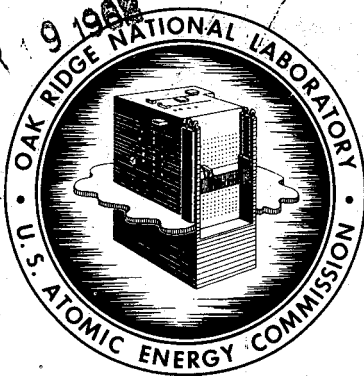


MAR 9 1962



MASTER

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

UNION
CARBIDE

ORNL - TM - 130

COPY NO. - 39

DATE - January 26, 1962

Hot Cell Demonstration of Zirflex and Sulfex Processes:

Report Number 2.

J. H. Goode and M. G. Baillie

ABSTRACT

Twelve Zircaloy-2 clad UO_2 specimens, irradiated in the NRX to about 15,500 Mwd/T and decayed about 9 months, have been declad and core dissolutions completed. The pellets were fractured but were essentially intact (i.e. had not fallen apart) when declad. The uranium losses ranged from 0.03 to 0.09%, due to solubility of U(IV) in the Zirflex reagent, and the plutonium losses from 0.01 to 0.04%. The core pellets were 99.5% dissolved in 4 M HNO_3 -0.1 M $\text{Al}(\text{NO}_3)_3$ in 5 hr, which was slightly faster than the rate of unirradiated pellets.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

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.

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 M NH_4F -1 M NH_4NO_3 was chosen to give a F/Zr mol ratio of 7 in the final decladding solution if 100% of the Zircaloy was dissolved. Makeup water was continuously added to the boiling solution during the decladding 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 before discharge to the plant vessel off-gas system.

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 4 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.

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 de-clad, the cores dissolved, and a solvent extraction run made in "Mini" mixer-settlers⁽¹⁾. These runs served mainly to test the equipment and operations in the hot cell prior to tests with highly-irradiated NRX specimens. 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. Late in December, 12 of the nominal 20,000 Mwd/T NRX specimens were de-clad and the cores dissolved.

2.0 FUEL SPECIMEN HISTORY

The irradiation specimens used in these experiments were fabricated at ORNL, according to ORNL-LR-Dwg C-21345, from Zircaloy-2 tubing and bar stock and UO₂ pellets under specifications outlined in the proposal for PRFR irradiations in the Chalk River NRX reactor⁽²⁾. The Mark I irradiation specimens were 4.5" long x 0.3125" OD and were filled with 7 uranium dioxide pellets manufactured by the Nuclear Material and Controls Corp. A "Numec" quality control report listed the following impurities in the 3.91% enriched uranium dioxide⁽³⁾:

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

The report also stated the density of the lot of pellets to be 95.9% of theoretical, exceeding the specifications of $94 \pm 1\%$. The ORNL Inspection Engineering Department, reporting on a 10% (306 pellets) sampling of the entire lot, determined that 278 exceeded specifications, 27 met, and only 1 pellet was below specification density. Of the 278 pellets exceeding specification, 184 were greater than 95.7% of theoretical⁽⁴⁾. The ORNL

Analytical Chemistry Division reported the O:U ratio of two random pellets to be 2.025 and 2.017. Each pellet was inspected as to diameter (0.2600 ± 0.0005 inch), length (0.500 ± 0.005 inch), and other dimensions before insertion into the Zircaloy-2 shell assembly in a helium atmosphere. The final end cap was welded into place without removal of the specimen from the helium atmosphere. Each assembly was then tested with dye penetrant, X-ray radiography, helium leak tested, vacuum tested, and finally pickled, weighed, autoclaved in water for 24 hours at 300°C and 1250 psi pressure, and reweighed. Any rod that gained more than 0.004 grams was rejected. Clearance between the UO_2 pellets and the 0.025" Zr-2 wall of the tubing was 0.00125".

Holder No. 2, containing 20 ThO_2 and 100 UO_2 fuel specimens, each clad in Zr-2, was inserted in the NRX reactor on 2/25/60, was irradiated for 327 days at peak fluxes varying between 3.9×10^{13} n/cm²/sec to 5.6×10^{13} n/cm²/sec, and was discharged on 4/3/61. The average irradiation was calculated to be 17,610 Mwd/T and the peak irradiation was calculated to be 20,600 Mwd/T⁽⁵⁾. Table 1 summarizes the irradiation history of Holder No. 2.

The surface temperature of the specimens was calculated to be between 207 and 214°F ⁽²⁾. Twelve specimens from the region of the highest flux were chosen for this series of experiments.

3.0 EXPERIMENTAL RESULTS

3.1 Decladding. The 12 specimens were declad in 11 experiments using as variables length of boiling, purge gas, and number of pins. The irradiated pins, each containing a nominal 31.25 grams UO_2 (27.51 g U after burnup) and 16.4 grams of Zircaloy-2, were declad in 6 M NH_4F -1 M NH_4NO_3 reagent, using 213 ml of solution per pin. Table 2 summarizes the conditions and results of each of the experiments and Table 3 presents average values for the series of experiments. It appears that the air purge gas in the dissolver increased the soluble uranium losses over those obtained with a nitrogen purge, however, the increase was of little significance. Length of contact of the exposed pellets to the boiling decladding reagent apparently had no effect on uranium or plutonium losses,

Table 1. Irradiation Data on NRX Holder No. 2--3264 g U + Th

Date	Days	Peak Flux	Kw*	Kwd
2/25-3/1/60	4.49	5.0×10^{13}	172	772
3/1-3/13	12.45	5.5	184	2290
3/14-3/20	5.86	5.5	180	1055
3/25-4/9	15.08	5.5	180	2710
4/10-5/1	21.14	5.5	180	3810
5/6-5/29	23.42	5.6	192	4500
6/2-7/3	29.15	5.0	172	5020
7/6-7/24	16.66	5.5	188	3130
7/29-8/21	23.25	5.5	188	4370
8/27-9/18	20.25	5.4	192	3890
9/23-10/16	21.3	5.6	200	4260
10/20-11/20	30.9	5.0	180	5560
11/25-11/30	2.65	4.8	172	455
11/30-12/14	13.4	4.4	160	2140
12/15-12/18	3.0	4.3	156	465
12/22-1/3/61	7.2	4.3	156	1133
1/4-1/23	17.1	4.5	164	2804
1/26-1/31	4.9	4.1	148	725
2/1-1/18	17.9	4.5	164	2935
2/19-2/26	6.9	4.1	141	973
3/2-3/26	24.0	4.1	151	3624
3/27-4/3	6.0	3.9	143	858
		(327 days)		57482
		Avg.	17610 Mwd/T	
		Peak	20600 Mwd/T	

* Measured value from water temperature at exit of holder.

nor did the number of pins exposed to the reagent.

Fig. 1 shows pin No. X-33, used in run 5 and 5B; note the striped effect believed due to expansion of the hot pellets against the Zircaloy jackets during irradiation. Unirradiated specimens were not striped, but were a continuous irridescent gold to violet color. Fig. 2 shows the same specimen (X-33) after 2 hr in boiling 6 M NH_4F -1 M NH_4NO_3 . The dissolution of one-half (8 grams) of the Zircaloy jacket, progressing from one end of the specimen, was peculiar to this single specimen out of the 16 in the Zirflex series. The remaining specimens dissolved by a general surface attack mechanism.

Note the great number of cracked, but still intact, pellets in the

Table 2. Summary of Zirflex Decladding of NRX-Irradiated Fuel Specimens

Run No.	5	5B*	6	7	8	9	10	11	12	13	14	15
Pin No.	X-33	X-33	X-13	X-12	X-9	X-116	X-60	X-90	X-36	X-11	X-115	X-57, X-86
Irrad: Mwd/T	15,150	15,150	15,150	15,150	15,150	15,750	15,750	15,750	15,750	---	---	---
Rate: Mw/T	46.3	46.3	46.3	46.3	46.3	48.2	48.2	48.2	48.2	---	---	---
Total Time: hr	2.0	3.0	10.0	8.0	6.0	4.0	3.0	3.0	3.0	3.5	4.1	3.0
Purge Gas**	none	none	none	none	none	none	none	nitrogen	nitrogen	air	air	air
Declad Vol: ml	213	213	213	213	213	213	213	213	213	213	213	426
Diluted Vol: ml	575	250	430	460	425	426	426	426	426	426	400	850
Sol. U-mg/ml	0.04	0.02	0.02	0.04	0.03	0.03	0.04	0.03	0.03	0.04	0.06	0.05
U Loss-%	0.08	---	0.03	0.07	0.04	0.05	0.06	0.04	0.04	0.07	0.09	0.08
Pu-c/m/ml	1.79×10^3	4.16×10^3	6.38×10^3	4.06×10^3	---	6.76×10^3	3.92×10^3	1.16×10^3	5.04×10^3	1.18×10^3	3.80×10^3	4.50×10^3
Pu Loss-%	0.01	---	0.02	0.02	---	0.04	0.02	0.01	0.03	0.05	0.01	0.01
Gr β -c/m/ml	1.99×10^7	3.96×10^7	4.15×10^7	3.99×10^7	3.61×10^7	4.27×10^7	4.10×10^7	4.18×10^7	---	2.94×10^7	4.88×10^7	3.33×10^7
Gr γ -c/m/ml	1.45×10^8	2.41×10^8	2.30×10^8	3.02×10^8	2.66×10^8	3.41×10^8	3.10×10^8	2.86×10^8	3.18×10^8	2.93×10^8	3.72×10^8	3.45×10^8
Condens. Vol.	405	---	1650	1250	1350	1300	660	1100	1000	1250	1450	1450
Cond. Rate: ml/hr	200	167	165	156	225	325	220	367	333	357	375	483
Cond. Gr γ c/m/ml	2.74×10^4	6.80×10^4	1.29×10^5	3.48×10^4	2.86×10^4	2.19×10^6	1.79×10^5	9.47×10^4	1.08×10^5	7.34×10^6	3.56×10^5	1.11×10^5

* Continuation of Run 5 after 10 day delay w/pellets exposed to air, water, etc.

** None means H_2O - NH_3 vapor.

Table 3. Average Values for Decladding Experiments

Zirflex Process, Zr-2-clad UO_2 specimens
15,150 to 15,750 Mwd/T Irrad.

	No Purge	N_2 Purge	Air Purge
No. Expts.	6	2	3
U Conc.*-mg/ml	0.03	0.03	0.05
U Loss-%	0.05	0.04	0.08
Pu α -c*/m/ml	4.51×10^3	3.11×10^3	3.16×10^3
Pu Loss-%	0.02	0.02	0.02
Gr β *-c/m/ml	3.72×10^7	4.18×10^7	4.05×10^7
Gr γ *-c/m/ml	2.62×10^8	2.97×10^8	3.37×10^8

*In diluted (1:1) decladding solution.

photographs (Fig. 2-5). The pellets appear to be whole when declad, but bumping during boiling and handling break them into smaller pieces. The greater number of intact pellets over those in the Westinghouse PWR specimens reported last month⁽⁷⁾ may be due to the slightly higher density of the NRX UO_2 , the smaller diameter of the pellets and/or the better heat transfer because of the expansion of the pellets against the jacket in the NRX specimens due to the original 0.001" clearance, versus up to 0.004" in the PWR pins. There does not appear to be any correlation of irradiation rate or length (total burnup) with degree of fracture since the PWR pins had both a lower irradiation rate, ~ 5 Mw/ton U and lower burnup, ~ 400 Mwd/Ton U.

Gross gamma activity in the decladding solution of the high burnup specimens ($2-3 \times 10^8$ Gr γ c/m/ml) was several orders of magnitude greater than that in the low burnup pins, making it a high level waste stream. Gamma scan indicated 1-2% of the activity was contributed by ruthenium and cesium, while the remainder was due to Zr-Nb activities. The bulk of this Zr-Nb activity was apparently due to activation of the Zircaloy cladding. This was verified by the fact that the ratio of Zr-Nb gamma activity to TRE β was 0.37 in the core solution, but was 280 in the decladding solution. The gamma activity (3×10^8 c/m/ml) was equivalent to 0.73% of the gamma activity in the core solution.

The soluble uranium losses (Table 2) ranged from 0.03 to 0.09% and

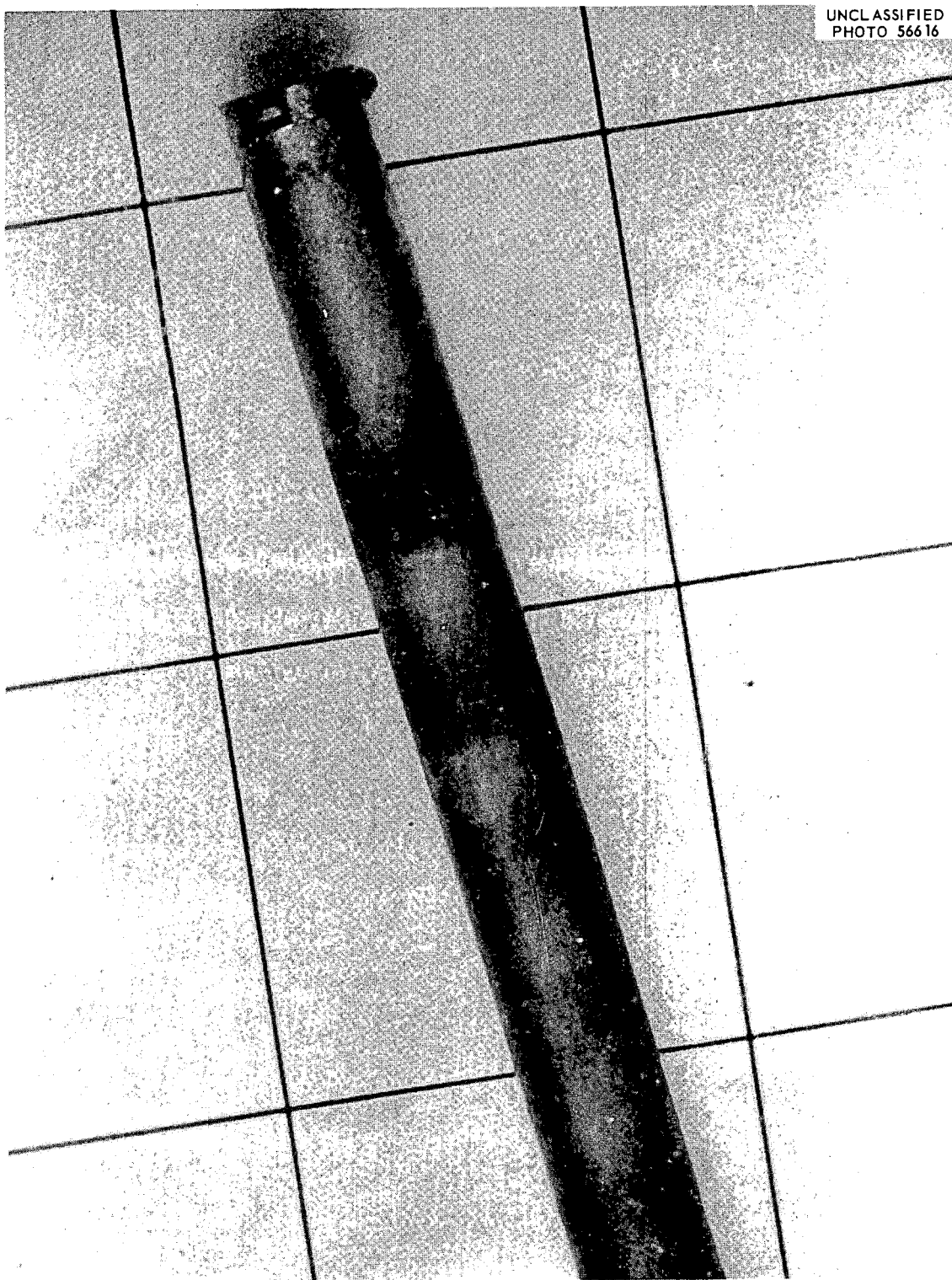


Fig. 1. Zircaloy-2 clad UO_2 fuel specimen X-33 after irradiation in NRX reactor to 15,150 Mwd/T. (Background is 1" grid.)



Fig. 2. Zircaloy-2 clad UO_2 fuel specimen X-33 after 2 hours in boiling 6 M NH_4F - NH_4NO_3 . Note the intact UO_2 pellet. (Background 1" grid.)



Fig. 3. UO₂ pellets from specimen X-9. Irradiated to 15,150 Mwd/T in NRX Reactor. (Background 1" grid.)



Fig. 4. UO₂ pellets from specimen X-13. Irradiated to 15,150 Mwd/T in NRX reactor. (Background 1" grid.)



Fig. 5. UO₂ pellets from specimen X-33. Irradiated to 15,150 Mwd/T in NRX reactor. (Background 1" grid.)

the plutonium losses from 0.01 to 0.04%. Length of exposure of the pellets to the decladding solution had little or no effect on losses of uranium and plutonium, nor did the use of a nitrogen purge gas in the decladding vessel over the normal steam-ammonia atmosphere. The use of an air purge, in Runs HZ 13-15, however, apparently increased the soluble uranium losses by a factor of about 1.5-2, although it is possible that this small change is the result of statistical variations. It can be seen from the solubility curves for U(IV) and U(VI) in Zirflex solutions (Fig. 6 and 7) 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/l, if conditions are controlled such that the U(IV) valence state is wholly maintained⁽⁶⁾. The fact that the losses did fall in this range for every experiment is strong evidence of the fact that the uranium was present in the quadra-valent 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, resulting in the presence of 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.

3.2 Corrosion of Ni-o-nel. A corrosion specimen of Ni-o-nel was placed in contact with the pins in a number of the cladding dissolutions. Its weight was periodically recorded to obtain an indication of the severity of corrosion of this material under Zirflex conditions.

The surface area of the specimen was about 6 in², its initial weight 84.1421 g, and the density of Ni-o-nel is 8.2 g/cm³. This means that a weight loss of 0.82, represents a corrosion to the depth of one mil. Table 4 gives the corrosion history of the specimen.

3.3 Core Dissolutions. The UO₂ pellets from the first 4 decladding experiments were combined for the first core dissolution experiment. Since the 5 M HNO₃ core dissolvent, used for the low burnup specimens, produced a 4 M HNO₃ feed, boiling 4 M HNO₃-0.1 M Al(NO₃)₃ was used as the dissolvent in these experiments. In contrast with the dissolution

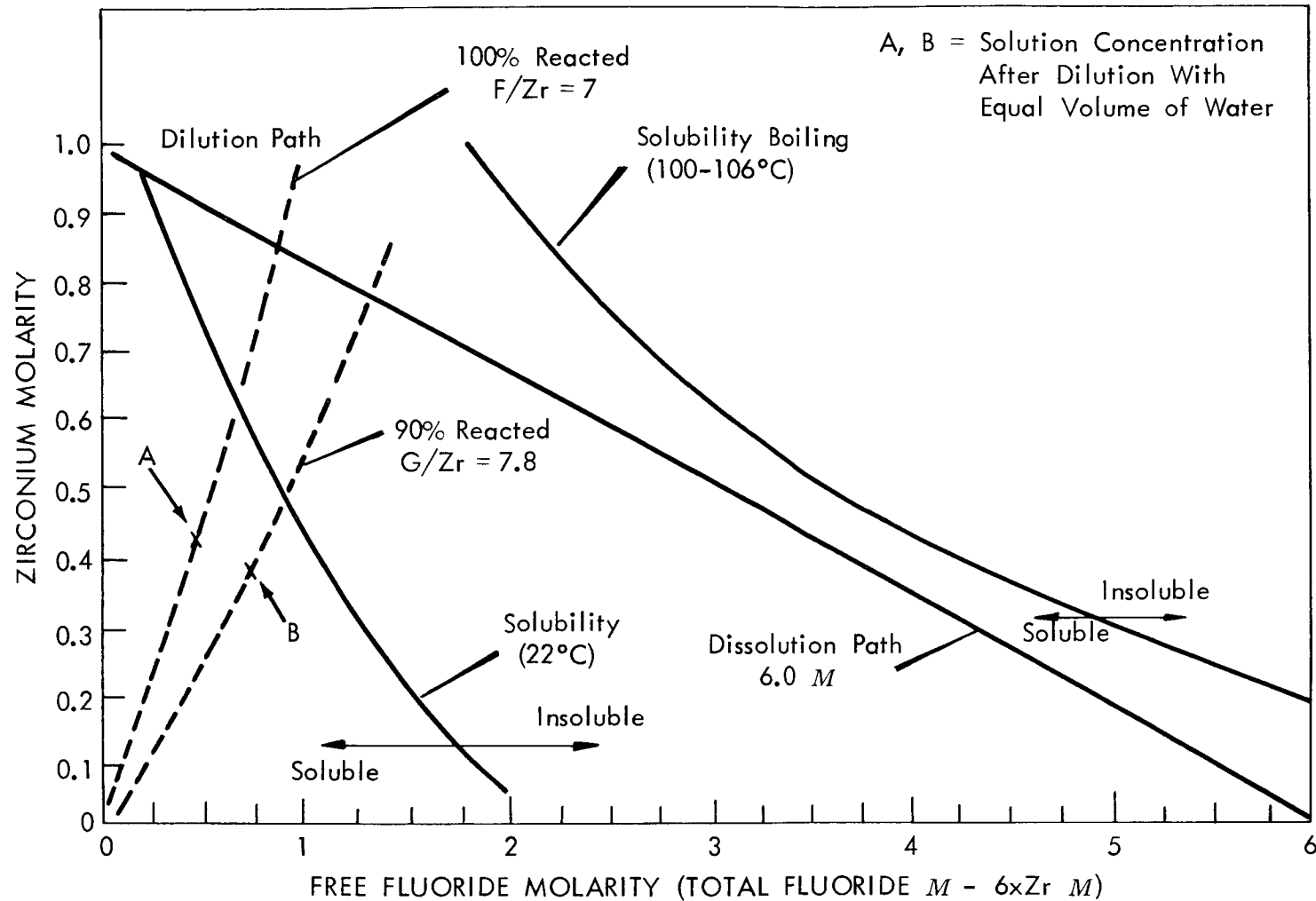


Fig. 6. Solubility of zirconium in ammonium fluoride solutions (adapted from Fig. 1, HW-65979).

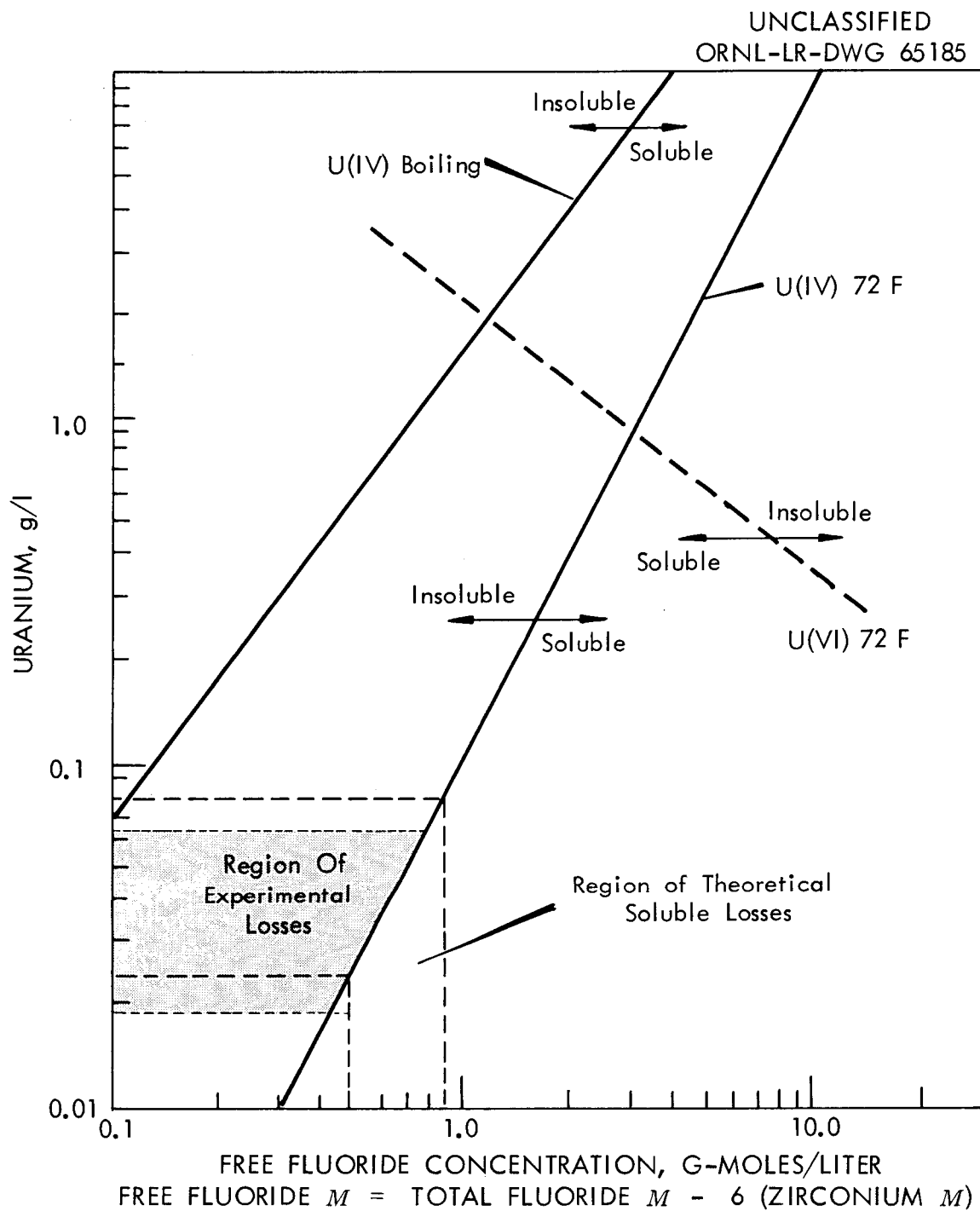


Fig. 7. Solubility of uranium in zirflex solutions (adapted from Fig. 9, HW-65979).

Table 4. Corrosion of Ni-o-nel in Zirflex Decladding

Specimen Weight	Weight Loss Since last weighing.	Treatment Since last weighing	Corrosion Rate-last weighing.	Overall Cor. Rate
Grams	Grams		mils/mo	mils/mo
84.1421	---	---	---	---
84.1276	0.0145 g	9.9 hr in Zirflex solution, 8.8 hr at B.P.	1.3	1.3
84.0605	0.0816 g	9.0 hr in Zirflex solution, 7.3 hr at B.P.	8.0	4.5

of the low burnup pellets, the reaction was not complete at the end of 45 minutes but continued for 3 hr, at which time the reaction appeared to stop. Filtration of the feed solution, which analyzed 106 g U/l, gave a thin layer of black solids on the filter paper which probably contained up to 4-5% of the uranium in the pellets. Complete dissolution of unirradiated pellets from the same batch of UO_2 required 6-7 hr.

Spectrographic analysis of the undissolved black residue is shown in Table 5. It is evident from this analysis that the major portion of the residue was undissolved UO_2 .

The core solution had a muddy green color, which appeared black through the lead glass windows of the cell. A very small amount of solid material was centrifuged from the core solution; spectrographic analyses of the solids and supernate appear in Table 5, and indicate the solids were very small particles of UO_2 that passed through the No. 2 filter paper. Table 6 presents a detailed analysis of the core solution.

Using Cs^{137} as a standard, the average burnup of the first 4 specimens was calculated to be 15,150 Mwd/T, and the second 4 was 15,750 Mwd/T. Ullmann further calculated (5) from the Cs^{137} analysis of 1.22×10^{10} d/m/ml on 12/28/61, the 106 mg U/ml, 3.62×10^7 second irradiation time, and 2.14×10^7 seconds decay time that the specimens had been irradiated in a pseudo flux of 1.75×10^{13} n/cm²/sec. With these assumptions he then calculated the concentration of the total Sr and Mo produced. His values of 5.1 µg/ml for Sr and 16.5 µg/ml for Mo compared very well with the spectroscopic analysis in Table 5 of 2-10 µg/ml for

Table 5. Spectrographic Analysis of High Burnup UO₂ Dissolutions
(VS = Very Strong, S = Strong, M = Moderate, W = Weak, VW = Very Weak,
T = Trace, FT = Faint Trace, -- = sought not Found, Numerals = µg/ml)

Element	Undissolved Black Residue	1 st Core Sol'n Solids	1 st Core Sol'n Supernate	2 nd Core Sol'n	Final Undissolved Residue
Ag	FT	FT	--	--	T
Al	S	T	VS	100-500	VW
B				--	--
Ba				25	--
Be		--	T	--	T
Ca	W	T	W	25-100	W
Cd	W			--	--
Ce		?	VW	100-250	--
Co				--	--
Cr	T			2	W
Cu				2	FT
Dy				--	
Eu				--	
Fe	W	VW	M	10	M
Gd				--	
Ho				--	
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			--	--
Sm				--	
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

Sr and about 25 µg/ml for Mo, indicating that all of the fission products were in solution.

A breakdown of the alpha activity of the core solution, based on pulse analysis of the gross alpha counting plate, the plutonium (TTA)

Table 6. Analysis of High Burnup UO₂ Core Solution
(α counted at 52% geom., β - γ at 18%)

U - 106 mg/ml
H ⁺ 3.74 M (?)
Gr α - 7.49×10^7 c/m/ml (39.6% 5.15 Mev α , 17.6% 5.50 Mev α , 39.9% 6.11 Mev α).
Pu α - 4.74×10^7 c/m/ml (77.0% 5.15 Mev α , 22.1% 5.50 Mev α , 0% 6.11 Mev α).
Gr β - 3.57×10^{10} c/m/ml
TRE β - 2.37×10^{10} c/m/ml
Gr γ - 1.92×10^{10} c/m/ml
Zr-Nb γ - 2.05×10^{11} d/m/ml
Ru γ - 2.08×10^9 c/m/ml
Cs ¹³⁷ γ - 1.22×10^{10} d/m/ml

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

Pu ²³⁹ + Pu ²⁴⁰ α :	2.96×10^7 c/m/ml
Am ²⁴¹ α :	0.27×10^7 c/m/ml
Cm ²⁴² α :	2.98×10^7 c/m/ml
Total α :	7.26×10^7 c/m/ml vs 7.49×10^7 Gr α c/m/ml.

The core pellets of the second 4 pins were refluxed for 3 hours in 1100 ml 4 M HNO₃-0.1 M Al(NO₃)₃, and the solution filtered through No. 2 filter paper. The spectrographic analysis of the second core solution is shown in Table 5; other analyses of the core solution showed 95.3 mg U/ml, 3.37 M HNO₃, 1.39×10^{10} Gr β c/m/ml, 1.36×10^{10} Gr γ c/m/ml, 6.69×10^7 Gr α c/m/ml, and 2.85×10^7 Pu α c/m/ml. The filter paper, containing the undissolved residue from the dissolution, was returned to the dissolver with 500 ml 4 M HNO₃-0.1 M Al(NO₃)₃, refluxed for another 3 hours, and filtered. This solution analyzed 0.51 mg U/ml, 2.55×10^6 Pu α c/m/ml, 3.68×10^9 Gr β c/m/ml, 2.48×10^9 Gr γ c/m/ml, and 7.12×10^6 Gr α c/m/ml after filtration. A few tenths of a gram of black solids, removed from the solution by the second filtration, were boiled for 3 hours in 475 ml 4 M HNO₃-0.05 M KF solution, cooled, and refiltered. The final light gray undissolved residue was analyzed spectrographically (Table 5), and appeared to be mainly ZrO₂ and corrosion products along with a trace of uranium. The filtrate analyzed

0.23 mg U/ml, 7.34×10^8 Gr β c/m/ml, 5.21×10^9 Gr γ c/m/ml, 1.48×10^5 Gr α c/m/ml, and 5.60×10^4 Pu α c/m/ml. Radiochemical analyses showed >99% of the gamma activity in the final filtrate was due to Zr-Nb, confirming the spectrographic analysis above. Table 7 presents a summary of the second core dissolution and cleanout, which indicates that the undissolved residue from core dissolution, which contained about 4% of the total uranium, also contained a higher ratio of β and γ activity to uranium than did the 95.3 mg U/ml core solution.

Dissolution of the UO_2 pellets from the third set of 4 fuel specimens was accomplished in 1100 ml 4 M HNO_3 -0.1 M $\text{Al}(\text{NO}_3)_3$ in 5 hours of re-fluxing. A total of 0.7 grams of undissolved solids remained. Assuming the solids to be all UO_2 , this amounts to about 0.5% of the total uranium in the pellets, giving 99.5% dissolution in 5 hours vs 96-97% dissolution for unirradiated pellets in the same length of time. These results confirm earlier work indicating that irradiated UO_2 dissolved more rapidly than unirradiated pellets.

3.4 Solvent Extraction. Two solvent extraction runs using the modified Purex flowsheet ⁽¹⁾ were completed, but detailed analyses are not available at this time. Preliminary results from the first of the runs show decontamination factor of 8×10^4 and 2×10^4 for β and γ , respectively on the uranium stream, between the AF and CU, and DF's of 4×10^4 and 7×10^3 for β and γ , respectively for plutonium, between the AF and BP. Uranium and plutonium losses were normal, and no operational difficulties were noted. Some of the black solids from the core solution collected at the interfaces in the extraction section of the "A" Bank, but caused no trouble.

4.0 FUTURE WORK

A third solvent extraction run is to be made about the middle of January to give additional data on mixer-settler stage requirements for uranium and plutonium extraction and stripping and decontamination from fission products. Zirflex decladding experiments are continuing on 10,000-11,000 Mwd/T and 5000 Mwd/T specimens while awaiting the arrival of the Sulfex specimens from Chalk River in February.

Table 7. Summary of Second High Burnup UO_2 Core Dissolutions

Solution	Vol, ml	Uranium		Plutonium		Activity Ratios, c/m/mg U		
		mg/ml	% of Total	c/m/ml	% of Total	Gr α	Gr β	Gr γ
Core	1100	95.3	96.0	2.85×10^7	95.6	7.02×10^5	1.46×10^8	1.43×10^8
1 st Cleanout	500	8.51	99.9	2.55×10^6	99.9	8.37×10^5	4.42×10^8	2.91×10^8
2 nd Cleanout	475	0.23	~100	5.60×10^4	~100	6.54×10^5	3.21×10^8	2.29×10^{10}

5.0 REFERENCES

1. R. E. Blanco and J. R. Flanary, "Hot Cell Demonstration of Zirflex and Sulfex Processes," ORNL-CF 61-5-37 (May 10, 1961).
2. Letter, J. A. Swartout to H. M. Roth, "PRFR Irradiations in the Chalk River NRX Reactor," (September 11, 1959).
3. Letter, F. Forscher, Nuclear Material and Controls Corp., to UCNC Purchasing Dept., (June 2, 1959).
4. Letter, ORNL Inspection Engineering Dept. to A. E. Goldman, ORNL Metallurgy Division.
5. J. W. Ullmann, unpublished data.
6. P. W. Smith, "The Zirflex Process, Terminal Development Report," HAPO, HW-65979 (August 20, 1960).
7. J. H. Goode and M. G. Baillie, "Hot Cell Demonstration of the Zirflex and Sulfex Processes. Report No. 1," ORNL-TM-111 (in press).

DISTRIBUTION

Internal

1. F. L. Culler
- 2-3. R. E. Blanco
4. K. B. Brown
5. J. C. Bresee
6. D. E. Ferguson
7. T. A. Gens
8. H. E. Goeller
9. M. E. Whatley
10. M. G. Baillie
11. J. R. Flanary
12. L. M. Ferris
- 13-17. J. H. Goode
18. E. L. Nicholson
19. R. H. Rainey
20. J. W. Ullmann
- 21-23. Laboratory Records
- 24-25. Central Research Library
26. Laboratory Records-RC
27. Document Reference Section

External

28. E. L. Anderson, AEC
29. F. R. Dowling, AEC
- 30-31. D. G. Karraker, SRL
32. J. J. McBride, ICCP
33. J. W. Morris, SRL
34. W. H. Reas, HAPO
35. V. R. Thayer, Wilmington
36. J. Vanderryn, ORO
37. W. E. Winsche, SRL
38. Research and Development, ORO
- 39-53. DTIE