LIA09831

Union Carbide, [illegible]

A. SUMMARY

The article by Messrs. Friend and Teeple of the International Nickel Company, while generally fair in its treatment of the other metals, leaves the impression that there is only one material to use in contact with hydrofluoric acid. [illegible] Further study of the reference material listed brings out the information that mild carbon steel is entirely suitable through a narrower temperature range than for Monel for the anhydrous acid and only for concentrations above [illegible] concentration range is where we find lead has a sufficiently low corrosion rate to enable its use under certain conditions. Rubber, Neoprene and many [illegible] plastics show excellent resistance to weak HF but begin to corrode in the concentration range of 60-80%. Like lead, in and above this range, the rate of corrosion increases with the concentration. There seems to be a drastic change in corrosive characteristics in this range.

Monel in a variety of applications with HF has proved to be resistant to all concentrations including anhydrous acid over a wide temperature range. Monel has proven useful as bubble caps in HF distillation columns, and in other installations where velocities are encountered has given longer service than copper and bronze. Copper is said to be a close second to Monel in resisting HF attack, though with a 175°F maximum in anhydrous acid and requirements of low velocity and absence of aeration when in contact with the dilute acid.

B. HISTORY

One of the earliest commercial uses of fluorine and its compounds came about in 19[illegible] with the development of Freon refrigerants. The first production of [illegible] hydrofluoric acid [illegible] was accomplished in [illegible]. The most important [illegible] from a tonnage [illegible], came about in 19[illegible] with the use of HF in the [illegible] of 100 octane gasoline and in other organic [illegible] corrosion problems [illegible] accentuated through the greatly expanded production of HF. The Department of Commerce "Facts for Industry" gives the total allocations of [illegible] from July 1, 19[illegible]-June 30, 19[illegible] as 83,000 short tons of 100% H₂F₂

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C. [illegible]

[illegible] of aviation [illegible] by [illegible] a catalyst [illegible] etching of glass.

D. [illegible]

Performance of HF may be divided:

1. The anhydrous acid or its water solutions of very high acid concentrations

2. The more dilute acid concentrations.

Lead is resistant to concentrations below 65 to 70% but not to higher concentrations of the anhydrous acid. At moderate temperatures mild carbon steel is resistant to anhydrous acid and to the higher acid concentrations above 75 to 80% HF but is corroded by lower concentrations. Among the unsatisfactory materials, the most readily attacked are those containing silica, such as glass, porcelain, enamelware, asbestos and certain silica cast irons. In HF acid, wood chars instantly while rubber polymerizes and hardens and most plastics are unsatisfactory. (5)

Mild steel is excellent for handling AHF and is used for storage tanks, shipping containers, pipes, fittings, valves and pumps. Apparently a protective coating forms on steel inhibiting further corrosion. This coating causes valves to freeze, unless operated at fairly frequent intervals, probably by cementing moving parts together. This is overcome by double valving and by making it a plant practice to open and close valves twice a day. For best resistance to HF a thoroughly deoxidized, dead melted or killed steel with a minimum of non-metallic inclusions is ideal. Because of lack of precise control, Bessemer steel is not used (5). The paragraph on lead is quoted below followed by abstracts on one or more paragraphs on other materials.

1. "Chemical lead appears to be usefully resistant to unaerated aqueous HF solutions under about 60 to 65 per cent concentration at temperatures up to about 175° F. Its corrosion rate is considerably increased by a high degree of aeration particularly in the more dilute solutions. Lead is not resistant to anhydrous acid nor to aqueous solutions above about 65 per cent concentration."

2. Monel is indicated to be the most generally useful material as it is said to be resistant to all concentrations including AHF over a wide temperature range. The tables show it as the most resistant except for platinum and silver. It will probably be used exclusively to handle the boiling solutions encountered in HF production. Straight Monel has given good service for bubble caps

[illegible]
castings or as a [illegible]

3. [illegible]

[illegible] to be [illegible] corrosion rates are [illegible] at higher temperatures.

4. Copper-Nickel Alloys.

The copper-nickel alloys (particularly 70% copper, 30% nickel) can be considered as [illegible] to Monel in general performance. These alloys are considerably less sensitive to velocity conditions and are resistant to [illegible] or high strength HF at higher temperatures than copper, though not to as high temperatures as Monel.

5. Nickel.

In AHF nickel is resistant even at considerably elevated temperatures and is one of the most resistant materials for high temperature operation. In dilute hydrofluoric acid solutions its corrosion resistance may be limited to temperatures below 170° to 180° F. In a commercial 60-65% acid it was corroded severely at atmospheric temperature, and its erratic performance in dilute commercial solutions is the result of depending upon the strength of the oxidizing conditions as to whether it will or will not form a protective oxide film when iron salts are present.

6. Inconel.

Inconel is resistant to aqueous hydrofluoric solutions at atmospheric temperature and sometimes up to 160° to 170° F. In anhydrous acid at elevated temperatures, Inconel is also said to be resistant but temperature limits have not been established.

7. Hastelloy Alloys.

Hastelloy alloys, A, B & C should demonstrate useful resistance to HF water solution of all concentrations for a considerable temperature range. Alloys A & B appear resistant up to the boiling point with alloy C resistant up to a somewhat lower temperature. Severe intergranular attack has been reported for Hastelloys A & B in 60 to 80% hydrofluoric acid. Hastelloy D, (10% silicon, 85% nickel) is resistant to hydrofluoric solutions at moderate temperatures.

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8. Carbon Steel.

As noted above, carbon steel is satisfactory above 50 to 60% and particularly resistant to anhydrous acid up to [illegible]° F. above which it is said to be subject to rapid attack. In the alkylation process temperatures are moderate and HF is substantially anhydrous so that carbon steel can be used for most of the major equipment except in the acid regeneration units.

9. Austenitic Stainless Steels.

Austenitic stainless steels Types 302, 304, 316, 321 and 347 have been found to be resistant to dilute aqueous HF at atmospheric temperatures but are subject to severe corrosion by the hot acid solutions. Types 304 and 316 were severely corroded by commercial 60-65% acid at atmospheric temperature. In impure 10% HF solution at [illegible]° F., both materials suffered transcrystalline cracking due to stress corrosion. In another case (b), cold worked 18-8 stainless suffered stress corrosion cracking in hot 40 to 60% acid.

All of these stainless steels are apparently resistant to AHF even at somewhat elevated temperatures. With some water present, Type 316 stainless was considerably more resistant than Type 304 stainless at 215° to 250° F.

10. Silver Brazing Alloys, Ni-Resist and Cast Iron.

The most favorable alloy found for use in joining Monel is RT (60% silver, 25% copper, 15% zinc) which has been found by galvanic test to be cathodic to Monel. From this it is apparent that for silver brazing Monel to be used in aqueous acid, an RT alloy composition should be used to avoid accelerated attack on the brazed joint.

The castiron alloy, Ni-Resist (13.5-17.5% nickel, 5.5-7.5% copper, 1.75-2.5% chromium) is resistant to dilute aqueous HF solutions at atmospheric temperature but not at elevated temperatures. It was appreciably corroded by commercial 60-65% acid at room temperature. Plain cast iron is attacked by HF over a wide concentration range even at atmospheric temperature. It is not considered suitable for use.

Table I

PLANT-CORROSION TEST IN STORAGE OF 40-60% HYDROFLUORIC ACID

Temperature; Atmospheric - 33 day Test Duration

Material	Corrosion Rate In. Per Yr.
Chemical Lead	0.003
Monel	0.008
Copper	0.003
Yellow Brass	0.007

In the above test the acid was diluted from 60 to 40% in storage tank. Test specimen immersed in solution in tank.

Table [illegible]

[illegible]	
Temperature: [illegible] F – [illegible] 23 days	
Material	Corrosion Rate [illegible]
[illegible]	[illegible]
Copper	[illegible]
Chemical Lead	[illegible]
[illegible] bronze	[illegible]
Monel	[illegible]
Nickel	>[illegible]
Inconel	0.15
18-8 Stainless 304	>0.21
18-8 Mo Stainless 316	>0.29
Mild Steel	0.17
Ni-Resist	0.13
Cast Iron	0.23

The acid in the above tests contains 15-25% Fluosilicic acid, 0.3-1.28% sulfuric acid and 0.01-0.03% iron. Test specimens immersed in solution in tank.

Table III

CORROSION TESTS IN HYDROFLUORIC ACID ALKYLATION PLANTS

Material	Regenerator Column Bottom Plant "C" Test No. 6 (See below)	Dehydrator Column Bottom Plant "C" Test No. 7 (See below)
Monel	0.007	0.022
"S" Monel	0.011	0.039
Nickel	0.018	0.068
Inconel	0.025	>0.13 (1)
Copper	0.13 (1)	>0.13 (1)
Silicon bronze	0.12 (1)	>0.12 (1)
18-8 Stainless Type 302	-----	-----
18-8 Stainless Type 304	0.11	>0.12 (1)
Chemical Lead	>0.13 (1)	0.13 (1)
Hastelloy A	0.0046	0.016
Hastelloy B	0.0043	0.018
Hastelloy C	0.0021	0.038
Mild Steel	0.15	>0.24 (2)
Duranetal "J"	0.003 (8)	0.009 (10)

Footnotes (Table III)

Test No. 6 - Bottom of regeneration column. Feed to column contained [illegible] per cent HF, 1.6 per cent water and oils. Test rack [illegible] grid plate of column. Feed 1[illegible] bbl. per day. Temperature; Ave. [illegible]° F., Max. [illegible]° F. Duration of test; 65 days.

Test No. 7 - Bottom of dehydrator column beneath bottom plate. Feed contained 89.3 per cent HF, and 1.6 per cent water. Feed rate 10 bbl. per day. Temperature; Ave. [illegible]° F., Max. [illegible] F. Duration of test; 65 days.

(1) Completely corroded away. Original thickness 0.0[illegible] in.
(2) " " " " " 0.062 in.
(3) Pitted to maximum depth of 0.005 in. during test.
(4) " " " " " 0.012 " " "

B. [illegible] INFORMATION

Protection of Workmen - Slight concentrations of AHF fumes cause [illegible] nasal and throat irritation. People who sunburn easily usually burn readily from fumes of AHF. Zinc oxide powder applied to exposed skin surfaces, minimizes the danger of burning. It is of great importance to maintain regular inspection of pipes, valves, etc., due to the hazard of hydrogen explosion when cutting into empty lines or tanks, especially if they contained weak acid. This can be minimized by adding dry ice to the receptacle or line before starting repair work. Equipment removed from HF service should be given a thorough alkaline wash before being handled.

First Aid Treatment for hydrofluoric acid burns.

1. Promptness
2. Prolonged and thorough flushing with water.
3. Treatment for shock.

List of Publications

1. A. C. Finger, "Fluorine Compounds in Organic Syntheses," Chemical and Metallurgical Engineering, 51, June 1944, pp. 101-103.

2. F. E. Frey, "Commercial Alkylation with Hydrogen Fluoride Catalyst," Chemical and Metallurgical Engineering, 50, November, 1943, pp. 126-128

3. M. E. Holmberg and F. A. Prange, "Corrosion in HF Alkylation," Industrial and Engineering Chemistry (Industrial Edition), 37, November, 1945, pp. 1030-1033.

4. R. A. Findley, "Mechanical Operation of HF Alkylation Units," National Petroleum News (Technical Section), 37, May 2, 1945, pp. R325, 386, 388.

5. C. M. Fohr, "How to Handle AHF with Safety," The Oil and Gas Journal, 42, July 22, 1943, pp. 39-42.

6. O. B. J. Fraser, "Stress-Corrosion Cracking of Nickel and Some Nickel Alloys," Symposium on Stress-Corrosion Cracking of Metals, Am. Soc. Testing Mat'ls. and Am. Inst. Mining and Met. Eng'rs. (1944) p. 464.

[illegible] the lower cost of lead may warrant interest for certain applications even though the lead corrosion rate may be greater. For instance:

at $0.[illegible] per pound, 15 lbs. sheet lead cost $[illegible] per sq. ft.
" " " " 20 lbs. " " " [illegible] " " "
" " " " 24 lbs. " " " [illegible] " " "
" " " " 30 lbs. " " " [illegible] " " "

at $0.44 per pound, 1/4 in. Monel cost 6.06 per sq. ft.
(Based on sheet costs only)