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INHIBITION OF CORROSION OF 304-L IN HNO_3-HF MIXTURES WITH ALUMINUM.

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INHIBITION OF CORROSION OF 304-L IN HNO_3-HF MIXTURES WITH ALUMINUM

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Chemical Research and Development
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April 5, 1962

HANFORD ATOMIC PRODUCTS OPERATION

RICHLAND, WASHINGTON

GENERAL ELECTRIC

INHIBITION OF CORROSION OF 304-L IN HNO_3-HF MIXTURES WITH ALUMINUM

Introduction and Summary

Type 304-L stainless steel is subject to severe corrosion by mixtures of nitric acid and hydrofluoric acid. However, at several points in HAPO separations processes, it is very advantageous to be able to use these particular acids in combination. To prevent serious corrosion of equipment, some means must be found to inhibit the corrosion of stainless steel in this system. Work performed at HAPO and other sites indicates that aluminum nitrate is an effective inhibitor in this system. The purpose of this report is to present data defining the aluminum-to-fluoride ratios necessary to achieve satisfactory inhibition.

Samples of type 304-L stainless steel were exposed to boiling solutions containing nitric acid, hydrofluoric acid, and aluminum nitrate at various concentrations. The data collected indicate that an aluminum-to-fluoride mole ratio of 5 to 6 is sufficient to produce almost complete inhibition in .01 M hydrofluoric acid solutions with nitric acid concentrations up to 10 molar. A mole ratio of 5 to 6 also produced good inhibition in 4 M nitric acid solutions with hydrofluoric acid concentrations up to 0.1 molar. It appears likely, although data were not collected to confirm this, that this same mole ratio may produce inhibition at a combination of the higher nitric and hydrofluoric acid concentrations.

Samples exposed in the vapor phase and at the interface of boiling solutions of aluminum-inhibited nitric-hydrofluoric acid did not exhibit any evidence of accelerated attack.

Detailed Discussion

At several points in HAPO separations processes, the use of nitric acid solutions containing small quantities of fluoride is desirable. However, stainless steel equipment is severely corroded by such solutions. While it is possible to tolerate a relatively high corrosion rate at one point in the process, such corrosion cannot be permitted in equipment downstream from this point. Some means must therefore be found to inhibit the corrosion of stainless steel by nitric-hydrofluoric acid mixtures. Work performed in HAPO laboratories and at other sites has indicated that aluminum nitrate is an effective inhibitor in this system. This report will present data which partially define the mole ratio of aluminum-to-fluoride necessary to achieve this inhibition.

Samples of type 304-L stainless steel - 1.5" x 0.5" x 0.25" - were prepared for exposure by heat treating at 1250 F for one hour and water quenching. All sample faces were ground to a 120 grit finish to remove oxide scale. The samples were passivated in 20 w/o nitric acid, dried with acetone, and weighed.

All samples were exposed to 200 ml solution in Kel-F bottles with Teflon condensers, as shown in Figure 1, for a minimum of five 24-hour periods. Most samples were exposed for a total of 200 to 300 hours. Individual period corrosion rates were calculated on the basis of total weight loss during that period, and the overall corrosion rate is an average of the individual period rates. All corrosion rates are expressed as mils penetration per month (.001"/month).

The investigation was designed to evaluate the effects of increasing nitric acid concentration at a given fluoride concentration, and increasing fluoride concentration at a given nitric acid concentration. The two parts of the investigation will be discussed separately.

A. Nitric Acid Effects

A total of 31 samples were exposed to boiling solutions of .01 M HF, with HNO_3 concentrations of 4, 6, 8, and 10 M, and aluminum-to-fluoride mole ratios ranging from 0 to 10. In addition, samples were exposed to 4, 6, 8, and 10 M HNO_3 to provide base rates for comparison. The data collected are shown in Figure 2.

Examination of the data in Figure 2 indicates that at concentrations of 4 and 6 M HNO_3, an aluminum-to-fluoride mole ratio of 4 produces good inhibition, and a mole ratio of 6 to 8 produces almost complete inhibition. At HNO_3 concentrations of 8 and 10 M, a ratio of 6 produces good inhibition, and a ratio of 8 to 10 is required for nearly complete inhibition.

If one were required to define the optimum aluminum-to-fluoride mole ratio for inhibition in the HNO_3 - .01 M HF system, one might select a value between 5 and 6. Although higher ratios may result in further inhibition, the absolute value of the corrosion rate decreases very slowly beyond this point.

In order to determine if accelerated corrosion occurs in either the vapor phase or at the liquid-vapor interface in inhibited solutions, samples of sensitized 304-L were exposed in these positions over boiling solutions of 6 M HNO_3 - .01 M HF - .04 M $Al(NO_3)_3$, and 8 M HNO_3 - .01 M HF - .05 M $Al(NO_3)_3$. The samples were exposed for 11 individual periods, or a total of 320 hours None of the samples exhibited any evidence of accelerated attack.

B. Hydrofluoric Acid Effects

The postulated mechanism of inhibition by aluminum in this system is the formation of an aluminum-fluoride complex ion. If this is correct, the mole ratio of aluminum-to-fluoride required for inhibition may increase with increasing fluoride concentration as a result of disassociation of the complex.

In order to determine if this is true, samples of type 304-L stainless steel were exposed to boiling solutions of 4 M HNO_3 with HF concentrations of .01, .05, 0.1, and 0.5 M, with aluminum-to-fluoride mole ratios ranging from 0 to 6. The data collected are shown in Figure 3.

The data in Figure 3 indicates that, within certain limits, increasing fluoride concentration does not significantly affect the corrosion rate at aluminum-to-fluoride mole ratios greater than two.

The data shown in Figure 3 at a fluoride concentration of 0.5 M are questionable, particularly at the higher aluminum-to-fluoride ratios. At these concentrations, the sample is exposed to a solution which is 50 volume percent $Al(NO_3)_3 \cdot 9\ H_2O$ and 50 volume percent 8 M HNO_3. The effective acid concentration seen by the sample surface is unknown, but one might expect it to be in the neighborhood of 8 M. If this is correct, the data at this point are not comparable to other data on the graph.

It would be desirable to investigate the effect of increasing HNO_3 concentration at the higher HF concentrations. This was not possible in these studies because of accelerated corrosion due to hexa-valent chromium produced from corrosion of the sample. The inhibiting effect of aluminum is masked by the intergranular corrosion resulting from the chromium.

C. Conclusions

Based on the data collected in this investigation, it appears that an aluminum-to-fluoride mole ratio of 5 to 6 is sufficient to produce almost complete inhibition of the corrosion of 304-L stainless steel by nitric acid solutions containing fluorides in the concentrations normally encountered in HAPO separations processes (on the order of .01 M). The data also indicate that this relationship may hold true at significantly higher fluoride concentrations.

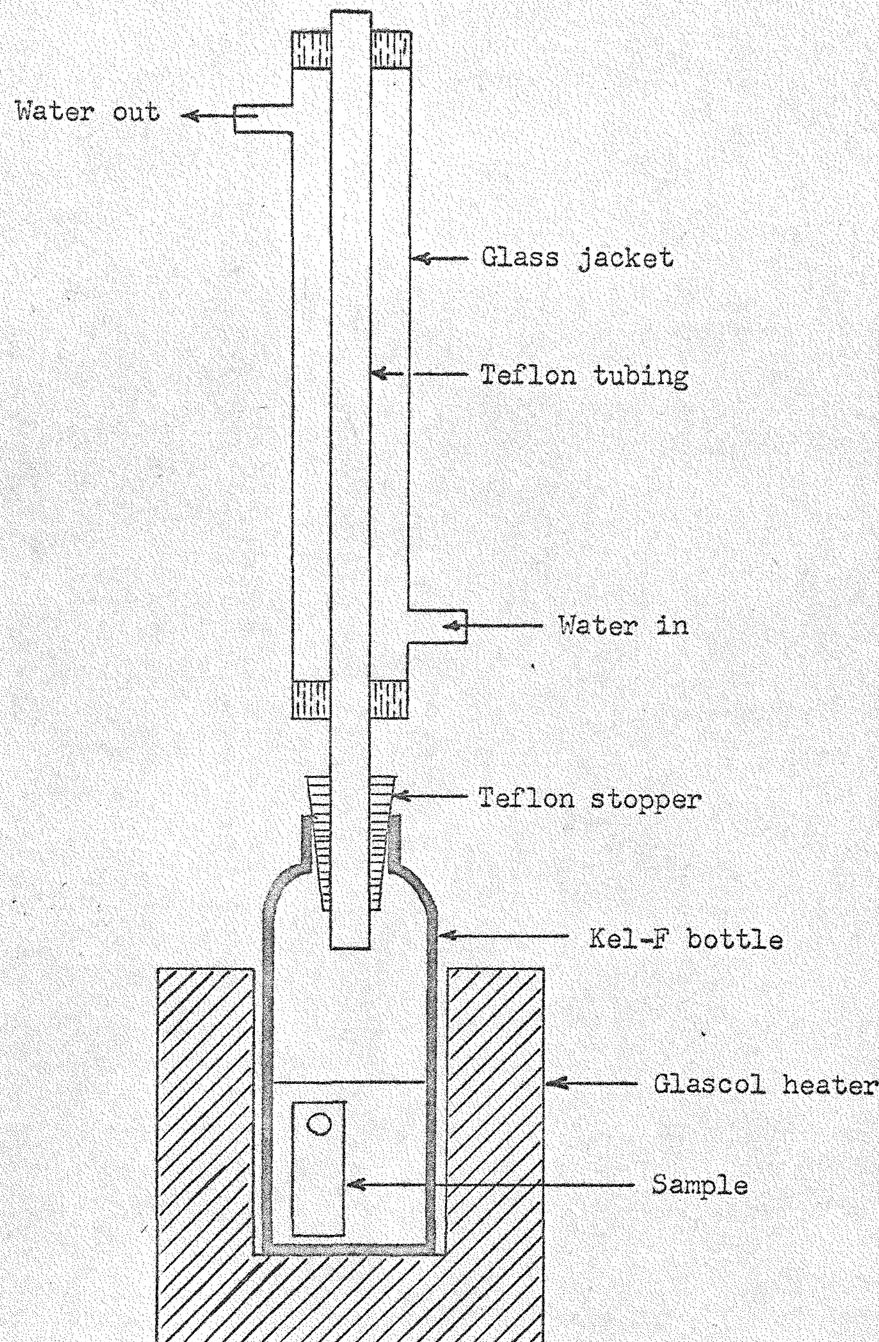

FIGURE 1

Drawing of equipment used for corrosion tests in boiling nitric-hydrofluoric acid solutions.

FIGURE 2

Corrosion Of 304-L By HNO_3 - .01M HF - ANN Solutions

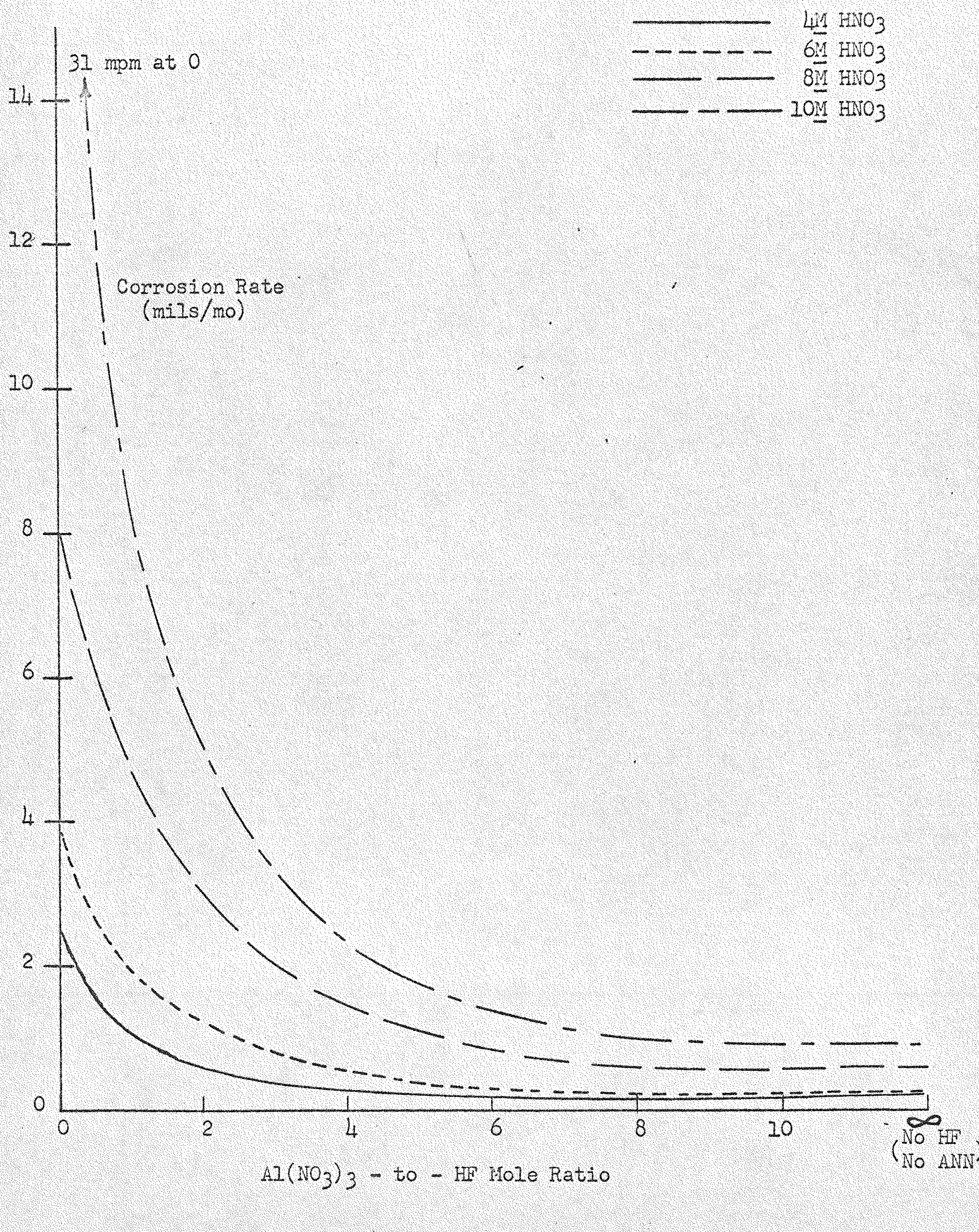

FIGURE 3

Corrosion Of 304-L By 4M HNO_3 - HF - ANN Solutions