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POWER REACTOR FUELS REPROCESSING PROGRESS REPORT ON CORROSION STUDIES

R. F. MANESS

AUGUST 26, 1959

HANFORD LABORATORIES

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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By

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Chemical Development
Chemical Research and Development Operation

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TABLE OF CONTENTS

POWER REACTOR FUELS REPROCESSING PROGRESS REPORT ON CORROSION STUDIES

I. INTRODUCTION

The Hanford Atomic Products Operation is currently developing technology for the reprocessing of certain low-enrichment (<5 percent U^{235}) power reactor fuels. The fuel elements concerned are of diverse geometry and composition. Fuel claddings include zirconium alloys, austenitic stainless steels, and aluminum. Core compositions include metallic uranium, uranium dioxide, and uranium-molybdenum alloys. Dissolvents capable of decladding these elements or dissolving them completely will represent environments more difficult to contain, from the corrosion standpoint, than those encountered in processing the usual aluminum-clad, uranium-cored production fuel elements.

Several processes for decladding or total dissolution of these various types of fuel elements have been developed. The Darex process (dilute aqua regia) is designed for total dissolution of stainless steel clad elements, while the Niflex process (HNO_3-HF mixtures) is intended for total dissolution of elements clad in either stainless steel or zirconium alloys. The Zirflex process (NH_4F-NH_4NO_3 solutions) is designed for decladding zirconium alloy clad elements, and the Sulfex process (sulfuric acid) is intended for decladding stainless steel clad fuels. Following either of the decladding procedures, the cores would be dissolved in nitric acid or in nitric acid - ferric nitrate solution. Other process variations under consideration include chopping the elements into relatively small pieces and the possibility, with chopped fuels, of dissolving the core material first with or without subsequent dissolution of the cladding.

It is apparent that several different feed preparation process combinations which will handle the entire spectrum of low enrichment fuels are possible. Corrosion studies pursuant to finding suitable materials of construction for process equipment to contain the various process solutions or combinations of process solutions were an integral part of the technology development program. This progress report summarizes corrosion studies performed at Hanford Laboratories in support of the Power Reactor Fuels Reprocessing program. Certain cladding and core dissolution rate data required to define process solutions are also reported.

II. OBJECTIVES

Specific objectives were changed as technology in the dissolution of the various fuel types was developed. However, the work reported may be divided into corrosion studies on candidate materials of construction for equipment for (1) the dissolution of Zircaloy cladding in ammonium fluoride-ammonium nitrate solutions, (2) the total dissolution of stainless steel clad fuels in nitric acid-hydrofluoric acid solutions and (3) the dissolution of stainless steel cladding in dilute sulfuric acid. A further objective was the determination of a single material of construction which could be used for a processing complex which would handle all of the low-enrichment fuels concerned. Extensive corrosion studies on materials of construction for the Darex process were performed at the Batelle Memorial Institute. Only confirmatory tests on the suitability of titanium for this process were done at Hanford Laboratories.

III. SUMMARY

A. Ammonium Fluoride-Ammonium Nitrate Systems (Zirflex)

The 300 series stainless steels, vacuum-melted Hastelloy F, Carpenter 20, Ni-o-nel, Haynes 25 and Incoloy 804 have satisfactory corrosion resistance to the solutions involved in the dissolution of zirconium or Zircaloy claddings in ammonium fluoride or NH_4F-NH_4NO_3

solutions. Titanium fails rapidly in these solutions. Appreciable reduction of the pH of these solutions makes them very corrosive to the stainless steels. Small amounts of fluoride are present during core dissolution following a Zirflex decladding. The corrosiveness of the resulting HNO_3-HF solutions toward stainless steel can be reduced to satisfactory levels by the addition of aluminum nitrate. The waste coating solution may be stored in mild steel after neutralization to a pH of eight to ten.

B. Nitric Acid - Hydrofluoric Acid Systems (Niflex)

Satisfactory dissolution rates for 304-L stainless steel cladding are obtained in 1 M HNO_3 - 2 M HF solutions. The minimum practical fluoride to stainless steel ratio is about five. Dissolution of 347 stainless steel in these solutions is slow. Among many materials studied, vacuum-melted Hastelloy F offers the best corrosion resistance to the HNO_3-HF solutions encountered during decladding. "As welded" weld metal is subject to severe preferential attack. The only solution yet found to this problem is a full solution anneal. Vacuum-melted Hastelloy F shows good resistance to solutions encountered in core dissolution, i. e., the decladding solution butted with nitric acid and aluminum nitrate.

C. Sulfuric Acid Systems (Sulfex)

Dissolution rates for both annealed 304-L and 347 stainless steel in three to four molar sulfuric acid are from five to ten mils per hour. Both Fe(III) and nitrate inhibits the dissolution of stainless steels by sulfuric acid; the passivation effect can be overcome by contacting the stainless steel with a less noble material such as mild steel. Attack of uranium metal and uranium dioxide cores by the decladding solution is accelerated by both Fe(III) and nitrate.

Vacuum-melted Hastelloy F and Ni-o-nel show adequate corrosion resistance to the H_2SO_4-stainless steel solutions concerned in sulfuric acid decladding. Ni-o-nel has better resistance than Hastelloy F to dilute sulfuric acid. However, the presence of dissolved stainless steel accelerates the attack on Ni-o-nel and decreases it on Hastelloy F "As welded" Hastelloy F shows preferential weld metal attack in sulfuric acid; Carpenter 20 and Carpenter 20Cb show stress cracking in sulfuric acid - stainless steel solutions. Ni-o-nel weldments and Hastelloy F welded with Ni-o-nel filler wire show no preferential attack in sulfuric acid or sulfuric acid - stainless steel solutions.

D. Core Dissolution

During uranium or uranium dioxide core dissolution in nitric acid following decladding, some sulfate (Sulfex decladding) or fluoride (Zirflex decladding) will be present due to incomplete rinsing or to the presence of solids (UF_4). Residual sulfate in the concentration range anticipated has no significant effect on the corrosion of 304-L stainless steel or vacuum-melted Hastelloy F by nitric acid. Fluoride present will increase the corrosion potential but can be effectively complexed by aluminum.

Corrosion rates of 304-L, vacuum-melted Hastelloy F, and Ni-o-nel in nitric acid solutions are not markedly increased by low concentrations (0.1 to 0.3 M) of ferric nitrate. However, at higher concentrations (~1 M) corrosion, of an intergranular nature, is severe.

The corrosion behavior of vacuum-melted Hastelloy F and Ni-o-nel in dichromate-containing solutions (simulated oxidizer solution) is similar to that of 304-L, i. e., low corrosion rates in stoichiometrically neutral or acid deficient solutions and high rates accompanied by severe integranular attack in acid solutions.

IV. EXPERIMENTAL AND DISCUSSION

A. Zirflex Process

In the Zirflex process(1), removal of Zircaloy cladding with NH_4F-NH_4NO_3 solutions is followed by dissolution of the uranium metal or oxide core in nitric acid or HNO_3-$Fe(NO_3)_3$ solution. The dissolution of zirconium in ammonium fluoride solution proceeds as shown in Equations (1) and (2).

$$Zr + 6NH_4F + 4H_20 \longrightarrow (NH_4)_2ZrF_6 + 4NH_4OH + 2H_2 \ldots (1)$$

$$NH_4OH \longrightarrow NH_3 + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The pH of the initial solution (ca. 6 M NH_4F) is about seven. This decreases to about four as the dissolved zirconium approaches one molar. In practice, the dissolution is stopped at a terminal zirconium concentration of about 0.85 M leaving about one molar free ammonium fluoride in solution. Hydrogen evolution may be suppressed by the addition of ammonium nitrate as shown by Equation (3).

$$Zr + 6NH_4F + 1/2\ NH_4NO_3 \longrightarrow (NH_4)_2ZrF_6 + 5NH_3 + 1\text{-}1/2\ H_2O \ldots (3).$$

Corrosion rates were determined for the austenitic stainless steels 304-L, 309 SCb and 316 and for Carpenter 20, vacuum-melted Hastelloy F, Ni-o-nel, Incoloy 804, and Haynes 25 (see Table I for nominal alloy compositions) in solutions simulating those produced by the dissolution of zirconium in ammonium fluoride and NH_4F-NH_4NO_3 solutions.

Many simple reflux boiling tests were made with these materials in which specimens were exposed to liquid and vapor phases and at the interface. In all cases, the specimens exposed in the liquid phase

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(1) HW-49633. "Dejacketing of Zircaloy Clad Fuel Elements with Ammonium Fluoride Solution." J. L. Swanson. April 15, 1957.

TABLE I

NOMINAL ALLOY COMPOSITIONS

Alloy	Cr	Ni	Fe	Co	Mn	Mo	Cu	Si	W	C	Nb
	Nominal Composition, Weight Per Cent										
304-L SS	19	10	bal	--	2	--	--	1	-	0.03	--
309 SCb SS	23	13	bal	--	2	--	--	1	-	0.08	Nb-Ta-10XC
316 SS	17	12	bal	--	2	2	--	1	-	0.08	--
Carpenter 20	20	29	bal	--	1	2	3	1	-	0.07	--
Hastelloy F*	22	45	bal	--	2	6.5	--	0.4	-	0.01	2
Ni-o-nel	21	40	bal	--	1	3	1.75	0.4	-	0.05	--
Multimet	21	20	bal	20	1	3	--	1	2.5	0.1	1
Incoloy 804	30	42	bal	--	1	--	--	1	-	0.05	--
Hastelloy X	22	45	bal	--	1	9	--	1	-	0.15	--
Haynes 25	20	10	2	50	1.5	--	--	1	15	0.15	--
Illium R	22	64	2.5	--	1	6.5	4	1	-	0.20	--

* Vacuum melted

had the highest corrosion rate. The majority of the tests were made in Teflon containers equipped with air-cooled polyethylene condensers followed by water-cooled glass condensers. Some tests were made in stainless steel and Hastelloy F equipment and some in glass. Abnormally low corrosion rates were obtained when glass equipment was used. Solution-volume to specimen-area ratio was normally 250 ml/sq. in. Exposure times varied from 24 to 1000 hr.

Results obtained in short-term tests are shown in Table II. The initial dissolver solution is relatively corrosive to stainless steel (ca. 15-20 mils/mo.) in the absence of an inhibitor. As the decladding reaction proceeds, the solution becomes appreciably less corrosive. Also, the corrosion rates are reduced markedly by small amounts of aluminum, copper, arsenic, or silicon in solution. These materials do not appear to interfere with the dissolution of zirconium. Long-term tests (1000 hr.) show that the corrosion rates are essentially constant with time. The mode of corrosion is general with some intergranular attack.

The corrosivity of NH_4F-NH_4NO_3 solutions is markedly decreased in the presence of actively dissolving zirconium. Vacuum-melted Hastelloy F, Ni-o-nel, and 304-L specimens showed overall corrosion rates of about one mil/month when exposed to the liquid phase in laboratory-scale dissolutions of Zircaloy-2 in 6 $\underline{M}$ NH_4F - 0.5 $\underline{M}$ NH_4NO_3. The dissolutions were made in Hastelloy F equipment and were terminated at a free ammonium fluoride concentration of about one molar. The corrosivity of Zirflex decladding solution was also evaluated in a recirculating type dissolver. The dissolver consisted of three one-inch-diameter sections of Haynes 25 tubing (slotted at top and bottom) placed in a four-inch-diameter Hastelloy F pot. Zircaloy was dissolved in the one-inch-diameter tubes. Corrosion specimens were placed both in the reservoir solution and within the

TABLE II

CORROSIVITY OF ZIRFLEX DECLADDING SOLUTION

CONDITIONS: 24 to 48-hour exposure to boiling solutions contained in Teflon or stainless steel.

Solution	Material	Corrosion Rate, Mils/Month
(1) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	304-L	11.4
(2) 6 $\underline{M}$ NH_4F	304-L	7.8
(3) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	304-L	21.0
(4) 4 $\underline{M}$ NH_4F	304-L	10.6
(5) 3 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	304-L	16.0
(6) 3 $\underline{M}$ NH_4F	304-L	4.1
(7) 2 $\underline{M}$ NH_4F	304-L	3.3
(8) 1 $\underline{M}$ NH_4F	304-L	1.3
(9) 0.75 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.5 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	304-L	6.0
(10) 0.83 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.0 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	304-L	4.4
(11) 1 $\underline{M}$ $(NH_4)_2ZrF_6$	304-L	nil
(12) 4 $\underline{M}$ NH_4F, 0.001 $\underline{M}$ SiO_2	304-L	5.1
(13) 4 $\underline{M}$ NH_4F, 0.01 $\underline{M}$ SiO_2	304-L	7.1
(14) 4 $\underline{M}$ NH_4F, 0.05 $\underline{M}$ SiO_2	304-L	1.9
(15) 4 $\underline{M}$ NH_4F, 0.10 $\underline{M}$ SiO_2	304-L	0.5
(16) 4 $\underline{M}$ NH_4F, 1 $\underline{M}$ $(NH_4)_2ZrF_6$	304-L	3.2
(17) 4 $\underline{M}$ NH_4F, 0.0 to 8.4 g Pyrex/l.	304-L	1.6
(18) 4 $\underline{M}$ NH_4F, 7.6 g. Pyrex/l.	304-L	0.01
(19) 4 $\underline{M}$ NH_4F, 0.1 $\underline{M}$ $Al(NO_3)_3$	304-L	2.2
(20) 4 $\underline{M}$ NH_4F, 0.01 $\underline{M}$ $Cu(NO_3)_2$	304-L	2.1
(21) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.001 $\underline{M}$ $Cu(NO_3)_2$	304-L	11.7
(22) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.005 $\underline{M}$ $Cu(NO_3)_2$	304-L	12.2
(23) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ $Cu(NO_3)_2$	304-L	3.4
(24) 0.83 $\underline{M}$ $(NH_4)_2ZrF_6$, 1 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ $Cu(NO_3)_2$	304-L	0.7
(25) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.001 $\underline{M}$ Cr_2O_3	304-L	17.9
(26) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.005 $\underline{M}$ Cr_2O_3	304-L	13.3
(27) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ Cr_2O_3	304-L	22.4
(28) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.05 $\underline{M}$ Cr_2O_3	304-L	2.7
(29) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.05 $\underline{M}$ $Cr(NO_3)_2$	304-L	5.3
(30) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.005 $\underline{M}$ $Ni(NO_3)_2$	304-L	41.2
(31) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ $Ni(NO_3)_2$	304-L	25.1
(32) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.005 $\underline{M}$ As_2O_3	304-L	2.0
(33) 4 $\underline{M}$ NH_4F, 0.001 $\underline{M}$ B_2O_3	304-L	2.7
(34) 4 $\underline{M}$ NH_4F, 0.01 $\underline{M}$ B_2O_3	304-L	4.4
(35) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	309SCb	9.6

TABLE II (Cont'd)

Solution	Material	Corrosion Rate, Mils/Month
(36) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ $Cu(NO_3)_2$	309SCb	3.4
(37) 0.75 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.5 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	309SCb	2.3
(38) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Carp 20	14.0
(39) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Carp 20	5.6
(40) 3 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Carp 20	2.3
(41) 1 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Carp 20	0.8
(42) 0.75 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.5 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Carp 20	1.3
(43) 0.83 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.0 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Carp 20	0.3
(44) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ $Cu(NO_3)_2$	Carp 20	1.8
(45) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.005 $\underline{M}$ As_2O_3	Carp 20	0.2
(46) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.1 $\underline{M}$ $Al(NO_3)_3$	Carp 20	3.4
(47) 6 $\underline{M}$ NH_4F	Hast. F	1.2
(48) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Hast. F	3.3
(49) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ $Cu(NO_3)_2$	Hast. F	0.9
(50) 4 $\underline{M}$ NH_4F	Hast. F	2.7
(51) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Hast. F	5.2
(52) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.005 $\underline{M}$ As_2O_3	Hast. F	1.3
(53) 0.75 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.5 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Hast. F	0.61
(54) 0.83 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.0 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Hast. F	0.23
(55) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Ni-o-nel	4.4
(56) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Ni-o-nel	2.0
(57) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.01 $\underline{M}$ $Cu(NO_3)_2$	Ni-o-nel	1.0
(58) 4 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3, 0.005 $\underline{M}$ As_2O_3	Ni-o-nel	0.8
(59) 2 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Ni-o-nel	1.1
(60) 0.75 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.5 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Ni-o-nel	0.34
(61) 0.83 $\underline{M}$ $(NH_4)_2ZrF_6$, 1.0 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Ni-o-nel	0.12
(62) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Incoloy 804	5.9
(63) 6 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3	Haynes 25	5.5

tubes. The reservoir solution was air sparged at a rate of 0.5 cc/min./ml. solution. The data obtained are shown in Table III.

TABLE III

CORROSIVITY OF ZIRFLEX DECLADDING SOLUTION IN RECIRCULATING TYPE DISSOLVER

Conditions: Zircaloy-2 dissolved in boiling 6 M NH_4F - 0.5 M NH_4NO_3 to terminal zirconium concentration of about 0.8 M.
Exposure hours = 200.

Average Corrosion Rate, Mils/Month(1)

Dissolver Solution			Reservoir Solution		
304-L	Hast. F	Ni-o-nel	Hast. F(2)	Ni-o-nel(2)	Hast. F(3)
2.0	1.1	2.0	1.1	2.4	1.3

Notes:

(1) Includes three runs in which corrosion rates were five to ten mils/month. Leaking gasket permitted two-fold concentration of solution.

(2) Weldment.

(3) Hastelloy F welded with Ni-o-nel.

Little or no difference in the corrosivity of the reservoir and dissolver solutions is noted. The weldments evaluated showed no preferential attack.

Samples of austenitic stainless steels (304-L, 347, 316) placed in a pilot plant Zirflex dissolver corroded at an average overall rate of about four mils/mo. in the absence of an inhibitor. Total exposure time was 110 hours about half of which was under decladding conditions and half under core dissolving conditions. Similarly exposed vacuum-melted Hastelloy F samples corroded at from one to two mils/mo. Heavily oxidized Zircaloy was dissolved in most of the pilot plant runs.

Consequently, the test coupons were exposed to the more corrosive initial decladding solution for a relatively large part of the exposure time. Pilot plant runs including a corrosion inhibitor have not been made.

Stressed specimens of 304-L and Hastelloy F showed no stress cracking after 700 hours exposure to boiling 6 M NH_4F - 0.5 M NH_4NO_3 - 0.01 M $Cu(NO_3)_2$ solution (liquid and vapor phase). No permanent effects on corrosion rates were induced by scratching 304-L specimens which were immersed in 6 M NH_4F or by anodic or cathodic activation. Corrosion rates for 304-L coupons immersed in air- or argon-sparged boiling 4 M NH_4F - 0.5 M NH_4NO_3 were comparable to those obtained in the absence of sparge.

An economic incentive exists for the use of ammonium acid fluoride vice ammonium fluoride as the Zirflex dissolvent. Laboratory-scale Zirflex dissolutions were made using 3 M NH_4HF_2 - 0.5 M NH_4NO_3 as the dissolvent. Hastelloy F specimens placed in the solution simultaneously with the Zircaloy showed a corrosion rate of about one mil/month. However, Hastelloy F corrodes at an excessive rate (about 85 mils/month) in boiling 3 M NH_4HF_2 - 0.5 M NH_4NO_3 in the absence of dissolving zirconium.

A few corrosion tests were made under heat transfer conditions, i. e., heat was supplied to the solution through the test specimens. As shown in Table IV, corrosion rates were about three-fold higher than those obtained with test specimens immersed in boiling solutions.

TABLE IV

CORROSIVITY OF ZIRFLEX DECLADDING SOLUTION HEAT TRANSFER CONDITIONS

Conditions: 24 to 72 hour exposure. Bulk metal temperature 140°C.

Solution	Material	Corrosion Rate, Mils/Month
6 M NH_4F, 0.5 M NH_4NO_3	304-L	38
6 M NH_4F, 0.5 M NH_4NO_3, 0.01 M $Cu(NO_3)_2$	304-L	11
0.75 M $(NH_4)_2ZrF_6$, 1.5 M NH_4F, 0.5 M NH_4NO_3	304-L	14
6 M NH_4F, 0.5 M NH_4NO_3	Hast. F	18
6 M NH_4F, 0.5 M NH_4NO_3, 0.005 M AS_20_3	Hast. F	6.2
0.75 M $(NH_4)_2ZrF_6$, 1.5 M NH_4F, 0.5 M NH_4NO_3	Hast. F	3.4

To simulate use of the same dissolver for decladding and core dissolution operations, coupons of 304-L and vacuum-melted Hastelloy F were exposed alternately to boiling 6 M NH_4F - 0.5 M NH_4NO_3 (eight hours) and boiling 10 M HNO_3 (16 hours). Seven cycles were completed. The coupons were given only a water rinse between exposures. Average corrosion rates obtained are shown in Table V.

TABLE V

CORROSION RATE OF 304-L AND HASTELLOY F ALTERNATE DECLADDING AND CORE DISSOLUTION CONDITIONS

	Average Corrosion Rate, Mils/Month	
	Decladding(1)	Core Dissolution(2)
304-L		
No inhibitor	12.4	0.6
0.01 M $Cu(NO_3)_2$	2.4	0.5
Hastelloy F		
No inhibitor	3.3	0.6
0.01 M $Cu(NO_3)_2$	0.9	0.6

Notes: (1) 6 M NH_4F, 0.5 M NH_4NO_3
(2) 10 M HNO_3

Corrosion of a stainless steel dissolver during the dissolution of fuel cores declad with NH_4F solution would be sensitive to any fluoride remaining as UF_4 or fluoride ion. If necessary, the UF_4 may be metathesized with NaOH or $Al(NO_3)_3$. Tests were made to determine the feasibility of dissolving the cores plus residual fluoride directly in HNO_3-$Al(NO_3)_3$ solutions. The tests were made under heat transfer conditions using stainless steel containers. The bulk metal temperature of the heat transfer test wafers was 140°C. Also, test coupons were suspended in the boiling solution. The test solutions simulated initial, mid-point, and final dissolver solutions at Al/F mole ratios of 6.25, 3.12, and 1.00. The fluoride ion concentration was held constant at 0.08 M. Assuming a feed containing 1.0 M UNH, this amount of fluoride represents two percent conversion of the uranium core to UF_4. The results of these tests are given in Table VI.

TABLE VI

DISSOLUTION OF FUEL CORES CONTAINING RESIDUAL FLUORIDE EFFECT OF Al/F RATIO ON 304-L CORROSION RATES

	Corrosion Rate, Mils/Month Al/F Mole Ratio 6.25	3.12	1.00
Initial			
Wafer	1.97	2.82	13.7
Coupon	1.33	1.62	8.25
Mid-Point			
Wafer	1.90 (0.96)*	3.20	6.50
Coupon	0.76 (0.32)*	1.57	3.46
Final			
Wafer	0.34	0.16	0.19
Coupon	0.04	nil	0.07

Initial - 10 M HNO_3, 0.02 M UNH, 0.08 M HF, $Al(NO_3)_3$

Mid-Point - 5 M HNO_3, 1.0 M UNH, 0.08 M HF, $Al(NO_3)_3$

Final - 1 M HNO_3, 1.4 M UNH, 0.08 M HF, $Al(NO_3)_3$

* plus 0.01 M $Cu(NO_3)_2$.

These data indicate fuel cores containing two percent UF_4 can be dissolved directly in HNO_3-$Al(NO_3)_3$ solution in a stainless steel dissolver without excessive corrosion. The requisite amount of $Al(NO_3)_3$ is less than that required for salting if the dissolver solution is to be processed in a Redox type solvent extraction system.

Vacuum-melted Hastelloy F offers good corrosion resistance to nitric acid solutions as shown by the data given in Table VII. The resistance of Hastelloy F to HNO_3-HF solutions is discussed in a following section of this report.

TABLE VII

CORROSION RATES OF VACUUM MELTED HASTELLOY F(1) IN HNO_3 SOLUTION

	Corrosion Rate, Mils/Month No. of 48 Hour Periods				
I. Huey Type Tests (Coupon immersed in boiling liquid)	1	2	3	4	5
65 w/o HNO_3	2.47	1.20	1.20	1.07	1.66
40 w/o HNO_3	1.32	0.37	0.41	0.37	0.14
II. Heat Transfer Tests(2)	720 Hour Exposure				
65 w/o HNO_3	1.4				
50 w/o HNO_3	2.4 (0.78)				
40 w/o HNO_3	0.38				

(1) Heat FV-150.

(2) Bulk metal temperature 135°C.

Ni-o-nel also offers good corrosion resistance to nitric acid. Welded Ni-o-nel specimens ("as welded") exposed to boiling 10 M HNO_3 for five 48-hour periods corroded at an average rate of 0.35 mil/month with no preferential attack or increase in corrosion rate with time.

To simulate corrosion of the underground waste storage tanks, 1020 mild steel coupons were exposed at 25 and 40°C to Zirflex decladding waste solution neutralized with 50 w/o NaOH to pH values between 5.5 and 9.3. The data obtained (cf Table VIII) indicate negligible attack on specimens exposed for five months to solutions at pH 8.5 and 9.3. Pitting attack was appreciable in solutions at lower pH

TABLE VIII

CORROSION RATES OF MILD STEEL IN NEUTRALIZED ZIRFLEX DECLADDING SOLUTION - EFFECT OF pH

CONDITIONS: Five-month exposure in closed polythene bottles.
Specimens suspended with Teflon tape.

	25 C				40 C			
	Wt. Loss, g		Max. Penetration, Mils*		Wt. Loss, g		Max. Penetration, Mils*	
pH	Liquid	Interface	Liquid	Interface	Liquid	Interface	Liquid	Interface
5.5	0.470	0.431	6.5	5.5	1.084	0.898	13	14
6.3	0.228	0.328	5.5	5.5	0.452	0.571	6.5	10.5
6.9	0.172	0.337	5.5	5.0	0.175	0.491	3.0	6.0
8.5	0.000	0.000	0.0	0.0	0.000	0.000	0.0	0.0
9.3	0.000	0.000	0.0	0.0	0.000	0.000	0.0	0.0

* Maximum pit penetration. Determined by direct measurement after belt grinding to depth of deepest pit.

values. Exposure of 1020 mild steel specimens to boiling neutralized Zirflex waste solution is currently in progress. Negligible corrosion has occurred after exposure for two months.

Mild steel specimens exposed for six months to a boiling solution composed of nine parts synthetic Redox neutralized waste and one part Zirflex waste solution showed negligible corrosion and no preferential attack. The specimens were exposed to liquid (at pH 10), vapor, and the interface.

A preliminary chemical flowsheet for decladding Dresden fuel elements (Zircaloy clad UO_2) in NH_4F-NH_4NO_3 solution is given in HW-60374 ("Non-Production Fuels Reprocessing Technology," A. M. Platt, R. J. Sloat, and R. E. Burns. May 14, 1959).

B. HNO_3-HF System (Niflex)

The Niflex process involves complete dissolution of fuels clad in either zirconium alloys or stainless steel. Cladding removal is accomplished with HNO_3-HF solutions. For core dissolution (U or UO_2), nitric acid is added to increase core dissolution rates and aluminum nitrate is added to reduce corrosion of the container. Preliminary flowsheets prepared by R. W. McKee for complete dissolution of Yankee and PRDC type fuel elements by the Niflex Process are given in Figures 7 and 8.

Zirconium dissolves much more rapidly than stainless steel in HNO_3-HF solutions as shown by the data given in Table IX.

TABLE IX

DISSOLUTION RATES OF 304-L AND Zr-3 IN HNO_3-HF SOLUTIONS

Conditions: One-hour exposure to boiling solutions in glass equipment.

	Dissolution Rate, Mils/Hour	
	304-L	Zr-3
2 M HNO_3, 1 M HF, 0.0 M $Al(NO_3)_3$	6.3	~80
2 M HNO_3, 1 M HF, 0.5 M $Al(NO_3)_3$	0.048	27
2 M HNO_3, 1 M HF, 1.0 M $Al(NO_3)_3$	0.003	10
2 M HNO_3, 1 M HF, 2.0 M $Al(NO_3)_3$	0.001	2.0

Since the stainless steel is the more difficult to dissolve of the two cladding materials, a somewhat detailed study of 304-L stainless steel dissolution rates in HNO_3-HF solutions was made to define needed solution compositions. Teflon containers equipped with air-cooled polythene condensers followed by water-cooled glass condensers were used in these studies. The results are shown in Figure 1 and Table X. The data indicate an optimum nitric acid concentration of about 1.0 M. At this nitric acid concentration satisfactory dissolution rates may be obtained in boiling solutions with HF concentrations of one molar, or less. However, higher HF concentrations would reduce the required dissolution and exposure time. The dissolution rate is approximately doubled for each 15°C rise in temperature.

No significant difference was noted in the dissolution rates of fully annealed vs. sensitized (two hours at 1250°F) 304-L stainless steel in 1 M HNO_3-2 M HF. The dissolution rate of 304-L was not changed as a result of heating the metal in air for two weeks at 400°C.

The dissolution of 347 stainless steel in HNO_3-HF solutions is difficult. One-hour dissolutions in 1 M HNO_3-1 M HF and 1 M HNO_3-2 M HF resulted in dissolution rates of 1.9 and 4.3 mils/hour, respec-

TABLE X

DISSOLUTION RATES OF 304-L IN HNO_3-HF SOLUTION

CONDITION: One-hour exposure in Teflon or polythene containers. 125 ml. solution/in^2 SS.

HF Molarity	Temp, °C	Dissolution Rate, Mils/Hour HNO_3 Molarity 0.0	0.5	1.0	2.0	5.0	10
0.5	Boiling	0.73	5.62	3.09	2.15	2.02	1.50
1.0	"	0.89	8.09	6.87	6.58	4.77	4.33
1.0	85	--	--	--	3.30	--	--
1.0	72	0.13	1.86	1.01	0.76	0.09	--
1.0	50	0.06	0.96	0.62	0.38	0.05	--
2.0	Boiling	1.55	11.4	12.0	13.4	9.62	8.61
2.0	85	--	--	5.92	6.10	--	--
4.0	72	--	--	11.2	--	--	--
4.0	50	--	--	3.19	--	--	--

tively. However, dissolution essentially stopped in 1 M HNO_3-2 M HF after the stainless steel concentration in solution reached 0.1 M. The dissolution rate of 304-L stainless steel in HNO_3-HF solutions is also dependent upon the concentration of stainless steel in solution. Quantitative data on this effect are shown in Figure 2. The dissolution rate decreases markedly as the stainless steel/fluoride mole ratio approaches 0.2. Some additional data on the effect of certain components of stainless steel on the 304-L dissolution rate are shown in Table XI.

TABLE XI

DISSOLUTION OF 304-L IN FLUORIDE CONTAINING SOLUTIONS

Conditions: One-hour exposure to boiling solutions contained in Teflon.

	Dissolution Rate, Mils/Hour
1 M HNO_3, 1 M HF	6.87
1 M HNO_3, 1 M HF, 0.17 M $Fe(NO_3)_3$	0.46
1 M HNO_3, 1 M HF, 0.17 M $Cr(NO_3$	2.37
1 M HNO_3, 1 M HF, 1.0 M CrO_3	0.02
2 M HF	1.55
2 M HF, 0.1 M CrO_3	0.02
1 M H_2SO_4, 1 M HF	1.88

Metals and alloys investigated as potential materials of construction for containing boiling HNO_3-HF solutions included Haynes 25, Multimet, Hastelloy X, vacuum-melted Hastelloy F, Illium R, Carpenter 20, 309 SCb, Incoloy 804, Ni-o-nel, platinum, tantalum, and gold. Of these materials only vacuum-melted Hastelloy F, Haynes 25, 309 SCb, platinum and gold exhibited promising corrosion resistance. Vacuum-melted Hastelloy F showed somewhat greater corrosion resistance than 309 SCb or Haynes 25 to the HNO_3-HF compositions of interest. Therefore, the experimental work was concentrated on this material. It was established early that only the vacuum-melted variety of Hastelloy F (0.02% C) offers useful corrosion resistance to HNO_3-HF solutions. The air melted alloy (0.05% C) experiences severe intergranular attack.

Corrosion rates for vacuum-melted Hastelloy F (heat FV-150) obtained in HNO_3-HF solutions contained in Teflon equipment are given in Table XII. Vapor and interface specimens invariably corroded less than specimens exposed to liquid. Hence, only liquid phase corrosion data are presented. Except for end-grain attack, corrosion was general and uniform at HF concentrations of two molar and less. Pitting attack occurred at higher HF concentrations. The corrosion rates of heats FV-153 and 155 (used in construction of a semiworks dissolver) in HNO_3-HF solutions were found to be two-fold higher than that of heat FV-150. The reason for this difference is not apparent from a comparison of composition and microstructure.

Stressed vacuum-melted Hastelloy F specimens exposed to boiling 1 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HF in liquid and interface positions showed no indication of stress corrosion cracking after 580 hours of exposure.

The corrosion rate of Hastelloy F decreases as stainless steel dissolves due to a decreasing nitric acid concentration and to the complexing of fluoride by the constituents of stainless steel. This effect is shown in Table XIII.

TABLE XII

CORROSION RATES OF HASTELLOY F* IN HNO_3-HF SOLUTION

Solution	Exposure Time, Hours	Temp, °C	Corrosion Rate, Mils/Month
0.5 M HNO_3, 1.0 M HF	24	Boiling	17
0.5 M HNO_3, 2.0 M HF	24	Boiling	26
1.0 M HNO_3, 0.5 M HF	24	Boiling	4.5
1.0 M HNO_3, 1.0 M HF	24	Boiling	14
1.0 M HNO_3, 2.0 M HF	21	Boiling	34
1.0 M HNO_3, 2.0 M HF	24	Boiling	30
1.0 M HNO_3, 2.0 M HF	48	Boiling	33
1.0 M HNO_3, 2.0 M HF	360	Boiling	36
1.0 M HNO_3, 2.0 M HF	580	Boiling	35
1.0 M HNO_3, 2.0 M HF, 0.3 M SiO_2	24	Boiling	3.9
1.0 M HNO_3, 2.0 M HF, 0.5 M As_2O_3	2	Boiling	915
2.0 M HNO_3, 0.5 M HF	24	Boiling	6.4
2.0 M HNO_3, 1.0 M HF	24	Boiling	14
2.0 M HNO_3, 2.0 M HF	24	Boiling	29
2.0 M HNO_3, 3.0 M HF	24	Boiling	101 pitting
5.0 M HNO_3, 0.4 M HF	29	Boiling	26
5.0 M HNO_3, 2.0 M HF	24	Boiling	140
6.0 M HNO_3, 1.0 M HF, 1.0 M $Al(NO_3)_3$	24	Boiling	2.8
6.0 M HNO_3, 2.0 M HF, 1.0 M $Al(NO_3)_3$	24	Boiling	6.8
9.0 M HNO_3, 0.4 M HF	7	Boiling	45
9.0 M HNO_3, 1.0 M HF, 1.0 M $Al(NO_3)_3$	24	Boiling	3.3
10 M HNO_3, 2.0 M HF	24	Boiling	320
13 M HNO_3, 0.25 M HF	4	Boiling	194
0.5 M HNO_3, 1.0 M HF	96	85	1.0
0.5 M HNO_3, 2.0 M HF	72	85	5.3
0.5 M HNO_3, 3.0 M HF	96	85	10
0.5 M HNO_3, 5.0 M HF	96	85	26 pitting
1.0 M HNO_3, 1.0 M HF	72	85	3.6
1.0 M HNO_3, 2.0 M HF	72	85	12
1.0 M HNO_3, 3.0 M HF	72	85	24
2.0 M HNO_3, 1.0 M HF	72	85	2.9
2.0 M HNO_3, 2.0 M HF	72	85	6.7
2.0 M HNO_3, 3.0 M HF	72	85	17 pitting
0.5 M HNO_3, 4.0 M HF	255	70	10
1.0 M HNO_3, 1.0 M HF	255	70	1.9
1.0 M HNO_3, 2.0 M HF	255	70	4.7
1.0 M HNO_3, 3.0 M HF	255	70	8.4
1.0 M HNO_3, 4.0 M HF	255	70	9.6

*Heat FV-150 (Vacuum melted)

TABLE XIII

HASTELLOY F CORROSION RATES DURING JACKET REMOVAL

Conditions: 304-L exposed to boiling 1 M HNO_3 - 2 M HF contained in Teflon in presence of Hastelloy F specimens.

Exposure Time, Hours	Conc. of SS, M	Corrosion Rate, Mils/Month
1	0.38	34
2	0.42	29
3	0.45	22
6	0.52	17

The above Hastelloy F corrosion data apply to "as-mill-annealed" metal. Weld metal attack of "as-welded" vacuum-melted Hastelloy F weldments fabricated by closely controlled metal-arc, inert-gas methods is severe in HNO_3-HF solutions (about 300 mils/month in 1 M HNO_3 - 2 M HF as determined by weight loss). Weldments produced using the electron beam technique also show severe weld metal attack. As-welded specimens show preferential weld metal attack in core dissolvent solutions (HNO_3-HF-stainless steel solutions butted with HNO_3 and $Al(NO_3)_3$) only at Al/F mole ratios less than one. Preferential weld metal attack in boiling 10 M HNO_3 is negligible. As-welded 309 Cb weldments also show severe preferential weld metal attack in HNO_3-HF solutions. As-welded Haynes 25 specimens show severe attack in the area adjacent to the weld area but no preferential weld metal attack in HNO_3-HF solutions. Weldments made with vacuum-melted Hastelloy F as base metal and Haynes 25 filler rod do show preferential weld metal attack when exposed to HNO_3-HF solutions.

Post-weld heat treatment studies of vacuum-melted Hastelloy F weldments show that weld metal attack is reduced to near that of base metal by a full solution anneal at 2150°F. Annealing at 2100°F is only partially effective while annealing at 1860°F is detrimental. The effect of post-weld heat treatment temperature on the corrosion resistance of vacuum-melted Hastelloy F weldments to HNO_3-HF solutions is shown graphically in Figure 3. The microstructure of a weldment before and after annealing is shown in Figure 4. Photographs of the segregated phase present in the dendritic weld metal is shown at higher magnifications in Figure 5. The root pass of some weldments showed greater corrosion resistance than the filler pass, presumably because of an annealing treatment of the root-pass metal when making the filler pass. The microstructure of one such weldment is shown in Figure 6. Heat treatments made as a function of time (one to three hours) at 2100 and 2150°F showed that no improvement in corrosion resistance occurs after one hour at temperature. No difference was noted in the corrosion behavior of air-cooled and water-quenched weldments. Weldments solution annealed at 2175 and 2200°F and water-quenched showed no preferential weld metal attack in boiling 1 $\underline{M}$ HNO_3 - 2 $\underline{M}$ HF solution. No cracking occurred. Appreciable scaling and pitting occurred during the solution anneal, however. The melting point of Hastelloy F is listed by the manufacturer (Haynes-Stellite Co.) as 2300°F. Weldments annealed at some unknown high temperature (defective furnace thermocouple) and water-quenched showed extensive cracking of the base metal.

Four laboratory-scale heats of modified vacuum-melted Hastelloy F were produced on-site. Weldments made from these heats (same metal used for both base and filler metal) were corrosion tested in HNO_3-HF and H_2SO_4-stainless steel solutions. The results are shown in Table XV.

TABLE XV

CORROSION RESISTANCE OF SOME HEATS OF MODIFIED VACUUM-MELTED HASTELLOY F

	Nominal Alloy Composition, Weight Percent						Corrosion Rate, Mils/Month	
	Cr	Ni	Mo	Fe	C	Nb	1M HNO_3-2M HF	4M H_2SO_4-10 g ss/l
1)	22	45	6	bal.	.01	-	32	6
2)	22	45	9	bal.	.01	-	27	7
3)	22	45	12	bal.	.01	-	147	27
4)	22	45	9	bal.	.01	1	134	14

Weld metal attack of weldments produced from heat No. 1) was somewhat less, and that of Heat No. 2) appreciably less, than that of standard vacuum-melted Hastelloy F weld metal. Weldments made from heats 3) and 4) showed appreciably higher base metal corrosion rates, in both test solutions, than the standard alloy. Weld metal attack was severe. In preliminary tests made with a sample of copper-bearing Hastelloy F obtained from the Haynes Stellite Company, no preferential weld metal attack occurred on exposure to boiling 1 M HNO_3 - 2 M HF. Further studies of weld metal modifications are in progress.

A laboratory-scale dissolver constructed of vacuum-melted Hastelloy F was run to failure in boiling 1 M HNO_3 - 2 M HF solution. Heat was supplied to the dissolver via a Glas-col mantle. The solution was changed twice a week to prevent excessive build-up of corrosion products. The dissolver was made from a section of four-inch-diameter welded pipe which was fabricated on-site. The pipe was annealed for one hour at 2100°F and water quenched prior to the time the bottom weld was made. The fabricated dissolver was annealed for one hour at 2125°F and water quenched. Failure of the dissolver at the bottom weld occurred after 1100 exposure hours. No preferential attack of the seam weld was noted.

TABLE XVI

SIMULATED DISSOLUTION OF 304-L CLAD FUELS IN HNO_3-HF SOLUTION

CONDITIONS: Dissolutions performed in boiling solutions contained in dissolver constructed of Hastelloy F.

	Final Decladding Solution	Hast. F Corrision Rate, Decladding	Initial Core Dissolving Solution	Hast. F Corrosion Rate, Core Dissolving	Final Feed Solution
(1)	0.34 M SS, 2.0 M F^-, ~0.3 M HNO_3	22 mils/month	0.23 M SS, 1.4 M F^-, ~2.0 M HNO_3, 0.81 M $Al(NO_3)_3$	2.0 mils/month	0.26 M SS, 1.5 M F, 0.54 M U, 0.91 M Al $(NO_3)_3$ ~0.0 M HNO_3
(2)	0.45 M SS, 2.0 M F^-, ~0.1 M HNO_3	30 mils/month	0.56 M SS, 2.5 M F^-,(1) ~3.0 M HNO_3, 1.47 M Al $(NO_3)_3$	3.8 mils/month	0.56 M SS, 2.5 M F^-, 0.76 M U, 1.47 M Al $(NO_3)_3$ ~0.0 M HNO_3
(3)	0.53 M SS, 3.0 M F^-,(2) ~0.1 M HNO_3	42 mils/month	0.37 M SS, 2.1 M F^-, ~2.5 M HNO_3, 0.81 M $Al(NO_3)_3$	4.8 mils/month	0.40 M SS, 2.3 M F^-, 0.48 M U, 0.91 M Al $(NO_3)_3$ ~0.5 M HNO_3
(4)	0.41 M SS, 2.0 M F^-, ~0.1 M HNO_3	25 mils/month	0.37 M SS, 1.8 M F, ~2.0 M HNO_3, 0.25 M SiO_3	10.7 mils/month	0.39 M SS, 1.9 M F^-, 0.24 M U, 0.28 M Si, ~1 M HNO_3
(5)	0.42 M SS, 2.0 M F^-, ~0.1 M HNO_3, 2.0 M NH_4NO_3	32 mils/month	0.27 M SS, 1.3 M F^-, ~1.5 M HNO_3, 0.6 M $Al(NO_3)_3$, 1.3 M NH_4 NO_3	1.0 mils/month	0.30 M SS, 1.4 M F^-, 0.24 M U, 0.65 M Al $(NO_3)_3$ ~0.5 M HNO_3, 1.4 M NH_4NO_3

Notes:

(1) Solution concentrated subsequent to $Al(NO_3)_3$ addition and prior to HNO_3 addition. Hastelloy F corrosion rate during concentration was one mil/month.

(2) Initially 2.0 M F^-. Additional HF butt as reaction subsided.

Several feed preparation runs were made in a one-liter dissolver constructed of vacuum-melted Hastelloy F. In all runs, stainless steel was dissolved in 1 M HNO_3 - 2 M HF. After the stainless steel dissolution, nitric acid and aluminum nitrate were added and uranium metal was dissolved. Data obtained in typical runs are given in Table XVI. The Hastelloy F corrosion rate was 25 to 30 mils/month during decladding (vs ~45 mils/month for 309 SCb) and about three mils/month during core dissolution. Continuous weight measurements of the dissolving uranium indicated a dissolution rate of about three to 5 g/cm^2-hr in most runs. The uranium dissolution rate was markedly reduced when Na_2SiO_3 (vice $Al(NO_3)_3$) was used to complex fluoride. Other uranium dissolution data are given in Table XVII.

TABLE XVII

DISSOLUTION RATE OF INGOT URANIUM

Conditions: Two-minute exposure to boiling solutions containing 0.22 M stainless steel 1.5 M HF, 0.86 M $Al(NO_3)_3$, and varying amounts of HNO_3 and U.

Dissolvent	Dissolution Rate, g/cm^2-hr.
1.96 M HNO_3, 0.0 M U	5.5
0.84 M HNO_3, 0.25 M U	3.8
0.29 M HNO_3, 0.35 M U	3.4
0.0 M HNO_3, 0.48 M U	2.5 (ppt. formed on cooling)

A single dissolution of U-8 w/o Mo alloy was made under conditions similar to those used in Run No. 1 (Table XVI). The dissolution rate was about two-fold lower than that observed for ingot uranium and the terminal solution contained about two volume percent of solids.

To simulate conditions during the storage of dissolver solutions obtained by HNO_3-HF dissolution of stainless steel clad fuels, 304-L stainless steel specimens were exposed for 3000 hours at 25 and 40°C to synthetic feed solutions contained in closed polythene bottles. The results of these tests, shown in Table XIV, indicate that ambient temperature storage of the dissolver solutions in stainless steel tanks is practical.

TABLE XIV

CORROSIVITY OF SYNTHETIC FEED SOLUTIONS TO 304-L STAINLESS STEEL

	Corrosion Rate, Mils/Month			
	25 C		40 C	
	Liquid	Interface	Liquid	Interface
1) 1 M UNH, 2 M HF, 0.5 M HNO_3, 0.45 M SS	0.02	0.03	0.05	0.08
2) 1 M UNH, 4 M HF, 0.5 M HNO_3, 0.45 M SS	0.10	0.35	0.56	0.97

Actual feed solutions would contain $Al(NO_3)_3$ in addition to the components of stainless steel. Thus, the free fluoride concentration and corrosivity of the solutions would be produced even further. Mild steel (1020) specimens exposed for 3000 hours at 40°C to solution 2) Table XIV after neutralization to pH 8.5 corroded at about 0.8 mil/month.

C. Sulfuric Acid System (Sulfex)

Dilute sulfuric acid can be used to dissolve preferentially stainless steel cladding.(2) Hanford Laboratories data(3) indicate little attack on irradiated uranium and uranium dioxide fuel cores exposed to boiling dilute sulfuric acid.

Data obtained on the dissolution rate of annealed 304-L stainless steel in boiling dilute sulfuric acid as a function of sulfuric acid and dissolved stainless steel concentration are shown in Figure 9. These data indicate the optimum initial sulfuric acid concentration is three to four molar. Higher concentrations would only unnecessarily increase the size of the off-gas system and aggravate corrosion problems. Sensitization of 304-L (one hour at 1250°F) increases the dissolution rate in boiling dilute sulfuric acid about two-fold. The dissolution rate of 347 stainless steel is only slightly less than that of 304-L. Boiling dilute sulfuric acid also dissolves 309 Cb stainless steel readily.

During the course of the Sulfex studies several 304-L specimens of unknown history were found to be passive in boiling 3.5 $\underline{M}$ H_2SO_4. In every case the specimens were activated by momentarily contacting them with mild steel while in the sulfuric acid solution. None of the specimens were passive in boiling 6 M H_2SO_4. Passive 304-L specimens were produced by the following techniques: 1) HNO_3-HF etch followed by exposure to 30 w/o HNO_3 at 70°C, 2) exposure to boiling 4 $\underline{M}$ HNO_3 - 0.5 $\underline{M}$ HCl solution, 3) removal of dissolving specimens from boiling H_2SO_4-ss solutions, and 4) long term (six month) exposure to air.

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(2) ORNL-2461. "Development of the Sulfex Process for Decladding Stainless-Steel-Clad Power Reactor Fuel Elements with Sulfuric Acid." J. R. Flanary, et al. March 30, 1959.

(3) HW-61428. "Rates of Reaction of Irradiated Uranium Dioxide and Uranium Metal with Sulfuric Acid." J. L. Swanson. August 13, 1959.

Methods (2) and (3) were the most effective; some specimens showed no attack after two hours exposure to boiling 3.5 M H_2SO_4. Dissolution was initiated in all cases by contact with mild steel or active stainless steel. Exposure of 304-L specimens for one month to water at 300°C did not produce passivation to boiling 3.5 M H_2SO_4.

The dissolution rate of 304-L in boiling 3.5 M H_2SO_4 containing as little as 0.01 M Fe(III) or 0.05 M NO_3 was essentially nil. Dissolution was initiated by contacting the 304-L with mild steel. However, dissolution of stainless steel in 3.5 M H_2SO_4 to the extent of 25 g/l followed by the addition of minor quantities of Fe(III) or nitrate produced a solution in which 304-L was not activated by contact with mild steel. Air sparging during the dissolution of stainless steel in sulfuric acid had no effect upon the rate or amount of stainless steel dissolved.

The effect of nitrate and ferric ion on uranium and sintered uranium dioxide dissolution rates in boiling sulfuric acid is shown in Table XVIII. It is apparent that the dissolver must be essentially free of nitrate and ferric ion for both decladding and core dissolution conditions.

Data obtained on the corrosion rates of vacuum-melted Hastelloy F, Carpenter 20, Ni-o-nel and Haynes 25 in sulfuric acid and in H_2SO_4-stainless steel solutions in simple reflux boiling tests are shown in Tables XIX through XXII. The corrosion rate of vacuum melted Hastelloy F in boiling 3.5 M H_2SO_4 is about 28 mils/month. However, the rate is reduced to about four mils/month in the system 3.5 M H_2SO_4 - 1 g ss/l. Further increases in the stainless steel concentration increases the corrosion rate. The corrosion rate in 3.5 M H_2SO_4-20 g ss/l is about ten mils/month. The corrosion rates of Ni-o-nel and Carpenter 20 in the sulfuric acid and H_2SO_4-stainless steel systems are essentially the same. Dissolved stainless steel increases the corrosivity towards both materials. The corrosion rates are two to 2.5 mils/month in

TABLE XVIII

CLADDING AND FUEL CORE DISSOLUTION RATES IN SULFURIC ACID EFFECT OF NITRATE AND FERRIC ION

CONDITIONS: One to three-hour exposures of annealed 304-L., ingot uranium, and sintered UO_2 to boiling 3.5 M H_2SO_4 containing varying amounts of nitrate and ferric ion.

		Dissolution Rate		
NO_3^-, M	Fe (III), M	304-L., Mils/hr	U, mg/cm^2 -hr	UO_2, mg/cm^2- hr
--	---	9.87	1.2	0.4
0.01	---	9.22	1.4	2.8
0.02	---	5.52	---	4.5
0.04	---	0.23	---	12
0.06	---	0.14	---	28
0.08	---	0.08	---	48
0.10	---	0.09	3.4	74
0.20	---	0.06	---	91
---	0.01	nil	5.1	19
---	0.02	nil	11	---
---	0.10	nil	---	88
---	0.20	nil	89	---

TABLE XIX

VACUUM MELTED HASTELLOY F CORROSION RATES
H_2SO_4 - STAINLESS STEEL SYSTEM

CONDITIONS: Exposure to boiling solutions. Fresh solution every 24 hours.

	Corrosion Rate, Mils/Month, Number of 24 hour periods										
Solution	1	2	3	4	5	6	7	8	9	10	Avg.
(1) 3.5 M H_2SO_4	27.4	29.7	27.8	29.1	32.5	30.1	21.3	33.1	30.3	28.2	28.9
(2) 3.5 M H_2SO_4, 1 g. ss/l.	3.87	4.73	3.85	3.08	5.10	5.66	3.99	6.77	5.66	5.02	4.77
(3) 3.5 M H_2SO_4, 5 g. ss/l.	7.44	6.66	3.54	4.71	5.29	5.19	6.62	4.96	5.78	5.68	5.59
(4) 3.5 M H_2SO_4, 10 g. ss/l.	6.85	6.97	9.61	5.95	6.97	7.00	9.87	9.60	8.12	8.02	7.90
(5) 3.5 M H_2SO_4, 20 g. ss/l.	15.6	8.99	8.26	12.9	9.43	9.49	6.93	7.34	13.0	9.88	10.2
(6) 4.0 M H_2SO_4	34.1	55.0	--	--	--	--	--	--	--	--	--
(7) 3.0 M H_2SO_4	21.0	12.6	11.4	--	--	--	--	--	--	--	--
(8) 3.0 M H_2SO_4, 0.05 M $Fe_2(SO_4)_3$	0.13	0.15	0.00	--	--	--	--	--	--	--	--
(9) 3.0 M H_2SO_4, 0.01 M $CuSO_4$	1.90	0.16	--	--	--	--	--	--	--	--	--
(10) 3.0 M H_2SO_4, 0.2 M HNO_3	0.11	--	--	--	--	--	--	--	--	--	--
(11) 3 M H_2SO_4, 10 g. ss/l., 0.05 M $Fe_2(SO_4)_3$	0.14	0.18	0.10	--	--	--	--	--	--	--	--
(12) 3 M H_2SO_4, 10 g. ss/l., 0.01 M NH_4NO_3	14.2	--	--	--	--	--	--	--	--	--	--
(13) 3 M H_2SO_4, 10 g. ss/l., 0.10 M NH_4NO_3	0.11	0.13	0.06	--	--	--	--	--	--	--	--

Note: Sulfuric acid concentration not corrected for that consumed in reaction with stainless steel.

TABLE XX

CARPENTER 20 CORROSION RATES
H_2SO_4 - STAINLESS STEEL SYSTEM

CONDITIONS: Exposure to boiling solutions. Fresh solution every 24 hours.

	Corrosion Rate, Mils/Month Number of 24-hour periods										
Solution	1	2	3	4	5	6	7	8	9	10	Avg.
(1) 3.5 $\underline{M}$ H_2SO_4	2.35	1.27	1.84	1.84	1.78	2.63	1.36	1.48	1.98	2.08	1.86
(2) 3.5 $\underline{M}$ H_2SO_4, 1 g ss/l.	3.48	3.12	3.01	3.15	2.12	2.58	2.23	3.31	2.54	3.73	2.93
(3) 3.5 $\underline{M}$ H_2SO_4, 5 g ss/l.	5.05	5.27	8.00	1.07	5.90	7.66	6.07	5.76	4.88	8.13	6.75
(4) 3.5 $\underline{M}$ H_2SO_4, 10 g ss/l.	12.1	7.30	4.76	10.3	9.59	9.17	8.48	10.5	13.3	8.95	9.42
(5) 3.5 $\underline{M}$ H_2SO_4, 20 g ss/l.	12.6	11.7	15.2	17.8	9.21	9.60	11.1	13.2	10.2	--	12.3
(6) 4.0 $\underline{M}$ H_2SO_4	2.70	2.24	3.57	2.63	2.89	--	--	--	--	--	2.81

Note:

Sulfuric acid concentration not corrected for that consumed in reaction with stainless steel.

TABLE XXI

NI-O-NEL CORROSION RATES
H_2SO_4 - STAINLESS STEEL SYSTEMS

CONDITIONS: Exposure of welded specimens to boiling solutions. Fresh solution every 24 hours.

Solution	Corrosion Rate, Mils/Month Number of 24-hour periods 1	2	3	4	5	6	7	8	9	10	Avg.
(1) 3 M H_2SO_4	3.31	2.45	1.93	2.58	2.38	2.42	2.06	2.42	2.26	1.65	2.35
(2) 3 M H_2SO_4, 10 g ss/l.	8.11	8.50	8.14	8.82	7.67	6.71	6.72	7.64	7.68	7.68	8.09
(3) 4 M H_2SO_4	3.31	3.15	3.74	2.52	2.84	4.77	2.01	2.56	3.11	3.00	3.10
(4) 4 M H_2SO_4, 10 g ss/l.	8.17	4.90	7.46	8.47	5.85	8.53	8.95	8.82	6.55	9.52	7.72
(5) 3.5 M H_2SO_4	1.99	2.03	--	1.96	2.98	--	--	--	--	--	2.28
(6) 3.5 M H_2SO_4, 5 g ss/l.	6.75	3.40	4.19	6.21	10.8	--	--	--	--	--	6.27
(7) 3.5 M H_2SO_4, 20 g ss/l.	6.54	9.43	5.33	6.51	7.42	--	--	--	--	--	7.05
(8) 3.5 M H_2SO_4, 50 g ss/l.	7.20	4.89	8.43	7.44	11.4	--	--	--	--	--	7.89

Note:

Sulfuric acid concentration not corrected for that consumed in reaction with stainless steel.

TABLE XXII

HAYNES 25 CORROSION RATES IN SULFEX SOLUTIONS

CONDITIONS: Sections of one-inch-diameter welded Haynes 25 tubing (as annealed by the fabricator) exposed for five 24-hour periods to boiling solutions as listed below.

	Average Corrosion Rate, Mils/Month		
Solution	Liquid	Vapor	Interface
2 M H_2SO_4	14	--	--
3 M H_2SO_4	22	3.6	--
4 M H_2SO_4	32	--	--
3.5 M H_2SO_4, 1 g ss/l.	6.1*	2.6	10*
3.5 M H_2SO_4, 5 g ss/l.	8.6*	--	--
3.5 M H_2SO_4, 10 g ss/l.	9.2*	--	--
3.5 M H_2SO_4, 20 g ss/l.	10*	2.9	8.4*
3.5 M H_2SO_4, 40 g ss/l.	11*	--	--

*Preferential weld metal attack.

3.5 M H_2SO_4 and ten to 12 mils/month in 3.5 M H_2SO_4-20 g ss/l. Corrosion of Haynes 25 in sulfuric acid and H_2SO_4-stainless steel systems is similar to that of Hastelloy F.

As-welded vacuum-melted Hastelloy F weldments showed moderate preferential weld metal attack in boiling dilute sulfuric acid and in H_2SO_4-stainless steel solutions. However, no preferential attack occurred after a solution anneal. Hastelloy F weldments welded with No. 65 Ni-o-nel wire did not show preferential weld metal attack in sulfuric acid and in H_2SO_4-stainless steel solutions even though not annealed. Welded Haynes 25 tubing (as annealed by the fabricator) showed preferential weld metal attack in H_2SO_4-stainless steel solutions. Preferential weld metal attack of as-welded Ni-o-nel weldments occurred when the weldments were made using coated electrodes. Weldments made using No. 65 welding wire did not show preferential attack. Carpenter 20 and Carpenter 20 Cb weldments in the as-welded condition showed preferential weld metal attack in H_2SO_4-stainless steel solutions. Stressed Carpenter 20 and Carpenter 20 Cb specimens showed stress cracking in boiling H_2SO_4-stainless steel solutions. The cracks occurred along the face of the coupon under compression. No stress cracking of Hastelloy F or Ni-o-nel was noted.

Data on the corrosion of vacuum-melted Hastelloy F in sulfuric acid and sulfuric acid-stainless steel systems under heat transfer conditions are given in Table XXIII.

TABLE XXIII

HASTELLOY F CORROSION RATES IN SULFEX SOLUTIONS HEAT TRANSFER CONDITIONS

Conditions: 240-hour exposure. Fresh solution every 48 hours. Bulk metal temperature 140°C.

Solution	Corrosion Rate, Mils/Month
4 M H_2SO_4	200
3 M H_2SO_4	150
3 M H_2SO_4, 5 g. ss/l	5.5
3 M H_2SO_4, 10 g. ss/l	1.5
3 M H_2SO_4, 20 g. ss/l	1.6
4 M H_2SO_4, 10 g. ss/l	8.7

Notes: 1) Crevice corrosion noted on all specimens. Severe on specimens exposed to H_2SO_4 only.

2) Sulfuric acid concentration not corrected for that consumed in dissolution of stainless steel.

The low corrosion rates obtained in the presence of dissolved stainless steel maybe be due to oxidation of Fe(II) to Fe(III).

The corrosivity of Sulfex decladding solution is markedly reduced in the presence of dissolving stainless steel. Vacuum-melted Hastelloy F and Ni-o-nel specimens exposed for four six-hour periods to boiling 3.5 M H_2SO_4 containing from zero to 50 g/l dissolved stainless steel corroded at rates of 2.2 and 1.1 mills/month, respectively. The corrosivity of Sulfex decladding solution was also evaluated in a recirculating type dissolver. The dissolver used was identical to the one used in previously described Zirflex dissolutions (Section IV-A). However, the solution was not air sparged. The data obtained are shown in Table XXIV.

TABLE XXIV

CORROSIVITY OF SULFEX DECLADDING SOLUTION IN A RECIRCULATING TYPE DISSOLVER

Conditions: 304-L stainless steel dissolved in 3.5 M H_2SO_4 to a terminal stainless steel concentration of about 50 g/l. Six-hour dissolutions. Total exposure = 200 hours.

Dissolver Solution			Reservoir Solution		
Hast. F(1)	Ni-o-nel(2)	Hast. F(3)	Hast. F(1)	Ni-o-nel(2)	Hast. F(3)
1.5	0.4	1.3	2.0	0.5	1.2

Notes: (1) Hastelloy F weldment fabricated using heat of Hastelloy F containing no niobium as weld metal.

(2) Standard weldment.

(3) Hastelloy F welded with Ni-o-nel.

No difference in the corrosivity of the reservoir and dissolver solutions is noted. The weldments showed no preferential attack.

Sulfate may not be quantitatively removed from the dissolver prior to dissolution of the fuel cores in nitric acid. Data showing the effect of residual sulfate on the corrosivity of nitric acid and nitric acid - uranyl nitrate solutions towards vacuum-melted Hastelloy F and 304-L stainless steel are given in Table XXV. The data show that sulfate (0.01 to 0.25 M) has no significant effect on the corrosivity of these solutions.

Equipment for containing spent Sulfex decladding solution may be constructed of 304-L stainless steel if Fe(III) (ca. one g/l) is added to the solution prior to transfer from the dissolver. Oxidants capable of oxidizing Fe(II), which is already present in the spent decladding solution, are also effective. Data showing the effect of Fe(III) on the cor-

TABLE XXV

EFFECT OF RESIDUAL SULFATE ON CORROSIVITY OF CORE DISSOLVENT SOLUTION

CONDITIONS: Specimens exposed to liquid phase of boiling solutions.

Solution	Corrosion Rate, Mils/Month 48 hr.	72 hr.	72 hr.
Hastelloy F			
10 M HNO_3, 0.01 M H_2SO_4	0.30	0.30	0.33
10 M HNO_3, 0.05 M H_2SO_4	0.45	0.26	0.36
10 M HNO_3, 0.25 M H_2SO_4	0.49	0.31	0.45
6 M HNO_3, 0.01 M H_2SO_4, 0.7 M $UO_2(NO_3)_2$	0.14	0.13	0.21
6 M HNO_3, 0.05 M H_2SO_4, 0.7 M $UO_2(NO_3)_2$	0.19	0.10	0.24
6 M HNO_3, 0.25 M H_2SO_4, 0.7 M $UO_2(NO_3)_2$	0.20	0.12	0.29
1.1 M HNO_3, 0.25 M H_2SO_4, 1.6 M $UO_2(NO_3)_2$	0.04	0.06	0.02
304-L			
10 M HNO_3, 0.25 M H_2SO_4	0.68	0.31	0.41
6 M HNO_3, 0.25 M H_2SO_4, 0.7 M $UO_2(NO_3)_2$	0.50	0.23	0.29
1.1 M HNO_3, 0.25 M H_2SO_4, 1.6 M $UO_2(NO_3)_2$	0.09	0.06	0.19

rosivity of spent Sulfex decladding solution to 304-L are given in Table XXVI. In many instances simulated spent Sulfex decladding solutions containing no added Fe(III) were found to be non-corrosive to 304-L. This effect may be due to air oxidation of Fe(II) to Fe(III). An air sparge of the spent decladding solution may be sufficient to produce a solution containable in 304-L stainless steel.

Preliminary corrosion tests were made to determine the feasibility of using 300 series stainless steels to contain dilute sulfuric acid at ambient temperatures. The corrosion rates of 304-L, 347, 309 Cb, and 316 were determined at 25°C in 3.5 $\underline{M}$ H_2SO_4 to be 40, 24, 5, and 0.1 mil/month, respectively (average of seven 24-hour periods). The 309 Cb corrosion rates were erratic (0.0 to 17 mils/month).

D. Core Dissolution

Following either the Sulfex or Zirflex decladding procedures, uranium or uranium dioxide cores will be dissolved in nitric acid. Current plans at HAPO provide for dissolution of U-Mo alloy cores in HNO_3-$Fe(NO_3)_3$ solutions. An appreciable reduction in the core dissolution cycle for uranium and uranium dioxide cores could be attained by dissolving them in HNO_3-$Fe(NO_3)_3$ solution as shown in Table XXVII.

The effects on corrosion rates of residual fluoride from Zirflex decladding, and sulfate from Sulfex decladding, present during dissolution of fuel cores in nitric acid, has already been discussed in the sections on Zirflex and Sulfex.

Data on the corrosion of 304-L, vacuum-melted Hastelloy F, and Ni-o-nel in boiling HNO_3-$Fe(NO_3)_3$ solutions are given in Table XXVIII. The corrosivity of HNO_3-$Fe(NO_3)_3$ solutions increases as either the ferric nitrate or nitric acid concentration is increased. "As-welded" vacuum-melted Hastelloy F and Ni-o-nel weldments show no preferential weld metal attack in boiling 5 $\underline{M}$ HNO_3-1 $\underline{M}$ $Fe(NO_3)_3$. Intergranular attack of both base and weld metal is severe, however.

TABLE XXVI

CORROSIVITY OF SPENT SULFEX DECLADDING SOLUTION EFFECT OF FERRIC ION

CONDITIONS: Sensitized 304-L specimens exposed for 18 to 48 hours to following solutions at 62 C.

Solution	Corrosion Rate,(1) Mils/Month
4 M H_2SO_4, 40 g ss/l.	238 (410)
4 M H_2SO_4, 25 g ss/l.	450
4 M H_2SO_4, 15 g ss/l.	368
4 M H_2SO_4, 40 g ss/l., 0.001 M $Na_2Cr_2O_7$ added	356
4 M H_2SO_4, 40 g ss/l., 0.002 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 40 g ss/l., 0.002 M $Fe_2(SO_4)_3$	nil
4 M H_2SO_4, 40 g ss/l., 0.004 M $Fe_2(SO_4)_3$	nil
4 M H_2SO_4, 25 g ss/l., 0.001 M $Fe(NO_3)_3$	nil
4 M H_2SO_4, 25 g ss/l., 0.005 M $Fe(NO_3)_3$	nil
4 M H_2SO_4, 25 g ss/l., 0.05 M $Fe(NO_3)_3$	nil
4 M H_2SO_4, 25 g ss/l., 0.10 M $Fe(NO_3)_3$	nil
4 M H_2SO_4, 25 g ss/l., 0.001 M $Na_2Cr_2O_7$ added	452
4 M H_2SO_4, 25 g ss/l., 0.002 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 25 g ss/l., 0.004 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 25 g ss/l., 0.006 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 25 g ss/l., 0.02 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 25 g ss/l., 0.002 M $Fe_2(SO_4)_3$	445
4 M H_2SO_4, 25 g ss/l., 0.004 M $Fe_2(SO_4)_3$	nil
4 M H_2SO_4, 25 g ss/l., 0.006 M $Fe_2(SO_4)_3$	nil
4 M H_2SO_4, 25 g ss/l., 0.01 M $Fe_2(SO_4)_3$	nil
4 M H_2SO_4, 15 g ss/l., 0.001 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 15 g ss/l., 0.002 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 15 g ss/l., 0.01 M $Na_2Cr_2O_7$ added	nil
4 M H_2SO_4, 15 g ss/l., 0.002 M $Fe_2(SO_4)_3$	nil
4 M H_2SO_4, 15 g ss/l., 0.004 M $Fe_2(SO_4)_3$	nil
4 M H_2SO_4, 15 g ss/l., 0.03 M $Fe_2(SO_4)_3$	nil

Note:

(1) Corrosion rates for specimens exposed to liquid phase. Interface specimens exposed to active solutions showed attack in liquid phase only. Solutions non-corrosive to liquid phase specimens were also non-corrosive to interface specimens.

TABLE XXVII

DISSOLUTION OF METALLIC URANIUM (INGOT) AND SINTERED URANIUM DIOXIDE IN NITRIC ACID - EFFECT OF FERRIC NITRATE

Initial Solution	Initial U Conc., M	Initial HNO_3 Conc., M(1)	Dissolution Rate,(2) g/cm^2-hr
Uranium			
9.0 M HNO_3	0.00	9.00	0.19
	0.49	7.04	0.20
	0.94	5.24	0.10
	1.44	3.24	0.13
	1.92	1.32	0.06
9.0 M HNO_3, 0.1 M $Fe\ (NO_3)_3$	0.00	9.00	0.50
	0.57	6.72	0.38
	1.13	4.48	0.40
	1.68	2.28	0.32
	2.13	0.48	0.36
9.0 M HNO_3, 0.3 M $Fe\ (NO_3)_3$	0.00	9.00	0.84
	0.56	6.76	1.23
	1.09	4.64	1.35
	1.66	2.36	1.30
	2.18	0.28	0.90
Uranium Dioxide			
9.0 M HNO_3	0.00	9.00	0.43
	0.52	6.92	0.28
	0.98	5.08	0.16
	1.40	3.40	0.03
9.0 M HNO_3 0.1 M $Fe\ (NO_3)_3$	0.00	9.00	3.20
	0.56	6.76	4.73
	1.24	4.04	5.01
	1.77	1.92	4.82
	2.26	-0.04	1.13
9.0 M HNO_3, 0.3 M $Fe\ (NO_3)_3$	0.00	9.00	4.78
	0.63	6.48	6.23
	1.39	3.44	5.71
	2.01	0.96	0.46
	2.43	-0.72	0.61

Notes:

(1) Calculated values
(2) Two-minute exposures

TABLE XXVIII

CORROSIVITY OF THE NITRIC ACID - FERRIC NITRATE SYSTEM

CONDITIONS: Specimens exposed to liquid phase of boiling solutions for specific periods.

		Corrosion Rate, Mils/Month					
		Exposure Hours					
Solution	Material	24	72	48	48	72	48
10 $\underline{M}$ HNO_3, 0.2 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.96	1.1	1.2	1.5	1.7	2.5
10 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	304-L	1.8	4.5	--	6.8	8.0	10*
10 $\underline{M}$ HNO_3, 0.6 $\underline{M}$ $Fe(NO_3)_3$	304-L	2.9	4.9	7.1	6.1	8.6	8.3*
5 $\underline{M}$ HNO_3, 0.2 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.36	0.30	0.22	0.32	0.27	0.11
5 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.48	0.65	0.56	0.63	0.65	0.63
5 $\underline{M}$ HNO_3, 0.6 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.95	1.1	1.2	1.6	1.8	1.7
5 $\underline{M}$ HNO_3, 0.8 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.73	2.6	4.4	8.0	8.4*	--
5 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$	304-L	--	--	3.1	4.1	7.1	9.1*
2 $\underline{M}$ HNO_3, 0.2 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.25	0.23	0.11	0.11	0.24	0.13
2 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.30	0.30	0.34	0.17	0.40	0.34
2 $\underline{M}$ HNO_3, 0.6 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.60	0.64	0.60	0.60	0.72	0.63
2 $\underline{M}$ HNO_3, 0.8 $\underline{M}$ $Fe(NO_3)_3$	304-L	0.56	0.72	0.98	1.2	1.2	--
2 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$	304-L	--	--	1.2	4.0	1.7	2.5*
0.5 $\underline{M}$ HNO_3, 0.2 $\underline{M}$ $Fe(NO_3)_3$	304-L	--	0.08	0.22	0.16	0.16	0.06
0.5 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	304-L	--	0.18	0.10	0.26	0.45	0.79
0.5 $\underline{M}$ HNO_3, 0.6 $\underline{M}$ $Fe(NO_3)_3$	304-L	--	0.41	0.41	0.54	0.70	0.59
0.5 $\underline{M}$ HNO_3, 0.8 $\underline{M}$ $Fe(NO_3)_3$	304-L	--	0.56	0.65	0.84	1.1	0.96
0.5 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$	304-L	--	0.67	0.43	1.0	0.97	--
10 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	1.0	2.4	5.6	13	22	37*
5 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	0.17	0.27	0.17	0.28	0.20	0.22
5 $\underline{M}$ HNO_3, 0.6 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	0.17	0.09	0.62	0.57	--	--
5 $\underline{M}$ HNO_3, 0.8 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	0.59	1.1	1.6	2.0	1.8	--
5 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	--	1.8	2.6	4.6	6.5	9.0*
2 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	nil	0.11	nil	nil	nil	0.10
2 $\underline{M}$ HNO_3, 0.8 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	--	0.14	0.22	0.37	--	--
2 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	0.35	1.1	0.65	--	--	--
0.5 $\underline{M}$ HNO_3, 0.2 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	--	0.06	0.03	0.08	nil	--
0.5 $\underline{M}$ HNO_3, 0.4 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	--	0.08	0.25	0.02	0.33	0.06
0.5 $\underline{M}$ HNO_3, 0.6 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	--	0.08	0.25	0.28	0.36	0.20
0.5 $\underline{M}$ HNO_3, 0.8 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	--	0.26	0.48	0.34	0.37	0.27
0.5 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$	Hastelloy F	--	0.35	0.33	0.60	0.49	0.25
2.7 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$, 0.46 $\underline{M}$ U, 0.11 $\underline{M}$ Mo	Hastelloy F	--	--	2.4	3.2	4.6*	
5 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$	Ni-o-nel	--	1.9	3.4	9.3	12	12*
2.7 $\underline{M}$ HNO_3, 1.0 $\underline{M}$ $Fe(NO_3)_3$, 0.46 $\underline{M}$ U, 0.11 $\underline{M}$ Mo	Ni-o-nel	--	--	2.1	3.2	5.2*	

*Heavy intergranular attack.

Corrosion rates of 304-L, vacuum-melted Hastelloy F, Ni-o-nel, and Carpenter 20 in selected HNO_3-HF-$Al(NO_3)_3$ solutions are given to Table XXIX. These data were obtained at a time when acid fluoride solutions were under study as a means of dissolving U-Mo alloy cores and are included here for reference purposes only.

The corrosion rates of vacuum-melted Hastelloy F, Carpenter 20, and 304-L, in simulated Redox oxidizer solutions ($UO_2(NO_3)_2$ - HNO_3 - $Na_2Cr_20_7$ are shown in Table XXX. The corrosivity of the solution increases greatly as the acidity increases from 0.0 to 1.0 $\underline{M}$ HNO_3. All three metals undergo severe intergranular attack in the high acid region. Preliminary data show the corrosivity of the system is not increased by the addition of macro amounts of ferric nitrate. Further work on these systems is planned.

TABLE XXIX

CORROSIVITY OF THE HNO_3-HF-$Al(NO_3)_3$ SYSTEM

CONDITIONS: Exposure to boiling solutions contained in Teflon. Fresh solution each 24-hour period.

Solution	Hast. F	Corrosion Rate, Mils/Month*		
		Carp. 20	304-L	Ni-o-nel
5 M HNO_3, 1.0 M HF, 1.0 M $Al(NO_3)_3$	2.5	3.0	8.6	5.6
4 M HNO_3, 1.0 M HF, 1.0 M $Al(NO_3)_3$	2.4	2.4	--	--
3 M HNO_3, 1.0 M HF, 1.0 M $Al(NO_3)_3$	1.1	1.9	3.3	1.9
2 M HNO_3, 1.0 M HF, 1.0 M $Al(NO_3)_3$	0.74	1.4	--	--
5 M HNO_3, 1.0 M HF, 0.5 M $Al(NO_3)_3$	5.6	16	68	19
4 M HNO_3, 1.0 M HF, 0.5 M $Al(NO_3)_3$	4.9	10	--	--
3 M HNO_3, 1.0 M HF, 0.5 M $Al(NO_3)_3$	3.3	7.0	15	12
5 M HNO_3, 0.5 M HF, 0.5 M $Al(NO_3)_3$	1.6	3.8	3.8	3.6
4 M HNO_3, 0.5 M HF, 1.0 M $Al(NO_3)_3$	0.63	1.9	0.69	--
4 M HNO_3, 0.5 M HF, 0.5 M $Al(NO_3)_3$	1.4	1.7	2.7	--
4 M HNO_3, 0.5 M HF, 0.25 M $Al(NO_3)_3$	3.6	10	37	--
3 M HNO_3, 0.5 M HF, 0.5 M $Al(NO_3)_3$	0.65	1.5	2.1	2.2
3 M HNO_3, 0.2 M HF, 0.4 M $Al(NO_3)_3$	0.04	0.36	0.19	--
3 M HNO_3, 0.2 M HF, 0.2 M $Al(NO_3)_3$	0.36	0.69	2.0	--
3 M HNO_3, 0.2 M HF, 0.1 M $Al(NO_3)_3$	1.2	3.3	7.3	2.2
2 M HNO_3, 0.5 M HF, 0.5 M $Al(NO_3)_3$	0.26	0.72	1.8	--

*Average of three 24-hour periods.

TABLE XXX

HASTELLOY F, CARPENTER 20, AND 304-L CORROSION RATES OXIDIZER CONDITIONS

Solution	Corrosion Rate, Mils/Month(1)		
	Hast. F	Carp. 20	304-L
1.0 UNH, 1.0 M HNO_3, 0.15 M $Na_2Cr_2O_7$	3.20 (1.7-5.1)(2)	6.21 (2.0-9.4)(2)	22.9 (1.0-44)(2)
1.0 M UNH, 0.0 M HNO_3, 0.15 M $Na_2Cr_2O_7$	0.18	0.16	0.12
1.0 M UNH,-0.2 M HNO_3, 0.15 M $Na_2Cr_2O_7$	0.14	0.12	0.12
1.0 M UNH, 0.0 M HNO_3, 0.10 M $Na_2Cr_2O_7$	0.11	0.13	0.10

Notes:

(1) Average of five 48-hour periods.

(2) Specimens exposed to solution containing 1.0 M HNO_3 exhibited heavy intergranular attack and an increase in corrosion rate with time as measured by weight loss. Parenthetical values represent the measured corrosion rate during first and fifth period respectively.

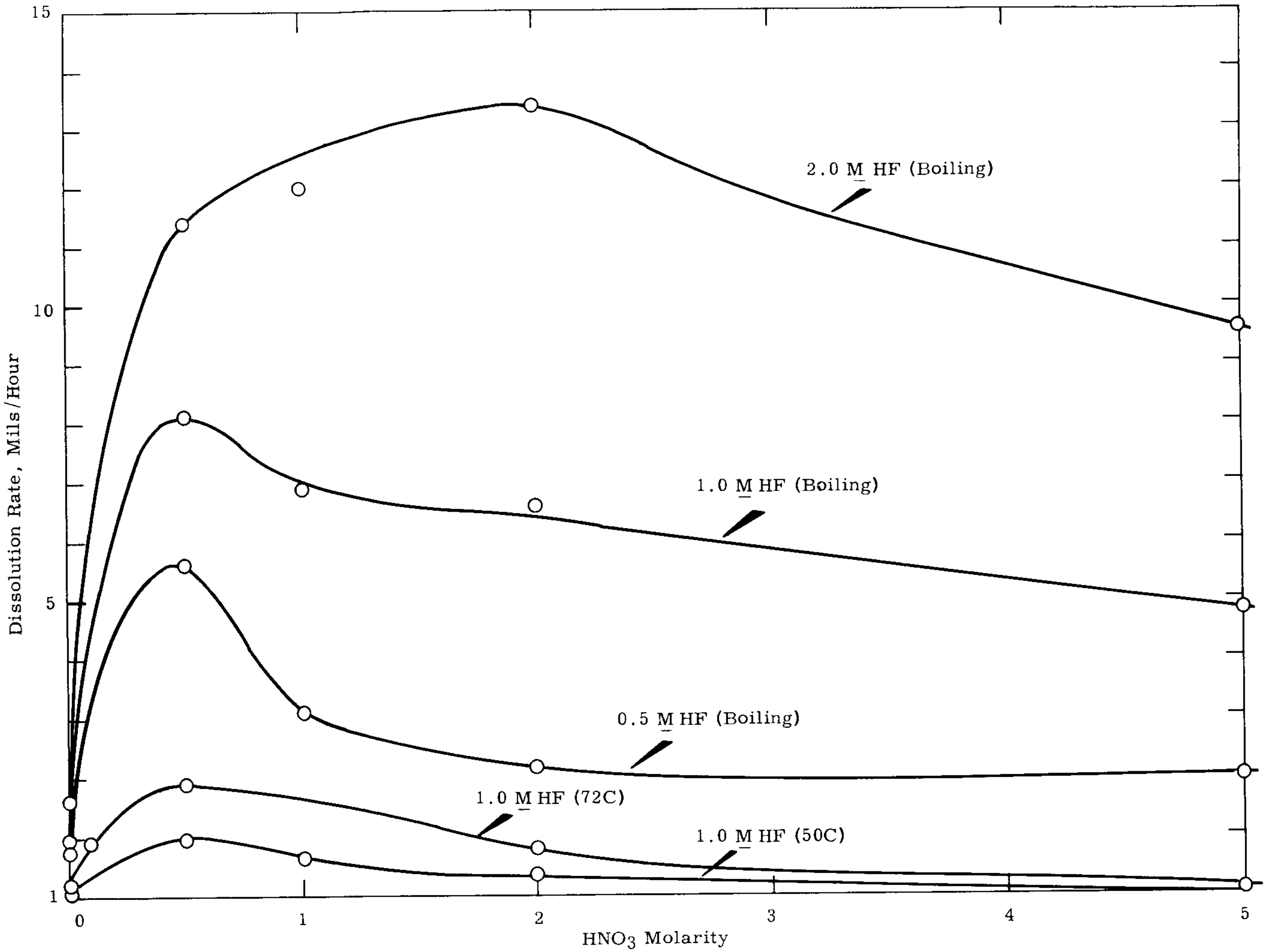


FIGURE 1

Dissolution Rates of 304-L in HNO_3-HF Solutions
Conditions: One-hour exposures in Teflon or
polythene containers.
125 ml solution/sq in. stainless steel

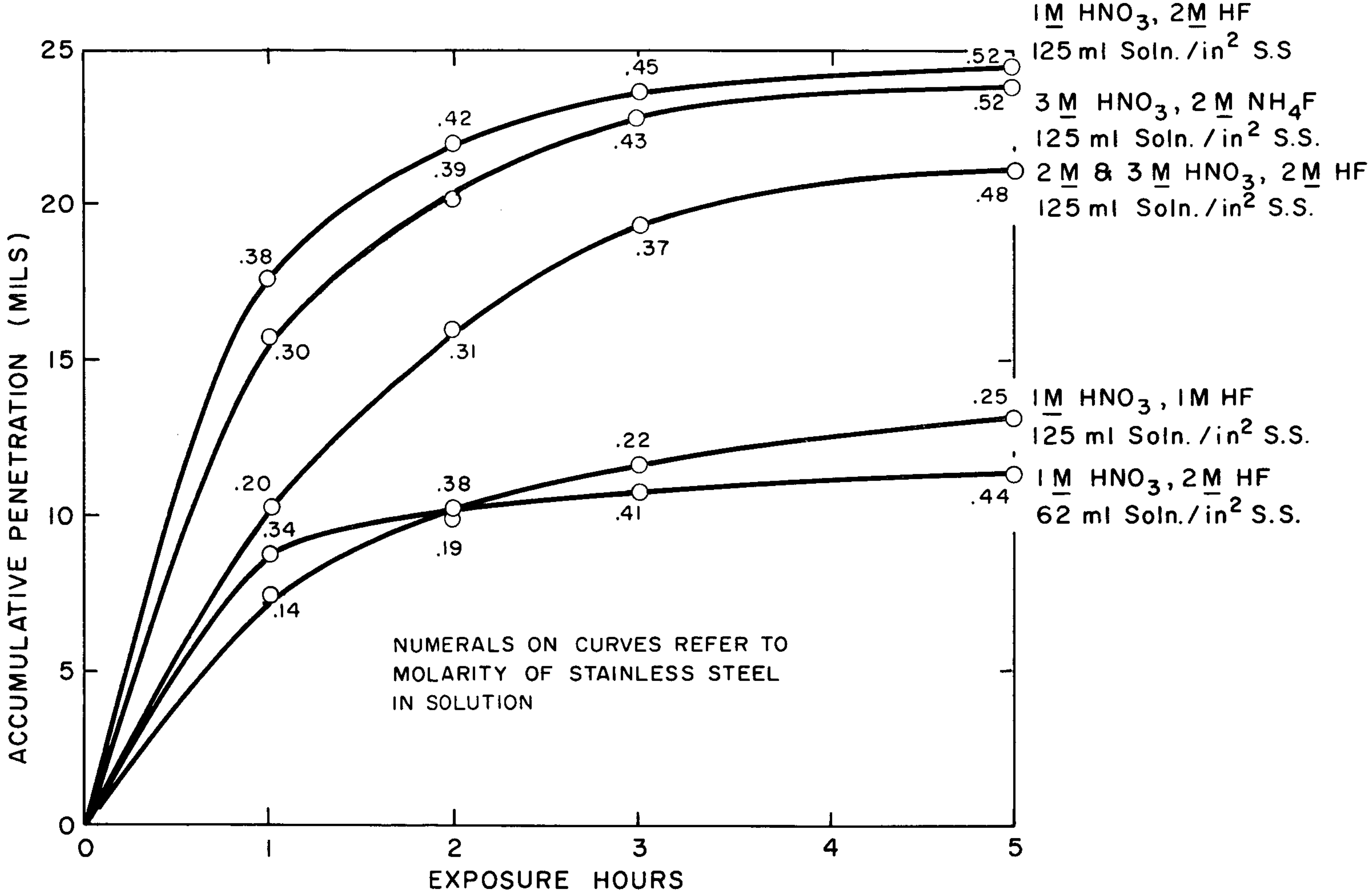
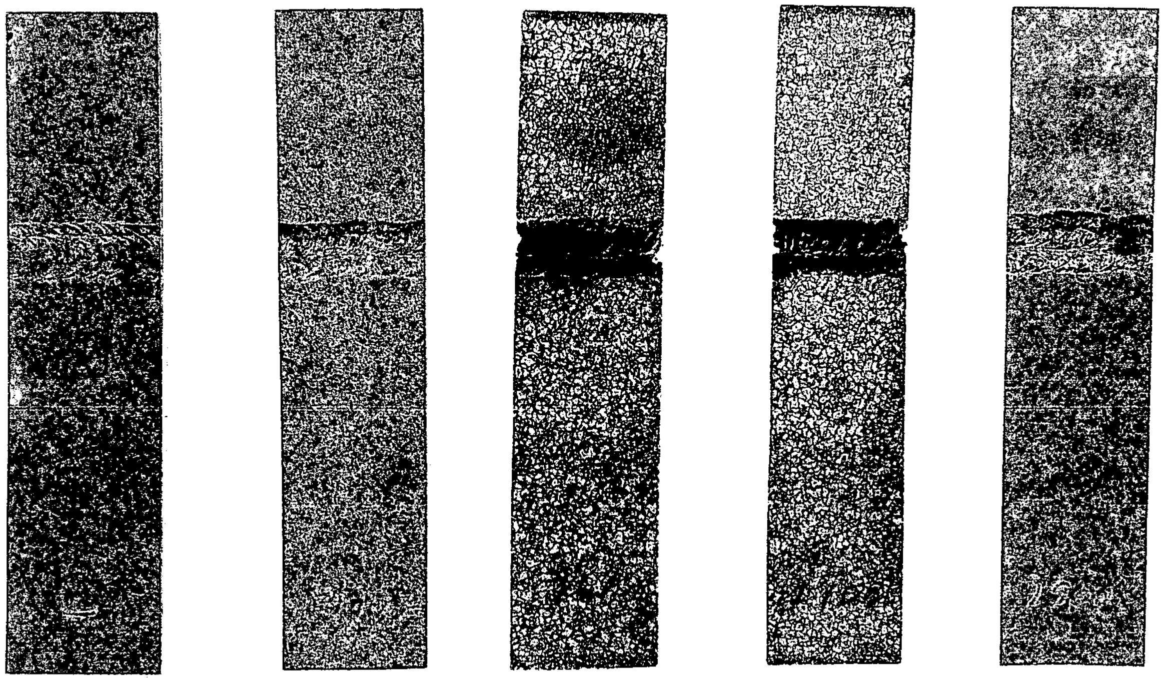


FIGURE 2

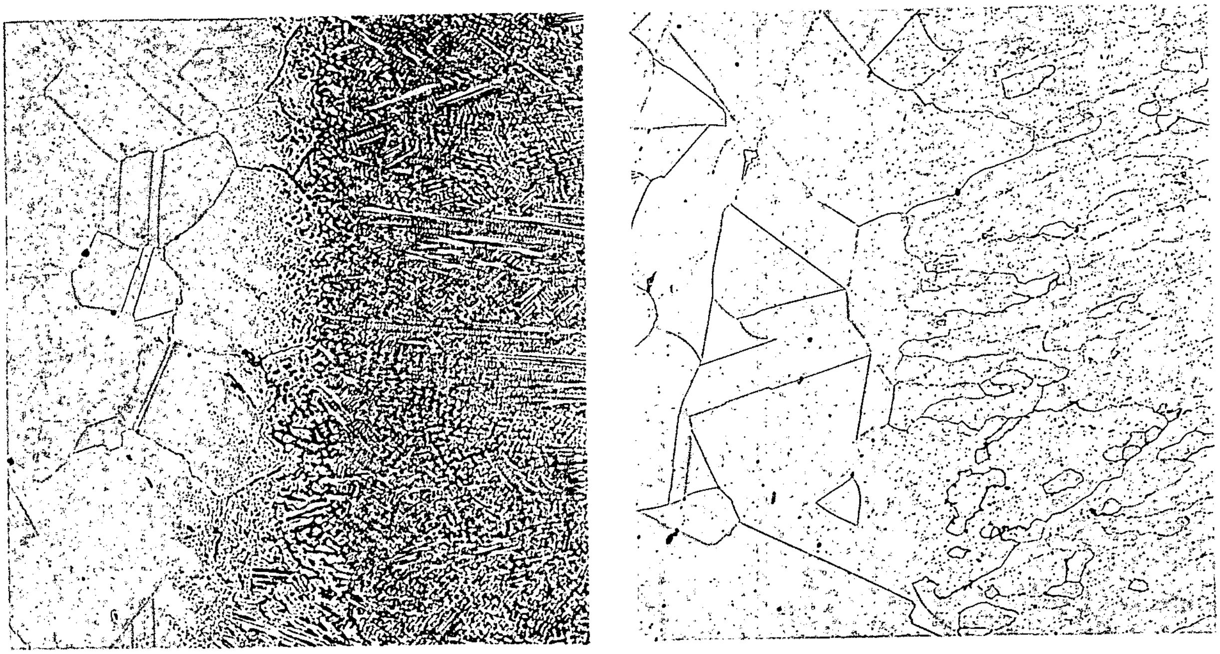
Dissolution of 304-L Stainless Steel in Boiling HNO_3-HF Solution



Conditions: Two 24-hour exposures to boiling $1\ \underline{M}\ HNO_3$, $2\underline{M}$ HF. All weldments solution annealed for one hour at 2100F followed by one-hour heat treatment at temperature indicated below. Weldments produced by the inert-gas shielded tungsten-arc process.

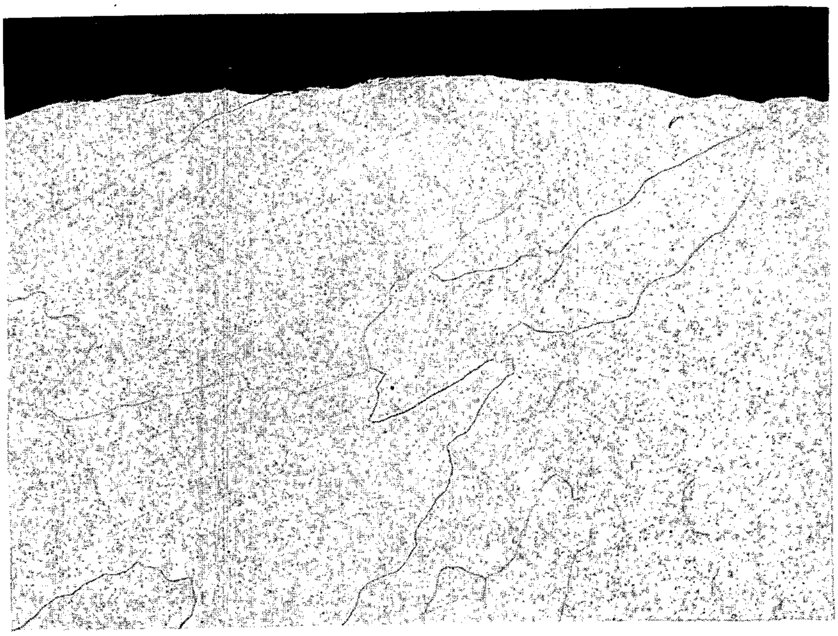
FIGURE 3

Corrosion of Vacuum Melted Hastelloy Weldments-Effect of Post-Weld Heat Treatments



As-Welded (100x) Annealed One Hour at 2100F (100x)

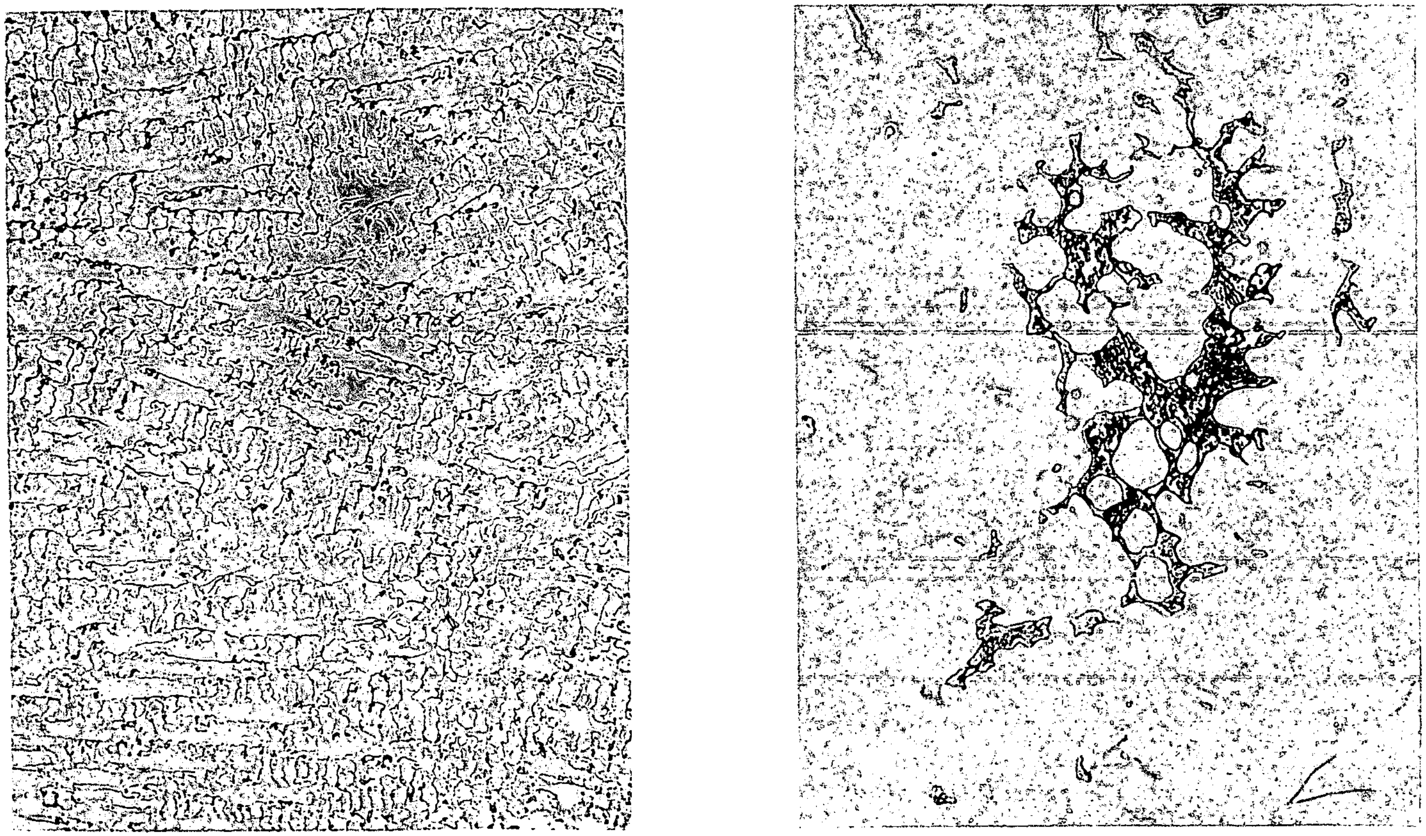
Junction between Parent and Weld Metal



Weld Metal Annealed One Hour at 2150F (100x)

FIGURE 4

Microstructure of Vacuum Melted Hastelloy F Weld Metal Effect of Annealing Temperature

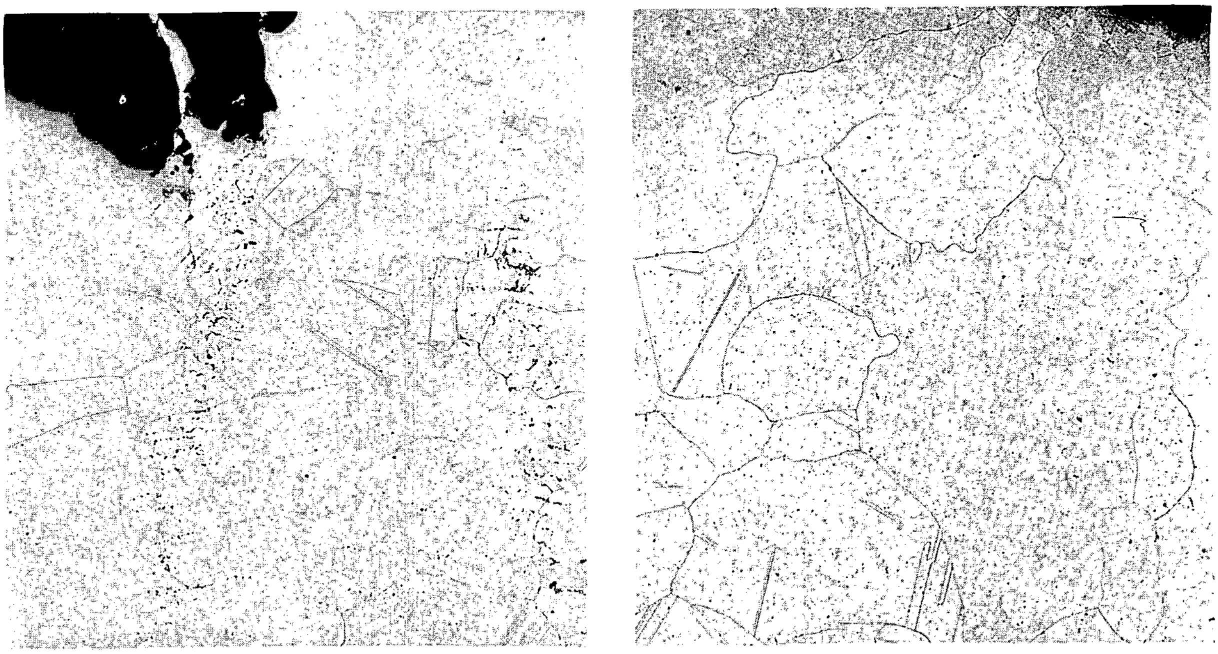


100 x

1000 x

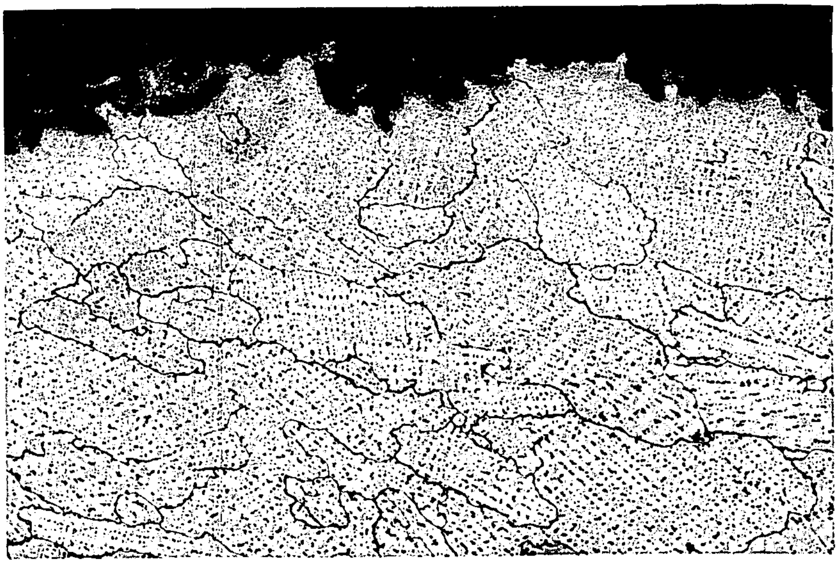
FIGURE 5

Photomicrographs of Vacuum Melted Hastelloy F Weld Metal in "As-Welded" Condition Showing Segregated Phase at High Magnification. Weldment Fabricated in Gloved Box. Helium Atmosphere.



Root Pass(100x)
Section 1

Root Pass(100x)
Section 2



Filler Pass (100x)

FIGURE 6

Photomicrographs of Vacuum Melted Hastelloy F Weld Metal. Sections of Weld Metal Were Cut from Flange of Pilot Plant Dissolver which was Annealed for Two Hours at Ca 2125F and Water Quenched

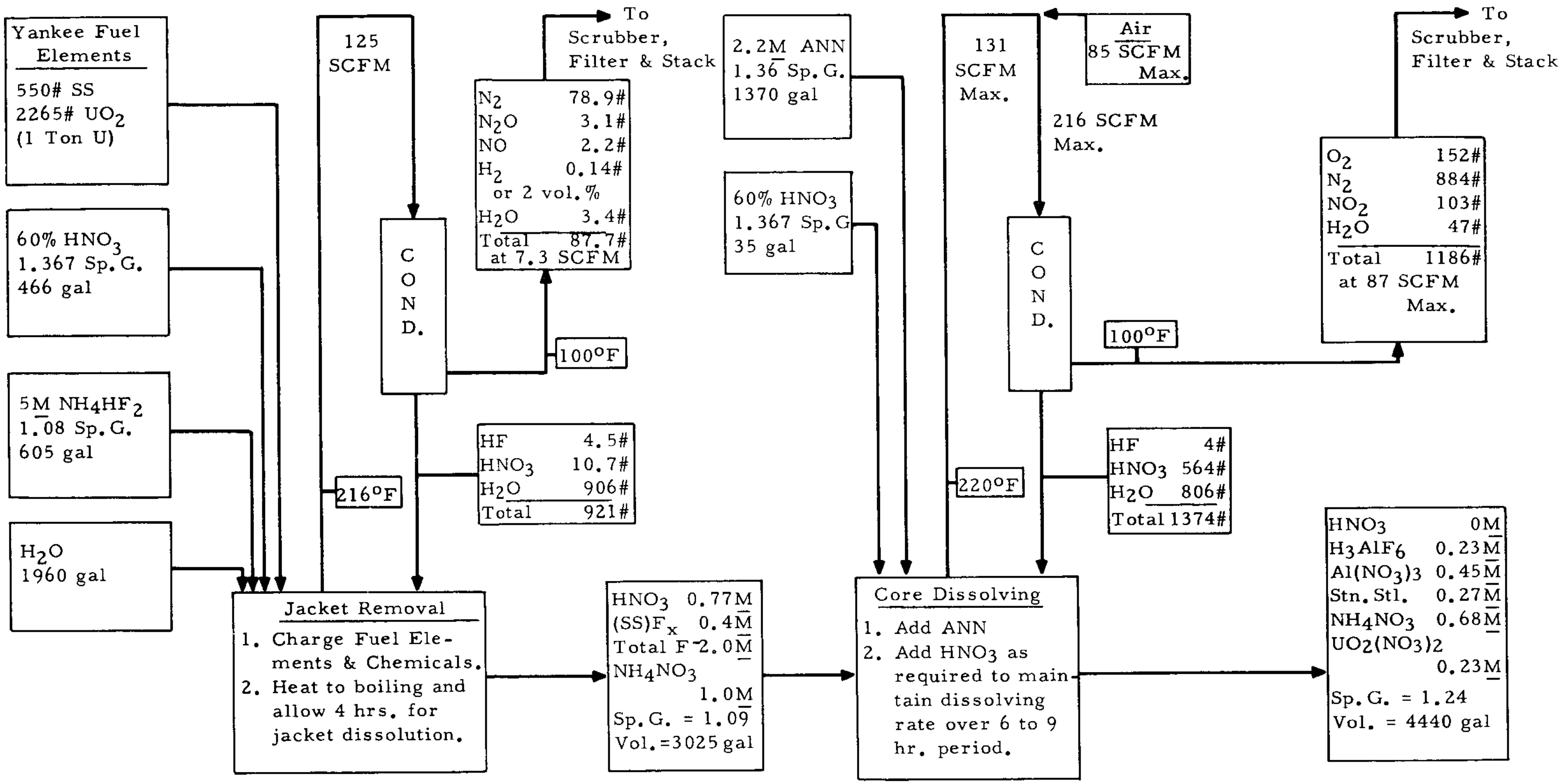


FIGURE 7

Niflex Flowsheet - Yankee Fuel Elements

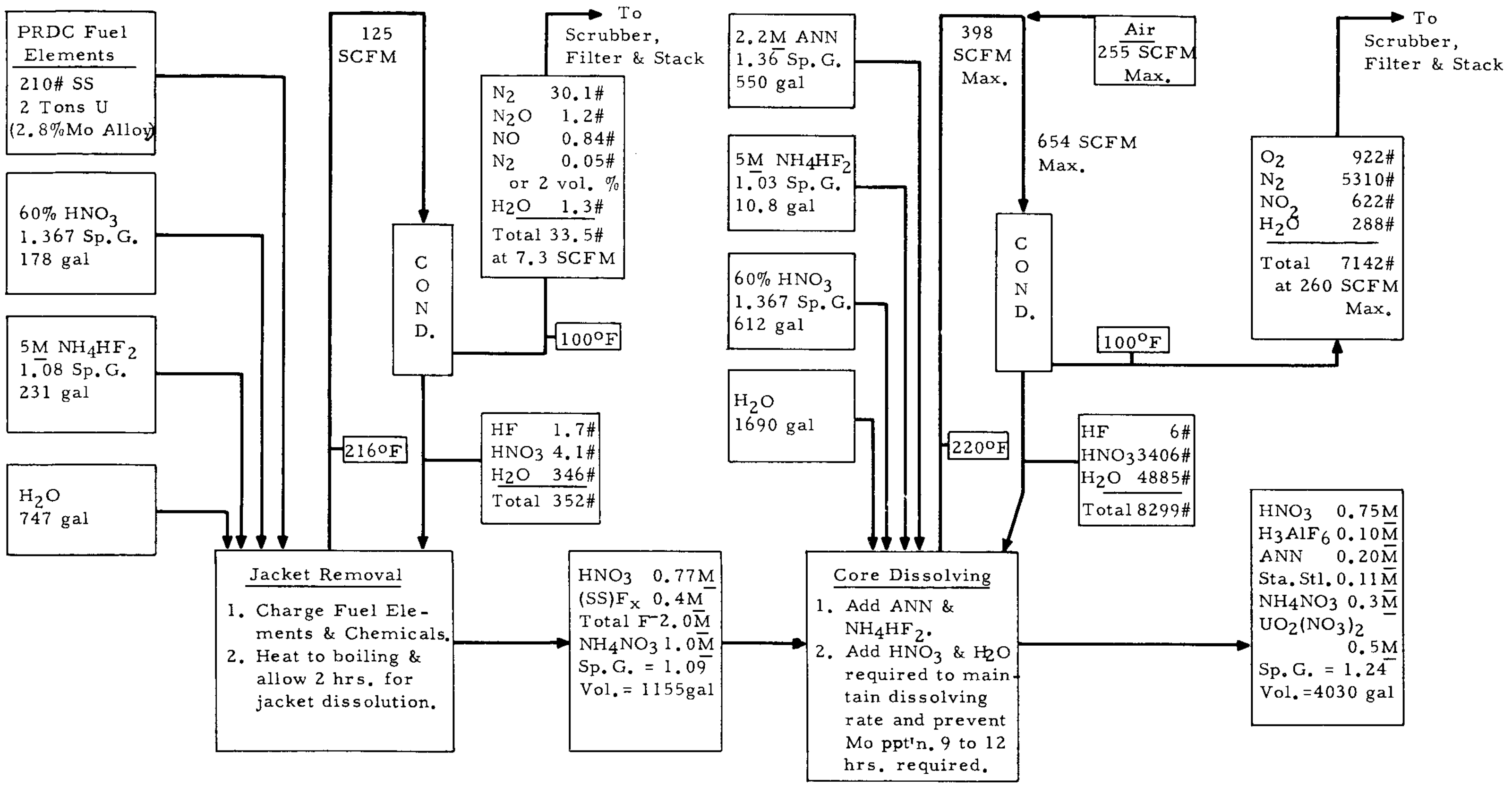


FIGURE 8

Niflex Flowsheet - PRDC Fuel Elements

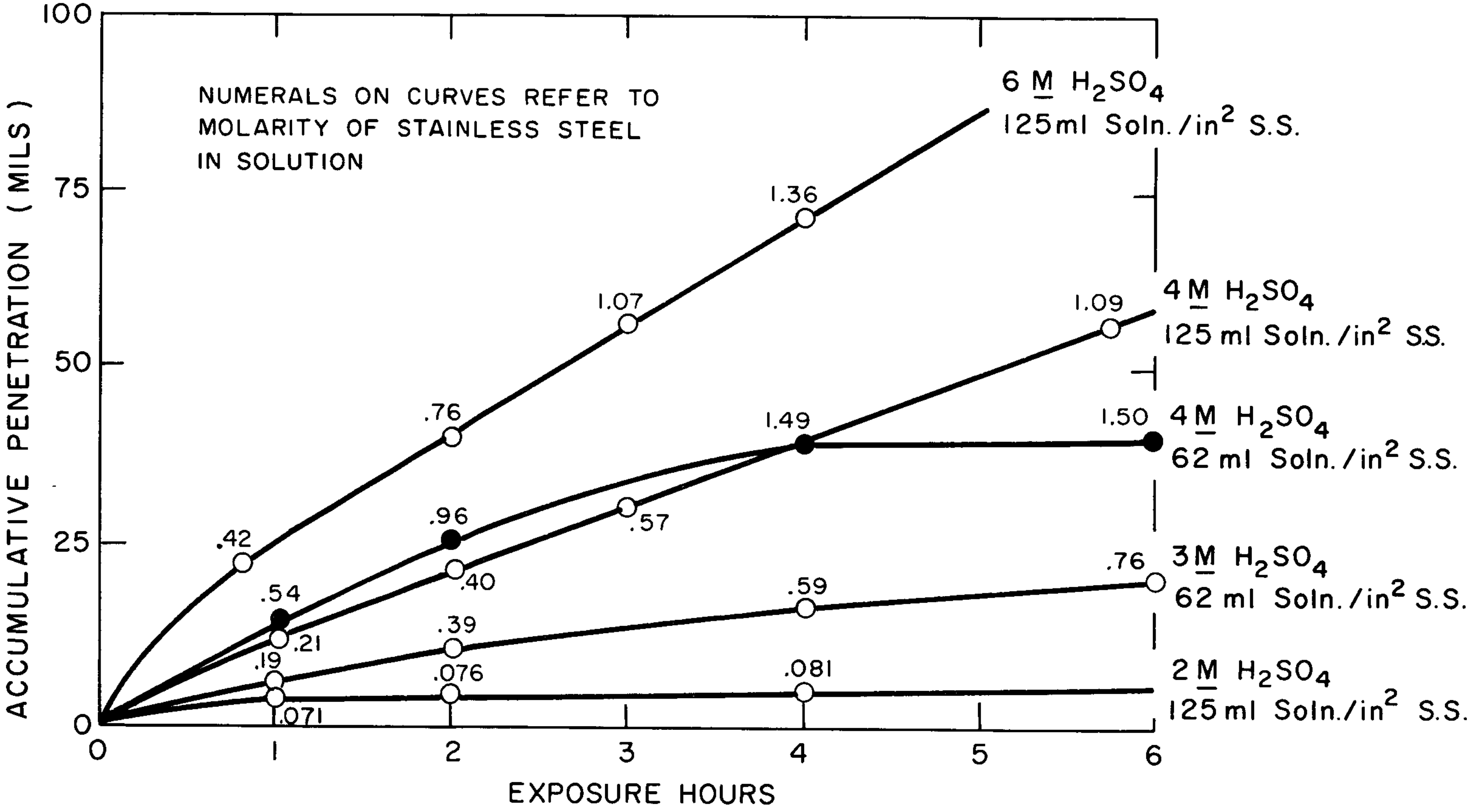


FIGURE 9

Dissolution of 304-L Stainless Steel in Boiling Sulfuric Acid

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