



# OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION



OAK RIDGE NATIONAL LABORATORY LIBRARIES



3 4456 0548473 0

ORNL-TM-22

COPY NO. - 22

DATE - October 11, 1961

## Dissolution of Zirconium Reactor Fuels in Titanium Equipment

T. A. Gens

### ABSTRACT

Continuous dissolution of Zircaloy-2 in a titanium dissolver appears practical using as a dissolvent refluxing 3 M  $\text{HNO}_3$ -1.2 M  $\text{HF}$ -0.4 M  $\text{HBF}_4$ -0.6 M  $\text{Cr(III)}$ -0.4 M  $\text{Cr(VI)}$ -0.46 M  $\text{Zr}$ . Dissolution and corrosion rates are 10  $\text{mg/cm}^2\text{-min}$  and 0.0  $\text{mil/mo}$  in short term tests, respectively. A stable product solution containing 0.36 M  $\text{Zr}$  is obtained after addition of aluminum nitrate to complex fluoride ion. Another reagent investigated for use in continuous dissolution is 16 M  $\text{HNO}_3$ -2.6 M  $\text{F}$ -0.025 M  $\text{HBF}_4$ -1.4 M  $\text{Zr}$  with short term titanium corrosion rates of 0.0  $\text{mil/mo}$ . However, Zircaloy-2 dissolution rates are only 3  $\text{mg/cm}^2\text{-min}$  in the latter reagent.

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.

### NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

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.

## 1.0 INTRODUCTION

The utility of a Darex (1) titanium dissolver would be greatly extended if the titanium vessel could be used in dissolution of reactor fuels containing zirconium as well as stainless steel. Since fluoride ion must be used in any practical aqueous dissolution of zirconium fuels, inhibition of the attack of fluoride ion on titanium using strong nitric acid, chromate ion, and fluoboric acid, singly or in combinations, was studied. All of these methods of inhibition have been briefly investigated previously (2,3). The most promising reagent found was dilute nitric-hydrofluoric acid containing both hexavalent chromium and fluoboric acid to inhibit titanium corrosion. Strong nitric-hydrofluoric acid with a small amount of fluoboric acid produces a more desirable solvent extraction feed solution but requires closer control of the reagent composition to limit corrosion and does not dissolve Zircaloy rapidly. Continuous dissolution experiments are needed to verify the batch laboratory results, since the batch results give only an indication of dissolution and corrosion rates under continuous conditions. A method of continuously monitoring the dissolvent composition will have to be developed before continuous dissolution experiments can be made. Further optimization of the dilute acid dissolvent is probably possible, since the dissolvent contains four reagents and many variations in concentrations are possible.

## 2.0 FLOWSHEET

The dissolvent for the proposed process (Fig. 1) is boiling 0.465 M Zr, 2.8 M F, 3 M HNO<sub>3</sub>, 0.4 M B, 0.6 M Cr(III), 0.4 M Cr(VI). The dissolvent concentration is held constant by monitoring the withdrawal stream and adding more reagent as needed. The reagent is 5.5 M HNO<sub>3</sub>-0.4 M HBF<sub>4</sub>-0.5 M (NH<sub>4</sub>)<sub>2</sub>CrO<sub>7</sub>-1.2 M HF. An instantaneous zirconium dissolution rate of about 10<sup>2</sup> mg/cm<sup>2</sup>-min and titanium corrosion rate of 0.0 mil/mo have been predicted from batch laboratory runs. The dissolver solution is stable indefinitely at the boiling point or at room temperature. Addition of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O to complex fluoride ion before Purex-type solvent extraction produces a 30% volume increase and yields a solution which is stable at room temperature but in which hydrolysis occurs on warming before the boiling point is reached. Addition of aluminum nitrate as a solution, rather than as the solid nona-hydrate used in the laboratory work, would produce a more dilute solvent extraction feed solution.

## 3.0 LABORATORY RESULTS

Alternating titanium and zirconium dissolution rate studies were made by immersing titanium or Zircaloy-2 in the various reagents and calculating rates by dividing weight losses by exposure times and the average geometric surface areas. Results were plotted as a function of the molar ratio of



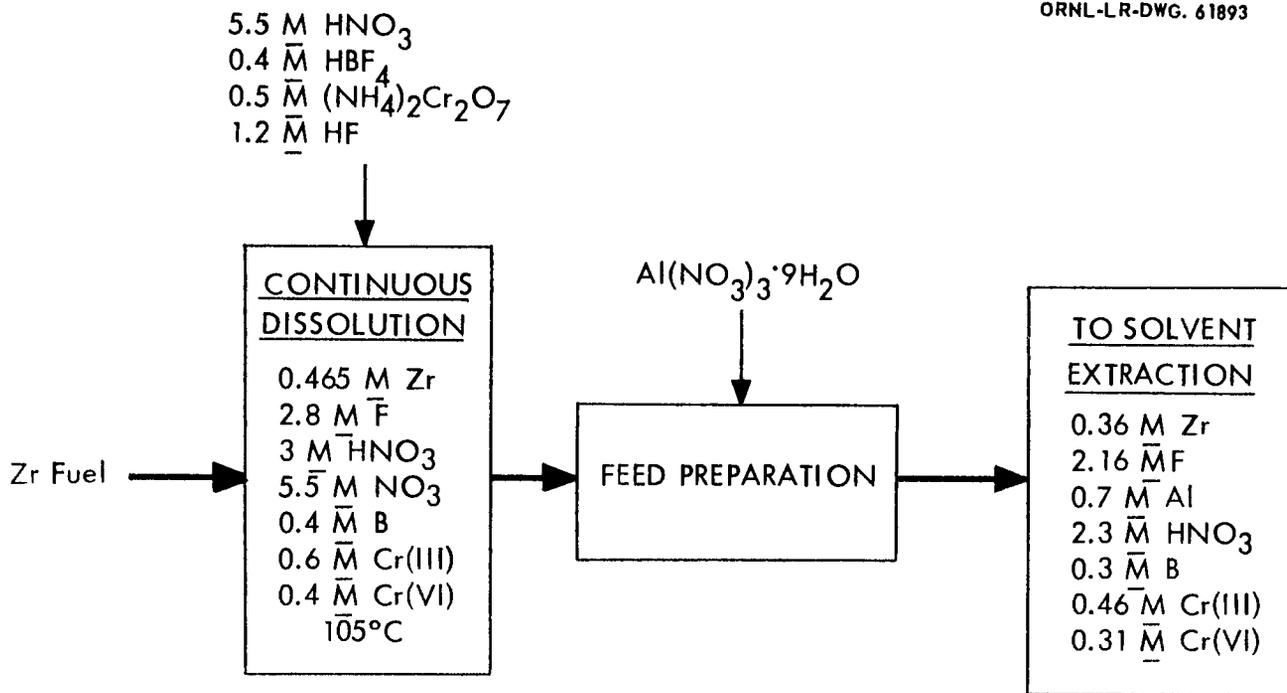


Fig. 1. Process for dissolving zirconium reactor fuels in Darex titanium equipment.

fluoride ion to dissolve zirconium (F/Zr). The averages of this ratio before and after immersion were used in the Zircaloy-2 dissolution rate studies. Titanium corrosion studies were usually made for 30 min and therefore cannot be considered as very accurate, although good reproducibility was observed in most cases. Longer term exposure always indicated corrosion rates equal to or less than those obtained in short exposure periods, so that the short term corrosion rates shown in this work are probably higher than would be obtained in continuous dissolution. Tin, which is present in Zircaloy-2 to about 1 wt %, was soluble in all experiments.

### 3.1 Dissolution in Dilute Nitric Acid

Dilute nitric acid provides little or no protection of titanium against fluoride, as does concentrated nitric acid (Sect. 3.2). Therefore, it was found necessary to add to the dilute nitric acid dissolvent both hexavalent chromium ion and fluoboric acid inhibitor to achieve sufficient protection. The hexavalent chromium ion probably serves to produce a protective oxide coat on titanium, preventing attack by fluoride ion. Fluoboric acid apparently also forms a protective white compound which coats the titanium surface. This coat is not sufficiently protective unless the reagent contains fluoride ion other than that supplied by hydrolysis of  $\text{HBF}_4$ , suggesting the coat is actually a fluoborate, not a borate compound.

The dilute nitric acid reagent studied most intensively was 3 M  $\text{HNO}_3$ -0.4 M  $\text{HBF}_4$ -HF with added chromium ions. The chromium was present as both hexavalent and trivalent chromium, since Cr(VI) is reduced to Cr(III) by dissolving zirconium alloys. In fact, the net result of dissolution always appeared to be reduction of Cr(VI) and oxidation of zirconium metal to Zr(IV) ions. No gas evolution was observed, and the green Cr(III) color developed as zirconium dissolved. It was necessary to always have more than the required stoichiometric amount (1.3 moles/mole of Zr) of Cr(VI) present to keep titanium corrosion rates low.

Effect of Fluoborate Concentration. The addition of up to 0.4 M  $\text{HBF}_4$  to 3 M  $\text{HNO}_3$  solutions containing dissolved zirconium and Cr(VI) had the surprising effect of decreasing titanium corrosion rates (Fig. 2). Increasing the fluoboric acid concentration above 0.4 M increased the corrosion rates. In 0.4 M  $\text{HBF}_4$  solutions the corrosion rates were less than 10 mils/mo, even in the initial solution with no dissolved zirconium, and decreased rapidly when the F/Zr ratio decreased below 6. The dissolution rate of Zircaloy-2 was still 4 mg-cm<sup>2</sup>-min in the 0.4 M  $\text{HBF}_4$  solution when the F/Zr ratio had decreased to 5. However, a white precipitate started forming in the solution at this point. Therefore only a very small operating range, in the area of F/Zr = 5 to 6, exists for this reagent unless titanium corrosion rates of about 10 mils/mo are accepted.



When hydrofluoric acid was added to 3 M HNO<sub>3</sub> containing dissolved zirconium and Cr(VI), it again appeared desirable to add 0.4 M HBF<sub>4</sub> to the dissolvent to increase the range over which titanium corrosion rates remained low (Fig. 3). Corrosion rates were higher when less than 0.4 M HBF<sub>4</sub> was added. The titanium corrosion dropped to 0.0 mil/mo before the F/Zr ratio reached 6 in the solution containing 0.4 M HBF<sub>4</sub>-1 M HF while the rate did not drop to 0.0 mil/mo until the F/Zr ratio reached 4 in the solution containing 0.1 M HBF<sub>4</sub>-1.4 M HF.

The Need for Cr(VI). Many attempts were made to avoid the use of Cr(VI) to inhibit titanium corrosion because of the necessity of using at least 1.3 moles of Cr(VI) per mole of zirconium dissolved. These attempts were successful only in 16 M HNO<sub>3</sub> solution, particularly if a small amount of fluoboric acid was present (Sect. 3.2). In 18 M acid containing fluoborate ion, Zircaloy-2 was passive. In 6-12 M HNO<sub>3</sub> containing hydrofluoric acid and 0.1-0.2 M HBF<sub>4</sub> the titanium corrosion rates were excessive at F/Zr ratios above 3, and Zircaloy-2 dissolution was too slow at ratios below 3. In 3 M HNO<sub>3</sub>, the titanium corrosion rate dropped rapidly to about 10 mils/mo when the F/Zr ratio decreased to 3.8 (Fig. 4), but a precipitate started forming at the same time. The addition of Cr(VI) to this reagent, however, caused the titanium corrosion rate to be much lower at high F/Zr ratios and to decrease essentially to zero at a F/Zr ratio of 6 (Fig. 4).

Selection of 3 M HNO<sub>3</sub>. Titanium corrosion rates in 0.2 M HBF<sub>4</sub>-0.2 M (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-3 M HNO<sub>3</sub> were constant at about 10 mils/mo until the F/Zr ratio decreased to 4 (Fig. 5). The corrosion rates were lower in 1 and 2 M HNO<sub>3</sub> but higher in 5 M HNO<sub>3</sub>. On the other hand, Zircaloy-2 dissolution rates were as high in 3 M HNO<sub>3</sub> as in 5 M HNO<sub>3</sub> and higher than in 1 and 2 M HNO<sub>3</sub> (Fig. 6). Therefore 3 M was selected as the optimum nitric acid concentration.

Effect of Hydrofluoric Acid Concentration. When 0.4 M HF was added to refluxing 3 M HNO<sub>3</sub>-0.4 M HBF<sub>4</sub>-Cr, the titanium corrosion rate increased and remained high until the F/Zr ratio dropped to 5 (rather than 6 without 0.4 M HF, Fig. 7). However, addition of 0.8-1.2 M HF actually served to increase the useful range of the dissolvent in titanium equipment, since although corrosion rates were initially higher, they dropped rapidly at higher F/Zr ratios. The initial titanium corrosion rate when the solution was made 1.2 M in HF was 1 in./mo, but this rate had dropped to 0.0 mil/mo at a F/Zr ratio of 9, where the Zircaloy-2 dissolution rate still exceeded 20 mg/cm<sup>2</sup>-min (Fig. 8). In a brief test with the dissolving Zircaloy-2 touching the titanium at an average F/Zr ratio of 26, the zircaloy-2 dissolution rate exceeded 30 mg/cm<sup>2</sup>-min and the titanium corrosion rate was 0.0 mil/mo. Dissolution was continued until the F/Zr ratio was decreased to 6, where the product was stable at the boiling point and room temperature. The lower titanium corrosion rates in this reagent containing 1.2 M HF apparently are caused by a thin white film which covers and protects the titanium. The rates were generally reproducible, although on some occasions the film did not form as expected and rates increased to as much as 10 mils/mo when previous tests indicated rates of 0.0 mil/mo. Several alternating exposures of the titanium to the reagent and to air led to formation of a highly protective film.

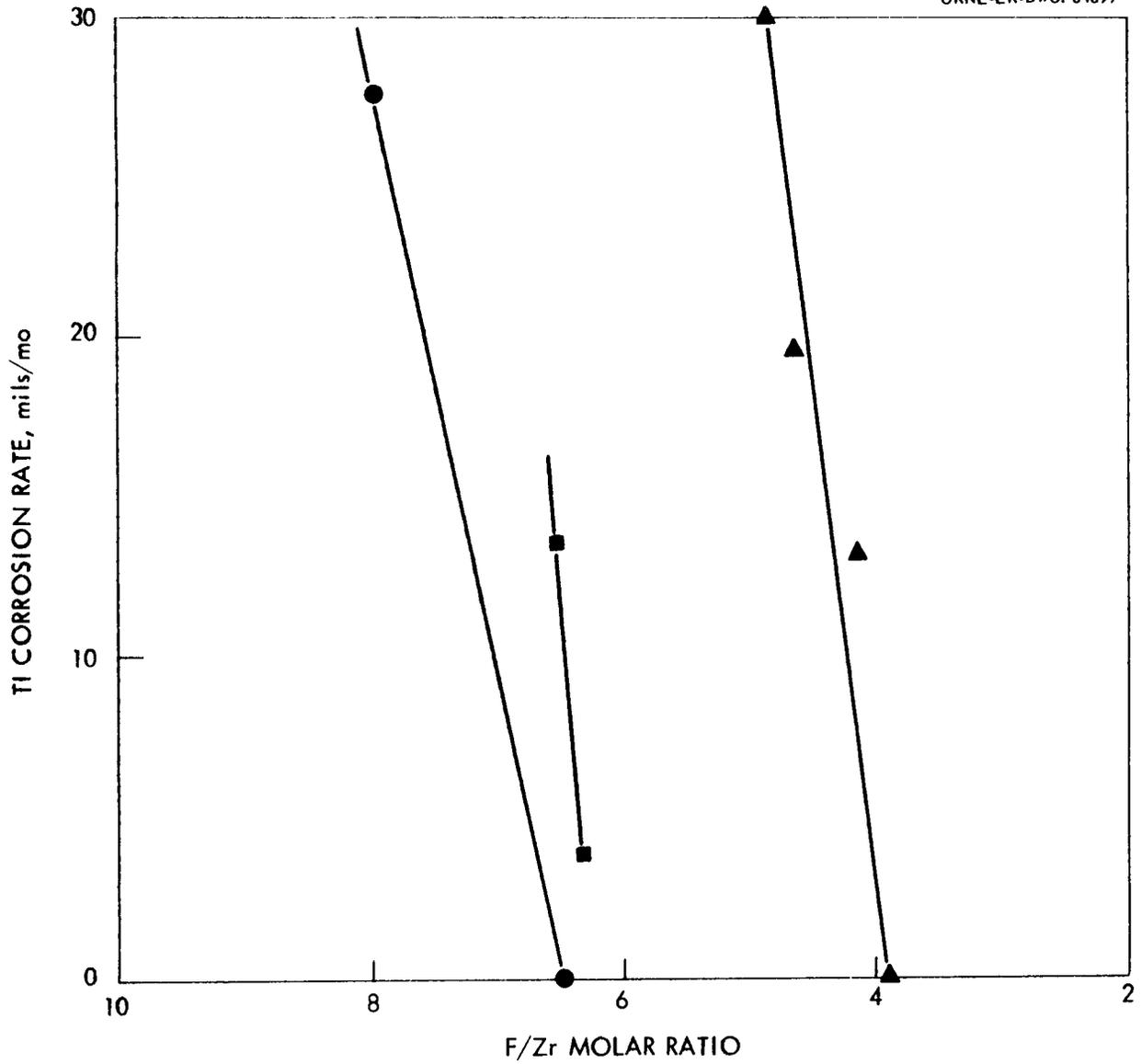


Fig. 3. Corrosion rates of titanium in refluxing 3 M HNO<sub>3</sub>-HBF<sub>4</sub>-HF-(NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-Zr solution. ▲, 1.4 M HF-0.1 M HBF<sub>4</sub>-0.8 M Cr; ■, 1 M HF-0.2 M HBF<sub>4</sub>-0.4 M Cr; ●, 1 M HF-0.4 M HBF<sub>4</sub>-1 M Cr.

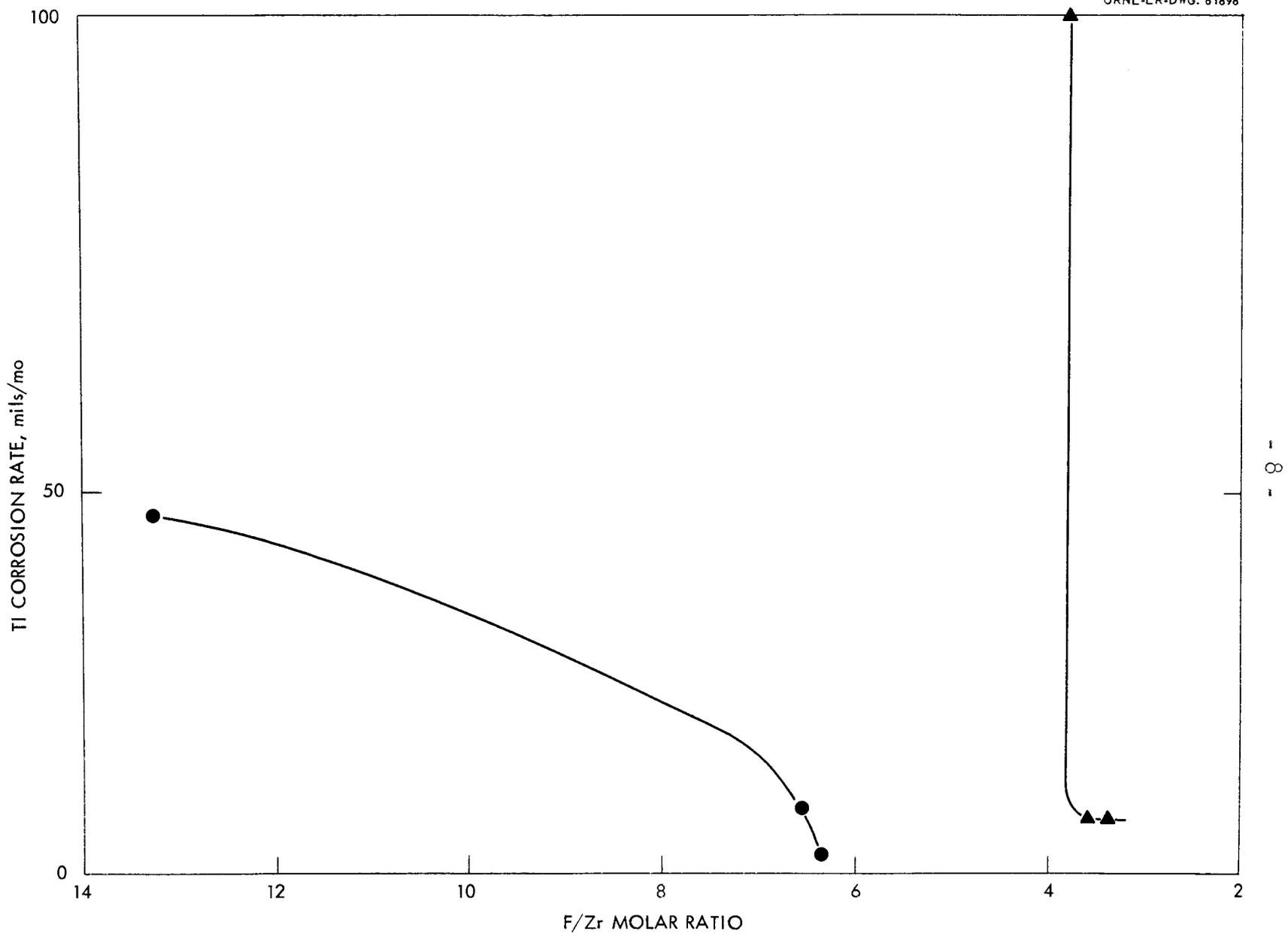
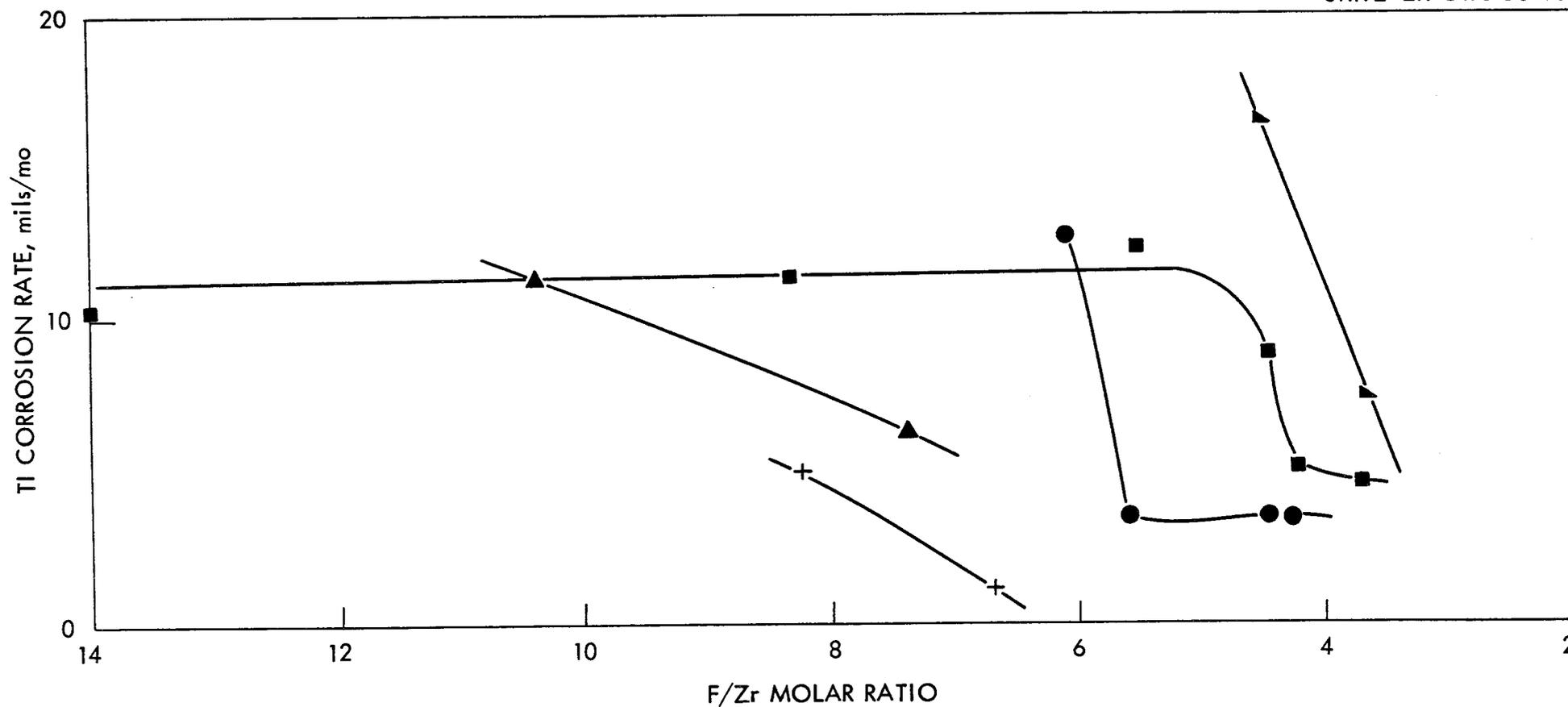


Fig. 4. Corrosion rates of titanium in refluxing 3 M HNO<sub>3</sub>-1 M HF-0.2 M HBF<sub>4</sub>. ●, 0.4 M Cr(VI) added.



- 6 -

Fig. 5. Titanium corrosion rates in refluxing 0.2 M HBF-0.2 M (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-HNO<sub>3</sub>. + , 1 M HNO<sub>3</sub>; ● , 2 M HNO<sub>3</sub>; ■ , 3 M HNO<sub>3</sub>; ▲ , 4 M HNO<sub>3</sub>; ▴ , 5 M HNO<sub>3</sub>.

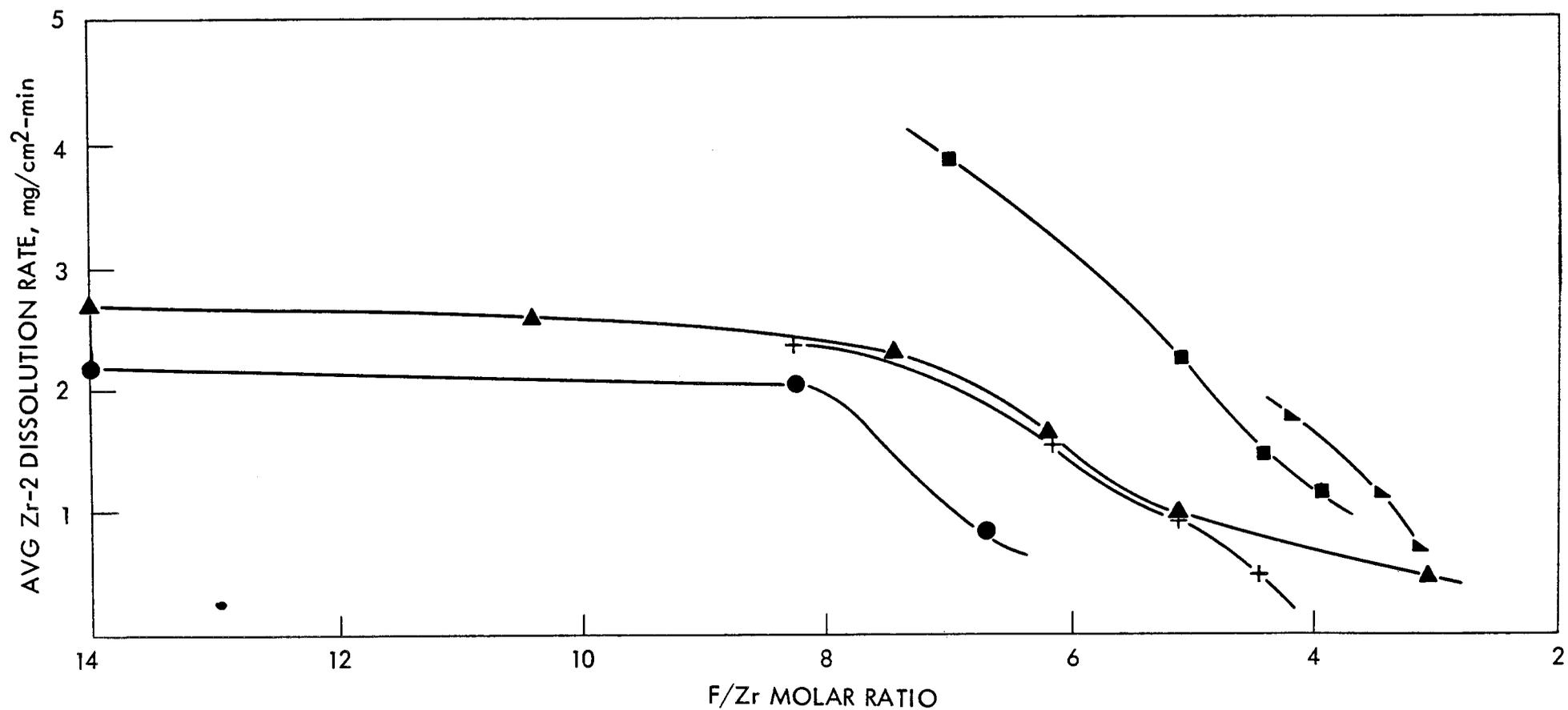


Fig. 6. Zircaloy-2 dissolution rates in refluxing 0.2 M HBF<sub>4</sub>-0.2 M (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-HNO<sub>3</sub>. ●, 1 M HNO<sub>3</sub>; + 2 M HNO<sub>3</sub>; ■, 3 M HNO<sub>3</sub>; ▲, 4 M HNO<sub>3</sub>; ▴, 5 M HNO<sub>3</sub>.

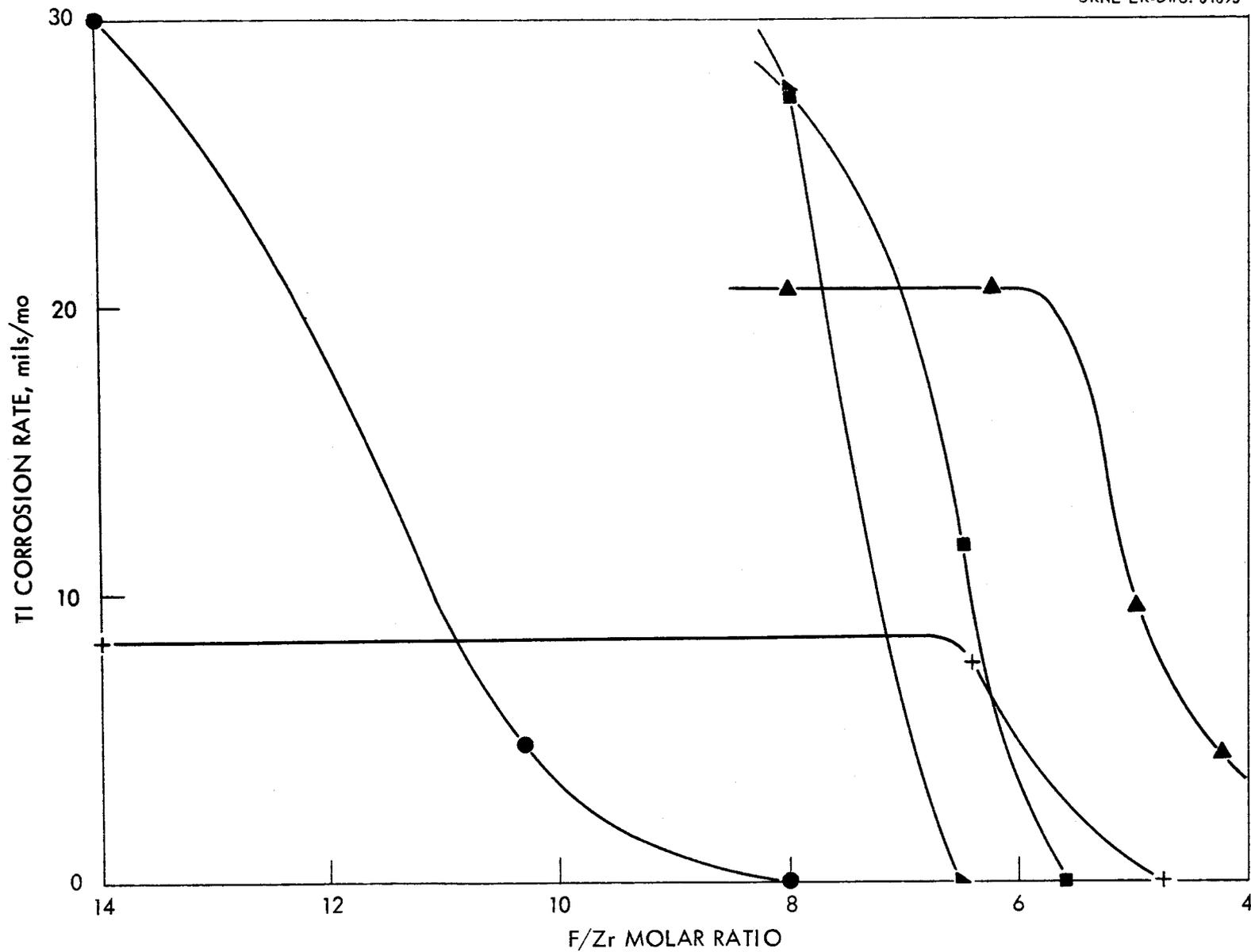


Fig. 7. Titanium corrosion rates in refluxing 3 M HNO<sub>3</sub>-0.4 M HBF<sub>4</sub>-0.4 to 1 M Cr-HF. +, 0.0 M HF; ▲, 0.4 M HF; ■, 0.8 M HF; ▼, 1.0 M HF; ●, 1.2 M HF.

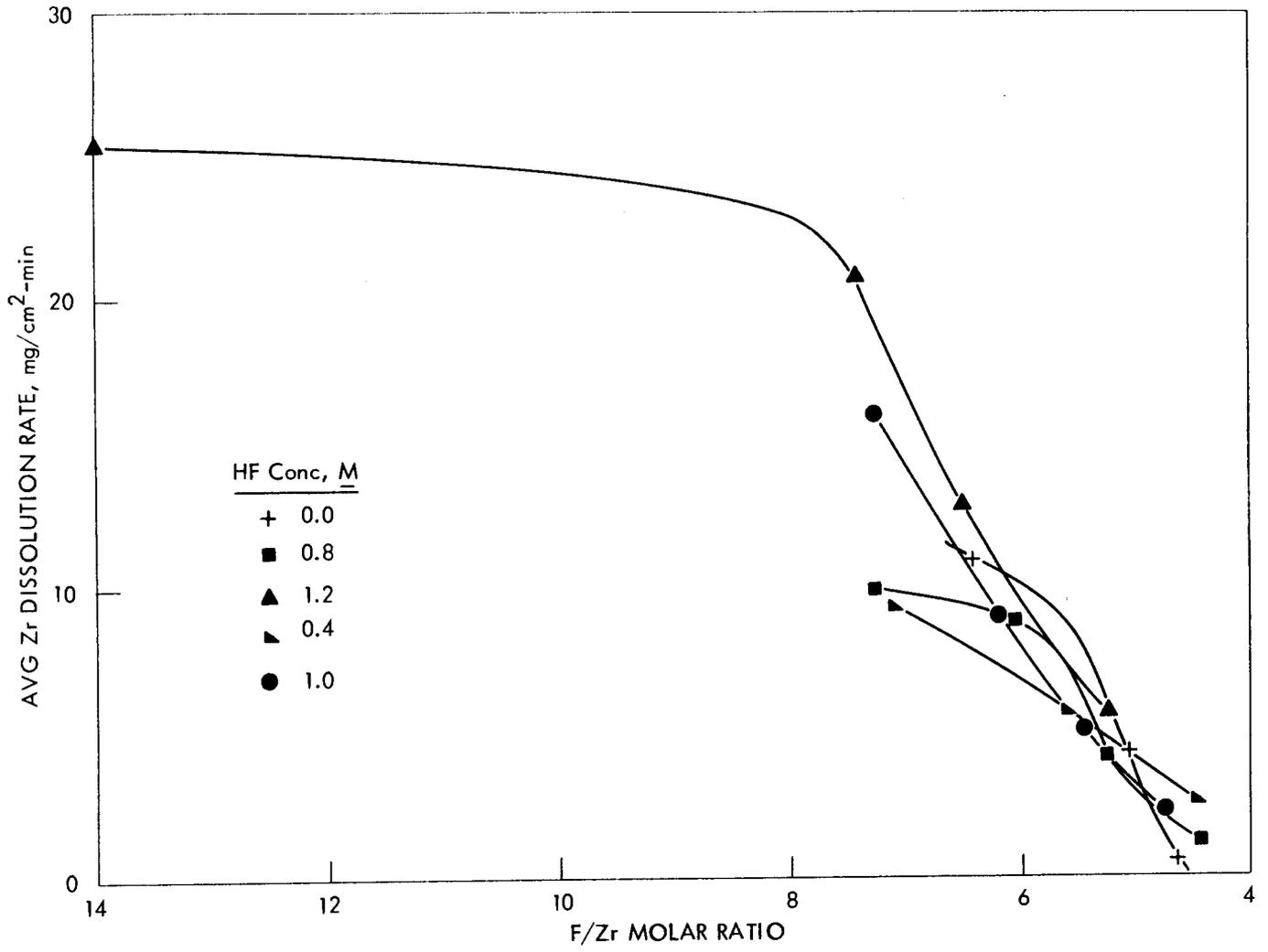


Fig. 8. Zirconium dissolution rates in refluxing 3 M HNO<sub>3</sub>-0.4 M HBF<sub>4</sub>-0.4 to 1 M Cr-HF.

### 3.2 Dissolution in Concentrated Nitric Acid

Strong nitric acid is known to inhibit corrosion of titanium (2). Use of strong nitric acid rather than hexavalent chromium ion to inhibit corrosion would be desirable because of the large amounts of chromium required due to its stoichiometric reduction by dissolving zirconium. An attempt to decrease the amount of hexavalent chromium ion reduced by dissolving in 18 M  $\text{HNO}_3$ -HF solution was unsuccessful. The chromium ion was still reduced in approximately stoichiometric amounts, even in the strong nitric acid.

In refluxing 16 M  $\text{HNO}_3$ -2.1 M F-Zr solutions, titanium corrosion rates decreased rapidly as the F/Zr ratio decreased below 2 (Fig. 9), but began to increase as this ratio decreased to 1.8. The decrease in rates as the F/Zr ratio approached 2 is in good agreement with the conclusion of Vander Waal et al (4) that one zirconium ion complexes only two fluoride ions in strong acid. When a small amount of fluoboric acid (0.025 M) was added to a similar dissolvent, the rate decreased as before but did not increase as the F/Zr ratio continued to decrease to 1.8 and below, probably because the fluoboric acid caused a white coat to form on the titanium.

Unfortunately, Zircaloy-2 dissolution rates were not very high in these dissolvents at F/Zr ratios below 1.9, where the titanium corrosion rates were acceptable. For example, in 16 M  $\text{HNO}_3$ -2.64 M F-0.025 M  $\text{HBF}_4$ , the Zircaloy-2 dissolution rate was about  $3 \text{ mg/cm}^2\text{-min}$  at a F/Zr ratio of 1.9 (Fig. 10). The presence of 0.025 M  $\text{HBF}_4$  apparently did not cause any decrease in the dissolution rates.

Rate studies were not made in more concentrated solutions because it was observed that uranium solubility decreased greatly above 1.7 M Zr. The product solutions shown in Fig. 10 were stable hot or cold and upon dilution and when the solution was made 0.01 M in uranium. Apparently the only feed adjustment necessary would be dilution with water to reduce nitric acid concentrations and permit solvent extraction with tributyl phosphate in organic diluent.

### 4.0 CONCLUSIONS

Batch laboratory data indicate dissolution of Zircaloy-2 in titanium is practical in dilute nitric-hydrofluoric acid containing hexavalent chromium ion and fluoboric acid. Because films form on both the titanium and dissolving Zircaloy-2, further work is needed to determine if the process can be operated continuously as shown in Fig. 1. Before the process can be run continuously, some method of continuously measuring the zirconium concentration in the dissolvent is needed. Corrosion measurements indicate that close control is not necessary to avoid excessive corrosion rates; however, close control is

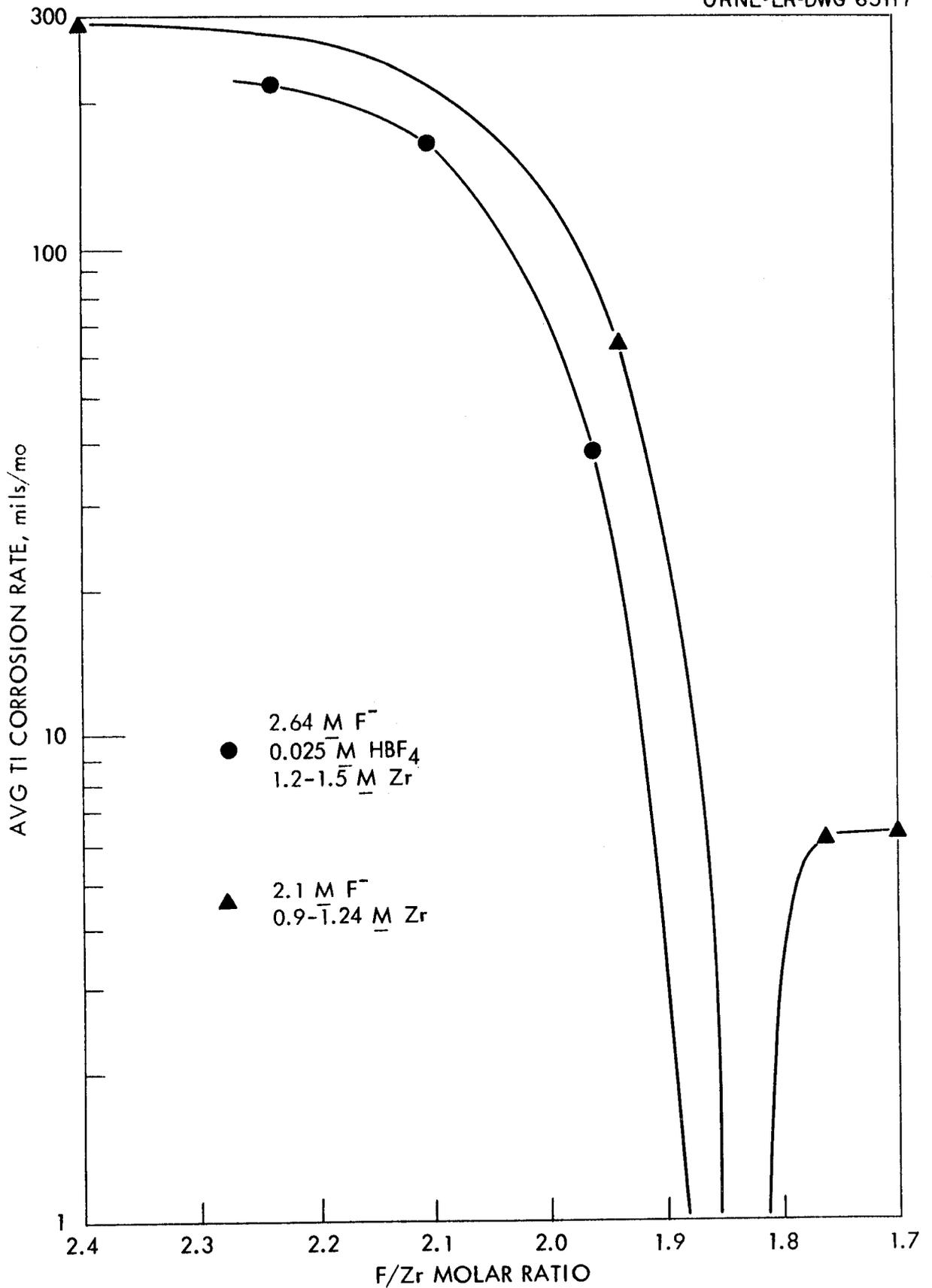


Fig. 9. Corrosion of titanium in refluxing 16 M HNO<sub>3</sub>-F<sup>-</sup>-BF<sub>4</sub><sup>-</sup>-Zr solutions.

UNCLASSIFIED  
ORNL-LR-DWG. 61894

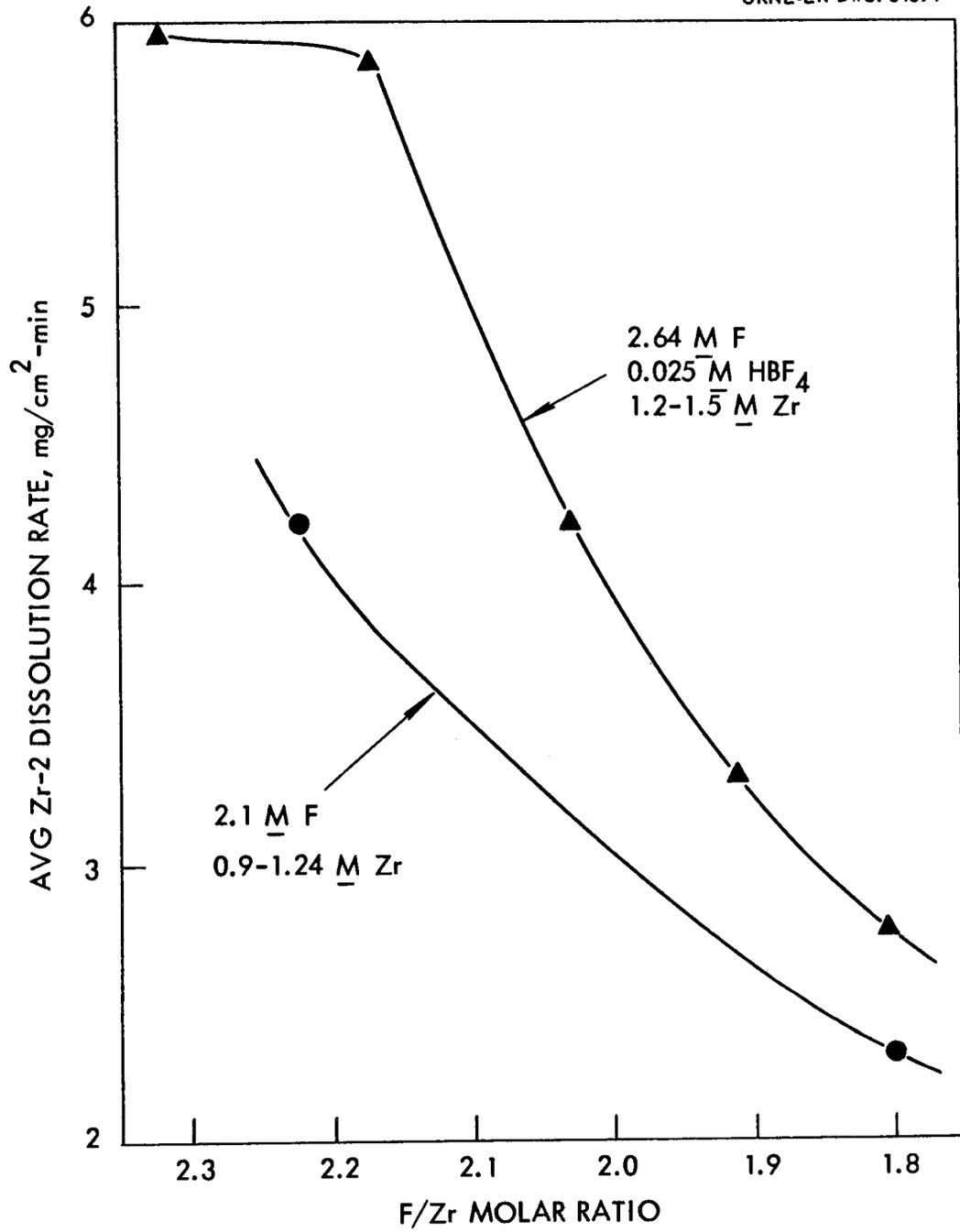


Fig. 10. Dissolution of Zircaloy-2 in refluxing 16 M HNO<sub>3</sub>-F<sup>-</sup>-BF<sub>4</sub><sup>-</sup>-Zr solutions.

needed to maintain the zirconium concentration near 0.47 M. At lower zirconium concentrations, it would be necessary to add more aluminum to complex fluoride not complexed by zirconium, or suffer high corrosion rates in the solvent extraction and waste storage equipment. At zirconium concentrations above about 0.5 M, a precipitate starts to form. At this point dissolution rates decrease rapidly. The precipitate can be dissolved by adding water. Control of the process by continuous colorimetric analyses of hexavalent or trivalent chromium may be possible.

The two disadvantages of low dissolution rates and need for close control to prevent excessive corrosion in the strong nitric acid dissolvent would appear to outweigh the advantage of a more desirable solvent extraction feed solution. High Zircaloy-2 dissolution rates are necessary to penetrate rapidly the oxide coat which forms on Zircaloy-2 in pressurized water.

#### 5.0 REFERENCES

1. W. E. Clark, J. R. Flanary, and F. G. Kitts, "The Darex Process: The Treatment of Stainless Steel Reactor Fuels with Dilute Aqua Regia," ORNL-2712 (in preparation).
2. W. E. Clark and T. A. Gens, "A Study of Dissolution of Reactor Fuels Containing Zirconium in a Titanium Vessel," ORNL-3118 (October 1961).
3. F. G. Kitts, "The Use of Boron for Fluoride Complexing in Thorex Dissolver Solutions," ORNL-CF-59-8-29 (August 1959).
4. E. M. Vander Wall, E. M. Whitener, and D. C. Bauer, "Dissolution of Zirconium and Zircaloy-2 in Nitric-Hydrofluoric Acid Mixtures at Reflux Temperatures," IDO-14497 (September 1959).

DISTRIBUTION

1. R. E. Blanco
2. W. D. Bond
3. J. C. Bresee
4. K. B. Brown
5. W. E. Clark
6. F. L. Culler
7. W. Davis, Jr.
8. D. E. Ferguson
9. L. M. Ferris
10. J. R. Flanary
11. T. A. Gens
12. H. E. Goeller
13. H. B. Graham
14. F. G. Kitts
15. E. L. Nicholson
16. R. H. Rainey
17. M. E. Whatley
18. E. L. Anderson, AEC, Wash.
19. J. A. McBride, IDO
20. C. M. Slansky, IDO
21. Jack Vanderryn, OR AEC
- 22-23. C. R. Library
24. Document Reference Section
- 25-27. Laboratory Records
28. Laboratory Records RC
- 29-43. DTIE
44. M. Skinner