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DISSOLUTION OF OXIDE-COATED
ZIRCONIUM AND ZIRCONIUM ALLOYS

J. F. Phillips, Jr.

April 1968

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DISSOLUTION OF OXIDE-COATED ZIRCONIUM
AND ZIRCONIUM ALLOYS
IN AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS

By

John F. Phillips, Jr.
Applied Chemistry Section
Chemistry and Chemical Engineering Department

April 1968

PACIFIC NORTHWEST LABORATORY
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DISSOLUTION OF OXIDE-COATED ZIRCONIUM
AND ZIRCONIUM ALLOYS
IN AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS

John F. Phillips, Jr.

INTRODUCTION

Zircaloy-clad nuclear fuel elements are declad (Zircaloy jackets dissolved) at Hanford Project chemical separations facilities by the Zirflex process. This process involves dissolution of the Zircaloy in a solution initially $5.5M \text{ NH}_4\text{F}-0.5M \text{ NH}_4\text{NO}_3$. The dissolution rate of Zircaloy metal in this solution is fairly rapid (10 - 20 mils/hr).

However, the fuel elements, prior to decladding, are coated with a black, hard, tightly-adherent and highly impervious zirconium oxide coating acquired during pre-use autoclaving and/or during exposure to hot water in nuclear reactors. Two types of zirconium oxide,⁽¹⁾ the black oxide (called "pre-transition oxide") just mentioned, and a less tightly adherent white oxide (called "transition oxide") may be observed. Because the white oxide usually indicates mechanical defects or chemical contamination, elements forming this oxide during pre-use autoclaving are rejected. In its simplest form, the Zirflex decladding process consists of dissolving Zircaloy in the initially $5.5M \text{ NH}_4\text{F}-0.5M \text{ NH}_4\text{NO}_3$ dissolvent, decanting the dissolver solution to waste, and rinsing the fuel cores with water to remove residual decladding solution.⁽²⁾ However, the black, tightly adherent oxide is an effective barrier to the Zirflex dissolvent. Dissolution of such oxide-coated cladding appears to start only at minute holes or defects, and to proceed by enlargement of these holes.⁽³⁾ Consequently, initial dissolving rates may be quite low and total decladding time excessive because of the limited area of bare Zircaloy available for rapid dissolution. During processing of Zircaloy-clad Shippingport and N-Reactor fuels in the Redox plant, difficulty in obtaining complete decladding in

reasonable times was experienced, and decladding procedure modifications, including partial decladding, leaching of the core material with nitric acid, and subsequent dissolution of residual Zircaloy were required.

In addition to long decladding time cycles, the slow initial dissolving rate experienced with the initially $5.5\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$ dissolvent was found to increase exposure of the dissolver to the relatively corrosive dissolvent, and to significantly increase conversion of uranium metal core material to uranium tetrafluoride. More than 5% conversion of uranium to uranium tetrafluoride was observed in some of the Zirflex decladding operations in the Redox plant. An extra process step, a metathesis of the UF_4 to hydrated uranium oxide, is required in the Purex plant to remove the fluoride.

During exploratory studies for alternatives or means to improve the Zirflex process, pitting or penetration of the oxide coating was observed to be much more extensive in $7.5-8\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$ than in the standard Zirflex dissolvent. More detailed studies were conducted to determine whether an improved process for dissolving oxide-coated Zircaloy cladding could be developed using $7.5-8\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$ as the dissolvent. Results of these studies are presented in this report.

SUMMARY

Pitting or pinholing of oxide-coated Zircaloy-2 coupons was markedly more rapid and extensive when the coupons were exposed to boiling $7.5-8\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$ than in similar exposure to the standard Zirflex dissolvent, $5.5\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$. As a consequence, attack by the more concentrated dissolvent was more uniform over the surface of the metal. Use of the more concentrated reagent for the initial attack on oxide-coated Zircaloy, based on laboratory-scale studies, shows strong promise as an improvement over the standard Zirflex process. Some

advantages of the more concentrated reagent over the standard Zirflex reagent indicated by these studies are as follows:

- Oxide-coated Zircaloy-2 is more rapidly and extensively pitted.
- Terminal zirconium concentration in the decladding solution can be reached more quickly.
- Higher terminal zirconium concentrations are possible.
- More extensive pitting of the oxide surface and more rapid completion of the decladding process should require less time exposure of the uranium metal core (per unit area) to the decladding solution, particularly when the concentration of fluoride not complexed by zirconium is high. This result is expected to reduce the attack on the uranium and the percent of uranium converted to uranium tetrafluoride. Experimental testing of this hypothesis has not been made.

EXPERIMENTAL

Included in this section are descriptions of experiments designed to measure pitting of oxide coating on Zircaloy-2 coupons, Zircaloy-2 dissolution rates, Zircaloy-2 decladding product solubility, stainless steel corrosion rates, and off-gas composition as a function of decladding composition.

PITTING OF OXIDE-COATED ZIRCALOY-2 BY AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS

The effectiveness of ammonium fluoride-ammonium nitrate solutions in pitting oxide-coated Zircaloy-2 was determined by exposing Zircaloy-2 coupons to 200 ml of boiling test solution and counting the number of pits formed on the faces of the coupon. The coupons were exposed for 10 min intervals and the pits, as seen through an 8X magnifying glass, were counted. Coupon dimensions were 1.3 cm x 2.4 cm x 0.076 cm.

OXIDE COATING OF ZIRCALOY-2 COUPONS*

Three groups of oxide-coated Zircaloy-2 coupons were examined for pitting characteristics. The first group was oxidized by steam autoclaving the coupons for various periods of time at 1500 psi and 400 °C. A second group was exposed to a simulated N-reactor environment, established by steam autoclaving the coupons at 400 °C and 1500 psi for 6 days and then exposing the coupons at 300 °C for various periods of time to high-oxygen-content water buffered to pH 10 with lithium hydroxide. The third group of coupons was exposed to simulated PRTR conditions for various periods. This environment was simulated by steam autoclaving the coupons for 6 days at 400 °C and 1500 psi, and then exposing the coupons at 300 °C to low-oxygen-content water buffered to pH 10 with ammonium hydroxide.

ZIRCALOY-2 DISSOLUTION RATE MEASUREMENT

Zircaloy-2 dissolution rates, as a function of dissolved zirconium, were determined by exposing an oxide-free Zircaloy-2 disk to 250 ml of boiling ammonium fluoride-ammonium nitrate test solution for a measured time period--usually 5 or 10 min. All test solutions were initially 0.5M in NH_4NO_3 . The disk was mounted in a Teflon holder in such a manner that 3.94 cm² was exposed to the solution. Dissolved Zircaloy-2 was calculated from coupon weight loss. In a typical experiment, a weighed amount of zirconium was completely dissolved to establish the desired zirconium concentration. Boiling was continued for at least 30 min and then a dissolution rate measurement was made. Steam evolution provided the only sparging.

SOLUBILITY MEASUREMENTS AT 50 °C

To determine the amount of dilution necessary to prevent precipitation of ammonium fluorozirconate salts from terminal decladding solutions, 10 ml of simulated decladding solution

* The Zircaloy-2 coupons were supplied by L. Charlot, Pacific Northwest Laboratory.

was prepared from ammonium heptafluorozirconate, ammonium fluoride, and ammonium nitrate. Water was added, one ml at a time, until the salt completely dissolved. The solutions were stirred at 50 °C for at least 30 min between water additions. Equilibrium was approached from the opposite side by slowly evaporating the decladding solution until precipitates just began to form. Terminal decladding solution compositions tested were calculated on the basis of the reaction:

DISSOLUTION OF OXIDE-COATED ZIRCALOY-2 IN 5.5M NH₄F-0.5M NH₄NO₃
AND 7.5M NH₄F-0.5M NH₄NO₃

Dissolution characteristics of oxide-coated Zircaloy-2 were examined by immersing a 1.6 cm x 6.5 cm Zircaloy-2 tube in 280 ml of ammonium fluoride-ammonium nitrate for short periods and measuring weight loss. The Zircaloy tube, prior to use, had been steam autoclaved for 90 days at 400 °C and 1500 psi. The tube wall thickness was ~0.1 cm. Because the ends of the tube were not oxide-coated, they were capped with Teflon. Total dissolution of the Zircaloy would have produced a solution about one molar in zirconium.

CORROSION OF 304-L STAINLESS STEEL BY AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS*

Solutions for corrosion rate measurements were obtained by dissolving a weighed amount of zirconium in boiling ammonium fluoride-ammonium nitrate solution. Test coupons were hung in the solution and the solution boiled under total reflux for a measured period of time. Corrosion rates were determined by weight loss.

* Corrosion rates were measured by R. F. Maness of Pacific Northwest Laboratory.

HYDROGEN EVOLUTION DURING ZIRCALLOY-2 DISSOLUTION

Hydrogen in the decladding process off-gas was determined by gas chromatography. Off-gas samples were first dried by passing the gases through solid potassium hydroxide. The dried gases were then collected in sample tubes. Two 7-foot columns in series, one packed with 100-mesh silica gel and the other with 100-mesh activated charcoal, were used to resolve the hydrogen from ammonia and traces of air and water vapor. The columns were operated at room temperature with nitrogen carrier gas and thermal conductivity detectors.

RESULTS

PITTING OF ZIRCALLOY-2 BY AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS

Results of experiments designed to estimate the pitting action of ammonium fluoride-ammonium nitrate solutions on oxide-coated Zircaloy-2 are shown in Tables I, II and III. In all experiments, the ammonium nitrate concentration was 0.5M. Columns 3 through 7 (Table I), and 3 through 6 (Tables II and III), show the number of pits per square centimeter formed on coupon faces in 10 min intervals.

Occasionally the coupons were overlaid with small patches of transition (white) zirconium oxide. The ammonium fluoride-ammonium nitrate failed in almost all cases, to pit the Zircaloy-2 at these places even when the adjacent pretransition oxide was badly pitted.

TABLE I. *Pitting of Steam-Autoclaved Zircaloy-2 by Ammonium Fluoride-Ammonium Nitrate Solutions*

Ammonium Fluoride Concentration, M	Autoclave Time, days	Pits/sq cm vs. Exposure Time, min				
		10	20	30	40	50
5.5	9	0.0	0.0	0.0	0.0	-
7.5	9	-	0.0	0.0	8.2	34.3
4.5	15	0.0	0.0	0.0	0.0	0.2
5.5	15	0.0	0.0	0.2	0.2	0.5
5.5	15	0.2	0.2	0.2	0.2	0.2
5.5	15	0.0	0.0	0.0	0.0	0.0
7.5	15	0.0	0.0	0.2	2.9	4.6
3.5	30	0.0	0.0	0.0	0.0	-
5.5	30	0.0	0.0	0.0	0.0	0.0
5.5	30	0.0	0.0	0.0	0.0	0.0
6.5	30	0.0	0.0	0.0	0.2	0.2
6.5	30	-	-	0.0	0.0	0.8
7.5	30	-	0.0	-	1.0	6.8

TABLE II. *Pitting of Zircaloy-2 Exposed to Simulated N-Reactor Environment by Ammonium Fluoride-Ammonium Nitrate Solutions*

Ammonium Fluoride Concentration, M	Exposure** Time, days	Pits/sq cm vs. Exposure Time, min				
		10	20	30	40	50
5.5	60	0.0	0.0	0.0	0.3	-
5.5	60	-	0.8	1.8	1.5	-
7.5	60	0.0	5.9	8.9	8.8	-
7.5	60	0.2	5.7	11.9	13.1	-
5.5	90	-	0.0	0.0	0.0	-
7.5	90	-	-	6.7	~16.0	-
5.5	150	-	0.0	0.0	0.0	-
7.5	150	0.7	0.7	3.4	5.9	-
5.5	180	-	0.0	0.0	0.0	-
7.5	180	0.7	11.6	19.3		
5.5*	150	0.2	0.7	~30.0	-	-
7.5*	150	-	-	~30.0	-	-

* These samples were not steam-autoclaved prior to exposure to the simulated reactor environment.

** All coupons, including those shown in Table III, were steam-autoclaved for 6 days at 400 °C and 1500 psi prior to reactor environment exposure. The second column of Tables II and III refers only to exposure time of the coupon to the simulated environment.

TABLE III. *Pitting of Zircaloy-2 Exposed to Simulated PRTR Environment by Ammonium Fluoride-Ammonium Nitrate Solutions*

Ammonium Fluoride Concentration, M	Exposure Time, days	Pits/sq cm vs. Exposure Time, min				
		10	20	30	40	50
5.5	120	0.0	0.2	0.2	0.2	-
7.5	120	0.0	2.3	2.9	6.9	-
5.5	150	0.0	0.0	0.0	0.0	-
7.5	150	0.0	3.9	5.2	-	-
5.5	180	0.0	0.0	0.0	-	-
7.5	180	0.0	1.5	4.9	7.5	-

Salient features of Table II and III data are the following:

1. Decladding reagents containing less than $5.5\text{M NH}_4\text{F}$ were relatively ineffective in pitting oxide-coated Zircaloy-2. In many instances, even after 40 min exposure to this reagent, no pits were found.
2. Exposure to $7.5\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$ caused a significantly larger number of pits than were formed at lower NH_4F concentration.
3. No decladding reagent tested was found to rapidly pit Zircaloy-2 coupons coated with transition oxide.
4. Decladding solution containing either 5.5M or $7.5\text{M NH}_4\text{F}$ was found to readily pit Zircaloy-2 exposed without steam-autoclaving to the N-reactor environment.

DISSOLUTION RATE OF UNOXIDIZED ZIRCALOY-2 IN SOLUTION INITIALLY $5.5\text{M NH}_4\text{F}$ $0.5\text{M NH}_4\text{NO}_3$ AND $7.5\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$

Shown in Tables IV and V are dissolution rates for oxide-free Zircaloy-2 in ammonium fluoride-ammonium nitrate solutions as a function of dissolved zirconium concentration. For ease of comparison, the data are graphed in Figure 1.

TABLE IV. *Dissolution Rates of Zircaloy-2 in Solutions
Initially 7.5M NH_4F -0.5M NH_4NO_3 versus
Dissolved Zirconium*

<u>Zirconium Concentration, M</u>	<u>Dissolution Rate, mg/ sq cm/min</u>
0.0000	25.2
0.0176	22.8
0.0256	21.6
0.0639	10.7
0.169	5.6
0.284	10.1
0.374	12.4
0.626	9.9
0.762	6.5
0.916	3.7

TABLE V. *Dissolution Rate of Zircaloy-2 in Solutions
Initially 5.5M NH_4F -0.5M NH_4NO_3 versus
Dissolved Zirconium*

<u>Zirconium Concentration, M</u>	<u>Dissolution Rate, mg/ sq cm/min</u>
0.002	27.3
0.084	22.6
0.210	20.3
0.487	8.4
0.667	4.5
0.737	3.0

DILUTION OF ZIRCALOY-2 DECLADDING SOLUTION NECESSARY TO PREVENT PRECIPITATION

Solution compositions and required dilution necessary to prevent precipitation of ammonium fluorozirconate salts from simulated zirconium decladding solution at 50 °C are shown in the following tabulation. Solution compositions were calculated on the basis of an initial decladding composition of 7.5M NH_4F -0.5M NH_4NO_3 .

<u>Zirconium Concentration, M</u>	<u>NH_4F Concentration, M</u>	<u>NH_4NO_3 Concentration, M</u>	<u>Dilution</u>
0.8	1.9	0.10	0.6:1.0
0.9	1.2	0.05	0.6:1.0
1.0	0.5	0.00	0.6:1.0

FIGURE 1. Instantaneous Dissolution Rates of Unoxidized Zircaloy-2 in 3.5M NH₄F-0.5M NH₄NO₃ and 7.5M NH₄F-0.5M NH₄NO₃

DISSOLUTION OF OXIDE-COATED ZIRCALOY-2 IN 5.5M NH₄F-0.5M NH₄NO₃
AND 7.5M NH₄F-0.5M NH₄NO₃

The data shown in Tables VI and VII were obtained during partial dissolution of an oxide-coated Zircaloy-2 tube in the standard Zirflex dissolvent (5.5M NH₄F-0.5M NH₄NO₃) and in 7.5M NH₄F-0.5M NH₄NO₃ solutions. The data represent a comparison of times required to reach given molarities of dissolved zirconium when using the two dissolvents. The data are also shown in graph form in Figure 2.

TABLE VI. *Dissolution of Oxide-Coated Zircaloy-2*
in 7.5M NH₄F-0.5M NH₄NO₃

<u>Zirconium</u> <u>Concentration, M</u>	<u>Time, hr</u>
0.005	0.25
0.011	0.50
0.055	0.75
0.060	1.00
0.089	1.50
0.102	1.75
0.135	2.00
0.165	2.25
0.207	2.50
0.393	2.84
0.486	3.00
0.560	3.25
0.601	3.50
0.668	3.75
0.690	4.00
0.715	4.25

Dissolvent: 280 ml solution initially 7.5M NH₄F-0.5M NH₄NO₃

Zircaloy-2: Tubing 1.6 cm in diameter by 6.5 cm long. Ends capped with Teflon to prevent dissolution in non-oxidized areas. Initial surface area about 63 cm².

TABLE VII. *Dissolution of Oxide-Coated Zircaloy-2
in 5.5M NH_4F -0.5M NH_4NO_3*

<u>Zirconium Concentration, M</u>	<u>Time, hr</u>
0.018	0.25
0.088	0.50
0.126	0.75
0.173	1.00
0.240	1.40
0.278	1.70
0.312	2.05
0.363	2.33
0.380	2.60
0.404	2.75
0.442	3.11
0.456	3.41
0.491	3.90
0.523	4.40
0.554	4.91

Dissolvent: 280 ml solution initially 5.5M NH_4F -0.5M NH_4NO_3

Zircaloy-2: Tubing 1.6 cm in diameter by 6.5 cm long. Ends capped with Teflon to prevent dissolution in non-oxidized areas. Initial surface area about 63 cm².

CORROSION OF 304-L STAINLESS STEEL BY AMMONIUM FLUORIDE-AMMONIUM NITRATE SOLUTIONS

Shown in Table VIII are 304-L stainless steel corrosion rates in boiling solutions initially 6M NH_4F -0.5M NH_4NO_3 and 7.5M NF -0.5M HNO_3 as a function of dissolved zirconium. These measurements were made in the absence of dissolving zirconium. Hence, no evolved ammonia was present to increase the pH and the corrosion rates are factors of 20 to 50 higher than would be expected in the presence of dissolving zirconium.

FIGURE 2. Partial Dissolution of Oxide-Coated Zircaloy-2 in 5.5M NH_4F -0.5M NH_4NO_3 and 7.5M NH_4F -0.5M NH_4NO_3

TABLE VIII. 304-L Stainless Steel Corrosion Rates

Solution Composition, M			Corrosion Rate, mils/mo.
NH_4F	NH_4NO_3	$(\text{NH}_4)_2\text{ZrF}_6$	
7.5	0.5	-	50
6.18	0.4	0.22	40
4.86	0.3	0.44	47
2.22	0.2	0.88	36
6.0	0.5	-	57
4.38	0.4	0.27	49
3.24	0.3	0.46	62
1.92	0.2	0.68	55

HYDROGEN EVOLUTION DURING ZIRCALOY-2 DISSOLUTION IN 7.5M NH_4F -0.5M NH_4NO_3

Results of hydrogen determinations on Zirflex process off-gas resulting from dissolution of Zircaloy-2 in 7.5M NH_4F -0.5M NH_4NO_3 are shown in the following tabulation. The gas when analyzed was dry. During actual dissolution, however, the off-gas will be diluted with water vapor, and the hydrogen concentration will be correspondingly lower.

<u>Zirconium Concentration</u>	<u>% Hydrogen (V/V)</u>
0.00 M	2.20
0.30 M	2.50

DISCUSSION

A solution of composition 5.5M NH_4F -0.5M NH_4NO_3 is presently used to remove Zircaloy-2 from N-reactor fuel. With this reagent, prolonged digest times were sometimes required to sufficiently pit the cladding for subsequent core leaching with nitric acid. This prolonged pitting time resulted in substantial conversion of core material to uranium(IV) fluoride.

Data in Tables I through III confirm the relative inability of 5.5M NH_4F -0.5M NH_4NO_3 to pit oxide-coated Zircaloy-2. Data in Table I also show ammonium fluoride-ammonium nitrate solutions

containing 3.5M, 4.5M and 6.5M NH_4F pit oxide-coated Zircaloy no better than those containing 5.5M NH_4F .

The relatively high initial dissolution rate of non-oxide-coated Zircaloy-2 (see Figure 1) in 5.5M NH_4F -0.5M NH_4NO_3 is another serious though less obvious disadvantage because, once pitted, the cladding is rapidly penetrated and the core is exposed to the relatively undepleted Zirflex reagent. Because this reagent so poorly pits the cladding, a substantial conversion of core material to uranium(IV) fluoride may occur during extended periods of exposure.

In contrast, a 40 min exposure of oxide-coated Zircaloy-2 to 7.5M NH_4F -0.5M NH_4NO_3 was found to produce a relatively large number of pits. The large number of these pits, in combination with the lower initial Zircaloy dissolution rate should result in a more uniform removal of cladding and exposure of the core to undepleted decladding reagent.

Two additional advantages of 7.5M NH_4F -0.5M NH_4NO_3 over 5.5M NH_4F -0.5M NH_4NO_3 are the higher possible terminal zirconium concentration and the decreased time required to reach this terminal concentration. Although Figure 2 indicates that 0.42M zirconium is reached faster in 5.5M NH_4F -0.5M NH_4NO_3 , current processing procedure calls for approximately a 0.75M terminal zirconium concentration. This concentration was actually reached much faster with 7.5M NH_4F -0.5M NH_4NO_3 than with 5.5M NH_4F -0.5M NH_4NO_3 . In fact, terminal zirconium concentrations of 0.85M are possible with moderately increased digest times.

Stainless steel (304-L) corrosion rates in 7.5M NH_4F -0.5M NH_4NO_3 appear comparable to corrosion rates in 5.5M NH_4F -0.5M NH_4NO_3 . Corrosion rates given in Table VIII were obtained when no Zircaloy was dissolving and hence with no ammonia being liberated. Consequently, these rates are at a factor of 20 to 50 higher than might actually be expected.

As in the present Zirflex Process, dilution of the spent decladding solution will be necessary to prevent precipitation. Addition of one liter of water to 0.6 liters of decladding solution will prevent precipitation of ammonium heptazirconate at 50 °C. Analysis of off-gas by gas chromatography showed that the evolution of hydrogen during dissolution of Zircaloy in 7.5M NH_4F -0.5M NH_4NO_3 is not markedly different than during dissolution of Zircaloy in 5.5M NH_4F -0.5M NH_4NO_3 .

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