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ZIRFLEX PROCESS FOR PWR BLANKET FUEL. II. REVISED FLOWSHEET

L. M. Ferris

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ORNL-2940

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

ZIRFLEX PROCESS FOR PWR BLANKET FUEL. II. REVISED FLOWSHEET

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OCT 26 1960

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ABSTRACT

A revised Zirflex process is presented for dissolution of PWR blanket fuel (UO_2 pellets clad in Zircaloy-2). The Zircaloy-2 is dissolved in 6 M NH_4F—1.0 M NH_4NO_3 and the core in 10 M HNO_3—0.1 M $Al(NO_3)_3$. It differs from the original in dilution of the decladding solution to about 0.1 instead of 0.5 M zirconium and addition of 0.1 M $Al(NO_3)_3$ to the core dissolvent to inhibit corrosion by fluoride sorbed on the pellets. Use of a downdraft condenser during the decladding is suggested to prevent return of ammonium hydroxide to the dissolver, thereby avoiding formation of insoluble $ZrO_2 \cdot 2H_2O$.

Two types of flowsheet demonstration experiments were performed: batch dissolutions of single unirradiated PWR blanket rods, and a series of successive dissolutions in which half a fuel rod was added at the start of each cycle and undissolved zirconium was allowed to accumulate. In 3 hr about 80% of the zirconium in a nonoxidized PWR rod dissolved in boiling 6 M NH_4F—1 M NH_4NO_3 (F to total Zr mole ratio of 6), leaving only the solid end caps. The soluble uranium loss was less than 0.07%. No precipitation occurred when the decladding solution was diluted to 0.1 M zirconium. When the surface of the zirconium had been oxidized, decladding required as long as 17 hr. In the series of successive dissolutions, the amount of undissolved zirconium increased with increasing number of cycles until it reached what appeared to be a steady-state amount after about 15 cycles. The steady-state amount of zirconium residue was roughly equal to the amount charged to the dissolver at the beginning of each cycle.

The solubilities of ZrF_4 in NH_4F-HNO_3 solutions and of UO_2F_2 in NH_4F solutions were determined.

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1.0 INTRODUCTION

This report summarizes the results of laboratory-scale experiments obtained since June 30, 1958 in the development of the Zirflex process for PWR blanket fuel. This fuel element is a 27-mil thick Zircaloy-2 tube (0.4 in. dia, 10.25 in. long) filled with UO_2 pellets.[1] A solid Zircaloy-2 end cap, containing about 10% of the zirconium, is located at each end of the fuel element. The Zirflex process is based on the dissolution of zirconium in boiling ammonium fluoride solutions,[2-5] with work on the process for zirconium-clad oxide fuels proceeding both at ORNL and HAPO. Modified Zirflex processes for dissolution of zirconium-uranium alloy fuels have recently been developed at ORNL.[6,7] Ni-o-nel, Hastelloy F, and several stainless steels are resistant enough to corrosion to allow both decladding and core dissolution in the same vessel.[8,9]

A tentative flowsheet for PWR blanket fuel was given in a previous report.[2] Questions unanswered in the earlier work were the effect of oxide coatings on the time required for dissolution of the cladding and the best method of handling the problem of carryover of fluoride to the core dissolvent. These, and other, questions have now been at least partially answered, the result being the revised flowsheet given here. This flowsheet has been tested batchwise and in a series of cyclic dissolution experiments. Several new problems arising mainly from the buildup of zirconium and solids, the ammonia off-gas, and precipitation of $ZrO_2 \cdot 2H_2O$ if ammonia is returned to the dissolver can best be solved by further study on a unit operations scale.

The author is indebted to K. S. Warren of the ORNL Chemical Technology Division for his study of the solubility of ZrF_4 in HNO_3-NH_4F solutions, and to E. S. Snavely and co-workers of the ORNL Reactor Experimental Engineering Division who conducted the cyclic dissolution experiments. Chemical and x-ray analyses were made by the groups of G. R. Wilson, W R. Laing, and R. L. Sherman of the ORNL Analytical Chemistry Division.

2.0 FLOWSHEET

The revised flowsheet (Fig. 1) differs from the one given in ORNL-2558[2] in the provision for incomplete dissolution of the zirconium by a high dilution of the decladding waste solution and in the addition of aluminum nitrate to the core dissolvent. Because of the solid end caps in the PWR fuel, it is doubtful that the zirconium can be completely dissolved in a reasonable time. The amount of zirconium per PWR subassembly was altered in compliance with Ullmann's recent tabulation.[1]

Based on laboratory experiments, the Zircaloy-2 tubing, which constitutes about 80% of the zirconium, is dissolved in about 3 hr with boiling 6 $\underline{M}$ NH_4F—1 $\underline{M}$ NH_4NO_3. The mole ratio of fluoride to total zirconium is 6 and the undissolved zirconium is present mainly as end caps. After the decladding, the solution is diluted to about 0.2 $\underline{M}$ zirconium and then filtered or centrifuged. The UO_2 core pellets are washed with about 1

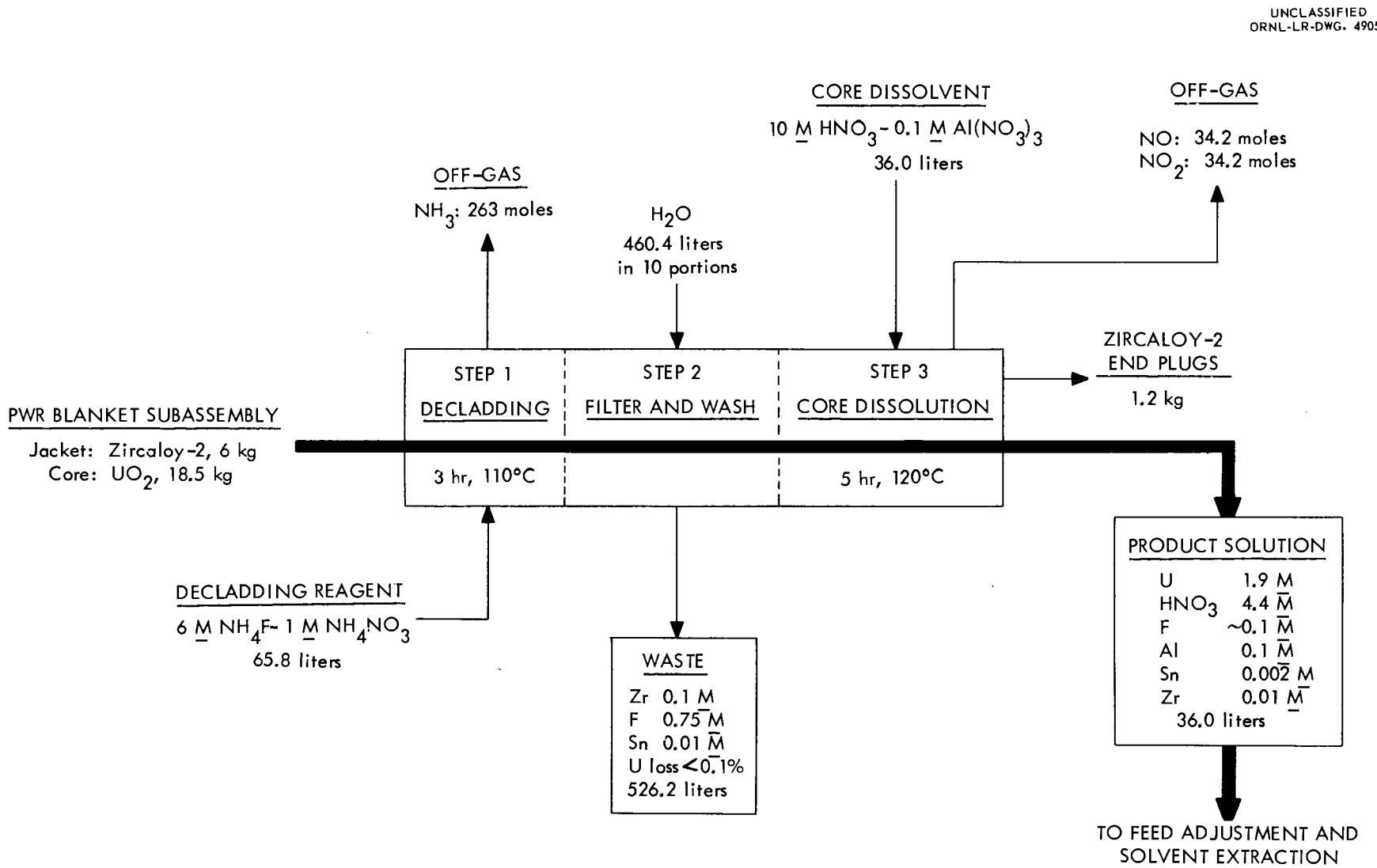

Fig. 1. Zirflex process for decladding and dissolution of PWR blanket fuel.

volume of cold water [or 0.05 M $Al(NO_3)_3$] in several portions to remove sorbed fluoride. The wash solution is added to the decladding solution, producing a final waste solution containing 0.1 M zirconium. This condition ensures that no $(NH_4)_3ZrF_7$ will precipitate even if the F/Zr ratio in solution is 20. Soluble uranium losses are expected to be less than 0.1%. The core pellets are dissolved in 5 hr in a volume of boiling 10 M HNO_3—0.1 M $Al(NO_3)_3$ sufficient to produce a solution containing 1.9 M uranium. The aluminum nitrate is required to inhibit corrosion by fluoride, which is carried over from the decladding operation. This product solution requires further adjustment before the uranium is recovered by solvent extraction.

When 0.75 to 1.0 M NH_4NO_3 is present in the decladding solution, the off-gas is essentially pure ammonia. According to Swanson,[4] only about 0.05 mole of hydrogen is evolved per mole of zirconium dissolved. The off-gas from the core dissolution is mainly NO and NO_2.

Since the Zircaloy-2 end caps accumulate with the dissolution of successive batches of fuel, a longer decladding time and/or a separate end cap dissolution step every three or four cycles will be required.

3.0 EXPERIMENTAL WORK

3.1 Dissolution Reactions

Dissolution of zirconium in ammonium fluoride solutions proceeds according to the reaction[3]

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

In the presence of ammonium nitrate the hydrogen is converted to ammonia:

$$2H_2 + 1/2\ NH_4NO_3 \longrightarrow NH_3 + 3/2\ H_2O$$

The latter point was substantiated by comparing the amount of nitrate remaining after a dissolution in 6 M NH_4F—1 M NH_4NO_3 with that computed from the stoichiometry in two runs,

Unreacted Nitrate, moles	
Calculated	Found
0.29	0.28
0.28	0.33

and by direct analysis of the gases evolved.[4] In the calculations the amount of nitrate consumed by reaction with tin in the Zircaloy-2 was considered negligible since only about 0.02 mole of tin was available for reaction for every 2 moles of hydrogen evolved.

The effect of ammonium nitrate concentration on the dissolution of tin in Zircaloy-2 was estimated as follows: Ten-gram specimens of Zircaloy-2 were completely dissolved in 6 M NH_4F solutions containing various amounts of ammonium nitrate. The weight of the insoluble residue, comprised mainly of tin, was determined in each case. The amount of residue decreased from about 0.34 g in 6 M NH_4F to about 0.01 g in 6 M NH_4F—1 M NH_4NO_3 (Fig. 2). Perhaps the optimum choice of ammonium nitrate concentration, if corrosion is to be minimized, is 0.75 M since the tin is almost completely dissolved, and, as determined by Swanson,[4] the amount of hydrogen evolved is only about 0.06 mole per mole of zirconium dissolved.

During each dissolution experiment a white solid accumulated in the condenser. Initially this was thought to be silica from the glass equipment, but more careful study showed it to be $ZrO_2 \cdot 2H_2O$ [or $Zr(OH)_4$]. Spectrographic analyses showed less than 10% of other metals present. Thermogravimetric analyses showed a weight loss on heating to 600°C in dry helium of 20% compared to 22.5% expected for the reaction $ZrO_2 \cdot 2H_2O \longrightarrow ZrO_2 + 2H_2O$. As expected, x-ray analysis of the residue after heating confirmed the presence of ZrO_2. Presumably, the hydrous oxide is formed when entrained solution comes in contact with ammonium hydroxide solution formed in the condenser. In fact, unless the ammonia is removed rapidly, the hydrous oxide accumulates in the dissolver and can lead to a much lower rate of dissolution than is usually experienced.[10] While actual dissolution conditions must be worked out in large-scale equipment, it appears that use of a downdraft condenser would aid measurably in decreasing the amount of solids formed.

3.2 Solubility Data

The solubilities of zirconium in ammonium fluoride and ammonium fluoride—nitric acid solutions and of uranyl fluoride in ammonium fluoride solutions were determined to aid in the selection of optimum process conditions.

Solubility of Zirconium in NH_4F Solutions. At 26°C, the solubility of zirconium in ammonium fluoride solutions decreased from 1 to about 0.03 M as the F/Zr mole ratio in solution increased from 6 [which corresponds to a saturated solution[11] of $(NH_4)_2ZrF_6$] to 200 (Fig. 3). The experiments were made by dissolving pure zirconium metal in boiling 6 M NH_4F to produce a series of solutions of widely varying F/Zr ratio. In each case a precipitate formed when the solutions were cooled to 26°C. The samples were then shaken periodically over a period of 3 weeks to ensure equilibrium before a sample of the supernatant solution was withdrawn for analysis.

These results are in excellent agreement with those of von Hevesy[11] and of Swanson[4] whose values are plotted for reference in Fig. 3. The equilibrium solid phase was $(NH_4)_3ZrF_7$ when the F/Zr mole ratio was greater than 7.[11] Since the solubility decreases rapidly with increasing F/Zr

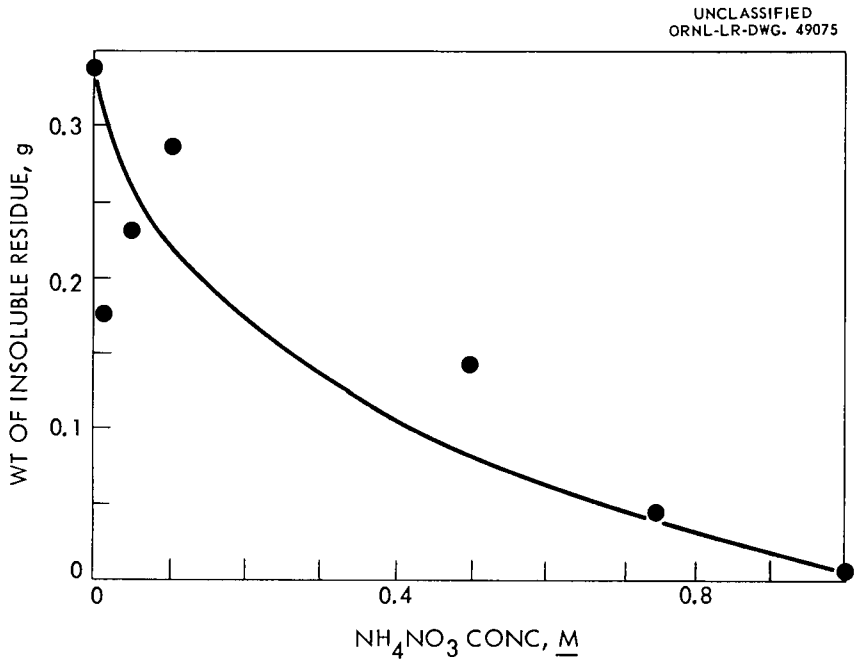

Fig. 2. Weight of tin residue after complete dissolution of 10-g samples of Zircaloy-2 in boiling 6 M NH_4F containing ammonium nitrate.

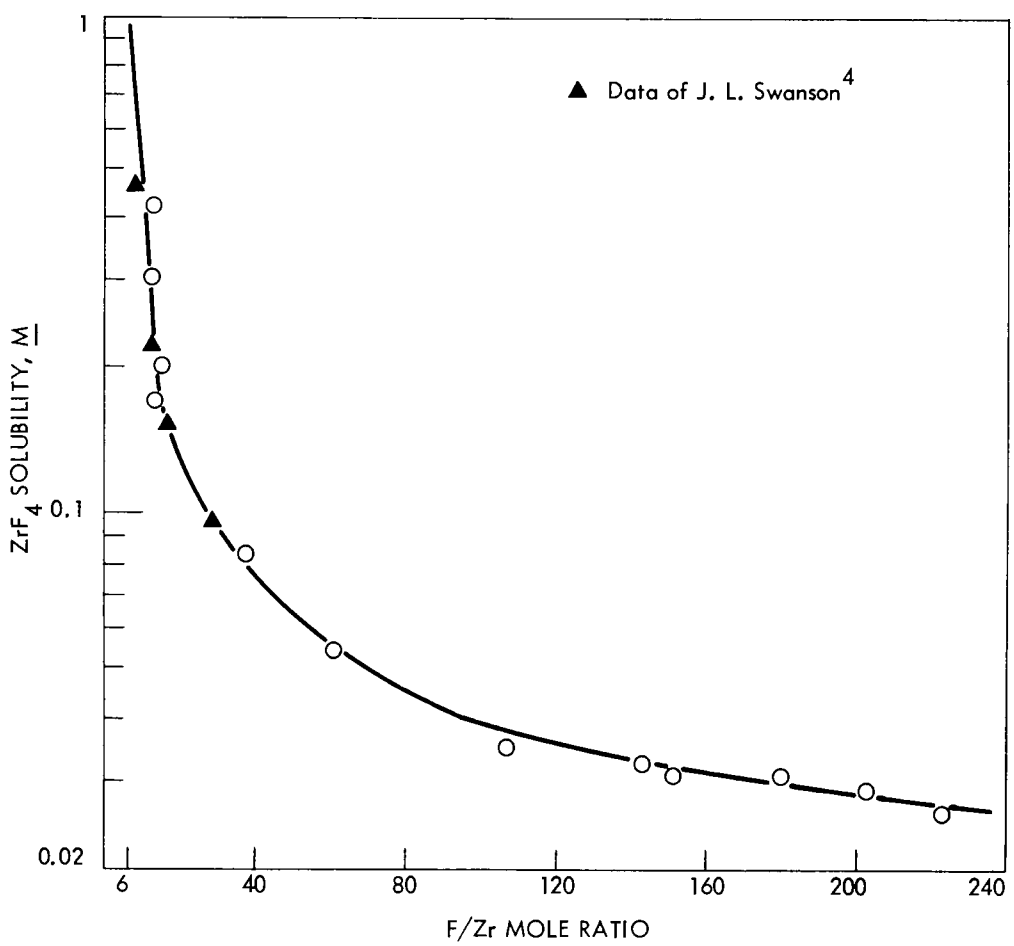

Fig. 3. Solubility of zirconium in ammonium fluoride solutions at 25°C.

ratio (or, in other words, with increasing amount of uncomplexed ammonium fluoride), the necessity for greatly diluting a Zirflex decladding solution is obvious. Under flowsheet conditions the mole ratio of fluoride to total zirconium is about 6; however, since dissolution of the zirconium is seldom complete, excess ammonium fluoride (a high F/Zr ratio) always remains in the solution. In most experiments, including the cyclic experiments (see below), the F/Zr ratio in the decladding solution was less than 20. Under these conditions the solubility is at least 0.1 M. To be certain that no precipitation occurs, the hot decladding solution probably should be diluted 8- to 10-fold.

Solubility of Zirconium in NH_4F—HNO_3 Solutions. The solubility of zirconium in ammonium fluoride—nitric acid solutions is of interest because of the possible cross-contamination of the process solutions. The presence of nitric acid in solution resulted in a higher zirconium solubility when the F/Zr ratio was less than about 8, but caused a lowering of the solubility at higher ratios. Data were obtained from solutions prepared by adding sufficient nitric acid to a series of NH_4F-$(NH_4)_2ZrF_6$ stock solutions to produce a precipitate and a variation in pH. After precipitation occurred, the samples were shaken periodically for about 3 weeks to ensure equilibrium. Data were interpreted in terms of the components NH_4F, ZrF_4, HNO_3, and H_2O.

In solutions where the F/Zr mole ratio was between 6 and 8, the solubility of ZrF_4 was increased by the addition of nitric acid (Fig. 4); when the F/Zr mole ratio was greater than 8, the solubility of ZrF_4 decreased with increasing nitric acid concentration. For example, at a F/Zr ratio of 10 the solubility of ZrF_4 decreased from 0.3 to 0.16 M as the nitric acid concentration increased from 0 to 6 M. The x-ray pattern of the equilibrium solid phase corresponded to that of $ZrF_4 \cdot H_2O$ reported by D'Eye.[12] These results show that traces of nitric acid from the core dissolvent would not cause precipitation in the decladding solution, but sufficient carryover of decladding solution into the 10 M HNO_3 core dissolvent could result in the precipitation of $ZrF_4 \cdot H_2O$.

Solubility of Uranyl Fluoride in Ammonium Fluoride Solutions. At 26°C the solubility of uranyl fluoride in ammonium fluoride solutions decreased from about 5 to 0.0025 M as the ammonium fluoride concentration increased from 0 to 5 M.[13] This study was undertaken to supplement data on the solubility of uranium fluorides in ammonium fluoride solutions. With these data the maximum soluble uranium losses that can occur if saturation is reached can be predicted. The solubility of UF_4 in zirconium fluoride—ammonium fluoride solutions has been reported by Swanson;[4] in the presence of radiation the uranium could be oxidized to U(VI).

Excess solid uranyl fluoride was added to solutions that initially contained ammonium fluoride in concentrations varying from 0.5 to 6 M. The solutions were maintained at constant temperature (within 0.1°C), with periodic shaking, for several days to ensure equilibrium. Four isotherms

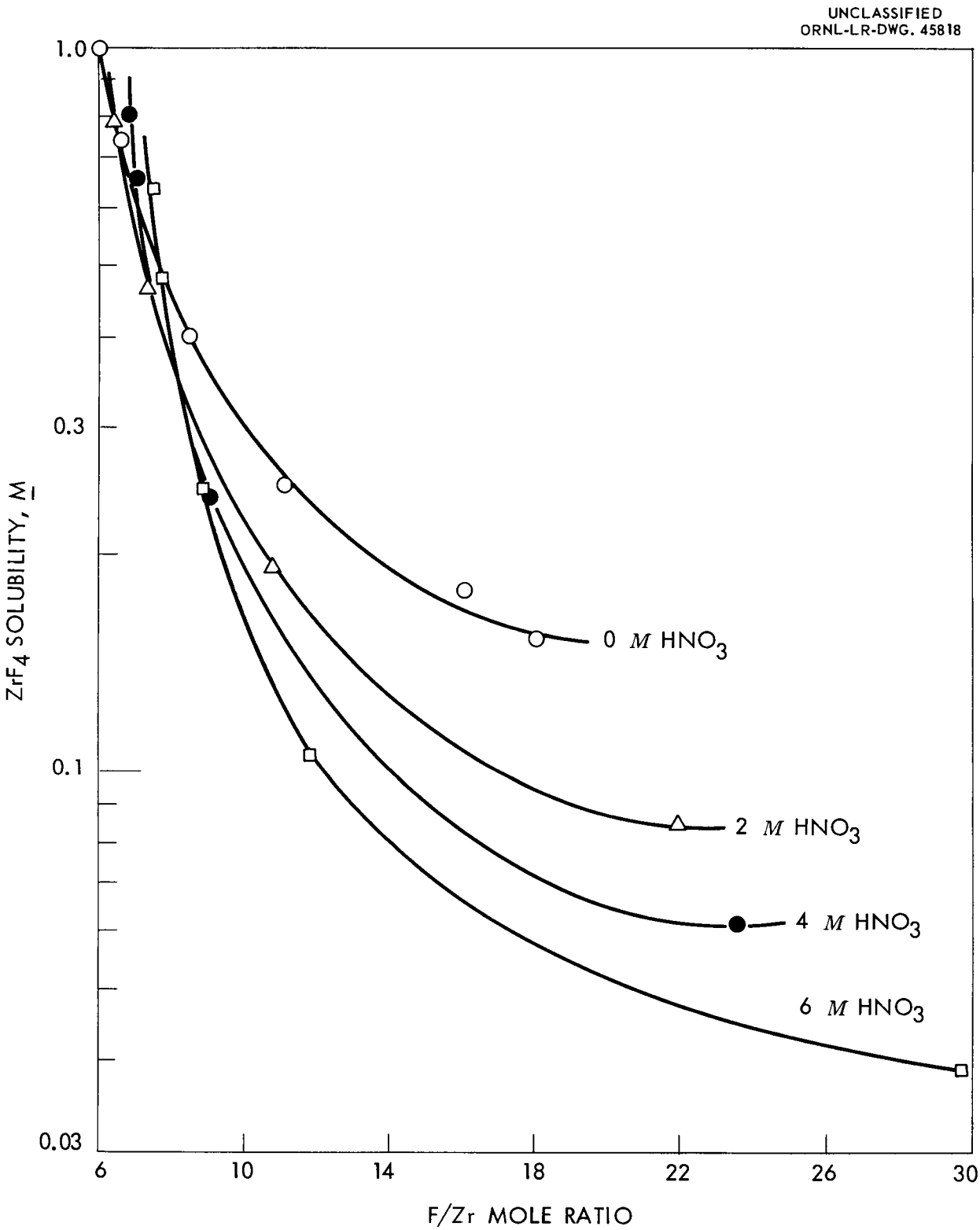

Fig. 4. Solubility at 25°C of ZrF_4 in ammonium fluoride - nitric acid solutions.

were obtained: 25, 40, 59.5, and 80°C. In addition to the solubility in NH_4F solutions, the solubility of UO_2F_2 was determined in 0.9 M $(NH_4)_2ZrF_6$ solution at 26, 59.5, and 80°C.

In ammonium fluoride solutions, the solubility of uranyl fluoride decreased rapidly with increasing ammonium fluoride concentration (Fig. 5). For example, at 26°C the solubility decreased from about 5.1[14] to 0.0025 M as the NH_4F concentration increased from 0 to 5 M. Solubilities were higher at the elevated temperatures. The equilibrium solid phase was identified by x-ray analysis as $(NH_4)_3UO_2F_5$. The solubility of UO_2F_2 at 26°C in 0.9 M $(NH_4)_2ZrF_6$ solution was about 50 times higher than that in 6 M NH_4F solution (Fig. 6). This means that as zirconium dissolves during the decladding step, the maximum attainable soluble uranium loss increases proportionally if uranium is oxidized to U(VI). If all the zirconium from a PWR blanket fuel rod is dissolved under flowsheet conditions to produce a 1 M $(NH_4)_2ZrF_6$ solution, the maximum soluble uranium loss, if the uranium is present as U(VI), would be about 10%.

3.3 Removal of Sorbed Fluoride from Core Pellets

In the flowsheet demonstration experiments reported in ORNL-2558,[2] the UO_2 core pellets were washed with cold water after decladding. As a result, the fluoride concentration in the solvent extraction feed solution was 0.1 to 0.2 M. Cold 0.05 M $Al(NO_3)_3$ solution was found to be an effective reagent for the removal of fluoride sorbed on the UO_2 pellets. The fluoride concentration in the 1.3 M $UO_2(NO_3)_2$ solution obtained from core dissolution was reduced to less than 0.015 M when cold 0.05 M $Al(NO_3)_3$ was used as the wash solution. Hot and cold water washes resulted in final fluoride concentrations of about 0.06 M (Table 1).

The optimum wash solution tested was 0.05 M $Al(NO_3)_3$. Uranium losses to the combined dejacketing-wash solution, however, increased with increasing aluminum nitrate concentration, and some difficulty was experienced in filtering solutions when the $Al(NO_3)_3$ concentration was greater than 0.05 M. Because of the difficulty in filtering and the fact that no difference in fluoride carryover was obtained in recent flowsheet demonstration experiments (see Sect. 3.2), it appeared advisable to add aluminum to the core dissolvent to complex the traces of fluoride that are inevitably carried over. In the earlier tests, where the fluoride carryover was much greater, the wash water was added in fewer portions than in the recent series.

For the washing tests, 30-g samples of UO_2 pellets were digested in about 100 ml of boiling 1 M ammonium hexafluozirconate solution for 3 hr. After the fluozirconate solution was removed by filtration, the pellets were washed with about 100 ml, in 10 portions, of the solution being tested. The pellets were then dissolved in 10 M HNO_3 and the resulting solution diluted to produce a simulated solvent extraction feed solution which was 1.3 M in uranium. This solution was analyzed for fluoride.

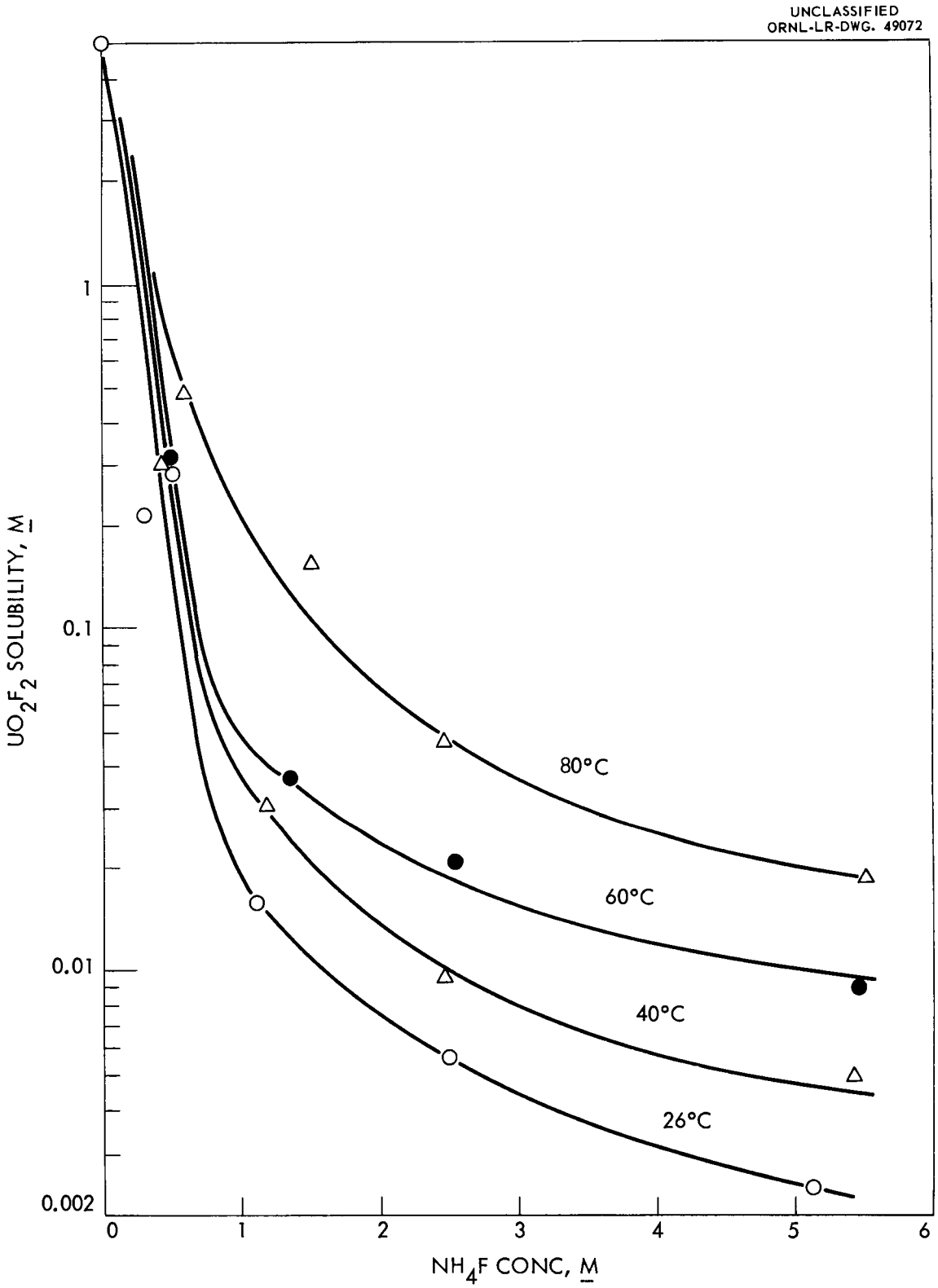

Fig. 5. Solubility of uranyl fluoride in aqueous ammonium fluoride solutions between 26 and 80°C.

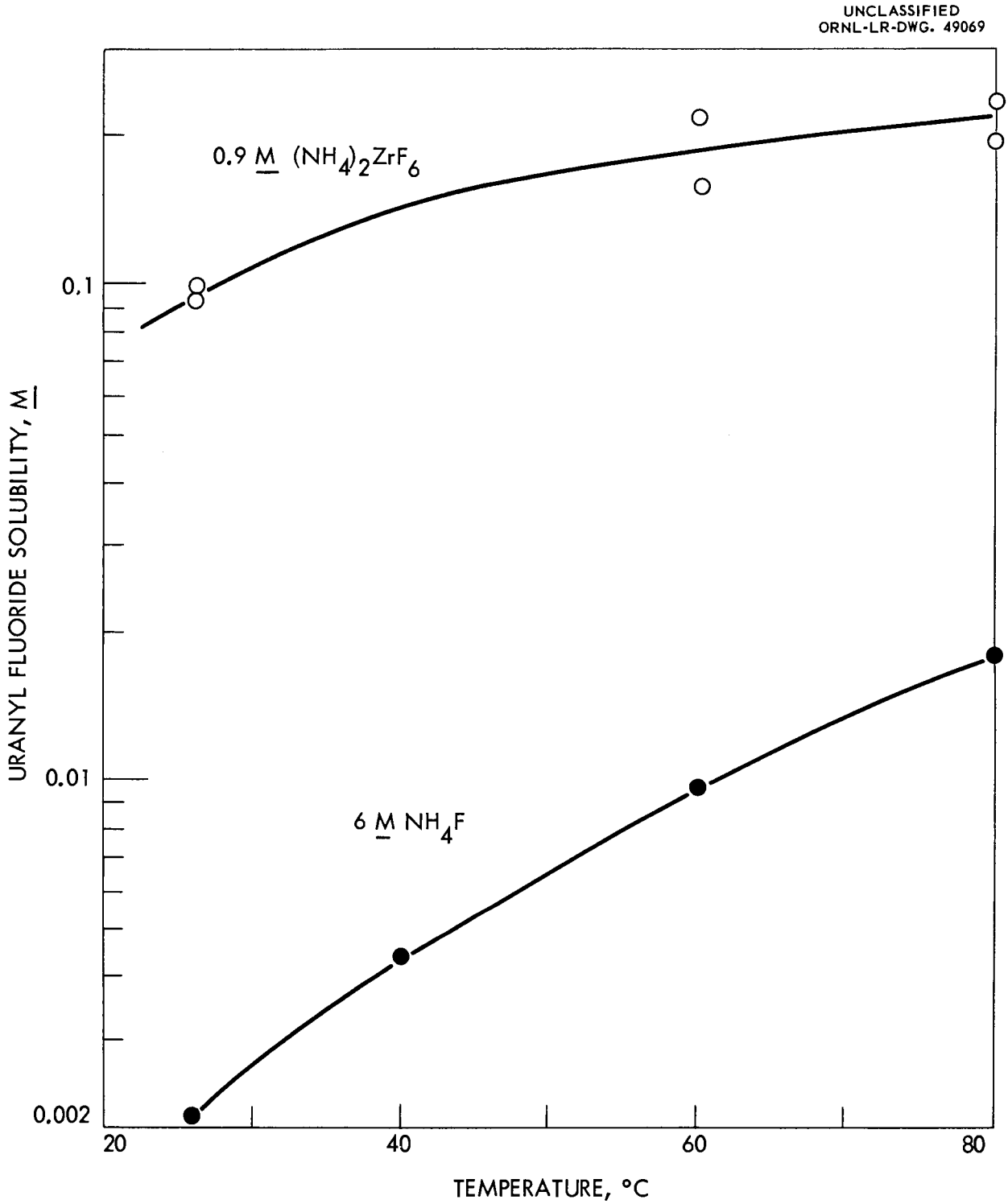

Fig. 6. Solubility of UO_2F_2 in 6 M NH_4F and 0.9 M $(NH_4)_2ZrF_6$ at various temperatures.

Table 1. Removal of Sorbed Decladding Solution from UO_2 Pellets

Uranium conc. in final nitrate solution: 1.3 M

Run No.	Wash Solution	F^- Conc. in Final Nitrate Solution, M	U Lost to Wash, %	U Material Balance, %
1	Cold H_2O	0.055	0.000	99.0
2	Hot H_2O	0.055	0.0024	97.3
3	Hot H_2O	0.051	0.0029	95.7
4	Cold 0.05 M $Al(NO_3)_3$	0.015	0.0055	93.6
5	Cold 0.05 M $Al(NO_3)_3$	0.003	0.0042	98.6
6	Hot 0.05 M $Al(NO_3)_3$	0.009	0.040	82.1
7	Hot 0.05 M $Al(NO_3)_3$	0.006	0.033	99.9
8	Cold 0.1 M $Al(NO_3)_3$	0.004	0.062	95.9
9	Cold 0.1 M $Al(NO_3)_3$	0.007	0.028	96.8
10	Hot 0.1 M $Al(NO_3)_3$	0.009	0.04	95.7
11	Hot 0.1 M $Al(NO_3)_3$	0.003	0.058	96.3
12	Cold 0.01 M HNO_3	0.055	0.004	98.3
13	Cold 0.01 M HNO_3	0.060	0.004	99.2

3.4 Flowsheet Demonstration Experiments

Batch Dissolution of Nonoxidized PWR Fuel Rods. Experiments were performed with nonoxidized PWR fuel rods to test the effects of using the dilute aluminum nitrate wash after decladding and of using only 0.5 M NH_4NO_3 in the decladding reagent. In the seven experiments performed, there appeared to be no advantage in using dilute aluminum nitrate as the wash solution after decladding. The fluoride concentration in the final uranyl nitrate product never exceeded 0.02 M even when cold water was used for the wash (Table 2). In the earlier flowsheet runs,[2] the wash water was added in three to five portions instead of the seven to ten used in the present series. This fact undoubtedly partially accounts for the present findings.

In the runs where the NH_4NO_3 concentration in the decladding reagent was 0.5 instead of 1 M, the weight of nitric acid—insoluble solids, mainly SnO_2 and ZrO_2, remaining after core dissolution increased by a factor of about 4. In dissolution of a PWR blanket fuel rod (45 g of zirconium, 1 g of tin, 130 g of uranium) according to the flowsheet shown

in Fig. 1 less than 0.07 g of solids remained when the decladding reagent contained 1 M NH_4NO_3 and 0.2 to 0.25 g when the ammonium nitrate concentration was 0.5 M (Table 3). Similar data with 0.75 M NH_4NO_3 were not obtained. Uranium losses to the nitric acid—insoluble residue were always less than 0.0025% (Table 2; see also Table 4.3, p. 10 of reference 2). Soluble uranium losses to the decladding solutions were always less than 0.07% (Table 2).

Table 2. Dissolution of Nonoxidized PWR Blanket Fuel Rods According to the Zirflex Process

Decladding reagent: boiling 6 M NH_4F—1 M NH_4NO_3
Core dissolvent: 10 M HNO_3

Run No.	NH_4NO_3 Conc., M	Decladding Time,[a] hr	Wash Solution	Uranium Loss, % In Decladding	Uranium Loss, % To HNO_3-insol. Residue	F^- Conc. in Final Product, M	Wt of HNO_3-insol. Residue, g
P-30	1.0	3	0.05 M $Al(NO_3)_3$	0.0055	-	0.010	0.031
-31	1.0	3		0.0052	-	0.02	-
-33	1.0	3.25		0.0016	-	0.02	0.064
-34	1.0	3	Cold H_2O	0.009	-	0.019	0.059
-35	0.5	3		0.069	0.0023	0.006	0.21[b]
-36	0.5	3		0.022	0.0008	0.006	0.25[b]
-37	0.5	3		0.056	0.0012	0.004	0.23[b]

[a]About 80% of the zirconium dissolved in each case.

[b]Residue mainly SnO_2 and ZrO_2.

Batch Dissolution of Oxidized PWR Fuel Rods. Several experiments were performed in an attempt to determine if a thick coating of ZrO_2 on PWR blanket fuel had a marked effect on the rate of decladding. The surface of the irradiated fuel should be well oxidized since it is expected to be in contact with pressurized water for about 750 days.[9] The few data obtained indicate that the rate of dissolution of oxidized fuel can be significantly lower; however, the behavior of the fuel specimens will be difficult to predict. Before definite conclusions can be drawn it will be necessary to test both irradiated and unirradiated specimens that have been subjected to high-temperature pressurized water for long periods of time.

Table 3. Dissolution of Oxidized PWR Blanket Rods According to the Zirflex Flowsheet

Run No.	Decladding Time, hr	Method of Oxidation	U Loss, % To Decladding Solution	U Loss, % To HNO_3-Insol. Residue
P-16	4	Autoclaved 30 days	0.014	0.0048
P-17	17		0.007	0.11
P-18	3		0.039	0.017
P-19	6		0.036	0.0006
P-20	2		0.084	0.0003
P-21	2		0.012	0.0003
P-22	2		0.010	0.00007
P-23	3		0.019	0.0002
P-24	1		0.042	0.0005
P-25	4	Heated 14 days in air at 400°C	0.014	0.0037
P-26	3		0.019	0.0079
P-27	4		0.016	0.017
P-29	3	Heated 16 days in air at 400°C	0.047	0.0001

In each experiment the oxidized fuel specimen was dissolved according to flowsheet conditions. The autoclaved specimens had been exposed at 300°C for 30 days at 2000 psi (1200 steam and 800 psi oxygen). Other specimens, fabricated at ORNL, were heated in air for 14 days at 400°C. One specimen, that used in run P-29, was fabricated by the Westinghouse Corporation, and may have been autoclaved for a short time prior to its shipment to ORNL. In all runs with autoclaved pins except run P-17, decladding was complete (i.e. the only zirconium remaining was present as end caps) in less than 6 hr. Uranium losses to the decladding solution were less than 0.08%, and showed no systematic variation with decladding time (Table 3). Only in run P-17 did the uranium loss to the nitric acid—insoluble residue exceed 0.005%.

Dissolution of the cladding of the autoclaved specimens and most of the air-oxidized specimens occurred through a pitting attack (specimen A in Fig. 7). The surface of an autoclaved pin is black. Specimen B (Fig. 7) was the one fabricated by Westinghouse and heated in air at 400°C for 16 days. Most of the surface is white. For some reason the ends of the pin retained their original black color. After a 3-hr exposure to boiling 6 M NH_4F—1.0 M NH_4NO_3, only the end caps of specimen B had dissolved.

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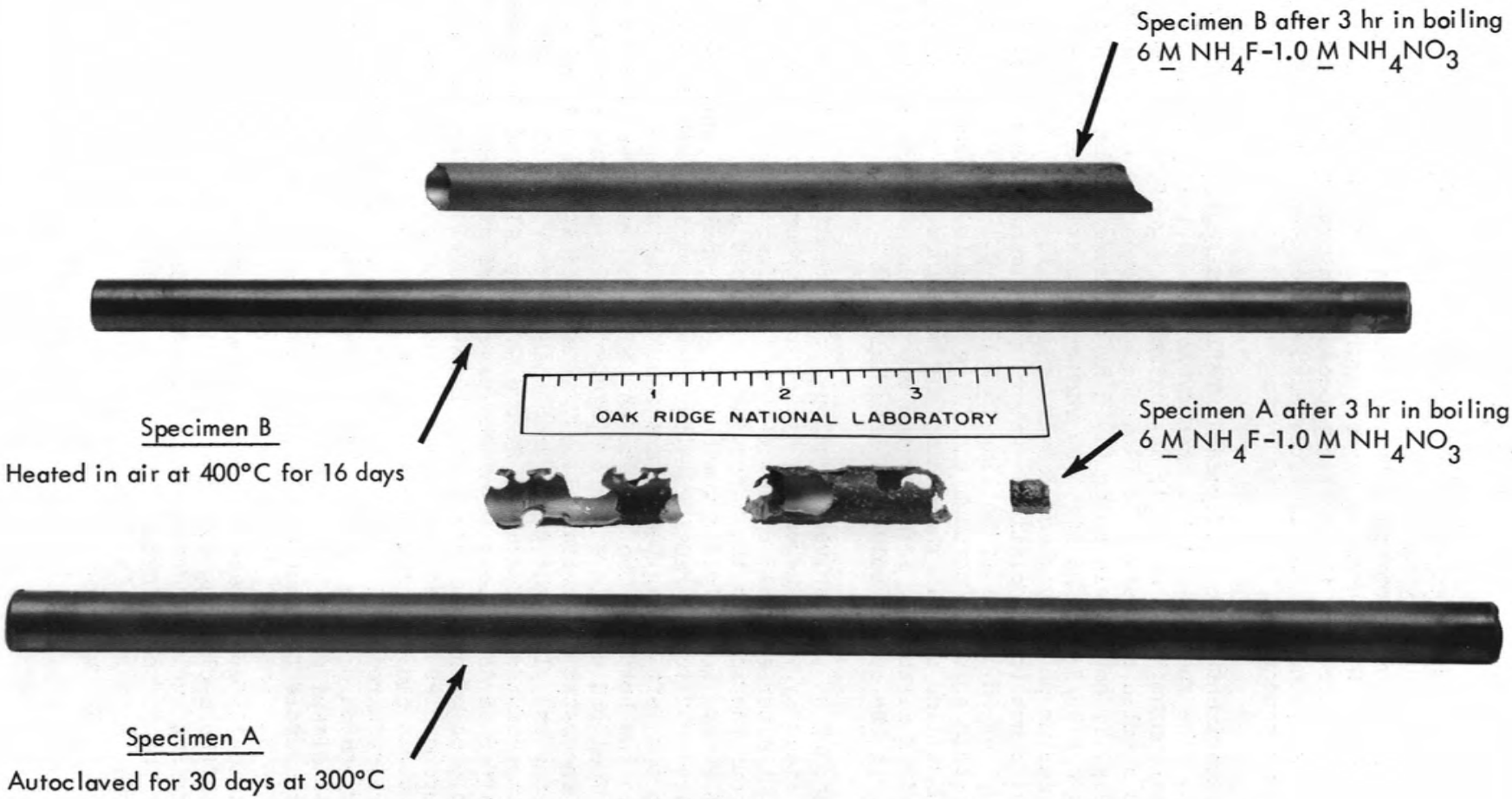

Fig. 7. Decladding of oxidized PWR rods in the Zirflex process.

Cyclic Dissolution Experiments. The cyclic dissolution experiments were performed by Snavely and co-workers of the ORNL Reactor Experimental Engineering Division to obtain data on corrosion of Ni-o-nel in the Zirflex process. Other data on the accumulation of end caps, formation of solids, and effect of the cyclic procedure on uranium losses were readily obtained by weighing all solids after each dissolution step and analyzing the solutions produced.

All experiments were performed in Teflon beakers fitted with Kel-F condensers. The fuel charge for each cycle was half a PWR blanket rod (24 g of zirconium, 75 g of UO_2); approximately 4 g of the zirconium was present as a solid end cap. The flowsheet followed was essentially that given in Fig. 1, each cycle being (1) 3 hr exposure of the fuel to 250 ml of boiling 6 M NH_4F—1 M NH_4NO_3; (2) vacuum filtration of the hot solution through a medium-porosity glass filter; (3) rinsing the container and contents with hot (85°C) distilled water; (4) dissolution of the core pellets in 5 hr in 150 ml of boiling 10 M HNO_3—0.1 M $Al(NO_3)_3$; (5) removal of this solution through the filter; and (6) a second rinsing with hot distilled water. The decladding solutions were diluted only to about 0.2 M zirconium, a fact which may account for the presence of $(NH_4)_3ZrF_7$ in the cooled solutions (see below).

The amount of undissolved Zircaloy-2 that remained in the dissolver increased steadily with increasing cycles and appeared to reach a steady-state amount after about 15 cycles (Fig. 8). After 15 cycles the residue weighed about the same as the zirconium introduced as a fresh fuel charge, i.e. about 24 g. Not only did the end plugs accumulate, but also part of the Zircaloy-2 tubing remained after several cycles (see Fig. 9a). The rod at the left in Fig. 9a is one-fourth of an untreated rod with an end plug at the bottom. The jackets on the right were remnants of two pieces of fuel rod used in a third cycle. They were extremely thin and had been penetrated in several places. The piece at the extreme right still had the end plug; the plugs from the two previous cycles are shown at the bottom of the photograph. Figure 9b shows all the zirconium remnants after seven cycles; seven end plugs were still present although only two pieces of jacket were left. Inspection of the residue after several more cycles showed that usually eight end plugs were present. Since a new end plug was introduced at the beginning of each cycle, eight cycles were required to dissolve one end plug. It is recommended that after every three or four cycles the residue be refluxed in 6 M NH_4F for 15-30 hr to dissolve out the zirconium residue. Increasing the decladding time in each cycle to about 6 hr would also be of great benefit.

In virtually every case an insoluble material passed through the filter with the decladding solution. The amount of this solid in solutions from successive cycles increased steadily and, in one series, was about 10 g after the fifteenth cycle (Fig. 10a). Chemical analyses of the solids showed that while the F/Zr mole ratio was varied and always less than 7, the F/NH_4 ratio was nearly constant at about 2.5 (Table 4).

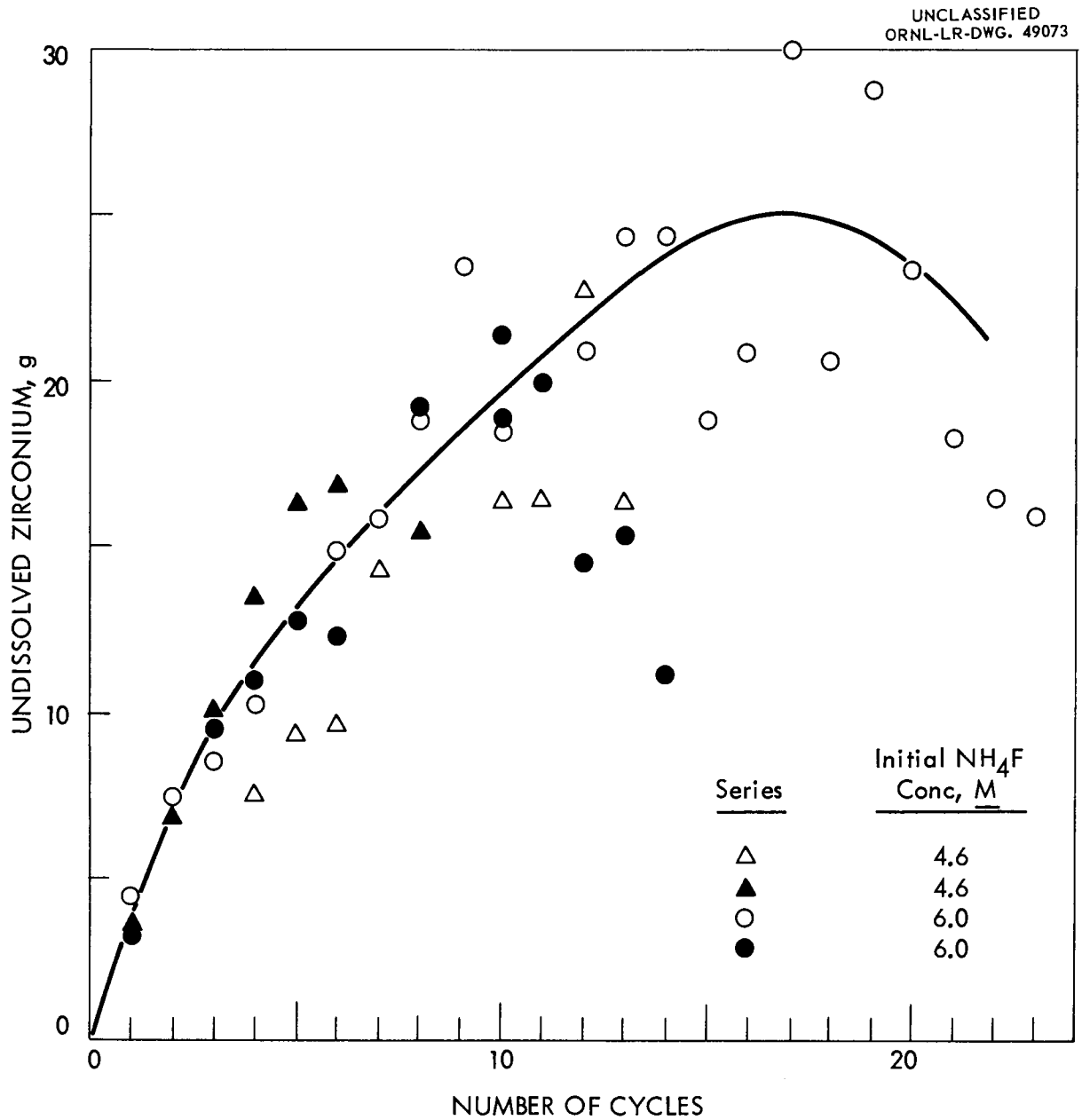

Fig. 8. End cap buildup during four series of cyclic dissolutions of PWR blanket fuel under conditions similar to the flowsheet shown in Fig. 1.

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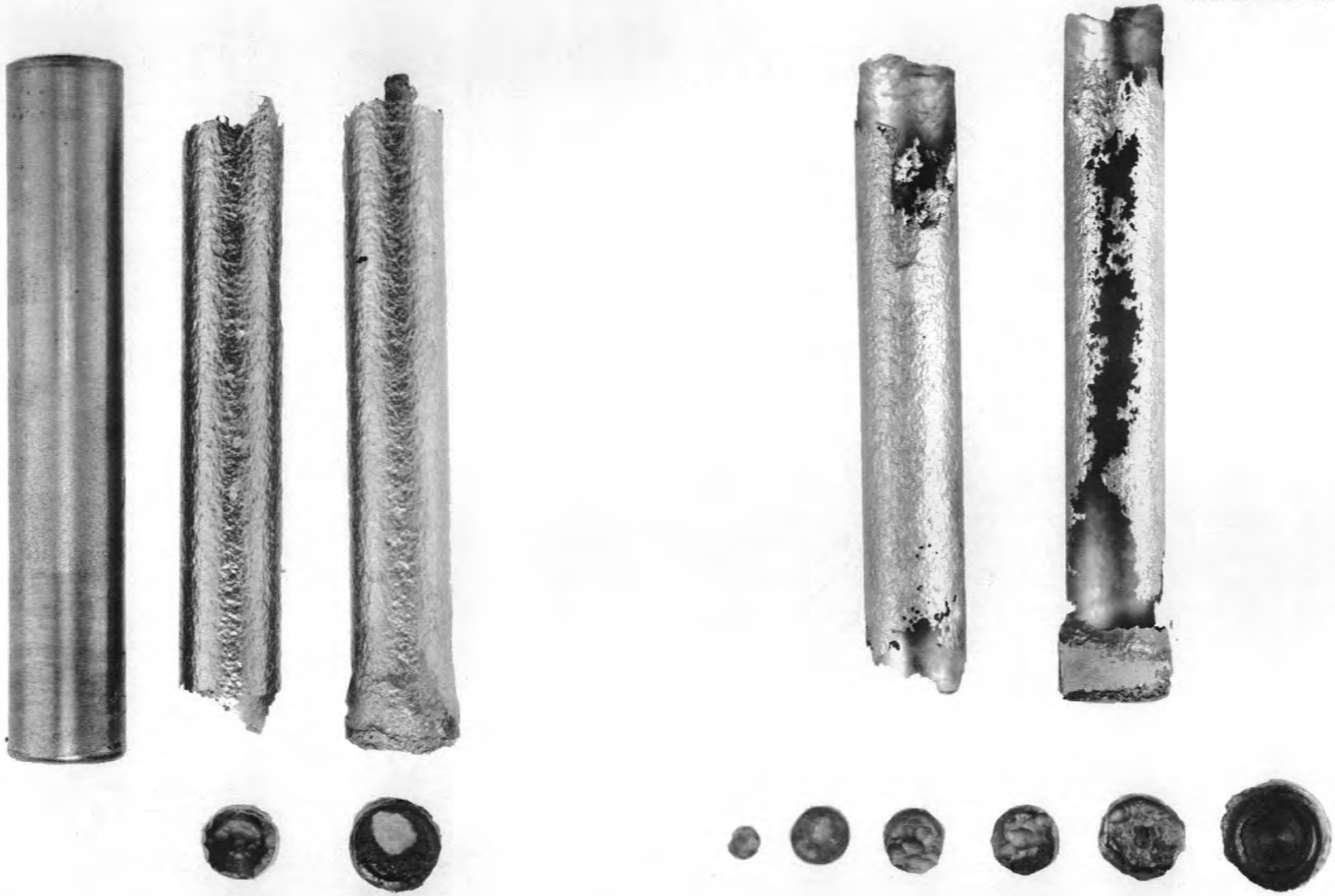

Fig. 9. Zircaloy cladding remaining after (a) three Zirflex cyclic tests (the rod on the left is an unused PWR fuel rod section) 2X; (b) seven Zirflex cyclic tests (2X).

Table 4. Analyses of Solids Found in Filtered Zirflex Decladding Solutions from Cyclic Tests

Run No.	Wt of Solids, g	Analysis of Solids F/Zr	F/NH_4	Sn, %	U Loss to Solids, %
D6Z-1	0.16	-	-	-	-
-3	0.17	4.35	2.46	9.6	0.0009
-5	1.86	2.35	2.47	4.4	-
-7	2.92	4.43	2.44	4.3	0.0044
-9	1.55	3.20	2.44	3.7	0.0073
-11	1.02	1.79	-	10.9	-
-13	1.02	5.33	2.63	7.8	0.0059
-15	10.51	2.59	2.65	1.0	-

Since a large fraction of the solids was water soluble, it was concluded that, in addition to the tin, they were comprised of mixtures of $(NH_4)_3ZrF_7$ (water soluble[11]) in which the F/NH_4 ratio is 2.33 (see also Sect. 3.1) and $ZrO_2 \cdot 2H_2O$. Since the solids carried virtually no uranium (losses were less than 0.01%) they can be slurried and jetted to waste. The presence of $(NH_4)_3ZrF_7$ in the solids indicates that the decladding solution should have been diluted to less than 0.2 M zirconium.

Solids, which were found by x-ray analysis to be mainly SnO_2, were found in all the filtered core dissolution product solutions. The amounts of solids found, though small, increased with increasing number of cycles; only about 0.5 g was found at the end of the fifteenth cycle (Fig. 10b).

Since most of the solid material found in both the decladding and core solutions was not formed by cooling the hot dissolver solutions, it was concluded that the increasing amount found at the end of each subsequent cycle was due to the gradual increase in pore size of the glass filter used for solid-liquid separations. It seems reasonable to assume that chemical attack of the glass occurred, particularly with repeated contact with hot ammonium fluoride—ammonium nitrate solutions.

The amount of uranium lost to the decladding solution also increased with increasing number of cycles to about 0.5% at the end of the fifteenth cycle (Fig. 11). Since core dissolution was complete in each cycle, i.e. no accumulation of UO_2 occurred, it is concluded that the apparent loss is due to passage of fine UO_2 particles, which were always present since PWR rods had been cut in half for these tests, through the filter which ultimately appear as part of the loss.

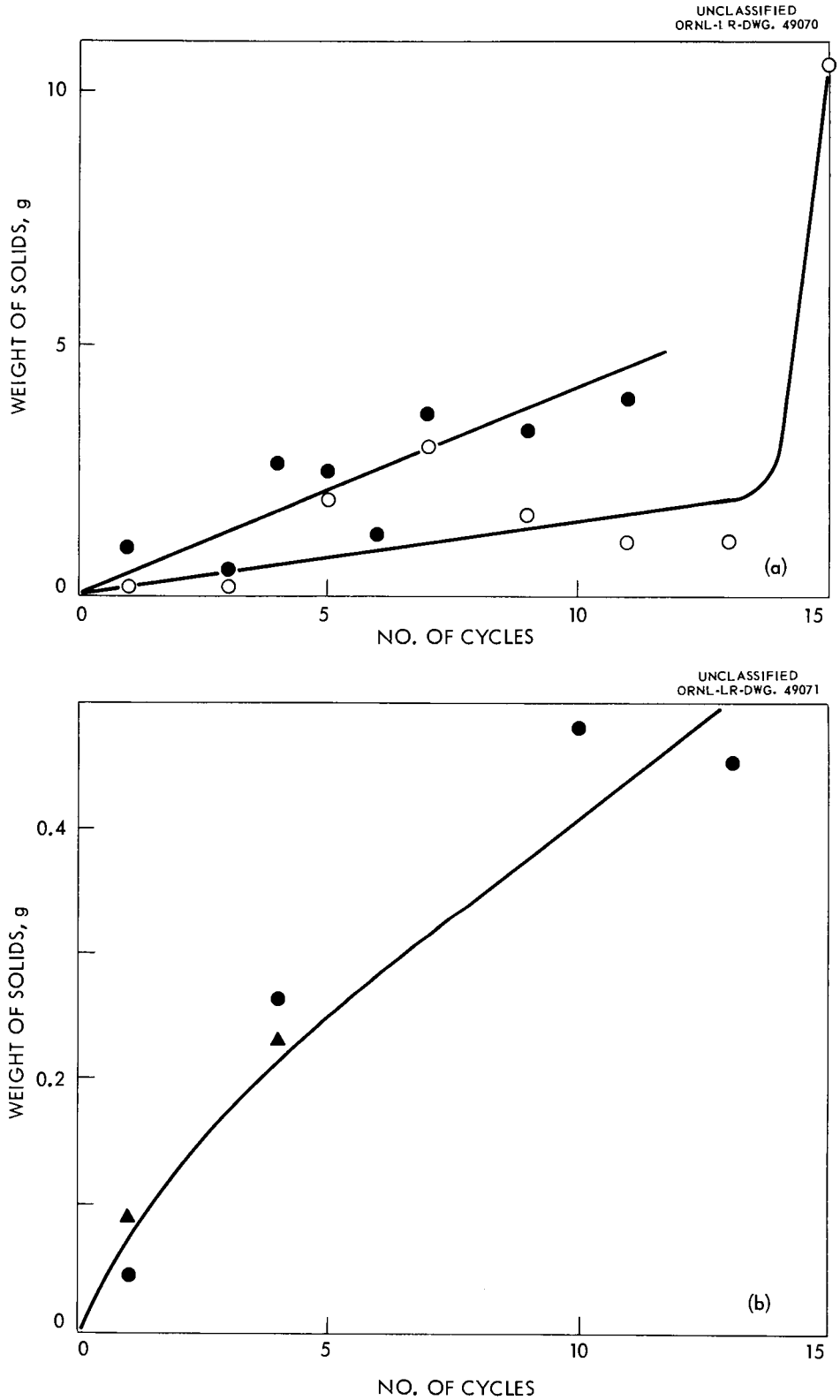

Fig. 10. Amount of solids formed in filtered (a) decladding solutions and (b) core dissolution solutions in Zirflex cyclic dissolution experiments. Solid in core solution is SnO_2. Solids buildup probably due to defective filter.

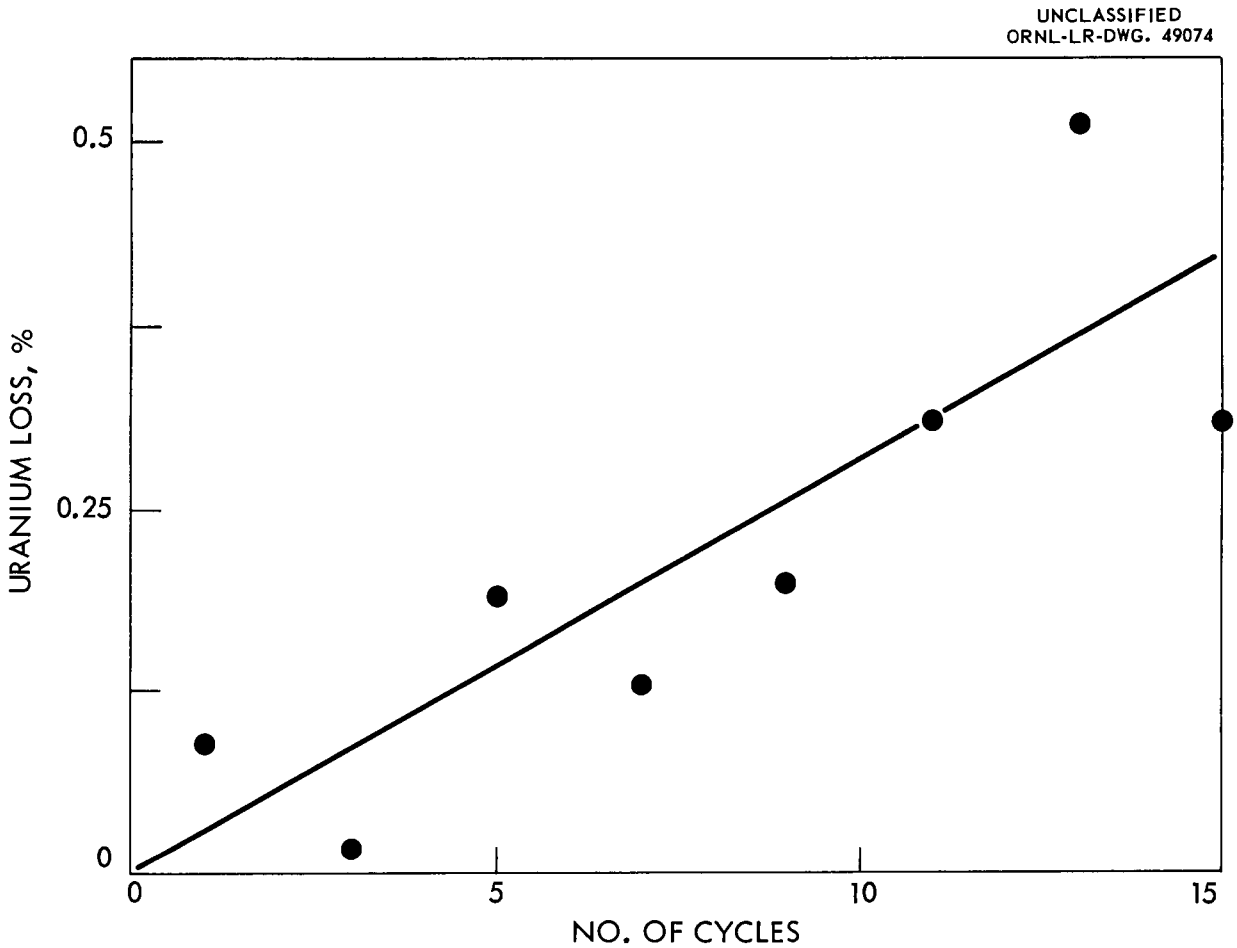

Fig. 11. Uranium decladding losses in cyclic dissolution experiments. Buildup probably due to defective filter.

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