Corrosion Resistance of NICKEL- CONTAINING ALLOYS in HYDROFLUORIC ACID, HYDROGEN FLUORIDE and FLUORINE

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NiDI

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Table 1

Nominal Compositions of Nickel Alloys in Use or Corrosion Tested

Composition, %	Ni	Fe	Cr	Mo	Cu	C	Si	Mn	Other
Stainless Steels									
AISI Type 304	9.5	70	18	–	–	.08 max	0.5	1.5	–
AISI Type 304L	10	69	18	–	–	.03 max	0.5	1.3	–
AISI Type 316	13	65	17	2.0 min	–	.08 max	0.5	1.7	–
AISI Type 316L	13	65	17	2.0 min	–	.03 max	0.5	1.8	–
AISI Type 317	14	61	19	3.0 min	–	.08 max	0.4	1.6	–
AISI Type 309Cb	13	64	21	–	–	–	1.0 max	2.0 max	Cb-Ta 5XC min
AISI Type 310	20	52	25	–	–	0.25 max	1.0 max	2.0 max	–
AISI Type 321	10	69	18	–	–	.08 max	1.0 max	2.0 max	Ti 5XC min
AISI Type 329	4.5	67	27	1.5	–	.07	0.5	0.6	–
AISI Type 347	11	68	18	–	–	.08 max	1.0 max	2.0 Max	Cb–Ta 1OXC min
AM 350	4.3	76	16.5	2.75	–	0.10	0.25	0.80	N 0.10
ARMCO* 17-7 PH	7	72	17	–	–	.09	1.0	1.0	Al 1.0
ARMCO* PH 15-7 Mo	7	72	15	2.5	–	.09	1.0	1.0	Al 1.0
Iron base-Nickel-Chromium-Copper-Molybdenum Alloys									
WORTHITE* Stainless	24	48	20	3.0	1.75	.07 max	3.25	0.6	–
CARPENTER* Stainless No. 20Cb	29	44	20	2.5	3.3	.07 max	0.6	0.75	Cb (+Ta) 0.6
CARPENTER* Stainless No. 20Cb-3	34	39	20	2.5	3.3	.07 max	0.6	0.75	Cb (+Ta) 0.6
ACI Type CN-7M (a)	29	44	20	2.0 min	3.0 min	.07 max	1.0	–	–
Nickel base-Iron-Chromium-Molybdenum Alloys									
INCOLOY* alloy 825	41.8	30	21.5	3.0	1.80	.03	0.35	0.65	Al 0.15; Ti 0.90
HASTELLOY* alloy 6	45	19.5	22.2	6.5	2.0	.03	0.35	1.3	W 0.6;
HASTELLOY* alloy F	47	17	22	6.5	–	.05 max	0.35	1.3	Cb–Ta 2.12; Cc 2.5 max
HASTELLOY* alloy X	48	18.5	22	9.0	–	0.10	1.0 max	1.0 max	Co 2.5 max; W 0.2–1.0
Nickel base-Chromium-Molybdenum Alloys									
ILLIUM* "B" alloy	52	1.15	28	8.5	5.5	.05	3.5	1.25	B .05
ILLIUM* "98" alloy	55	1.0	28	8.5	5.5	.05	0.7	1.25	–
ILLIUM* "G" alloy	56	6.5	22.5	6.4	6.5	0.20	0.65	1.25	–
ILLIUM* "R" alloy	68	1	21	5.0	3.0	.05	0.7	1.25	–
Nickel base-Molybdenum-Chromium Alloys									
HASTELLOY* alloy N	69	5	7	17	–	.08 max	1.0 max	0.8 max	–
HASTELLOY* alloy C	54	5	15.5	16	–	.08 max	1.0 max	1.0 max	Co 2.5 max; W 4; V 0.4 max
Nickel base-Molybdenum Alloy									
HASTELLOY* alloy B	61	5	1 max	28	–	.05 max	–	–	Co 2.5 max; Other 3
Nickel base-Silicon Alloy									
HASTELLOY* alloy D	82	2 max	1 max	–	3.0	0.12 max	9	–	Co 1.5 max; Other 2
Nickel-Alloyed Cast Irons									
Ni-Resist (Type 1)	15.5	69	2.5	–	6.5	2.8	2.0	1.2	–
Ni-Resist (Type 3)	30	62	3.0	–	0.5 max	2.6 max	1.5	0.6	–
Nickel-Copper Alloys									
MONEL* alloy 400	66	1.35	–	–	31.5	0.12	0.15	0.90	–
MONEL* alloy K-500	65	1.0	–	–	29.5	0.15	0.15	0.60	Al 2.80; Ti 0.50
ACI M-35 Nickel-Copper alloy	64	3.5 max	–	–	29	0.35 max	2.0	1.50	–
Nickel-Copper alloy 505	64	2.0	–	–	29	.08	4.0	0.80	–
Nickel-Copper alloy 506	64	1.5	–	–	30	0.10	3.2	0.80	–
Copper-Nickel alloy CA 715	30	0.55	–	–	67	–	–	1.00 max	Pb .05 max; Zn 1.0 max
Copper-Nickel alloy CA 710	20	0.75	–	–	74	–	–	1.00 max	Pb .05 max; Zn 1.0 max
Copper-Nickel alloy CA 706	10	1.0	–	–	86.5	–	–	1.00 max	Pb .05 max; Zn 1.0 max
Copper-Nickel alloy CA 720	41	2.0	–	–	55.7	–	–	1.25	–
Nickel									
Nickel 200	99.5	0.15	–	–	.05	.06	.05	0.25	–
Nickel 201	99.5	0.15	–	–	.05	.01	.05	0.20	–
DURANICKEL* alloy 301	94.0	0.15	–	–	0.15	0.55	0.25	0.25	Al 4.5; Ti 0.50
Nickel base-Chromium Alloys									
CORRONEL alloy 230	55.0 min	5.0 max	36	–	1.0 max	.08 max	.06 max	1.0 max	Ti 1.0 max; Al 0.5 max
INCONEL* alloy 600	76.0	7.2	15.8	–	0.10	.04	0.20	0.20	–
INCONEL* alloy 625	60.0	5.0 max	21.5	9.0	–	0.10 max	0.50 max	0.50 max	Cb (+Ta) 3.65
INCONEL* alloy X750	73.0	6.75	15.0	–	.05	.04	0.30	0.70	T1 2.50; Al 0.80; Cb 0.85
Iron-Nickel-Chromium Alloy									
INCOLOY* alloy 800	32.0	46.0	20.5	–	0.30	.04	0.35	0.75	–

* See page 35 for registered trademarks.

(a) Cast "20" alloys, such as DURIMET* 20, ALLOYCO* 20, etc.

Corrosion Resistance of Nickel-Containing Alloys in Hydrofluoric Acid, Hydrogen Fluoride and Fluorine

• Introduction

The industrial usage of hydrofluoric acid, hydrogen fluoride and fluorine is relatively new, as compared with many heavy chemicals. Until the first two decades of the twentieth century, only aqueous hydrofluoric acid and calcium fluoride, "fluorspar," were of any commercial significance. With the development of methods for large scale production of anhydrous hydrogen fluoride in 1931 and, from it, fluorine, a new frontier in fluorine chemistry was made possible.

The objective of this bulletin is to present the corrosion resistant characteristics of nickel and nickel-containing alloys in hydrofluoric acid, hydrogen fluoride, fluorine, and some fluorine containing compounds, with the hope that such information will be helpful to those responsible for material selection. The compositions of the alloys mentioned are shown in Table 1.

If it is possible to generalize, it may be said that hydrofluoric acid, hydrogen fluoride, and fluorine are less corrosive to many metals and alloys than are their other halide counterparts. They readily react with many metals to form metallic fluoride films, which, depending upon conditions, may be thin, adherent, and protective to further reaction. This is frequently the case with high nickel alloys, with the result that a number of such nickel-containing alloys are used in the handling of the fluorine family of compounds.

• Corrosion by Hydrofluoric Acid

Hydrogen fluoride is readily soluble in water over a wide concentration range, the water solutions being referred to as hydrofluoric acid. Commercially, this acid is marketed in concentrations from 30 to 70 per cent, the latter being a common grade. An azeotropic mixture of 38.2 per cent occurs, having a boiling point of 234 F (112 C). Thus, concentrations greater than 38.2 per cent cannot be produced by evaporation, and must be made by absorption of anhydrous hydrogen fluoride in water.

Nickel-Copper Alloys

The nickel-copper. alloys, typified by MONEL alloy 400, and modifications of this composition, exhibit excellent corrosion resistance to hydrofluoric acid over a wide range of acid concentrations and temperatures. Its corrosion resistance is less affected by acid concentration, temperature, or velocity than it is by the amount of oxygen in contact with the solution. Air, or oxygen, in aqueous solutions of the acid accelerates corrosion, as shown in Table 2, for tests in 25 and 50 per cent solutions. In the nitrogen purged tests, these alloys developed an adherent

Table 2

Laboratory Tests, Showing Effects of Aeration on Corrosion of Nickel-Copper Alloys

	Corrosion Rate, mils per year			
	Saturated with Air (a)		Purged with N_2 (b)	
Material	86 F (30 C)	176 F (80 C)	86 F (30 C)	176 F (80 C)
	25% Hydrofluoric Acid (C.P. Grade)			
MONEL alloy 400	37	11	0.2	2.4
ACI M-35 Nickel-Copper alloy	19	19	0.6	1.3
Nickel-Copper cast alloy 505	9	21	0.2	0.2
Nickel-Copper cast alloy 506	19	22	0.4	0.4
	50% Hydrofluoric Acid (C.P. Grade)			
MONEL alloy 400	8	39	<0.1	0.5
ACI M-35 Nickel-Copper alloy	6	37	0.5	2.0
Nickel-Copper cast alloy 505	3	46	0.4	2.0
Nickel-Copper cast alloy 506	7	44	0.2	1.0

Velocity: 42 to 73 ft/min.
(a) 1-day tests.
(b) 2-day tests.

brown fluoride film, as contrasted with a loose, nonadherent film in the aerated tests.

The effect of oxygen has been further explored in the studies of Pray, et al,[1] whose data for both liquid and vapor phase corrosion of Alloy 400 are shown in Table 3. These studies indicate that a slight increase in corrosion rate results with 500 ppm oxygen in the purge gas, and that a substantial increase may occur with more than 1500 ppm oxygen. Edwards[2] conducted similar studies in boiling 40 per cent hydrofluoric acid, Table 4, concluding that for successful practical use of Alloy 400 with this acid concentration, the oxygen in blanketing gas should be maintained at low levels, of the order of less than 0.1 per cent.

Table 3

Effect of Oxygen on Corrosion of MONEL alloy 400, 70/30 and 90/10 Copper-Nickel Alloys

Purge Gas, Nitrogen, Plus Oxygen As Shown	Corrosion Rate, mils per year-4-Day Tests					
	MONEL alloy 400		70/30 Copper-Nickel		90/10 Copper-Nickel	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
ppm 0_2	**Boiling 38% Hydrofluoric Acid 234 F (112 C)**					
<5	9.5	6.8	3.5	3.2	2.4	2
<500	17	12	2.6	2.9	2.9	3
1500	31	49	12	43	11	53
2500	29	18	13	48	13	42
3500	34	54	18	54	17	61
4700	53	107	30	144	53	170
10,000	46	25	20	80	18	83
ppm 0_2	**Boiling 48% Hydrofluoric Acid 226 F (108 C)**					
<5	11	3	3	1	2	1
<500	22	4	7	12	-	-
1500	28	24	7	30	7	40
2500	27	9	13	42	11	54
3500	34	29	19	60	17	65
4700	43	83	22	91	29	118
10,000	48	75	29	132	36	156

Using a purge gas containing 1 per cent oxygen in nitrogen (equal to 10,000 ppm oxygen), Braun, et al,[3] surveyed the effect of acid concentration on the corrosion behavior of Alloy 400 at 140 F (60 C) in liquid, interface, and vapor phase exposures, Figure 1. These tests indicate that for liquid exposure the acid concentration had little effect on corrosion rate, and that interface and vapor phase exposures were more corrosive with a maximum corrosion rate at about 40 per cent acid.

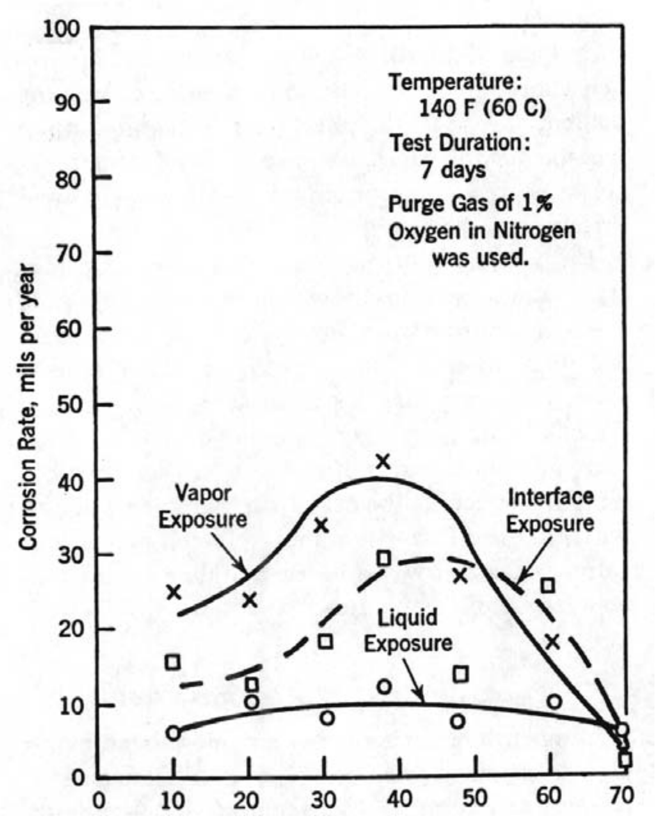
Schussler[4] conducted 30-day tests of Alloy 400 in 5 and 48 per cent hydrofluoric acid solutions at 150 F (66 C), both fully and partially immersed. Low corrosion rates with uniform attack prevailed for specimens fully immersed. However, in the partial immersion, the surfaces exposed to the aerated

Table 4

Effect of Oxygen on Corrosion of MONEL alloy 400

Laboratory Test: 1000 hours (41.5 days).
40% Hydrofluoric Acid Boiling-266 F (130 C).

Vol. % Oxygen In Hydrogen Purge Gas	Corrosion Rate, mils per year	
	Liquid	Vapor
0	11	1
0.1	21	2
1.0	75	12
Air Blanket (No Hydrogen)	22	1000



Hydrofluoric Acid Concentration, per cent by weight

Fig. 1 - Effect of hydrofluoric acid concentration on corrosion of MONEL alloy 400.

vapors corroded at considerably higher rates and in a non-uniform manner.

Results of a variety of other laboratory tests of Alloy 400 in hydrofluoric acid solutions are listed in Table 5. In those tests where the corrosion rate was high, it will be noted that air or oxygen was present.

In anhydrous acid, the effect of aeration is considerably less severe than for aqueous solutions, and, in the absence of oxygen, Alloy 400 exhibits excellent corrosion resistance up to at least 300 F (149 C), the highest temperature at which it was tested.

Effect of Weld Metal Composition for Joining Nickel-Copper Alloy 400

Until recently, little attention has been given to the effects which weld metal composition might have on the corrosion behavior of welded Alloy 400 structures in hydrofluoric acid media. As has been shown above, acid solutions of low oxygen content are not particularly corrosive.- In such solutions, minor alloy composition variations would not be expected to demonstrate significant differences in corrosion resistance behavior, and, for such media, choice of welding electrode has not been critical.

Table 5

Laboratory Corrosion Tests

						Corrosion Rate, mils per year	
HF, %	**Temp, F**	**Aeration**	**Agitation**	**Test Duration, Days**	**Other Comments: Re Test Condition**	**Nickel 200**	**MONEL alloy 400**
0.5	150	Slight	–	14	Some air over liquid	30	13
5.0	150	Slight	–	14	Some air over liquid	26	20
8.7	136	None	None	0.67	–	–	8
10	60	None	None	30	–	<0.1	<0.1
10	70	Slight	None	–	Open to air	–	9
25	176	Saturated	None	2	–	–	33
30	70	Slight	None	–	Open to air	18	8
30	70	None	None	4	–	–	4
35	230	Slight	None	2	Air over liquid	110	47
35	248	None	None	6	Nitrogen purge	–	1
35	248	Saturated	None	2	Air purge	–	294
40 to 60	70	–	–	33	In storage tank	–	3
45	275	–	–	?	–	–	3
48	70	Slight	None	?	Open to air	9	<0.1
48	150	Some	None	13	Air over liquid	74	17
48	240	None	None	8	In closed bomb	9	1
50	70	–	–	4	–	–	5
60	70	–	–	2	–	–	15
70	70	None	None	8	In closed bomb	1	<0.1
70	122	None	None	4	In closed bomb	–	4.2
70	240	None	None	8	In closed bomb	44	18
90	40	None	None	0.2	In closed bomb	–	1.3
90	70	None	None	1	–	–	0.8
90	70	None	Slight	1	–	–	1.5
93	70	None	None	8	In closed bomb	6	3
98	70	None	None	8	In closed bomb	–	2
98	130	None	None	8	In closed bomb	1	1
98	240	None	None	8	In closed bomb	3	2
98	93-110	Slight	None	3.6	Air in vapor	2.3	2.5
99.5	50	None	None	35	–	–	0
100*	50	None	None	35	–	–	0
100	70	None	None	1	–	–	0
100	70	Slight	None	1	Open to air	–	4.8
100	122	None	None	4	In closed bomb	–	0.5
100	100	None	None	8	In closed bomb	–	1
100	300	None	None	8	In closed bomb	3	1

• Anhydrous.

Where air or oxygen can not be completely excluded, choice of welding products can be important to the corrosion behavior of welded joints. This was pointed out by Dickenson and Watkins[5] during the start-up of a prototype plant for the recovery of hydrofluoric acid, wherein air could not be excluded. Certain weld deposits suffered accelerated attack, while others were unaffected. The attacked welds contained columbium, a constituent of one of the conventional electrodes for welding Alloy 400. Dickenson demonstrated the adverse effect of columbium in weld deposits on Alloy 400 by laboratory tests in 40 per cent hydrofluoric acid. Using plates welded with the three commercial welding products available at that time, a bare filler metal and two coated electrodes, only the columbium-containing deposit from one of the coated electrodes suffered attack.

Additional laboratory tests, Table 6, have been made to assess the effect of weld metal composition in both aerated and deaerated acid. These results support the findings of Dickenson and Watkins, and point out the accelerated corrosion likely to be encountered in aerated acid from the use of a columbium-containing electrode. As a weld deposit specimen, Test 1, the columbium-containing material suffered accelerated attack in both aerated and deaerated acid. As a weld deposit on Alloy 400 plate, Test 2, the columbium-containing deposit suffered accelerated attack in the aerated acid. The columbium-free materials, on the other hand, performed equal to the base alloy with no indication of accelerated attack as a weld deposit. Columbium-free welding products are preferred for the fabrication of Alloy 400 equipment for hydrofluoric acid service.

Table 6

Laboratory Corrosion Tests in 40% Hydrofluoric Acid

Test 1–Corrosion of as-deposited weld metal
Test Duration: 16.5 Days. Temperature: 158 F (70 C)

Material	Corrosion Rate, mils per year Solution Nitrogen Deaerated	Solution Aerated
MONEL filler metal, argon arc	8	70
MONEL coated electrode, Cb-free	3.6	67
MONEL coated electrode, Cb-containing	28	104
MONEL alloy 400, argon arc	8	79

Test 2–Corrosion of MONEL alloy 400 welded specimens, (bead on plate)
Test Duration: 12 Days. Temperature: 158 F (70 C)

Weld deposit made from	Corrosion Rate, mils per year Solution Nitrogen Deaerated	Solution Aerated
MONEL filler metal	2	42
MONEL coated electrode, Cb-free	2	41
MONEL coated electrode, Cb-containing	2	52 (a)
MONEL alloy 400 base plate, no weldment	2.5	70

(a) Weld deposit was preferentially attacked.

Composition (%) of Weld Deposits, Test 1

	C	Ti	Al	Si	Mn	Fe	Cu	Ni	Other
Filler metal	.01	2.29	.05	0.50	0.4	<0.2	30	bal	–
Coated electrode, Cb-free	0.33	0.41	0.78	0.50	2.5	0.7	30	bal	–
Coated electrode, Cb-containing	.05	0.84	0.39	0.50	1.5	1.3	30	bal	2.08 Cb
Alloy 400 base plate	0.12	<.01	.01	.08	1.20	1.65	29.15	bal	–

Effects of Stress

Alloy 400 and modifications of this alloy have been found to be subject to stress corrosion cracking in moist aerated vapors of hydrogen fluoride and to a much lesser extent in aerated solutions of the acid. Both transgranular and intergranular cracking have been observed. Copson and Cheng[6] have noted cracking to be more prevalent under conditions where the corrosion rate is high, i.e., where oxygen is present. Similar cracking susceptibility was observed for Nickel 200, INCONEL alloy 600, age-hardened DURANICKEL alloy 301 and age-hardened INCONEL alloy X-750. However, in the un-aged condition, DURANICKEL alloy 301 and INCONEL alloy X-750 exhibited a high level of resistance to stress cracking in the Copson and Cheng studies, and have been employed in applications where stress relieving of Alloy 400 was not feasible.

In practice, the occurrence of stress corrosion cracking may be minimized or avoided either by altering the hydrofluoric acid environment by excluding oxygen, or by heat treatment of the equipment to reduce stress. While internal stress can be relieved by a full anneal, a stress relief treatment for one hour at 1000 to 1200 F (530 to 650 C) followed by a slow cool has been found to be a practical treatment for fabricated structures of Alloy 400.

Silver Brazing Alloys for Joining Nickel-Copper Alloy 400

In some instances, it may be more desirable to fabricate Alloy 400 components by brazing rather than by welding. The resulting brazed joint is likely to have a relatively small exposed surface area of braze alloy as compared with the area of the adjacent base metal. For this reason, it is desirable to select a brazing alloy which not only has adequate corrosion resistance but is also somewhat cathodic to the base metal. In the corrosion tests, Table 7, a brazing alloy of 60 per cent silver, 25 per cent copper, 15 per cent zinc and an alloy of 50 per cent silver, 15 per cent copper, 15.5 per cent zinc, and 18 per cent cadmium, both exhibited useful corrosion resistance. When coupled to an equal area of Alloy 400, the higher silver alloy was cathodic, whereas the lower silver alloy was anodic. Braun, et al,[3] report excellent corrosion resistance for a 72 per cent silver, 28 per cent copper brazing alloy in boiling 38 and 48 per cent hydrofluoric acid. In a galvanic couple test this brazing alloy was cathodic to Alloy 400.

These results indicate that for Alloy 400 equipment to be used in aqueous hydrofluoric acid solutions a brazing alloy of at least 60 per cent silver should be used to avoid accelerated attack of the joint.

High concentrations of hydrofluoric acid at temperatures of 235 to 300 F (113 to 150 C) may cause embrittlement of some silver brazing alloys, as shown by the results of Tests 2 and 3, Table 18. The use of brazed joints for these conditions appears to be of questionable merit, and should be investigated for the particular operating conditions before selecting this means of fabrication.

Copper-Nickel Alloys

The copper-nickel alloys, typified by alloys CA 715 (70 per cent copper, 30 per cent nickel) and CA 706 (90 per cent copper, 10 per cent nickel) may be expected to exhibit corrosion resistance similar to nickel-copper Alloy 400 in unaerated aqueous hydrofluoric acid, based on limited available data. However, the corrosive effects of aeration in the vapor phase are likely to be even more severe with the higher copper alloys. Braun[3] evaluated 70/30 copper-nickel for the acid concentration range of 10 to 70 per cent, with oxygen present in a purge gas in contact with the solution, Figure 2. It will be observed that interface and vapor exposures were much more corrosive than immersed exposure for acid solutions up to about 50 per cent concentration. Pray, et al,[1] explored the effect of oxygen for both 70/30 and 90/10 copper-nickels, and their data are shown in Table 3 along with that for Alloy 400. The adverse effect of increasing oxygen on the corrosion behavior is quite apparent, especially in vapor phase exposure. Schussler's[4] studies confirm these observations, and indicate that, for partial immersion conditions with an air atmosphere, attack can be very severe at the liquid level. It is suspected that oxygen converts the cuprous fluoride corrosion product film to the cupric state which, in effect, alters the corrosive media in contact with the metal, producing a more corrosive condition.

Based on the limited data available, it would appear that the copper-nickel alloys can be expected to have good corrosion resistance to unaerated aqueous hydrofluoric acid solutions of all concentrations up to boiling temperatures, but only limited resistance to aerated solutions.

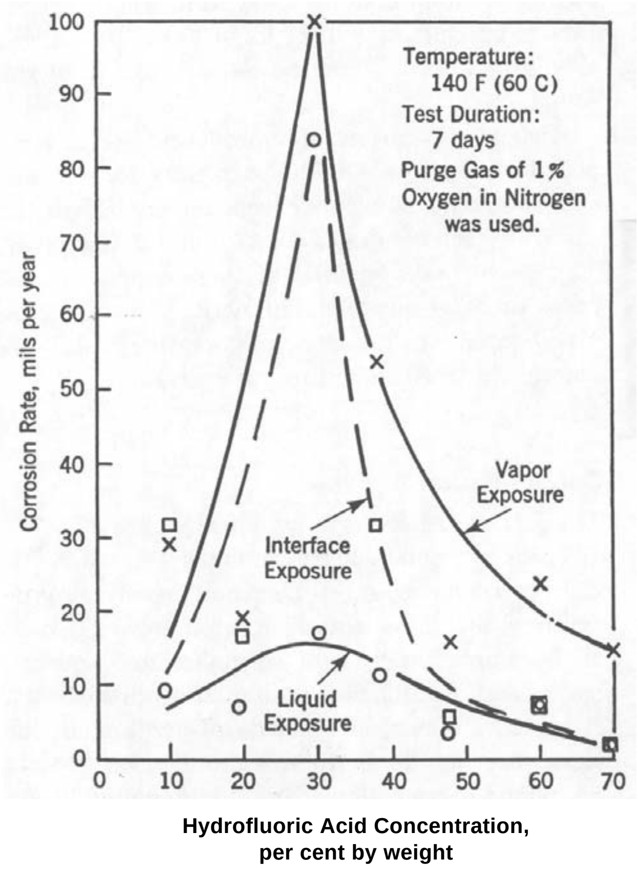


Fig. 2 – Effect of hydrofluoric acid concentration on corrosion of 70/30 copper-nickel alloy.

Nickel 200

Nickel 200 is not as resistant as Alloy 400 to aqueous hydrofluoric acid, either air-free or aerated. It has received less attention in corrosion studies, and quantitative data are less complete, Table 5. The presence of air or oxygen in aqueous solutions tends to accelerate the corrosion of Nickel 200 to a greater extent than Alloy 400, and the usefulness of Nickel 200 would appear to be limited to completely oxygen-free solutions at temperatures below 170 to 180 F (77 to 82 C). In tests in anhydrous hydrogen fluoride, Nickel 200 was resistant at 300 F (150 C), and is one of the more resistant materials for hot gaseous hydrogen fluoride (see discussion, page 13).

Nickel-Chromium Alloys

While corrosion test data is rather limited, the nickel-chromium alloys, typified by INCONEL alloy 600, are resistant to dilute aqueous solutions at ambient temperatures, or to essentially anhydrous hydrogen fluoride, but may be corroded at a significant rate in hot aqueous solutions. The presence of ferric salts in the acid is favorable to the performance of Alloy 600, Table 7. For hot gaseous hydrogen fluoride, Alloy 600 is one of the more resistant alloys (see discussion, page 13).

Table 7

Plant Corrosion Test in Impure 12% Hydrofluoric Acid

Media: Approximately 12% Hydrofluoric Acid.
0.2% Fluosilicic Acid.
1 g/l Ferric Oxide as Ferric Salts.

Process: Scrubbing of fluorine gas from a chemical process.

Test Duration: 7 Days.

Temperature: 182 F (83 C)

Material	Corrosion Rate, mils per year
MONEL alloy 400	12
Nickel 200	4
INCONEL alloy 600	9
Copper	13
Silicon Bronze	9
Stainless Type 302	160 (a)
Stainless Type 316	700 (a)
50% Ag–15% Cu–15.5% Zn–18% Cd Silver Solder	9
60% Ag–25% Cu–15% Zn Silver Solder	11
Pure Silver	0.5
Galvanic Couples of:	
MONEL alloy 400	8
to	
50% Ag Silver Solder	17
MONEL alloy 400	15
to	
60% Ag Silver Solder	6

(a) Specimens perforated by stress corrosion cracking at machined edges and letter code stamping. Corrosion rate only approximate, since pieces of specimen were lost as a result of cracking.

Chromium-Nickel Stainless Steels and Chromium-Nickel-Molybdenum-Iron Alloys

Laboratory corrosion test data for aqueous solutions of hydrofluoric acid are shown in Table 8. These data indicate that the family of chromium-nickel-iron alloys shown have rather limited re-

Table 8

Laboratory Tests of Nickel Stainless Steels and Cr-Ni-Mo-Fe Alloys in Aqueous Hydrofluoric Acid Solutions

No Aeration.

No Agitation (except for boiling tests).

HF, %	Temp, F	Test Duration, Days	Corrosion Rate, mils per year				
			Type 304	Type 316	Type 309Cb	CARPENTER Stainless No. 20	INCOLOY alloy 825
.05	140	10	12	–	10	–	–
0.1	140	10	25	–	27	–	–
0.15	140	10	47	–	44	–	–
0.2	140	10	62	–	54	–	–
10	60	30	0.4	<0.1	–	–	–
20	216	3	–	–	–	–	41
38	230	2	–	2000	–	–	–
38	Boiling	4	–	–	–	–	10
48	Boiling	4	–	–	–	–	9
50	140	35	–	–	–	–	2
65	140	35	–	–	–	–	5
70	140	35	–	–	–	–	5
70	70	42	–	49	–	15	14
90	40	0.2	35		–	–	–
90	70	1	30	–	–	–	–
90	70	1	11*	–	–	–	–
98	93-111	3.5	–	2	–	–	–

* Velocity of 0.4 to 1.45 ft/sec in test.

sistance to hydrofluoric acid solutions. They may resist dilute solutions or practically anhydrous acid at room temperature, but are not useful for service at higher temperatures.

In corrosion tests in plant process media involving hydrofluoric acid, as will be illustrated later in this bulletin, the stainless steels generally exhibit poor corrosion resistance in hot media. In certain circumstances, the molybdenum-containing alloys exhibit greater resistance than the molybdenum-free alloys.

Stainless steels may be subject to stress corrosion cracking by hot hydrofluoric acid solutions. In the tests shown in Table 7, specimens of Types 302 and 316 stainless steels suffered severe transgranular stress cracking at stamped identification marks and machined edges. In these media, general corrosion was also quite severe.

HASTELLOY Alloys

Laboratory corrosion data for the HASTELLOY alloys, shown in Tables 9 and 10, indicate that alloys B and D are probably the most versatile for temperatures above room temperature. The effect of oxygen on corrosion of these alloys is not indicated, except for HASTELLOY alloy C, Table 10, where aeration had a considerably greater accelerating effect in 50 per cent acid than in 65 per cent acid.

Table 9

Laboratory Tests of HASTELLOY Alloys in Aqueous Hydrofluoric Acid Solutions

HF, %	Temp, F	Test Duration, Days	Corrosion Rate, mils per year HASTELLOY alloys ...				
			B	C	D	F	N
5	Room	5	4	1	6	2	1.5
25	Room	5	5	5	6	12	3.0
40	Room	–	2.6	2.9	1	–	–
40	130	–	1	10	2.6	–	–
45	Room	5	3	6	4	15	4.6
50	Boiling	4	–	180	–	–	–
60	Room	–	1.6	3.6	2.4	–	–
65	Boiling	4	–	17	–	–	–
98	93 to 111	3.6	4	1	–	–	–

Table 10

Effect of Aeration on the Corrosion of HASTELLOY Alloy C

35-day tests, at 140 F (60 C)

HF, %	Atmosphere Over Solution	Corrosion Rate, mils per year	
		Liquid	Vapor
50	N_2 Purge	29	24
50	Air	180	66
65	N_2 Purge	8	10
65	Air	15	17

ILLIUM Alloys

ILLIUM "R" has shown reasonably good corrosion resistance in air-free acid in the tests of Braun, et al,[3] Table 11, but suffered accelerated attack when oxygen was present. Schussler[4] reported severe pitting and significant corrosion rates for ILLIUM "R" in both 5 per cent and 48 per cent acid, the attack being especially severe at liquid level in partial immersion tests.

ILLIUM "98" is being successfully used in the handling of hydrofluoric acid vapors and condensate as they occur in the production of hydrofluoric acid by reaction of sulfuric acid and fluorspar.

Table 11

Effect of Aeration on the Corrosion of ILLIUM "R"

35-day tests, at 140 F (60 C)

HF, %	Atmosphere Over Solution	Corrosion Rate, mils per year Liquid	 Vapor
50	N_2 Purge	9	3
50	Air	110	13
65	N_2 Purge	8	1
65	Air	41	13

• Corrosion by Liquid Fluorine

Fluorine is a very reactive element which, in the case of metals, combines to form the metal fluoride. At very low and moderate temperatures these fluoride films may be insoluble, adherent and protective, with the result that very low corrosion rates prevail.

At atmospheric pressure, fluorine is a liquid at –363 to –306 F (–220 to –188 C). Kleinberg and Tompkins[7] found that most of the common metals and alloys were highly resistant to liquid fluorine at these low temperatures so long as the metal system was free from organic contamination. Among the alloys which they evaluated were Nickel 200, MONEL alloy 400, Type 304 stainless steel, and ARMCO PH 15-7 Mo stainless steel. In 1-year tests in liquid fluorine at –320 F, Kleinberg and Tompkins obtained corrosion rates for these alloys of less than .01 mil per year. No significant differences in tensile properties of the alloys were observed between liquid fluorine and liquid nitrogen exposure for the 1-year period.

At room temperature, 86 F (30 C), these investigators observed that metallic fluoride films on these alloys developed to a thickness of 6 to 12 Angstrom units within an exposure period of about 200 min-

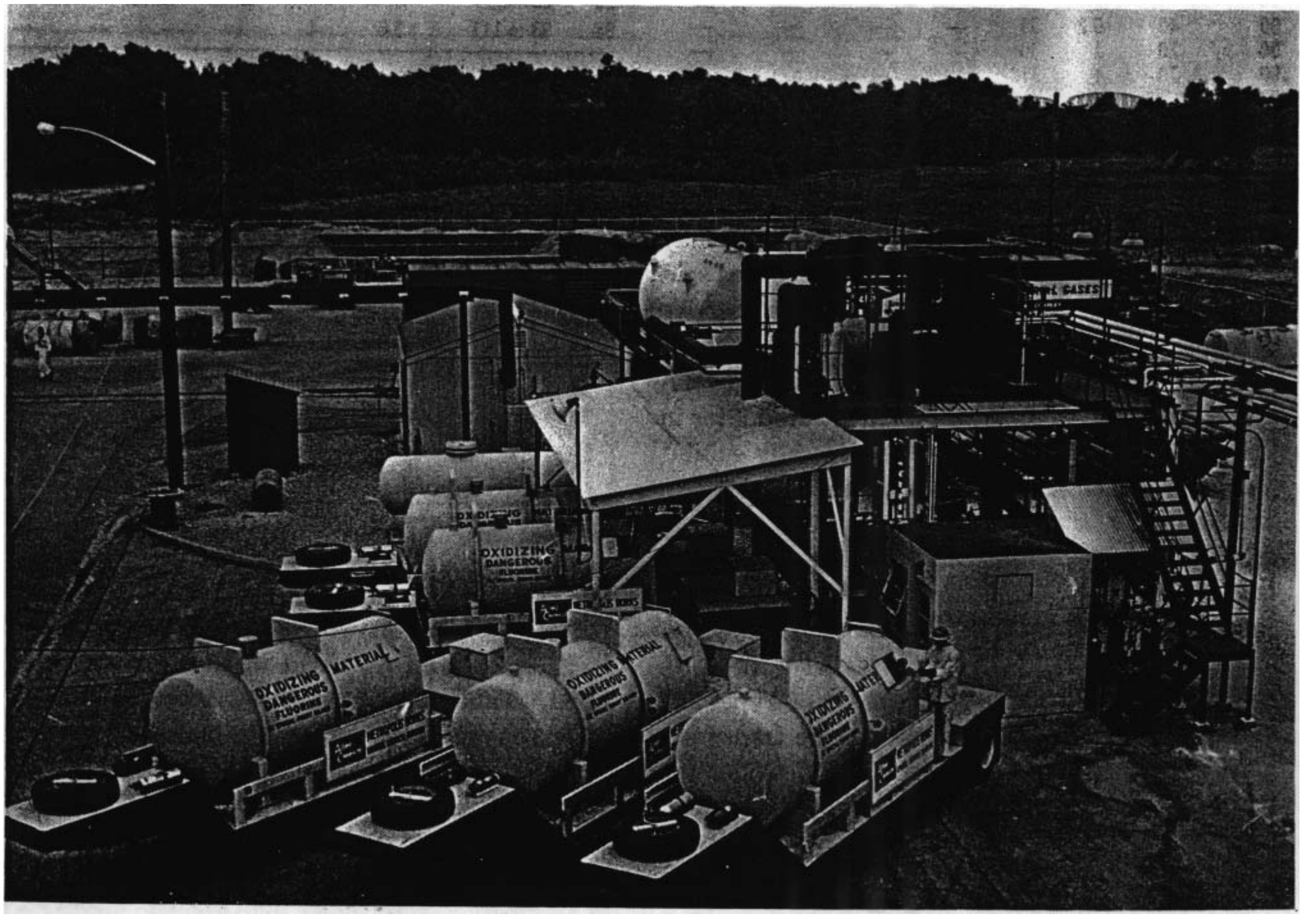


Fig. 3 – ICC-authorized tanks for bulk shipments of liquid fluorine. Each loss-free, Dewar-type tank consists of three concentric shells and heads. The highly corrosive fluorine is contained in an inner shell of nickel-copper alloy 400.

Courtesy of Allied Chemical Corporation.

utes, with practically no further reaction beyond this time. These investigators suggest exposure of metallic equipment to ambient temperature fluorine to develop a fluoride film as an advisable, though not required, pretreatment for liquid fluorine service.

Gundzik and Feiler[8] conducted tests with Nickel 200 and Types 321 and 347 stainless steel alternately exposed to liquid and gaseous fluorine over a 3½-month period. All three alloys were essentially unaffected by this exposure, and corrosion rates calculated from very minor weight changes were of the order of less than 0.03 mpy.

In the handling of liquid fluorine, there is concern that sudden impact or rupture may cause ignition of the metal container. Tests with dynamite cap explosions against tubes filled with liquid fluorine have failed to cause ignition of Nickel 200, Alloy 400, and Types 304, 347 and 316 stainless steels.

Tensile tests[10] to fracture in liquid fluorine have not caused ignition of AM 350, Types 301 and 304L stainless steels, nor INCONEL alloy X-750. Alloy 400 is being used for "Dewar-type" tanks for the transportation of liquid fluorine, as illustrated in Figure 3.

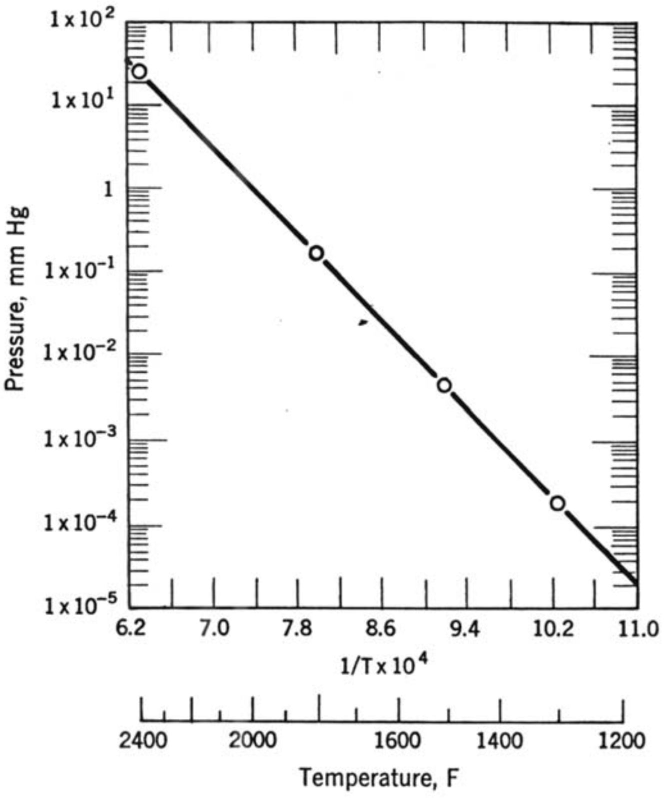


Fig. 4 – Vapor pressure of nickel fluoride.

• Corrosion by Hot Gaseous Fluorine

Nickel 200 and Alloy 400 have received considerable attention for applications involving contact with hot fluorine gas because of the formation on their surfaces of a dense nickel fluoride reaction product. The vapor pressure of nickel fluoride as a function of temperature, shown in Figure 4, would indicate that the fluoride film might offer considerable protection up to reasonably high temperatures.

Goodwin and Lorenzo[11] have reported the ignition temperature for nickel in fluorine as 2075 F (1135 C).

Steunenberg, et al,[12] conducting experiments with nickel in fluorine at temperatures of 570 to 1110 F (300 to 600 C) observed that at 570 and 750 F (300 and 400 C) a logarithmic reaction rate law governed; but at higher temperatures a parabolic reaction rate prevailed, Figure 5. Their work suggests that corrosion rates based on short-time exposures for a single time period may be much higher than rates based on long time exposure, especially at temperatures over 750 F (400 C).

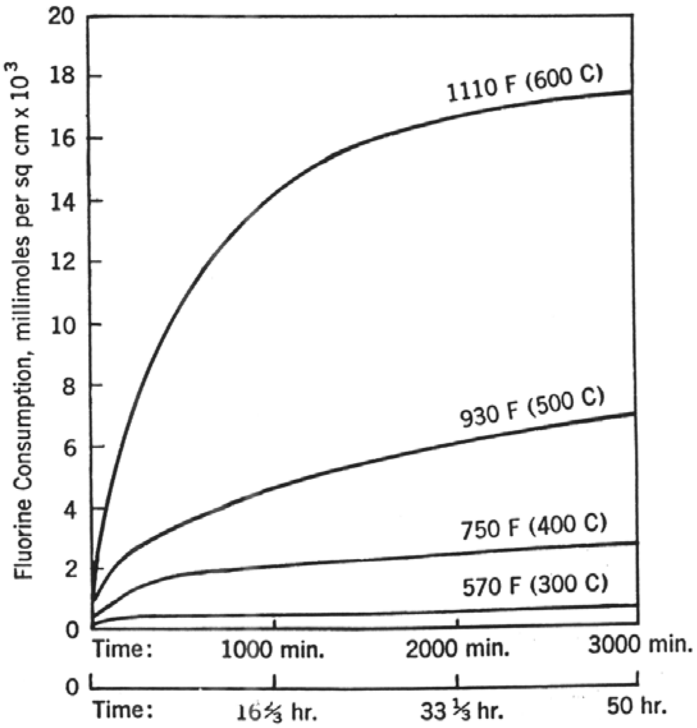


Fig. 5 – Consumption of fluorine by a nickel vessel–effect of time.

Jarry, Fischer, and Gunther[13] have studied the mechanism of the nickel-fluorine reaction at 1110 to 1300 F (600 to 700 C), at which temperature the parabolic rate prevails. Using radioactive marker experiments, they determined that the fluorine, rather than the nickel, migrates through the fluoride scale during the course of the reaction. Fluorine reaches the nickel surface either by gross movement through pores or cracks in the fluoride scale or by some transport process through the bulk of the scale. They reason that a mechanism involving fluorine transport through the scale is more probable in view of the parabolic reaction rate in this temperature range.

The determination of quantitative corrosion data in hot gaseous fluorine has, unfortunately, usually been limited to short test periods, which are likely to yield abnormally high rates for conditions where a parabolic reaction rate prevails. Data available from three studies are presented in Tables 12, 13 and 14, and should be interpreted more as guides than as quantitative values. Results shown in Table 12 are those of Myers and DeLong[14] for nickel-containing alloys in tests of 4 to 15 hours duration. The fluorine employed in their studies contained a small amount of oxygen, and it is possible that the reported results are higher than would prevail for oxygen-free fluorine. Data shown in Table 13 are from the work of Steindler and Vogel[15] for tests of from 4 to 6 hours duration, employing a commercial high purity fluorine supply (99.5 per cent or better). Their corrosion rates are based in one case on a calculation from weight gain, and in the second case from measured film thickness.

Data shown in Table 14 are from the studies of R. B. Jackson[16] for test periods of from 5 to 120 hours, and are based mainly on weight gained in the formation of fluoride films. Alloys showing very high rates of corrosion at higher temperatures suffered weight losses, indicating that the corrosion product films were not protective.

Jackson's studies indicate that Nickel 200 and Alloy 400 develop dense, uniform fluoride films, and have useful resistance to at least 1000 F (540 C). His work supports the reaction rate observations of Jarry, et al,[13] both at low and high temperatures. Increasing the pressure of the fluorine gas increased the corrosion rate of both Nickel 200 and Alloy 400 at 1000 F (540 C), but not at 700 F (370 C) or lower temperatures.

While the results of these three studies do not necessarily provide identical corrosion rates, they do indicate the acceptable corrosion resistance of both Nickel 200 and Alloy 400 to temperatures approaching 950 to 1000 F (510 to 540 C). Alloy 600, ILLIUM "R," and the nickel stainless steels would appear to be limited to much lower temperatures, as indicated by these results.

Table 12

Corrosion of Nickel-Containing Alloys by Fluorine

(Based on tests of 4 to 15 hours duration)

Temperature:	**F 392**	**482**	**572**	**662**	**752**	**842**	**932**	**1112**	**1202**	**1292**
	C 200	**250**	**300**	**350**	**400**	**450**	**500**	**600**	**650**	**700**
Material	**Corrosion Rate, mils per year**									
Nickel 200	–	–	–	–	8	23	60	350	190	410
MONEL alloy 400	–	–	–	–	6	18	24	720	960	1800
INCONEL alloy 600	–	–	–	–	455	1150	740	2000	1560	6000
Stainless Type 347	Nil	1740	2550	6200	9500	–	–	–	–	–
Stainless Type 309Cb	Nil	Nil	900	5500	8000	–	–	–	–	–
Stainless Type 310	Nil	Nil	370	4250	6750	–	–	–	–	–
Sheet Steel (.007% Si)	Nil	192	48	2.4	144	3600	–	–	–	–
SAE 1030 Sheet Steel (Trace Si)	24	96	108	Nil	180	6500	–	–	–	–
SAE 1020 Sheet Steel (0.22% Si)	455	5750	8000	1770	6500	18,000	–	–	–	–

As will be discussed later, in connection with the fluorination of uranium tetrafluoride to the hexafluoride, Alloy 400 has been a useful alloy for equipment operating at temperatures of 800 to 1000 F (430 to 540 C).

Table 13

Corrosion of Nickel-Containing Alloys by Fluorine (99.5% Pure Fluorine)

(Based on tests of 4 to 6 hours duration)

Temperature:	F 1020	1200	1380
	C 550	650	750
Material	Corrosion Rate, mils per year		
Nickel 200	4.4 (a)	59 (a) 314 (b)	353 (a) 816 (b)
MONEL alloy 400	–	41 (a)	2900 (a) 3500 (b)
INCONEL alloy 600	3200 (a) 4800 (b)	7100 (a) 6000 (b)	24,000 (a) 25,600 (b) 33,500 (c)

(a) Calculated from weight gain after exposure.
(b) Calculated from film thickness after exposure.
(c) Calculated from weight loss after exposure.

Table 14

Corrosion of Nickel-Containing Alloys by Gaseous Fluorine

Temperature:		F 80	400	700	1000
		C 27	204	370	538
Material	Exposure Time, hours	Corrosion Rate, mils per year			
MONEL alloy 400	5	2.4	0.5	1.9	29.8
	24	0.5	0.5	1.7	11.3
	24 (*)	–	0.7	2.4	21.3
	120	0.2	0.1	1.2	7.2
Nickel 200	5	1.0	3.3	1.7	24.5
	24	0.9	0.5	1.2	16.1
	24 (*)	–	0.3	0.5	44.5
	120	0	0.1	0.4	13.8
Stainless Type 304	5	1.7	6.1	1565	–
Stainless Type 304L	24	0.6	7.5	6018	–
	120	0	25.4	–	–
Stainless Type 347	5	2.7	4.0	4248	–
ILLIUM "R"	5	1.5	6.0	12.7	4038
INCONEL alloy 600	5	1.1	0.6	78.0	3451

All tests made In flowing gaseous fluorine, except (*) which were conducted In bombs at Initial pressure of 250 psi.

• Corrosion by Hot Gaseous Hydrogen Fluoride

Myers and DeLong's[14] work with fluorine was extended to include some studies of the effect of anhydrous hydrogen fluoride and a hydrogen fluoride-steam mixture at elevated temperatures. Their results for nickel-containing alloys are shown in Tables 15 and 16. Nickel 200, Alloy 400, and Alloy 600 all exhibit useful corrosion resistance in hot hydrogen fluoride to 1110 F (600 C), while the nickel stainless steels do not have suitable utility at 930 F (500 C), the lowest temperature for which data are available. Mixtures of hydrogen fluoride and steam did not adversely affect the corrosion behavior of Nickel 200 and Alloy 400, the only alloys included in this combined media.

Table 15

Corrosion of Nickel-Containing Alloys by Anhydrous Hydrogen Fluoride at Elevated Temperatures

Test Duration: 4 to 15 hours (estimated)

Temperature:	F 932	1022	1112
	C 500	550	600
Material	Corrosion Rate, mils per year		
Nickel 200	36	–	36
MONEL alloy 400	48	48	72
INCONEL alloy 600	60	–	60
Stainless Type 304	–	–	530
Stainless Type 347	7200	18,000	7000
Stainless Type 309Cb	230	1680	6600
Stainless Type 310	480	4000	12,000
SAE 1020 Steel	610	580	300

Table 16

Corrosion of Nickel 200 and MONEL alloy 400 in Hydrogen Fluoride-Steam Mixture at Elevated Temperatures

Test Duration: Variable from test to test, but between 4 and 15 hours

Temperature:	F 1022	1112	1202	1292	1382
	C 550	600	650	700	750
Material	Corrosion Rate, mils per year				
Nickel 200	31	72	108	144	120
MONEL alloy 400	–	24	60	156	204

As with hot fluorine, short time tests in gaseous hydrogen fluoride can yield inaccurate corrosion rates because of the parabolic reaction rates prevailing. The Myers and DeLong data are felt to be abnormally high in view of the short test periods employed. Data in Table 17, for tests of 36 hours duration, in the hydrofluorination of metal oxides, indicate considerably lower rates for the nickel base alloys, and the outstanding behavior of HASTELLOY alloy C and INCONEL alloy 600.

Table 17

Corrosion Tests in Hydrogen Fluoride Gas

Temperature: 930 to 1110 F (500 to 600 C)

Test Duration: 36 hours

7 lb HF per hour at 4 psig was passed through a laboratory furnace for hydrofluorination of metal oxides.

Material	Corrosion Rate, mils per year	Comments
HASTELLOY alloy C	0.3	Iridescent tarnish film
INCONEL alloy 600	0.7	Iridescent tarnish film
HASTELLOY alloy B	2	Black film
Nickel 200	9	Black film
Nickel 201	14	Black film
MONEL alloy 400	13	Adherent dark film
MONEL alloy K-500	16	Adherent dark film
70/30 Copper-Nickel	16	Adherent dark film

As will be noted later, INCONEL alloy 600 has been used almost universally in the hydrofluorination of uranium dioxide with hydrogen fluoride at temperatures of 900 to 1000 F (480 to 540 C) and of aluminum oxide at 700 to 1100 F (370 to 590 C).

Nickel 200 and 201, and Alloy 400 are subject to intergranular embrittlement by sulfur compounds at temperatures above about 600 F (316 C). Alloy 600 resists the deleterious effects of sulfur compounds to temperatures of 1000 to 1200 F (540 to 650 C), and is the preferred material when such compounds may be present.

• Hydrofluoric Acid Manufacture

Hydrofluoric acid is conventionally produced by the reaction of concentrated sulfuric acid with "acid grade" fluorspar, containing about 98 per cent calcium fluoride. The reaction unit, or generator, may be either a rotary kiln or a U-shaped covered trough equipped with a screw conveyor. The gaseous hydrogen fluoride, along with undesirable but unavoidable contaminants such as silicon tetrafluoride, and sulfur compounds, are condensed for further separation and purification. Granular calcium sulfate "anhydrite," the other reaction product, is discharged from the exit end of the kiln.

Little information has been disclosed by producers regarding materials of construction for the various steps in their processes. Carbon steel has been useful for rotary kiln construction, utilizing replaceable steel linings for the more severe corrosion zones. HASTELLOY alloy C has been successfully employed as a welded-in-place strip lining for the feed end of rotary kiln generators, and CARPENTER Stainless No. 20Cb for the lining of the exit end where the calcium sulfate is removed by screw conveyor or similar mechanism. Steel rails may be employed inside the generator, tumbling as the kiln rotates, to keep the reacting mass from agglomerating. This mechanical action, while beneficial to the process, can cause mechanical damage to the alloy linings.

One process for the production of anhydrous hydrofluoric acid, described by Rogers & Muller,[17] employs a special premixer, called a "Ko-kneader," which produces thorough mixing of the reactants and accelerates their subsequent reaction in the kiln. The wetted parts of the Ko-kneader have been constructed from a 35 per cent nickel, 15 per cent chromium, 4.5 per cent molybdenum alloy of European manufacture.

The hot gases leaving the kiln, consisting of hydrogen fluoride gas, entrained sulfuric acid, and silicon tetrafluoride, are severely corrosive. In recent years, cast piping of ILLIUM "98" has provided economical service in several plants. In the process of cleaning the kiln gases to remove the entrained solids and sulfuric acid, mixtures of sulfuric acid, hydrofluoric acid and water are encountered. In one plant, where sulfuric acid is the major constituent, and temperatures are of the order of 200 F (93 C), CARPENTER Stainless No. 20Cb has provided reasonable service in spite of a measurable corrosion rate.

Following the cleaning step, the gases are condensed to crude anhydrous hydrofluoric acid in carbon steel condensers. Residual hydrogen fluoride in the gases leaving these condensers is absorbed in concentrated sulfuric acid. At the ambient temperatures of this operation, carbon steel has a moderate corrosion rate, and both CARPENTER Stainless No. 20Cb-3 and Type 316 stainless have been found to be quite resistant and preferred for absorber construction.

The crude anhydrous hydrofluoric acid from the initial condensing step is double distilled to yield a high purity product. In the first distillation column the low boiling impurities, sulfur dioxide and silicon tetrafluoride, pass overhead and are returned to earlier process streams for recovery. This column and its reboiler can be of carbon steel.

In the second distillation column, the hydrogen fluoride is driven overhead, with the column "bottoms" consisting of a ternary mixture of hydrogen fluoride as the major constituent, sulfuric acid, and water. Carbon steel performs well for the upper portion of this column, MONEL alloy 400 being useful for the lower portion and the reboiler. The purified anhydrous hydrogen fluoride is condensed and stored in carbon steel equipment.

In one plant, a 70 per cent aqueous hydrofluoric acid grade is produced by mixing controlled quantities of anhydrous acid and water in a mother liquor of 70 per cent acid. Because the reaction is exothermic, cooling is required, and MONEL alloy 400 heat exchangers are employed for this part of the process equipment.

• Fluorine Production and Handling

For many years, fluorine was manufactured on a small scale as needed, and used immediately, because it was considered too difficult to keep in a pure condition. After 1940, however, the need arose for storing and transporting the gas in large quantities. It was found that the gaseous fluorine can be safely handled in cylinders of welded Nickel 200 or MONEL alloy 400 at pressures as high as 400 psi. This is possible because fluorine reacts only superficially with these metals, rapidly forming a thin and adherent coating of fluoride which protects the metal from further attack. Such a film also forms on brass, iron, aluminum, magnesium, and copper; hence, these metals are considered satisfactory for handling fluorine at room temperature.

One major fluorine producer suggests the following procedure as a surface pretreatment for flourine service:

"The corrosion resistance of all the materials of construction used with fluorine depends upon the formation of a passive fluoride film. Therefore, before any equipment, lines or fittings are put into service they must be thoroughly cleansed of all foreign matter, flushed with a non-aqueous degreasing and preliminary drying solvent such as acetone, trichloroethylene or carbon tetrachloride, thoroughly purged with a stream of dry nitrogen, and passivated. The passivating procedure consists of slowly displacing the dry nitrogen in the system by bleeding fluorine (at essentially atmospheric pressure, and at a nominal rate of 0.1 to 0.3 mol of fluorine per hour for laboratory-sized systems-greater for large systems) into the system. The displacement procedure is continued until a piece of filter paper or a swatch of cotton held close to the exit by means of long metal forceps begins to burn. The system is then valved off and the working pressure of fluorine is applied. After 5 to 10 minutes, passivation is assumed to be complete. The fluorine is then vented and the system is sealed until put into service.

"Passivation may also be achieved by the use of chlorine trifluoride in the manner described above for fluorine, with the additional step of purging and displacing the chlorine trifluoride with dry nitrogen prior to sealing off the system."

Electrolytic Cells and Electrodes

Gaseous fluorine is commonly produced by the electrolysis of anhydrous hydrogen fluoride from a molten bath of KF • 2HF. Extensive data on materials of construction of fluorine cells have been published. Experience has shown that economical and lasting electrolytic cells for fluorine generation at medium temperatures of 212 to 300 F (100 to 150 C) may be constructed with carbon anodes and an Alloy 400 container having a steel water-jacket. The advantages of Nickel 200 and Alloy 400 containers become even more pronounced in high temperature cells at 480 to 570 F (250 to 300 C).

The anode, as the place where the fluorine is deposited, is probably the most fertile source of cell difficulty. Much of the early work was done with Nickel 200 anodes; they have, therefore, received considerable study, and have revealed a number Of important advantages as well as defects. Nickel 200 anodes in cells operated at moderate temperatures have the advantages of eliminating polarization difficulties to which carbon anodes are occasionally prone. They can operate successfully in a wider range of temperature and hydrogen fluoride concentration than carbon anodes, and, being more rugged, are well suited to resist the occasional minor explosions that may be expected from a fluorine-producing cell. Another important consideration is that Nickel 200 anodes are not adversely affected by the presence of water in the electrolyte.

Nickel 200 does exhibit lower current efficiency than carbon, particularly at lower temperatures, and on being corroded produces a sludge which may tend to foul the electrolyte. Copper, iron, silver, magnesium, and Alloy 400 anodes have also been evaluated, but all were found to be less satisfactory than Nickel 200 at temperatures below 300 F (150 C).

While carbon anodes are widely used, they also have disadvantages in that they require anhydrous electrolyte and are reported to be subject to contamination by carbon fluorides which may cause swelling due to the formation of an interstitial compound of carbon monofluoride. Breakage rate can be high in the rugged environment of the fluorine cell, although this difficulty has been overcome to some extent by impregnation with copper. High current capability, power efficiency and electrolyte economy have been decisive factors in the adoption of carbon anodes in many fluorine production plants.

Since Nickel 200 anodes function well in wet electrolytes it is customary to start off with a few of them in cells of the latest design to eliminate water by a preliminary electrolysis. It has been said that without the development of the Nickel 200 anode-type of generator for large-scale use, the fluorine program in the United States would have been considerably delayed.

The cathodes, where hydrogen is formed, are often constructed of steel, sometimes the cell wall being used for this purpose. In German plants, silver cathodes and cell walls of magnesium have been used. MONEL alloy 400 screen diaphragms, gas-welded at the joints and silver-soldered into place, have proved very satisfactory for separating the anode and cathode cell compartments; such screens and skirts have been widely adopted. The electrolyte container and other cell hardware have also been constructed of MONEL alloy 400 with good results. In a notably safe and efficient 600-ampere cell operated at 530 F (275 C), serious difficulties due to sludge accumulations in the electrolyte were practically eliminated when Alloy 400 was adopted for all metal parts exposed to the hot melt.

Pumps, Piping and Cylinders

The fluorine gas is frequently compressed into a liquid by diaphragm pumps directly connected to the cells. In one experimental pump, Alloy 400 diaphragms (20 gauge and 13-inch diameter) and heads (3 ½-inch thick) were found to be in excellent condition after more than 500 hours of operation. On the strength of these favorable results, two additional pumps about 6 times as large were installed. Only occasional replacement of diaphragms was reported during 18 months of continuous operation.

Liquid fluorine may be stored in clean dry copper or steel cylinders. For maximum safety it is recommended, by some producers, that cylinders be made of Alloy 400 or Nickel 200, as it is difficult to ignite these metals under ordinary conditions.* One observer reports that Nickel 200 cylinders containing fluorine at pressures up to 20 atmospheres were not corroded after one year of use. (A superficial protecting layer of nickel fluoride was present on the surface.)

Valves

The maintenance of tight valves presents one of the most difficult problems in connection with the handling of fluorine. When the valve is operated there is an obvious tendency towards removal of protective films by abrasion, with resultant leakage across the seat and around the stuffing box. Nickel 200 and Alloy 400 are preferred for valve stems and seats because the film of fluoride formed on them is thin, adherent and protective. TEFLON is often used as a packing material for atmospheric or low-pressure use, and as a seat matched to Alloy 400 or Nickel 200 components.

At higher pressures, diaphragm and bellows-

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* A fire hazard exists with fluorine in the presence of water and grease which may be present as contaminants.

sealed valves, and needle valves of Alloy 400 packed with TEFLON or its equivalent are used. Nonmetallic seats or discs are not recommended by some authorities for high pressure use. Double valves are a wise precaution where it is imperative that leaks be prevented.

As a safety precaution when operating with pure fluorine at high pressures the valves should be equipped with extension handles passing through shields of concrete, brick or metal.

As an example of the seriousness of this potential problem, undetected slow leaks around defective packing have been known to ignite and destroy any kind of metal valve if conditions permitted the heat of reaction to accumulate up to the kindling point of the metal.

Disposal of Fluorine

The unique nature of fluorine operations frequently leaves considerable amounts of gas not completely used up in the process, plus an awkward disposal problem for the excess gas. For obvious reasons this highly reactive gas cannot be vented to the atmosphere. Excess fluorine must be disposed of completely by chemical reaction.

The well-known reaction with water suggests itself immediately as a simple way to convert fluorine to relatively harmless compounds, and this reaction has been investigated by a number of observers as a disposal method. Fluorine has two ways of dealing with water, even under conditions that are apparently identical. Fluorine sometimes burns quietly under water with a purple flame. At other times it reacts smoothly and more slowly without visible flame. Suddenly it may shift to the flame reaction, producing a violent explosion. Hence the reaction with water is not considered suitable. The reaction of fluorine with ordinary low-temperature steam has also been reported to be uncontrollable and subject to violent explosions.

Smiley and Schmitt[18] have reported that the disposal problem can be successfully solved by permitting preheated fluorine to react with superheated steam. By this method fluorine is converted to hydrogen fluoride without formation of potentially explosive by-products. This reaction at elevated temperature produces a large amount of heat, most of it in the vicinity of the fluorine/steam mixing nozzle.

MONEL alloy 400 has proven to be a suitable material of construction for the reactor nozzle, spray disposal tower, and particularly for the reactor chamber, where the gaseous hydrogen fluoride/ steam mixture prevails at elevated temperatures. Where elevated temperatures of approximately 750 F (400 C) exist in the fluorine preheater, Alloy 400 was chosen because of its good corrosion resistance to high temperature attack.

• Hydrofluoric Acid Alkylation Processes

Petroleum refineries employ the hydrofluoric acid alkylation process for increasing the octane value of gasoline. The essential feature of alkylation is the reaction of certain olefins from the cracking units with isobutane in the presence of hydrofluoric acid as a catalyst to form saturated branch chain hydrocarbons. The end product, known as alkylate, has very high antiknock properties. During World War II, alkylate was required as an addition to aviation gasoline, and subsequently became a common constituent of many motor fuels.

The most corrosive conditions in hydrofluoric acid alkylation plants normally exist in the acid-regeneration column and its preheater, and the acid-dehydrating column. As the alkylation process proceeds, the hydrofluoric acid gradually becomes contaminated with high-molecular-weight organic material and water which remain dissolved in the acid. A portion of the acid is continuously removed from the cycle, heated, and distilled from the organic material in the regeneration column. A portion of the overhead acid and water from the column goes to the dehydrating column where substantially anhydrous hydrogen fluoride is distilled overhead and the water removed from the bottom as a hydrofluoric acid solution of 38 to 45 per cent concentration.

In order to determine the performance of metals and alloys in these units under operating conditions, corrosion tests have been made in various parts of the regeneration equipment in three refineries. In one refinery tests were made in the top of the acid-regeneration column and in the inlet and outlet ends of the preheater. Tests were also made in the top of a hydrogen fluoride stripper tower. In a second refinery, tests were made in the top and bottom of the regeneration column. In the third

Table 18

Corrosion Tests in Hydrofluoric Acid Alkylation Plants

TEST CONDITIONS

Test 1: Inlet side of preheater channel. Liquid composition: 79 to 92 per cent HF, 0.8 to 2.5 per cent water, remainder isobutane and acid-soluble oil. Temperature: Avg. 120 F, max 135 F (avg. 49 C, max 57 C). Duration of test: 111 days.

Test 2: Outlet side of preheater channel. Composition same as Test 1. Temperature: Avg. 235 F, max 260 F (avg. 113 C, max 127 C). Duration of test: 111 days.

Test 3: Top of regeneration column just below vapor outlet. Composition: 90 to 95 per cent HF and 5 to 10 per cent isobutane. Acid phase: 90 to 95 per cent HF, 0.5 to 2.5 per cent water, 1.0 to 5.0 per cent oil. Temperature: Avg. 275 F, max 300 F (avg. 135 C, max 149 C). Pressure 120 to 150 psi. Duration of test: 70 days.

Test 4: Top of regeneration column. Composition: equal parts of 93 per cent HF and isobutane vapor. Temperature: Avg. 215 F, max 220 F (avg. 100 C, max 104 C). Duration of test: 49 days.

Test 5: Bottom of regeneration column in acid tar containing 1 to 10 per cent HF-Water in a 1:1 ratio. Average temperature: ,250 F (121 C). Duration of test: 49 days.

Test 6: Bottom of regeneration column. Feed to column contains 85.2 per cent HF, 1.6 per cent water and oils. Test made beneath grid plate of column. Feed 194 bbl. per day. Temperature: Avg. 220 F, max 250 F (avg. 104 C, max 121 C). Duration of test: 45 days.

Test 7: Bottom of dehydrator column beneath bottom plate. Feed contains 89.3 per cent HF, and 1.6 per cent water. Feed rate 15 bbl. per day. Temperature: Avg. 225 F, max 250 F (avg. 107 C, max 121 C). Duration of test: 45 days.

Test 8: Top of HF stripper column above top tray. Composition of vapor 10 per cent HF and 90 per cent light hydrocarbons. Temperature: Avg. 110 F, max 150 F (avg. 43 C, max 66 C). Duration of test: 117 days.

	Corrosion Rate, mils per year							
	Regenerator Preheater		Regenerator Column				Dehydrator Column	HF Stripper Column
Material	Inlet Plant A Test 1	Outlet Plant A Test 2	Top Plant A Test 3	Top Plant B Test 4	Bottom Plant B Test 5	Bottom Plant C Test 6	Bottom Plant C Test 7	Top Plant A Test 8
MONEL alloy 400	0.3	0.5	0.5	0.5	7.5	7.1	22	0.7
Nickel-Copper alloy 505	–	–	–	1.4	10	11	39	–
Nickel 200	1.1	3.5	13	14	11	18	68	0.7
INCONEL alloy 600	0.8	19	0.7	25	23	25	>130[1]	0.5
70/30 Copper-Nickel	1.1	6	0.7	5.3	21	–	–	1.3
Copper	19	>52[1]	>82[1]	>120[1]	>120[1]	>130[1]	>130[1]	3.4
Silicon Bronze	12	>50[1]	>79[1]	–	–	>120[1]	>120[1]	6.9
Stainless Type 302	–	–	–	>110[1]	36	–	–	–
Stainless Type 304	–	–	–	63[4]	45	11	>120[1]	–
Stainless Type 316	–	–	–	1	1.5	–	–	–
HASTELLOY alloy B	–	–	–	3	4	4.5	15	–
HASTELLOY alloy C	–	–	–	2	14	2.1	36	–
Mild Steel	27	>100[2]	>160[2]	200[5]	36[7]	150	>240[2]	18
DOWMETAL J	40	19	3	3[6]	14	3[8]	9[10]	0.2
Aluminum 1100	–	–	–	35	>120[1]	–	–	–
Chemical Lead	–	–	–	–	–	>130[9]	>130[9]	–
Brazing Alloy (60 Ag, 25 Cu, 15 Zn)	1.2	>26[3]	17[11]	–	–	–	–	1.6
Brazing Alloy (50 Ag,15 Cu, 15.5 Zn,18 Cd)	0.8	18[11]	19[11]	–	–	–	–	1.4

Legend:
> Greater than.
1. Completely corroded away. Original thickness 0.032 in.
2. Completely corroded away. Original thickness 0.062 In.
3. Completely corroded away. Original thickness 0.015 In.
4. Perforated by pitting. Original thickness 0.032 in.
5. Perforated by pitting. Original thickness 0.062 in.
6. Pitted to maximum depth of 0.002 In. during test.
7. Pitted to maximum depth of 0.008 in. during test.
8. Pitted to maximum depth of 0.006 In. during test.
9. Completely corroded away. Original thickness 0.032 In.
10. Pitted to maximum depth of 0.012 In. during test.
11. Specimens embrittled during test.

refinery, tests were made in the bottom of the regeneration column and in the bottom of the dehydration column. The results of these corrosion tests are given in Table 18. The operating conditions existing during each test are given as reported by the refineries in which the tests were made.

It will be noted that Alloy 400 exhibited optimum corrosion resistance in these plant tests. This alloy has found wide use for valves, valve trim, pumps, instruments, acid rerun fractionating columns, and in heat exchangers, where corrosive attack is especially severe. In the reboiler of the flash tower, where a mixture of acid, water, and oil is handled at 300 F (150 C), Alloy 400 tubes and clad steel shells are commonly employed.

Plant equipment experience for a 2500 barrels per day alkylation unit after approximately seven years of operation has been described in considerable detail by Forry and Schrage.[19] These authors cite specific uses of Alloy 400, as well as carbon steel, for vessels, exchangers, piping, heaters, pumps, valves, and instrumentation throughout a plant which was placed in operation in 1958.

A rather thorough treatment of corrosion experience at another refinery is given in Phillips Petroleum Company's book, "Hydrofluoric Acid Alkylation."[20]

• Uranium Refining

Hydrogen fluoride and fluorine have been useful reactants in the refining of uranium oxide concentrates to produce uranium hexafluoride. The fundamental steps involve hydrogen reduction of ore concentrates to UO_2, hydrofluorination of this oxide to UF_4 with hydrogen fluoride, and the fluorination of UF_4 to UF_6, the hexafluoride.

In one process for hydrofluorination of "brown oxide," UO_2 to UF_4 at elevated temperatures, presumably in the 900 to 1100 F (480 to 590 C) range, Meyer, et al,[21] cite the use of INCONEL alloy 600 for a series of horizontal reactors, equipped with HASTELLOY alloy C reactor screws which move the product through each reactor. Corrosion rates for INCONEL alloy 600 in this hydrofluorinator system, based on 80 days of plant operation, ranged from less than 0.1 mpy at the feed end to 0.3 mpy at the discharge end.

The production of uranium hexafluoride from ore concentrates by fluid bed refining techniques has been described by Ruch, et al.[22] The ore concentrate, primarily U_3O_8, is sized for optimum fluid bed processing and reduced to crude UO_2 by hydrogen in a Type 304 stainless steel reductor operating in the range of 1000 to 1200 F (530 to 650 C).

The hydrofluorination of the UO_2 to crude UF_4 is accomplished in two separate reactor stages operating in series. Anhydrous hydrogen fluoride is both the reactant and the fluidizing medium, and is fed to the bottom of the secondary reactor. These reactors, made of INCONEL alloy 600, operate at 900 to 1100 F (480 to 590 C). The UF_4 is then fluorinated to UF_6, using gaseous fluorine with calcium fluoride as the fluid bed. The fluorinator vessels, consisting of a main reaction vessel and several clean-up reactors on the exit gases, are all made of MONEL alloy 400, and operate in the 800 to 1000 F (480 to 530 C) range. The UF_6 is then condensed in primary cold traps and transferred to distillation equipment for separation of impurities. A low boiler fractionating column, operating at about 200 F (93 C) and 85 psia at the condenser, and a high boiler column, operating at 240 F (116 C) and 95 psia, are of MONEL alloy 400 construction. Corrosion tests in pilot plant distillation equipment indicated the following materials to be resistant in the order shown: Nickel 200 (0.2 mpy), Alloy 400, Alloy 600, copper, Type 304 stainless steel, and mild steel (3 mpy). UF_6 vapors were found to be more corrosive than the liquid.

Similar uses of INCONEL alloy 600 for fluid bed hydrofluorination of uranium dioxide to uranium tetrafluoride have been mentioned by Hawthorn,[23] Hueston,[24] and Levey, et a1.[25] Hawthorn also refers to the use of a MONEL alloy 400 distillation column for the recovery of aqueous hydrofluoric acid associated with the hydrofluorination equipment.

Heymann and Kelling[26] have reported results of corrosion studies of several materials in uranium hexafluoride at 176 F (80 C). These studies have indicated extremely low corrosion rates for Nickel 200, Alloy 400, and a 19 per cent chromium–11 per cent nickel stainless steel.

Piping for handling uranium hexafluoride at the Atomic Energy Commission gaseous diffusion plant at Portsmouth, Ohio,[27] has been of steel construction with 0.003- to 0.005-inch thickness of nickel plating.

• Glass Etching

Aqueous solutions of hydrofluoric acid, and solutions of ammonium bifluoride and sodium fluosilicate, are useful reagents for the etching of glassware. When using hydrofluoric acid, fluosilicic acid and fluosilicates are produced during the etching reaction.

MONEL alloy 400 has been commonly used for glass etching equipment in processes employing aqueous hydrofluoric acid solutions at room temperature. Results of spool tests in plant equipment, shown in Tables 19 and 20, indicate that usefully low corrosion rates prevail for Alloy 400, both immersed in the etching bath and in the vapors or spray chamber areas above the bath. It is recommended that the alloy be used in the stress-relieved condition to preclude the possibility of stress corrosion cracking, especially in the vapor phase.

In processes employing ammonium bifluoride for the etching reagent, corrosion of a number of nickel-containing alloys may be of considerable magnitude, as illustrated by the data in Table 21. The usefulness of Nickel 200 or Alloy 400 may be limited to components such as conveyor equipment where a dated life can be justified. Apparently, measurably good life can be expected for 70/30 copper-nickel equipment.

Table 19

Plant Corrosion Test Hydrofluoric Acid Etching of Glass Television Tubes

Media: 8% Hydrofluoric Acid with unknown amount of Fluosilicic Acid.

Test Duration: 120 days.

Temperature: Room.

Material	Corrosion Rate, mils per year		
	Test 1	Test 2	Test 3
	In Solution Tank	In Spray Chamber Above Solution Tank	In Fume Duct From Spray Chamber
MONEL alloy 400	4	5	4
ACI M-35 Nickel-Copper Alloy	2	3	–
Nickel-Copper alloy 505	2	4	–
Nickel 200	6 (a)	3 (15-mil pits)	7 (sl. pitting)
DURANICKEL alloy 301	7 (a)	6	7 (13-mil pits)
INCONEL alloy 600	6 (b)	9	7
Stainless Type 304	17 (c)	25	8
Stainless Type 316	13 (c)	9	3
ACI Type CN-7M	7 (d)	2	1
CARPENTER Stainless No. 20	6 (d)	2	1
WORTHITE	8 (d)	5	3
HASTELLOY alloy B	4	6	11

(a) Original thickness 0.031 in.; perforated by pitting on one edge.
(b) 0.028 In. maximum pitting.
(c) Corroded away at one edge; original thickness 0.031 in.
(d) Corrosion non-uniform, one area of specimen more severely attacked.

Table 20

Plant Corrosion Tests in Glass Etching Process

Test 1: Immersed in 40% hydrofluroric acid solution storage tank. 33 days.
Room temperature.

Test 2: In fume duct 8 ft above etching tank ahead of vent fan. 33 days.
Room temperature.

Test 3: In fume duct 24 ft above etching tank on exhaust side of vent fan. 68 days
Room temperature

Material	Corrosion Rate, mils per year		
	Test 1	Test 2	Test 3
MONEL alloy 400	3.1	<0.1	<0.1
Nickel 200	–	<0.1	<0.1
INCONEL alloy 600	–	<0.1	<0.1
Stainless Type 304	–	<0.1	<0.1
Copper	2.7	0.1	<0.1
Yellow Brass	7.2	0.2	0.1
Chemical Lead	2.5	1.0	1.0

Table 21

Plant Corrosion Tests in Process for Etching Glass Bulbs

Media: Ammonium Bifluoride 35.0%.
Sodium Fluosilicate 11.5%.

Test duration of 30 days at 60 to 80 F (16 to 27 C), immersed in etching solution during usage; no aeration or agitation.

Material	Corrosion Rate, mils per year
70/30 Copper-Nickel	5
Copper	22
MONEL alloy 400	29
Nickel 200	30
INCONEL alloy 600	22
Stainless Type 316	40
Stainless Type 302	165
Stainless Type 304	177
Ni-Resist(Type 1)	17
Cast Iron	586

Note: No pitting observed during test.

• Pickling of Cast Iron

One use of hydrofluoric acid is for the pickling of cast iron, particularly for the removal of casting mold sand from the iron surface. Results of corrosion tests, Table 22, in pickling baths operated at room temperature and at 170 F (77 C) illustrate the good corrosion resistance of Alloy 400 at both temperatures, and of several alloys at room temperature.

Table 22

Plant Corrosion Tests in 6% and 10% Hydrofluoric Acid Pickling Solutions

Test specimens immersed in pickling tanks used for pickling cast iron.

Material	Corrosion Rate, mils per year		
	6% HF Temperature: 170 F (77 C)		10% HF Temperature: Room
	Test 1 4-Day	Test 2 28-Day	Test 3 30-Day
MONEL alloy 400	0.8	0.2	<0.1
Nickel 200	350	(a)	<0.1
INCONEL alloy 600	63	68	<0.1
Stainless Type 304	1100	(a)	0.4
Stainless Type 316	–	–	<0.1
Ni-Resist (Type 1)	880	541	1.0
Cast Iron	(b)	(b)	220

(a) Specimens completely corroded away. Original thickness 0.032 in.
(b) Specimens completely corroded away. Original thickness 0.187 in.

Table 23

Laboratory Corrosion Test in Pickling Bath for Cast Iron

Media: Hydrofluoric Acid–5%
Sulfuric Acid–5%
Ferrous Sulfate–10%
Alternate immersion test of 40 hours, at 120 F (49 C).

Material	Corrosion Rate, mils per year
MONEL alloy 400	195
Nickel 200	79
INCONEL alloy 600	108
Stainless Type 304	393
Stainless Type 316	191
Carbon Steel	840

Some pickling baths contain about 5 per cent each of sulfuric acid and hydrofluoric acid, and are operated hot. Laboratory tests have indicated that such baths may be quite corrosive, especially if aerated, Table 23. These results indicate that users of such baths should conduct tests under their specific conditions of operation prior to selecting alloys for such service.

• Pickling of Special Steels

Sulfuric Acid-Hydrofluoric Acid Pickling Baths:
Hydrofluoric acid may be added to sulfuric acid to assist the pickling of special grades of steel, such as those of high silicon content. Corrosion tests conducted in one such bath in a pilot plant operation are shown in Table 24. In the absence of aeration, a number of high nickel alloys exhibited reasonably good resistance to general corrosion, although some suffered pitting attack and crevice corrosion. HASTELLOY alloy D, Alloy 400, 70/30 copper-nickel, and ILLIUM "G" and "R" alloys corroded uniformly, and at rates which would justify their use in this media. Most of the high nickel base alloys containing chromium, and the nickel-chromium-iron-molybdenum alloys, suffered pitting attack as well as evidence of stress accelerated corrosion in cold worked areas. Type 316 stainless was completely corroded away.

Nitric Acid-Hydrofluoric Acid Pickling Baths:
In the pickling of stainless steels and several chromium-containing nickel base alloys to remove hot rolling or hot forging scale, mixed acid baths of nitric acid and hydrofluoric acid are frequently employed. Such baths contain from 10 to 20 per cent nitric acid, and up to 3 to 5 per cent hydrofluoric acid. While it is customary to line the pickling tanks with non-metallic components, there are needs for metallic equipment such as pickling crates, baskets, and chain for the handling of the work in these operations. A limited amount of corrosion testing has been conducted in such baths, Table 25.

Many alloys which would be highly resistant to nitric acid solutions are severely corroded by the mixed acids. Alloys of high chromium and nickel contents appear to have the best corrosion resistance, as evidenced by the behavior of CORRONEL alloy 230 (36 per cent chromium), Type 329 stainless steel (28 per cent chromium), and Type 310 stainless steel (25 per cent chromium). The behavior of these alloys may be affected considerably by a slight increase in bath temperature. For example, in a bath of 10 per cent nitric acid, 2 per cent hydrofluoric acid, CORRONEL alloy 230 had a corrosion rate of 4 mpy at 149 F (65 C), and 11 mpy at 158 F (70 C). At 2 per cent hydrofluoric acid there is some indication that these baths may be considerably less corrosive, as shown in Test 3 of Table 25. At one stainless steel processing plant, a tank made of Type 316L stainless was found, after two years, to have lost little thickness handling a pickling bath of 10 to 12 per cent nitric acid, 1 to 2 per cent hydrofluoric acid at operating temperatures up to 135 F (57 C), whereas a second tank handling 15 per-cent nitric, 5 per cent hydrofluoric acid at 140 to 150 F (60 to 65 C) suffered a corrosion rate of about 65 mpy.

At another plant, INCOLOY alloy 825 was found to be quite serviceable in pickling crate service in a bath of 12 to 15 per cent nitric acid, 3 to 5 per cent hydrofluoric acid at 140 F (60 C). In a 428-day test under normal usage, involving alternate immersion and removal of the crates from the bath, INCOLOY alloy 825 pins corroded at a rate of 9 mpy, which is acceptable for this service. Neither INCOLOY alloy 800 nor INCONEL alloy 600 has been found to be as suitable in this service.

Nickel 200, Alloy 400, HASTELLOY alloy B, and the copper-nickels are all severely corroded by nitric acid, as well as the nitric acid-hydrofluoric acid mixtures, and should not be considered for these applications.

Table 24

Plant Corrosion Tests in Acid Pickling of Silicon-Containing Steel

Media: 25 to 35% Sulfuric Acid
4 to 8% Hydrofluoric Acid

31-day test, immersed in pilot pickling tub, no aeration, agitated by movement of steel strip through bath.

Temperature: 120 to 175 F, avg. 135 F (49 to 80 C, avg. 57C).

Material	Corrosion Rate, mils per year	Max Attack in Crevice, mils
ILLIUM "6"	5	None
ILLIUM "R"	6	None
HASTELLOY alloy D	6	None
MONEL alloy K-500	7	None
MONEL alloy 400	7	None
Chemical Lead	7	None
70/30 Copper-Nickel	8	None
HASTELLOY alloy C	4	2
HASTELLOY alloy N	4	15
HASTELLOY alloy B	4	10
INCONEL alloy 625	5	2
HASTELLOY alloy F	6	5
HASTELLOY alloy 6	6	8
INCOLOY alloy 825	6 (*)	13
CARPENTER Stainless No. 20Cb	7 (*)	11
CARPENTER Stainless No. 20Cb-3	7 (*)	22
ACI Type CN-7M	7	2
WORTHITE	11	5
ILLIUM "B"	25	–
CORRONEL alloy 230	111	–
Tantalum	>3500	Corroded away
Stainless Type 316	>7000	Corroded away

* Stress accelerated attack in the area of codes. Stress corrosion cracking did stamped not occur.

Table 25

Plant Corrosion Tests in Baths for Pickling Stainless Steels

Test 1: 15% Nitric Acid, 3% HF, by vol.
Test Duration: 4 days.
Temperature: 85 to 135 F, avg. 120 F (30 to 57 C, avg. 49 C).
Moderate aeration and little agitation.

Test 2: 20% Nitric Acid, 3% HF, by vol.
Test Duration: 2 days.
Temperature: 120 F (49 C)
Moderate agitation; no aeration.

Test 3: 10% Nitric Acid, 2% HF, by vol.
Test Duration: 23 days.
Temperature: 120 F (49 C).
Moderate agitation; no aeration.

	Corrosion Rate, mils per year		
Alloy	Test 1	Test 2	Test 3
CORRONEL alloy 230	8	–	–
Stainless Type 329	12	43	–
Stainless Type 310	21	–	–
CARPENTER Stainless No. 20	59	151	–
ACI Type CN-7M	66	–	<1
INCOLOY alloy 825	–	185	–
Stainless Type 309	161	–	–
Stainless Type 317	106	–	<1
Stainless Type 316	820	950	<1
Stainless Type 304	>3000	>2700	<1
Stainless Type 347	>3000	–	–
Stainless Type 321	>3000	–	–
HASTELLOY alloy F	43	–	–
HASTELLOY alloy X	56	–	–
HASTELLOY alloy C	123	380	5
ILLIUM "98"	104	–	–
INCOLOY alloy 800	140	–	–

• Compounds of Fluorine

Both hydrofluoric acid and fluorine are basic raw materials for the production of fluorine-containing compounds which find a wide range of commercial utilization. Their role in the production of uranium for nuclear fuel elements is probably their best known commercial application. Organic compounds containing fluorine have unique properties, and the possible compounds which may have future markets are almost limitless. Fluoboric acid, fluosilicic acid, salts of these acids, and other inorganic compounds are commercial products employed by industry.

Corrosion data available for these several compounds, obtained from laboratory tests or processes involving specific compounds are dealt with below.

Fluoboric Acid

Fluoboric acid, HBF_4, is generally produced by dissolving boric acid in hydrofluoric acid. Results of a corrosion test in a 32 per cent fluoboric acid solution storage tank, Table 26, indicate the relative corrosion behavior of a number of nickel-containing alloys. This acid is often present, along with substantial quantities of either lead or tin fluoborate, in plating baths for the electroplating of lead or tin. Results of corrosion tests in such plating baths are shown in Tables 27 and 28. Since avoidance of undesirable metallic contamination of plating baths is highly desirable, corrosion resistance criteria for bath-handling equipment may be more critical than for many other industrial applications. These corrosion test results indicate that HASTELLOY alloys B and C exhibit a high order of corrosion resistance.

Table 26

Plant Corrosion Test in Fluoboric Acid

Media: 32% HBF_4
1.5% H_3BO_4 (Boric Acid)
Balance: Water

Test Duration: 30 days. Temperature: Avg. 75 F (avg. 24 C).

No aeration; no agitation.

Test made in a storage tank, where solution was changed every other day.

Material	Corrosion Rate, mils per year	Maximum Pitting During Test, mils
MONEL alloy 400	1.2 and 3.5	None
Nickel 200	1.3	2
INCONEL alloy 600	1.3	3
70/30 Copper-Nickel	1.4	None
90/10 Copper-Nickel	1.6	None
Silicon Bronze	1.8	None
Stainless Type 304	4.4	6
Stainless Type 316	3.7	None
Stainless Type 309	2.3	5
Stainless Type 310	2.6	6
ACI Type CN-7M	2.0	–
HASTELLOY alloy B	1.0	–
Ni-Resist (Type 1)	7.6	–
Chemical Lead	24.0	–

Table 27

Plant Corrosion Test in Fluoboric Acid Plating Baths for Tin, Lead, and Antimony Plating

Test of 59 days duration during which separate plating baths were present for the plating of the above metals. In all baths 3.5 oz/gal each of boric acid and fluoboric acid were present, with appropriate amounts of eithertin, lead, or antimony fluoborate.

Temperature: 70 F (21 C). No aeration.

Material	Corrosion Rate, mils per year
MONEL alloy 400	0.7
Nickel 200	1.1
INCONEL alloy 600	1.2
INCOLOY alloy 825	1.0
Stainless Type 304	0.3
Stainless Type 316	0.3
HASTELLOY alloy B	<0.1
HASTELLOY alloy C	<0.1
70/30 Copper-Nickel	0.6
Ni-Resist (Type 1)	3.3

Table 28

Plant Corrosion Test in Tin Plating Bath

Media: 18% Stannous Fluoride
14% Fluoboric Acid
Small amounts of proprietary chemical additives.

365-day test, immersed in plating bath, at 125 F (52 C).

No aeration; agitation by constant solution recirculation.

Material	Corrosion Rate, mils per year
HASTELLOY alloy B	0.1
HASTELLOY alloy C	0.2
ILLIUM "R"	0.3
INCOLOY alloy 825	0.3
HASTELLOY alloy F	0.3
CARPENTER Stainless No. 20	0.3 (a)
INCONEL alloy 600	0.4 (b)
Stainless Type 316	1.0
Stainless Type 304	5.6

(a) Pitting to 1 mil depth In center crevice area.
(b) Pitting to 11 mil depth in center crevice area.

Fluosilicic Acid

Fluosilicic acid, H_2SiF_6, is readily formed by the reaction of silicon tetrafluoride with water, and is frequently encountered as a by-product either from hydrogen fluoride production or from the production of phosphoric acid by the acidulation of phosphate rock. The limited corrosion data that have been accumulated in fluosilicic acid from laboratory and plant tests are shown in Tables 29 to 34. While these data are not sufficient to permit extensive discussion regarding alloy behavior, they do indicate that several nickel-containing alloys may have useful corrosion resistance in the handling of this acid. In the absence of strongly oxidizing conditions, Alloy 400, Alloy 600, and HASTELLOY alloy C appear useful, whereas the austenitic stainless steels may suffer pitting attack.

Table 29

Laboratory Tests of MONEL alloy 400 in Fluosilicic Acid Solution

Test Duration: 96 hours. No aeration.

Acid Concentration, %		Temp, F	Corrosion Rate, mils per year
H_2SiF_6	HF		
10	0	75	3.7
10	30	75	2.4
20	0	75	2.4
20	30	75	2.2
30	0	75	1.1
35.2	0	75	1.5
22	0	175	15
22	2	175	9

Table 30

Plant Corrosion Test in Storage of Fluosilicic Acid and Sodium Fluosilicate

135 days in 6 to 9% H_2SiF_6 at 100 F (38 C).

28 days in saturated sodium fluosilicate at ambient temperature. Agitated with air.

Material	Corrosion Rate, mils per year
MONEL alloy 400	1.5
Nickel 200	1 (a)
INCONEL alloy 600	1
Chemical Lead	8.8
Stainless Type 304	1.7 (b)
Ni-Resist (Type 1)	6
Cast Iron	156

(a) Pitted to 2 mil depth.
(b) Pitted to 7 mil depth.

Fluosilicic acid, like hydrofluoric acid, may cause stress corrosion cracking of Alloy 400, and stress relieving is recommended for equipment for such service, especially if the media is aerated.

Sodium Fluosilicate

Results of corrosion tests, Table 35, in the making of sodium fluosilicate by the reaction of fluosilicic acid with sodium chloride, indicate useful corrosion resistance for HASTELLOY alloy B, Alloys 400 and 600, and Nickel 200.

Zinc Fluosilicate

Results of corrosion tests in the making of zinc fluosilicate at two different plants are shown in Table 36. The conditions in the crystallizer, Test 2, are apparently considerably more corrosive than those for Test 1, probably due to the greater degree of agitation and hydrochloric acid acidity prevailing. HASTELLOY alloy C shows superior corrosion resistance in both tests, and has been employed as evaporator tubing in the plant where Test 2 was conducted.

Table 31

Plant Corrosion Test in Fluosilicic Acid

49-day test in 12 to 13% fluosilicic acid plus undescribed impurities from wet process phosphoric acid.

Specimens exposed at two locations submerged in unfiltered acid storage tank, extensive aeration, but little agitation.

Temperature: 140 to 165 F (60 to 74 C).

Material	Corrosion Rate, mils per year
INCONEL alloy 625	0.5, 1.0
ILLIUM "98"	2 , 2
HASTELLOY alloy 6	1 , 3
HASTELLOY alloy F	2 , 7
INCOLOY alloy 825	2 , 6
HASTELLOY alloy C	5 , 7
CARPENTER Stainless No. 20 Cb-3	3 ,10
ILLIUM "G"	22 , 26
ILLIUM "R"	5 , 29
Stainless Type 317	5 , 27
ACI M-35 Nickel-Copper alloy	26 , 61
MONEL alloy 400	39 , 69
HASTELLOY alloy B	32 , 71
Stainless Type 316	40 , 78
Red Brass	42 , 91
Antimonial Lead	130 , >240 (*)

* Corroded away during test.

Table 32

Plant Corrosion Test in Fluosilicic Acid of 9 to 25% Concentration

90-day test, submerged in acid at 145 F (63 C), with some aeration and agitation.

Material	Corrosion Rate, mils per year	Pitting
MONEL alloy 400	2	None
Nickel 200	12	None
INCONEL alloy 600	1	None
Stainless Type 302	38	Severe pitting (*)
Stainless Type 316	6	Considerable pitting (*)
Mild Steel	>124	Corroded away

* Pit depth not determined.

Table 33

Plant Corrosion Test in 20% Fluosilicic Acid

28-day exposure in recycle tank of den fume scrubber.

Temperature: 130 to 140 F (54 to 60 C).

Extensive aeration. Flow at 0.5 ft/sec.

Material	Corrosion Rate, mils per year
ILLIUM "G"	3.4
CARPENTER Stainless No. 20	3.3 (*)
INCOLOY alloy 825	4.6
HASTELLOY alloy C	5.2
HASTELLOY alloy F	6.4
Stainless Type 316L	5.3
Stainless Type 317	4.9
Stainless Type 329	81.0

* 1 mil pitting during test.

Table 34

Plant Corrosion Test in 22% Fluosilicic Acid

Spool exposed for 94 days in fluosilicic acid weir box, at 120 to 182 F (49 to 83 C). No aeration, considerable flow.

Material	Corrosion Rate, mils per year
MONEL alloy 400	3
ACI M-35 Nickel-Copper alloy	3
Nickel 200	18
INCONEL alloy 600	5
Silicon Bronze	2
Stainless Type 316	2 (a)
Ni-Resist (Type 1)	5
Cast Iron	>3000 (b)

(a) 14 mil pitting, max.
(b) Corroded away during test.

Table 35

Plant Corrosion Test in the Manufacture of Sodium Fluosilicate

3.5% fluosilicic acid reacted with 4.7% sodium chloride precipitates out sodium fluosilicate, and a mother liquor of saturated sodium fluosilicate, with some sodium chloride and hydrochloric acid.

Test Duration: 35 Days.

Temperature: 80 F (27 C).

No aeration; some agitation.

Material	Corrosion Rate, mils per year	Pitting, mils
MONEL alloy 400	11	None
Nickel 200	10	None
INCONEL alloy 600	10	None
Stainless Type 302	3	10
Stainless Type 316	1	5
HASTELLOY alloy B	3	None
Chemical Lead	13	None
Ni-Resist (Type 3)	9	None
Cast Iron	116	None
Mild Steel	39	None

Table 36

Plant Corrosion Tests in Zinc Fluosilicate Production

Test 1: 30 to 36% by wt. zinc fluosilicate solution, plus 1 % free fluosilicic acid.

Temperature: 60 to 80 F (16 to 27 C); some agitation.

70-day test, immersed in neutralization tank.

Test 2: Concentrated zinc fluosilicate, plus 1% free fluosilicic acid and 0.5 to 1.0% HCI.

Temperature: 106 to 116 F (41 to 47 C).

22.4-day test, in a vacuum crystallizer; considerable agitation.

Material	Corrosion Rate, mils per year	
	Test 1	**Test 2**
HASTELLOY alloy C	0.3	0.1
ILLIUM "R"	–	7
HASTELLOY alloy B	–	83
NICKEL 200	5	111
MONEL alloy 400	5	160
INCONEL alloy 600	5 (a)	126
Stainless Type 316	1	9 (b)
Stainless Type 302	2.4 (a)	–
ACI Type CN-7M	–	12 (b)
CARPENTER Stainless No. 20	–	11 (c)

(a) Pitting to 4 mil max depth.
(b) Pitting to 20 mil max depth.
(c) Pitting to 17 mil max depth.

Table 37

Plant Corrosion Test in Production of Ammonium Bifluoride

Media: Essentially ammonium bifluoride, which varied from highly alkaline with ammonia to highly acid with HF. Impurities include small amounts of hydrofluosilicic acid, sulfuric acid, and traces of iron. Tank emptied and filled each working day. Over weekends, cold ammonium bifluoride mother liquor left in tank.

Temperature: Room temperature to boiling.

No aeration, but some agitation.

28-day test.

Material	Corrosion Rate, mils per year	Max Pitting During Test, mils
MONEL alloy 400	8	None
Nickel 200	14	7
INCONEL alloy 600	29	None
Stainless Type 304	77	None
Stainless Type 316	47	None
Ni-Resist (Type 1)	67	None
Cast Iron	124	None
Mild Steel	93	None
Copper	14	None
Lead	>214	*

* Specimens corroded away during test.

Table 38

Field Corrosion Tests in Ammonium Bifluoride Solutions

Test 1:15% solution. No aeration or agitation, 70 to 80 F (21 to 27 C).

33-day exposure.

Test 2: 10% solution. Moderate aeration, 77 F (25 C).

61-day exposure.

Test 3: 50% to anyhydrous. Solution heated to 390 F (200 C) to evaporate water, cooled to 77 F (25 C) and diluted.

Cycle repeated once a day for 10 days.

Material	Corrosion Rate, mils per year		
	Test 1	Test 2	Test 3
MONEL alloy 400	<0.1	–	7.7
Nickel 200	1		8.8
INCONEL alloy 600	1	2.2	8.7
Ni-Resist (Type 1)	6	11	–
Cast Iron	150	–	–
INCOLOY alloy 825	–	0.5	7.1
Stainless Type 316	–	10	–
HASTELLOY alloy F	–	4.6	–
CARPENTER Stainless No. 20	–	1.3	–
HASTELLOY alloy C	–	1.1	8.4
Stainless Type 304	–	11	–
ACI Type CN-7M	–	–	9.6

• Inorganic Fluorides

Limited corrosion data and reference to alloy uses with fluoride salts have been accumulated either through laboratory and plant corrosion tests or proven satisfactory use in service. Such information as is available is presented in the following discussion and tabular data.

Aluminum Fluoride

The electrolytic refining of aluminum requires aluminum fluoride, AlF_3, as a constituent of the electrolyte. Since insufficient quantities of aluminum fluoride occur naturally, it must be produced by one or more chemical means. One process employs the hydrofluorination of aluminum oxide, or hydroxide, at temperatures of 750 to 1100 F (400 to 600 C). One plant employing this process uses INCONEL alloy 600 for a fluid bed reactor. After four years of continuous operation this equipment has provided trouble-free service from a corrosion resistance standpoint.*

Ammonium Bifluoride

Ammonium bifluoride is made either by directly reacting ammonia and hydrogen fluoride in gaseous form and cooling the reactant to form the solid product, or by reacting the two constituents in an aqueous media. Results of a corrosion test in the latter process, Table 37, indicate the usefulness of Alloy 400 for this reaction. Results of other tests in aqueous solutions of the bifluoride are shown in Table 38. Ammonium bifluoride, along with hydrofluoric acid, is used for etching or frosting of glass, as mentioned earlier in this bulletin.

Boron Trifluoride

In the anhydrous liquid, Table 39, corrosion rates for Alloy 400, Alloy 600, and Types 304 and 316 stainless steels are usefully low at 300 to 400 F (150 to 200 C). Boron trifluoride is frequently used as a catalyst for organic reactions, often as an ether complex. Results of plant tests involving its use in the polymerization of organics are shown in Tables 40 and 41. Under the conditions prevailing in Table 40, it is presumed that the presence of water caused some hydrolysis to hydrofluoric acid, which,

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* Private communication.

along with the aeration prevailing, caused substantial corrosion of Nickel 200, Alloy 400 and carbon steel. Under the conditions prevailing in Table 41, moisture was not reported, and most of the alloys exposed demonstrated satisfactory corrosion resistance. In the use of boron trifluoride for catalytic functions, alloy evaluation under the specific conditions prevailing is indicated.

Boron-10 has a valuable place in the atomic energy program as a good neutron absorber. It is used in reactor shielding and in control instruments. In preparation, dimethyl ether is first reacted with boron trifluoride to form a complex. The next step is to separate the two isotopes of boron. The complex is introduced into six, fractionation columns which are connected to work as a single unit. B-10 tends to concentrate in the liquid phase, while the B-11 concentrates in the vapor phase. The columns are filled with Cannon protruded packing. From the point where boron trifluoride enters the system, the tanks, columns, column packing, reboilers, condensers, and pumps are practically all made of MONEL alloy 400.

Table 39

Plant Corrosion Test in Boron Trifluoride

Media: Essentially anhydrous boron trifluoride at 300 to 400 F (150 to 204 C).

155 days exposure.

Specimens exposed in shell of a condenser, under wash by condensing liquid.

Material	Corrosion Rate, mils per year
Nickel 200	8*
MONEL alloy 400	1.3
INCONEL alloy 600	<0.1
Stainless Type 304	<0.1
Stainless Type 316	<0.1
Carbon Steel	29

* Pitting to 19 mil max depth during test.

Table 40

Plant Test in Polymerization Reaction with Boron Trifluoride Catalyst

Media: Polymerization of cresols with boron trifluoride. Also present were aromatic solvents and traces of water.

Temperature: 203 F (95 C).

Test Period: 15 days.
Violent agitation.
Moderate aeration.

Material	Corrosion Rate, mils per year
MONEL alloy 400	48
Nickel 200	65
INCONEL alloy 600	2
Stainless Type 304	1.3
Stainless Type 316	1.1
CARPENTER Stainless No. 20	1.2
INCOLOY alloy 825	1.1
Mild Steel	185

The next step is to combine the B-10 enriched complex with a potassium fluoride-ethyl alcohol-water mixture to form potassium fluoborate salt. The reaction occurs in a Nickel 200 kettle and the salt is filtered and dried in MONEL alloy 400 equipment. The final step is the electrolysis of the fluoborate salt in a cell at 1400 F (760 C). The anode of the cell is a carbon pot surrounded by a heat resistant INCONEL alloy 600 shell. The cathode is a MONEL alloy 400 pipe on which the elemental boron deposits. Alloy 400 has been found to last ten times as long as other materials used in this service. It maintains a clean surface so the product can be easily removed. The boron is ground, washed with water, then with acid, dried and packed in cans. Alloy 400 equipment is used in the water wash.

Table 41

Field Tests in Polymerization of Several Hydrocarbon Compounds with Boron Trifluoride Catalyst

Test Duration: 162 days.

	Corrosion Rate, mils per year	
	Test 1	Test 2
Material	40 to 115 F (4 to 46 C) Moderate Aeration, Pump Circulation Liquid	60 to 100 F (15 to 38 C) Extensive Aeration Vapor
MONEL alloy 400	2.5	1.4
Nickel 200	2.0	1.3
70/30 Copper-Nickel	4.1	1.0
Ni-Resist (Type 1)	3.7	1.5
Cast Iron	3.7	5.0
Steel	3.2	2.0
Stainless Type 304	1.0	<0.1
Stainless Type 316	0.1	<0.1
INCONEL alloy 600	1.2	0.5
INCOLOY alloy 825	0.3	0.1
HASTELLOY alloy C	<0.1	<0.1

Oxygen-Fluoride Compounds

Oxygen difluoride (OF_2) has been of interest as a possible oxidizer for spacecraft propulsion. Ozone difluoride (O_3F_2), when dissolved at low concentrations in liquid oxygen, may also find applications in the same field. Compatibility studies of several materials with these compounds have been reported by Tiner, et al.[28] Corrosion data for nickel-containing alloys included in these studies, shown in Table 42, indicate that at the low temperatures prevailing, these alloys all exhibit a very high level of corrosion resistance. Stress corrosion tests and impact sensitivity tests indicated no adverse effects for any of the nickel-containing alloys.

Table 42

Alloys Evaluated in Oxygen-Fluoride Liquid Oxidizers

	Corrosion Rate, mils per year		
	Oxygen Difluoride	**Ozone Difluoride Liquid Oxygen**	
	at -110 F (-79 C) 21-day	**at -320 F (-196 C) 12-month**	
Material	Liquid	Liquid	Vapor
Nickel 200	.01	.001	.001
MONEL alloy 400	.02	.001	.001
INCONEL alloy X-750	.06	Nil	.001
90/10 Copper-Nickel	.01	.001	.001
60/40 Copper-Nickel	.01	.001	Nil
Stainless Type 301	.01	.002	Nil
Stainless Type 316	.01	.002	.001
Stainless Type 347	Nil	.001	.001
PH 15-7 Mo Stainless	.01	.001	Nil
AM 350 Stainless	Nil	.002	Nil
AM 355 Stainless	.01	Not Tested	
RENÉ 41	.05	.001	Nil

Sodium Fluoride

MONEL alloy 400 has been used for the drying of sodium fluoride crystals. A corrosion test of 336-hours, wherein specimens were attached to a rake in the dryer at 200 F (93 C), indicated a corrosion rate of 6 mpy for MONEL alloy 400.

Sodium Acid Fluoride NaF-HF

The production of sodium acid fluoride from soda ash by reaction with excess hydrofluoric acid may be rather corrosive to many alloys, as indicated by the data in Table 43, Test 1. Aeration of the reaction, while not specifically indicated in this test, is suspected as the accelerating factor in the corrosion of Alloy 400 and the copper-nickel alloys. The reacted salt solution, even with aeration, was found to be considerably less corrosive, as indicated by the data for Test 2.

Table 43

Plant Corrosion Tests in Sodium Acid Fluoride

Test 1: Saturated solution containing 85 grams per liter of sodium acid fluoride and 30 grams per liter of hydrofluoric acid, plus crystalline sodium acid fluoride.30-day test in reaction tank, 175 F (80 C); some liquid flow, and some air entrainment in process.

Test 2: Solution of 38 grams per liter of sodium acid fluoride, plus some crystals. 30-day test in solution holding tank, 50 F (10 C). Air agitation.

	Corrosion Rate, mils per year	
Material	**Test 1**	**Test 2**
MONEL alloy 400	69	4
Nickel-Copper alloy 505	40	–
Nickel 200	88	20*
INCONEL alloy 600	118	13
70/30 Copper-Nickel	111	–
80/20 Copper-Nickel	–	9
90/10 Copper-Nickel	128	–
HASTELLOY alloy B	85	–
HASTELLOY alloy C	25	–
HASTELLOY alloy D	89	–
Stainless Type 304	70	2
Stainless Type 316	43	1
Stainless Type 309	44	–
Stainless Type 310	74	–
ACI Type CN-7M	32	–
WORTHITE	30	–
ILLIUM "G"	35	–
Ni-Resist (Type 1)	273	27
Chemical Lead	10	3

* Perforated at spacer.

Stannous Fluoride

Stannous fluoride, which finds commercial usage as an additive to toothpaste for the prevention of decalcification of teeth, is made by reacting stannous oxide with hydrofluoric acid. Corrosion tests, Table 44, in the crystallization of the reacted salt, indicate that the salt is probably not corrosive, but that the corrosion observed was due to the residual hydrofluoric acid present in the crystallizing media.

Table 44

Plant Test in Crystallization of Stannous Fluoride

Media: 30 to 50% stannous fluoride.
2 to 7% hydrofluoric acid.

Test of 30 days duration, submerged in solution, aerated and agitated.

Temperature: 80 to 210 F (27 to 99 C)

Material	Corrosion Rate, mils per year
HASTELLOY alloy C	3
CARPENTER Stainless No. 20	3.4 (a)
INCOLOY alloy 825	4
HASTELLOY alloy B	5
Nickel 200	6 (b)
MONEL alloy 400	6

(a) Incipient pitting.
(b) Pitting to 2 mil depth.

Other Metal Fluorides

The results of laboratory corrosion tests in hot concentrated solutions of several other metal fluorides are shown in Table 45. The copper fluoride solution was found to be more corrosive than the others. Silver demonstrated very good corrosion resistance in all baths. 70/30 copper-nickel, copper, and Alloy 400 would be expected to perform well in barium fluoride solutions, whereas 70/30 copper-nickel would be preferred in handling copper fluoride. Alloy 400 is shown to be superior in handling both chromium fluoride and potassium-titanium fluoride under the indicated conditions. Alloy 400 has been employed for dryers in the conversion of these concentrated liquors to solid dry product.

• Halogen Fluorides

The liquid compounds, bromine trifluoride, bromine pentafluoride and chlorine trifluoride are used as intermediates for fluorination of other compounds, especially organic compounds. They are readily made by mixing fluorine and the other halogen constituent in appropriate proportions and reacting at 390 to 570 F (200 to 300 C). Nickel 200 has been employed for such reactors. The gaseous reaction product is condensed in refrigerated nickel condensers. Receiver and shipping cylinders may be of mild steel.

Chlorine monofluoride, while not of major industrial use as yet, is conveniently prepared by reacting chlorine and chlorine trifluoride in a Nickel 200 reactor at 750 to 930 F (400 to 500 C). This product has potentialities as a special fluorinating agent for organic compounds.

Bromine Trifluoride

In recent years there has been interest in the possible use of bromine trifluoride for the separation of uranium and fission products from spent fuels of nuclear reactors. Results of static laboratory corrosion tests[29] in bromine trifluoride and a mixture of uranium hexafluoride and bromine trifluoride, shown in Tables 46 and 47, suggest that Nickel 200, Alloy 400, Alloy K-500, and Alloy 600 all exhibit a high order of corrosion resistance to these media. Alloy 800, chromium-nickel stainless steel, and steel had measurable, but possibly useful, corrosion rates in these media. Strickland, et al,[30] have described

Table 45

Laboratory Corrosion Tests in Concentrated Solutions of Metallic Fluorides

Temperature: 185 F (85 C). Test Duration: 7 days. No aeration, or agitation.

	Corrosion Rate, mils per year							
	Barium Fluoride		Copper Fluoride		Chromium Fluoride		Potassium-Titanium Fluoride	
Material	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
MONEL alloy 400	5.3	0	30	9	7	3.4	2.5	0
70/30 Copper-Nickel	3.3	0.2	1.4*	4.5	27	17	21	0
Copper	3.4	0.2	18	0.5	18	31	25	0
Silver	0.2	0.1	0	0	0.2	0	0.2	0
Stainless Type 304	–	–	150* (P)	23	–	–	–	–
Stainless Type 316	–	–	260* (P)	43	–	–	–	–
CARPENTER Stainless No. 20	–	–	110	27	–	–	–	–

* Coated with copper fluoride after test. (P) Pitted.

operation of a pilot plant for fluorination of spent uranium fuel elements using bromine trifluoride, in which MONEL alloy 400 was used for process equipment and piping, and nickel as porous filter elements and tower packing.

Table 46

Laboratory Corrosion Tests in Bromine Trifluoride

Tests conducted in nickel boiler equipped with air-cooled reflux condensers.

	Corrosion Rate, mils per year			
	Test 1 650 hours 158 F (70 C)	Test 2 20 weeks 257 F (125 C)		
Material	**Liquid**	**Liquid**	**Vapor**	**At Inter-face**
Nickel 200	.04	No loss	No loss	No loss
Nickel 200, Welded	.02	No loss	No loss	No loss
MONEL alloy 400	0.1	<.01	No loss	No loss
MONEL alloy 400, Welded	0.1	<.01	No loss	No loss
MONEL alloy K-500	0.2	<.01	<.01	<.01
INCONEL alloy 600	.08	.03	<.01	.01
DURANICKEL alloy 301 (a)	Not tested	0.3	0.1	0.3
INCOLOY alloy 800 (a)	Not tested	3.6	1.3	3.2
Stainless Type 304 (b)	Not tested	3.4	2.8	3.6
Carbon Steel (b)	Not tested	7.8	4.9	7.7

(a) In test 4 weeks.
(b) In test 1 week.

Table 47

Laboratory Corrosion Data

Media: 10% uranium hexafluoride
90% bromine trifluoride

Temperature: 257 F (125 C)

Tests conducted in nickel boilers equipped with air-cooled reflux condensers.

		Corrosion Rate, mils per year		
Material	**Test Period, Weeks**	**Liquid**	**Vapor**	**At Inter-face**
Nickel 200	11	.01	.01	.02
Nickel 200, Welded	11	<.01	<.01	No loss
MONEL alloy 400	11	0	.04	<.01
MONEL alloy 400, Welded	11	0	<.01	<.01
MONEL alloy K-500	11	<.01	<.01	<.01
INCONEL alloy 600	11	.02	.02	.01
DURANICKEL alloy 301	4	<.01	.05	.02
INCOLOY alloy 800	4	2.5	0.7	1.2
Stainless Type 304	4	4.1	2.5	2.9
Stainless Type 347	1	5.8	2.4	3.3
Mild Steel	1	9.0	6.8	5.2

Mecham, et al ,[31] have reported on the operation of a pilot plant for the decontamination of irradiated uranium by a fluoride volatility process. MONEL alloy 400 and Nickel 200 were employed for the equipment, and corrosion studies in the dissolver were made for 600 hours in the halogen medium, results of which are shown in Table 48. The process involved several steps, as follows:

Step I:
Dissolution of the aluminum cladding on the uranium slugs in aqueous caustic.

Step II:
Bromine trifluoride dissolution, at 250 F (120 C) and 2 atmospheres pressure. Because the solution was recycled, it also contained a few per cent of uranium hexafluoride and bromine pentafluoride.

Step III:
Bromine produced in the solution was regenerated by adding fluorine gas, at room temperature.

Step IV:
Fractionation of the dissolver solution leaving the dry residue of nonvolatile fission products, which are then washed away with aqueous aluminum nitrate wash.

Table 48

Corrosion of Nickel 200, MONEL alloy 400 and INCONEL alloy 600 in Volatile Fluoride Pilot Plant Dissolver*

Material	Penetration, mils	Comments
Submerged in Liquid		
MONEL alloy 400	0.7 to 0.8	No pitting.
Nickel 200	0.6 to 1.0	Some minute pits.
MONEL alloy 400 Nickel 200, Welded	0.7	Small scattered pits.
INCONEL alloy 600	2.7 to 2.8	General attack, pitting.
INCONEL alloy 600, Welded	8.9	Attacked and pitted, particularly the edges.
Exposed to Vapor		
MONEL alloy 400	0.3 to 0.4	Good appearance.
Nickel 200	0.3 to 0.4	Good appearance.
MONEL alloy 400–Nickel 200, Welded	0.3	Good appearance.
INCONEL alloy 600	6.7 to 7.9	Severe attack; edges pitted.
INCONEL alloy 600, Welded	5.8	Attacked and pitted; weld thinned.

• 600 hours in halogen medium 60 to 320 F (15 to 160 C)
25 hours in aqueous wash and decanting medium 60 to 140 F (15 to 60 C)

Table 49

Alloys Having Favorable Resistance to Chlorine Trifluoride, Perchlorylfluorine, and 3 to 1 Mixture of These

MONEL alloy 400
Nickel 200
Stainless Type 347
ARMCO PH 15-7 Mo Stainless (Cond. RH 1050)
AM 350 Stainless (SCT-850)

Table 50

Laboratory Corrosion Tests in Wet Perchloryl Fluoride

Test Duration: 21-day; liquid and vapor exposures.

Temperature: 86 F (30 C).

Corrosion Rate, mils per year			Comments
Material	**Liquid**	**Vapor**	L=Liquid V-Vapor
MONEL alloy 400	3.8 (a)	6.2 (a)	L: General etch and few shallow pits. V: Severe pitting and etching.
Nickel 200	2.4 (a)	1.1 (a)	L: Etch and fine pitting. V: Smaller area of etch and pitting.
INCONEL alloy 600	0.9	0.4	L and V: Scattered deep pinpoint pits.
INCOLOY alloy 800	0.4	.01	L: A few pits; one specimen only. V: Unchanged.
INCOLOY alloy 825	.05	.04	L and V: Unchanged.
ILLIUM "6" alloy	0.4	0.2	L and V: Unchanged.
ILLIUM "98" alloy	1.7	0.3	L and V: Fine etch.
ILLIUM "R" alloy	0.2	0.2	L and V: Ripple etch at one edge.
HASTELLOY alloy C, Wrought	1.9	1.6	L and V: Satin smooth.
HASTELLOY alloy C, Cast	0.1	0.2	L and V: Several fine shallow pits.
70/30 Copper-Nickel	2.2	2.2	L: Light scattered etch.
18% Nickel Silver	11.4	5.5	L and V: Shallow pitting at support and general etch.
Stainless Type 304	0.6	4.0	L: A few crater-like pits at support hole. V: As for L, but more severe.
Stainless Type 316	0.4	2.1	L: Pitting and etch at support hole. V: As for L, but more severe.
Stainless Type 347	2.7	7.7	L and V: Crater-like pits at support hole.
CARPENTER Stainless No. 20Cb	0.1	0.5	L and V: One or two pits at support hole.
Low Carbon Steel	8.5 (a)	13.3 (a)	L and V: Etched and pitted over all.

(a) Water content of perchloryl fluoride = 0.2%
For all other tests, water content = 1%

Chlorine Trifluoride and Perchloryl Fluoride

Chlorine trifluoride, ClF_3, perchloryl fluoride, ClO_3F, and a 3 to 1 mixture of the two, have recently received interest as possible storable liquid oxidizers for missile use. Rather extensive studies of material compatibility with these compounds have been reported by Grigger and Miller .[32] Their tests of one year's duration have shown a number of nickel-containing alloys, Table 49, to have very favorable corrosion behavior. Welding and stress had no adverse effects on the corrosion behavior of these alloys in the anhydrous liquids at 86 F (30 C). Corrosion rates for all alloys shown were less than .01 mpy. Liquid flow at 100 ft/sec through orifices of Nickel 200 and the stainless steels did not cause erosion. Tests indicated that these oxidizers were not shock sensitive in contact with Nickel 200 or stainless steels. The presence of moisture[33] in these fluorides was found to increase corrosion rates somewhat and cause pitting attack on certain alloys, Table 50.

• Molten Fluoride Salts

Molten fluoride salt mixtures, as carriers for fissile materials, and as non-fuel coolant salts for nuclear reactor systems, have been of interest due to their stability under radiation and their low vapor pressure at relatively high operating temperatures. Alloy selection for equipment to handle such salts has received considerable study, especially by W. D. Manly, et al.[34] Because the temperature range of use may be from 1000 to 1650 F (550 to 900 C), useful alloys must combine not only adequate resistance to the fluoride salts, but resistance to air oxidation and good elevated temperature strength. The molten salts of interest have included mixtures of sodium fluoride, lithium fluoride, potassium fluoride, beryllium fluoride and zirconium fluoride as solvents for uranium or uranium-thorium fluoride fuels.

Preliminary studies indicated that nickel base alloys and stainless steels offered the most promise for these salts, but in both alloy systems the attack increased with chromium content of the alloy. Alloy 600 appeared promising, but was found to suffer attack by formation of subsurface voids due to selective attack and outward diffusion of chromium. Oxidation-reduction reactions appear to be involved with the overall formation of chromium fluoride in the salt. In systems wherein the reaction is temperature-dependent, the greatest attack occurs at the hotter metal wall temperatures, and chromium crystals deposit at cooler temperatures, a phenomenon referred to as chromium mass transfer.

The studies of Manly, et al, included HASTELLOY alloy B, which exhibited excellent resistance to the fluoride salts up to 1830 F (1000 C), but, unfortunately, had poor air oxidation resistance and structural characteristics under cyclic elevated temperature conditions. Their alloy development work was extended to the nickel-molybdenum system with sufficient chromium to provide both adequate oxidation resistance and elevated temperature structural properties. From this work emerged an alloy of 15 to 18 per cent molybdenum, 6 to 8 per cent chromium, 5 per cent iron (max), 0.5 per cent titanium/aluminum, balance nickel, first called "INOR-8," and now the commercial HASTELLOY alloy N. This alloy has excellent resistance to hot fluoride salts in the temperature range of 1300 to 1600 F (700 to 870 C) and good resistance to chromium mass transfer.

This alloy has been employed for the hydrofluorinator in the Oak Ridge National Laboratory Fluoride Volatility Process for the reprocessing of zirconium-clad highly enriched uranium fuel elements or homogenous fluoride salt mixtures. In this vessel, the uranium and zirconium are converted to their respective tetrafluorides. In a second reactor, constructed of Nickel 201 (former designation, low-carbon nickel), the uranium tetrafluoride is further oxidized to uranium hexafluoride by contact with elemental fluorine. The nature and extent of corrosion of these alloys in this process has been described by Miller, et a1,[35] Goldman and Litman,[36, 37, 38] and Youngblood, et a1,[39] the latter authors reporting the condition of the equipment after 40 operating runs. The HASTELLOY alloy N hydrofluorinator, which was exposed to gaseous hydrogen fluoride and a molten mixture of sodium fluoride, lithium fluoride, and zirconium tetrafluoride at 1040 to 1200 F (500 to 650 C), was observed to corrode primarily by bulk-metal loss. Except for the bottom area, where a corrosion rate of 0.14 mil/hr of hydrogen fluoride exposure was measured (and felt to be of questionable accuracy), the maximum rate in the remainder of the vessel was .028 mil/hr of hydrogen fluoride exposure (8.1 mil per month of exposure to molten salt).

The Nickel 201 fluorinator, which was exposed to the molten salt and fluorine at about 930 F (500 C), had significant bulk-metal losses and some evidence of intergranular corrosion. Its maximum bulk-metal loss occurred in the lower vapor region at a rate of 0.9 mil/hr of fluorine exposure. Corrosion tests of other alloys during operation of the fluorinator indicated that HASTELLOY alloy N and an alloy of 79 per cent nickel, 4 per cent molybdenum, balance iron, show promise of improved corrosion resistance for the fluorination step.

• Organic Compounds of Fluorine

Fluorocarbons

Because the size of the fluorine atom is small as compared with that of other halogens there is no steric factor restricting the replacement of hydrogen in hydrocarbons by fluorine. Thus, many compounds containing only carbon and fluorine are possible with a wide range of structures. Such compounds are known as "fluorocarbons."

Of greatest industrial importance is the reaction of chlorine-containing compounds with anhydrous hydrofluoric acid, with or without a catalyst, to form a fluorinated compound. Two unsaturated fluorocarbons, tetrafluoroethylene and hexafluoropropene, are of commercial importance, being the starting material for fluorine-containing polymers.

Little information is available regarding alloys employed for carrying out these reactions. Presumably, steel is adequate, if the reactants are essentially water-free. Since hydrogen chloride is a by-product of the reaction, that portion of process equipment employed for its recovery or disposal must be of materials capable of resisting hydrochloric acid.

"Halofluorocarbons," compounds containing carbon, fluorine, and at least one other halogen, usually chlorine, are produced in large quantities, finding use principally as refrigerants and propellants for "Aerosol" dispensers. Because these compounds are quite stable and chemically inert, they are not particularly corrosive to many metals and alloys. Stability studies[40] have indicated that Nickel 200, MONEL alloy 400, and 18 per cent chromium–8 per cent nickel stainless steel were unaffected when exposed to FREON 12, dichloro-difluoromethane, in sealed PYREX tubes for periods of six and twelve months at 150 F (66 C). MONEL alloy 400 was also unaffected when exposed to dry FREON 12 vapor at 235 F (113 C) for test periods extending up to twenty weeks.

Processes have been described[41] for the polymerization of tetrafluoroethylene to produce the granular polytetrafluoroethylene, TEFLON. Such reactions may be carried out under considerable pressure, at temperatures up to 465 F (240 C), in the presence of water and a variety of catalysts. Corrosion resistant reactor vessels are preferred to prevent introducing metallic impurities. Stainless steel, HASTELLOY alloys and nickel, as well as silver and tantalum are reported[41] to be satisfactory as liner materials.

Extrusion of Fluorocarbon Plastics

In processes for the extrusion of fluorocarbon plastics, at temperatures above their melting points, which can be as high as 900 F (480 C), some breakdown to fluorine or hydrogen fluoride may occur to cause corrosion of the extruding equipment. HASTELLOY alloy C has been reported[42] to be a highly successful alloy for components of extrusion equipment such as crosshead bodies, dies, and guider tips for the coating of wire, and the helical screws of molding and extrusion machinery.

Electrochemical Fluorination of Organics

In recent years, an electrochemical process has been employed for the production of organic compounds of fluorine. This was first used by Simons[43] and his associates at Pennsylvania State College in 1941. The organic substance is dissolved in anhydrous hydrofluoric acid, to which an alkali metal fluoride may be added to render the solution conductive. Operating at 4 to 8 volts, hydrogen is produced at the cathode, the fluorine atom replacing hydrogen in the compound. The process is quite versatile, and a great variety of compounds is capable of being produced.

The cell consists of a steel container in which is suspended an "electrode pack" made up of thin sheets of high purity nickel placed close together in a vertical position. These sheets are alternately connected to form anodes and cathodes much like the plates of a storage battery. Depending upon their boiling points, the fluorocarbons produced are either recovered from the top of the cell as gases, or drained from the bottom as liquids.

REFERENCES

1. Pray, H. A., Fink, F. W., Friedl, B. E., and Braun, W. J., "Corrosion Resistant Materials for Hydrofluoric Acid," Atomic Energy Commission, Battelle Memorial Institute Report 268, June 15, 1953.
2. Edwards, W. T., "Aqueous Corrosion in the Atomic Energy Industry," First International Congress on Metallic Corrosion, 1961, p. 442.
3. Braun, W. J., Fink, F. W., Ericson, G. L., "The Corrosion of Monel and 70/30 Cupro-Nickel in Hydrofluoric Acid," Atomic Energy Commission, Battelle Memorial Institute Report No. 1237.
4. Schussler, Mortimer, "Metal Materials for Handling Aqueous Hydrofluoric Acid," *Industrial & Engineering Chemistry,* Jan., 1955 (Vol. 47, No. 1), pp. 133-139.
5. Dickenson, F. S., and Watkins, B., "Use of Welding in Chemical Plants in the UK AEA," *British Welding Journal,* Oct., 1960 (Vol. 7, No. 10), pp. 643-651.
6. Copson, H. R., and Cheng, C. F., "Stress Corrosion Cracking of Monel in Hydrofluoric Acid," *Corrosion,* Dec., 1956 (Vol. 12, No. 12), pp. 647t-653t.
7. Kleinberg, S., and Tompkins, J., "Compatibility of Various Metals with Liquid Fluorine," Air Products & Chemicals, Inc., ASDTDR, 62-250, May, 1962.
8. Gundzik, R. M., and Feiler, C. E. (Lewis Flight Propulsion Laboratory), NACA (currently NASA) TN#3333, Dec., 1954. "Corrosion of Metals of Construction by Alternate Exposure to Liquid and Gaseous Fluorine."
9. Sterner, C. J., and Singleton, A. H., "The Compatibility of Various Metals with Liquid Fluorine," TR60-819 under Air Force Contract AF 33(616)6515, Air Products, Inc., Allentown, Pa. (March, 1961.)
10. Richards, H. T., and Hanson, M. P., "Influence of Fluorine Environments on the Mechanical Properties of Several Sheet Alloys," NASA TN D-1706: NASA-Lewis Research Center, Cleveland, Ohio (April, 1963).
11. Godwin, T. W., and Lorenzo, C. L., "Ignition of Several Alloys in Fluorine," Paper Presented at American Rocket Soc., Nov. 17-21, 1958, N. Y. C.
12. Steunenberg, R. K., Seiden, L., and Griffin, H. E., ANL 5924, Chemical Engineering Div., Summary Report, July, Aug., Sept., 1958.
13. Jarry, R. L., Fischer, J., and Gunther, W. H., "The Mechanism of the Nickel-Fluorine Reaction," *J. Electrochem. Soc.,* April, 1963, pp. 346-348.

REFERENCES (Continued)

14. Myers, W. R., and DeLong, W. B., "Fluorine Corrosion," *Chemical Engineering Progress,* 1948 (Vol. 44, No. 5), pp. 359-362.

15. Steindler, M. J., and Vogel, R. C., "Corrosion of Materials in the Presence of Fluorine at Elevated Temperatures," Argonne National Laboratory, ANL5662, Jan., 1957, 21 pp.

16. Jackson, R. B., General Chemical Division, Allied Chemical Company, "Corrosion of Metals and Alloys by Fluorine," Contract AF 04 (611) -3389.

17. Rogers, W. R., and Muller, K., "Hydrofluoric Acid Manufacture," *Chemical Engineering Progress,* May, 1963 (Vol. 59, No. 5), pp. 85-88.

18. Smiley, S. H., and Schmitt, C. R., "Continuous Disposal of Fluorine," *Industrial & Engineering Chemistry,* Feb., 1954 (Vol. 46, No. 2), pp. 244-247.

19. Forry, Keith, and Schrage, Charles, "Trouble-Shooting HF Alkylation," *Hydrocarbon Processing,* Jan., 1966 (Vol. 45, No. 1), pp. 107-114.

20. Also reproduced as: "Corrosion Limits Metals That Can Be Used for Construction of HF Alkylation Units," *National Petroleum News,* Aug. 7, 1946 (Vol. 38, No. 32), pp. R618-R628.

21. Meyer, F. H., Podlipec, F. J., and Kato, T. R., "Corrosion Problems Associated with Uranium Refining," *Corrosion,* 1959 (Vol. 15), pp. 168t-170t.

22. Ruch, W. C., Peterson, D. A., Gaskill, E. A., and Tepp, H. G., "Production of Pure Uranium Hexafluoride from Ore Concentrate," Allied Chemical Corp. Reprint V-52, Nuclear Engineering & Science Conference, April 6-9, 1952.

23. Hawthorn, E., "Uranium Tetrafluoride Manufacture with Fluidized Solid Techniques," *Nuclear Power,* March, 1960, pp. 120-123.

24. Hueston, F. H., "Nuclear Grade Uranium Tetrafluoride-by the Moving Bed Process," *The Canadian Journal of Chemical Engineering,* Feb., 1960, pp. 29-32.

25. Levey, R. P., et al, "Fluid Bed Conversion of U0, to UF,," *Chemical Engineering Progress,* March, 1960 (Vol. 56, No. 3), pp. 43-48.

26. Heymann, D., and Kelling, F. E. T., "Corrosion of Some Metals and Alloys in Uranium Hexafluoride," *Corrosion Technology,* May, 1958, pp. 148-158.

27. "Piping the Atom," *Heating, Piping and Air Conditioning,* July, 1955, pp. 91-94.

28. Tiner, N. A., English, W. D., and Toy, S. M., "Compatibility of Structural Materials with High Performance O-F Liquid Oxidizers," AFML-TR-65-414, Nov., 1965.

29. Schnizlein, J. G., Steunenberg, R. K., and Vogel, R. C., "Corrosion Studies Pertinent to Bromine Trifluoride," ANL 5557, April, 1956.

30. Strickland, G., Horn, F. L., acid Johnson, R., "Pilot Plant Fluorination of Uranium Fuel Elements by Bromine Trifluoride," Preprint 21, Session 34, Nuclear Engineering and Science Conference, March 17-21, 1958.

31. Mecham, Wm. J., Lumatainen, R. C., Kessie, R. W., and Seefeldt, Waldemar B., "Decontamination of Irradiated Uranium by a Fluoride Volatility Process," *Chemical Engineering Progress,* Feb., 1957 (Vol. 53, No. 2), pp. 72F-77F.

32. Grigger, J. C., and Miller, H. C., "The Compatibility of Welded Structural Materials with Chlorine Trifluoride, Perchloryl Fluoride and a Mixture of These," *Air Force Laboratory Tech. Documentary Report* No. ML-TDR-64-22, Feb., 1964.

33. Grigger, J. C., and Miller, H. C., "Effect of Chlorine Trifluoride and Perchloryl Fluoride on Construction Materials," *Materials Protection,* Sept., 1964, pp. 53-57.

34. Manly, W. D., et al, "Metallurgical Problems in Molten Fluoride Systems," Second International Conference of the Peaceful Uses of Atomic Energy, A/CONF.15/P/1990, June, 1958.

35. Miller, P. D., et al, "Construction Materials for the Hydrofluorinator of the Fluoride-Volatility Process," BMI-1348 (June 3, 1959).

36. Litman, A. P., and Goldman, A. E., "Corrosion Associated with Fluorination in the Oak Ridge National Laboratory Fluoride Volatility Process," ORNL-2832 (June 5, 1961).

37. Goldman, A. E., and Litman, A. P., "Corrosion Associated with Hydrofluorination in the Oak Ridge National Laboratory Fluoride Volatility Process," ORNL-2833 (Nov., 1961).

38. Litman, A. P., "Corrosion of Volatility Pilot Plant Mark I INOR-8 Hydrofluorinator and Mark III `L' Nickel Fluorinator after Fourteen Dissolution Runs," ORNL-3253, Feb. 9, 1962.

39. Youngblood, E. L., Milford, R. P., Nicol, R. G., and Ruch, J. B., "Corrosion of the Volatility Pilot Plant INOR-8 Hydrofluorinator and Nickel 201 Fluorinator During Forty Fuel-Processing Runs with Zirconium-Uranium Alloy," ORNL-3623, March, 1965.

40. "Stability and Corrosive Properties of `Freon 12' Dichlorodifluoromethane," Technical Bulletin B-5, E. I. du Pont de Nemours & Company.

41. U. S. Patent 2,393,967, M. M. Brubaker (to E. I. du Pont de Nemours & Co.).
    U. S. Patent 2,394,243, R. M. Joyce, Jr. (to E. I. duPont de Nemours & Co.).
    U. S. Patent 2,534,058, M. M. Renfrew (to E. I. duPont de Neracurs & Co.).

42. *Haynes Alloy Digest,* May, 1963 (Vol. 14, No. 5).

43. Simons, J. H., et al, *Journal of the Electrochemical Society* 1949 (Vol. 95), pp. 47, 53, 55, 59, 64.

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CEB-1	"Resistance of Nickel and High Nickel Alloys to Corrosion by Sulfuric Acid"
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