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THE EFFECT OF FLUORIDE ON THE CORROSION OF STAINLESS STEEL IN THE PRESENCE OF EXCESS Al^{+3} ION

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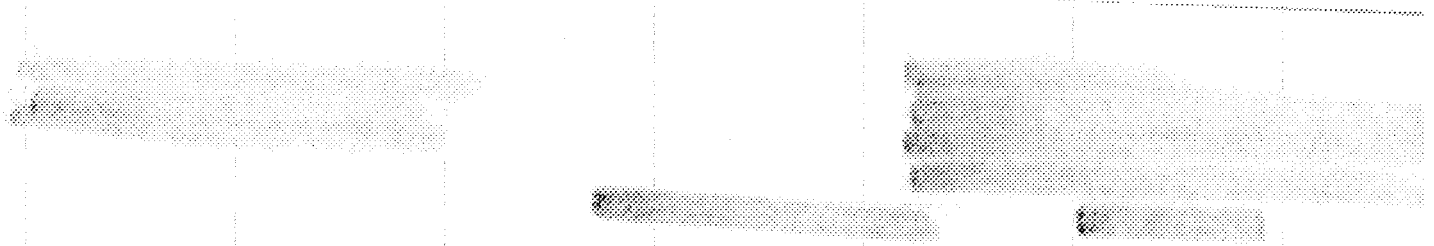


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INTRODUCTION

The study of the effect of fluoride ions on uranium containing solutions has led to the problem of their effect on the corrosion rates of stainless steel equipment. Mr. I. R. Higgins made some rough checks on the inhibiting effect of Al^{+3} ions on solutions containing fluoride. The results of these tests showed a decided drop in the rate of attack when the ratio of Al^{+3} to F^{-1} reached 1.5:1. There was no appreciable advantage in raising the aluminum-fluorine ratio above 2:1.

The Corrosion Group was then asked to make a quantitative evaluation of the rate and nature of corrosion in a sulphuric acid, uranyl nitrate solution with and without the presence of aluminum inhibited fluoride.

ABSTRACT

Corrosion tests of Type 347 stainless steel for two weeks in boiling uranyl nitrate, sulphuric acid media, with and without additions of Al^{+3} and F^{-1} in a 2:1 mole ratio, were made. The results show that although the presence of aluminum greatly reduces the deleterious effect of fluoride, the corrosion rates are still three to four times greater than when no fluoride is present.

TEST CONDITIONS

Sample Preparation. Samples of Type 347 stainless steel in the unwelded, fully annealed conditions were machined to one inch diameter rounds, one-fourth inch thick with one-fourth inch hole in the center. All flat surfaces were then polished on 80 and 120 grit paper successively.

The polished samples were measured, degreased in acetone and alcohol, dried and weighed before being exposed to the corroding media.

Corrosion Media. Two solutions were used in this investigation. Both solutions were maintained at boiling under total reflux.

I	250 g U/l as	$UO_2(NO_3)_2$
	3.5 M	H_2SO_4
	0.08M	HF
	0.16M	$Al(NO_3)_3$
II	250 g U/l as	$UO_2(NO_3)_2$
	3.5 M	H_2SO_4

Test Apparatus. Two liters of solution were placed in a three liter three-necked distilling flask and heated with a 375 watt infrared lamp. The samples were suspended by means of a glass hook through the center holes. Semi-immersed samples were so located that approximately 50% of the area was in the gas and 50% in the liquid phase.

TEST RESULTS

The tests were run for a period of two weeks in all. The samples were removed, dryed and weighed at the end of one week. The weight losses for each 168 hour period and for the total period are in Table I. Penetration rates are calculated only for the cumulative weight loss.

TABLE I

Corrosion Rates of Stainless Steel Samples

Sample	Solution	Condition	Weight Loss (MDD)			Penetration Rate (mils per year)
			1st week	2nd week	Cumulative	
1	I	Total Immersion	94.5	78.5	86.5	15.6
2	I	Total Immersion	107.1	81.0	94.2	17.0
3	I	Semi-Immersion	86.6	74.1	80.3	14.5
4	I	Semi-Immersion	91.1	74.3	82.7	14.9
5	II	Total Immersion	27.1	20.4	23.8	4.3
6	II	Total Immersion	32.6	22.5	27.5	5.0
7	II	Semi-Immersion	27.8	19.5	23.7	4.3
8	II	Semi-Immersion	24.5	17.6	21.4	3.9

It is interesting to note that the solution containing fluoride (I) had taken on a decided blue-green color at the end of the test while the other (II) retained its original yellow-orange tint.

The decrease in rate of attack for the two successive weeks of exposure is probably due not only to a depletion in the active ingredients, but also to the formation of a protective film on the stainless steel. This is substantiated by the fact that in Solution II where the samples acquired a thin tightly adherent bronze colored film, the corrosion rate for the second week was an average of 71% of the original, whereas in Solution I the samples showed a clean bright etched appearance and the corrosion rate for the second week averages 82% of the original rate.

All surfaces of samples exposed to Solution I are completely covered with tiny pits of approximately uniform size and depth, two mils in diameter and one mil deep. Figures 1 and 2 are photographs of samples as removed from test. They clearly show the difference in corrosion attack between the fluoride and non-fluoride-containing solutions. There is no appreciable difference in attack on totally immersed and semi-immersed specimens.

CONCLUSIONS

The results of this investigation clearly indicate that the presence of Al^{+3} ions in twice the concentration of F^{-1} ions will have a beneficial effect on corrosion rates. However these rates will still be three to four times as high as in similar solutions without fluoride additions. Specifically the rates in the uranyl nitrate, sulphuric acid solutions tested averaged 15.5 mpy with inhibited fluoride present and only 4.4 mpy without the fluoride. In addition, the type of attack changed from uniform surface removal to one with strong pitting tendencies with the addition of hydrofluoric acid.

ACKNOWLEDGMENTS

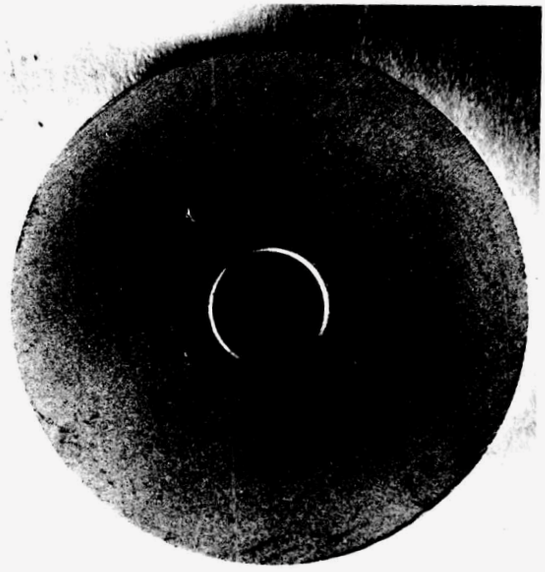
The author wishes to express his appreciation to:

I. R. Higgins for the basic work in determining the necessary amount of Al^{+3} for effective inhibition.

L. Fairchild and J. Brown for the preparation of samples and testing media.

H. Barker for the photographs of the samples after exposure.

FIGURE I
TOTAL IMMERSION SAMPLES



SOLUTION I
Mag. 2.5 X

SOLUTION II
Mag. 2.5 X

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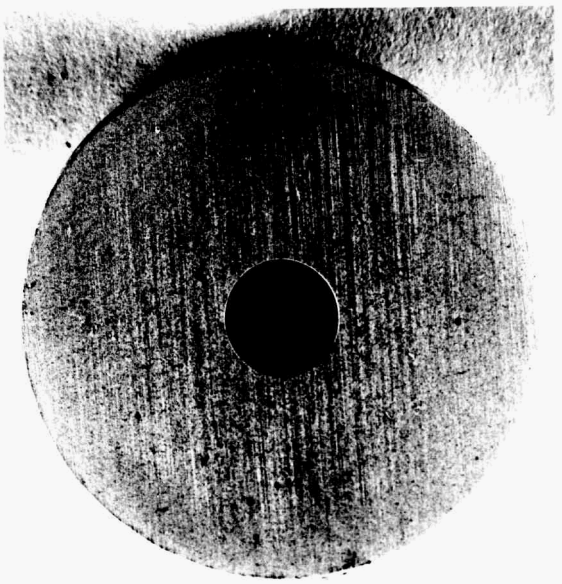
FIGURE 2
SEMI IMMERSION SAMPLES



SOLUTION I
Mag. 2.5 X

SOLUTION II
Mag. 2.5 X

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