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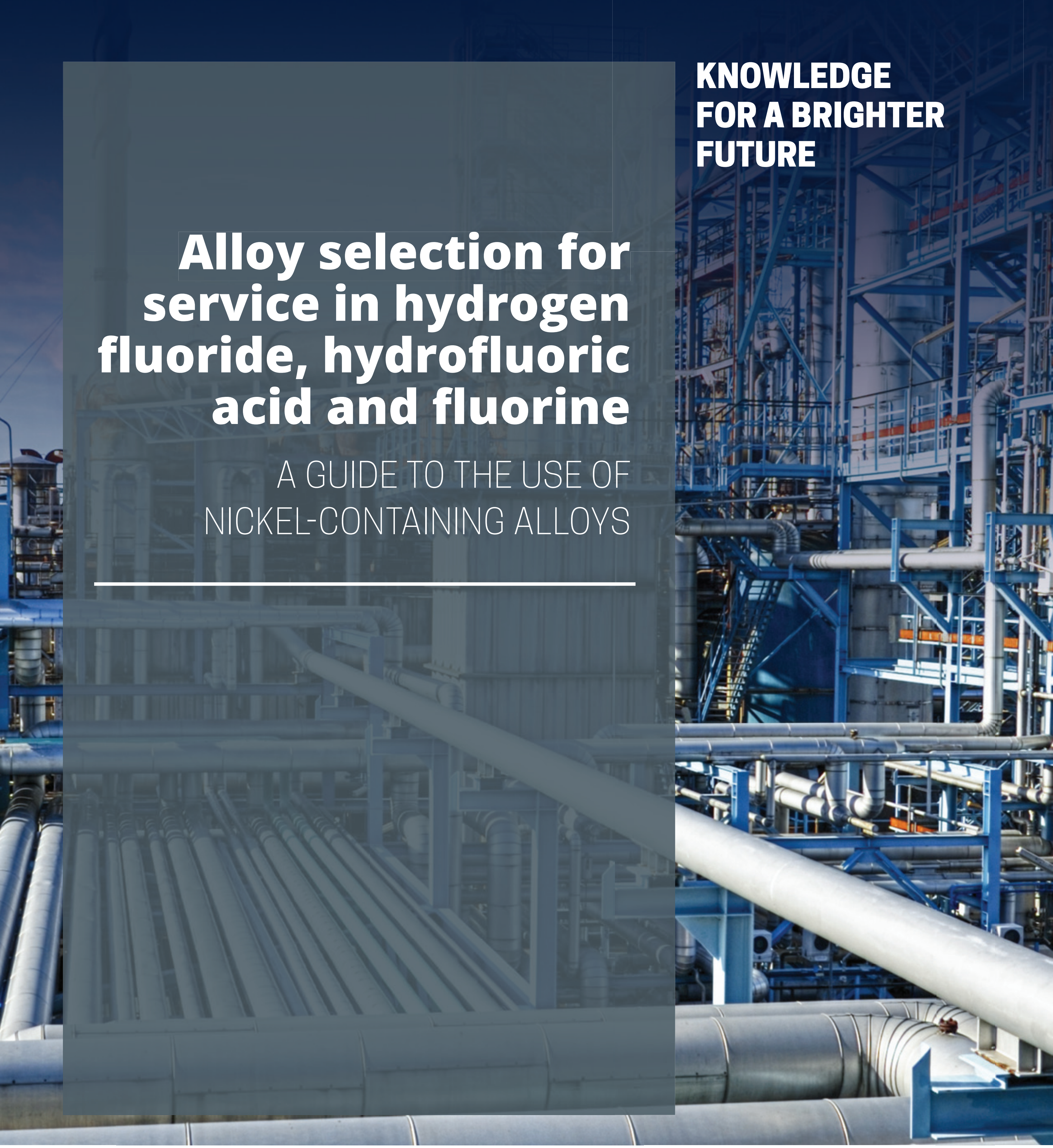
Alloy selection for service in hydrogen fluoride, hydrofluoric acid and fluorine

A GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS



Nickel INSTITUTE
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A GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS

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Introduction

Hydrogen fluoride (HF) is a gas at room temperature. When dissolved in water it forms hydrofluoric acid. Hydrogen fluoride and hydrofluoric acid are available in four grades:

- anhydrous hydrogen fluoride (AHF),
- 70% hydrofluoric acid,
- 48% reagent-grade hydrofluoric acid, and
- 49% electronic-grade hydrofluoric acid.

These chemicals are extremely hazardous, inflicting serious burns and breathing the vapours can cause lung damage.

AHF is the starting material for the production of most fluorine compounds. One of the main uses of AHF is in the manufacture of hydrofluorocarbons (HFCs), e.g. CF_3CH_2F, CF_3CF_2H, $CF_3CH_2CH_2F$ and CH_2F_2 which are non-ozone-depleting replacements for the chlorine-containing chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). The HFCs are widely used in refrigeration and air conditioners and CF_3CH_2F is the propellant used in inhalers to deliver the drugs for the treatment for asthma attacks. HCFCs are used to make the fluorinated polymers, polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). HF is also used in a number of manufacturing processes, e.g., petroleum alkylation, uranium isotope treatments, aluminium manufacture, etc. It is also used in specialised metal cleaning and pickling solutions to, for example, remove welding slag.

This publication describes the behaviour of nickel-containing alloys and the specific nature of their reactivity with AHF and hydrofluoric acid, considered separately. The behaviour of other metals commonly used in the manufacture or handling of these chemicals is also discussed. *Table 1* lists the main nickel-containing alloys and their UNS number considered in this introductory publication.

Table 1 Nominal composition of nickel-containing alloys used in hydrogen fluoride and hydrofluoric acid systems.

		Nominal composition, %						ASTM Spec.[b]	
Alloy	UNS number[a]	Ni	C	Cr	Mo	Cu	Fe	Plate	Seamless tube and pipe
Group I – Commercially pure (C.P.) nickel and nickel-copper alloys									
200	N02200	99.5	0.08	-	-	-	0.2	B162	B161
400	N04400	66.5	0.2	-	-	-	1.2	B127	B165
K500	N05500	66.5	0.25	-	-	Bal	1.2	B127	B165
M35-1	N24135	66	0.2	-	-	30	1.2	-	-
Group II – Chromium-containing nickel alloys									
600	N06600	76	0.08	15.5	-	-	8	B168	B167
825	N08825	42	0.03	21.5	3	2.25	30	B424	B163
625	N06625	61	0.05	21.5	9	-	2.5	B443	B444
31	N08031	31	0.02	27	6.5	1.2	15	B582	B622
G-3	N06985	48	0.01	22	7	2	19	B582	B622

Alloy	UNS number[a]	Ni	C	Cr	Mo	Cu	Fe	Plate	Seamless tube and pipe
Group II *cont'd* – Chromium-containing nickel alloys									
G-30	N06030	42	0.01	29.5	5	1.8	15	B582	B622
690	N06690	61	0.02	29	-	-	9	B168	B167
C-22/622	N06022	56	0.01	21.5	13.5	-	4	B575	B622
C-276	N10276	58	0.01	15.5	16	-	5.5	B575	B622
59	N06059	60	0.01	23	15.5	-	0.7	B575	B622
686	N06686	56	0.01	21	16	-	2.5	B575	B622
C-2000	N06200	57	0.01	23	16	-	1.5	B575	B622
CW2M	N26455	Bal	0.01	16	16	-	1	-	-
CX2M	N26022	Bal	0.01	23	15.5	-	1	-	-
CX2MW	N26059	Bal	0.01	21	13	-	4	-	-
CW6M	N30107	Bal	0.03	18	18	-	1	-	-
Group III - Nickel-molybdenum alloys									
B-2	N10665	69	0.01	1	28	-	2	B333	B622
B-3	N10675	65	0.01	1.5	28.5	-	1.5	B333	B622
N3M	N30003	Bal	0.01	-	31	-	1	-	-
N7M	N30007	Bal	0.03	-	31	-	1	-	-
Copper-nickel alloys									
90/10	C70600	10	-	-	-	90	-	B171	B466
70/30	C71500	30	-	-	-	70	-	B171	B466
Precipitation hardenable stainless steel									
15-7Mo	S15700	7	0.04	15	2.1	-	Bal	A693	-
Austenitic stainless steels									
304L	S30403	8	0.02	18	-	-	Bal	A240	A312
316L	S31603	10	0.02	16.5	2.1	-	Bal	A240	A312
321	S32100	9	0.04	17	-	-	Bal	A240	A312
347	S34700	9	0.04	17	-	-	Bal	A240	A312
20	N08020	33	0.02	19.5	2.2	3.2	Bal	A240	B729
CN7M	N08007	29	0.04	20	2.3	3.5	Bal	-	-
904L	N08904	24	0.01	20	4.5	1.5	Bal	A240	A312
6%Mo[c]	S31254	18	0.01	20	6.2	0.7	Bal	A240	A312
6%Mo[c]	N08367	24	0.01	21	6.2	-	Bal	A240	A312
6%Mo[c]	N08926	25	0.01	20.5	6.2	1	Bal	A240	A312
7%Mo	S32654	22	0.01	24	7.3	0.5	Bal	A240	A312

a - UNS numbers beginning with an "N" indicate a nickel alloy, but the definition of a nickel alloy is different than that used by ASTM.

b - in ASTM specifications, most nickel alloys fall into the "B" specifications. However, due to a redefinition of a nickel alloy, a few alloys such as Alloy 20 are being reclassified as stainless steels, and will be included in the "A" specifications. That work is still in progress.

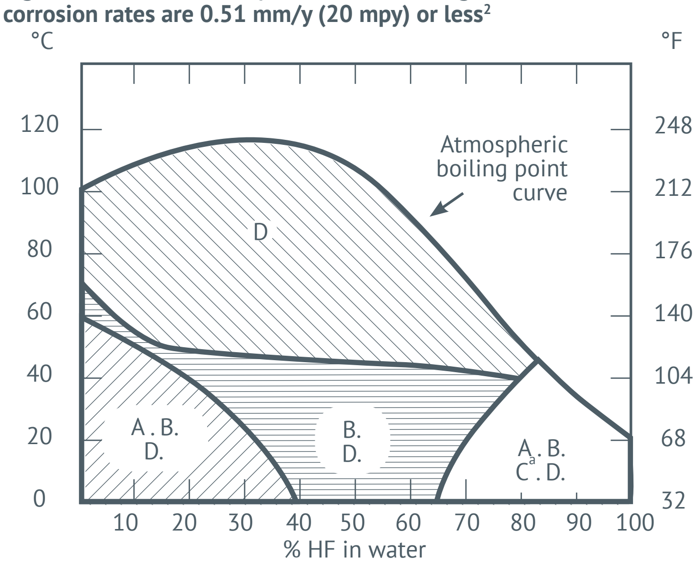
c - the 6%Mo alloys are a series of stainless steels, many of which are proprietary, all with roughly 6%Mo content and roughly equivalent in performance.

A more detailed discussion of all aspects of materials selection for these fluorine-based chemicals is available elsewhere.[1] An overview of the corrosion resistance of various materials in HF is shown in *Figure 1*. These data were compiled from laboratory tests and experience in low-flow, low-oxygen commercial HF and AHF and include wrought and cast alloys. Higher velocity conditions or the presence of contaminants may make some of these materials unsuitable.

CORROSION BEHAVIOUR — ANHYDROUS HYDROGEN FLUORIDE (AHF)

A small amount of HF is recovered from the Wet Process production of phosphoric acid.[3] However, the vast majority is produced by one of several proprietary processes starting with digestion of fluorspar (calcium fluoride; CaF_2) with hot concentrated sulphuric acid. Various high-nickel alloys must be employed, depending on the specific chemistry, to handle the combination of sulphuric and halogenated acids which result. *Figure 2* shows a typical manufacturing process and provides a summary of the materials of construction involved.

Figure 1 Metals and alloys for HF service: regions where observed corrosion rates are 0.51 mm/y (20 mpy) or less[2]



A — Alloy 200, G-3, G-30, 600, 20, 825, CN7M

B — Alloy C-22, 59, C-2000, 686, C-276, B-2, B-3, N3M, N7M, CW2M, CX2M, CX2MW, CW6M

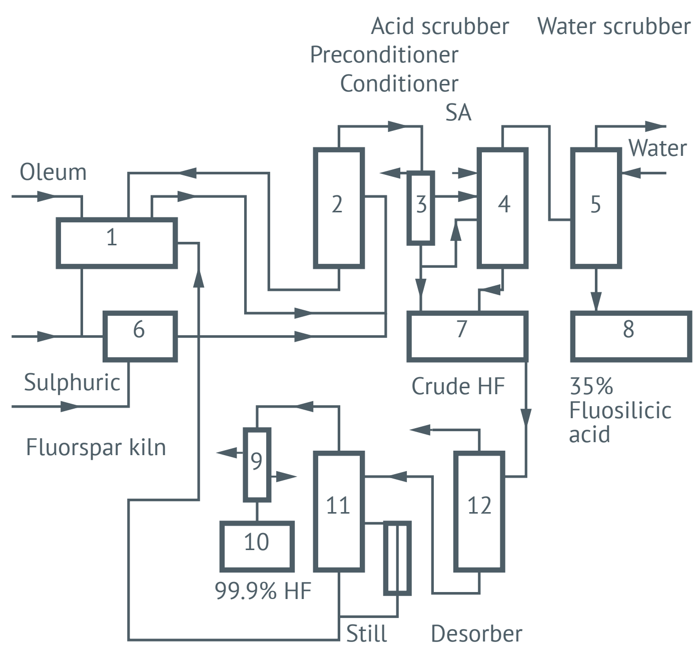
C — Carbon steel [a]

D — 90/10, 70/30, 400, M35-1, gold, platinum, silver, molybdenum

[a] *Carbon steel sometimes suffers hydrogen stress cracking (HSC), hydrogen embrittlement (HE), or hydrogen-induced cracking (HIC). To avoid excessive corrosion, the velocity for 70% Aqueous HF on carbon steel is typically limited to 0.6 m/s (2 ft/s). The velocity limit for carbon steel in liquid AHF service is typically 1.8 m/s (6 ft/s).*

AHF contains a maximum of 400 ppm water and at ambient temperatures is not very corrosive. Some metals and alloys, however, are velocity-sensitive (depending upon the tenacity of the protective film of metallic fluorides). Others are subject to hydrogen embrittlement (HE), depending upon their metallurgical structure and/or mechanical history. The boiling point of AHF is 19.5 °C (67.1 °F) but corrosion data has been reported in the 500-600 °C (930-1110 °F) range and some process operations, e.g., hydrofluorination reactions are conducted at intermediate temperatures: aluminium oxide at as low as 370 °C (700 °F).[2]

Figure 2 Process diagram of a hydrofluoric acid plant and designation of typical materials of construciton



1. Carbon steel	5. N10665	9. N10665
2. Carbon steel	6. N10665 lined steel	10. Carbon steel
3. Ni-Cr-Mo (N10276)	7. NiCu (N04400)	11. N10665
4. Ni-Mo (N10665)	8. Rubber-lined steel	12. N04400

Carbon steels and cast irons

AHF is traditionally stored and shipped in steel containers, corrosion rates being less than 0.12 mm/y (5 mpy) in both liquid and vapour phases to about 66 °C (150 °F) because of a protective film of a complex iron oxide/fluoride. The velocity limit imposed by survival of such films is 1.8 m/s (6 ft/s). Good steel quality, fabrication and design are required to prevent several possible forms of hydrogen-related damage, i.e., blistering, delamination, embrittlement and cracking. The upper limit for HF *vapour* is about 300 °C (570 °F). Low-alloy steels are often less resistant than carbon steel.

Both the brittle characteristics and siliceous constituents in cast irons effectively preclude their use in AHF.

Stainless steels

Conventional austenitic grades tolerate higher temperatures than carbon steel, about 100 °C (212 °F) in liquid AHF. They are often utilised for valves, pumps, instrumentation and bolting, although Type 301, Type 302 and Type 303 should be avoided.

Fluorides do not cause stress-corrosion cracking (SCC) directly but do aggravate susceptibility of *sensitised* grades to intergranular SCC.

Nickel and its alloys

The chromium-free Alloy 400 (N04400) is usually the material of choice, based on both cost and corrosion resistance. It is widely used for valves, valve trim, pumps and piping to at least 100 °C (212 °F). Its major weakness is a propensity to fail by SCC in the event of ingress of air and moisture, its inherent copper content producing the cupric fluoride (CuF_2) which is the specific responsible agent. In this instance, thermal stress relief may delay onset of SCC but will not completely remove the risk of cracking.

Alloy 200 (N02200) has about the same general corrosion resistance and is immune to SCC. However, far and away the most reliable and cost-effective alloy is Alloy 600 (N06600), which is the material of choice especially for vaporisers (which are easily contaminated by air). Higher nickel-molybdenum and nickel-chromium-molybdenum alloys offer no advantage in AHF, although Alloy C-276 (UNS N10276) is probably the most readily available alloy for bellows and instrument parts. Alloy 600 has been successfully used at temperatures of 370–590 °C (700–1095 °F) in the hydrofluorination of metal oxides.

It should be noted that weld deposits containing niobium or titanium compounds are subject to selective attack in AHF and should be avoided.

Copper and its alloys

In the absence of oxygen, zinc- and silicon-free copper alloys are resistant to AHF. Copper has been used for a distillation column for AHF and it is especially useful for flexible tubing connections. It is, however, velocity-sensitive. 70–30 cupronickel is insensitive to velocity effects and has been used in heat exchangers and other equipment involving relatively high flow rates.

Other metals

The reactive metals (i.e., titanium, zirconium and tantalum) do not resist fluorides in any form.

Silver is very resistant, but only in the absence of sulphur contamination. The other precious metals are resistant and platinum rupture disks have shown nil corrosion in the manufacture of AHF.

CORROSION BEHAVIOUR – HYDROFLUORIC ACID

When AHF is combined with water, it forms a relatively weak reducing acid. Although monobasic, it has the ability to form oligomers [$(HF)_N$] and compounds like ammonium bifluoride, NH_4HF_2. AHF is “very soluble” in water but, commercially, it is available in three grades, i.e., 70% hydrofluoric acid (B.P. 66.6 °C: 152 °F), 48% hydrofluoric acid (C.P. “Reagent Grade”) and as a 49% “Electronic Grade”.[3] Since the azeotrope is 38.2% (B.P. 112 °C: 234 °F) these grades cannot be produced by evaporation but must be made by dilution of AHF. Like AHF, hydrofluoric acid is extremely hazardous, inflicting serious and slow-healing burns which require speedy medical treatment.

Hydrofluoric acid is quite different from the AHF in its corrosion characteristics, most often requiring high-nickel alloys, plastics or elastomers for its commercial applications, e.g., pickling operations, acid treatment of oil wells, etc.

Carbon steel

Carbon steel can be used under quiescent conditions for acid above 64% but the rates are prohibitive at 60% HF. The temperature limit for 70% hydrofluoric acid is not more than 32 °C (90 °F). Steel rarely finds practical application, nor do alloy steels because of hydrogen embrittlement and other hydrogen-related phenomena.

Stainless steels

The martensitic and ferritic grades of stainless steel find no application in this service, problems due to hydrogen-assisted cracking and velocity effects adding to a lack of resistance to general corrosion.

The conventional austenitic grades likewise find little application. The molybdenum-free grades, e.g., Type 304L (S30403), show a rate of <0.025 mm/y (1 mpy) in 10% HF at 16 °C (60 °F) but >0.25 mm/y (10 mpy) in 0.05% acid at 60 °C (140 °F). Type 304 bolting is used in lieu of alloy steel for *external* bolting around HF operations. Type 316L (UNS S31603) has good resistance to *general* corrosion below about 10% acid at about 25 °C (77 °F) but is subject to pitting and is not recommended. These grades are less resistant than carbon steel in 70% acid.

Higher stainless alloys like Alloy 20 (N08020) and Alloy 825 (N08825) offer only limited improvement and niobium and titanium constituents in weldments suffer preferential attack. However, Alloy 20 castings may be used for pumps and valves in 70% acid at ambient temperature.

Alloys such as 904L (N08904), 31 (N08031), 6%Mo (S31254, UNS N08367, UNS N08926) and 7%Mo (S32654) have reasonable resistance to weak acid (<10%) especially if chlorides are present.[5]

Chromium-free nickel alloys

These comprise Alloy 200, Alloy 400 and Alloy B-2 (UNS N10665) and their derivative forms. In general, they resist aqueous HF solutions in the absence of oxygen or more powerful oxidising species.

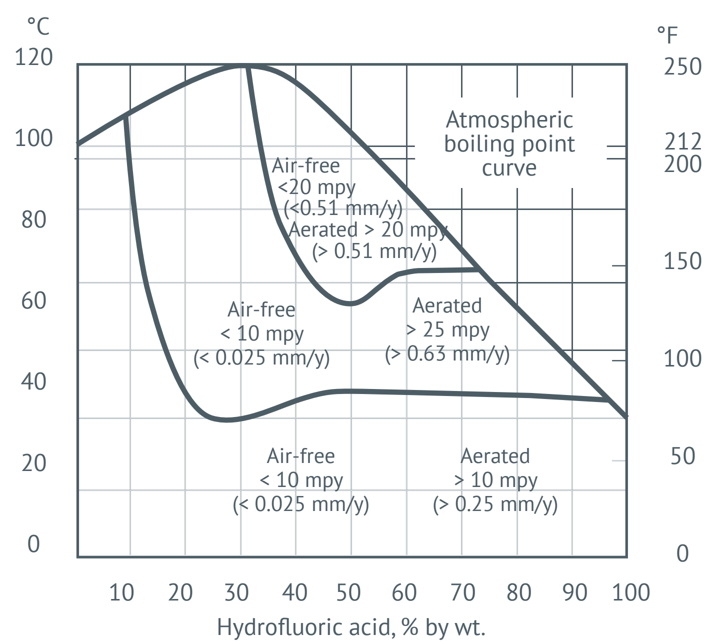
The least expensive and most commonly preferred material is Alloy 400, which is preferred for up to 120 °C (250 °F) for all concentrations. *Figure 3* shows an iso-corrosion chart for Alloy 400 in hydrofluoric acid.[6] An adherent protective film of brown fluoride salts is formed under anaerobic conditions, the film being quite resistant to velocity and impingement effects. Rates are usually <0.05 mm/y (2 mpy) up to at least 80 °C (175 °F). Weldments must not contain niobium, which is preferentially attacked.

Corrosion of Alloys 400 and K500 (N05500) increases dramatically with ingress of air or oxygen. Furthermore, SCC occurs in the *vapour* space from the formation of CuF_2, a specific agent for this type of cracking. Also, corrosion in the liquid phase is autocatalytic, due to the accretion of cupric ions, although SCC is not a problem therein.

Alloy 400 can be stress relieved at temperatures between 400 °C and 595 °C (750 °F and 1100 °F). For nearly complete removal of internal stress a hold time at temperature of up to about 3 hours may be required. This heat treatment will relieve stresses induced by cold working operations and welding with only a slight decrease in strength and a slight increase in ductility.

Nickel e.g., Alloy 200, is resistant, as long as air is absent, below 80 °C (176 °F) but less so than Alloy 400, and is more expensive and difficult to fabricate. The nickel-molybdenum alloys, e.g., Alloy B-2, are no more resistant than Alloy 400 (sometimes less so) and are not economically justified.

Figure 3 Iso-corrosion chart for Alloy 400 (N04400) in hydrofluoric acid.



Chromium-bearing nickel alloys

Alloy 600 offers an advantage over Alloy 400 in not being susceptible to cracking by (nor conducive to formation of) CuF_2 but the welding rods typically contain too much niobium, which can be a problem at elevated temperature.

The Ni-Cr-Mo alloys, e.g., Alloy C-276 and derivative compositions, are generally less resistant than Alloy 400 and Alloy 600. However, they are superior for operations for reprocessing nuclear wastes, which involve hot 16% acid. The preferred material for pumps and valves for 70% HF at ambient temperature is the CN7M (N08007) (Alloy 20 equivalent) casting alloy.[4]

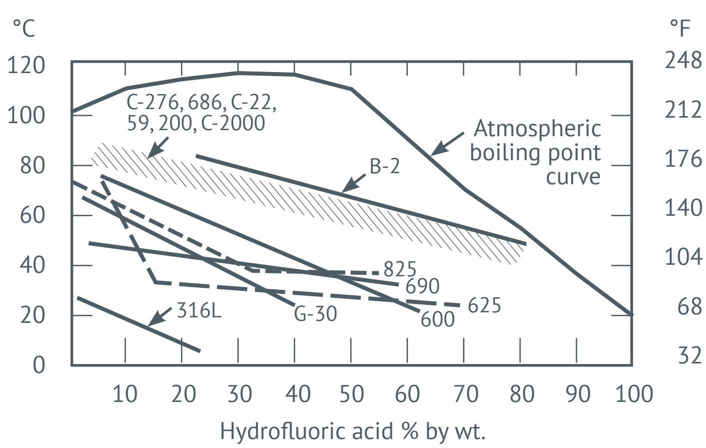
The corrosion resistance of various nickel-base alloys is shown in *Figure 4*.

Copper and its alloys

Conventional grades of copper, bronzes and brasses are resistant only in the total absence of oxygen or other oxidants. Even then, they are subject to autocatalytic attack due to accretion of cupric ions. They are also subject to velocity effects, dealloying and SCC.

Cupronickels, e.g., 90/10 (C70600) and 70/30 (C71500), have useful resistance to HF solutions, in the absence of dissolved oxygen or other oxidising agents. Corrosion rates are highest in the 20–40% range, especially at the liquid/vapour interface. Alloy 70/30 has been successfully used in AHF coolers subjected to interim water washes and is less susceptible to SCC than is Alloy 400.

Figure 4 Summary hydrofluoric acid isocorrosion chart showing 0.51 mm/y (20 mpy) lines for the various alloys examined



Other metals

All refractory metals are severely attacked by HF.

In the absence of air or sulphur contamination, silver has been used to resist hydrofluoric acid, e.g., in HF alkylation units. Gold and platinum are completely resistant.

CORROSION BEHAVIOUR – FLUORINE

Fluorine (F_2) is a yellow-green gas, analogous in many ways to the other halogen gases. A highly oxidising medium, all equipment must be thoroughly cleaned of any residual organic contaminants because of possible ignition.

Many common metals and alloys are resistant to *dry* fluorine, relying for their performance on a thin protective film of metal fluoride. A passivating pre-treatment with fluorine or chlorine trifluoride is required before storage.

Carbon steel and cast iron

Cast irons are not considered for this service because of their brittle nature and the susceptibility to corrosion of siliceous constituents.

Carbon steels with less than 0.01% silicon can resist fluorine up to 350 °C (660 °F) but corrosion increases rapidly with silicon content and they are subject to ignition in some circumstances. Historically, fluorine gas has been compressed and stored in steel cylinders and fluorine gas has been transported in steel piping with no problems except an accretion of white iron fluorides, which may accumulate in restricted areas of the system. Currently, steels find no practical application in this service.

Stainless steels

As with HF, martensitic and ferritic grades of stainless steel find no application.

At temperatures in the range of -220 °C (-364 °F) to -188 °C (-306 °F), Type 304 and 15-7Mo (S15700) were unattacked. At 30 °C (85 °F), a 6-12 angstrom thick film develops in about 3 hours, with no further reaction.[7] Type 321 (S32100) and Type 347 (S34700) stainless steel were completely resistant to fluorine in both liquid and vapour, <0.0025 mm/y (0.1 mpy) over a 3½-month exposure. In liquid fluorine, neither external explosions nor tensile tests to fracture caused ignition of the common austenitic grades. However, such grades lose passivity and corrode very rapidly above approximately 200 °C.

Nickel and its alloys

The nickel alloys were also unaffected by the ignition tests described above. Their resistance to high-temperature gaseous fluorine depends largely on the volatility of the fluoride corrosion products.

Chromium-free nickel alloys

Alloy 400 is used for the internal container in 3-layer Dewar-type tanks for bulk shipment of liquid fluorine. A dense metal fluoride protective film is formed. In the vapour, some attack would occur if there is ingress of oxygen and one might expect some SCC if moisture were to form the expected mixture of hypo- and hydrofluoric acid. Alloy 400 is recommended for valve seats.

Nickel alloy 200

Like Alloy 400, Alloy 200 resists liquid fluorine but is not commonly used because of its higher cost than for the nickel-copper alloy. Both Alloy 200 and Alloy 400 resisted fluorine to at least 370 °C (700 °F) with rates below 0.1–0.12 mm/y (4–5 mpy), as shown in *Table 2*.[7] Actually, these data are derived from relatively short-term tests, which tend to indicate higher rates than would actually obtain. Other data suggest that temperatures as high as 540 °C (1000 °F) can be tolerated.

Alloy B-2 is resistant <0.05 mm/y (2 mpy) to liquid fluorine at ambient temperatures but has a higher rate in fluorine gas <0.5 mm/y (20 mpy). It finds no application because it is more expensive than the Mo-free alloys.

Chromium-bearing nickel alloys

Alloy 600 is satisfactory at ambient temperatures and, lacking copper, is not susceptible to SCC in the event of ingress of moisture. However, as shown in *Table 2*, its corrosion resistance is not acceptable above perhaps 204 °C (400 °F), being an order of magnitude higher than for the chromium-free grades.

Table 2 Corrosion by hot gaseous fluorine mm/y (mpy)[7]

Material	Time (hrs.)	27 °C (80 °F)	204 °C (400 °F)	370 °C (700 °F)	530 °C (1000 °F)
Alloy 400	5	0.061 (2.4)	0.013 (0.5)	0.048 (1.9)	0.76 (29.8)
	120	0.005 (0.2)	0.002 (0.1)	0.030 (1.2)	0.18 (7.2)
Alloy 200	5	0.025 (1.0)	0.084 (3.3)	0.043 (1.7)	0.62 (24.5)
	120	0 (0)	0.002 (0.1)	0.010 (0.4)	0.35 (13.8)
Alloy 600	5	0.028 (1.1)	0.015 (0.6)	1.98 (78)	88 3451

The Ni-Cr-Mo alloys have no application in fluorine service.

Copper and its alloys

Copper tubing has been used to handle fluorine but any ingress of moisture causes catastrophic attack, in a manner similar to chlorine. Zinc and silicon-bearing alloys are to be avoided.

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