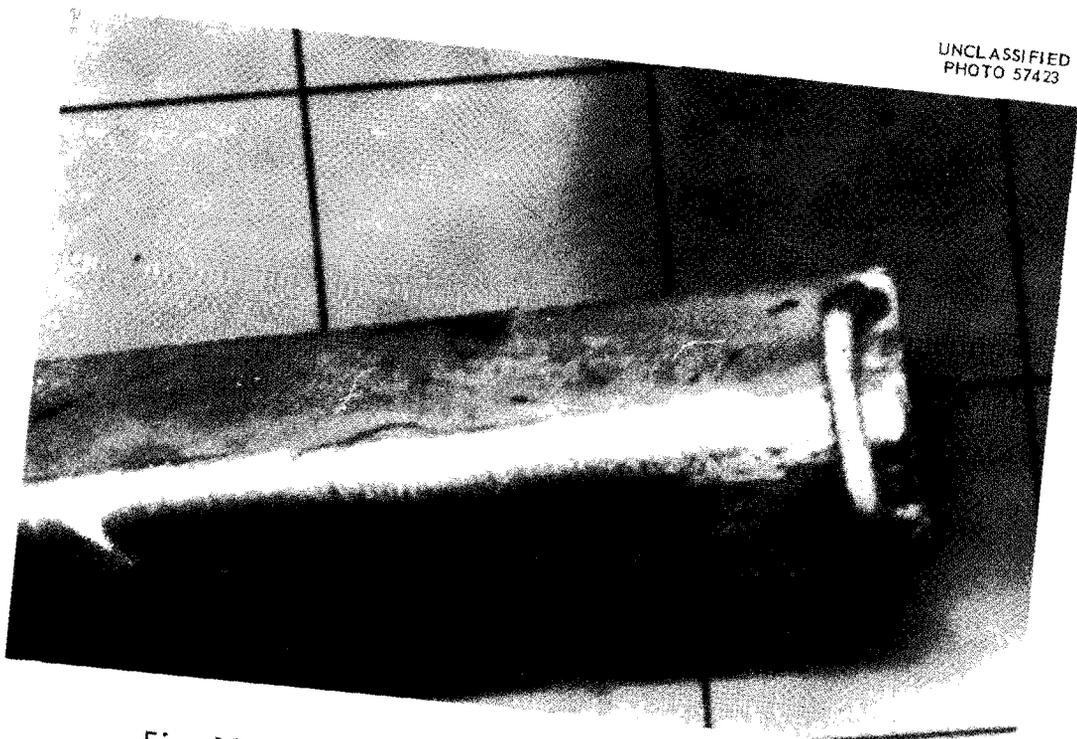


Fig. 13. Bottom of corrosion specimen after HZ-22.

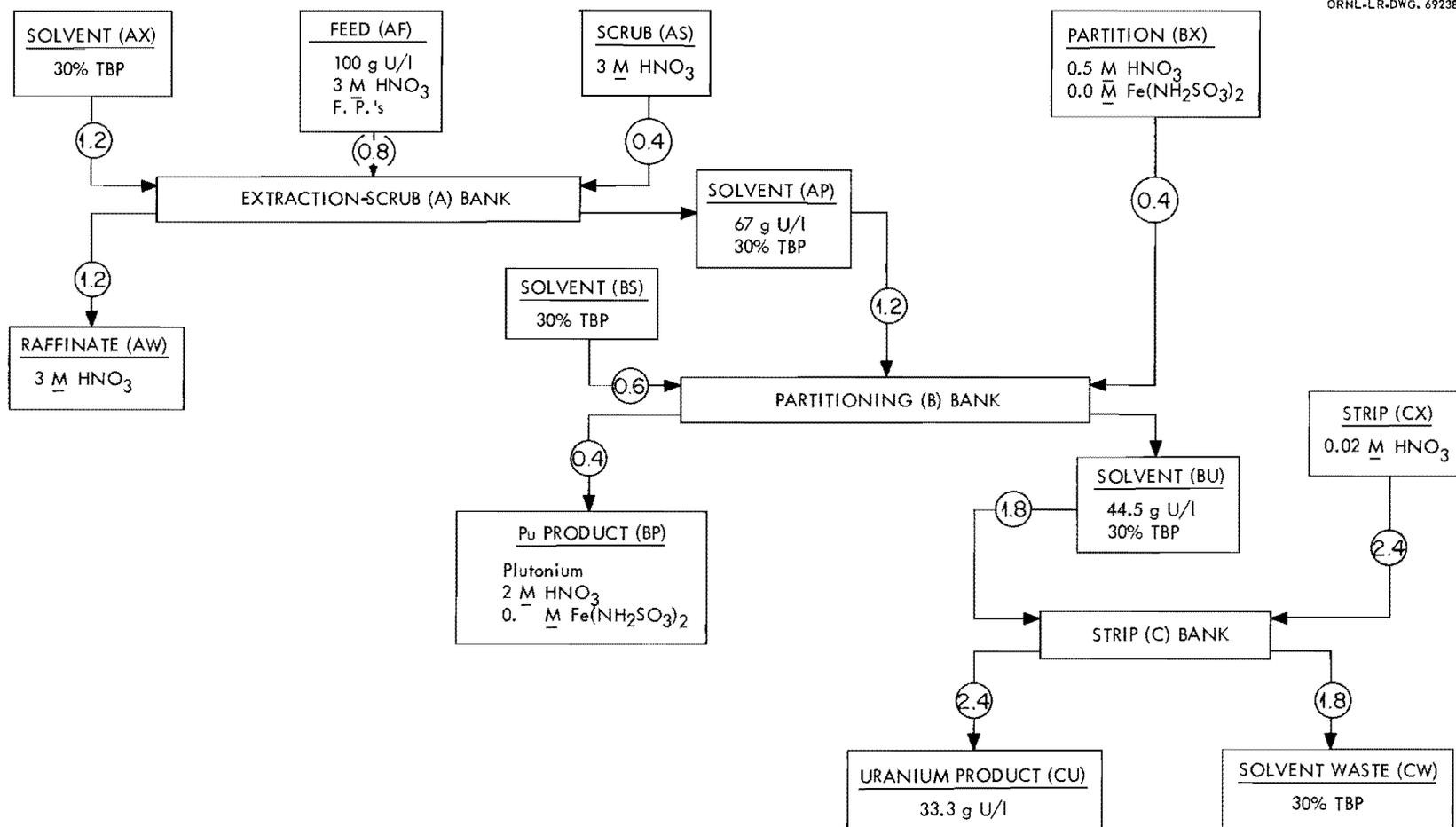


Fig. 14. Flowsheet for modified Purex solvent extraction (flows in ml/minute).

Table 4. Composition of Feed Solutions in Solvent Extraction Runs (a)

Run No.	U mg/ml	H ⁺ M	Gr α c/m/ml	Pu α c/m/ml	Gr β c/m/ml	TRE β c/m/ml	Gr γ c/m/ml	Zr γ c/m/ml	Nb γ c/m/ml	Ru γ c/m/ml	Cs γ c/m/ml
HMS-2 ^(b)	96.4	3.4	7.1 ⁷	4.2 ⁷	3.2 ¹⁰	2.0 ¹⁰	1.5 ¹⁰	5.1 ⁹	6.2 ⁹	1.5 ⁹	2.1 ⁹ (Cs ¹³⁷)
HMS-3 ^(c)	90.9	2.7	6.9 ⁷	3.9 ⁷	2.5 ¹⁰	1.7 ¹⁰	1.1 ¹⁰	1.3 ⁹	3.0 ⁹	1.3 ⁹	4.1 ⁹
HMS-4 ^(d)	95.8	3.0	4.8 ⁷	2.8 ⁷	1.7 ¹⁰	1.4 ¹⁰	1.1 ¹⁰	1.9 ⁹	3.9 ⁹	6.1 ⁸	3.0 ⁹
HMS-5 ^(e)	89.8	3.2	1.6 ⁸	2.8 ⁷	1.6 ¹⁰	1.2 ¹⁰	1.1 ¹⁰	6.2 ⁹	(Zr-Nb)	1.4 ⁹	2.5 ⁹

- (a) Colorimetric uranium analysis, Gr α and Pu α counted at 52% geometry, Gr β and TRE β at 10% geometry, and gamma at 18-21% geometry. (7.1⁷ c/m/ml in table = 7.1 x 10⁷ c/m/ml)
- (b) Feed for HMS-2 made up of core dissolutions from HZ-5-12. Gr α activity about 40% 5.15 Mev, 18% 5.50 Mev, and 40% 6.11 Mev.
- (c) Feed for HMS-3 made up of core dissolutions from HZ-13-15 plus 475 ml feed from HMS-2. Gr α activity 44% 5.15 Mev, 19% 5.50 Mev, and 35% 6.11 Mev; Pu α 75% 5.15 Mev, 25% 5.50 Mev.
- (d) Feed for HMS-4 made from 700 ml feed from HMS-3 and 300 ml from HZ-3 core dissolution plus 0.1 M diacetyl monoxime additive.
- (e) Feed for HMS-5 made from 600 ml of core dissolutions from HZ-19-20, 400 ml from HZ-17, and 0.05 M oxalic acid additive.

Table 5. Decontamination Factors of Modified Purex Solvent Extraction
Runs

Run	Sample	DF (β)	DF (γ)	Other D.F.
HMS-1 **	CU-1	7.2×10^4	7.6×10^3	
	CU-2	5.3×10^4	7.7×10^3	
	BP-1	2.0×10^4	1.2×10^3	
	BP-2	2.6×10^4	1.3×10^3	
	AP-1	5.5×10^3	1.8×10^3	
	AP-2	5.4×10^3	1.8×10^3	
HMS-2	CU-1	3.3×10^4	-	
	CU-2	2.7×10^4	1.4×10^4	
	CU-3	8.1×10^4	2.1×10^4	5.9×10^3 (Zr γ), 3.2×10^4 (Ru γ)
	BP-1	9.8×10^2	2.0×10^4	9.8×10^3 (Zr-Nb γ), 5.0×10^3 (Ru γ)
	BP-2	9.8×10^2	2.1×10^4	
	BP-3	-	-	
	AP-1	-	-	
	AP-2	-	-	
HMS-3	AP-3	4.4×10^4	5.9×10^3	1.2×10^4 (Zr-Nb γ), 1.7×10^3 (Ru)
	CU-1	7.7×10^3	1.7×10^3	1.3×10^3 (Zr-Nb γ), Ce ¹⁴⁴ present in quantity.
	CU-2	6.3×10^3	1.0×10^3	
	BP-1	1.3×10^4	2.0×10^3	2.6×10^3 (Zr γ)
	BP-2	1.3×10^4	2.3×10^3	
	AP-1	2.5×10^3	9.0×10^2	1.1×10^3 (Zr γ)
	AP-2	2.5×10^3	8.3×10^2	1.1×10^3 (Zr-Nb γ)
HMS-4	CU-1	1.6×10^4	2.7×10^3	3.7×10^2 (Zr γ)
	CU-2	1.7×10^4	3.9×10^3	5.3×10^2 (Zr γ)
	BP-1	-	4.2×10^3	8.6×10^2 (Zr γ) Ru not detected
	BP-2	-	6.1×10^3	1.3×10^3 (Zr γ)
	AP-1	2.9×10^3	1.9×10^3	4.5×10^2 (Zr γ)
	AP-2	3.0×10^3	1.6×10^3	3.2×10^2 (Zr γ)
HMS-5	CU-1	2.0×10^4	1.5×10^4	1.3×10^4 (Zr-Nb γ), 8.3×10^3 (Ru γ)
	CU-2	1.2×10^5	3.1×10^4	2.1×10^4 (Zr-Nb γ), 3.2×10^3 (Ru γ)
	BP-2	1.2×10^4	3.0×10^3	(Zr-Nb γ) Ru γ)
	AP-1	1.7×10^4	3.0×10^3	

** Run HMS-1 was made with a much lower activity feed than in the other four runs, and due to its long decay time of about 3 years did not contain the shorter-lived fission products, such as zirconium or niobium. Gross β and γ activities were 1.2×10^7 and 3.3×10^7 c/m/ml, respectively.

Run HMS-4. This run was made under identical conditions to those in run HMS-3. However, before the feed solution was pumped into the "A" bank, it was made 0.1 M in diacetyl monoxime, and digested at 80°C for two hours, as recommended by C. Blake⁽⁵⁾. This compound ($\text{c} - \overset{\text{O}}{\parallel} \text{c} - \overset{\text{NOH}}{\parallel} \text{c} - \text{c}$) is believed to complex some of the fission products in the aqueous phase, reducing their extractability, and thus improving decontamination factors. Run HMS-4 was started without emptying the mixer-settler units after run HMS-3, and it was observed that dark colored crud built up in the "A", "B", and "C" banks as the run progressed. Once again, this apparently did not affect the mixer-settler operation. The D.F.'s obtained in this run are given in Table 5.

Run HMS-5. The conditions in this run were again identical with those in Run HMS-3. A second additive, 0.05 M oxalic acid, a degradation product of the oxime, was tested using the same treatment as with the diacetyl monoxime in Run HMS-4 (Table 5).

2.5.2 Decontamination Factors. Decontamination factors for the AP, BP, and CU streams for β and γ activity, and in some cases for specific fission products are given in Table 5. Run HMS-3 is taken as a standard run, and the factors obtained in other runs have been compared with those from Run HMS-3 in Table 6.

It is evident from Tables 5 and 6 that the decontamination factors from gross activity are unchanged at the higher activity levels. Negligible Zr, Nb, Ru, Cs, and Ce were detected in both the plutonium and uranium products.

The treatment of the feed solution with diacetyl monoxime in Run HMS-4 gave improved decontamination from both gross β and γ by a factor of about 2, although decontamination from zirconium was reduced. The oxalic acid treatment used in Run HMS-5 gave vastly improved decontamination factors from both β and γ activity in the uranium product up to a factor of 19. Decontamination of the plutonium product was unaffected.

2.5.3 Uranium and Plutonium Losses. Table 7 gives the average uranium and plutonium losses for the five runs. Uranium losses to the waste stream

Table 6. Comparison of DF's with Standard Run

Run	Sample	$\frac{DF(\text{Run } x)}{DF(\text{Run } 3)}$ (β)	$\frac{DF(\text{Run } x)}{DF(\text{Run } 3)}$ (γ)	Other Comparison	Comment
HMS-2	Not compared due to different scrubbing conditions.				
HMS-3 *	Standard run.				
HMS-4 *	CU-1	2.1	1.6		Conditions identical with those in HMS-3.
	CU-2	2.7	3.9		
	BP-1	-	2.1	0.43 (Zr γ)	
	BP-2	-	2.7	0.13 (Zr γ)	
	AP-1	1.2	2.1	0.41 (Zr γ)	
	AP-2	1.2	1.9		
HMS-5 *	CU-1	2.6	8.8	10 (Zr-Nb γ)	Conditions identical with those in HMS-3.
	CU-2	19.1	3.4		
	BP-1	0.93	1.4		
	BP-2	0.93	1.4		
	AP-1	6.8	3.3		
	AP-2	-	-		

* Runs HMS-3, 4, and 5 were made with approximately 3.5 theoretical extraction stages and 4.5 theoretical scrub stages in the "A" bank, 2.5 theoretical scrub stages and 5.5 theoretical partitioning stages in the "B" bank, and 4 theoretical stripping stages in the "C" bank.

were less than 0.01% in all runs where 3.5 theoretical extraction stages were available in the "A" bank. Losses of uranium to the plutonium product were also about 0.01%. The high loss of uranium to the CW stream is largely due to lack of stages in the "C" bank. However, it is interesting to note that the oxime additive in Run HMS-4 appears to have resulted in better stripping of the uranium in the "C" bank. Apart from this, the additives did not affect uranium extraction. Plutonium losses to the AW were considerably higher than the uranium losses due to lack of stage, but again it is interesting to observe that the plutonium losses in Run HMS-4 were much lower than for either of the other two comparable runs, in both the AW and CW streams. Lower losses of plutonium to the CU stream were ob-

Table 7. Average Uranium and Plutonium Losses in Mini Mixer-Settler Modified Purex Runs

Stream	Percent Loss of Uranium			Percent Loss of Plutonium		
	AW	BP	CW	AW	CU	CW*
HMS-1	0.004	0.0001	2.2	0.53	0.77	0.01
HMS-2	0.07	0.0003	7.0	4.0	0.07	0.01
HMS-3	0.004	0.009	-	0.32	2.3	0.02
HMS-4	0.006	0.015	0.42	0.06	0.25	0.01
HMS-5	0.001	0.014	2.2	0.20	0.43	0.03

* Calculated from Gross α count of organic sample.

served with both of the additives. No positive explanation for the reduced plutonium losses to the AW is apparent. However, one possible explanation is that the pretreatment, particularly in Run HMS-4, resulted in more of the plutonium being present in the desirable Pu(IV) state. Additional work in this area is planned.

Alpha pulse analysis of the AW stream indicated about 2% of the gross α activity was due to Pu²³⁹ (5.15 Mev), about 10% had a 5.5 Mev energy, and about 85% had a 6.11 Mev energy. Pulse analysis of the plutonium α activity in the AP, BP, and CU, as well as the AF, showed about 75% 5.15 Mev and 25% 5.50 Mev energies. Pulse analysis of the gross α activity in the CW stream showed that 84% had an energy of 6.11 Mev, 6.7% had an energy of 5.50 Mev and 9.2% had an energy of 5.15 Mev. This indicates that about 90% of the gross α activity in the CW streams is due to americium and curium, thus the loss figures quoted in Table 7 for plutonium to the CW stream are high by about a factor of 10.

2.5.4 Radiation Effects on Solvent. To determine whether there were any radiation effects to the solvent, 250 ml of stripped solvent (CW) from Run HMS-3 was scrubbed with three successive equal volumes of 5% Na₂CO₃ and then with one equal volume of 0.1 N HNO₃. This cleaned organic was then subjected to a "Z" test, along with a fresh sample as a control. Table 8 shows the extent of activity retained in both samples after contacting them with zirconium tracer, and again after scrubbing to remove all possible activity.

Table 8. Activity Retention in Process Solvent (Z-Test)

	Decontamination		
	Before Scrub	After Scrub	Factor
Control sample	7.29×10^4 c/min/ml	3.39×10^3 c/min/ml	21.5
CW from HMS-3	1.13×10^5 c/min/ml	8.16×10^4 c/min/ml	1.4

Table 8 shows that the scrub reduced the activity level in the control sample by a factor of 15 g; 4 more than that in the used solvent. This indicates that some degradation has occurred in the single pass of solvent. The total dose to the solvent in one pass was estimated as about 0.6 watts/liter. Further work on radiation degradation of TBP-Amsco solvent and TBP-dodecane solvent is planned.

3.0 DISCUSSION AND CONCLUSIONS

A total of 22 Zirflex decladding experiments were made using specimens of UO_2 clad in Zircaloy-2, which had been irradiated from 182 to 17,700 Mwd/t. Losses of uranium and plutonium to the decladding solutions were on the order of 0.05%, apparently due to solubility of U(IV) and Pu(IV). The decladding solution contained solids (mainly ZrO_2 , CaF_2 , and up to 2 w/o uranium) that required separation to produce a clear, diluted decladding waste; these solids amounted to about 0.3 w/o of the original specimen. The presence of UO_2 fines in the decladding solution indicates that some means of solution clarification and recycle of the solids to the dissolver is probably necessary in a plant. The decladding reaction is smooth, requiring about 2 1/2 hours. About 10% of the original Zircaloy in these specimens remains as a heel as undissolved end caps. Under flow-sheet conditions of continuous removal of the steam and ammonia vapors from the dissolver with water makeup, no precipitation was noted in the hot concentrated decladding solution nor in the diluted, cold decladding waste solution.

Dissolution of the irradiated UO_2 core pellets in 4 M HNO_3 required about 5 hours for completion at the higher irradiation levels investigated. Irradiation increased the rate of dissolution over that of unirradiated UO_2 ,

with greater than 90% in solution within 2 hours versus 43% in the un-irradiated pellets. Three to four additional hours were required to completely dissolve the remaining 10%, which probably had been sintered by the high temperature in the center of the pellets during irradiation.

The effect of organic additives for feed pretreatment prior to solvent extraction showed factors of 2-10 in better decontamination from fission products in the CU and BP streams without disturbing uranium and plutonium equilibria. Additional runs will be made to confirm these effects. Preliminary data indicate that degradation of the Amsco-TBP solvent occurred in one cycle through the mixer-settlers, which exposed the solvent to about 0.6 watt-hours per liter.

4.0 CURRENT AND FUTURE WORK

Sulfex Process. Start-up runs were made using 2 intact WCAP specimens from Westinghouse irradiations 1-3 and 2-1. The capsules were discharged from the MTR late in 1957 and 1 or 2 of the 3 pins per capsule examined at KAPL. KAPL reported burnups of 550-1900 Mwd/TU. The identification of the specimens will be made from ORNL burnup analyses and data reported in YAEC-158⁽⁶⁾. The loss of uranium from the low density UO_2 to 4 to 6 M H_2SO_4 decladding solutions was about 2.5%. Decladding required 2-3 hours, leaving an end cap heel.

ORNL irradiation specimens with burnups between 8500 and 25,000 Mwd/T have been charged into the hot cell, and the Sulfex program was started during the week of 3/19/62 using NRX specimens irradiated to a nominal 25,000 Mwd/T and decayed 120 days.

Purex Process. Experiments are planned to determine the effects of radiation damage to the TBP-Amsco solvent upon repeated recycle through the modified Purex process using feed solutions made from the most highly irradiated UO_2 specimens. The use of a dodecane "Adakane", will also be evaluated.

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APPENDIX A.

Revised Method for Burnup Calculations from Cs¹³⁷ Analysis

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

$$Y = 6.15\%$$

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

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

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

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

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

$$(5) \frac{\text{Cs}^{137} \text{ d/m}}{\text{mg U}} \times \frac{1}{4.51 \times 10^{-8} \times 6.15 \times 10^{-2}} \times \frac{238}{6.02 \times 10^{20}} \times \frac{100}{1 - \lambda t} \times \frac{9.65 \times 10^5}{1 - \frac{\%}{100}}$$

$$= \frac{1.38 \times 10^{-4}}{(1 - \lambda t)(1 - \frac{\%}{100})} \times \frac{\text{Cs}^{137} \text{ d/m}}{\text{mg U}}$$

$$(6) \text{Mwd/TU charged} = \frac{1.38 \times 10^{-4}}{(1 - \lambda t)(1 - \frac{\%}{100})} \times \frac{\text{Cs}^{137} \text{ d/m}}{\text{mg U}}$$

For example, in Run HZ-22, WAPD-PWR pin #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 or 1.02×10^6 minutes from the date of mid-irradiation. The uranium analysis of the sample was 109 mg U/ml and the Cs¹³⁷ analysis was 4.62×10^9 d/m/ml.

On the basis of these results:

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

$$1 - \lambda t = 0.954$$

$$1 - \frac{\%}{100} = 0.99$$

$$(1-\lambda t)\left(1-\frac{\%}{100}\right) = 0.953$$

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

Substituting in equation (6):

$$\frac{1.38 \times 10^{-4}}{0.953} \times 4.24 \times 10^7 = \underline{6.15 \times 10^3 \text{ Mwd/TU charged}}$$

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