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DECLADDING OF ZIRCALOY CLAD URANIUM DIOXIDE FUELS
BY ACIDIC FLUORIDE SOLUTIONS

By

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Chemical Development Operation
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September 23, 1960

HANFORD ATOMIC PRODUCTS OPERATION

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DECLADDING OF ZIRCALOY CLAD URANIUM DIOXIDE FUELS BY ACIDIC FLUORIDE SOLUTIONS

I. Introduction

Current processes for dissolving Zircaloy cladding include neutral fluoride solutions ($\text{NH}_4\text{F} - \text{NH}_4\text{NO}_3$) for preferentially decladding uranium or uranium dioxide fuels,⁽¹⁾ and acid fluoride solutions for total dissolution of such fuels as Zircaloy clad U-Zr alloys.⁽²⁾ An acidic fluoride dissolution system which would preferentially remove Zircaloy cladding from uranium or uranium dioxide fuels would avoid the problem of ammonia removal associated with the Zirflex Process. This report summarizes experimental work which show the feasibility of the latter approach.

II. Summary and Conclusions

Satisfactory Zircaloy dissolution rates, relatively low container corrosion rates, and low loss of uranium dioxide to the decladding solution may be obtained with a decladding solution containing hydrofluoric acid and low concentrations of nitric acid. The nitric acid addition (made to dissolve tin present in Zircaloys) may be made subsequent to decladding. The latter technique is preferable from the corrosion standpoint. The heat of dissolution is sufficient to maintain a high Zircaloy dissolution rate. No applied heat is necessary or desirable.

III. Experimental and Discussion

A. Zircaloy Dissolution

Considerable data are available on the rate and mechanism of the dissolution of reactor grade zirconium in hydrofluoric and nitric-hydrofluoric acid solutions.^(3,4) The zirconium dissolution rate has been shown to be directly proportional to the un-ionized hydrofluoric acid concentration. For a given un-ionized hydrofluoric acid concentration the rate is independent of the HF_2^- , H^+ , F^- , or NO_3^- concentration over a wide range. The diffusion of un-ionized hydrofluoric acid from the bulk solution through a diffusion film to the solid surface is postulated as the slow step; the energy of activation for this process is 3.3 kcal/mole.⁽³⁾ Other reported activation energies are 2.4⁽⁴⁾ and 5.8⁽²⁾ kcal/mole.

Instantaneous dissolution rates of Zircaloy-2 determined in this investigation are shown in Figure 1 as a function of temperature and "free" fluoride ion concentration (total fluoride - 4x dissolved Zircaloy; $\text{F}-4\text{Zy}$). Deviation from linearity may be due to ionization of ZrF_4 (especially at temperatures near boiling) which decreases the un-ionized hydrofluoric acid concentration by formation of HF_2^- . The plot of $\log R$ vs \log dissolution rate shown in Figure 2 indicates an average apparent activation energy of 6.1 kcal. The heat of reaction was estimated to be 22,000 cal/mole Zircaloy-2 in 0.25 M HNO_3 - 2 M HF and 140,000 cal/mole in 2 M HF.

The above data were obtained on unoxidized Zircaloy. Direct use of these data to estimate dissolution time cycles for decladding Zircaloy-clad fuel elements is not possible because of the corrosion resistant oxide film which forms on the elements during reactor operation. Dissolutions of oxidized Zircaloy-clad uranium dioxide pellets were made to simulate the decladding of a spent fuel element. The pellets were about three inches long and about one-half inch in diameter. The uranium dioxide core was clad in 32 mil Zircaloy-2 tubing. End caps were 1/4-inch plugs of Zircaloy-2, each of which weighed about eight grams. The over-all composition was about 55 g UO_2 and 35 g Zircaloy-2 per pellet. Prior to use the pellets were etched² in hydrofluoric acid and exposed for 22 hours to 1150 psi steam at 400 C. Some pellets were given an additional 48 hour exposure at 425 C in a commercial argon atmosphere. Solution temperature - time data for several dissolutions are given in Figures 3 and 4. All runs were made in a one-liter Hastelloy F pot with no applied heat. In 0.25 M HNO_3 - 4 M HF, dissolution of steam treated pellets started immediately. Decladding was essentially complete in three hours. In 0.25 M HNO_3 - 3 M HF there was an induction period of about one-half hour; about four hours (total exposure) were required for complete Zircaloy-2 dissolution. The dissolution rate was prohibitively slow in 0.25 M - 2 M HF solution. As shown in Figure 3 a higher maximum temperature was attained, at constant fluoride concentration, when nitric acid was present during Zircaloy-2 dissolution because of the higher heat of reaction. The maximum dissolution rate was independent of the presence of nitric acid.

Pellets given a 48-hour exposure at 425 C in a commercial argon atmosphere (last 8-16 hours in air), in addition to the 72-hour exposure to 1150 psi steam, required eight hours for complete decladding in 0.25 M HNO_3 - 4 M HF solution (see Figure 4). However, decladding in 4 M HF solution was complete in three hours if preceded by a one-hour exposure to boiling 0.25 M HF. As shown in following sections of this report, the latter method is preferable from the standpoint of corrosion of nickel-base container materials.

Two small coupons of Zircaloy were available which had been exposed to 363 C water for 21 months. The oxide film on these specimens was comparable to that formed on the pellets treated with both steam and air. An initial fluoride concentration of four molar was required (at 25C) to penetrate the oxide film at a reasonable rate.

Complete dissolution of Zircaloy-2 in fluoride solutions requires a F/Zr mole ratio of about five. At lower ratios Zircaloy-2 cycled between a passive and an active condition during the final portion of the dissolution. The dissolution rate increased with increasing agitation of the solution. Quantitative data on this effect are available in the literature. (3)

An off-gas analysis taken near the mid-point of a Zircaloy-2 dissolution run in 0.25 M HNO_3 - 2 M HF solution gave the following composition: N_2 - 13.3 v/o, H_2 - 74.6 v/o, NO - 2.3 v/o, and N_2O - 8.8 v/o. Increasing the nitric acid concentration reduces the amount of hydrogen produced. (2)

B. Uranium Dioxide Core Loss

Uranium dioxide core losses during decladding were estimated by exposing small and large (one pound) quantities of unclad sintered UO_2 pellets to acidic fluoride decladding solutions. Typical data obtained by exposing single unclad sintered UO_2 pellets (previously etched in nitric acid) to boiling acid fluoride solutions are given in Table I. Experiments with unetched pellets gave somewhat lower but erratic waste loss data.

Table I

Uranium Loss to Acid Fluoride Decladding Solutions -
Sintered UO_2 Pellets

Exposures of 20 to 180 min. to boiling solutions contained in Zeflon.

Solution	UO_2 Loss, g./g. Pel. Hour
1. 0.5 M HNO_3 , 2 M HF , 0.40 M Zr	0.00
2. 0.25 M HNO_3 , 2 M HF , 0.40 M Zr	0.10
3. 0.25 M HNO_3 , 3 M HF	0.05
4. 0.25 M HNO_3 , 3 M HF , 0.40 M Zr	0.01
5. 0.25 M HNO_3 , 2 M HF , 0.1 M NH_2SO_3H , 0.40 M Zr	0.00
6. 2 M HF , 0.40 M Zr	0.00

These data show that the uranium loss is highly dependent upon the nitric acid concentration. In Run 5 (Table I) sulfamic acid was added subsequent to dissolution of the zirconium. Runs with similar solutions in which sulfamic acid was added prior to zirconium dissolution resulted in increased rather than decreased waste losses. The effects of urea additions were similar to those obtained with sulfamic acid.

Experiments similar to those discussed above were made with one pound batches of sintered uranium dioxide pellets. About ten weight percent of the UO_2 was present as fines produced from grain fallout after exposure to nitric acid. Exposure periods varied from one to three hours. Erratic data were obtained from these experiments with uranium losses varying from 0.02 to 0.2 w/o per hour of exposure to boiling 0.25 M HNO_3 , 2 M HF , 0.40 M Zr .

Uranium dioxide loss data obtained from experiments which simulated the decladding of spent fuel elements (see Figures 3 and 4) are given in Table II.

Table II

Uranium Losses During Acid Fluoride Decladding
of Zircaloy Clad Uranium Dioxide Pellets

<u>Initial Solution</u>	<u>Exp. Time, Hr.</u>	<u>Max Temp., °C</u>	<u>UO₂ Loss, w/o</u>
0.25 M HNO ₃ + 0.1 M HF	3	93	0.16
0.25 M HNO ₃ + 0.1 M HF	4	89	0.06
0.25 M HNO ₃ + 2 M HF	6	62	0.069
3 M HF ⁽¹⁾	4	66	0.07
0.1 M HF ⁽²⁾	3	73	0.08

Notes:

- (1) Solution made 0.25 M in HNO₃ one-half hour prior to termination of run.
 (2) Solution butted to 0.25 M HNO₃ + 0.1 M NH₂SO₃H 15 min prior to termination of run.

These data indicate low uranium loss to the decladding solution is obtained irrespective of the method of nitric acid addition. Nitric acid consumption is apparently nearly complete before a significant amount of the UO₂ core is exposed to the decladding solution.

The attack of acid fluoride decladding solution on metallic uranium is relatively rapid. A rate of 20 mg/cm² hr was determined (via weight loss) in a one-hour exposure of ingot uranium to boiling 0.25 M HNO₃ + 0.1 M HF + 0.1 M Zn solution.

Corrosion

The corrosivity of acid fluoride decladding solution precludes 304 stainless steel as a material of construction. Vacuum-melted nickel-base alloys were investigated and found to be sufficiently corrosion resistant. The compositions of alloys investigated are shown in Table III.

Table III

Nominal Composition of Candidate Alloys

<u>Alloy</u>	<u>Weight Percent</u>							
	<u>Ni</u>	<u>Cr</u>	<u>Fe</u>	<u>Mo</u>	<u>Cu</u>	<u>C</u>	<u>Ti</u>	<u>Nb</u>
Hastelloy F ^(a)	45	22	bal	6	0	.02	0	2
HAPC No. 4 ^(a)	45	22	bal	6	0	.02	1	0
HAPC No. 11 ^(a)	45	22	bal	6	2	.02	1	0
HAPC No. 20	50	25	bal	6	1	.02	1	-

(a) These are experimental alloys small heats of which were prepared at Battelle Memorial Institute.

Corrosion rates for alloy HAP0 No. 11 in 0.25 M HNO_3 - 2 and-3 M HF as a function of temperature are given in Figure 5. The desirability of limiting the temperature of the initial solution to 50 C or less is apparent. The corrosivity of decladding solution containing dissolved Zircaloy as a function of free fluoride concentration (F - 4 Zy) at 75 C and at the boiling point is given in Figure 6. The corrosivity decreases markedly with decreasing free fluoride concentration, especially at boiling temperatures.

Corrosion rates determined in runs simulating the decladding of spent fuel elements are given in Table II.

Table II

Corrosion Data Obtained During Acid Fluoride Decladding
of Zircaloy Clad Uranium Dioxide

Initial Solution	Expo. Time. Hr.	Max. Temp. °C	Terminal F/Zy	Corr. Rate, Mills Mo.		
				Alloy		
				4	11	20
0.25 M HNO_3 + 2 M HF	3	93	5.3	8.2	5.9	4.3
0.25 M HNO_3 + 3 M HF	4	80	8.8	9.8	6.6	4.7
0.25 M HNO_3 + 2 M HF	6	73	7.7	2.1	1.9	1.2
3 M HF	4	68	6.6	1.2	0.7	0.4
3 M HF	3	73	6.6	9.8	0.7	0.2

*Preceded by one-hour exposure to boiling 0.25 M HF.
Corrosion rate is for total exposure.

From the corrosion standpoint, the optimum operating procedure is to declad in hydrofluoric acid only. Nitric acid is added subsequent to decladding to dissolve tin.

Corrosion attack on the nickel-base alloys by acid fluoride decladding solution is largely general with some intergranular attack. Weldments of the HAP0 alloys were not preferentially attacked. Hastelloy F weldments exhibited some preferential attack in the weld metal and in the sensitized area adjacent to the weld. No heat transfer surfaces are required during decladding since sufficient heat to maintain rapid Zircaloy dissolution is supplied by the heat of reaction.

The free fluoride concentration in spent decladding solution is low. However, any fluoride carried from the decladding to the core dissolution step should be complexed with excess Al(III) prior to core dissolution to minimize corrosion of the dissolver.

References

- 1) HW-49633. "Dejacketing of Zircaloy-clad Fuel Elements with Ammonium Fluoride Solution." J. L. Swanson. April 15, 1957.
- 2) DO-14497. "Dissolution of Zirconium and Zircaloy-2 in Nitric Hydrofluoric Acid Mixtures at Reflux Temperatures." E. M. VanderWall et al. April 13, 1960.
- 3) J. Smith and R. Hill. J. Electrochem Soc. 105, 117-21 (March 1958).
- 4) E. M. VanderWall and E. M. Whitener. Ind. & Eng. Chem. 51, 915 (January 1959).

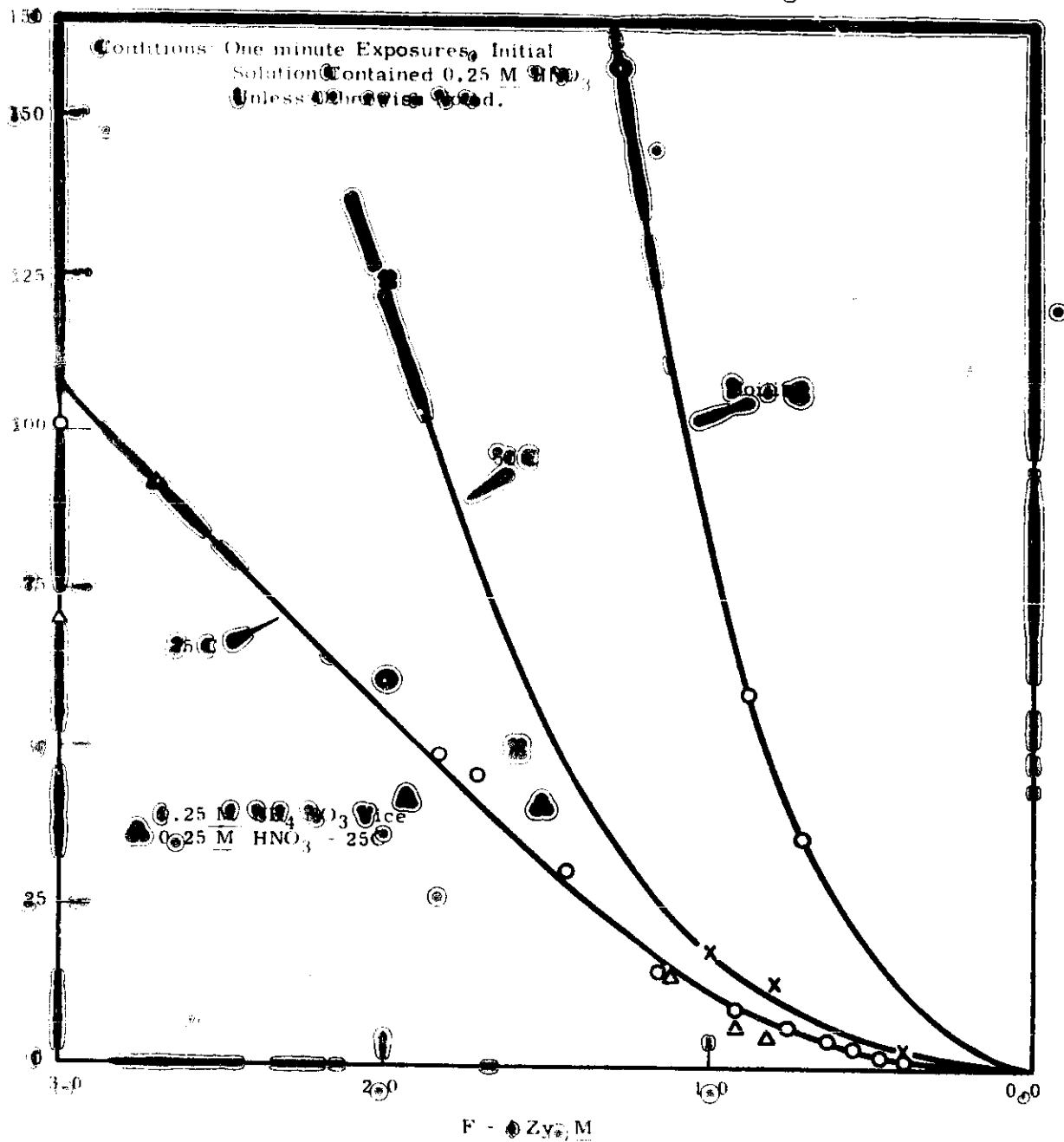


FIGURE 1
Instantaneous Dissolution Rates of Zircaloy
Effect of Temperature and "Free" Fluoride Concentration



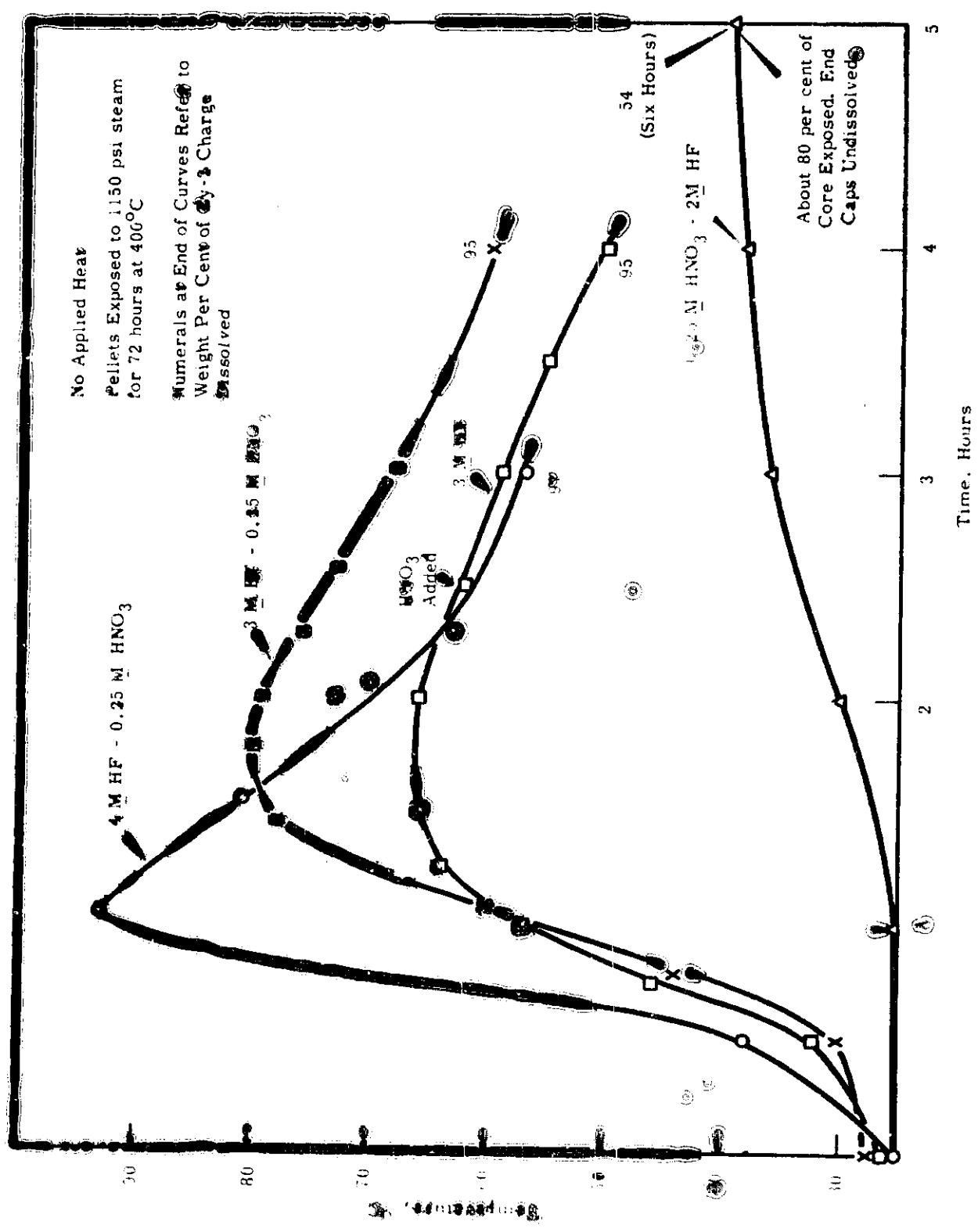
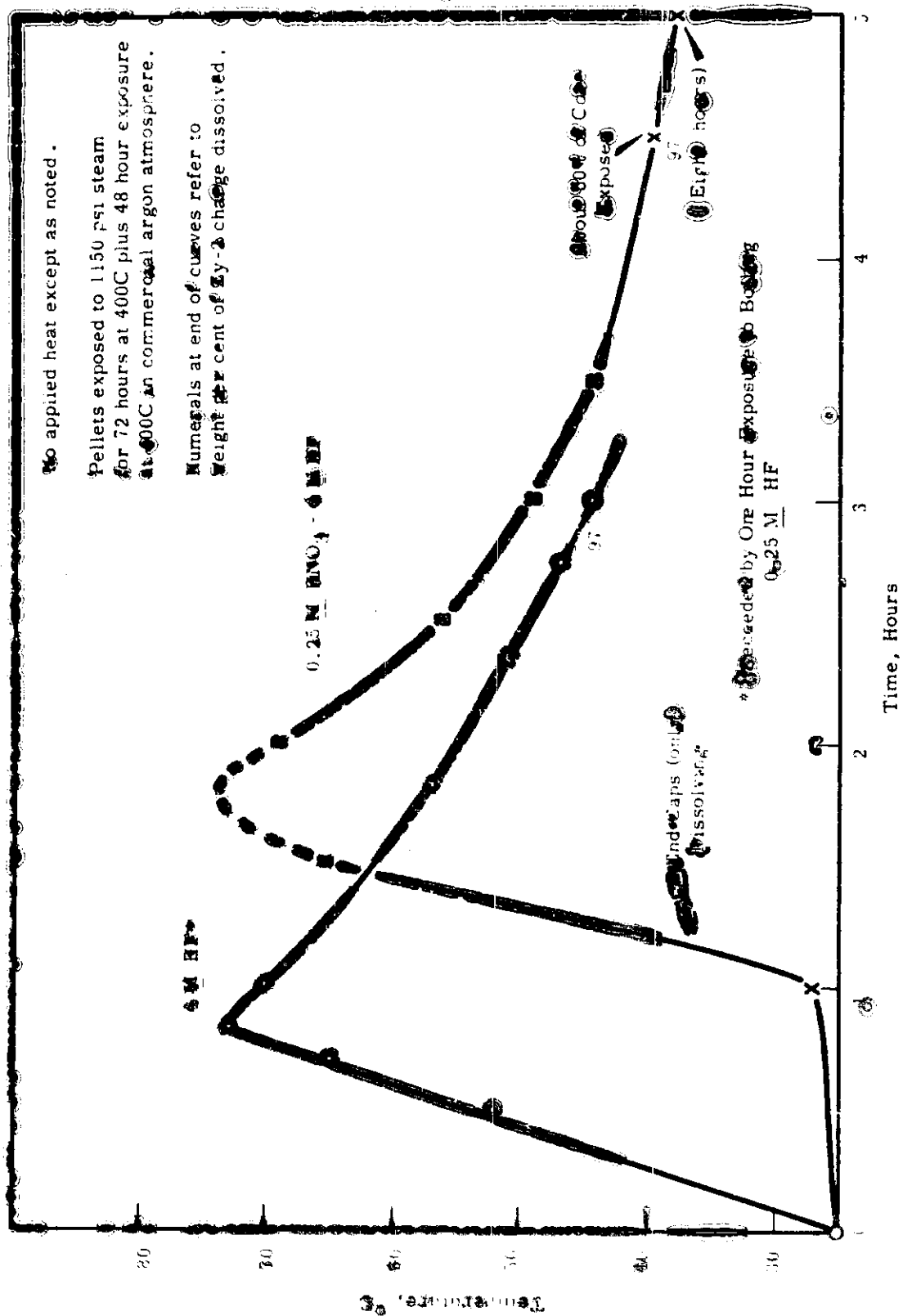


FIGURE 3
Decladding of Oxidized Zircaloy 2-Clad Uranium Dioxide



No applied heat except as noted.

Pellets exposed to 1150 psi steam for 72 hours at 400C plus 48 hour exposure at 600C in commercial argon atmosphere.

Numerals at end of curves refer to weight per cent of Zn^{++} change dissolved.

0.25 M PNO₂ - 6 M D₂O

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IndoCaps (only)

Approved by One Hour Exposure to Boring 0-25 M HF

Exposed

(1) Employees

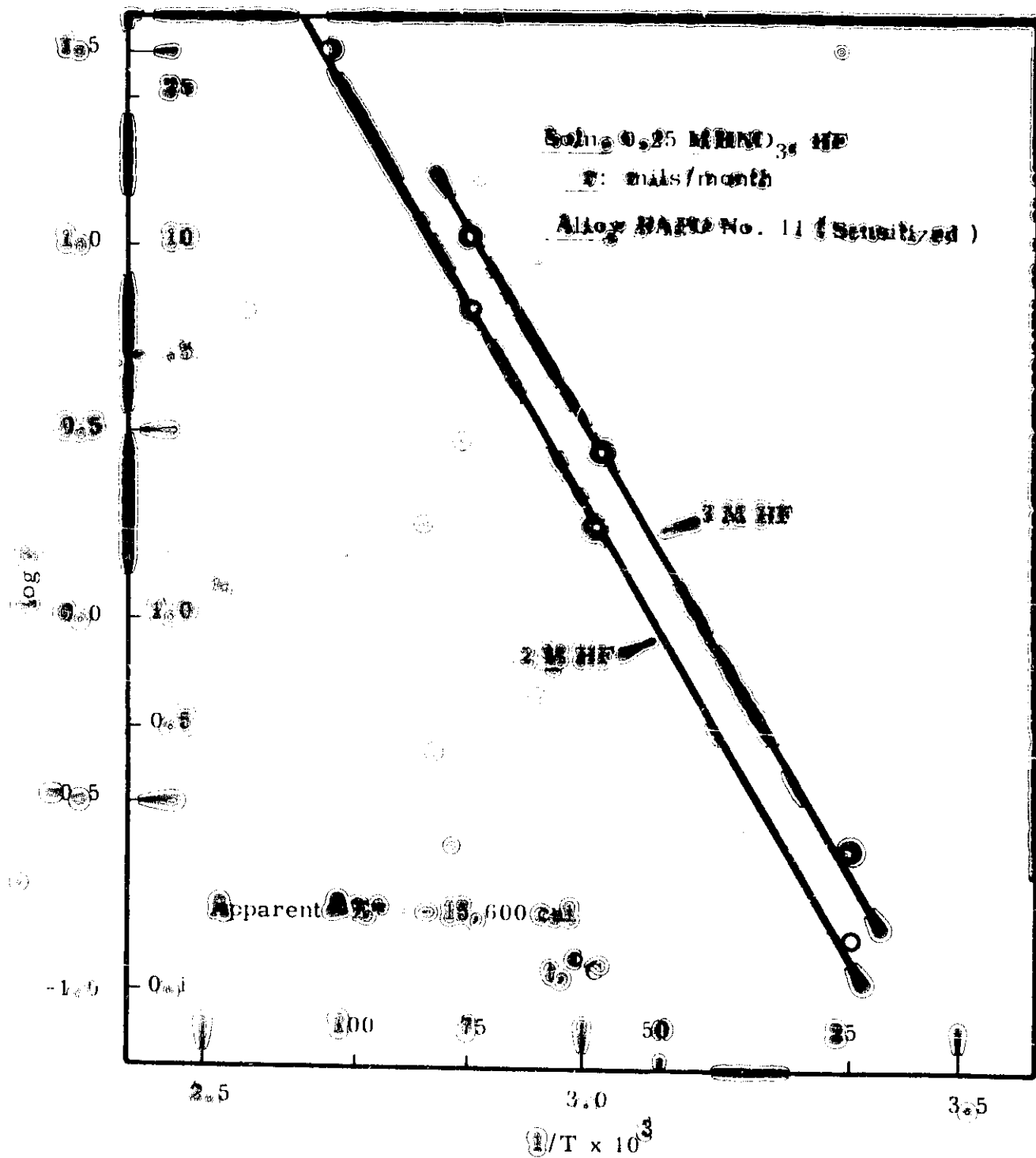


FIGURE 5
Corrosivity of Acid Fluoride Solution
Effect of Temperature

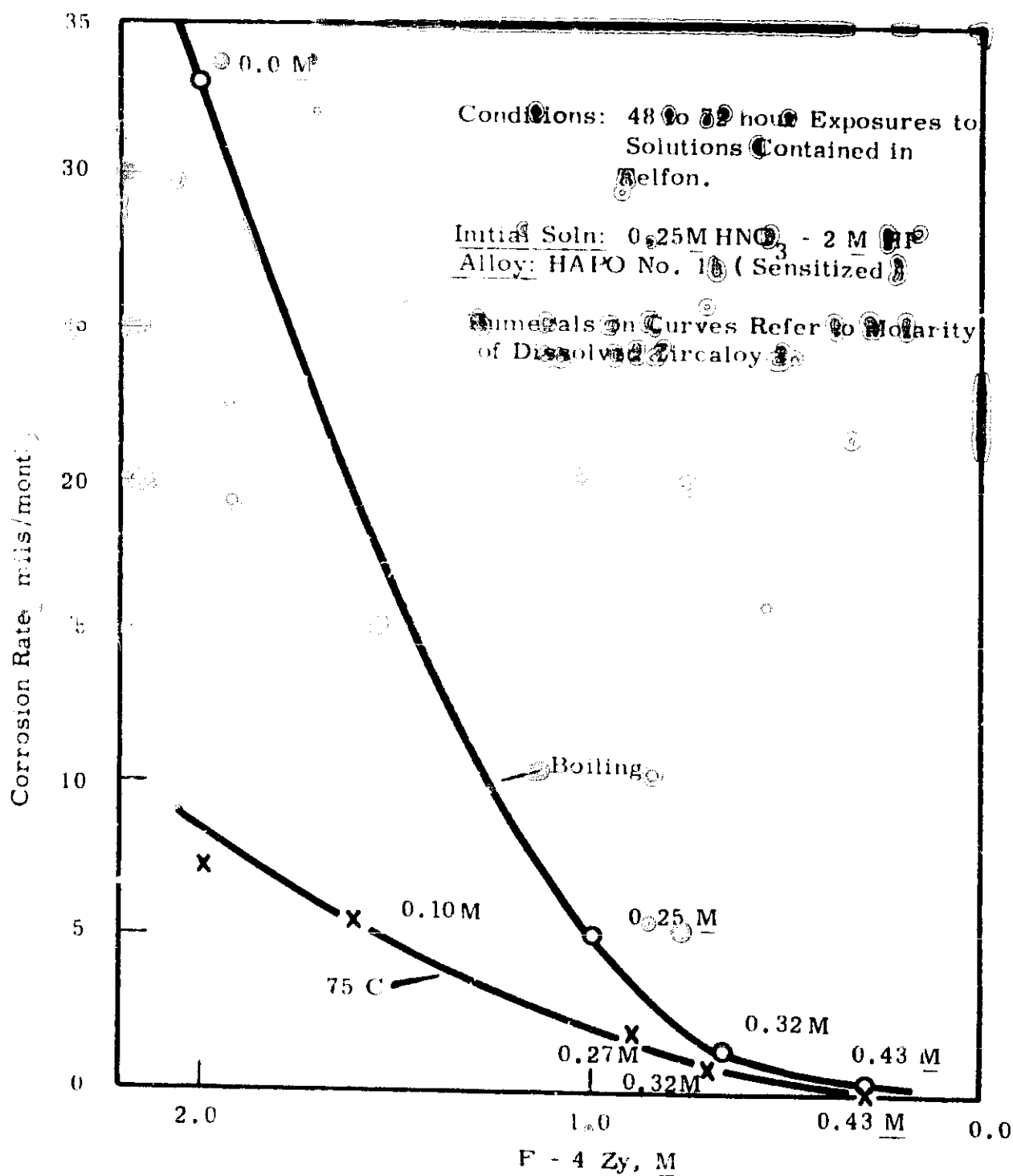


FIGURE 6
Corrosivity of Acid Fluoride Solution
Effect of "Free" Fluoride Concentration