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Richland, Washington
September 16, 1954

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INHIBITION OF FLUORIDE-CATALYZED CORROSION OF STAINLESS STEELS

INTRODUCTION:

All of the flowsheets currently being considered for the Thorex process call for the presence of from 0.05 to 0.075 M fluoride during the dissolution step. Considerable concern is being evidenced over the possible effects of fluoride on both plant equipment corrosion and solvent extraction operation in the Thorex process. Accordingly, a study of the dissolution of thorium and thoria was made in an effort to either eliminate the need for fluoride or to discover a way to use an amount small enough to be harmless to the equipment and process. This study revealed no alternate catalyst or dissolving media capable of dissolving thorium and/or thoria. It also established the fact that the concentration of fluoride cannot be reduced appreciably if an acceptable dissolution rate is to be maintained (1).

Since fluoride apparently will be present in the Thorex process, a series of experiments has been conducted to demonstrate the magnitude of its corrosive behavior and to test a number of substances as possible corrosion inhibitors.

SUMMARY AND CONCLUSIONS:

Corrosion tests of type 309 SCb, 347, and 304 L stainless steel coupons demonstrated the accelerated corrosion caused by the presence of fluoride ions in solution. The effects of several metal cations upon this fluoride-catalyzed corrosion were also determined. The following conclusions were drawn from these tests:

1. The presence of 0.1 M HF in boiling nitric acid solutions causes very rapid corrosion of stainless steels (300 - 900 mils/year), However, the presence of 1 M Th in solution will reduce this corrosion rate to an acceptable level.

2. Although several metal cations will inhibit fluoride corrosion, zirconium produces the best inhibition of those tested, reducing the corrosion rate approximately 25-fold.

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3. Titanium and vanadium oxides were too insoluble to give the needed concentrations of cations in solution to inhibit corrosion.

4. Vapor phase corrosion of type 309 SCb stainless steel is approximately equal to the liquid phase corrosion of the same steel.

5. Ammonium silicofluoride apparently hydrolyzes completely in boiling nitric acid to give six moles of active fluoride ion per mole of ammonium silicofluoride and is equally corrosive.

6. Further corrosion work is needed in equipment which could simulate more closely the Thorex dissolving cycle and a nitric acid recovery system.

EXPERIMENTAL:

1. Procedure

The stainless steel coupons used in this study were furnished by the Corrosion group of the Metallurgy Unit. All of the coupons were given a standard, desensitizing pretreatment consisting of a twenty-minute immersion in 24% HNO_3 at 60°C. The apparatus used consisted of a one-liter stainless steel pot fitted with a stainless steel reflux condenser. Provision was made for suspending samples in the vapor phase as well as immersing them in the boiling solution. The reproducibility of the corrosion data obtained using this apparatus was established by preliminary runs made in duplicate. Therefore, the numbers reported in this document were obtained from single determinations, in order to gather as much information as possible from the limited number of coupons available.

The corrosion rates were all determined at boiling temperatures (100-110°C); they were calculated from careful measurements of the initial dimensions and of the weight losses of the individual coupons. Stainless steels 347, 304L, and 309 SCb were tested in the boiling liquid phase. The best of these, 309 SCb, was also tested in the vapor phase.

2. Results:

Since thorium forms a tight complex with fluoride, the need for a corrosion inhibitor is expected to be greatest in the pots where thorium is absent, i.e., the nitric acid recovery system or waste concentrators. Therefore, most of the determinations were made in nitric acid-hydrofluoric acid solutions in the absence of thorium. In order to accelerate the corrosion rate and thereby reduce the time required for each individual experiment, 13 M HNO_3 - 0.1 M HF solutions were used rather than the lower concentrations which would actually occur in the process. The results of these experiments are recorded in Part A of Table I. Three corrosion tests on 347 stainless steel were made in 6.5 M HNO_3 and are recorded in Part C of Table I. These tests indicate corrosion to be less than half that at the higher HNO_3-HF concentrations. Although all of the polyvalent ions tests showed some inhibiting effect upon corrosion, zirconium appears to be by far the best inhibitor. When 0.2 M zirconium was used as inhibitor, the corrosion rate in 13 M HNO_3 - 0.1 M HF was lowered by factors ranging from 19 to 33 for the different steels tested. This experimentally observed fact is in agreement with the theory that the corrosion inhibition is the result of a cation-fluoride complex. Complexing constants

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reported by several investigators (2), (3), (4) indicate that, of the cations tested, zirconium forms the tightest complex with fluoride (complexing constants reported for room temperature in dilute acid, however). Vanadium and titanium, which might conceivably have given better results from a consideration of their charge and ionic radius, were too insoluble to produce the necessary concentrations of cation in solution.

One experiment was made to ascertain whether or not the corrosive effect of fluoride is independent of the form in which it is added. Previous results (1) indicated that ammonium silicofluoride will accelerate thorium dissolution at the same rate as six times its molar concentration of hydrofluoric acid. From the results in Part A of Table I it is apparent that 0.0167 M NH_4SiF_6 acts very nearly the same as 0.1 M HF, bearing out the conclusion that ammonium silicofluoride is completely hydrolyzed in boiling nitric acid.

In order to test the supposition that a high thorium concentration would adequately protect stainless steel equipment from fluoride corrosion, the two experiments recorded in Part B of Table I were conducted. The concentrations of 1.0 M Th and 6.0 M HNO_3 were picked to simulate an intermediate point in the dissolution scheme. Since little increase in thorium dissolution rate results from increasing the hydrofluoric acid concentration above 0.1 M, this concentration was selected as the probable maximum concentration in the dissolver pot. The corrosion data obtained from these runs indicate that 1.0 M thorium was a very effective corrosion inhibitor under the conditions used. No additional improvement resulted when 0.1 M Zr was added in addition to the thorium. In fact, corrosion appeared slightly higher for the run containing zirconium (these numbers probably fall within the limits of experimental error).

The presence of fluoride apparently causes a general pitting attack of stainless steel surfaces. Figure 1 shows both this pitting attack and the inhibiting effect of zirconium ions in solution. Figure 1-A shows the general uniform attack of nitric acid alone. Figure 1-B shows the general pitting attack caused by fluoride ions. Figure 1-C demonstrates the corrosion inhibition caused by the presence of 0.1 M zirconium. These photomicrographs were taken on a dark field at 100x magnification.

DISCUSSION:

Although the corrosion rates of the stainless steel samples tested were lowered to the 15-40 mil/year range by the presence of 0.1 to 0.2 M Zr, additional gains are needed if the desired equipment life spans are to be realized. This is especially true when one considers the accelerated corrosion generally experienced at welds, hot spots, etc.

Due to the preliminary nature of this study, no attempt was made to measure the depth of the pits caused by fluoride corrosion. The true nature and extent of these pits would, of course, need to be defined by any further experiments of a more thorough nature. In fact, establishment of optimum conditions for the Thorex dissolving and nitric acid recovery cycles will, in general, require such additional experiments conducted over extended periods with conventional corrosion study facilities.

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TABLE I

STAINLESS STEEL CORROSION RATES
(Boiling Temp.)

	HF Conc. M	Additive	Rate (mils/year) 309 SCb liquid	309 SCb vapor	347 liquid	304L liquid	Time Boiled hrs.
A. 13 M (60%) HNO_3	0.0	None	8.2	6.5	15	12	11
	0.0	0.0167 M NH_4SiF_6	300	250	620	440	6
	0.1	None	360	370	870	670	7
	0.1	0.1 M $Th(NO_3)_4$	85	89	150	140	6
	0.1	0.1 M $Al(NO_3)_3$	82	92	140	140	7
	0.1	TiO_2*	210	280	430	380	6
	0.1	V_2O_5*	120	160	240	240	6
	0.1	0.05 M $ZrO(NO_3)_2$	32	36	57	48	10
	0.1	0.1 M $ZrO(NO_3)_2$	21	22	38	34	5
	0.1	0.2 M $ZrO(NO_3)_2$	15	20	26	24	11
B. 6 M HNO_3; 1 M $Th(NO_3)_4$	0.1	None	1.3	0.3	7.1	8.6	17
	0.1	0.1 M $ZrO(NO_3)_2$	5.1	7.0	11	12	17
C. 6.5 M HNO_3	0	None	--	--	5.9	--	12
	0.05	None	--	--	104	--	12
	0.05	0.1 M ANN	--	--	12	--	9

*Added as solids which would have given 0.2 M solutions had they completely dissolved.

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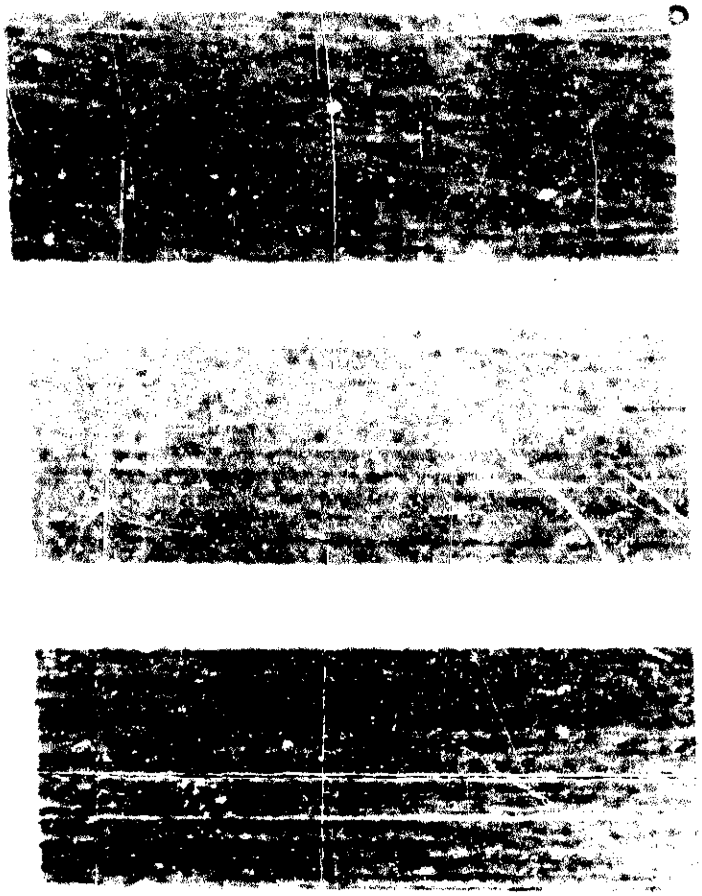

CONDITIONS

A. 13 M HNO_3
11 hours exposure
100-110°C

B. 13 M HNO_3
0.1 M HF
7 hours exposure
100-110°C

C. 13 M HNO_3
0.1 M HF
0.1 M $Zr(NO_3)_4$
5 hours exposure
100-110°C

Figure 6

309 SCb STAINLESS STEEL COUPONS
FROM HNO_3-HF CORROSION STUDIES
(100X Magnification)

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