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HYDROFLUORIC ACID DECLADDING OF ZIRCONIUM-CLAD POWER REACTOR FUEL ELEMENTS

W. E. Clark
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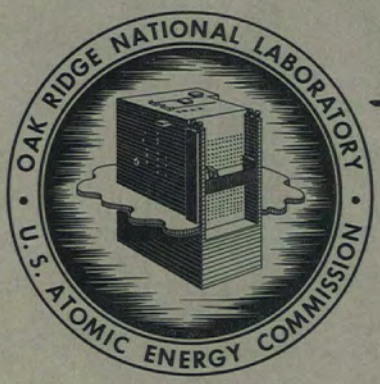

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Errata for ORNL-2460

On page 5 under "Reactions" the two $\triangle$ H values should be negative. Minus signs should therefore be inserted before the numerical values of 1.845.2 and 303.55.

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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ABSTRACT

A detailed flowsheet is presented for the removal of Zircaloy-2 cladding from a UO_2 core (as in the Commonwealth Edison fuel) by dissolution in hydrofluoric acid to give a F/Zr ratio of 4.5/1 in the solution. The core is dissolved in 8 M HNO_3 for subsequent removal of fission products by solvent extraction. In tests on unirradiated prototypes, uranium loss to the fluoride solution was as little as 0.16%. Dissolution data on uranium metal and U-10% Mo alloy indicate that these cores can be declad similarly. U-Zr alloys cannot be so stripped while U-Nb is somewhat doubtful. It appears that pure zirconium cladding can be removed about as easily as Zircaloy-2. One container constructed of Carpenter 20 (niobium stabilized) stainless steel can probably be used for both dissolution steps.

CONTENTS

1.0 INTRODUCTION

Though the use of zirconium and its alloys in fuel elements for nuclear reactors is desirable because of corrosion resistance and neutron economy, it presents a considerable problem in fuel reprocessing since these materials cannot be dissolved in the conventional dissolvents under ordinary conditions. Hydrofluoric acid, in which zirconium and many of its alloys dissolve readily, is objectionable in reprocessing streams because of its extreme corrosiveness in the acid solutions usually used. With fuel elements clad with zirconium or its alloys this difficulty can be eliminated by using HF only for removing the cladding, the core material being subsequently dissolved in a different reagent. This decladding process has the advantages of a rapid dissolution rate, a low-activity waste solution containing practically all the zirconium, and the elimination of all except traces of fluoride from subsequent processing steps.

A relatively large amount of information is available on the dissolution of zirconium and Zircaloy-2 in HF.[1,2] Exhaustive laboratory dissolutions were therefore considered unnecessary.

2.0 FLOWSHEET

The flowsheet proposed for decladding and dissolution of Commonwealth Edison fuel elements (Fig. 1, Table 1) uses 5 M HF initially, followed by addition of the remainder of the acid as 27 M HF during the second half hour of the reaction so as to give a final concentration of 9 M fluoride in the solution and a F^-/Zr ratio of 4.5/1. Under these conditions the decladding step requires about 2 hr for completion, and 2.5 hr is allowed to provide a safety factor. If for any reason an end cap should become passive it would pass through the nitric acid cycle without attack and would dissolve in the fresh acid in the next decladding cycle. The core dissolvent is 8 M HNO_3 at 90°C with a contact time of 5.5 hr. Dissolution of UO_2 is complete in this time. Dissolution time could be decreased greatly by using more concentrated nitric acid.

From the decladding solution $ZrF_4 \cdot 3H_2O$ crystallizes slowly over a period of several days as a hard mass of agglomerated crystals which adhere to the container. The composition of these crystals was determined independently at ICPP and at ORNL.[3,4] At HF concentrations above 12 M other crystalline species appear. The feasibility of draining off the supernatant acid, adding make-up HF, and recycling and storing the solid $ZrF_4 \cdot 3H_2O$ as low-activity-level waste has not been thoroughly evaluated. The principal technical difficulties appear to be the slowness with which the crystallization occurs and the difficulty of removing the hard agglomerated crystals from the container for transfer to storage. The $ZrF_4 \cdot 3H_2O$ can be immediately precipitated by adding acetone to the decladding solution (Fig. 2). Under these circumstances the crystals formed are small, do not adhere

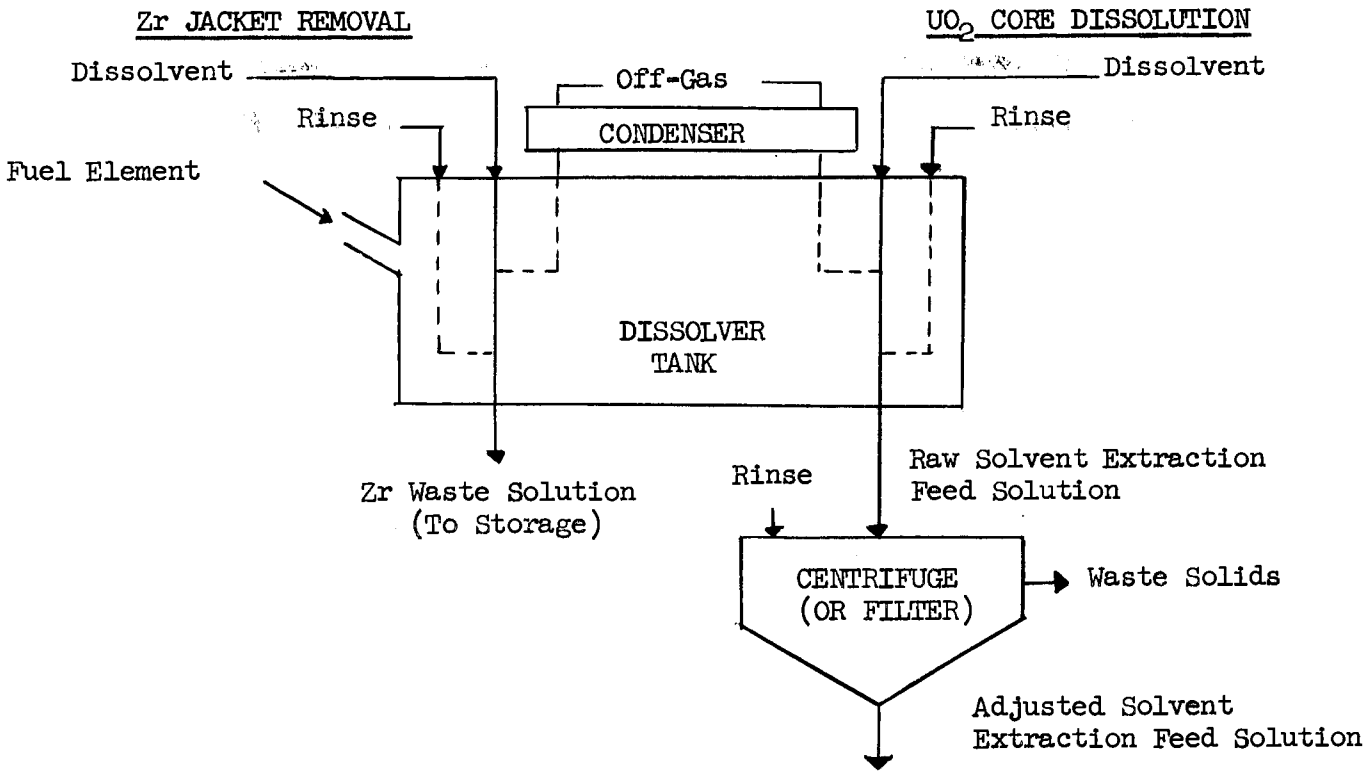

Fig. 1. Flowsheet for Zircaloy-2 Cladding Removal with HF (Commonwealth Edison Fuel).

Reactions:

$Zr^{o} + 4HF \longrightarrow ZrF_4 + 2H_2\uparrow$; $-\Delta H_{(max)} \cong 1{,}845.2$ kcal/subassembly

$2UO_2 + 6HNO_3 \longrightarrow 2UO_2(NO_3)_2 + NO + NO_2 + 3H_2O$; $-\Delta H = 303.55$ kcal/subassembly

The ΔH value for the first reaction is taken from ANL-4922, pp. 9-10; that for the second is calculated from values given in Handbook of Chemistry and Physics, 33rd ed., Chemical Rubber Publishing Co.

Procedure:

1. Add fuel to dissolver and add 4 liters of water and two 1-liter volumes of 27 N HF such that final volume is 6.0 liters at 9.0 N F^- ($F^-/Zr^{++} = 4.5/1$). The first volume is added immediately; after about 20 min the second volume is added slowly over a period of ~15 min. The temperature is held at >90°C for a total of 2 hr after the first acid solution is added.
2. Drain off dejacketing solution and rinse cores with 3 liters of water.
3. Add 7 liters of 8 M HNO_3 and reflux for 5 hr.
4. Centrifuge (or filter) dissolver solutions.
5. Rinse dissolver tank and centrifuge (or filter) with enough additional water to adjust core solution to solvent extraction feed conditions.

Table 1. Stream Compositions and Volumes in Removal of Zircaloy-2 Cladding with Aqueous HF

Basis: one Commonwealth Edison subassembly

Stream No.	Vol, liters	Mass, kg	Specific Gravity	U[a] M	U[a] kg	Zr M	Zr kg	Sn[b] M	Sn[b] kg	H^+ M	H^+ kg	F^- M	F^- kg	NO_3 M	NO_3 kg	H_2O moles	H_2O kg	H_2 moles	H_2 kg	NO moles	NO kg	NO_2 moles	NO_2 kg
Streams in																							
1		4.67			3.07		1.1		<0.017														
2	6.0	6.40	1.067							9.0	0.054	9.0	1.03			295.5	5.32						
4	3.0	3.00	1.000													166.6	3.00						
6	7.0	8.74	1.249							8.0	0.056			8.0	3.47	289.5	5.21						
8	1.0	1.00	1.000													55.5	1.00						
10	0.6	0.60	1.000													33.3	0.60						
		24.41			3.07		1.1		<0.017		0.110		1.03		3.47		15.13						
Internal streams																							
9	8.0	12.81	1.599	1.61	3.07	Trace	<0.02	<0.017		2.15	0.017	Trace		5.37	3.47	364.0	6.56						
Streams out																							
3	557.3 (STP)	0.063														0.8	0.14	24.1	0.049				
5	9.0	10.45	1.160	<0.005[d]	<0.007	2.0	1.1			1.0	0.006	9.0	1.03			461.3	8.31						
7	298	0.50														0.4	0.007			6.45	0.19	6.45	0.30
11	8.6	13.40	1.557	1.5	>3.06	Trace	~0.016	<0.017		2.0	0.017	Trace		5.0	2.67	397.3	7.16						
12		negligible				Mostly ZrO_2																	
		24.41			3.07		1.1		<0.017		0.023		1.03		2.67		15.62		0.049		0.19		0.30

[a] U as UO_2 pellets or UO_2^{++} (oxygen = 0.48 kg not included but considered in the total column).

[b] Sn^0 is insoluble in HF and is not expected to present a problem other than foaming upon addition of the core dissolvent.

[c] Exclusive of 0.5 kg of stainless steel mechanically removed.

[d] U loss to Zr waste solution ~0.2%.

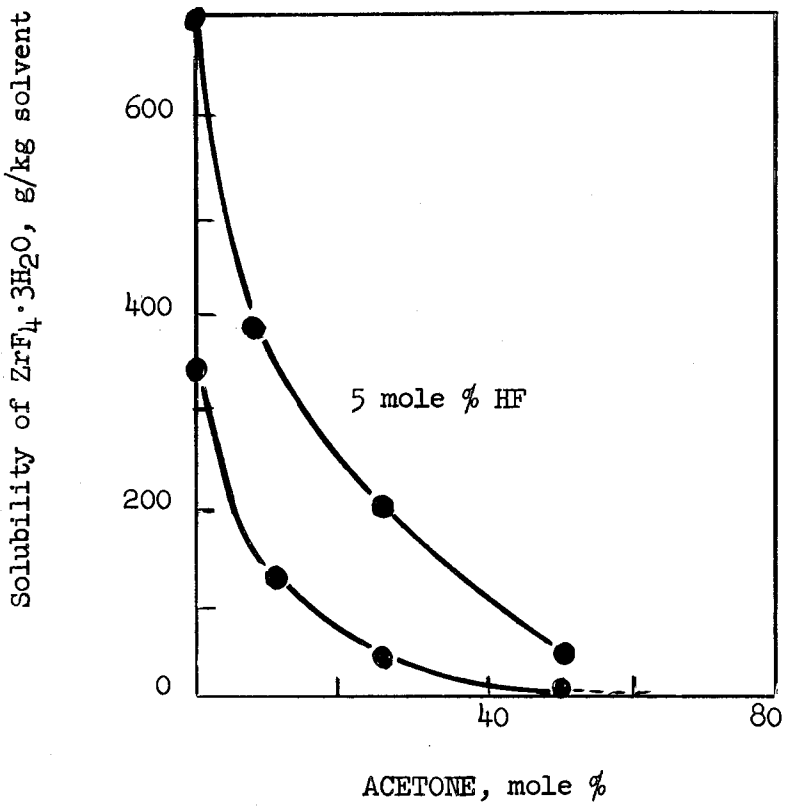

Fig. 2. Solubility of $ZrF_4 \cdot 3H_2O$ in Aqueous HF--Acetone System.[5] (Data obtained by R. K. McMullan, ORNL summer participant.)

to each other, and can be readily handled. The feasibility of separating the acetone from the HF solution for possible recycle has not been investigated.

3.0 EXPERIMENTAL RESULTS

Data obtained in 2.5-hr dissolutions of UO_2 pellets and several uranium alloy rods indicated that cladding can be removed from UO_2 and U-10% Mo cores, but not from U-2% Zr and perhaps not from U-10% Nb cores by HF, with only slight loss of uranium to the decladding solution (Table 2). The uranium losses were generally in line with the solubility of UF_4 in HF as reported by Argonne.[1]

Dissolution rates of zirconium and Zircaloy-2 were high even in the presence of relatively high concentrations of dissolved zirconium, while rates in more concentrated acid, e.g., 9 M, without any zirconium were too high to allow the reaction to be readily controlled (Table 3, Fig. 3).

Since the reaction of HF with zirconium is exothermic (-12.05 kcal/mole), the temperature of the dissolution system is difficult to control except

Table 2. Dissolution of Various Core Materials in HF

Material	Initial HF Conc. M	Temp., °C	Dissolution Rate (2-15 min exposure), mg/cm^2·min	Solution Uranium Conc. (2.5 hr reflux), mg/ml
UO_2	5	90	0.15	0.6
	9	90	0.08	0.35
	12	90	0.036	0.3
	12	25	0.062	----
U-10% Mo	2	90	0.26	----
	5	90	0.06, 0.11	1.46
	9	90	0.013, 0.2	1.75
	12	90	0.025, 0.58	1.07
	12	25	0.11	----
U-2% Zr	5	90	7.1	0.433[a]
	9	90	7.73	a
	12	90	4.24	a
	12	25	1.09	----
U-10% Nb	5	90	0.032[b]	0.63
	9	90	0.06	----
	12	90	0.14	0.036
	12	25	0.036	----

[a] Voluminous residues of UF_4 were obtained. At acid concentrations above 5 M practically all solution was absorbed by this solid phase.

[b] More prolonged exposure resulted in attack corresponding to a dissolution rate of ~28 mg/cm^2·min.

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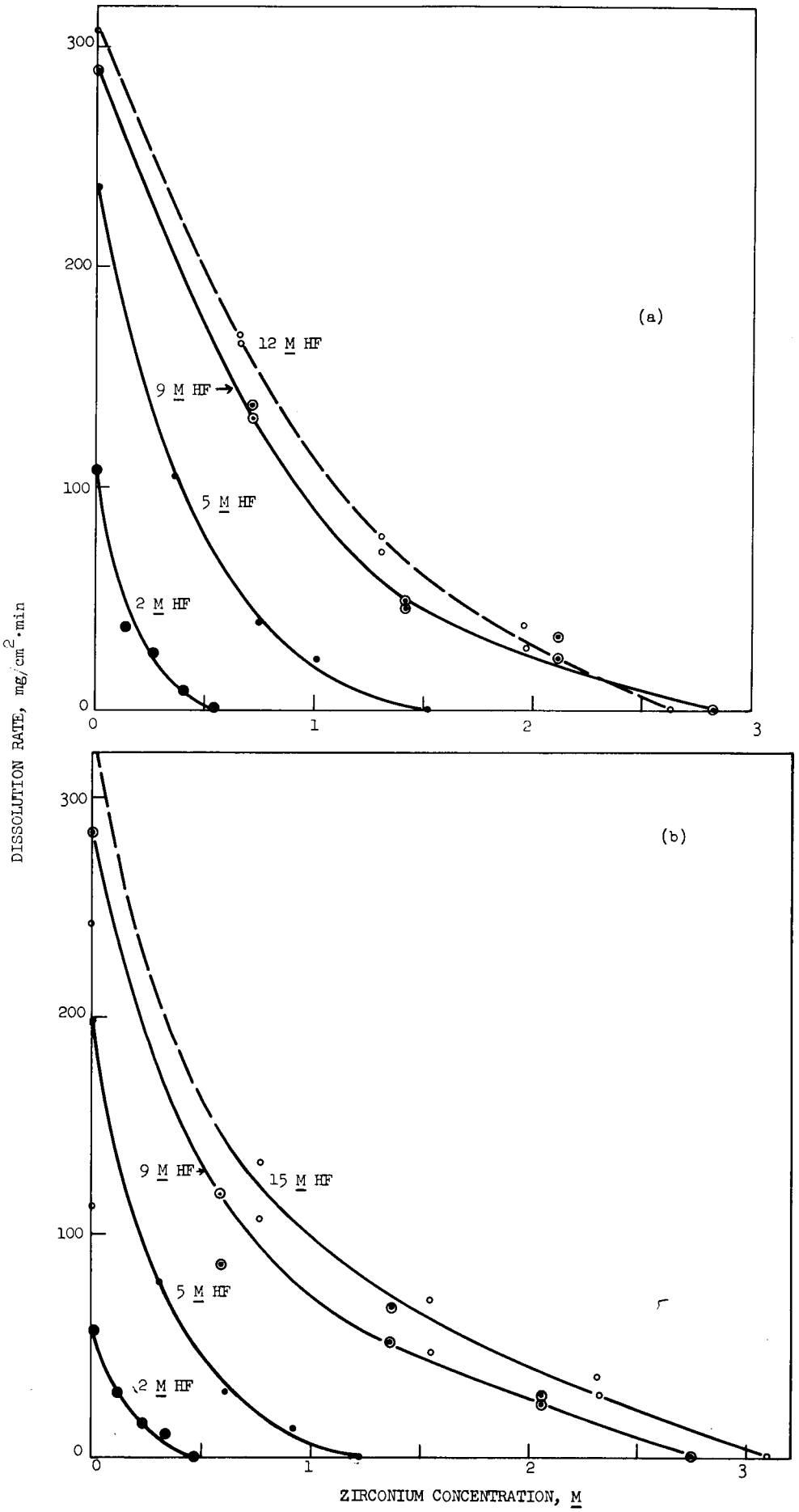

Fig. 3. Dissolution of (a) Zirconium and (b) Zircaloy-2 in Aqueous Hydrofluoric Acid. Temperature: 90°C to boiling. Each point represents a 2 minute dissolution experiment.

Table 3. Dissolution of Pure Zirconium and Zircaloy-2 in Hydrofluoric Acid Solutions of Various Percentage Saturations[a] with Zirconium

Conditions: t = 2.0 min; T = 90°C to boiling

HF Conc, M	Dissolution Rate, mg/cm^2·min				
	0%	25%	50%	75%	100%
			Zirconium		
2	108.2	46.6	25.7	6.9	0.0
5	236.5	105.5	38.5	22.9	0.0
9	242.6 289.6	137.3 130.1	44.1 58.4	22.9 32.8	0.0
12	300.9	164.9 168.6	70.8 78.0	26.9 39.2	0.0
			Zircaloy-2		
2	56.8	29.7	15.2	5.7	0.0
5	78.7	78.1	28.7	6.6	0.0
9	284.3	119.6 87.7	67.0 51.4	23.4 27.7	0.0
12	118.6 242.2	133.1 106.5	70.7 47.0	35.9 27.9	0.0

[a]The percentage saturations given represent the following molarities:

Saturation, %	Zr Conc. from Zr Metal, M				Zr Conc. from Zircaloy-2, M			
	2 M HF	5 M HF	9 M HF	12 M HF	2 M HF	5 M HF	9 M HF	12 M HF
25	0.14	0.30	0.71	0.66	0.11	0.31	0.59	0.77
50	0.27	0.75	1.41	1.31	0.22	0.61	1.37	1.55
75	0.41	1.13	2.12	1.97	0.33	0.92	2.06	2.31
100	0.54	1.51	2.82	2.62	0.45	1.22	2.74	3.09

at the boiling point. In most of these experiments the dissolvent was heated to 90°C and the metal added. With both zirconium and Zircaloy-2 samples the heat of reaction then raised the temperature to the boiling point.

In experiments with small sections of obsolete PWR fuel elements (UO_2 rod clad with 20-mil Zircaloy-2), uranium losses in dejacketing (Table 4) were somewhat lower than in the preliminary tests with bare UO_2 pellets. UO_2 pellets clad with 30-mil Zircaloy-2 (prototype Commonwealth Edison fuel elements) were declad with HF under conditions expected in actual decladding operations. Uranium losses were satisfactorily low (Table 5).

Scouting experiments with a mixture of hydrofluoric and nitric acids, with and without added aluminum nitrate, as a complete dissolvent for zirconium-containing fuel elements showed generally unfavorable dissolution rates (Tables 6, 7, and 8; Figs. 4 and 5). The results show that the F^-/Zr ratio must be equal to or greater than unity for practical dissolution rates to be obtained even in the presence of excess nitric acid. No further effort has been made to develop these systems.

Table 4. Removal of Zircaloy-2 Jackets from UO_2 Cores with Hydrofluoric Acid

Final F/Zr ~ 20/1 in every case

HF Conc., M	Initial and Maximum Temperatures, °C	Dissolution Rate, $mg/cm^2 \cdot min$	Final U Conc. in Solution, mg/ml	U Loss to Solution, %
2	25-36	20.9	0.055	0.19
5	25-60	184.1	0.057	0.096
10	25-95	164.9	0.02	0.05
15	25-104	126.9	0.052	0.06

Table 5. Dissolution of Commonwealth Edison Fuel Prototypes

Temperature: 90°C to boiling
Final F/Zr = 4.5/1 for complete decladding in each case

Dejacketing							Core Dissolution in 8 M HNO_3		
		Final Conc.						Final Conc.	
Initial HF Conc., M	Time, hr	Zr, M	H^+, M	U, mg/ml	U Loss, %	Remarks	Time, hr	U, mg/ml	H^+ M
9	2.25	1.7	1.0	4.8	0.47	Very rapid reaction; almost half of solution evaporated	5	413.6	2.9
5	2	2.8	1.8	1.15	0.16	Half of acid added after 15 min; 20% of solution evaporated			
5	2.5	1.7	0.31	1.84	0.30	Half of acid added slowly over a period of~1 hr; portions of end caps remained undissolved; 15% of solution evaporated	5	412	2.7

Table 6. Dissolution of Zircaloy-2 in HNO_3-HF Mixtures Containing Zr^{4+}

0.5 M HF			0.1 M HF		
HNO_3, M	Zr, M	Dissolution Rate[a] mg/cm^2·min	HNO_3, M	Zr, M	Dissolution Rate,[a] mg/cm^2·min
4	0.1	3.10	4	0.1	0.11
	0.3	0.99		0.3	Neg
	0.5	Ppt		0.5	Neg
6	0.1	6.03	6	0.1	0.0031
	0.3	1.14		0.3	Neg
	0.5	Ppt		0.5	Neg
8	0.1	7.24	8	0.1	0.012
	0.3	Ppt		0.3	Neg
	0.5	Ppt		0.5	Neg
13	0.1	9.81	13	0.1	0.080
	0.3	Ppt		0.3	Neg
	0.5	Ppt		0.5	Neg

[a]"Ppt" indicates the formation of a precipitate during preparation of the reagent and therefore discontinuation of the experiment.

Table 7. Dissolution of Zircaloy-2 in 13.1 M HNO_3-0.004 M HF

Temperature: 90°C
Time: 2 hr

Experiment[a]	Zr in Final Solution, M	F/Zr Ratio Obtained	Remarks
1	0.0036	1.1	White precipitate
2	0.0027	1.5	White precipitate
3A	0.00063	6.4	White precipitate
3B	0.0027	1.5	White precipitate
4A	0.0075	0.54	White precipitate
4B	0.0091	0.44	White precipitate

[a]Metal specimens used in experiments 3A and 4A were rinsed and re-used in experiments 3B and 4B, respectively.

Table 8. Dissolution of Zircaloy-2 in the Fluoride--Aluminum Nitrate System

Temperature: 25°C
Dissolution time: 15-30 min

Solution Composition,[a] M			Dissolution Rate, mg/cm^2·min	Solution Composition,[a] M			Dissolution Rate, mg/cm^2·min
HNO_3,	F^- as KF	Al^{3+}		HNO_3	F^- as HF	Al^{3+}	
0	0.095	0.31	0.34	0	0.21	0.32	0.17
3	0.19	0.32	0.30	3	0.10	0.21	0.55
7	0.18	0.31	0.29	7	0.05	0.13	0.43
10.5	0.12	0.21	0.20	10.5	0.009	0.08	0.26

[a]Solutions were intended to be 0.35 M in $Al(NO_3)_3$, and 1 M in KF or HF as indicated. Since precipitation occurred in all cases the clear supernatant liquids were used as dissolvents. The fluoride and aluminum concentrations were determined by analysis.

4.0 ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Dr. R. K. McMullan of the University of Texas who investigated the solubility and the crystal structure of the ZrF_4 hydrates, of R. L. Sherman of the ORNL Analytical Chemistry Division for x-ray crystallographic studies, of J. F. Talley of the Chemical Technology Division for laboratory work, and of P. W. Thomason, G. R. Wilson, W. R. Laing, and C. E. Lamb of the ORNL Analytical Chemistry Division for analytical work.

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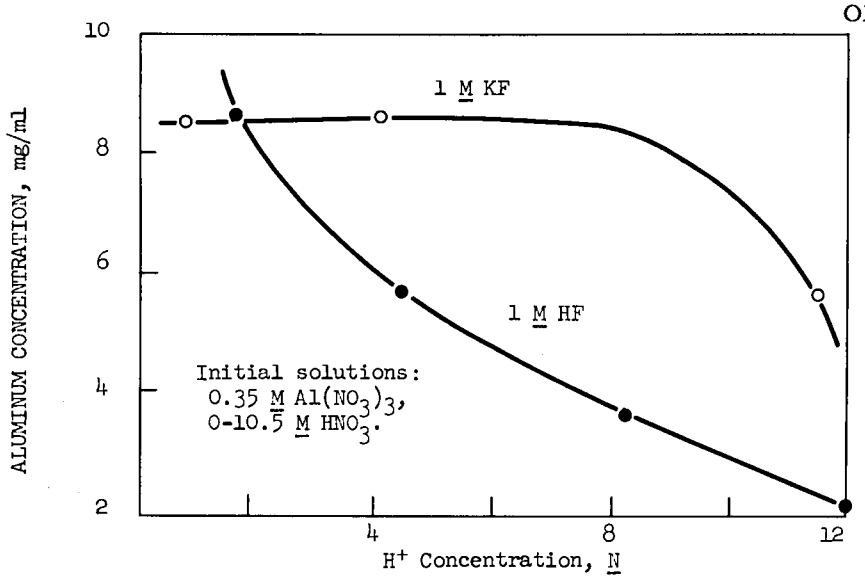

Fig. 4. Solubility of Aluminum Nitrate in Nitric Acid--Hydrogen Fluoride Systems at 25°C.

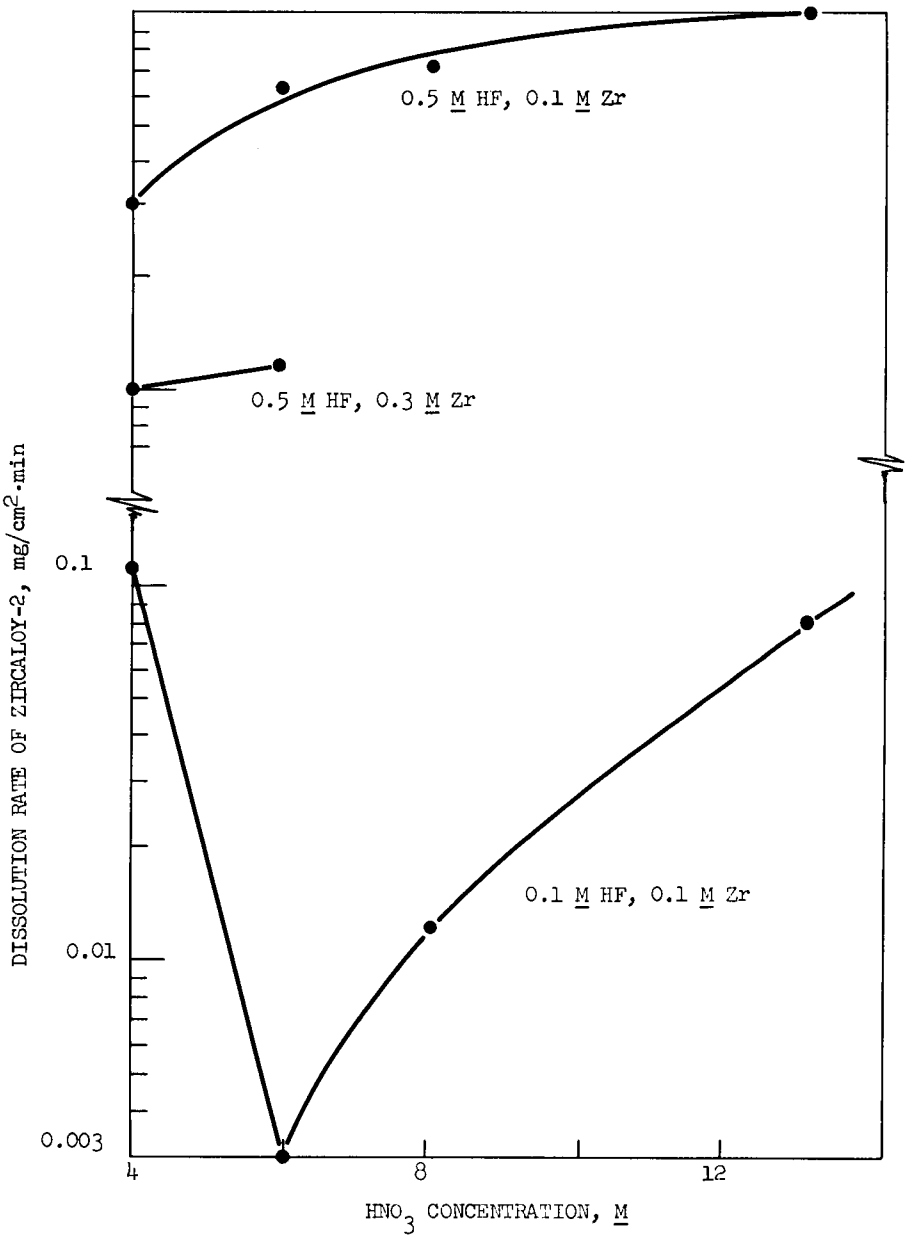

Fig. 5. Dissolution of Zircaloy-2 in HNO_3-HF Containing Zr^{4+}.

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