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October 12, 1959

DISSOLUTION OF STAINLESS STEEL CLAD POWER REACTOR FUELS WITH NITRIC ACID AND HYDROFLUORIC ACID

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RICHLAND, WASHINGTON

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DISSOLUTION OF STAINLESS STEEL CLAD POWER REACTOR FUELS WITH NITRIC AND HYDROFLUORIC ACID

INTRODUCTION

The processing of irradiated fuels from power and propulsion reactors is planned by Hanford Atomic Products Operation as part of the Atomic Energy Commission's interim reprocessing scheme. The several chemical processes proposed for the reprocessing of these fuels may be divided into two categories: first, total dissolution processes which dissolve both fuel element cladding and core material and, second, selective dissolution processes which dissolve either cladding or core material. The Niflex process uses a nitric and hydrofluoric acid solution for the total dissolution of stainless steel clad uranium fuel elements.

The nitric and hydrofluoric acid system has been used industrially as a metal pickling agent; but, it has not been applied generally to the total dissolution of stainless steel. Consequently, the application of the Niflex process for the dissolution of stainless steel clad fuels was studied on a pilot plant scale. The pilot plant data and supporting laboratory information are summarized in this report.

SUMMARY

The Niflex process employs one to two molar nitric acid and two molar hydrofluoric acid for the dissolution of 304-L stainless steel cladding. Dissolution rates of stainless steel are initially 10 mils per hour, but decrease markedly after the first hour. As a result two to five hours are required to dissolve a 10 mil cladding.

The stainless steel decladding reaction is apparently quite complex. As dissolution proceeds, the free fluoride ion concentration is rapidly reduced through a complex bonding with the stainless steel components. To obtain complete dissolution a fluoride to stainless steel mol ratio near 6 is needed. At the end of the decladding reaction a stainless steel concentration near 0.4 molar is normally attained.

Following the dissolution of the cladding, aluminum nitrate is added to complex the fluoride and thereby inhibit corrosion of the dissolver during the dissolution of the core in nitric acid.

Core dissolution rates for sintered UO_2 average 50 to 70 mils per hour and metallic uranium rates average 30 mils per hour. At the end of the core dissolution, the stainless steel concentration is about 0.2 molar and the uranium concentration ranges up to 0.5 molar.

Equipment corrosion is a major problem with the Niflex process. The best construction material now available is vacuum melted Hastelloy F* although even this material corrodes at a rate of 15 to 30 mils per month. Heat treatment after welding is generally required to prevent excessive weld corrosion.

* Haynes Stellite Company

The Niflex process was reasonably successful in laboratory and pilot unit tests, but further development is necessary. A more suitable material of construction is needed. Also, the chemical reaction mechanism must be firmly determined to establish optimum concentrations and solution volumes.

DISCUSSION

Dissolution Rates

The rate of dissolution of 304-L stainless steel in Niflex dissolver solution is highly dependent on both the concentrations of reactants and by products (stainless steel) in solution. Initial dissolution rates are about 6 to 10 mils per hour. However, as shown by Fig. 1 and Table I, these rates rapidly decrease as the stainless steel concentration increases. Over-all rates of dissolution are two to three mils per hour. Hence, four to five hours are required to dissolve greater than 97 percent of a 10 mil cladding.

The dissolution rates of 304-L stainless steel are affected by the fluoride ion concentration, the nitric acid concentration and the source of fluoride ion. Further treatment of the reaction kinetics is shown in Appendix A.

Increasing the fluoride ion concentration increases the dissolution rate of stainless steel as shown in Fig. 2. The effect of the fluoride ion concentration was determined to be approximately first order if a reaction is assumed which "complexes" four moles of fluoride per mole of stainless steel dissolved. Use of hydrofluoric acid instead of ammonium bifluoride as the source of fluoride ion gives slightly higher over-all dissolution rates possibly because of the greater total acidity of the solution. Since over-all rates for the acid and the bifluoride were within two to three mils per hour, however, the bifluoride is generally preferred because of convenience in handling.

Rates in the top section of the dissolver were somewhat higher than those in the bottom section of the dissolver (see Fig. 1). Also, any residual pieces of stainless steel were always located along the bottom portion of the charge. Additional runs are necessary to pinpoint the reason for this phenomena.

The optimum nitric acid concentration is dependent on the fluoride concentration as shown by Fig. 3. For a solution two molar in fluoride ion, the optimum nitric acid concentration is about two molar; nitric acid concentrations below or above two molar reduce the dissolution rate.

Chemistry

Although the nitric acid-hydrofluoric acid system has been applied industrially to the pickling of stainless steel, the chemical reaction has not been determined. Attempts to determine the reaction are complicated by the array of possible stainless steel-fluoride complexes. The iron, chromium, and nickel in stainless steel form fluoride complex ions which complex from about three up to six moles of fluoride per mole of stainless steel. (See Table II). Assuming that the metals are in the oxidation states Fe^{+3}, Cr^{+3}, and Ni^{+2}, and straight fluoride compounds are formed, the lowest mole ratio of fluoride to stainless steel dissolved is 2.8 to 1.

With complex ion formation, as shown in Table II, the lowest complex combination is 3.95 moles of fluoride per mole of stainless steel. On this basis fluoride to stainless steel ratios in excess of four would be required to obtain total dissolution in a reasonable time. Actually fluoride to stainless steel ratios from five to six were required in the pilot plant to obtain complete dissolution in four to five hours. Thus, apparently the highest complex combination of 5.6 moles of fluoride per mole of stainless steel is formed.

In the Niflex reaction, the hydrogen ion is apparently the reducing agent. If the hydrogen produced in the reaction were completely evolved, assuming the formation of straight fluoride compounds, the production rate would be 1.4 moles of hydrogen per mole of 304-L stainless steel dissolved. However, an average of only 0.35 moles of hydrogen were evolved per mole of stainless steel dissolved in the pilot plant. Oxygen material balances show this low rate is the result of back oxidation of the hydrogen to form water.

Off-Gases

The off-gases evolved from the dissolver include hydrogen, hydrogen fluoride, and oxides of nitrogen. The combined peak rates of these gases were 1.4 moles per mole of stainless steel dissolved; however, the average evolution rate for a 5 hour run was 0.57 moles per mole of stainless steel dissolved.

Since hydrogen concentrations in air of less than four percent by volume are non-explosive, air dilution can be employed for concentration control. Assuming a peak 304-L stainless steel dissolution rate of 10 mils per hour and a hydrogen evolution rate of 0.7 moles per mole of stainless dissolved, 0.034 scfm of hydrogen would be evolved per square foot of 304-L stainless steel charged. Hence, an air flow rate to the dissolver of 0.82 scfm per square foot of stainless steel would limit the hydrogen content of the off-gases to four percent.

In addition to hydrogen, oxides of nitrogen appear in the off-gases. These are apparently formed by the decomposition of nitric acid under the dissolver conditions. Rates for the oxides of nitrogen averaged 0.2 moles per mole of stainless steel dissolved. The rate of volatization and entrainment of hydrogen fluoride averaged 0.07 moles per mole of stainless steel dissolved.

Concentrations and Volumes

Concentrations used in the Niflex process are primarily controlled by the corrosion of the Hastelloy F vessel. Therefore, as indicated under the corrosion discussion, the fluoride concentration is limited to two molar. This, in turn, sets the nitric acid concentration at two molar for maximum dissolution rates.

The initial volume of solution is determined by the fluoride to stainless steel ratio. This ratio must be between five and six to obtain near 100 percent dissolution of the stainless steel. Assuming a fluoride to stainless steel ratio of 6 at two molar fluoride concentration, a solution volume of 6.6 gallons is required per pound of stainless steel charged.

Following cladding dissolution this volume is further increased by the addition of aluminum nitrate and nitric acid. The aluminum is needed to prevent excessive corrosion at the higher nitric acid concentrations required to complete core dissolution. Assuming an aluminum-to-fluoride ratio of 1 and, using 2.6 molar aluminum nitrate and 13 molar nitric acid, the final solution would be 0.15 molar in uranium and 0.19 molar in stainless steel. Hence, volumes as high as 6,650 gallons per ton of uranium occur for a typical fuel with a uranium-to-stainless steel weight ratio of 3.6 (Yankee). These volumes can be substantially reduced if higher fluoride concentrations are used. However, a material of construction which can resist higher fluoride concentrations is needed.

Corrosion[1]

Vacuum melted Hastelloy F (less than .02 percent carbon) is currently the most promising material of construction for the Niflex process. The corrosion rates for a two molar fluoride solution are near 20 to 35 mils per month. Increasing the fluoride concentration to three molar increases the corrosion rate by a factor of 3 to 4, as shown in the following tables. This necessarily limits the fluoride concentration to about two molar.

Since corrosion rates are generally high, the relative corrosion rates of the material to be dissolved and those of the vessel must be considered. Obtaining the maximum dissolution of stainless steel per mil of Hastelloy F sacrificed is desirable. As shown by the table below, one-quarter to one-half inch of stainless steel may be dissolved per mil of Hastelloy F vessel sacrificed. Based on instantaneous rates and on an assumed 100 tons of stainless steel clad fuels processed per year in one-ton batches, only two to four mils of the dissolver vessel would be sacrificed per year. On an integrated basis up to 20 mils would be sacrificed. Therefore, current anticipated stainless steel clad fuels (less than 100 tons per year) can be safely processed in a vacuum melted Hastelloy F vessel.

Materials of construction other than Hastelloy F have been investigated, but those tested to date show either excessive attack of the weld metal or of the areas adjacent to the welds.[1] However, vacuum melted Ni-o-nel* approaches Hastelloy F and corrosion rates in the Niflex solutions range from those of Hastelloy F to a factor of two greater.

Welds of Hastelloy F with Hastelloy F filler corrode at rates near 300 mils per month. However, a full solution anneal at 2150 F reduces the weld metal attack to near that of the base metal. If Ni-o-nel is used as a filler for welding Hastelloy F, preferential weld metal attack does not occur and heat treatment is not required.

Corrosion in Nitric and Hydrofluoric Acid Solutions[1]

Concentration M HNO_3	Concentration M HF	304-L Stainless Steel Rate, mils/mo.	Hastelloy F Rate mils/mo.	Rate Ratio Stainless Steel to Hastelloy F
1	0.5	2160	4.5	480
2	2	9730	29	335
1	2	8640	34	254
2	3	16560**	101	164
5	2	6840	140	49
10	2	6120	320	19

*International Nickel Company
**Extrapolated Value

Equipment

All components of the equipment in contact with solution or vapor were constructed of vacuum melted Hastelloy F ($>$ 0.02 percent carbon). Pieces were welded with air melted Hastelloy F wire* by an inert-gas-shielded tungsten electrode. The equipment was heat treated at 2125 F for one hour and water quenched to obtain maximum corrosion resistance of the welds.

The equipment for the pilot runs was arranged as shown in Figure 4. The dissolver is an 8-foot long 9-inch diameter tube connected to a 2' x 2' x 2-1/2' vapor box. The condenser is a 10-foot long 6-inch I.D. jacketed tube with a 4-1/4-inch O.D. cooling tube inside. Vapor flows through the annular area to the scrubbing tower. The tower is an 8-inch diameter, 10-foot long pipe which contains 1-inch stainless steel raschig rings. Scrub solution is recirculated through the tower from an auxiliary receiver tank. Off-gases discharge into the building stack through the off-gas vacuum control system.

Important variables such as temperature, off-gas flow, and weight of stainless steel sheet were monitored during operations. Temperature was determined by thermocouples, off-gas flow was measured by an orifice meter, and the weight of stainless steel sheet was measured by a modified pneumatic differential transmitter or an electronic strain gage. Other instrumentation was conventional.

*Wire was ordered as vacuum melted but later tests indicated 0.05 percent carbon which seriously reduced the vessel life.

Procedure

The charge of stainless steel sheet was suspended on the weighing rod and the nitric acid solution charged. (See flowsheet, Figure 5). After heating the solution to boiling, fluoride was added as 5 to 6 molar ammonia fluoride or 60 percent hydrofluoric acid. The addition generally took 10 to 30 minutes. All other procedures were conventional.

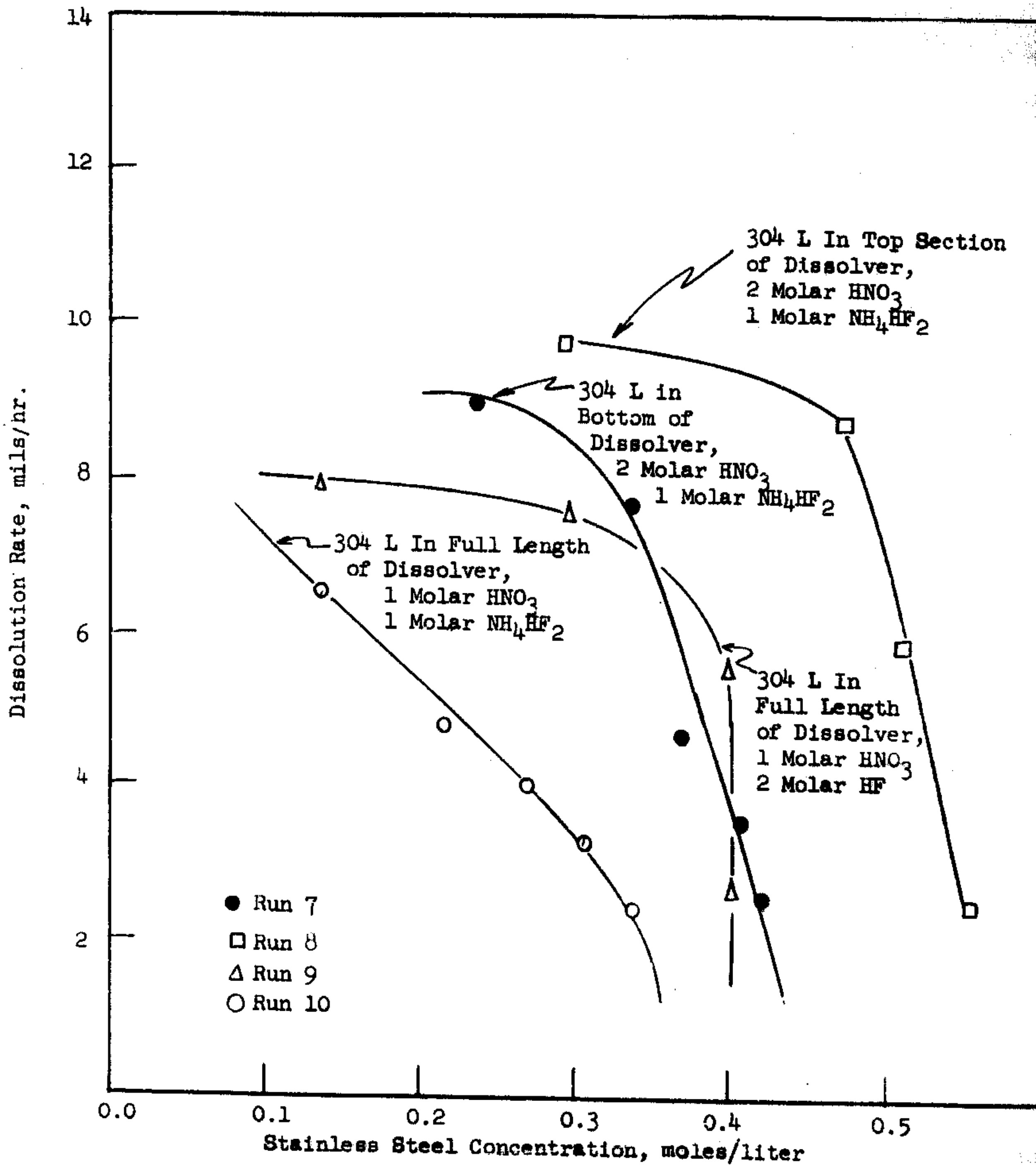


FIGURE 1 - DISSOLUTION RATE OF 304 L STAINLESS STEEL AS A FUNCTION OF 304 L CONCENTRATION

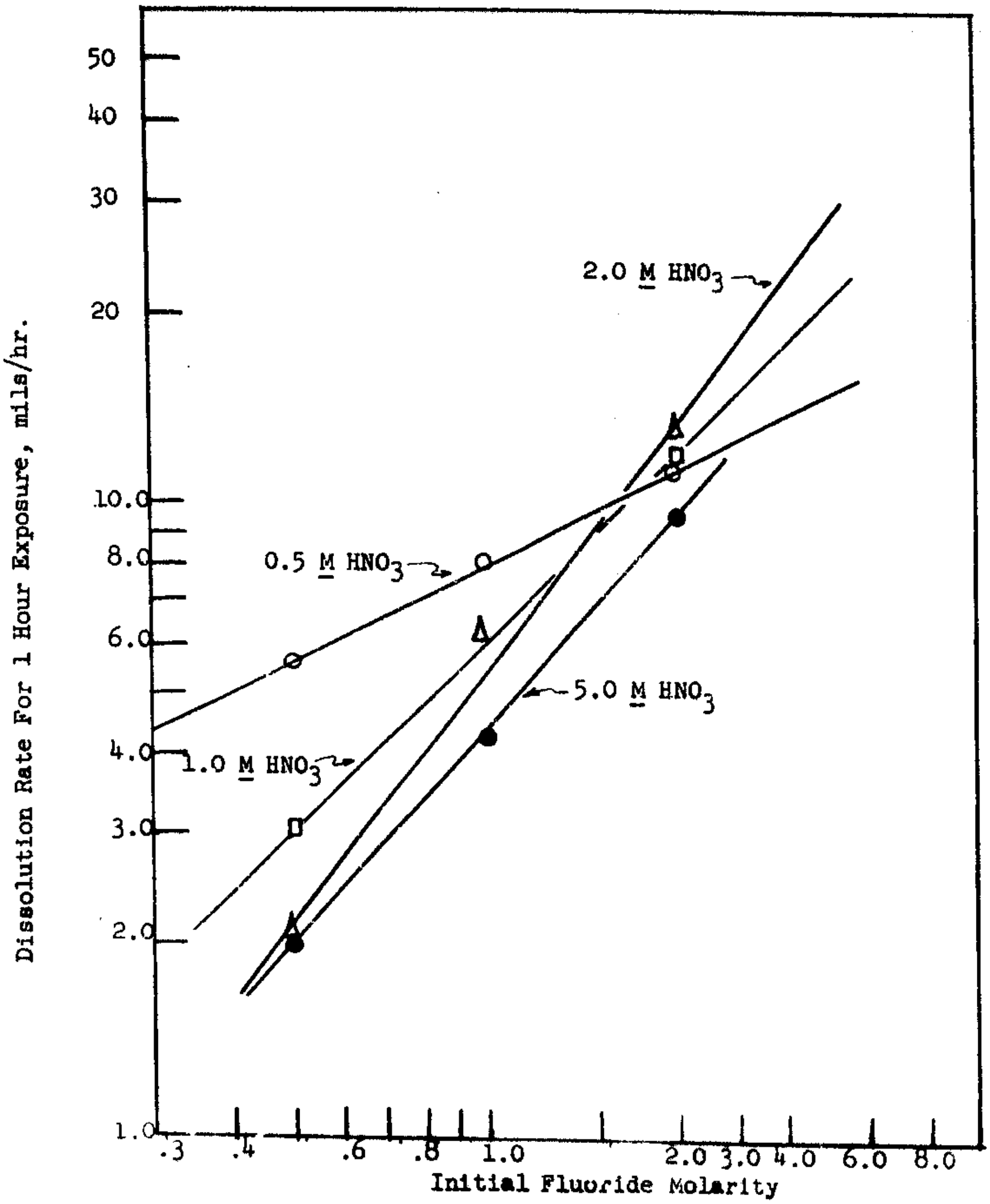


FIGURE 2 - 304 L STAINLESS STEEL DISSOLUTION RATES AS A FUNCTION OF FLUORIDE ION CONCENTRATION (1)

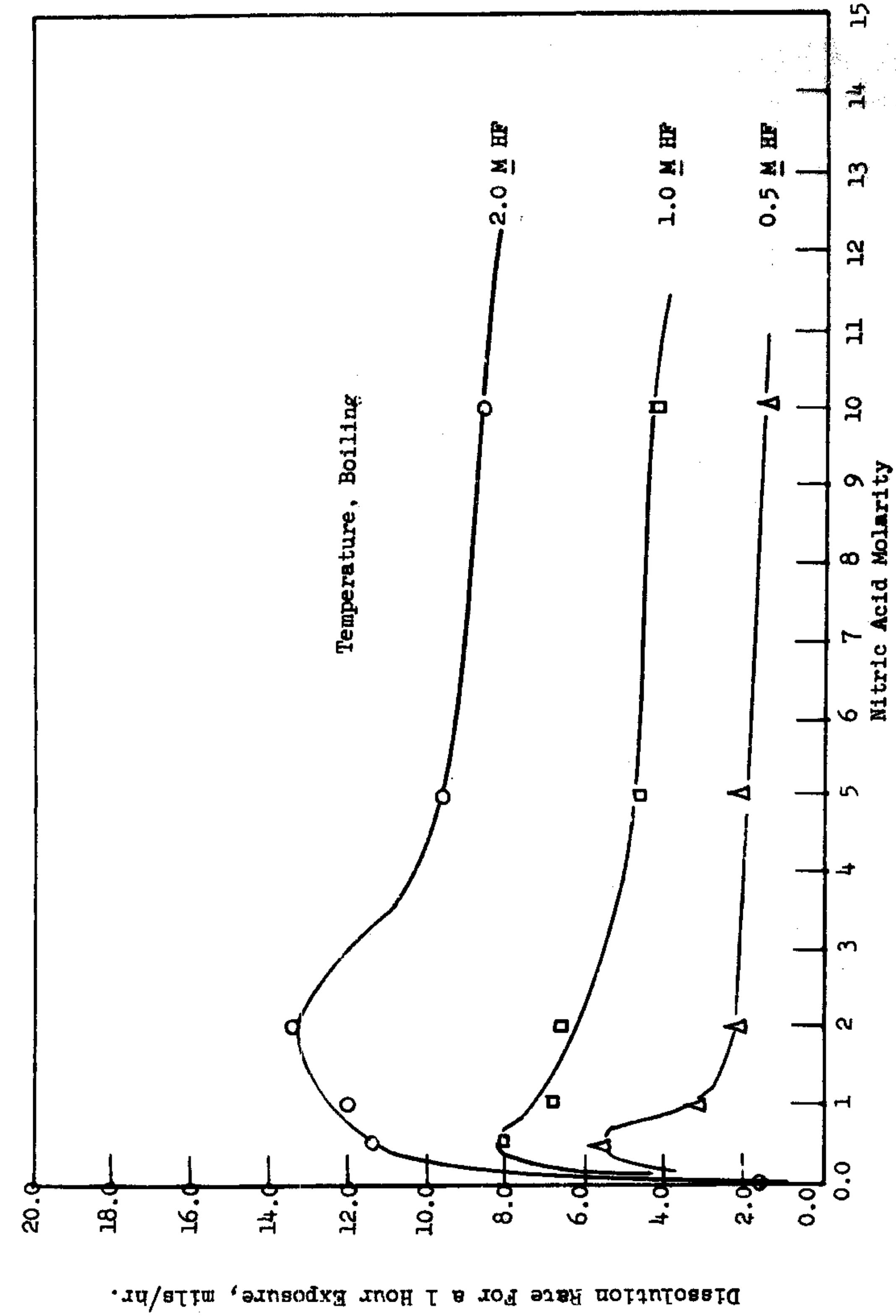


FIGURE 3 - DISSOLUTION RATES OF 304 L STAINLESS STEEL AS A FUNCTION OF NITRIC ACID CONCENTRATION AT VARIOUS HF CONCENTRATIONS(1)

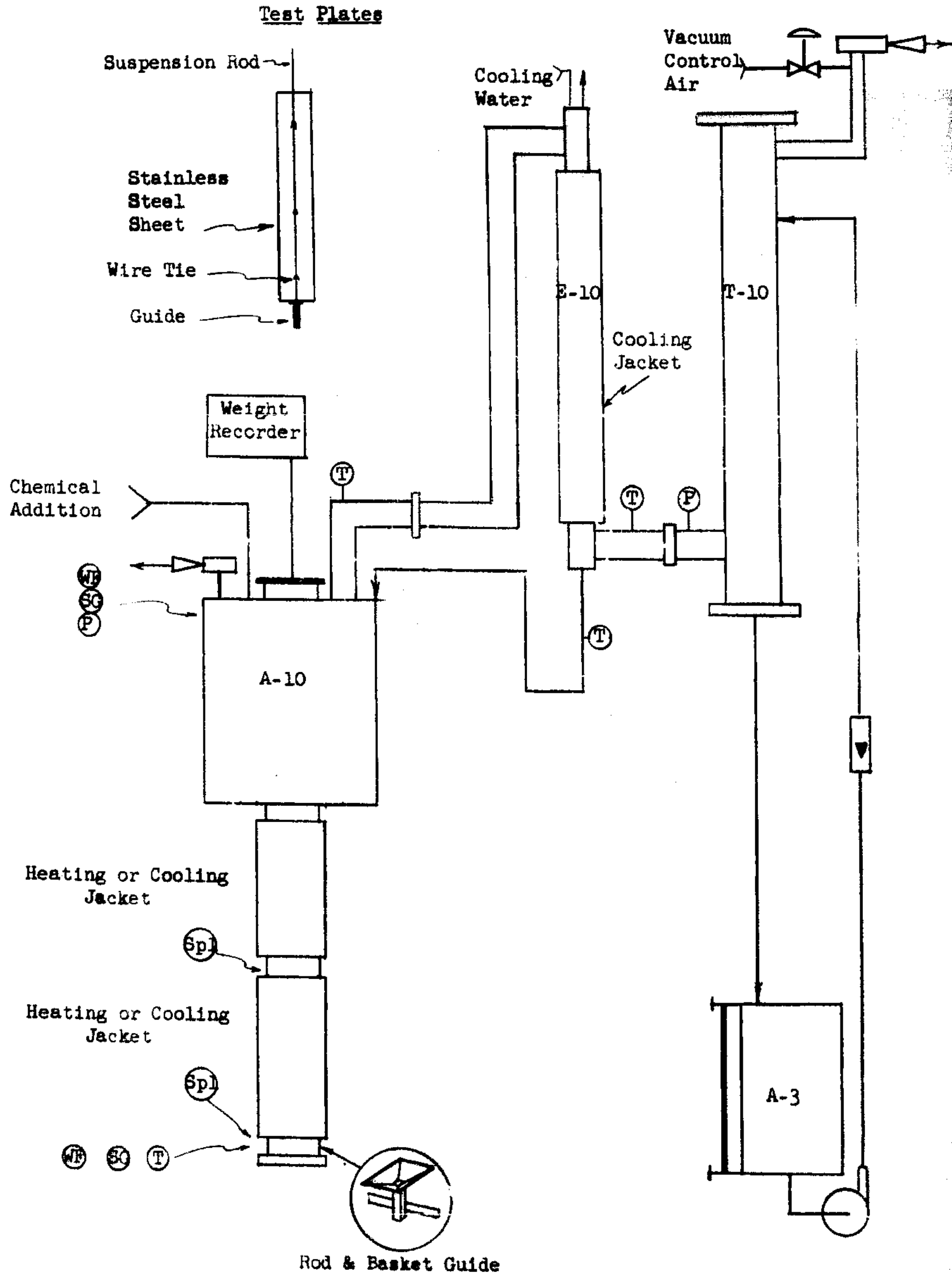
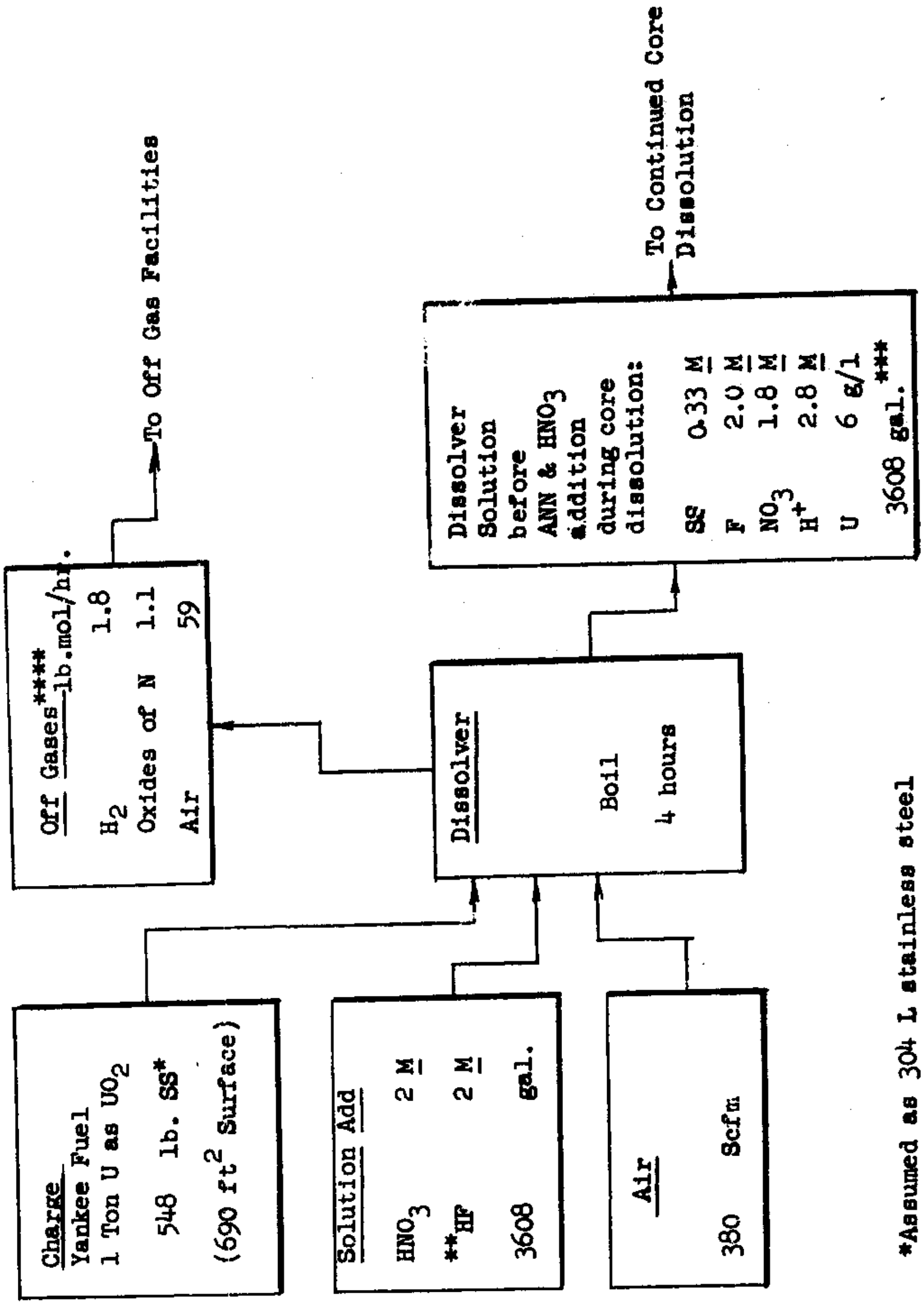


FIGURE 4 - PILOT PLANT DISSOLVER



*Assumed as 304 L stainless steel
**Alternate 1 M NH_4HF_2
***Assume no water loss to off gases
****Average rates based on 10 mils/hour.

FIGURE 5 - NIFLEX FLOWSHEET FOR DISSOLUTION OF 304 L STAINLESS STEEL

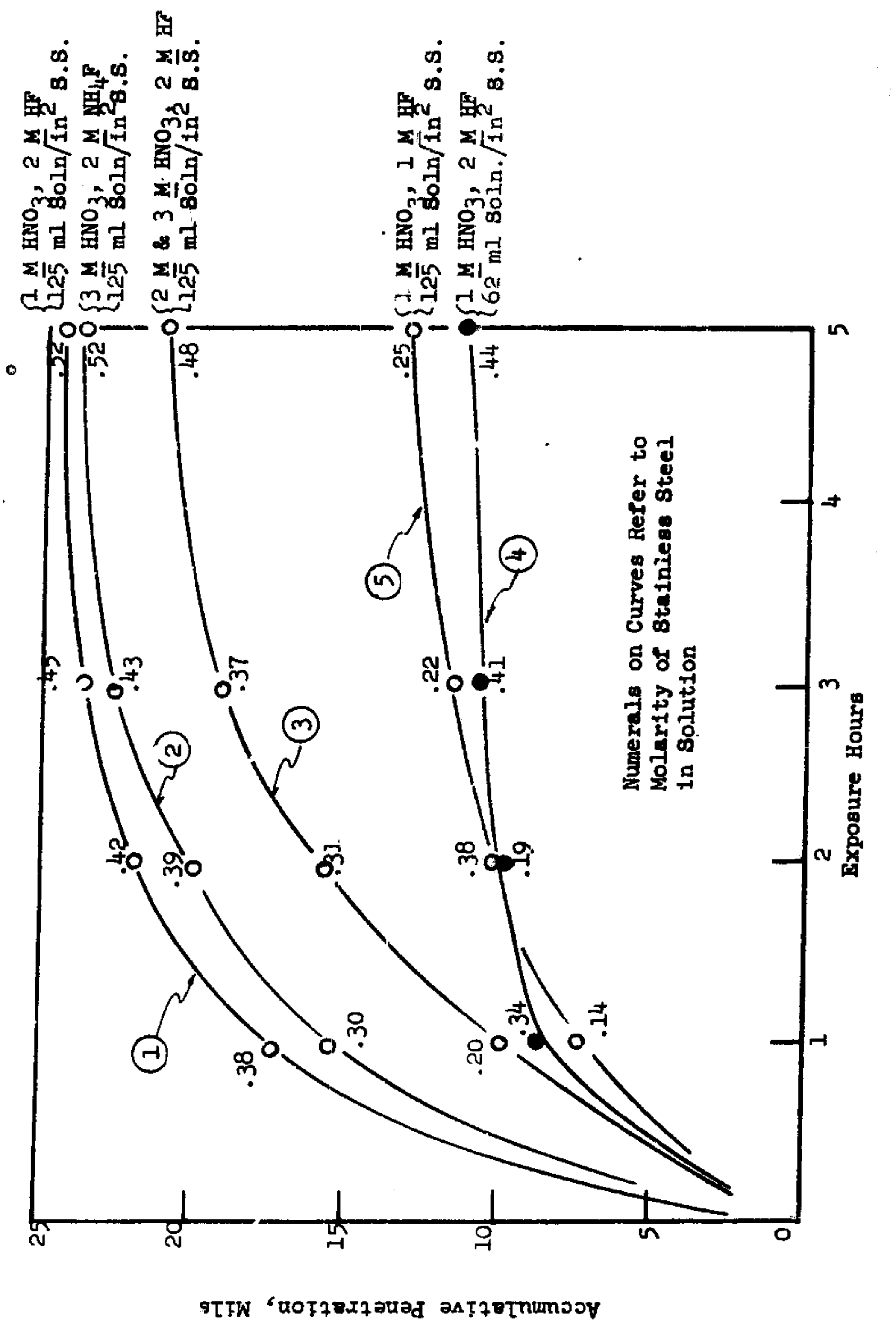


FIGURE 6 - DISSOLUTION OF 304 L STAINLESS STEEL IN BOILING HNO_3 - HF SOLUTION (1)

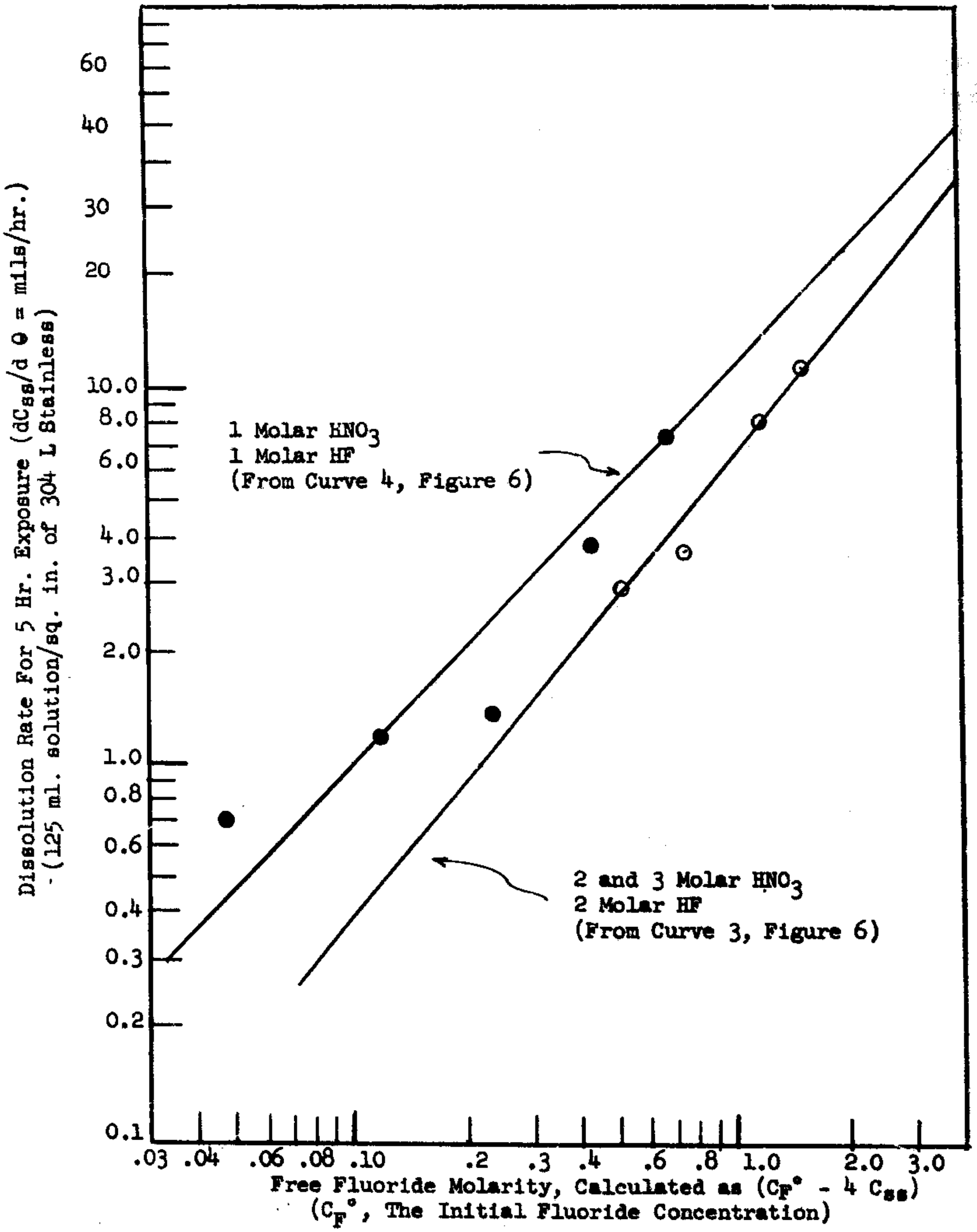


FIGURE 7 - 304 L STAINLESS DISSOLUTION RATE AS A FUNCTION OF FREE FLUORIDE ION CONCENTRATION (1)

TABLE I - RATE OF DISSOLUTION OF 304-L STAINLESS STEEL

Run	Source of Fluoride	Molarity F^-* (nominal)	Molarity HNO_3* (nominal)	Placement In Dissolver	Rate, First Hr. (mils/hr.)	Overall Rate (mils/hr.)	Percent Dissolution
1	NH_4HF_2	2	1	Full length	6.2	1.9	58.7
6	NH_4HF_2	2	2	Full length	8.4	2.6	91.1
7	NH_4HF_2	2	2	Bottom Section	9.0	2.6	97.4
8	NH_4HF_2	2	2	Top Section	9.9	2.7	97.7
9	HF	2	2	Full length	7.9	2.7	99.8
10	NH_4HF_2	2	1	Full length	6.4	2.5	85.2

* Initial Concentrations

TABLE II - FERRIC, CHROMIC AND NICKEL COMPLEX FLUORIDE IONS (2 and 3)

Ion Valence	Ferric	Chromic	Nickel
-3	FeF_6	CrF_6	
-2	FeF_5	CrF_5	NiF_4
-1	FeF_4	-	NiF_3

TABLE III

NIFLEX PILOT PLANT RUNS, SUMMARY OF 304-L STAINLESS STEEL DISSOLUTION STEP

Dissolvent Nominal Conditions					Operating Conditions		Results				Final Solution Analysis					Off-Gases	
Run No.	HNO_3 M	F M	NH_4^+ M	F/SS Mol Ratio	Scfm Air per ft.[2] SS	Boil-Up gs/hr.ft.[2] SS	Diss. Rate During 1st Hr. mils per hr.	Final % Diss.	Moles NO_3 Consumed (3) per mol SS dissolved	Moles H^+ Consumed(3) per mol SS Dissolved	SS M	F M	NO_3 M	H^+ M	U g/l	Peak Reaction Gas Rate Scfm/ft.[2] SS	Purpose
1	1	2	1	3	.34	-	6.2	37	0.19	1.24	.32	1.8	1.0	1.2		-	F/SS Ratio at Saturation
2	2	2	1	3	.29	1.1	8.4	65	0.29	4.2	.43	1.6	1.9	1.4		0.16	F/SS Ratio at Saturation
3	2	2	1	5	.30	0.7	5.4	90	0.59	2.7	.45	1.6	1.8	1.7		0.24	Total Dissolution
4	2	2	1	5	.33	0.6	10.5	90	0.61	3.52	.48	1.9	1.9	-		0.18	Total Dissolution
5	2	2	1	5	.34	0.6	9.2	93	0.71	3.36	.42	1.6	1.9	1.6		0.23	Eliminate Hastelloy F Contact
6	2	2	1	5	.34	0.1	8.4	91	0.81	3.25	.39	1.8	1.9	1.9		0.08	Changed Fluoride Add to Bottom
7	2	2	1	5	.55	0.9	9.0	97	0.51	3.63	.42	1.8	2.8	1.6		0.12	Rates in Bottom Section
8	2	2	1	-	.52	0.6	9.9	98	0.45	4.79	.56	2.2	2.5	2.0		0.10	Rates in Top Section
9	2	2	0	5	.46	0.5	7.8	99.8	0.70	2.62	.41	2.2	1.9	2.8		0.15	Use HF
10	1	2	0	6	.38	0.5	6.4	85	0.27	6.30	.34	2.1	0.9	1.4		0.21	F/SS Ratio
11	2	2	1	6	.45	0.6	10.7	98.9	0.18	3.12	.43	2.2	2.1	2.1		0.21	F/SS Ratio
12	2	2	1	7	.34	0.7	-	94	0.72	3.20	.27	1.4	1.7	1.5	4.3	-	Total Dissolution
13	2	2	1	8	.43	0.6	-	99.8	0.44	4.50	.29	1.6	1.9	2.0	5.0	0.11	Total Dissolution
14	2	2	1	7	.48	1.0	-	86	3.30	7.84	.30	1.6	1.0	0.2	13	0.23	Total Dissolution

1. Run 1 used 44 mil sheet, Run 2 through 11 used 24 mil sheet. Run 12 through 14 used 10 mil cladding.
2. Run 12 and 13 were clad 1/2" sintered UO_2 pellets. Run 14 was SS clad uranium rod 3/4" in diameter.
3. Based on nominal charge values and end analysis before addition of AHN.
4. All runs were operated 4 to 5 hours for SS dissolution.
5. All runs used ammonium bifluoride except run 9

APPENDIX

REACTION KINETICS AND MECHANISM

The dissolution rate of 304-L stainless is shown by Figure 3 to be influenced both by the nitric acid and fluoride ion concentration. The rate equations for the dissolution process, however, show that the reaction kinetics are dependent only on the free fluoride ion concentration; the nitric acid affects the rate in some unexplained way. The rate equations at various nitric acid concentrations follow:

Dissolution Rate Equation for 304-L Stainless*
(V/A = 125 ml solution/sq. in. of metal)

Nitric Acid Molarity	Rate Equation $dC_{ss}/d\Theta$ = mils/hr.
0.5	$dC_{ss}/d\Theta = 8.0\ (C_{F^-}{}^{**})^{0.50}$
1.0	$dC_{ss}/d\Theta = 6.1\ (C_{F^-})^{0.98}$
2.0	$dC_{ss}/d\Theta = 5.5\ (C_{F^-})^{1.3}$
5.0	$dC_{ss}/d\Theta = 4.4\ (C_{F^-})^{1.2}$

* Based on data of Figure 3
** C_{F^-} in moles/liter

The dissolution rate of 304-L stainless decreases rapidly as the stainless steel concentration of the solvent solution increases. The kinetic equations show that this decrease in rate must result from a drop in free fluoride ion concentration. The decrease in free fluoride ion concentration is probably a result of the formation of metal-fluoride complex ions. Several complex fluorides of the metal constituents of stainless steel are known; some of these are presented in Table II.

The free fluoride ion depletion per mole of stainless dissolved is determined by what complexes are formed. Assuming the dissolved metals are in the oxidation states Fe^{+3}, Cr^{+3} and Ni^{+2}, the lowest possible mole ratio of fluoride to stainless for complex formation is 3.95 to 1. Based on this ratio, the dissolution rate as a function of fluoride ion concentration was determined for curves 3 and 4 of Figure 6; the results which confirm the above basis are presented in Figure 7. The rate equations for Figure 7 are as follows:

Acid Molarity HNO_3	HF	Rate Equation* ($dC_{ss}/d\Theta$ = mils/hr.)
2 & 3	2	$dC_{ss}/d\Theta = 6.5 \ (C_{F^-})^{1.22}$
1	1	$dC_{ss}/d\Theta = 11 \ (C_{F^-})^{1.05}$

* V/A = 125 ml of solution/sq. in. of metal

The order of these equations confirms that previously obtained and indicates that the reaction is approximately first order for the above acid concentrations.

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