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DISSOLUTION OF LMFBR FUELS: SURVEY OF THE CORROSION OF SELECTED ALLOYS IN HNO_3-HF SOLUTIONS

Walter E. Clark
R. E. Blanco

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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DECEMBER 1971

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ABSTRACT

Corrosion data are compared for a number of candidate alloys in boiling HNO_3-HF solutions of widely varying concentrations. Corronel 230, welded with strip from the parent sheet, showed the most satisfactory performance of the alloys tested in solutions that were 3 to 10 *M* in HNO_3 and 0.05 to 1.0 *M* in HF. The long-term corrosion rate in 7 *M* HNO_3--0.05 *M* HF was 1.6 mils/month. Although type 309SCb stainless steel may be competitive in some parts of this range, Corronel 230 seems to offer an added margin of safety. The presence of complexing agents for fluoride (e.g., Al^{3+}) and of dissolution products (e.g., UO_2^{2+}, rare earths) drastically reduces the overall corrosion rates of all these alloys. In such solutions, the sensitivity of weldments to attack may be the factor that decides feasibility of use.

Titanium may be usable in 12 to 15 *M* HNO_3 solutions that are 0.003 *M* in HF; the corrosion rate in 15 *M* HNO_3--0.003 *M* HF was 1.8 mils/month. Al-6061 was almost completely resistant to boiling HNO_3-HF mixtures in which the concentration of HNO_3 was 15.6 *M* or higher.

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1. INTRODUCTION

The aqueous processing of nuclear power reactor fuels that contain separate phases of PuO_2 or ThO_2 requires dissolvents other than simple nitric acid. In order for the resulting solutions to be processed by well-developed nitric acid solvent extraction techniques, the final solution should still be predominantly nitrate. The usual approach to the problem has been to add varying amounts of fluoride to the nitric acid dissolvent to increase dissolution rates and solubilities of the fuel components. Unfortunately, the fluoride also seriously increases the corrosion rates of conventional

materials of construction. Previous work[1] has shown that unirradiated PuO_2-UO_2 is soluble in simple nitric acid if (1) the fuel contains less than about 40% PuO_2, and (2) the PuO_2 is in solid solution in the UO_2. Thus, the use of fluoride would not be required in the processing of Liquid Metal Cooled Fast Breeder Reactor (LMFBR) fuels if these conditions could be met. However, at the present time, the fabrication specifications for LMFBR fuel do not require that the fuel be soluble in nitric acid. In addition, the overall effect of irradiation conditions (burnup, linear heat rating, etc.) on the solubility of the irradiated fuel has not been determined. Also, fuel processing plants will probably have to be capable of handling fuel elements that fail prior to the desired irradiation levels, as well as unirradiated fuel that does not meet specifications. Early results from the current testing program with irradiated fuel at ORNL[2] are encouraging and indicate that (1) fuels which were soluble in nitric acid initially will exhibit solubilities of greater than 99% in nitric acid at burnups of up to 98,000 MWd/ton, and (b) irradiation tends to increase the solubility of fuels in nitric acid in instances where about 15% of the PuO_2 was insoluble initially. However, the fuel processing plant must consider (and may be forced to use) HNO_3-HF solutions to dissolve nitric acid-insoluble residues.

A considerable amount of work has been done on the containment of HNO_3-HF solutions during the past 15 to 20 years, but the results have not been summarized in a form that would allow a convenient comparison of various candidate materials for constructing a dissolver. This report attempts to provide such a comparison, primarily for solutions that contain no additives for complexing fluoride or otherwise decreasing corrosivity. The absence of complexing agents is important for the dissolution of LMFBR PuO_2-UO_2 fuels containing PuO_2 in a separate phase. For example, previous data indicate that the addition of aluminum to complex the fluoride to reduce both the amount of free fluoride present and the corrosivity of the solution causes the dissolution rate of PuO_2 to decrease to ineffective levels.[1] Also, some data indicate that, because the plutonium fluoride complex is so strong, large amounts of fluoride (up to an F/Pu atom ratio of 1 in solution) are required to maintain satisfactory dissolution rates at high plutonium concentrations (i.e., maintain a satisfactory instantaneous

concentration of free F^-, probably >0.05 *M* F). Thus, both large total amounts of fluoride and relatively high concentrations of free fluoride are apparently necessary to dissolve PuO_2 in order to achieve the concentrations required for fuel processing plants. This contrasts with the case of ThO_2, in which dissolver solutions of 13 *M* HNO_3--0.10 *M* Al--0.04 *M* F can be used to rapidly dissolve ThO_2 or ThO_2-UO_2 oxides to form solutions that are 1.0 *M* in thorium.[3] The free fluoride concentrations are low enough in this case to permit the use of 309SCb stainless steel as a material of construction.[4,5]

The primary purpose of this report is to evaluate the available corrosion data of greatest potential interest to the development of LMFBR fuel processing. The secondary purpose is to survey corrosion in HNO_3-HF mixtures very briefly and to present some unpublished data developed at ORNL on this subject.

An attempt has been made to arrange the data to indicate trends. Individuals interested in using a particular dissolvent with a given average load of a specific solute and/or fluoride complexing agent should, nevertheless, run confirmatory tests under their exact conditions. Some of the results presented were obtained in work carried out at ORNL.[6] The first data on Corronel 230 were obtained from Edwards in the United Kingdom.[7] The data on type 309SCb stainless steel come from a variety of sources, the most comprehensive of which is a report by Kranzlein.[8] Likewise, the information on Hastelloy F was derived from several sources, although the work at Hanford in support of the Niflex dissolution process[9,10] is the single most important source. Other data on these and additional alloys were generated at Battelle Memorial Institute.[11]

2. DATA

The results reported here are primarily for exposures in boiling solutions. In most instances, specimens were periodically removed for examination and weighing and were then replaced in the solution. The reader is referred to the original sources for questions concerning the experimental procedures. Nominal compositions of the alloys

included in this summary are listed in Table 1. Many other alloys were eliminated from consideration in the original test programs and are not mentioned in this report.

Dissolution of LMFBR fuels at reasonable rates requires the use of a dissolvent with an effective nitric acid concentration of at least 7 *M*, preferably 8 *M* or higher. A small, but undetermined, amount of fluoride must also be present in the free (i.e., uncomplexed) state in order for the dissolution of bulk PuO_2 to proceed at a reasonable rate. The presence of free fluoride markedly increases the corrosion rates of candidate alloys, as shown in Fig. 1 for titanium and Ni-o-nel. Similar quantitative data are lacking for other alloys of interest; qualitatively, however, it is safe to assume that other candidate materials will follow the same general pattern.

Data obtained for the three candidate alloys, 309SCb stainless steel, Haynes 25, and Corronel 230* in 7 *M* HNO_3--0.05 *M* HF are plotted in Fig. 2. Hastelloy F was also tested, but it was found to corrode at rates of 20 mils/month or greater. Corronel, by far the most resistant of the alloys tested, had a corrosion rate that leveled off at about 1.6 mils/month after about 72 hr of exposure (Table 2). The addition of UO_2^{2+} and rare earths to give final concentrations of 0.24 *M* and 0.06 *M*, respectively, decreased the corrosion rates of all candidate alloys to a few tenths of a mil per month and decreased the margin by which Corronel excelled the others (Fig. 2 and Table 3).

The data for Corronel 230 are summarized in Table 4 and Figs. 3 and 4. More data are needed for a comprehensive picture of the corrosion resistance of this alloy, but it is obvious that corrosion rates of less than 2 mils/month are obtainable in 6 to 10 *M* HNO_3 solutions that are also 0.05 *M* in HF. Weldments are preferentially attacked in all solutions having fluoride concentrations of 0.5 *M* or higher. Data for welded specimens are lacking in solutions with lower fluoride contents.

Type 309SCb stainless steel was used in constructing the Thorex dissolver.[4,5] As noted above (Fig. 2, Table 2), the corrosion rate of this alloy in 7 *M* HNO_3--0.05 *M* HF was several times greater than that of Corronel 230 and increased with exposure

*Obtained from the Huntington Alloys Division of the International Nickel Company. Specimens were welded using strips cut from the parent metal instead of weld rod.

Table 1. Nominal Compositions (in wt %) of Alloys Tested

Alloy	Element																		
	Fe	Cr	Ni	Co	Mo	Cu	Mn	Ti	W	Al	Mg	Nb	Ta	Si	C	P	S	N	H
Corronel 230	5.0[a]	35-37	Bal	-	-	1.0[a]	1.0[a]	1.0[a]	-	0.5[a]	-	-	-	0.6[a]	0.08[a]	-	-	-	-
Hastelloy F	21	22	45	2.5	6.0	-	1.7	-	1.0	-	-	2.2[b]	0.9[b]	1.0	0.01-0.02[b]	-	0.07-0.015[b]	-	-
BMI-HAPO 20[c]	16	25	50	-	6	1	0.6	1.0	-	-	-	-	-	0.4	0.02	-	-	-	-
EB-4358[c]	24[d]	23	45	-	3.5	2.25	-	-	-	-	-	---2.25---		-	-	-	-	-	-
EB-5459[c]	34[d]	23	35	-	3.5	2.25	-	-	-	-	-	---2.25---		-	-	-	-	-	-
Ni-o-nel	32.0	21.4	40.0	-	3.0	1.8	0.6	10XC[i]	-	0.1	-	-	-	0.4	0.05[a]	-	-	-	-
Haynes 25	2	20	10	50[d]	1.5	-	-	-	15	-	-	-	-	1.0[a]	0.15[a]	-	-	-	-
Haynes 150	20	28	e	50	e	-	0.65	-	-	-	-	-	-	0.75	0.8	-	-	-	-
Type 309SCb stainless steel[f]	63[d]	23	13	-	-	-	-	-	-	-	-	10XC[i]	-	-	0.08	-	-	-	-
Type 347 stainless steel	70[d]	18	11	-	-	-	-	-	-	-	-	10XC[i]	-	-	0.08	-	-	-	-
Titanium 45A	0.25[a]	-	-	-	-	-	-	Bal	-	-	-	-	-	-	0.08[a]	-	-	0.05[a]	0.015[g]
Aluminum, Al-1100	1[h]	-	-	-	-	0.2[g]	-	-	-	99.0[i]	-	-	-	1[h]	-	-	-	-	-
Aluminum, Al-6061	-	0.25	-	-	-	0.25	-	-	-	Bal	1	-	-	0.6	-	-	-	-	-

[a]Maximum.

[b]Hanford vacuum-melted material.

[c]Experimental alloy.

[d]Or specified as "balance".

[e]As low as possible.

[f]No longer being produced.

[g]Maximum for sheet stock, grades 35A to 75A.

[h]Maximum Fe + Si = 1%.

[i]Minimum.

[j]Ten times the carbon content.

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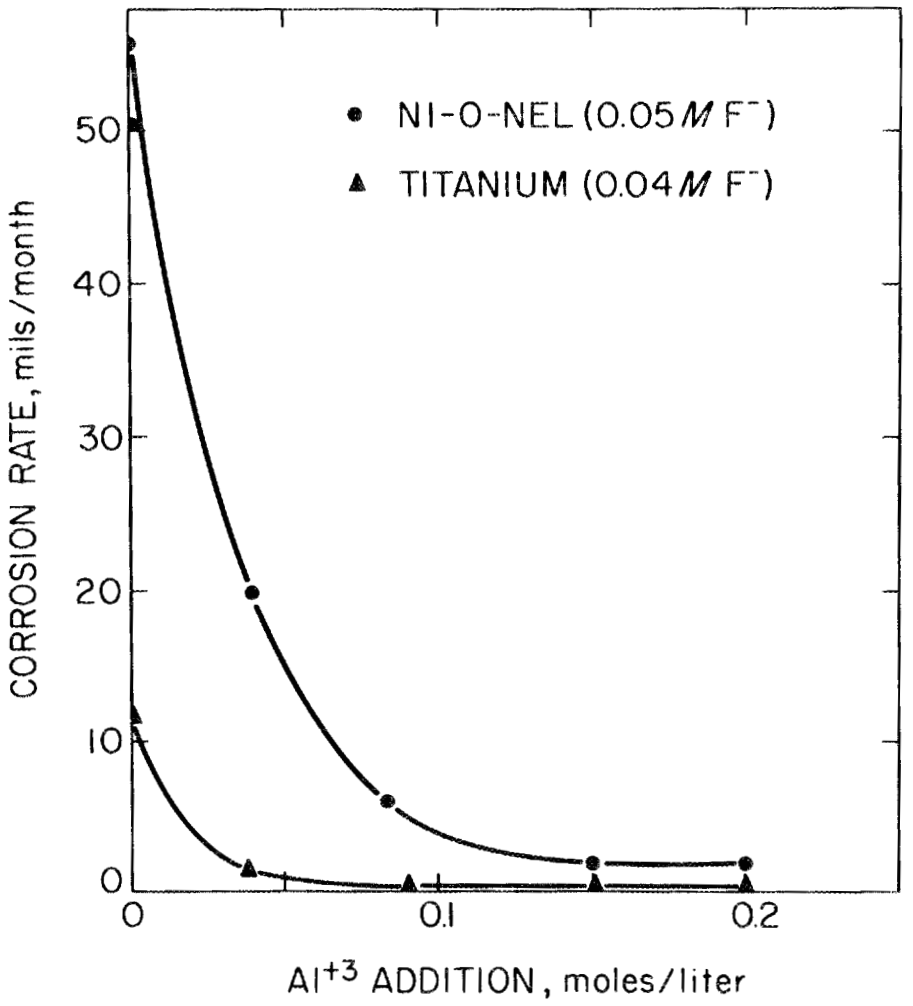

Fig. 1. The Effect of a Complexing Agent (Al^{3+}) on the Corrosion of Ni-o-nel and of Titanium in 13 M HNO_3--0.04 to 0.05 M NaF.

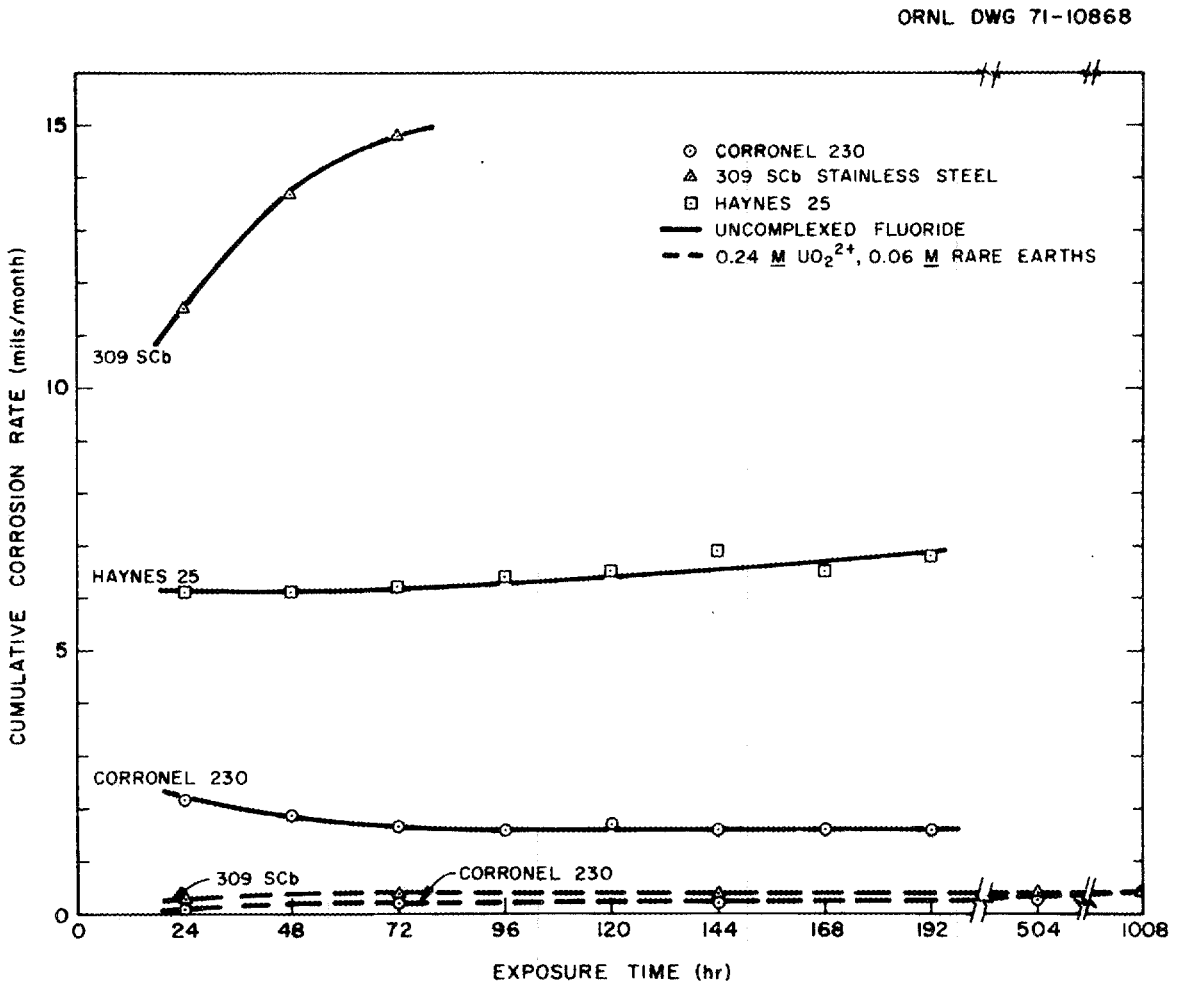

Fig. 2. Corrosion of Candidate Alloys in Boiling 7 *M* HNO_3--0.05 *M* HF as a Function of Exposure Time.

Table 2. Corrosion Rates (in mils/month) for Candidate Alloys in Boiling 7.0 *M* HNO_3--0.05 *M* HF

Alloy	Position[a]	Exposure Time (hr)							
		24	48	72	96	120	144	168	192
309SCb	V	5.6	6.2	7.0					
	I	10.8	12.8	14.0					
	S	11.5	13.7	14.8					
Haynes 25	V	3.4	3.4	3.4	3.4	3.5	3.5	3.3	3.4
	I	5.4	5.6	5.6	5.8	6.0	6.3	5.7	6.2
	S	6.1	6.1	6.2	6.4	6.5	6.9	6.5	6.7
Hastelloy F	V	11.4	13.2	15.1					
	I	21.3	25.5	28.0					
	S	23.6	28.2	31.7					
Corronel 230	V	1.5	1.4	1.3	1.2	1.2	1.2	1.1	1.1
	I	2.1	1.8	1.7	1.6	1.5	1.5	1.5	1.5
	S	2.2	1.9	1.7	1.6	1.7	1.6	1.6	1.6

[a]V = in the vapor phase.
I = at the vapor-liquid interface.
S = in solution.

Table 3. Corrosion Rates (in mils/month) for Candidate Alloys in Boiling Solutions of the Composition 7.0 *M* HNO_3--0.05 *M* HF--0.25 *M* UO_2^{2+}--0.06 *M* Rare-Earth Oxides

Alloy	Position[a]	Exposure Time (hr)							
		24	72	144	240	504	672	840	1008
309SCb	V	0.2	0.3	0.3	0.3	0.2	0.2	0.2	0.2
	I	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	S	0.3	0.4	0.4	0.4	0.4	0.4	0.5	0.5
Haynes 25	V	0.6	0.7	0.5	0.5	0.5	0.6	0.6	0.6
	I	0.8	0.9	0.8	0.7	0.6	0.7	0.7	0.7
	S	0.9	0.9	0.8	0.7	0.6	0.6	0.6	0.6
Hastelloy F	V	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.5
	I	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.5
	S	0.6	0.6	0.6	0.5	0.5	0.5	0.4	0.4
Corronel 230	V	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.1
	I	<0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3
	S	0.1	0.2	0.2	0.2	0.3	0.4	0.4	0.4

[a]V = in the vapor phase.
I = at the vapor-liquid interface.
S = in solution.

Table 4. Corrosion of Corronel 230 in Refluxing HNO_3-HF Solutions

Concentration (M)		Alloy Condition	Test Period (hr)	Corrosion Rate (mils/month)		
HNO_3	HF			Vapor	Interface	Solution
-	1.0	Welded	24	8.1	55.7	64.5
-	1.0		48	8.6	64.4	72.0
-	1.0		72	8.6	66.0	78.0
1.0	3.0		4	Dissolved		
3.0[a]	0.1	Unwelded	322	-	-	3.3
3.0[a]	1.0	Unwelded	322	-	-	6.6
4.0	0.3	Welded	24	2.5	3.8	4.0
			48	2.1	3.7	3.7
			72	2.2	3.8	3.8
			96	2.2	3.8	3.8
4.0	0.3	Unwelded	48	1.7	2.4	2.6
			144	1.2	1.7	1.9
			161[b]	1.2	1.8	2.0
			257	1.4	1.8	2.1
4.0	5.0	Unwelded	24	47.2	45.8	57.8
			48	47.0	46.1	61.2
			79	46.8	46.4	62.5
			103	44.5	45.8	62.8
6.0[a]	0.1	Unwelded	322	-	-	4.3
6.0[a]	1.0	Unwelded	322	-	-	22.7
7.0	0.05	Unwelded	24	1.5	2.1	2.2
			96	1.2	1.6	1.6
			192	1.1	1.5	1.6
7.0[c]	0.05	Unwelded	24	0.1	0.1	0.1
			504	0.1	0.2	0.3
			1008	0.1	0.3	0.4
9.0[a]	0.1	Unwelded	322	-	-	5.8
9.0[a]	1.0	Unwelded	322	-	-	28.8
10.0	0.5	Unwelded	24	28.0	43.1	50.9
			48	30.4	45.3	56.3
			72	32.9	47.8	59.3
10.0	0.5	Unwelded	48	42.3	43.3	63.5
			72	42.6	43.7	62.0
			96	39.5	43.8	59.9
10.0	1.0	Welded	24	62.3	86.4	109.5
			48	65.7	92.0	115.7
			72	68.4	96.0	113.1
10.0	1.0	Unwelded	24	36.8	56.1	55.4
			48	37.4	58.9	56.4
			79[b]	38.4	60.1	56.3
			103	38.4	60.3	56.2
10.0	5.0	Unwelded	24	64.8	157.3	178.7
			48	63.1	155.3	178.6
			65[b]	61.2	156.6	179.2
			89	57.3	153.6	172.9
12.0[a]	0.1	Unwelded	325	-	-	10.0
12.0[a]	0.2	Unwelded	300	-	-	22.7
12.0[a]	1.0	Unwelded	300	-	-	79.7

[a]UKAEA data (see ref. 7).

[b]Equipment failure resulted in variable exposure times.

[c]UO_2^{2+} and rare-earth oxides added to give concentrations of 0.24 M and 0.06 M respectively.

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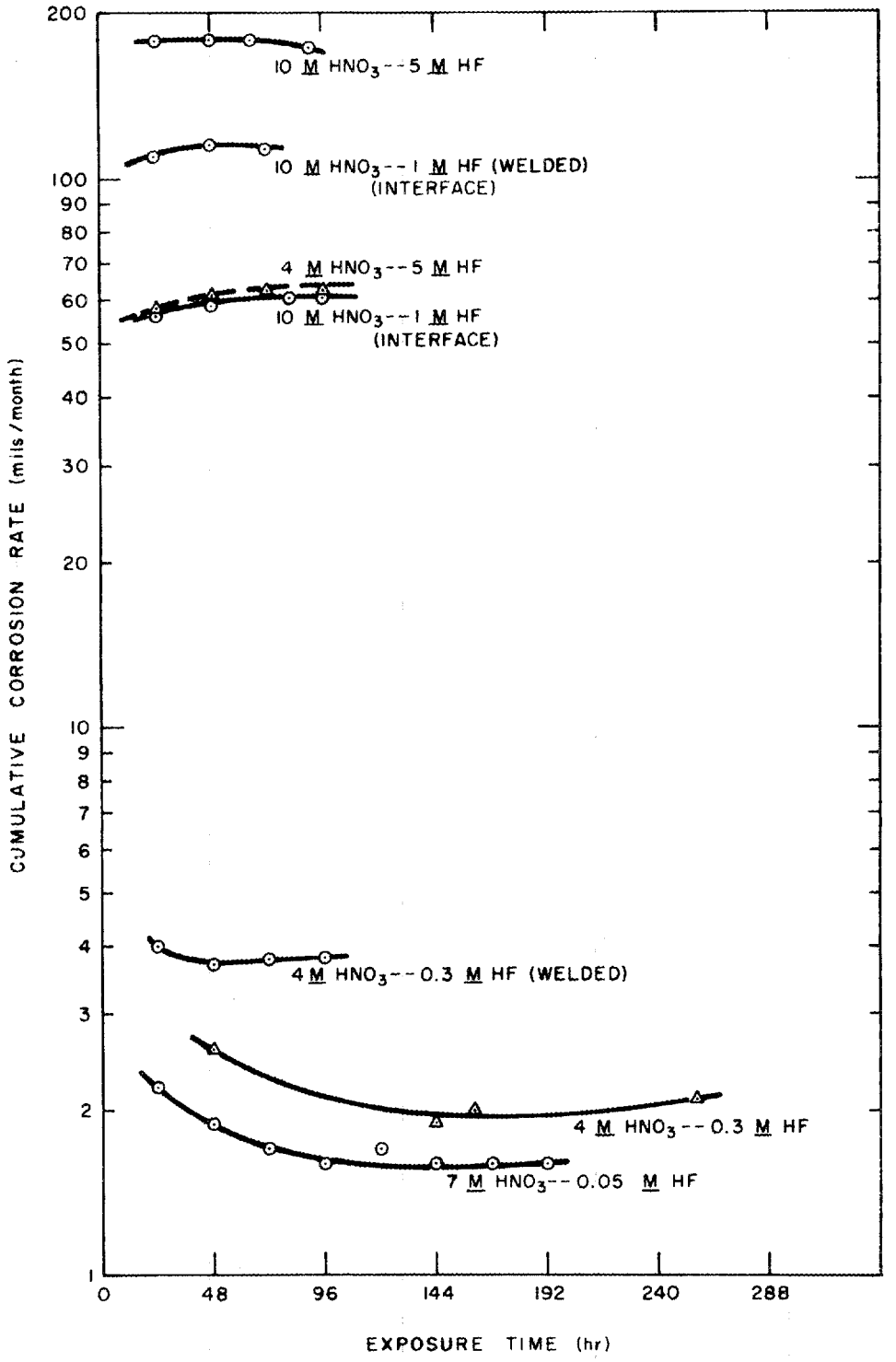

Fig. 3. Corrosion Rates for Corronel 230 in Various Concentrations of HNO_3-HF as a Function of Exposure Time.

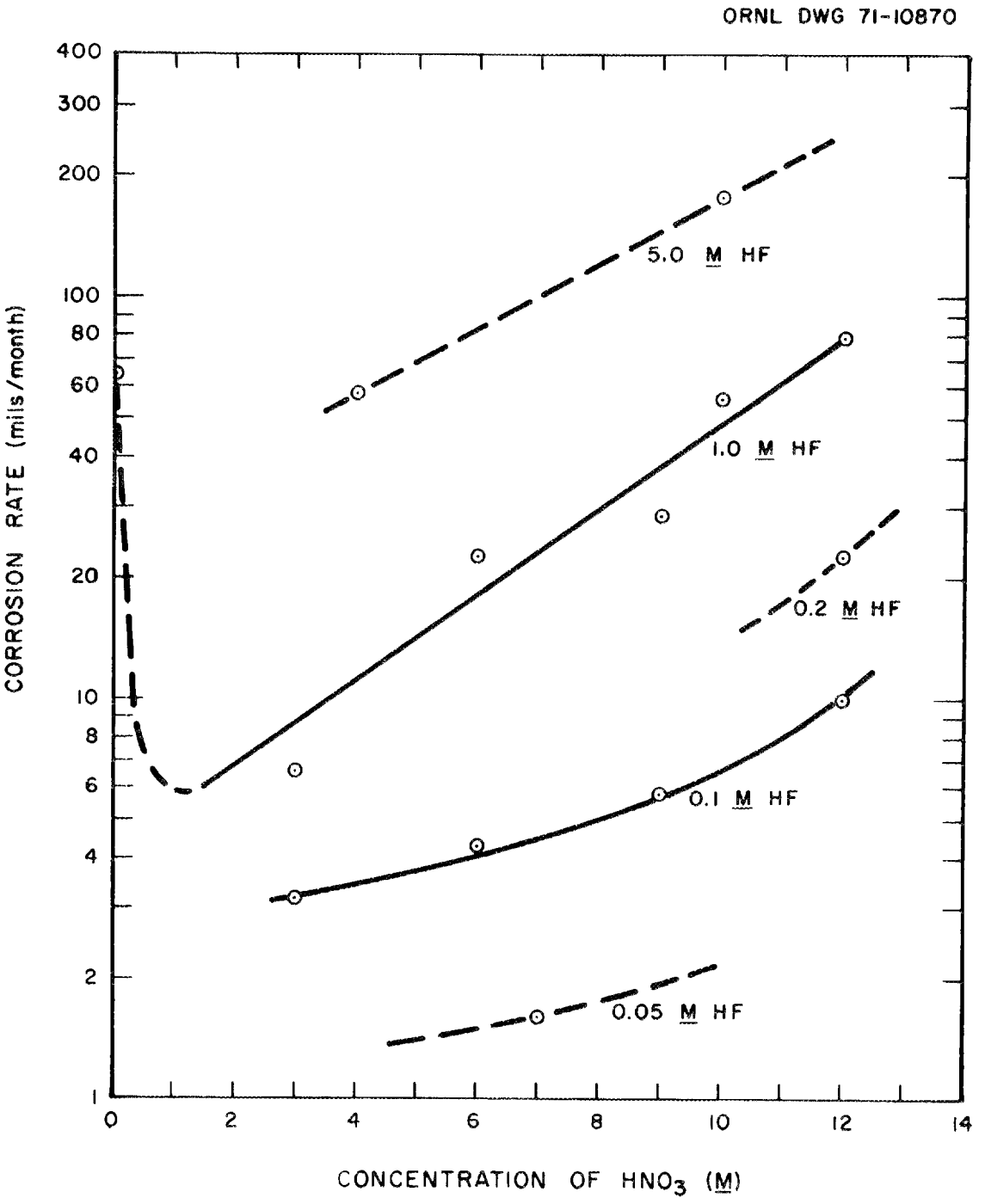

Fig. 4. Corrosion of Corronel 230 as a Function of HNO_3 Concentration at Various Concentrations of HF. Exposure times varied from 72 to 322 hr.

time. The corrosion of type 309SCb stainless steel as a function of HNO_3 and HF concentrations was also studied by Kranzlein[8] (Fig. 5) and by Webster[12] (Figs. 6 and 7). Corrosion rates range up to 3 mils/month in HNO_3 concentrations equal to or greater than 7 *M* as the free fluoride concentration increases to about 0.02 *M*. Weldments corrode much more rapidly (Figs. 7 and 8). Data from ORNL[6] (Table 5) and the UKAEA[7] are consistent with these results.

Hastelloy F performs best in relatively weak nitric acid (e.g., 1 *M* HNO_3-- 2 *M* HF, Niflex process). Limited tests show Haynes 25 to be superior to either type 309SCb or Hastelloy F in 7 *M* HNO_3--0.05 *M* HF but inferior to Corronel 230 (Table 2, Fig. 2).

Tests on titanium in a variety of HNO_3-HF combinations show that corrosion rates on the order of 3 to 4 mils/month are obtained in HNO_3 concentrations of 12 to 15 *M* and HF concentrations up to 0.005 *M* (Figs. 9 and 10, Table 6). Some local attack was observed at the lower ($\leq$ 12 *M*) HNO_3 concentrations when the HF concentration was 0.05 *M*. The presence of 0.002 *M* H_3BO_3 had no effect on the corrosion of titanium in these solutions. Rates were lowest at the higher (12 to 15 *M*) HNO_3 concentrations and at the lower HF concentrations; in 15 *M* HNO_3--0.003 *M* HF, the maximum rate was 2.2 mils/month (Table 6). A nitric acid concentration of about 6 *M* seems to be the most aggressive toward titanium in the presence of HF (Fig. 10). Pitting attack has been observed in a rectifying column above a continuously boiling Thorex solution in which the fluoride in the solution was well complexed.[11] In Thorex dissolvent [13 *M* HNO_3--0.05 *M* HF--0.04 to 0.1 *M* $Al(NO_3)_3$] and in other Thorex process solutions, corrosion rates were generally low and specimens were remarkably free of localized attack at weldments or elsewhere.

The addition of moderate amounts of fluoride-complexing agents decreases the corrosion of titanium in HNO_3-HF mixtures drastically (Fig. 1). In long-term exposures in 10 *M* HNO_3--0.5 *M* NaF--0.75 *M* $Al(NO_3)_3$, both welded titanium and unwelded Corronel 230 corroded at rates of about 1.4 to 1.5 mils/month for the first 24 hr; however, after 408 hr, the corrosion of titanium had decreased to 0.2 to 0.3 mil/month vs 0.7 mil/month for Corronel (Fig. 11, Table 7). Neither of the alloys suffered local attack.

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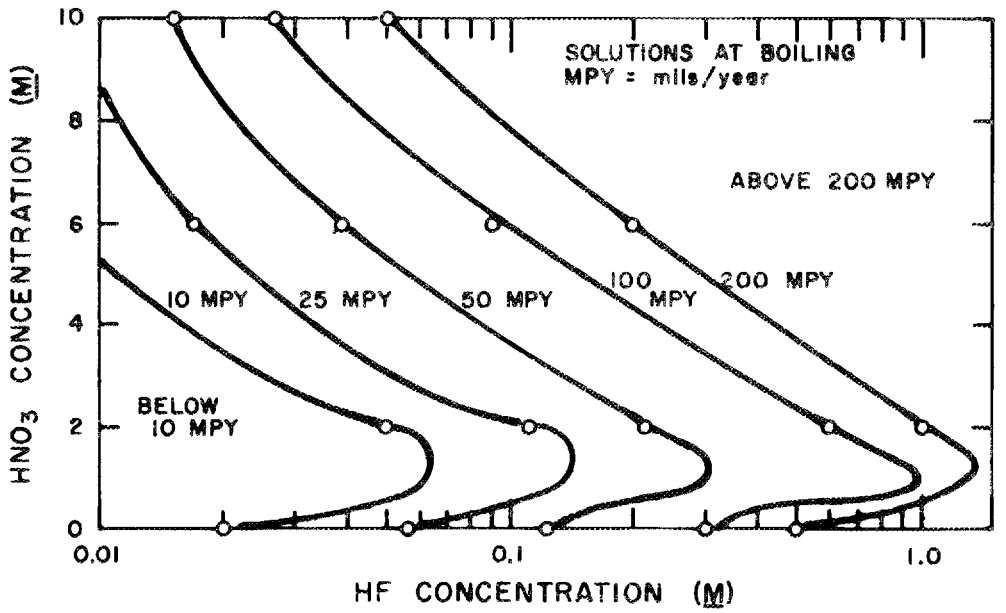

Fig. 5. Corrosion of 309SCb in HNO_3-HF Solutions. (Redrawn from Fig. 5 in ref. 8.)

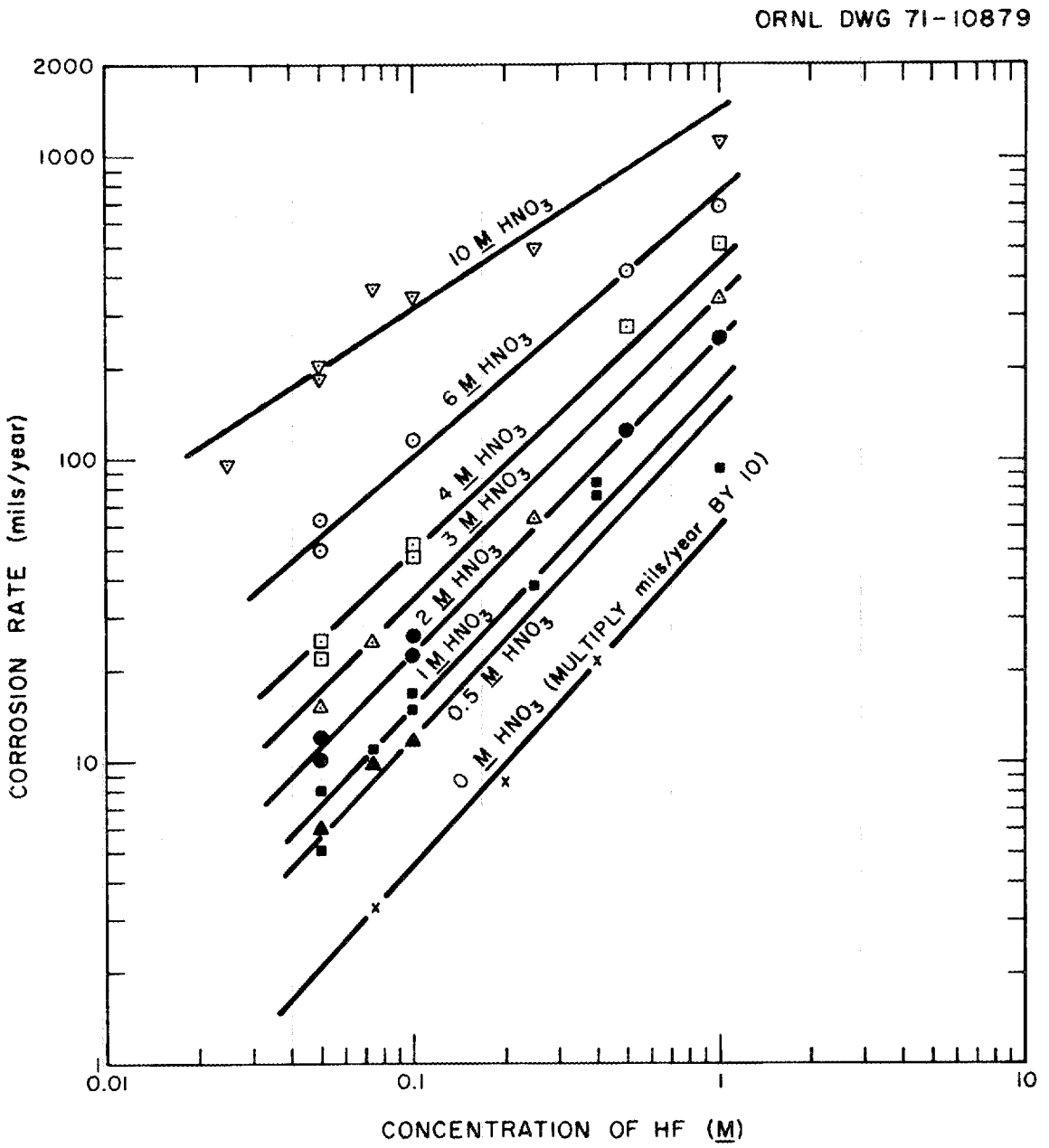

Fig. 6. Corrosion Rate of 309SCb in Boiling HF-HNO_3 as a Function of HF Concentration. (Redrawn from Fig. 5 in ref. 12.)

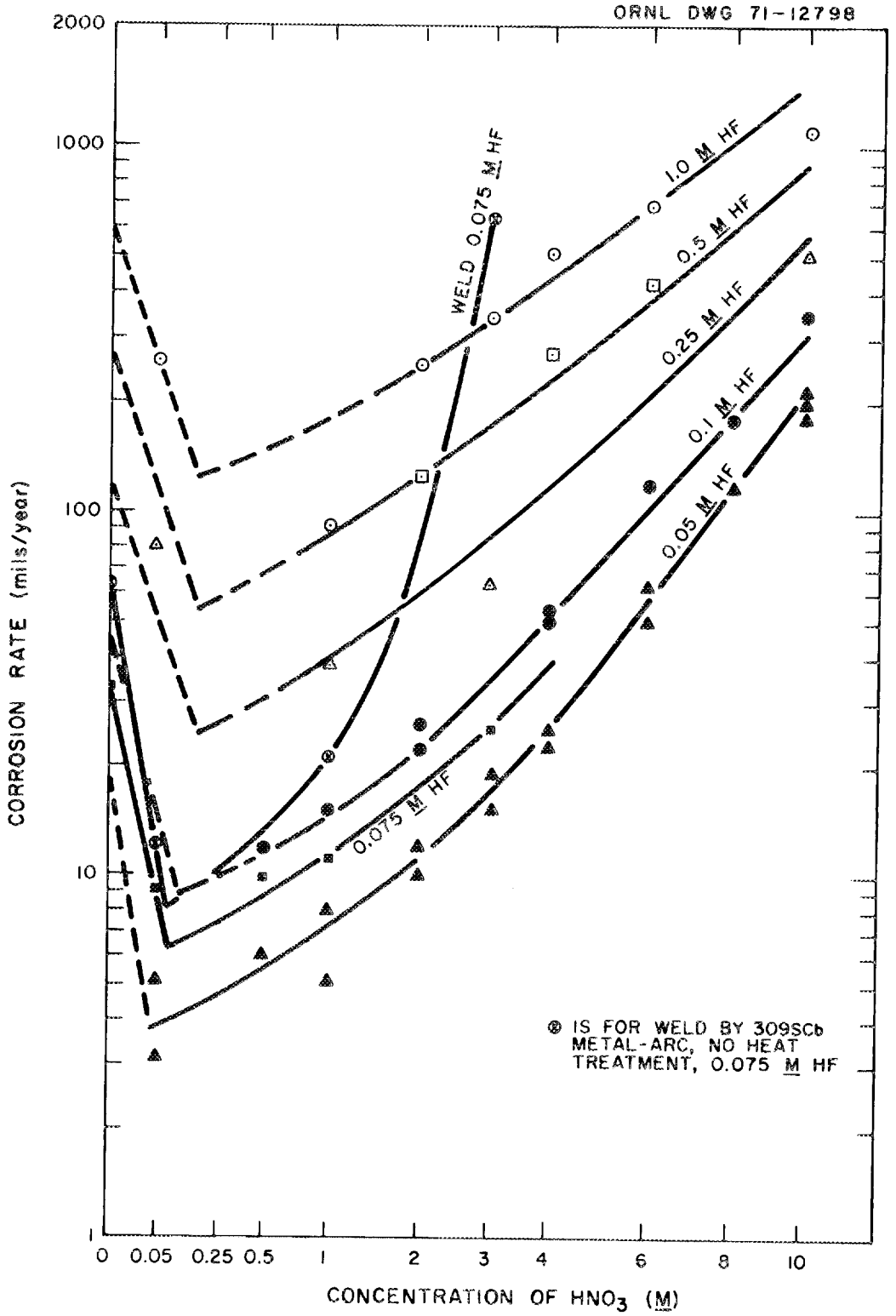

Fig. 7. Corrosion Rate of 309SCb in Boiling HF-HNO_3 as a Function of HNO_3 Concentration. (Data taken from ref. 12.)

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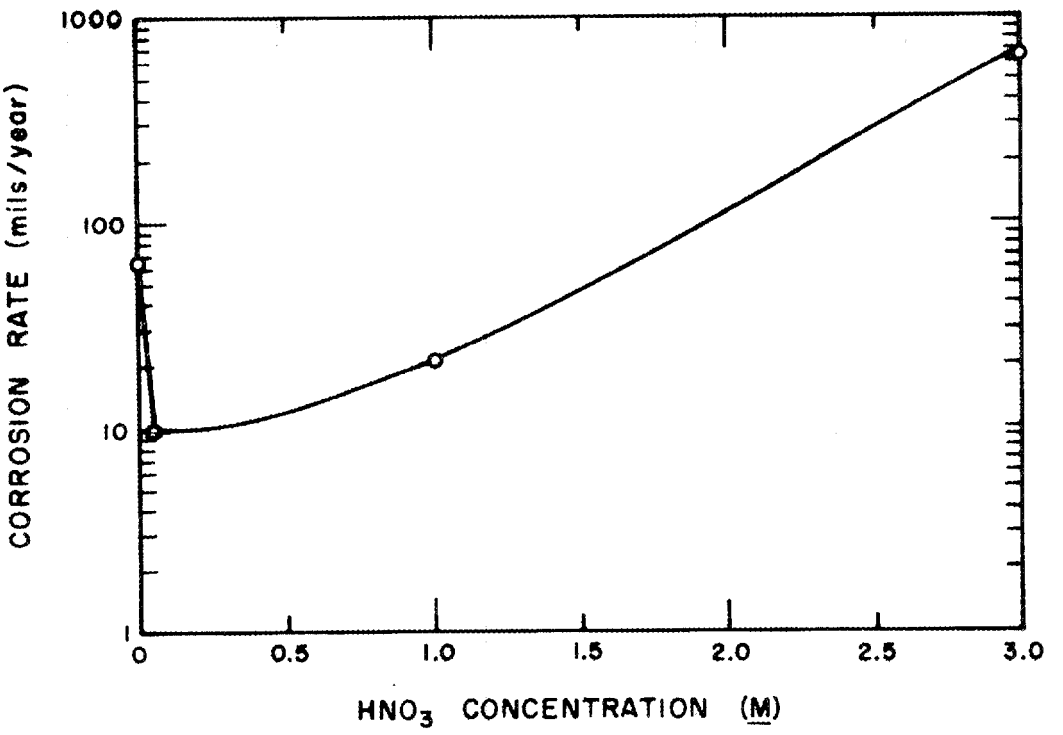

Fig. 8. Corrosion of 309SCb Welds in Boiling 0.075 *M* HF as a Function of HNO_3 Concentration. (Redrawn from Fig. 5 of ref. 8.)

Table 5. Corrosion Rates of Type 309SCb Stainless Steel in Various Mixtures of Nitric and Hydrofluoric Acid

(Test period: 24 hr)

HNO_3 Concentration (M)	Corrosion Rate (mils/month)					
	0.05 M HF			0.005 M HF		
	V[a]	I[a]	S[a]	V[a]	I[a]	S[a]
3.0	0.9	1.6	1.7	0.2	1.0	1.0
	1.0	2.0	1.4	0.5	1.0	0.9
	1.0[b]	2.0[b]	1.4[b]			
6.0	2.8	5.3	5.1	1.1	2.1	2.0
	2.6	4.8	5.1	1.1	2.2	2.0
	2.3[b]	4.6[b]	5.0[b]			
	2.9[b]	5.0[b]	5.3[b]			
9.0				1.2	2.2	2.1
				1.4	2.3	2.1
12.0	32	45	46	3.7	5.1	4.7
	31	45	45	3.8	4.6	4.6
	17[b]	30[b]	33[b]			
	20[b]	36[b]	39[b]			
15.0	48	55	56			

[a]V = in vapor phase; I = at the vapor-liquid interface; S = in solution.

[b]Solution was also 0.002 M in H_3BO_3.

ORNL DWG 71-10874

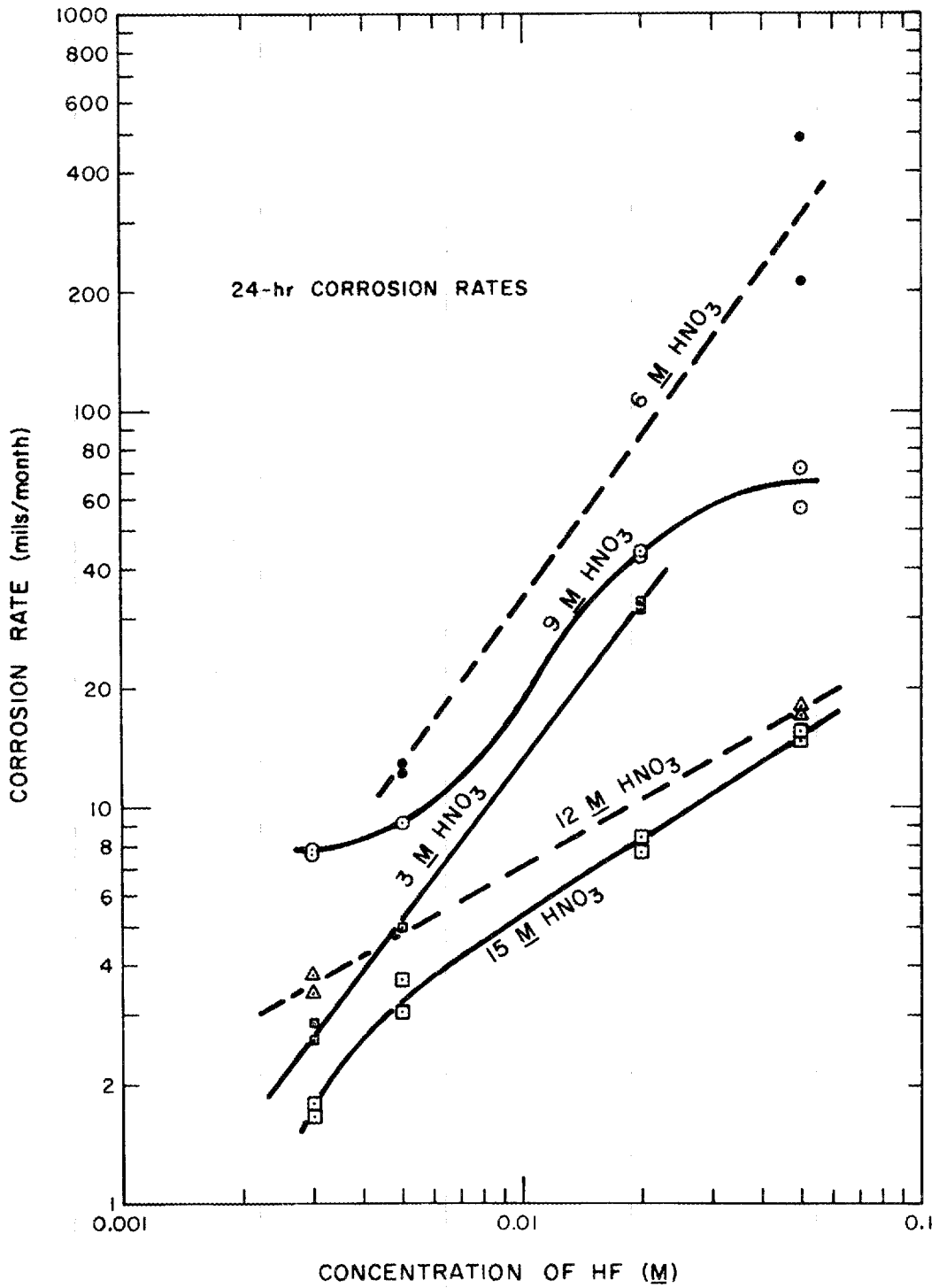

Fig. 9. Corrosion of Titanium in HNO_3-HF Mixtures as a Function of HF Concentration.

ORNL DWG 71-10877

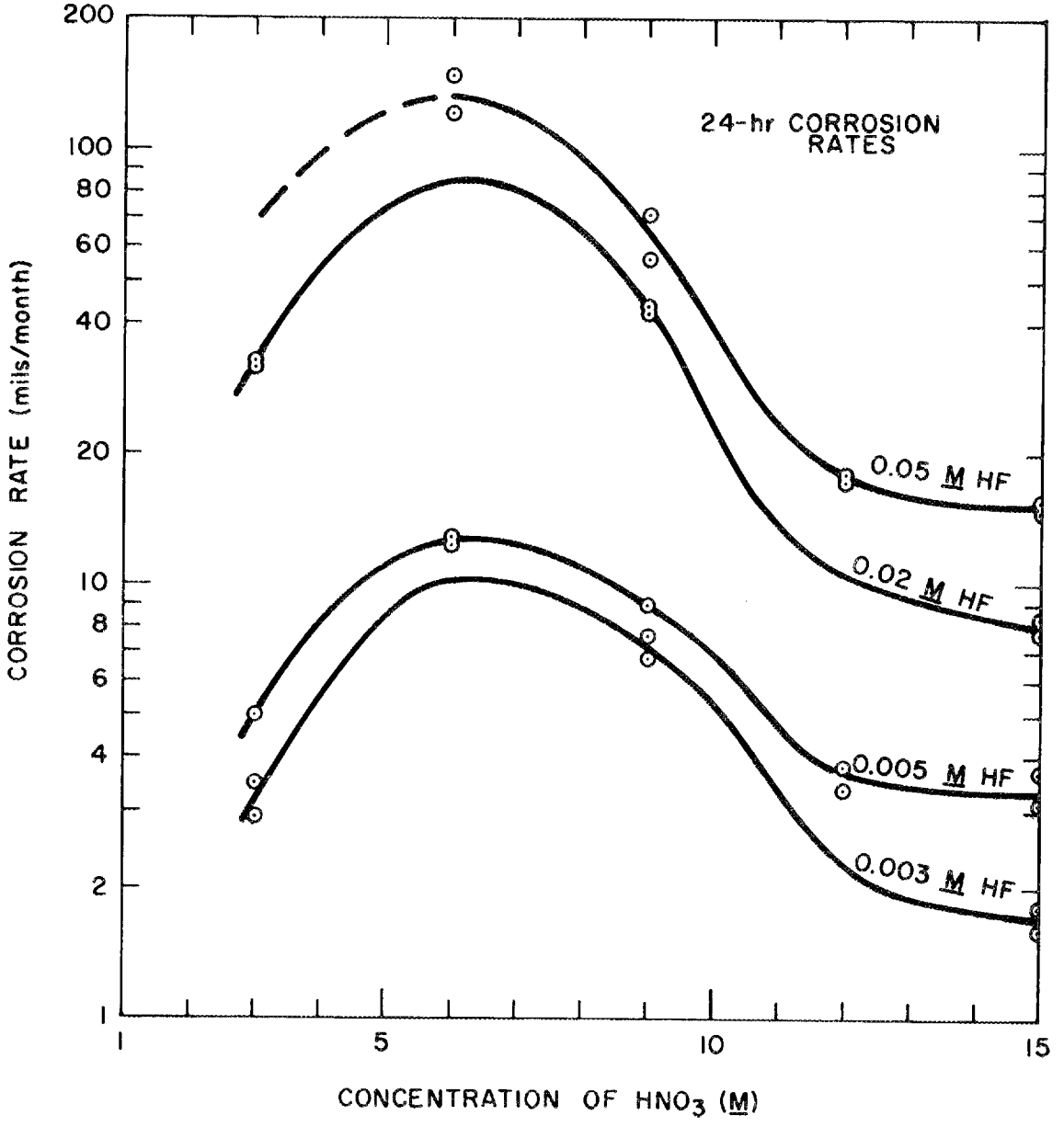

Fig. 10. Corrosion of Titanium in HNO_3-HF Mixtures as a Function of HNO_3 Concentration.

Table 6. Short-Term Corrosion Rates of Titanium-45A in Various Mixtures of Nitric and Hydrofluoric Acid

Test Period: 24 hr

HNO_3 Concentration (M)	Corrosion Rate (mils/month)											
	0.003 M HF			0.005 M HF			0.02 M HF			0.05 M HF		
	V[a]	I[a]	S[a]	V[a]	I[a]	S[a]	V[a]	I[a]	S[a]	V[a]	I[a]	S[a]
3.0	0.3, 0.3	2.4, 2.4	2.6, 2.9	0.1	4.8	5.0	0.2, 0.2	29, 26	33, 32			
	0.4,[b] 0.4[b]	2.8,[b] 3.1[b]	3.2,[b] 3.5[b]	0.2	5.2	5.0	0.6,[b] 0.5[b]	1.8,[b] 60[b]	56,[b] g[b]			
6.0				0.8	8.3	12.2				0.6	147	149
				0.8	7.9	12.9				0.4	136	121
9.0	1.0, 0.5	4.7, 4.4	7.8, 7.7	1.3	6.1	9.1	4.3, 7.0	30, 48	43, 44	4.6	49.5	56.5
	0.7,[b] 0.5[b]	7.8,[b] 6.1[b]	6.0,[b] 6.9[b]	1.6	6.7	9.1	2.4,[b] 1.8[b]	32,[b] 26[b]	54,[b] 40[b]	3.7	42.6	71.3
12.0				1.1	4.6	3.8				4.6	51.8	17.7
				1.3	2.9	3.4				4.2	48.1	17.4
15.0	0.1, g	2.1, 2.2	1.7, 1.8	1.1	3.8	3.7	0.6, 1.0	8.7, 9.4	8.4, 7.8	4.6	23.1	14.8
	0.4,[b] 0.1[b]	0.7,[b] 1.5[b]	2.2,[b] 1.6[b]	1.0	2.7	3.1	1.1,[b] 1.3[b]	9.6,[b] 6.6[b]	7.7,[b] 8.7[b]	5.9	26.2	15.6

[a] V = in vapor phase; I = at the vapor-liquid interface; S = in solution; g = slight weight gain.

[b] Solution also contained 0.002 M H_3BO_3.

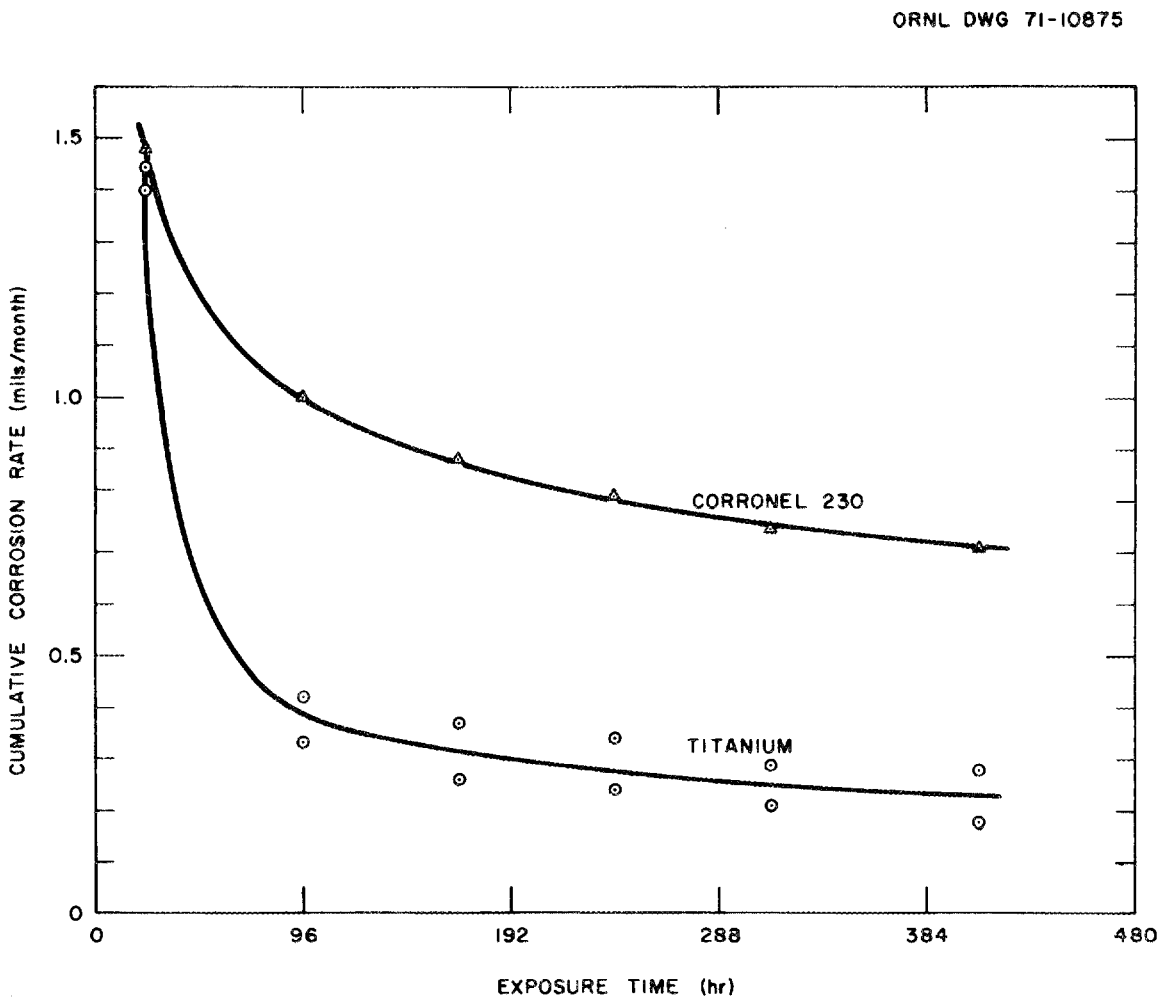

Fig. 11. Corrosion of Corronel 230 and of Titanium in 10 *M* HNO_3--0.5 *M* NaF--0.75 *M* $Al(NO_3)_3$.

Table 7. Corrosion of Welded Specimens of Titanium-45A and Unwelded Specimens of Corronel 230 in Boiling 10.0 *M* HNO_3--0.5 *M* NaF--0.75 *M* $Al(NO_3)_3 \cdot 9H_2O$ Solutions

Test Period (hr)	Alloy	Corrosion Rate (mils/month)		
		V[a]	I[a]	S[a]
24	Titanium-45A	0.10, 0.24	0.35, 0.56	1.40, 1.44
	Corronel 230	1.02	1.28	1.48
96	Titanium-45A	0.01, 0.04	0.32, 0.35	0.33, 0.42
	Corronel 230	0.90	0.93	1.00
168	Titanium-45A	0.01, 0.03	0.18, 0.21	0.26, 0.37
	Corronel 230	0.85	0.85	0.88
240	Titanium-45A	0.02, 0.04	0.16, 0.20	0.24, 0.34
	Corronel 230	0.82	0.78	0.81
312	Titanium-45A	<0.01, 0.02	0.13, 0.16	0.21, 0.29
	Corronel 230	0.80	0.75	0.75
408	Titanium-45A	<0.01, 0.02	0.11, 0.16	0.19, 0.28
	Corronel 230	0.78	0.71	0.71

[a]V = in vapor phase; I = at the vapor-liquid interface; S = in solution.

Aluminum and its alloys tend to passivate in very concentrated (>15.6 *M*) nitric acid containing HF. The use of an aluminum dissolver is, therefore, theoretically possible. When the ORNL corrosion tests on aluminum (Table 8) and on 309SCb, 304L, and 347 stainless steels (Table 9) were made, the disintegration and leaching of graphite fuels was being considered. Specimens of 6061 Al exposed for 192 days in solutions that were 22 to 23 *M* in HNO_3 and 1 to 2 *M* in HF gained, rather than lost weight except in the vapor phase, where the rate of attack amounted to only about 0.1 mil/month. The presence of dissolved uranium and undecomposed graphite had no accelerating effect. This resistance to corrosion appears to be due to a combination of passivation and the formation of a protective fluoride film. The erratic rates observed in solutions 14 to 15.6 *M* in HNO_3 and 1 to 2 *M* in HF (Table 8) and the fact that corrosion is more rapid at low temperatures than in the refluxing solution are indications that such a mechanism may be operating. Rates in boiling 22 to 23 *M* HNO_3 solutions that were 1 to 2 *M* in HF were consistently immeasurably low in the liquid phase and were 0.2 mil/month or less in the vapor for exposure times as long as 312 hr.

Type 309SCb stainless steel suffered an overall attack of about 0.3 mil/month in 23 *M* HNO_3--1 *M* HF during exposures of up to 312 hr. The heaviest attack was on the specimen exposed at the liquid-vapor interface. In the presence of graphite and dissolved UO_2, 309SCb depassivated after 72 hr of exposure and corroded at excessive rates (~28 mils/month) in a pitting type of attack. Types 304L and 347 stainless steels corroded at moderate rates (≦5 mils/month) in 22 *M* HNO_3--1 *M* HF (Table 9).

Comparative data for candidate materials are summarized in Tables 10, 11, and 12 for the three HNO_3 concentration ranges of 0 to 4 *M*, 6 to 13 *M*, and 13 to 23 *M* HNO_3, respectively.

3. DISCUSSION

Corronel 230 is clearly the most resistant material studied in 7 to 10 *M* HNO_3 solutions having an uncomplexed fluoride concentration of about 0.05 *M*. The corrosion rate of 1.6 mils/month found in 7 *M* HNO_3--0.05 *M* HF can be expected to

Table 8. Corrosion of 6061-T6 Aluminum[a] in HNO_3-HF Solutions

Test Period (hr)	Temperature (°C)	Concentration (M)		Corrosion Rate (mils/month)		
		HNO_3	HF	In Vapor Phase	At Vapor-Liquid Interface	In Solution
24	Boiling	14	1	b	b	b
48				0.6	b	b
72				0.4	b	b
96				0.5	b	1.0
24	60	14	1	3.3	2.8	8.6
48				2.9	2.7	4.3
72				3.2	6.1	4.3
96				3.1	8.1	4.3
24	Boiling	14	2	2.6	<0.1	1.7
48				3.8	0.7	1.9
72				3.6	1.0	2.1
96				3.5	1.7	3.2
24	Boiling	14	3	5.0	2.1	5.4
48				4.3	2.2	3.8
72				4.6	2.5	4.3
96				4.7	2.5	4.6
24	Boiling	14	4	3.4	1.9	5.8
48				4.9	3.5	7.9
72				5.2	4.2	8.1
96				5.7	4.5	8.5
24	Boiling	15.6	2	b	b	b
48				<0.1	b	b
72				b	b	b
96				<0.1	0.3	0.6
24	~31	15.6	2	0.5	16.0	28.2
48				1.3	18.4	28.7
72				1.7	18.4	28.4
96				1.6	20.4	28.5
24	Boiling	18	1	0.9	0.4	<0.1
48				0.5	0.2	<0.1
72				0.3	0.1	b
96				0.3	0.1	<0.1
24	Boiling	18	5	0.8	0.4	<0.1
48				0.6	0.3	0.1
72				0.3	0.1	<0.1
96				0.3	0.1	<0.1
24	Boiling	20	1	0.6	<0.1	b
48				0.3	0.1	0.1
72				0.2	<0.1	b
				0.1	<0.1	<0.1
24	Boiling	20	1	0.1	<0.1	0.2
48				<0.1	<0.1	0.1
72				<0.1	<0.1	<0.1
96				<0.1	<0.1	<0.1
24[c]	Boiling	22	2	b	b	b
48				0.1	b	b
72				0.2	b	b
24	Boiling	23	1	<0.1	b	b
48				<0.1	<0.1	b
96				<0.1	b	b
144				<0.1	b	b
312				<0.1	b	b

[a]Type 6061 aluminum was received in "F" temper and tested in T6 condition (solution heat treatment followed by artificial aging).

[b]Specimens gained weight during exposure period.

[c]Solution contained 40 to 50 g of uranium and 20 g of carbon per liter.

Table 9. Corrosion (in mils/month) of Types 304L, 309SCb, and 347 Stainless Steel, and 1100 Aluminum in Boiling 22 to 23 *M* HNO_3--1 to 2 *M* HF

Test Period (hr)	Concentration (*M*)		304L			309SCb			347			1100 Al		
	HNO_3^-	HF	V[a]	I[a]	S[a]	V[a]	I[a]	S[a]	V[a]	I[a]	S[a]	V[a]	I[a]	S[a]
24[b]	22	1	0.1	1.3	4.3				0.1	1.3	4.9			
48			0.1	1.4	3.9				0.1	1.3	4.6			
24	22	2							<0.1	0.4	0.4			
48									0.2	0.5	0.5			
72									0.1	0.5	0.5			
96									0.1	0.5	0.5			
24	23	1				<0.1, <0.1	0.6, 0.6	0.2, 0.3						
48						<0.1, <0.1	0.7, 0.8	0.4, 0.4				c	c	c
96						<0.1, <0.1	0.6, 0.7	0.2, 0.3				<0.1	c	c
144						<0.1, <0.1	0.4, 0.6	0.2, 0.3						
192						<0.1, <0.1	0.3, 0.4	0.1, 0.2				c	c	c
216						<0.1, <0.1	0.3, 0.4	0.1, 0.2						
312						<0.1, <0.1	0.2, 0.3	0.1, 0.2						
96	23	1				<0.1, <0.1	1.1, 0.2	15.7, 24.7[c]				c	c	c

[a]V = in vapor phase; I = at the vapor-liquid interface; S = in solution.

[b]These solutions contained 50 g of dissolved uranium and 20 g of solid graphite per liter.

[c]Pitting occurred.

Table 10. Corrosion of Candidate Alloys in Solutions Varying in Composition from 0 to 4 M in HNO_3 and from 0.1 M to 5 M in HF

Solution Composition (M)			Exposure Temperature (°C)	Exposure Time (hr)[a]	Candidate Materials and Corrosion Rates (mils/month)[b]									
					Corronel 230		Type 309SCb Stainless, Welded	Hastelloy F, Welded[c]	EB-4358, Welded	EB-5459, Welded	Type 347 Stainless, Welded	BMI-HAPO 20, Welded	Al-6061 -T6 Unwelded	Ni-o-nel, Welded
HNO_3	HF	Other			Welded	Unwelded								
0.0	1.0	-	Boiling	48	72[d]	43.7	-	-	-	-	-	-	-	-
0.0	1.0	Cu^{2+} (trace)[e]	Boiling	72	-	24.7	-	-	-	-	-	-	-	-
0.25	4.0	-	50	100	-	-	-	-	-	-	0.9[f]	-	-	-
0.5	1.0	-	Boiling	24	-	-	103(l)[g]	17[h]	-	-	-	-	-	-
0.5	2.0	-	Boiling	24	-	-	-	26[h]	-	-	-	-	-	-
1.0	0.5	-	Boiling	24	-	-	-	4.5[h]	-	-	-	-	-	-
1.0	0.5	-	60	312	-	2.8	-	-	-	-	-	-	-	-
1.0	1.0	-	Boiling	24	-	-	8.6(l)[a]	14[h]	-	-	-	-	-	-
1.0	2.0	-	Boiling	580	-	-	-	35[h]	-	-	-	20-29[h,i]	-	>150[h]
1.0	3.0	-	Boiling (104)	4	-	Disint.	585(l)[g]	133[g]	184[g]	203[g]	-	-	-	-
				20	-	-	463(l)[g]	123[g]						
1.0	3.0	-	60	312	-	5.0(V)	-	-	-	-	-	-	-	-
2.0	0.5	-	Boiling	24	-	-	-	6.4[h]						
2.0	1.0	-	Boiling	24	-	-	-	14[h]	-	-	-	-	-	-
2.0	2.0	-	Boiling	24	-	-	-	29[h]	-	-	-	-	-	-
2.0	2.0	-	Boiling	24	-	-	-	101[h]	-	-	-	-	-	-
3.0	0.1	-	60	500	-	0.13[j]	1.3[j]	0.5[j]	-	-	-	-	-	-
3.0	1.0	-	Boiling	322	-	0.67[j]	167[j] ≥9(l)[a]	-	-	-	-	-	-	-
			60	500	-	0.63[j]	28.3[j]	6.2[j]	-	-	-	-	-	-
4.0	0.3	-	Boiling	96	3.8	4.0(l)	-	-	-	-	-	-	-	-
4.0	1.0	-	Boiling	4	-	-	-	-	-	-	-	-	9600	-
			50	4	-	-	-	-	-	-	-	-	4600	-
4.0	5.0	Boiling	Boiling	103	-	62.8	-	-	-	-	-	-	-	-

[a] Data from DP-486, ref. 8. Exposure time, 240 hr.

[b] (V) and (l) indicate that the maximum rates listed were observed on specimens exposed in vapor and at the vapor-liquid interface respectively.

[c] Vacuum-melted alloy except as indicated.

[d] Catastrophic weld attack.

[e] From inadvertent contamination. Exact concentration undetermined.

[f] Hanford data, HW-68426; ref. 10.

[g] Preferential weld attack and deep end-grain pitting.

[h] Hanford data, HW-61662, HW-68426; refs. 9, 10.

[i] Depending upon heat-treatment.

[j] UKAEA data. No information on welding. Presumably normal industrial alloy.

Table 11. Corrosion of Candidate Alloys in Solutions Varying in Composition from 6 *M* to 13 *M* in HNO_3 and from 0.05 to 5 *M* in HF

Composition of Solution (*M*)			Exposure		Candidate Materials and Corrosion Rates (mils/month)									
					Corronel 230		Type 309SCb Stainless,	Hastelloy F,	EB-4358,	EB-5459,	Haynes-25,	Haynes-150,	Ti-45A,	Al-6061 -T6
HNO_3	HF	Other	Temperature (°C)	Time (hr)[a]	Welded[b]	Unwelded	Welded	Welded	Welded	Welded	Welded	Unwelded	Welded	Unwelded
6.0	0.1	-	Boiling	96	-	-	-	-	-	-	8.9	5.6	-	-
6.0	0.5	-	Boiling	72	-	-	-	-	-	-	49.4	24.2	-	-
6.0	1.0	-	Boiling	322	-	Disint.	-	-	-	-	-	-	-	-
7.0	0.05	-	Boiling	72	1.7	-	14.8	31.7	-	-	6.2	-	-	-
				192	1.6	-	-	-	-	-	6.7	-	-	-
7.0	0.05	0.24 UO_2^{2+}, 0.06 rare earths	Boiling	1008	0.4	-	0.5	0.4	-	-	0.6	-	-	-
9.0	0.4	-	Boiling	7	-	-	-	45	-	-	-	-	-	-
9.0	1.0	-	Boiling	322	-	28.9	Disint.	-	-	-	-	-	-	-
10.0	0.5	-	Boiling (116)	8	-	-	224[c,d]	260[c,d]	482[c,d]	500[c,d]	-	-	-	-
				36	-	-	212[c,d]	-	-	-	-	-	-	-
				96	-	59.9[c]	-	-	-	-	-	-	-	-
10.0	0.5	-	60	312	-	2.83	-	-	-	-	-	-	-	-
10.0	0.5	0.75 $Al(NO_3)_3$	Boiling	408	-	0.78(V)[c]	-	-	-	-	-	-	0.28	-
10.0	1.0	-	Boiling	4	-	-	-	-	-	-	-	-	-	1100
				24	100	56.1(I)	113	-	-	-	-	-	-	-
				103	113	60.3(I)	93[e]	-	-	-	-	-	-	-
10.0	2.0	-	Boiling	24	-	-	-	320[f]	-	-	-	-	-	-
10.0	5.0	-	Boiling	89	-	173	-	-	-	-	-	-	-	-
12.0	0.1	-	Boiling	500	-	12[f]	-	-	-	-	-	-	-	-
12.0	1.0	-	Boiling	24	-	-	-	-	-	-	-	-	-	105(V)
		-	-	300	-	79.9[f]	367[f]	-	-	-	-	-	-	-
12.0	1.0	-	60	500	-	6.3[f]	65.7[f]	58.3[b]	-	-	-	-	-	-
13.0	0.1	-	Boiling	72	-	-	-	-	-	-	72.3	46.8	-	-
13.0	0.25	-	Boiling	4	-	-	-	194[g]	-	-	-	-	-	-
13.0	0.5	-	Boiling	48	-	-	-	-	-	-	250.4	168.1	-	-
13.0	1.0	-	Boiling	-	-	-	-	-	-	-	-	-	85(V)[c]	-

[a]Vacuum-melted alloy.

[b]Welded according to supplier's directions.

[c]Acid etch.

[d]Severe acid etch plus preferential weld attack (knife-line attack on 309SCb).

[e]Data from DP-486 (ref. 8). Exposure time, 240 hr.

[f]UKAEA data.

[g]Hanford data (HW-61662, ref. 9).

Table 12. Corrosion of Aluminum, Al-6061-T6,[a] and Other Materials in Solutions Varying in Composition from 13 *M* to 23 *M* in HNO_3 and from 0 to 2 *M* in HF

Composition of Solution						Corrosion Rate (mils/month)[b]					
HNO_3 (*M*)	HF (*M*)	U(as UO_2) (g/liter)	Graphite (g/liter)	Exposure Temperature (°C)	Exposure Time (hr)	Al-6061 T6,[a] Unwelded	Al-1100, As-Rolled	Type 309SCb Stainless, Welded	Type 347 Stainless, Welded	Corronel 230, Unwelded	Titanium 45A, Welded
13	1.0	-	-	Boiling	24	85(V)[c]	-	-	-	-	-
14	1.0	-	-	~ 25	96	59.1	-	-	-	-	-
		-	-	~ 50	4	-	4600				
		-	-	~ 60	96	8.1(I)	-	-	-	-	-
		-	-	Boiling (106)	96	1.0	-	-	-	-	-
		-	-	-	192	85(V)[c]	-	-	-	-	-
14	2.0	-	-	Boiling	96	3.5(V)	-	-	-	-	-
14	3.0	-	-	Boiling	96	4.7(V)	-	-	-	-	-
14	4.0	-	-	Boiling	96	8.5	-	-	-	-	-
14	5.0	-	-	Boiling	72	4.4	-	-	-	-	-
14	5.0	-	-	~ 25	48	313	-	-	-	-	-
15.6	1.0	-	-	Boiling	4	d	-	-	-	-	-
15.6	2.0	-	-	Boiling	72	0.6	-	-	-	-	-
15.6	2.0	-	-	~ 31	96	28.5	-	-	-	-	-
18	1.0	-	-	Boiling	96	0.3(V)	-	-	-	-	-
18	5.0	-	-	Boiling	96	0.3(V)	-	-	-	-	-
20	0	-	-	Boiling	24	-	127	-	-	1.8(I)	0.18(I)
		-	-	-	168	-	-	-	-	7.01(V)[e]	0.07(I)
		-	-	-	720	-	-	-	-	5.5(V)[e]	-
20	0.023[f]	-	-	Boiling	19	-	134	-	-	-	-
20	1.0	-	-	Boiling	96	0.1(V)	-	-	-	-	-
20	1.0	50	20	Boiling	72	< 0.1	-	-	-	-	-
22	1.0	40	20	Boiling	48	-	-	-	4.6[g]	-	-
22	2.0	-	-	Boiling	96	0.5	-	-	-	-	-
22	2.0	50	20	Boiling	72	0.5	-	-	0.5	-	-
23	1.0	-	-	Boiling	192	0.1(V)	d	0.4(I)	-	-	-
23	1.0	50	20	Boiling	96	< 0.1(V)	d	24.7[h]	-	-	-

[a] T6 condition.

[b] Rates listed are maximum observed and are for specimens exposed in solution phase unless interface (I) or vapor (V) is indicated.

[c] Rate < 0.1 mil/month at interface and in solution.

[d] Denotes weight gain.

[e] Intergranular attack.

[f] Nominal. Concentration was reported as 300 ppm.

[g] Comparable rate for Type 304L was 3.9.

[h] Pitting attack.

increase somewhat slowly as the HNO_3 concentration increases, and more rapidly as the concentration of free fluoride increases. The presence of low concentrations of dissolution products will decrease the rate of attack. Consequently, a maximum corrosion rate of 1.6 mil/month would be expected only during the initial dissolution period. The rate would probably decrease to 1.0 mil/month or less after a significant amount of dissolution products appear in the solution. If the free fluoride concentration can be reduced to less than about 0.02 *M*, type 309SCb stainless steel may be usable, although Corronel would still be preferable. Weldments will doubtless suffer the maximum attack for both alloys.*

Titanium is a possible candidate for use in 12 to 15 *M* HNO_3 solutions that have free fluoride concentrations up to about 0.003 *M*. Corrosion rates were about 1.8 mils/month in 15 *M* HNO_3--0.003 *M* HF (Fig. 9) in these laboratory tests and should be lower in an operating dissolver owing to the presence of dissolution products. Little or no local attack should occur at this level of fluoride. However, it must be determined whether a fluoride concentration this low is sufficient to dissolve PuO_2 satisfactorily. There is a possibility that titanium might resist higher concentrations of fluoride in stronger (16 to 20 *M*) HNO_3, but data are lacking in this concentration range.**

A third possibility would be dissolution of the fuel in an aluminum dissolver*** using a dissolvent that was 22 to 23 *M* in HNO_3 and 1 to 2 *M* in HF, although the use of such concentrated nitric acid solutions may be undesirable. Results of corrosion tests are encouraging, but data under actual dissolution conditions are needed to ensure that the passivity persists throughout the entire dissolution cycle. Results of tests

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*Type 309SCb (columbium-stabilized type 309) stainless steel is no longer routinely produced. Type 309S, the extra low-carbon variety of 309, is available and is presumably free from much of the difficulty from carbide precipitation near weldments, which is characteristic of the regular grades of austenitic stainless steels. There is, in fact, relatively little difference in the resistance of types 304L, 347, and 309SCb stainless steels to HNO_3-HF solutions.[4,5]

**Titanium has been known to react explosively with red fuming nitric acid (i.e., >20 *M* HNO_3) but is resistant to lower concentrations.

***Mercury should be absent in such a dissolution process.

in which the stainless steels were exposed in these concentrated solutions indicate that a dissolver fabricated of stainless steel could possibly be used in the above range; however, more corrosion tests are required before a final recommendation can be made.

The present state of knowledge indicates that the combination of a dissolver fabricated of Corronel 230 and a dissolvent of 7 to 8 *M* HNO_3 having a free fluoride concentration no higher than 0.05 *M* is the most effective for the processing of LMFBR fuels.

4. ACKNOWLEDGEMENT

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