MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0059783 3

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

2

ORNL-3118
UC-10 – Chemical Separations Processes
for Plutonium and Uranium

Abst.
3.4

A STUDY OF DISSOLUTION OF REACTOR FUELS CONTAINING ZIRCONIUM IN A TITANIUM VESSEL

W. E. Clark
T. A. Gens

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

Printed in USA. Price $0.50. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D.C.

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.

ORNL-3118

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

A STUDY OF DISSOLUTION OF REACTOR FUELS CONTAINING ZIRCONIUM IN A TITANIUM VESSEL

W. E. Clark
T. A. Gens

Technicians:

J. F. Talley
E. R. Johns

DATE ISSUED

OCT 9 1961

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0059783 3

ABSTRACT

Titanium, which serves adequately as the construction material in processes which have been proposed for dissolution of reactor fuels containing stainless steel, might also be used for the dissolver vessel in dissolution of fuels containing zirconium. Titanium was corroded at rates as low as 2-20 mils/month during dissolution of zirconium alloys at rates of 0.3-1.2 mils/min ($\sim$5-20 mg/cm^2 . min) in 6 M NH_4F or 0.5 M HBF_4 containing dissolved zirconium, 0.4-0.6 M chromate, and 0.5-6 M NH_4NO_3 or HNO_3. In 16 M HNO_3-0.58 M Cr-1.9 M F-0.5 M Zr, the Zircaloy-2 dissolution rate was >0.1 mil/min and the titanium corrosion rate <3 mils/month. Aggressive localized corrosion, apparently associated with chromate depletion, was observed in the ammonium fluoride and fluoboric acid dissolvents.

CONTENTS

		Page
1.0	Introduction	4
2.0	Scouting Experiments	5
2.1	Effect of Additives on Titanium Corrosion and Zirconium Dissolution Rates	5
2.2	Zirconium Solubility in Acid Fluoborate	14
2.3	Test Procedures	14
2.4	Discussion and Conclusions	15
3.0	Strong Nitric Acid-Chromate Protection of Titanium Against Dilute Fluoride	15
3.1	Flowsheet	16
3.2	Titanium Corrosion Rates	17
3.3	Zircaloy Dissolution Rates	20
3.4	Discussion and Conclusions	21
4.0	References	22

1.0 INTRODUCTION

Scouting tests were made to indicate the feasibility of dissolving zirconium alloy fuels in titanium equipment. A promising dissolution method, based on inhibition of titanium corrosion observed when chromate was present in the dissolver, was examined in more detail. The adoption of titanium as the material of construction for Darex (stainless steel—containing fuel, dilute aqua regia reagent) processing equipment plus the surprisingly satisfactory performance of titanium in the Thorex dissolvent (1) led to the hope that process conditions could be developed that would allow zirconium-containing fuel elements to be dissolved in titanium processing equipment.

The dissolution and corrosion behavior of titanium and zirconium are very similar. The principal difference from a practical point of view is that titanium is the more resistant of the two in oxidizing solutions while zirconium is more resistant under reducing conditions and is more readily attacked by fluoride solutions. This is postulated as resulting from the greater stability of fluozirconate complexes compared to that of fluotitanates. The value of k for dissociation of the hexafluozirconate ion, $ZrF_6^{=} \rightleftharpoons ZrF_4 + 2F^-$ has been reported (2) as 6×10^{-34}. Values determined (3) for the formation of intermediate complexes of zirconium and fluoride are

$$ZrF^{4+} + HF \rightleftharpoons ZrF^{3+} + H^+ \qquad k_1 = 6.3 \times 10^5$$

$$ZrF^{3+} + HF \rightleftharpoons ZrF_2^{2+} + H^+ \qquad k_2 = 2.1 \times 10^4$$

$$ZrF_2^{2+} + HF \rightleftharpoons ZrF_3^{+} + H^+ \qquad k_3 = 6.7 \times 10^2$$

These data leave no doubt as to the stability of fluoride complexes of zirconium, but, unfortunately, comparable quantitative data for the corresponding titanium complexes are not available.

Two distinct types of titanium behavior applicable to the present problem have been recognized. The first type is due to the well-known phenomenon of passivity usually observed in oxidizing environments, in which aggressive corrosion of the metal ceases rather abruptly when a critical potential is reached. The excellent resistance of titanium to many usually

corrosive solutions can be explained by the fact that for titanium this potential has an unusually active (negative) value (4). The second type depends on the fact that the rate of attack of titanium in acidic ammonium fluoride solutions decreases rather abruptly with increase in the concentration of ammonium fluoride above certain rather high values in the range 4-6 M. The potential behavior of the titanium in these solutions is markedly different from that in the former case in that the potential of the metal continues to decrease with increasing ammonium fluoride concentration even though the corrosion rate decreases (5). Attempts have been made (5) to explain this phenomenon on the basis of a "salt film" coupled with hydrogen overvoltage effects, but no current explanation of the effect is entirely satisfactory (6).

In the present study, the behaviors of zirconium and titanium were investigated simultaneously in a variety of solutions chosen to accentuate the known differences in the chemical resistance of the two metals. The greater number of exposures were made in fluoride solutions to which oxidizing agents had been added.

The writers acknowledge the assistance of the Analytical Chemistry groups headed by C. Feldman and G. R. Wilson who analyzed residual solids and saturated solutions from selected experimental runs. A number of the corrosion tests were run by members of the Reactor Chemistry Division, notably L. Rice, E. S. Snavely, and D. N. Hess. The helpful suggestions and encouragement of R. E. Blanco are gratefully acknowledged.

2.0 SCOUTING EXPERIMENTS

Aqueous processing of zirconium-uranium alloys presents a particularly difficult problem since it is desirable that sufficient oxidant always be present to oxidize uranium to the hexavalent state in order to avoid formation of insoluble uranium tetrafluoride. In the case of uranium-zirconium alloys containing more than 75% uranium, sufficient fluoride must be present to prevent explosion of the alloy in the oxidizing solution (7).

2.1 Effect of Additives on Titanium Corrosion and Zirconium Dissolution Rates

Chromate in Acid Fluoride Solution. In experiments aimed at complete dissolution of 93% zirconium—7% uranium alloy in hydrofluoric and fluoboric

acids in the presence of various additives (Table 1), chromate clearly decreased the corrosion rate of titanium, although no quantitative relations can be drawn from the data. Aluminum and iron were considerably less effective than chromate. Corrosion rates were lowest, 4.1-7.1 mils/month, in a solution containing 0.5 M HBF_4, 3 M HNO_3, and 0.6 M chromate [0.3 M $(NH_4)_2Cr_2O_7$]. The effect of acid concentration was not clear-cut, although it appeared that HNO_3 up to about 3 M increased the alloy dissolution rate. In every case the dissolution rate of Zircaloy-2 was satisfactory in acid fluoride solutions, with penetration rates varying from 0.3 to 0.5 mil/min (Table 2). In most cases the Zircaloy dissolved at a remarkably uniform rate. In some cases the square billets used retained their original shape and square corners after having lost three-quarters of their weight, and had a shiny surface very similar in appearance to an electropolished finish.

The overall corrosion rate of titanium coupons was 68.4 mils/month in 0.5 M HBF_4—3 M HNO_3—0.3 M $(NH_4)_2Cr_2O_7$ that was dissolving 93% uranium—7% zirconium coupons (prototype EBWR core alloy). Excess ammonium dichromate solution was added at intervals during the 3-hr dissolution to maintain an appreciable concentration of Cr(VI). The final solution was 0.31 M in uranium, 0.17 M in zirconium, and 0.27 M in niobium. A white precipitate was visible in the final solution after cooling. Dissolution of the EBWR specimen was irregular, and not all the Zircaloy-2 cladding was removed.

Other 3-hr dissolution tests of this same type were run with refluxing solutions under the conditions:

(1) Initial solution: 0.5 M HBF_4—3 M HNO_3—0.3 M $(NH_4)_2Cr_2O_7$, 100 ml; 25 ml of 0.05 M $(NH_4)_2Cr_2O_7$ added in three separate charges of ~8 ml each at ~40-min intervals

(2) Initial solution: 0.5 M HBF_4—5 M HNO_3—0.6 M CrO_3, 100 ml

In each case the overall corrosion rate of the titanium was 170 mils/month. The titanium specimen used in test 1 suffered particularly severe localized corrosion in the vapor phase. The EBWR dissolution specimen, though heavily attacked, still retained a part of its zirconium cladding. The resultant solution was 0.17 M in zirconium, 0.29 M in uranium, and 0.003 M in niobium.

Table 1. Corrosion of Titanium during Dissolution of 93% Zirconium—7% Uranium Alloy in Acid Fluoride Solutions

Specimens exposed 1 hr in boiling solution, in solution phase only

Solution Composition, M						Zr-U Alloy Dissolution Rate, mils/min	Titanium Corrosion Rate, mils/mo
K_2CrO_4	HNO_3	HF	HBF_4	$Fe(NO_3)_3$	CH_3COONH_4		
--	--	3	--	1	1	Satis	3770
--	--	1	--	1	1	Local[a]	0
--	--	--	1	1	0.5	>0.52	2170
--	--	--	1	1	--	>0.5	2040
--	--	--	0.5	1	0.25	0.58	134.2
--	--	1.5	--	--	1	Local[a]	824
0.25	--	1.5	--	--	--	Local[a]	26.2
0.25	--	1	--	0.6	--	Local[b]	630
0.25	--	--	0.5	--	--	0.33	3840
0.25	--	--	0.5	1	--	Local[a]	1.31
0.25	--	--	1	1	0.25	≤0.66	14.5
0.5	6	--	0.5	1	--	0.72	3.2
0.1	3	--	0.5	0.5	--	>1.0	513
0.1	3	--	0.5	--	--	>1.0[c]	101

[a]Highly localized attack; probably unsatisfactory from a practical dissolution standpoint.

[b]Localized attack; possibly satisfactory from a practical dissolution standpoint.

[c]Solution also contained 0.5 M $Al(NO_3)_3$.

The zirconium cladding of the specimen from solution 2, on the other hand, was completely dissolved and the final solution was 0.26 M in zirconium, 0.69 M in uranium, and 0.002 M in niobium. White precipitates were observed in both solutions on cooling.

Chromate in Neutral Fluoride Solution. In almost neutral ammonium fluoride dissolutions (modified Zirflex), chromate also appeared to be the most important factor in decreasing corrosion (Table 3). Nitrate was slightly beneficial, and the effect of buffers (e.g. citrate) was not

Table 2. Corrosion of Titanium during Dissolution of Zircaloy-2 in Acid Fluoride Solutions

Specimens exposed 1 hr in boiling solution, in solution phase only

Solution Composition, M							Zircaloy Dissolution Rate, mils/min	Titanium Corrosion Rate, mils/mo
$CrO_4^=$	HNO_3	HF	HBF_4	$Fe(NO_3)_3$	$Al(NO_3)_3$	NH_4F		
0.1[a]	3	--	0.5	--	0.5	--	0.82	249
0.1[a]	6	--	0.5	--	0.5	--	0.66	562
0.1[a]	9	--	0.5	--	0.5	--	1.18	730
0.3[a]	3	--	0.5	--	0.5	--	0.92	132
0.1[a]	0	--	0.5	--	0.5	--	0.32	4553
0.1[a]	1	--	0.5	--	0.5	--	0.36	27.2
0.6[b]	6	--	0.5	--	0.5	--	0.66	78.8
0.2[b]	6	--	0.5	--	0.5	--	0.66	159.4
0.6[b]	6	2	--	--	0.5	--	0.82	91
0.6[b]	6	--	0.5	--	1.0	--	0.66	42
0.6[b]	3	--	0.5	1	--	--	0.39	22.0
0.6[b]	3	--	0.5	0.5	--	--	0.52	13.9
0.6[b]	3	--	0.5	0.2	--	--	0.66	23.9
0.6[b]	3	--	0.5	--	--	--	0.66	4.1
0.6[b]	3	--	0.5	--	--	--	0.69	7.1
0.8[b]	3	--	0.5	1	--	--	0.46	18.0
0.4[b]	3	--	0.5	1	--	--	0.59	36.8
0.2[b]	3	--	0.5	1	--	--	0.82	45.5
--	3	--	0.5	1	--	--	1.02	920
0.6[b]	3	--	0.5	--	--	1	0.66	12.5
0.3[a]	--	--	0.5	0.5	--	2	~0.17	24.5
0.3[a]	--	--	0.5	--	0.5	2	~0.27	50.8

[a]Added as CrO_3.

[b]Added as $(NH_4)_2Cr_2O_7$.

Table 3. Corrosion of Titanium during Dissolution of Zircaloy-2 in Modified Zirflex Solutions

Specimens exposed 1 hr in boiling solution, in solution phase only

Solution Composition, M					Zircaloy-2 Dissolution Rate, mils/min	Titanium Corrosion Rate, mils/mo
$(NH_4)_2Cr_2O_7$	NH_4NO_3	NH_4F	$(COO)_3(NH_4)_3$	H_2O_2		
0.1	1	6	--	--	0.49	55.7
0.1	1	6	0.1	--	0.79	2.1
0.1	1.5	6	0.1	--	0.36	15.1
0.1	2	6	0.1	--	0.30	18.6
0.1	0.5	6	--	--	0.62	271
0.2	1	6	--	--	0.72	2.0
0.3	1	6	--	--	0.62	10.5
--	1	6	--	--	0.79	635
0.3	--	6	--	--	0.62	33
0.3	0.5	6	--	--	0.59	8.0
--	1	6	--	0.1	0.79	779
--	1	6	0.1	0.1	0.75	508
--	--	6	0.1	0.1	0.69	1650
--	--	6	--	0.1	0.62	1790
0.1	1.5	--	0.1	--	0.033	20[c]
0.1	1	5	0.3	--	0.62	310
0.1	--	5	0.3	--	0.49	357
0.2	1	6	--	--	Poss. satis[a]	25.8
0.2	1	6	--	--	Satis[b]	23.2

[a]EBWR core alloy, 2.5 hr exposure; green precipitate observed in cold solution.

[b]EBWR core alloy, 3 hr exposure; green precipitate observed in cold solution. Alloy composition is 93.5% uranium, 1.5% niobium, 5% zirconium.

[c]Solution also contained 2 M NH_4BF_4.

clearly significant. Peroxide, in contrast to other oxidants, accelerated corrosion, perhaps because it caused reduction of Cr(VI) to a lower valence state. Rates were minimum, 2 to 10 mils/month, in solutions 6 M in NH_4F, 0.5 to 1 M in NH_4NO_3, and 0.1 to 0.3 M in $(NH_4)_2Cr_2O_7$.

The substitution of ammonium fluoborate for ammonium fluoride not only did not decrease the corrosion of the titanium but also decreased the

dissolution rate of Zircaloy-2 by a factor of ~20. The dissolution of Zircaloy-2 was satisfactory in all ammonium fluoride solutions tested, though usually a large amount of solids was present in the container at the end of the experiment. Most of these solids redissolved on reheating or dilution with water.

Other Additives. Scouting dissolution-corrosion tests were run in a number of miscellaneous solutions. Chloride-nitrate mixtures were unsatisfactory because of both low dissolution rates and high corrosion rates (Table 4). The addition of molybdate to the Thorex dissolvent did

Table 4. Corrosion of Titanium and Dissolution of Zircaloy-2 in Miscellaneous Solutions

Specimens exposed 1 hr in boiling solution, in solution phase only

Solution Composition	Titanium Corrosion Rate, mils/mo	Zircaloy-2 Dissolution Rate, mils/min
Zero or Low Fluoride		
6 M HCl—1 M HNO_3	27.4	0.033
6 M HCl—1 M $Fe(NO_3)_3$	6.1	0.033
6 M HCl—1 M HNO_3--0.05 M HBF_4	434	0.2
6 M HCl—1 M $Fe(NO_3)_3$—0.05 M HBF_4	583	0.23
6 M HCl—1 M $Fe(NO_3)_3$—1 M CrO_3	1.1	0
15.8 M HNO_3—0.04 M NH_4F—0.5 M MoO_3 (slurry)	72	0.033
10 M HNO_3—0.04 M NH_4F—0.5 M $(NH_4)_6Mo_7O_{24}$	79.6	0.033
Acid, High Fluoride		
6 M NH_4F—1 M HF	55	1.18
6 M NH_4F—1 M HF--0.1 M $(NH_4)_2Cr_2O_7$	76.5	0.69
6 M NH_4F—0.5 M HBF_4	87.0	1.08

not result in a satisfactory dissolution rate. Perhaps the most interesting solutions studied in this series were those listed as "Acid, High Fluoride" in which titanium showed the previously described (5,6) decrease in corrosion

rate with increased fluoride concentration. The failure of chromate to further decrease the corrosion rate (i.e. to <55 mils/month) in this solution is not surprising in view of the low potential of the titanium.

Corrosion in Consecutive Dissolution Tests. In consecutive dissolution tests the overall corrosion rate of titanium in neutral ammonium fluoride dissolvent was almost three times that in acid fluoborate, 15.8 vs 5.7 mils/month (Fig. 1). The difference in rates based on the final linear slopes of weight loss vs number of dissolutions was even greater,

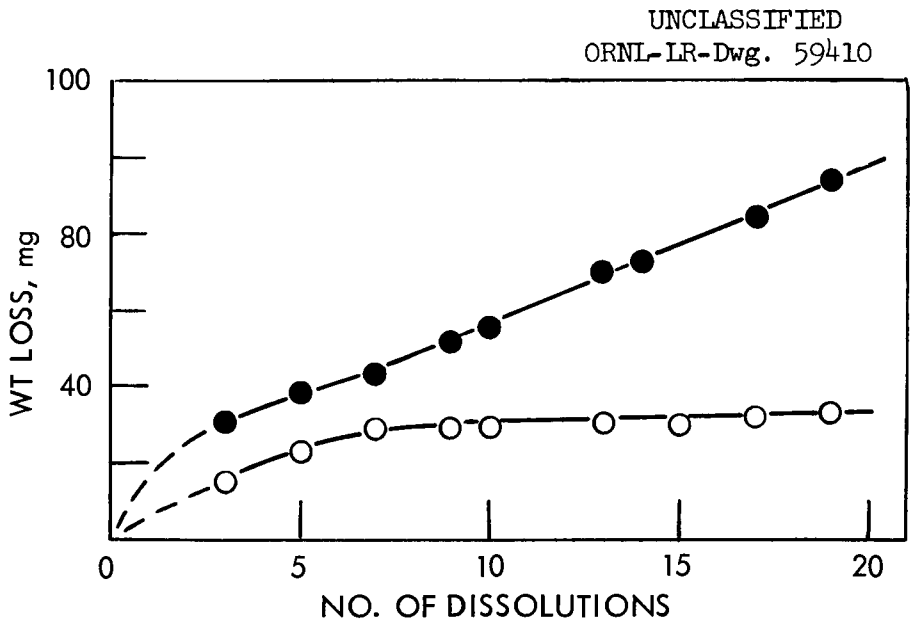

Fig. 1. Corrosion of titanium during cyclic dissolution of Zircaloy-2. Nominal cycle time = 1 hr.

	Dissolvent	Corrosion Rate, mils/mo Overall	Final
●	6 M NH_4F—1 M NH_4NO_3—0.2 M $(NH_4)_2C_2O_4$	15.82	13.6
○	0.5 M HBF_4—3 M HNO_3—0.3 M $(NH_4)_2Cr_2O_7$	5.72	1.21

with the fluoborate curve leveling off at 1.2 mils/month vs a steady rate of 13.6 mils/month for the ammonium fluoride solutions. There was, however, some pitting in the area just above the interface in the fluoborate solution, while in the ammonium fluoride solution there was roughening over essentially the whole area of the specimen, which was covered with a dark deposit or residue. The consecutive dissolutions (19) in each reagent were made in all-plastic reflux systems to eliminate any effect of products of fluoride attack on the glass. The titanium corrosion specimens were strips that extended from the bottom of the pot into the vapor phase, with ~1/3 below the level of the solution.

Effect of Ferric Chromate.* Dissolution tests (8) indicated that 7% uranium—93% zirconium alloy can be dissolved in 1 M hydrofluoric acid containing ferric ion. In a solution 1 M in hydrofluoric acid and 0.2 M in ferric dichromate, the liquid phase corrosion rate varied from 17 mils/month at 24 hr to 9 mils/month at 294 hr:

24 hr	72 hr	144 hr	294 hr
17.2	13.6	10.8	8.7
18.1	13.9	13.3	8.9

Effect of Palladium.* Short-term corrosion tests were run on titanium 45A and titanium—0.2% palladium alloy specimens in various boiling solutions of ammonium fluoride—ammonium nitrate and fluoboric acid—nitric acid with and without simultaneous dissolution of zirconium. The results (Table 5) indicate that neither titanium nor the precious metal alloy can be expected to withstand Zirflex dissolvent in the absence of zirconium, even with chromate additions. The addition of the precious metal to the titanium appears to offer no advantage for use in this particular solution.

Effect of Nitric Acid.* In a series of 24-hr tests titanium specimens were exposed to boiling 0.5 M fluoboric acid—0.3 M ammonium dichromate plus 3 to 15 M nitric acid, both with and without the presence of dissolving zirconium. The results (Table 6) indicated that increasing the concentration of nitric acid above about 3 M increased the corrosion rate with

*Tests carried out by personnel of the Reactor Experimental Engineering Division, ORNL.

Table 5. Corrosion of Titanium-45A and of Titanium—0.2% Palladium Alloy in Boiling Fluoride-containing Solutions

Test period: 24 hr

Solution	Specimen	Corrosion Rate, mils/mo		
		Vapor	Interface	Solution
6.0 M NH_4F—1.0 M NH_4NO_3	Ti-45A	59.0	>500[a]	>500[a]
	Ti-0.2% Pd	13.0	>500[a]	>500
6.0 M NH_4F-1.0 M NH_4NO_3 —0.2 M $(NH_4)_2Cr_2O_7$	Ti-45A	4.3	41.0	41.0
	Ti-0.2% Pd	7.4	52.0	59.0
6.0 M NH_4F—1.0 M NH_4NO_3 —0.2 M $(NH_4)_2Cr_2O_7$, dissolving Zr present	Ti-45A	2.0	8.5	10.0
	Ti-0.2% Pd	0.2	5.0	9.0
6.0 M NH_4F—0.5 M NH_4NO_3 —0.5 M HF	Ti-45A	13.0	211.0	>500
	Ti-0.2% Pd	190[b]	>500	>500[b]
0.5 M HBF_4—0.3 M $(NH_4)_2Cr_2O_7$ —3 M HNO_3	Ti-45A	3.1	40.0	50.0
	Ti-0.2% Pd	Wt gain	90.0	110.0
0.5 M HBF_4—0.3 M $(NH_4)_2Cr_2O_7$ —3 M HNO_3, dissolving Zr present	Ti-45A	0.5	16.0	19.0
	Ti-0.2% Pd	0.4	16.0	22.0

[a]Specimen disintegrated.
[b]Test stopped before 24 hr because of rapid disintegration of specimen.

Table 6. Corrosion Rates of Titanium-45A in 0.5 M Fluoroboric Acid—0.3 M Ammonium Dichromate

Test period: 24 hr

HNO_3 Solution, M	Corrosion Rate, mils/mo					
	No Zirconium Present			Dissolving Zirconium Present		
	Vapor	Interface	Solution	Vapor	Interface	Solution
3.0	3.1	40.0	50.0	0.5	16.0	19.0
9.0	19,16	110,120	150,150	1.6,1.1	66,130	140,140
12.0	4.7,35	170,175	260,295	2.9,2.0	110,29	110,110
15.0	1.0, 1.9	180,210	270,270	1.7,1.7	94,77	180,190

or without the presence of zirconium. These results, however, are not in agreement with those in solutions much lower in free fluoride, where both dichromate and more concentrated nitric acid produced a decided reduction in titanium corrosion rates (Figs. 3a and b, Sect. 3.0).

2.2 Zirconium Solubility in Acid Fluoborate

The concentration of zirconium in solution in acid fluoborate dissolvent was about the same as that in almost neutral ammonium fluoride solution:

0.5 M HBF_4—3 M HNO_3—0.3 M $(NH_4)_2Cr_2O_7$	0.29 M Zr(IV)
6 M NH_4F—1 M NH_4NO_3—0.2 M $(NH_4)_2Cr_2O_7$	0.33 M Zr(IV)

These two tests were run with 150 ml of refluxing dissolvent, which was allowed to react to completion (4.5 to 5 hr) with excess Zircaloy-2; the solutions were cooled and centrifuged to remove solids, and the zirconium concentration of the supernatant was determined.

2.3 Test Procedures

The majority of the tests were of a scouting nature to find a set of conditions that would justify running full-scale corrosion tests. The usual test therefore consisted in dropping loose specimens of titanium and Zircaloy-2 or 93% zirconium-7% uranium alloy into the boiling solution in a round-bottomed glass flask equipped with a reflux condenser. Tests were allowed to run 1 hr, after which the solution was poured off and the specimens were dried and weighed. The corrosion rate of the titanium was calculated from the weight loss and the apparent area of the specimen while the dissolution rate of the alloy specimen was estimated by micrometer measurement of the dimensions of the specimen before and after the test. The corrosion results given for titanium are very approximate, particularly for the lower rates, since in these cases the weight losses of the specimen were extremely small and approached the same order of magnitude as the weighing error. When the attack on the dissolution specimen was too small to be measured accurately or was extremely localized, the attack was considered unsatisfactory from the standpoint of a practical dissolution process.

2.4 Discussion and Conclusions

Titanium equipment could probably be safely used for dissolution of zirconium as an interim method or on an emergency basis, but careful control of the process would be required. In general, acid solutions appear better both from the standpoint of solids in solution and from that of corrosion of titanium than the ammonium fluoride solutions. They are not, however, suitable for use in decladding processes since they attack the core materials.

Oxidants (e.g. chromate) protect the titanium by raising its potential above that required for passivation. Local depletion of the chromate [an anodic controlling inhibitor (9,10)] will therefore lead to aggressive local attack of the same general nature as that observed with iron and its alloys in solutions that contain slightly less than enough inhibitor to maintain complete protection. Reduction of chromate by actively dissolving zirconium makes it difficult to ensure that the chromate concentration is kept above that required for complete passivation.

From the behavior of titanium in the solutions studied there appears to be a slight possibility of finding a cathodic controlling inhibitor that would be effective when used in conjunction with the decrease in corrosion rate observed in concentrated fluoride solutions. If this type of inhibitor can be found, the probability of aggressive localized corrosion will be greatly diminished (4). However the low values of the potential assumed by titanium in these solutions (4) indicate that the observed phenomenon may be due to such a mechanism. If so, the corrosion rates observed may be about as low as can be attained in this type of solution.

3.0 STRONG NITRIC ACID-CHROMATE PROTECTION OF TITANIUM AGAINST DILUTE FLUORIDE

Further attempts were made to develop a satisfactory strong nitric acid dissolvent for zirconium alloys in titanium equipment because of the potential advantages of strong nitric acid: (a) It passivates titanium (11) and significantly protects it from fluoride concentrations up to 0.05 M (12); (b) It oxidizes back to Cr(VI) part of the chromate additive that has been

reduced to Cr(III) by dissolving zirconium (13); (c) It produces an off-gas containing 0.1% each of hydrogen and nitrous oxide (14), 6% hydrogen being considered explosive in the presence of NO and NO_2 (15). Further work is planned on an accurate method of monitoring the mole ratio of fluoride to dissolving zirconium, and on corrosion of stainless steel or titanium in steam-stripping and of stainless steel in nitric-hydrofluoric acid containing zirconium at F/Zr ratios less than 4.

3.1 Flowsheet

An unproved flowsheet (Fig. 2) is presented only to illustrate how the process might be applied to 6.3% uranium-Zircaloy-2 (PWR seed), to give an estimated uranium concentration in the solvent extraction feed of 0.013 M. This would increase plant throughput and decrease waste volumes over those in the hydrofluoric acid process in use at Idaho (16) and the proposed aqueous ammonium fluoride dissolution [modified Zirflex (17)], in which the feed uranium concentrations are 0.0015 and 0.007 M, respectively.

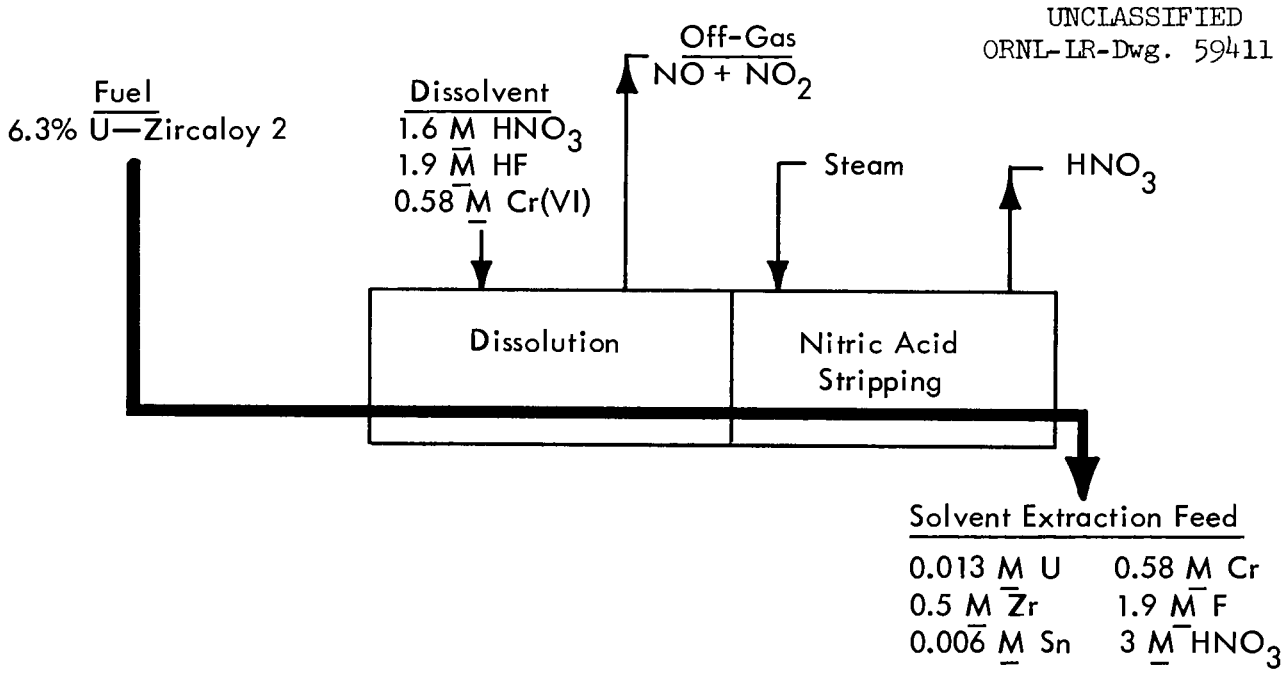

Fig. 2. Suggested process for dissolving reactor fuels containing zirconium in a titanium vessel.

The reagent, 16 M HNO_3--1.9 M HF—0.58 M Cr(VI), was selected to yield a product solution 0.5 M in zirconium, F/Zr = 3.8. The dissolvent is added slowly and continuously to a solution loaded with dissolution products, the rate of addition being equal to the rate of product removal so that reagent concentrations in the dissolver are almost constant at a level approximately equal to that in the product-withdrawal stream. The fluoride is replenished at the same rate at which it is complexed by the dissolving zirconium, this rate being determined by measuring the F/Zr ratio in the product.

A fuel reaction rate of 2 mg/cm^2.min (7.4 mils/hr) for high-zirconium alloys can be predicted from measured reaction rates, and a fuel element 70 mils thick or a clad 30 mils thick would dissolve in 3-5 hr. If the dissolution rate should actually be less, the zirconium (and uranium and tin) concentration in the solution would be lower with a constant rate of reagent addition, and a greater total volume of reagent would be needed. Oxide-coated Zircaloy would probably be more troublesome than in processes such as the Zirflex (18), in which the average Zircaloy dissolution rate is approximately the same as with the constant-rate dissolution proposed here, but the initial rate is perhaps 10-fold higher.

Titanium corrosion rates in the product solution should be satisfactory, <3 mils/month, if the zirconium concentration is high enough to produce a F/Zr ratio less than 5, but would increase rapidly if the F/Zr ratio should increase above 5.

The product is steam-stripped to decrease the nitric acid concentration to solvent extraction (tributyl phosphate) feed concentrations.

3.2 Titanium Corrosion Rates

Titanium corrosion rates were investigated in refluxing 3-15 M HNO_3 containing up to 0.05 M HF and no zirconium, and in refluxing 16 M HNO_3 containing 0.1-1.8 M HF, 0-1 M Cr, and enough dissolved zirconium to yield F/Zr ratios as low as 2. Vapor phase and interface corrosion rates have not yet been measured.

Nitric acid conconcentrations up to 9 M gave little indication of protecting titanium against dilute fluoride, but 15 M definitely protected the titanium, the corrosion rate being less than 15 mils/month at fluoride concentrations below 0.5 M (Fig. 3a). Corrosion rates were high, nearly

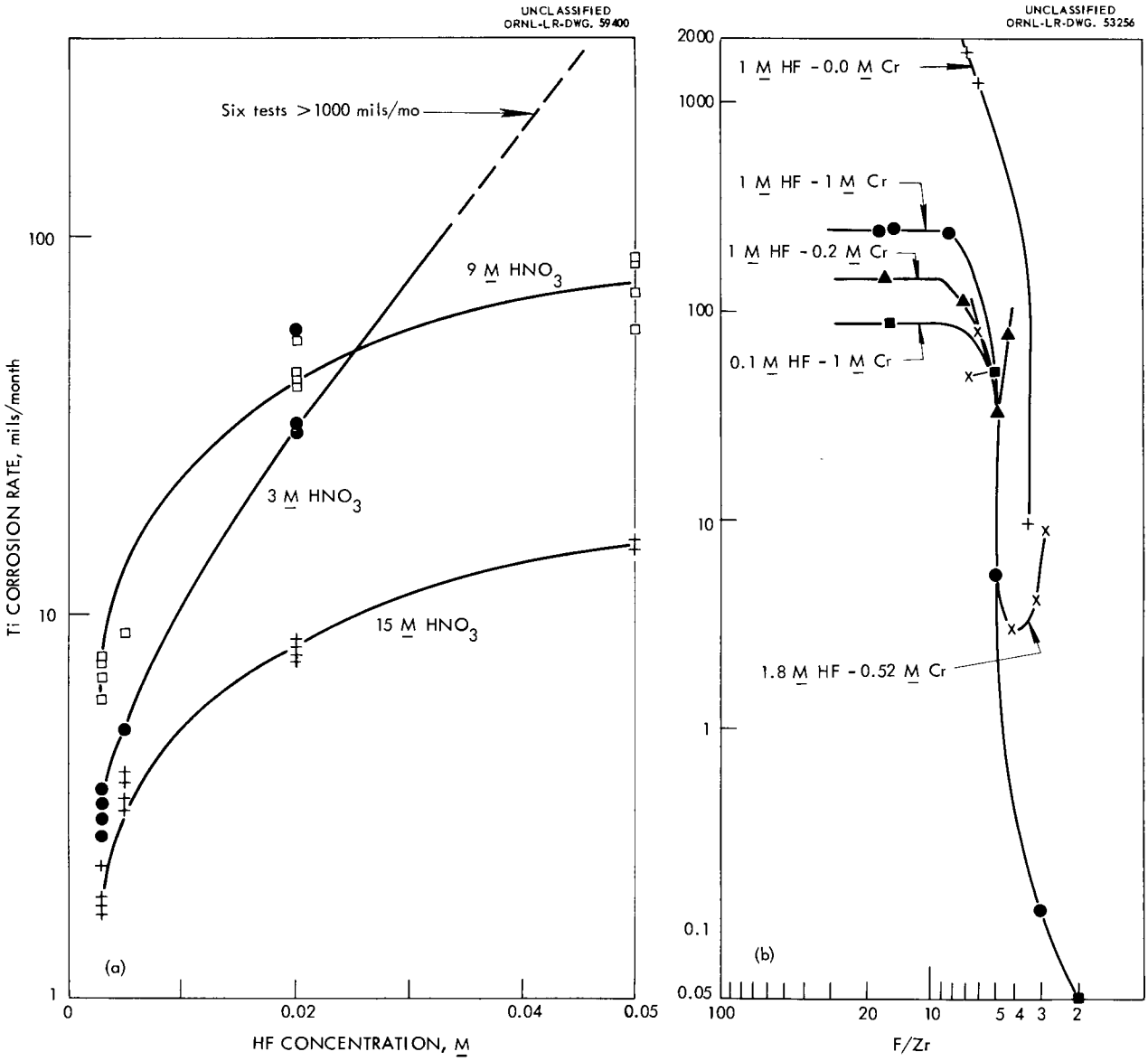

Fig. 3. Corrosion of (a) titanium 45A in various mixtures of nitric and hydrofluoric acids (12) (solution specimens only); and (b) titanium 65A in refluxing 16 M nitric acid--zirconium solution.

100 mils/month, in solutions containing 0.1 M HF when the F/Zr ratio was >5 (Fig. 3b). In the presence of Cr(VI) rates dropped very rapidly, by two orders of magnitude, as the F/Zr ratio was decreased below 5 but in the absence of Cr(VI) did not drop significantly until it was <3.5.

In 16 M HNO_3—1 M HF—0.2 M chromium the corrosion rate of titanium decreased rapidly as the F/Zr ratio decreased to 5, but increased rapidly when still more zirconium was put into solution (Fig. 3b). The corrosion rate was minimum in this run when the zirconium concentration was 0.2 M, the same as the chromium concentration, showing the importance of chromium being in its highest valence state. The color changed from deep red to green at this point, showing that the Cr(VI) had been reduced to Cr(III). Apparently, only about 10% of the oxidation of zirconium was performed by nitric acid, the remainder being by chromium.

The addition of 0.1 M $KMnO_4$ to 16 M HNO_3—1 M HF—0.2 M chromium did not conserve the Cr(VI); the decrease in corrosion rates ceased at the same zirconium concentration, 0.2 M. However, the permanganate did prevent a rapid increase in corrosion rates as more zirconium was dissolved, holding the rates to about 20 mils/month until a F/Zr ratio of 3.5 was approached and a further decrease in rates occurred.

Although chromium depressed the zirconium dissolution rate at the higher fluoride concentrations investigated (Sect. 3.3), it may be desirable to use high enough chromium and fluoride concentrations to produce a product solution containing at least 0.5 M zirconium. The most desirable product solution is probably close to that at the minimum of the 1.8 M HF—0.52 M chromium curve in Fig. 3b, where the F/Zr ratio is 3.9 and the zirconium concentration is 0.5 M. Since a F/Zr ratio below 4 is needed to permit further treatment of the product solution without adding large amounts of aluminum to complex fluoride, slightly more Cr(VI) should be used to significantly decrease the corrosion rates during dissolution. Solutions of 0.6 M zirconium in 16 M HNO_3—1.8 M HF—0.52 M chromium were stable several days at 25°C. Therefore the most desirable product solution appears to be about 16 M HNO_3—1.9 M HF—0.58 M chromium—0.5 M zirconium, F/Zr = 3.8. Such solutions containing 0.013 M uranium remained stable when stored two weeks at 25°C.

The dissolution rate of 7% uranium--zirconium alloy in the recommended reagent was 2.6 mg/cm^2.min, both with no uranium and 0.013 M in uranium. Increasing the nitric acid content to 18 M increased the Zircaloy-2 and 7% uranium—zirconium dissolution rates to 2.5 and 3.7 mg/cm^2.min, respectively, in the recommended reagent containing no uranium and to 2.0 and 2.8 mg/cm^2.min, respectively, when 0.013 M uranium was present.

In a continuous process the final zirconium concentration would be slightly higher than 0.5 M to produce an average zirconium concentration of 0.5 M. A continuous process is particularly applicable to enriched fuels such as the PWR seed, where a critically safe small-volume dissolver is needed. A batch process would probably be more difficult to operate because of the requirement that the F/Zr ratio be kept below 5 and the dependence of the zirconium dissolution rate on total fluoride as well as the F/Zr ratio (Sect. 3.3).

3.3 Zircaloy Dissolution Rates

In 16 M HNO_3 containing 0.1 M HF, the Zircaloy-2 dissolution rates increased as the chromium content of the solution increased from 0 to 1 M (Fig. 4). For example, at a F/Zr ratio in solution of 4, rates were 0.21, 0.29, and 0.48 mg/cm^2.min in 0, 0.2, and 1 M chromium, respectively. In contrast, in 16 M HNO_3 containing 1 M HF, the Zircaloy-2 dissolution rates decreased as the chromium content of the solution increased from 0.2 to 1 M, with dissolution rates of 4.1 and 1.4 mg/cm^2.min in 0.2 and 1 M chromium, respectively, at a F/Zr ratio in solution of 4. This depressing effect of chromium on Zircaloy-2 dissolution rates at higher fluoride concentrations is also seen in the curve for 16 M HNO_3—1.8 M HF—0.52 M chromium where, despite the higher fluoride concentrations, dissolution rates were lower than in 16 M HNO_3—1 M HF—0.2 M chromium.

In each experiment the Zircaloy-2 was immersed in the reagent for 15, 15, 30, 120, and 120 min, and the average dissolution rate based on weight loss and average surface area and the average F/Zr ratio in solution were calculated. In each case, the volume of reagent used in cubic centimeters was 20 times the initial Zircaloy-2 surface area in square centimeters. These rates at different F/Zr ratios, while not directly comparable, agree qualitatively with rates previously reported for dissolution of zirconium in nitric-hydrofluoric acid (14).

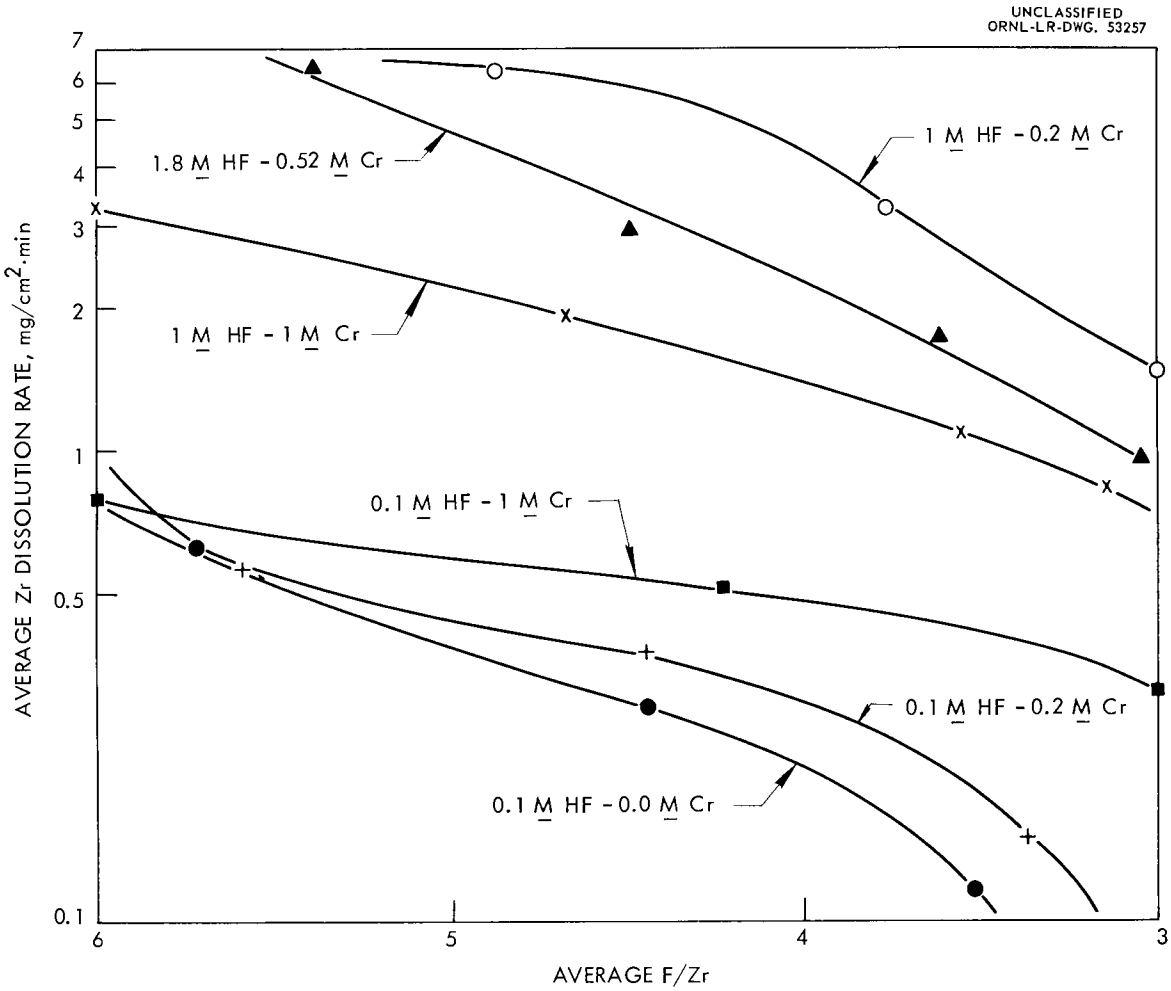

Fig. 4. Dissolution of zirconium in 16 M HNO_3—HF—$(NH_4)_2Cr_2O_7$.

3.4 Discussion and Conclusions

The selection of reagent concentrations to develop an operable flowsheet in the range of F/Zr ratios in solution of 5-3.5 should be possible, since titanium corrosion rates (Fig. 3b) are low but zirconium dissolution rates are still moderately high in this region (Fig. 4).

The only satisfactory alternative to keeping a high chromium concentration in the reagent is, apparently, to decrease the zirconium concentration, unless a means of conserving the Cr(VI) can be devised. Purging the system with nitrogen, using a downdraft condenser to prevent return of nitrous acid to the dissolver, or increasing the nitric acid concentration should conserve some Cr(VI). Acceptance of a higher F/Zr ratio (up to 5) in the

product solution would produce higher zirconium dissolution rates without significantly increasing titanium corrosion rates. This procedure would probably require the addition of some fluoride complexer, such as aluminum, to the solution before solvent extraction.

4.0 REFERENCES

1. C. L. Peterson, P. D. Miller, J. D. Jackson, and F. W. Fink, "Construction Materials for Various Head-end Processes for the Aqueous Reprocessing of Spent Fuel Elements," BMI-1375 (Aug. 28, 1959).
2. R. C. G. da Costa, Anales real. soc. espan. fis. y chim. (Madrid), Ser. B, 50: 799-808 (1954) [Chem. Abs. 49: 8734 (1955)].
3. R. E. Connick and W. H. McVey, J. Am. Chem. Soc., 71: 3182 (1949).
4. M. Stern and H. Wissenberg, J. Electrochem. Soc., 106: 755 (1959).
5. M. E. Straumanis and C. B. Gill, J. Electrochem. Soc., 101: 10 (1954).
6. M. E. Straumanis, S. T. Shih, and A. W. Schlechten, J. Electrochem. Soc., 102: 573 (1955).
7. R. Larsen, R. S. Shor, H. M. Feder, and D. S. Flikkema, "A Study of the Explosive Properties of Uranium-Zirconium Alloys," ANL-5135 (July 1954).
8. "Monthly Progress Report for Chemical Development Section B," for October 1959, ORNL-CF-59-12-20; March 1960, ORNL-CF-60-4-36; April 1960, ORNL-CF-60-5-106; July 1960, ORNL-CF-60-7-76.
9. U. R. Evans, "Metallic Corrosion, Passivity and Protection," Edward Arnold and Co., London, 2nd Ed., 1946, pp. 534-61.
10. H. H. Uhlig, "Corrosion Handbook," John Wiley and Sons, Inc., New York, 1948, pp. 905-8.
11. Ibid., p. 329.
12. L. Rice, Oak Ridge National Laboratory, Oak Ridge, Tennessee, private communication to W. E. Clark (June 1, 1960).
13. R. E. Blanco, "New Fuel Processing Procedures in Preparation for Solvent Extraction," in "Reactor Fuel Processing Costs: Papers Presented at the Idaho Symposium, January 18-20, 1956," IDO-14363 (Pt. II), p. 416.

14. E. M. Vander Wall, E. M. Whitener, and D. L. Bauer, "Dissolution of Zirconium and Zircaloy-2 in Nitric-Hydrofluoric Acid Mixtures at Reflux Temperatures," IDO-14497 (April 1960).

15. K. S. Warren, "A Survey of Potential Vapor-phase Explosions in Darex and Sulfex Processes," ORNL-2937 (December 1960).

16. D. G. Reid, C. E. Stevenson, R. B. Lemon, and F. K. Wrigley, "Zirconium Alloy Fuel Reprocessing," P/526, Proc. 2nd Internatl. Conf. Peaceful Uses Atomic Energy, Geneva, 1958, Vol. 17, UN, New York, p. 145.

17. T. A. Gens, "Modified Zirflex Process for Dissolution of 1-10% U-Zr Alloy Fuels in Aqueous NH_4F-NH_4NO_3-H_2O_2: Laboratory Development," ORNL-2905 (March 1960).

18. J. L. Swanson, "The Zirflex Process," P/2429, Proc. 2nd Internatl. Conf. Peaceful Uses Atomic Energy, Geneva, 1958, Vol. 17, UN, New York, p. 155.

ORNL-3118
UC-10 — Chemical Separations Processes
for Plutonium and Uranium
TID-4500 (16th ed., Rev.)

INTERNAL DISTRIBUTION

1. Biology Library
2-3. Central Research Library
4. Reactor Division Library
5. ORNL — Y-12 Technical Library
Document Reference Section
6-25. Laboratory Records Department
26. Laboratory Records, ORNL R.C.
27. E. D. Arnold
28. R. E. Blanco
29. G. E. Boyd
30. J. C. Bresee
31. K. B. Brown
32. F. R. Bruce
33. C. E. Center
34. W. E. Clark
35-36. F. L. Culler
37. D. E. Ferguson
38. L. M. Ferris
39. J. H. Frye, Jr.
40. T. A. Gens
41. J. H. Gillette
42. H. E. Goeller
43. A. T. Gresky
44. W. R. Grimes
45. C. E. Guthrie
46. C. W. Hancher
47. C. S. Harrill
48. A. Hollaender
49. A. S. Householder
50. R. G. Jordan (Y-12)
51. W. H. Jordan
52. M. T. Kelley
53. F. G. Kitts
54. J. A. Lane
55. T. A. Lincoln
56. S. C. Lind
57. K. Z. Morgan
58. J. P. Murray (K-25)
59. D. Phillips
60. H. E. Seagren
61. M. J. Skinner
62. J. A. Swartout
63. E. H. Taylor
64. J. W. Ullmann
65. W. E. Unger
66. A. M. Weinberg
67. M. E. Whatley
68. C. E. Winters
69. R. G. Wymer
70. J. W. Youngblood
71. C. E. Larson (consultant)
72. D. L. Katz (consultant)
73. T. H. Pigford (consultant)
74. H. Worthington (consultant)

EXTERNAL DISTRIBUTION

75. Division of Research and Development, AEC, ORO
76-585. Given distribution as shown in TID-4500 (16th ed., Rev.) under Chemical Separations Processes for Plutonium and Uranium category (75 copies — OTS)