DP - 429

METALLURGY AND CERAMICS
(TID-4500, 15th Ed.)

CORROSION OF STAINLESS STEEL IN THOREX PROCESS SOLUTIONS

by

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December 1959

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

Printed for
The United States Atomic Energy Commission
Contract AT(07-2)-1

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ABSTRACT

The corrosion of 304L and 309SCb stainless steel was studied in HF-HNO_3 solutions proposed for the Thorex process. Except for the dissolving and waste evaporation steps in the Thorex process, corrosion of 304L and 309SCb is not expected to exceed that experienced in the Purex process. To minimize the high initial corrosion rate of 309SCb in the boiling HF-HNO_3 dissolving solution, a heel of thorium should be maintained in the dissolver. The corrosion rate of 304L in the low activity waste evaporator can be reduced by adding one mole of aluminum per mole of fluoride to the evaporator feed.

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INTRODUCTION

In the Thorex process for the separation of U^{233} from irradiated thorium, the dissolution of thorium in HNO_3 requires the addition of HF to catalyze the reaction and to prevent formation of a protective film on the thorium. The addition of HF to the process solutions introduces a corrosion problem when these solutions are handled in stainless steel equipment. The objective of the work described in this report was to evaluate the seriousness of the corrosion problem that would arise if the Thorex process were operated in some existing stainless steel equipment in the Separations Area of the Savannah River Plant. The results of laboratory corrosion tests are reported here; corrosion data obtained during experimental dissolutions are given in DP-399.

SUMMARY

Except for the dissolving and waste evaporation steps in the Thorex process, corrosion of the stainless steel equipment in the Separations Area is not expected to exceed that experienced with the Purex process for separating plutonium from irradiated uranium.

The dissolver solutions, 10M HNO_3 and from 0.05 to 0.1M HF, corrode wrought 309SCb at a rate of from 205 to 365 mpy (mils per year). A corrosion rate of approximately 25 mpy is considered to be the maximum allowable rate for satisfactory service life. Welds of 309SCb corrode up to a rate 20 times higher than the wrought metal. As thorium dissolves, the corrosion rate of 309SCb decreases until at a concentration of 1.0M $Th(NO_3)_4$ the corrosion rate is less than 10 mpy. To minimize the severe initial corrosion in the HF-HNO_3 dissolver solution, a heel of thorium should be maintained in the dissolver.

In the evaporation cycle the corrosion rate of 304L exceeds 110 mpy in simulated low activity waste solutions after concentration. The addition of aluminum to complex the fluoride in a molar ratio of 1:1 reduced the corrosion rate of 304L to 22 mpy. No preferential weld corrosion occurs when 304L is welded with 308L filler rod. However, 347 welds corrode preferentially.

DISCUSSION

PROCEDURE

Conventional gravimetric corrosion test procedures were used. Generally, tests were conducted for five 48-hour periods. At temperatures below the boiling point, tests were run in "Saran" pipe sections or polyethylene containers in constant temperature water baths. "Teflon"-lined spool pieces were used for tests at boiling point. All coupons were supported on "Teflon" sample holders.

RESULTS

RESISTANCE OF VARIOUS ALLOYS TO THOREX SOLUTIONS

Tests at 50°C

The relative corrosion resistance of a variety of alloys was evaluated in simulated Thorex solutions to determine whether existing plant equipment was adequate for handling HF-HNO_3 solutions. For screening tests a solution of 10.3M HNO_3 and 0.33M HF at 50°C was used. Additions of $Th(NO_3)_4$ were made to simulate the solution after part of the thorium had been dissolved. Also, the effect of aluminum in the HF-HNO_3 solution was studied. Results are reported in the following table.

Corrosion of Alloys
in Simulated Thorex Solutions at 50°C

Solution Composition, M					Corrosion Rate, mpy							
HF	HNO_3	$Th(NO_3)_4$	$Al(NO_3)_3$	AlF_3	304L	309SCb	310	329	347	430	446	Carp. 20
0.33	10.3	-	-	-	93	31	23	110	264	230	139	71
0.33	10.3	0.012	-	-	66	30	22	106	236	145	61	74
0.33	10.3	0.122	-	-	3.5	2.7	2.0	1.8	3.8	4.8	4.1	3.3
0.33	10.3	-	0.176	-	9.0	6.0	5.0	7.0	19	17	6.0	9.0
-	10.3	-	-	0.33	8.0	6.0	7.0	8.0	20	19	7.0	9.0

Of the wrought alloys tested, 310 had the lowest corrosion rate in the HF-HNO_3 solutions. However, the corrosion rate of 309SCb was only slightly higher than 310, so that replacement of the existing 309SCb equipment would not be justified. Type 304L and Carpenter 20 were next in corrosion resistance.

Thorium complexed the fluoride and reduced the corrosion rate of stainless steel. At 50°C the addition of 0.122M $Th(NO_3)_4$ lowered the corrosion rate of all the alloys to less than 5 mpy in the 10.3M HNO_3 and 0.33M HF solution. From the corrosion data, it appeared that each mole of thorium was able to complex at least 4 moles of fluoride at 50°C.

Aluminum also complexed the fluoride and reduced the corrosion rate of stainless steel in HF-HNO_3 solutions. Addition of 0.176M $Al(NO_3)_3$ lowered the corrosion rate of all the alloys to less than 20 mpy. In 10.3M HNO_3 solutions containing 0.33M AlF_3 the corrosion rates of the alloys were approximately the same as in the 10.3M HNO_3 solutions containing 0.33M HF and 0.176M $Al(NO_3)_3$. From this corrosion data it appeared that each mole of aluminum was able to complex about 3 moles of fluoride in HF-HNO_3 solutions at 50°C.

Tests at Boiling

Dissolving experiments by Separations showed that a solution containing 10M HNO_3 and between 0.05 and 0.1M HF gave a reasonable time cycle for the Thorex process.[1] Therefore, corrosion tests of the various alloys were conducted in the following boiling HF-HNO_3 solutions that were designed to simulate process solutions at various stages.

Corrosion of Alloys
in Boiling Simulated Thorex Solutions

Solution Composition, M					Corrosion Rate, mpy							
HF	HNO_3	$Th(NO_3)_4$	$Al(NO_3)_3$	$NaNO_3$	304L	309SCb	309	310	329	347	Carp. 20	Tantalum
0.075	10.3	-	-	-	390	290	150	233	452	710	390	22
0.05	10.3	-	-	-	205	143	105	-	-	450	-	-
0.075	10.3	0.09	-	-	61	37	-	30	68	138	49	-
0.075	0.5	2.0	-	-	1.5	1.0	-	-	-	-	-	-
0.009	5.6	-	-	1.47	27	13	-	13	22	38	20	-
0.07	-	-	0.6	-	Nil	Nil	-	Nil	Nil	Nil	Nil	-

Although tantalum, 309, and 310 corroded at lower rates than 309SCb or 304L, their corrosion resistance was not superior enough to warrant replacing available 309SCb and 304L process equipment.

The addition of 0.09M $Th(NO_3)_4$ to boiling 10.3M HNO_3 and 0.075M HF solutions reduced the corrosion rate of 309SCb from 290 to 37 mpy and of 304L from 390 to 61 mpy.

In a boiling 0.075M HF, 0.5M HNO_3, and 2.0M $Th(NO_3)_4$ solution, which represented the solution after completion of the dissolving cycle, the corrosion rates of both 304L and 309SCb were less than 2 mpy.

An estimated low activity waste solution containing 0.009M HF, 5.6M HNO_3, and 1.47M $NaNO_3$ corroded 304L at 27 mpy and 309SCb at 13 mpy.

The waste from the first-cycle solvent extraction contactors was estimated as 0.07M HF and 0.6M $Al(NO_3)_3$. The corrosion rate of stainless steel in this solution was negligible.

CORROSION OF 304L AND 309SCb

To define further the corrosion behavior of 304L and 309SCb, a series of corrosion studies at varying HF, HNO_3, and $Th(NO_3)_4$ concentrations were conducted at 60°C and the boiling point.

Tests at 60°C

Effect of HF

The effect of HF on the corrosion of 304L and 309SCb was studied in 10M HNO_3 at 60°C. Results were as follows:

Effect of HF on the Corrosion of Stainless Steel in 10M HNO_3 at 60°C

HF, M	Corrosion Rate, mpy 304L	Corrosion Rate, mpy 309SCb
0.025	12	10
0.05	25	27
0.075	47	44
0.1	62	54

The corrosion rate was a linear function of the HF concentration for both 304L and 309SCb.

Effect of $Th(NO_3)_4$

The effect of $Th(NO_3)_4$ concentration on the corrosion rate of 304L and 309SCb in $HF-HNO_3$ solutions is reported in the following table.

Corrosion Rates of Stainless Steel in 10M HNO_3 Solutions Containing HF and $Th(NO_3)_4$ at 60°C

	Corrosion Rate, mpy			
	304L		309SCb	
$Th(NO_3)_4$, M	0.05M HF	0.1M HF	0.05M HF	0.1M HF
0	25	62	27	54
0.003	12	45	12	42
0.01	11	31	8.7	20
0.02	6.0	14	4.1	9.7
0.03	-	6.1	3.4	4.0
0.3	1.2	1.9	1.0	1.3
0.9	0.4	1.0	0.2	0.6

The corrosion rates of both 304L and 309SCb decreased with an increase in $Th(NO_3)_4$ concentration. In the 60°C solutions each mole of thorium complexed about 4 moles of fluoride, reducing the corrosion rate to less than 10 mpy.

Weld Corrosion Resistance

Welded samples of both 304L and 309SCb corroded at much higher rates than wrought samples as reported in the following table. Samples of 304L were electric-arc welded with 347 filler rod, and 309SCb was electric-arc welded with 309SCb filler rod.

Corrosion of Welded Stainless Steel in 10M HNO_3 Solutions Containing HF and $Th(NO_3)_4$ at 61°C

Solution Composition, M			Corrosion Rate, mpy	
$Th(NO_3)_4$	HF	HNO_3	304L-AW	309SCb-AW
0.003	0.05	10.0	32	44
0.03	0.05	10.0	6.3	4.7
0.3	0.05	10.0	1.4	1.0
0.003	0.1	10.0	80	115
0.03	0.1	10.0	8	5.4
0.3	0.1	10.0	2.2	0.6

The higher corrosion rates of the welded samples were due to preferential corrosion of the 309SCb and 347 welds.

Samples of all weld metals were tested and the results were as follows:

Corrosion of All-Weld-Metal Samples at 61°C in 10M HNO_3 and 0.05M HF Solutions Containing $Th(NO_3)_4$

	Corrosion Rate, mpy		
	$Th(NO_3)_4$, M		
Type	0.003	0.03	0.3
308L	55	15	1.6
308	150	12	1.2
309SCb	260	8	0.7
347	270	13	1.3

The resistance of 308L weld metal was superior, as has been noted in other work.[2,3] Twice the $Th(NO_3)_4$ concentration needed for wrought metal was required to reduce the corrosion rate of the weld metal to about 10 mpy.

Tests at Boiling

304L in $HF-HNO_3-Th(NO_3)_4$

The corrosion rate of 304L increased with either an increase in HF or HNO_3 concentration and decreased with an increase in $Th(NO_3)_4$ concentration. The corrosion data are summarized in the following table. The results are shown graphically in Figure 1 for 0.05M HF and in Figure 2 for 0.1M HF solutions. In each figure, isocorrosion curves show the combinations of HNO_3 and $Th(NO_3)_4$ required to obtain a specified corrosion rate with the HF concentration held constant.

Corrosion Rates of 304L
in Boiling $HF-HNO_3-Th(NO_3)_4$ Solutions

		Corrosion Rate, mpy						
		HNO_3, M						
$Th(NO_3)_4$, M	HF, M	10	8	6	4	2	1	0.5
0	0.05	344	226	151	114	104	85	63
0.003	0.05	206(430)*	178	-	96	54	-	45
0.03	0.05	66(139)	38	-	9.8	2.6	-	0.4
0.1	0.05	33	17	-	3.7	1.4	-	0.3
0.2	0.05	20	8.4	-	-	-	-	-
0.3	0.05	14(22)	6.0	-	0.9	-	-	-
0.6	0.05	-	4.2	-	1.1	0.5	-	-
0.8	0.05	7.4	-	-	-	-	-	-
1.0	0.05	-	4.0		1.5	0.8	-	-
1.5	0.05	-	-		1.7	0.7	-	0.2
0.03	0.075	96	-	-	-	-	-	-
0.3	0.075	15	-	-	-	-	-	-
0.8	0.075	5.8	-	-	-	-	-	-
0	0.1	591	421	-	213	201	-	103
0.003	0.1	575	368	-	168	-	-	-
0.02	0.1	-	-	-	-	-	-	29
0.03	0.1	183	80	-	24	5.1	-	6.3
0.1	0.1	64	34	-	6.2	1.9	-	0.4
0.2	0.1	-	-	-	-	-	-	0.2
0.3	0.1	33	15	-	3.4	1.6	-	0.2
0.6	0.1	19	10	-	4.0	1.6	-	-
0.8	0.1	13	-	-	-	-	-	-
1.0	0.1	12	7.6	-	3.5	1.8	-	0.1
1.5	0.1	-	-	-	-	-	-	0.2

* ( ) Designates samples arc welded with 347 filler rod.

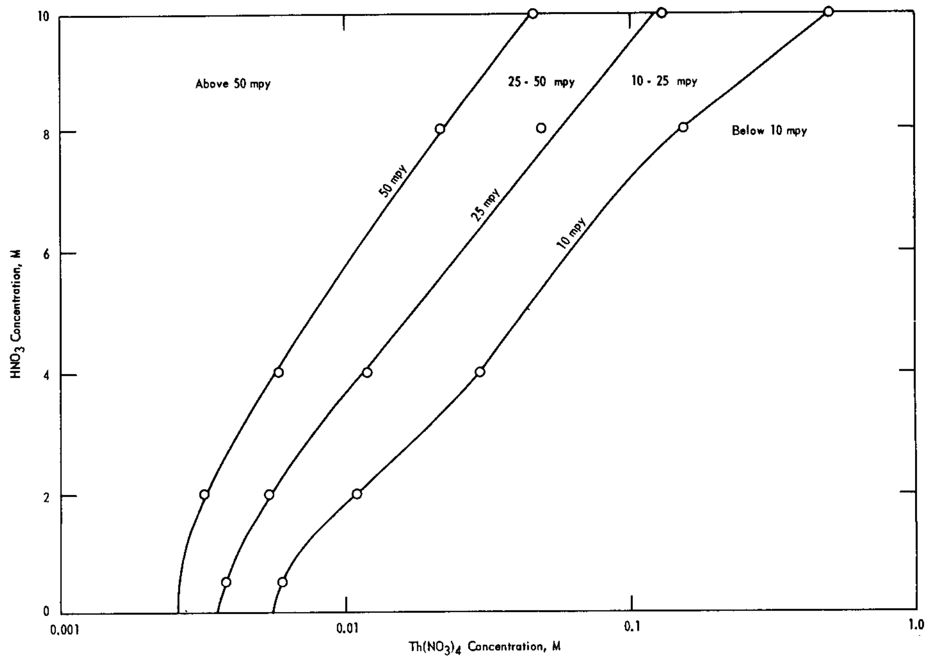

FIGURE 1 – CORROSION OF 304L IN BOILING 0.05M HF SOLUTIONS CONTAINING HNO_3 AND $Th(NO_3)_4$

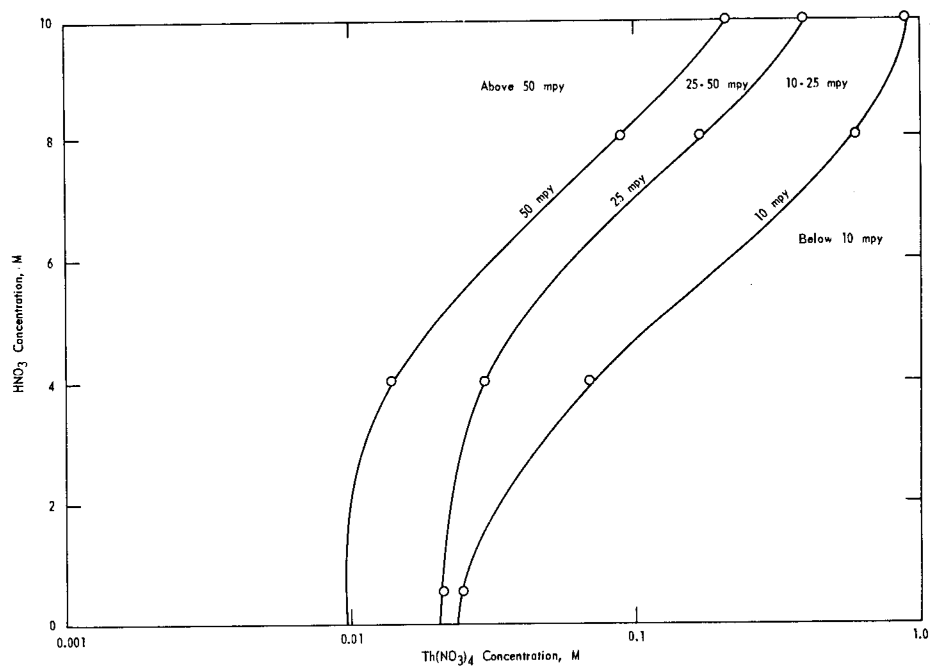

FIGURE 2 – CORROSION OF 304L IN BOILING 0.1M HF SOLUTIONS CONTAINING HNO_3 AND $Th(NO_3)_4$

During a dissolving cycle without a metal heel, the corrosion would start at a high rate, corresponding to the upper left corner of the Figure 1. As dissolving proceeds, the HNO_3 concentration would decrease and the $Th(NO_3)_4$ concentration would increase, so that the corrosion rate would follow a band across the figure to the lower right corner. With a minimum $Th(NO_3)_4$ concentration of 0.13M, the corrosion rate of 304L was below 25 mpy in 0.05M HF and 10M HNO_3. In 0.1M HF and 10M HNO_3 solutions about 0.4M $Th(NO_3)_4$ was required to reduce the corrosion rate of 304L to 25 mpy.

309SCb in HF-HNO_3-$Th(NO_3)_4$

The corrosion resistance of 309SCb was superior to 304L in boiling HF-HNO_3-$Th(NO_3)_4$ solutions. The following table summarizes the corrosion data for 309SCb. As for 304L, the corrosion rate of 309SCb increased with either an increase in HF or HNO_3 concentration and decreased with an increase in $Th(NO_3)_4$ concentration.

Corrosion Rates of 309SCb
in Boiling HF-HNO_3-$Th(NO_3)_4$ Solutions

		Corrosion Rate, mpy						
		HNO_3, M						
HF, M	$Th(NO_3)_4$, M	10	8	6	4	2	1	0.5
0.05	0	206	117	52	23	12	8.0	6.0
0.05	0.003	140(365)*	86	-	20	7.2	-	4.3
0.05	0.03	36(170)	22	-	5.0	1.9	-	0.1
0.05	0.1	18	11	-	2.9	0.5	-	0.2
0.05	0.2	15	7.1	-	-	-	-	-
0.05	0.3	12(25)	6.6	-	0.6	-	-	-
0.05	0.6	-	0.5	-	0.4	0.3	-	-
0.05	0.8	4.1	-	-	-	-	-	-
0.05	1.0	-	4.2	-	0.5	1.2	-	-
0.05	1.5	-	-	-	0.8	0.4	-	0.1
0.075	0.03	57	29	-	-	-	-	-
0.075	0.3	12	-	-	-	-	-	-
0.075	0.6	-	4.2	-	-	-	-	-
0.075	0.8	2.7	-	-	-	-	-	-
0.1	0	364	186	-	51	23	-	12
0.1	0.003	363	164	-	39	-	-	-
0.1	0.02	-	-	-	-	-	-	5.0
0.1	0.03	80	39	-	7.2	2.8	-	1.0
0.1	0.1	35	19	-	4.7	1.3	-	0.2
0.1	0.2	-	-	-	-	0.4	-	0.1
0.1	0.3	23	10	-	3.1	0.5	-	0.1
0.1	0.6	15	8.0	-	2.6	0.2	-	-
0.1	0.8	9.2	-	-	-	-	-	-
0.1	1.0	10	5.6	-	1.8	0.5	-	-
0.1	1.5	-	-	-	-	-	-	0.1

* ( ) Designates samples arc welded with 309SCb filler rod.

Figures 3 and 4 show isocorrosion curves for the corrosion rate of 309SCb as a function of HNO_3 and $Th(NO_3)_4$ concentration for 0.05 and 0.1M HF solutions, respectively. To minimize corrosion of 309SCb to 25 mpy in 0.05M HF and 10M HNO_3 solutions, 0.064M $Th(NO_3)_4$ was required. In 0.1M HF and 10M HNO_3 solutions a 0.19M $Th(NO_3)_4$ concentration was required to reduce the corrosion rate of 309SCb to 25 mpy.

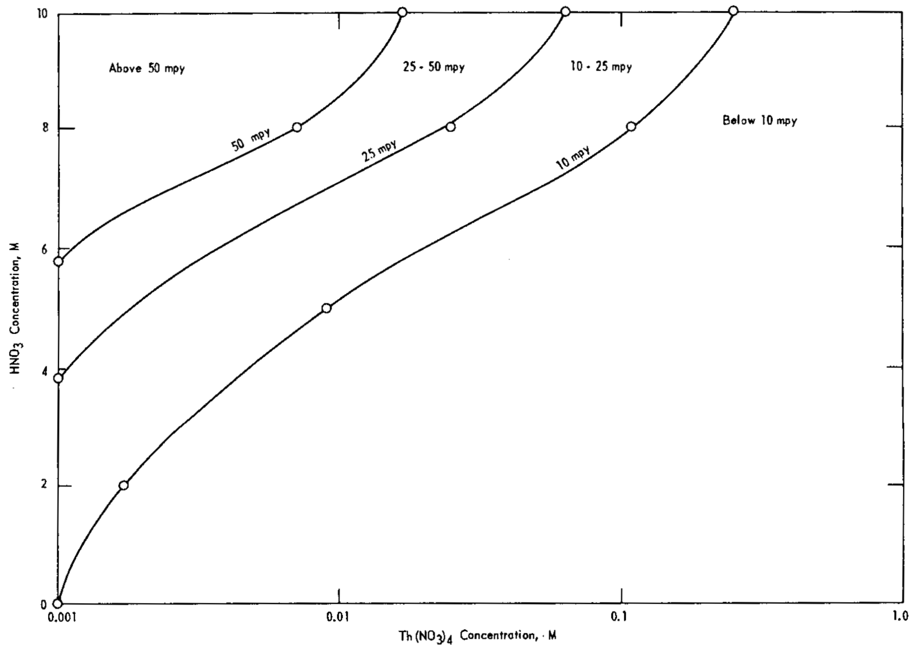

FIGURE 3 – CORROSION OF 309 SCb IN BOILING 0.05M HF SOLUTIONS CONTAINING HNO_3 AND $Th(NO_3)_4$

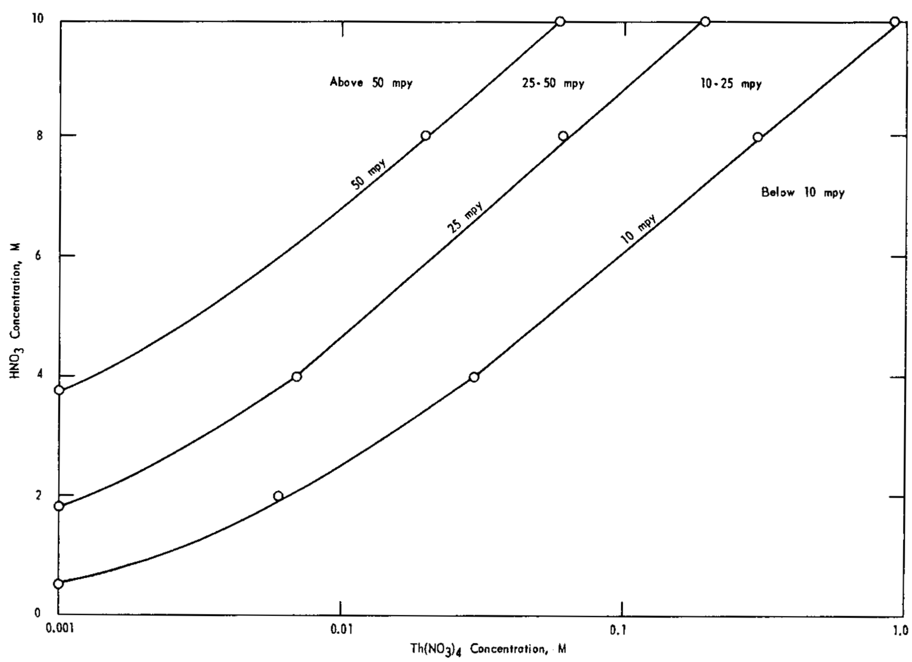

FIGURE 4 – CORROSION OF 309 SCb IN BOILING 0.1M HF SOLUTIONS CONTAINING HNO_3 AND $Th(NO_3)_4$

Although thorium reduced the corrosion rate of 309SCb in boiling HF-HNO_3 solutions, a much higher thorium-to-fluoride ratio was required to decrease the corrosion rate to an acceptable value at the boiling point than was required at 60°C. In 60°C solutions, each mole of thorium was able to complex 4 moles of fluoride. However, in boiling 10M HNO_3 at least 2 moles of thorium per mole of fluoride were required to reduce the corrosion rate of 309SCb below 25 mpy.

Waste Solutions

The corrosion of 304L and 309SCb during simulated concentration of the low activity waste solutions is reported in the following table.

Corrosion of Stainless Steel
in Boiling Low Activity Waste Solutions

Solution Composition, M				Corrosion Rate, mpy	
HNO_3	HF	Na_2SO_4	$NaNO_3$	304L	309SCb
1.26	0.006	0.004	0.015	4	0.3
3.2	0.02	0.016	0.51	19	10
5.0	0.04	0.024	1.0	68	26
6.8	0.06	0.04	1.5	112	56

As the waste is concentrated, the corrosion rate of the evaporator increases. Although rates were determined for both 304L and 309SCb, the present waste evaporators are constructed of 304L.

Effect of Aluminum - To reduce the corrosion rate during evaporation, the effect of adding $Al(NO_3)_3$ to the concentrated waste solution was studied.

Effect of Aluminum on Corrosion of Stainless steel
in a Boiling Concentrated Low Activity Waste Solution
6.8M HNO_3, 0.06M HF, 0.04M Na_2SO_4, 1.5M $NaNO_3$

	Corrosion Rate, mpy	
$Al(NO_3)_3$, M	304L	309SCb
0	112	56
0.02	69	30
0.04	30	16
0.06	22	10
0.12	6	6

A ratio of 1 mole of $Al(NO_3)_3$ per mole of fluoride was required to reduce the corrosion rate of 304L to 22 mpy in the concentrated waste solution. About 0.03M $Al(NO_3)_3$, or half the amount required for 304L, gave a 309SCb corrosion rate of about 23 mpy.

Effect of Cr^6 - Corrosion of stainless steel in Thorex solutions introduces Cr^6 into the process solutions. Since Cr^6 is known to accelerate the corrosion of stainless steel,[4] additions of CrO_3 were made to simulated Thorex solutions to determine the resulting corrosion effects.

Effect of Cr^6 in Boiling Thorex Solutions

Solution Composition, M					Corrosion Rate, mpy	
HNO_3	Na_2SO_4	$NaNO_3$	CrO_3	$Th(NO_3)_4$	304L	309SCb
3.06	-	-	0.1	2.0	168	396
3.06	-	-	0.3	2.0	350	1100
6.8	0.2	0.63	-	-	9	2.8
6.8	0.2	0.63	0.1	-	600	542
6.8	0.2	0.63	0.3	-	1300	1530

Severe corrosion of both 304L and 309SCb occurred with 0.1M Cr^6 additions to the process solutions. Generally, the resistance of 309SCb was inferior to that of 304L in the solutions containing Cr^6.

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