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Alloys to resist chlorine, hydrogen chloride and hydrochloric acid

by C.M. Schillmoller

NiDI Technical Series Nº 10 020

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Gaseous chlorine at low temperatures and in the absence of moisture is not severely corrosive and is commonly handled by carbon steel. Dry hydrogen chloride (HCl) behaves in a similar way. However, the strongly acidic hydrochloric acid is harmful to steel.

Each of these three substances is discussed under various conditions. Materials considered include the high-nickel alloys, stainless steels, high-molybdenum alloys, titanium, zirconium and tantalum.

CORROSION CHARTS

Corrosion is a very complex process. Seemingly unimportant variables, such as small amounts of moisture, impurities, or the presence of metal chlorides, can change the corrosion picture completely.

To present corrosion data in concise form, a variety of methods has been proposed. Basically the author is opposed to the presentation of information via simplified charts if this alone is used for selecting materials of construction. However, concise and condensed information is valuable in that it presents an overall view of the situation and can be used for screening purposes, thus minimizing the number of materials to be tested or considered.

How far can one go in condensing information and still have it be of substantial value? Figures 1, 2 and 3 attempt to condense corrosion data so that the general picture can be obtained at a glance. Nickel and high-nickel alloys are among the few proven metallic materials that show good corrosion resistance in chlorine, hydrogen chloride and hydrochloric acid. These alloys are, of course, not new to the chlor-alkali industry, being more or less standard selections in caustic, brine and salt processing.

Table 1 provides a brief description of the alloys commonly in use, their UNS number (Unified Numbering System) and the tradenames under which they are known. References in the text to Alloy 200, Alloy 400 and so on correspond

Table 1
Alloys commonly used in Cl_2 and HCl systems.

Materials	Reference in text	Nominal composition, % Ni	Cr	Mo	Cu	Fe	ASTM/ ASME B number	UNS number	Most common Tradenames
Nickel									
Nickel	Alloy 200	99.6	—	—	—	—	161-163	N02200	Nickel 200
Low-carbon nickel	Alloy 201	99.6	—	—	—	—	161-163	N02201	Nickel 201
Nickel-copper alloys									
Nickel-copper alloy	Alloy 400	67	—	—	31	1.5	163-165	N04400	Monel 400
Nickel-chromium-iron alloys									
Nickel-chromium-iron alloy	Alloy 600	76	15	—	—	8	163-168	N06600	Inconel 600
Nickel-iron-chromium alloy	Alloy 800	32	21	—	—	46	163-407	N08800	Incoloy 800
Nickel-iron-chromium-molybdenum-copper alloy	Alloy 825	42	21	3	2.3	30	163-423	N08825	Incoloy 825
High-molybdenum alloys									
Nickel-chromium-molybdenum-iron alloy	Alloy 625	61	21.5	9	—	4	443-446	N06625	Inconel 625
Nickel-chromium-molybdenum-iron alloy	Alloy C-4	63	16	15	—	2	575-622	N06455	Hastelloy C-4
Nickel-chromium molybdenum-iron alloy	Alloy C276	58	16	15	—	6	575-622	N10276	Hastelloy C276
Nickel-iron-chromium molybdenum-copper alloy	Alloy G	48	23	7	2	20	588-622	N06007	Hastelloy G
Nickel-molybdenum-iron alloy	Alloy B-2	68	—	28	—	1.5	333-622	N10665	Hastelloy B-2

NOTE:
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Hastelloy is a registered trademark of Haynes International

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to the tradenames as the UNS numbering system does not always permit immediate recognition.

In the chemical process industries, the common design parameter for tubing, valve trim and internals is 0.075 mm/year (0.003 in/yr) maximum corrosion rate, while for vessels and pipe, an upper corrosion rate of 0.50 mm/yr (0.020 in/yr) is frequently adopted, with a corrosion allowance of 3 to 6 mm (1/8 to 1/4 in.). This should provide a safe life of ten years or more. The charts summarize the limits of usefulness for the various alloys.

CHLORINE

Gaseous chlorine (Cl_2) at ambient temperatures and in the absence of moisture is not severely corrosive, and is commonly handled in carbon steel. Usually, a more resistant alloy such as Alloy 400 or Alloy C-276 is specified for critical parts such as valve trim, stem, instrumentation and orifice plates in chlorine pipelines. In contrast, wet chlorine is extremely corrosive to steel and nickel alloys, and requires Alloy C-276 or titanium. The upper limit of usefulness of carbon steel in dry chlorine is around 200°C (390°F), at which temperature the protective effects of the corrosion products disappear.

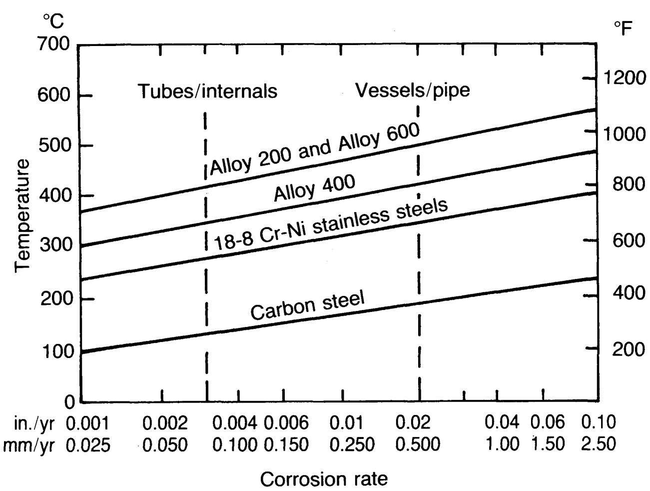

Figure 1
Upper design limits for various alloys in chlorine.

Figure 1 provides a guide to the selection of various alloys for dry chlorine, and indicates design parameters for tubes/internals and vessels/pipe components.

The surface coating of chlorides on the alloys tends to provide protection up to a temperature level at which melting, vaporization or decomposition removes such films. The corrosion rate appears proportional to the vapor pressure of the metal chlorides.

Alloy 200 and Alloy 600 are those alloys most commonly used for reactors, coils, agitators and piping in the 250-500°C (480-930°F) range. Carbon steel can still be used below 150°C (300°F). When the plant is not in operation, proper shutdown procedures should be used to keep the units dry or free from chlorine, so as to prevent attack by wet residual chlorine on the steel or nickel. In the case of AISI 304 or 316 stainless steel, which can be used up to 350°C (660°F), the presence of moisture during shutdown also raises the possibility of stress corrosion cracking. A temperature of 500°C (930°F) seems a prudent upper limit for nickel in dry chlorine.

Example

Ethylene is to be reacted with chlorine in the presence of a ferric chloride catalyst, to produce ethylene dichloride (EDC). The reactor temperature is 60-100°C (140-210°F). The process is exothermic; water cooling removes the heat of reaction.

Figure 1 indicates that carbon steel can be used for the reactor and auxiliary equipment, provided that the chlorine feedstock is dry, and that proper control of temperature is maintained by thorough mixing of the reactants to prevent hot spots and runaway temperatures. Intimate mixing can be assured by using EDC as a reaction medium. Alloy 200 should be considered for reactor internals and critical components if experience shows difficulty in controlling temperatures below 150°C (300°F), or if it is desirable to operate above this temperature.

HYDROGEN CHLORIDE GAS

Dry hydrogen chloride (HCl) behaves similarly to Cl_2, and carbon steel will suffice up to 250°C (480°F), above which Alloy 200 is usually specified. Figure 2 provides a guide to the selection of various alloys in dry HCl gas. Upper corrosion limits of 0.075 and 0.50 mm/yr are shown as design parameters for certain components. It is believed that these limits are conservative. In operations above the dewpoint the presence of moisture does not appreciably increase the corrosion rates, unless the temperature drops and the moisture condenses. In that case hydrochloric acid is formed which is highly corrosive.

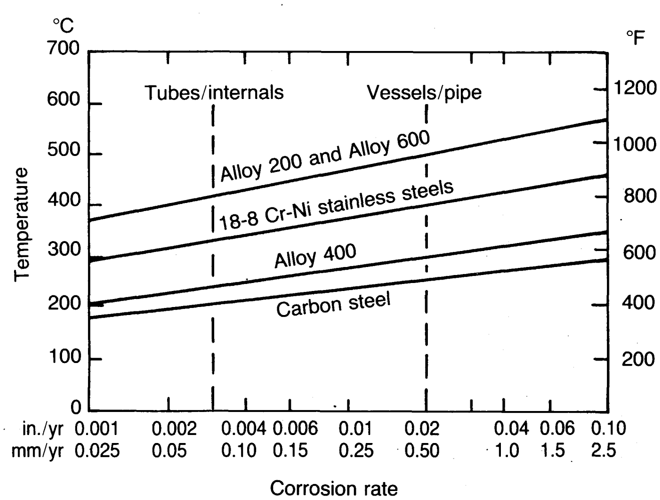

Figure 2
Upper design limits for various alloys in hydrogen chloride.

It must be pointed out that there are many variables, and that even small amounts of addition agents to control catalyst activity, for example, may exert an influence on the tenacity and vapor pressure of the protective corrosion scales. Therefore, absolute corrosion rates for different temperatures are difficult to predict in both Cl_2 and HCl gas systems. Even so, Figures 1 and 2 should be sufficiently accurate to serve as a guide.

The performance of Alloy 200 in dry as well as wet HCl gas has been consistently good. In cyclic operating conditions, particularly in the presence of air or oxygen, Alloy 600 and Alloy 825 offer good all-around resistance. It is prudent to assume that AISI 304 and 316 stainless steels would be subject to chloride stress-corrosion-cracking conditions during shutdown, despite various precautions that may be taken.

Example

Ethylene is to be reacted with dry HCl gas and oxygen (O_2) in the presence of copper chloride catalyst in a fixed-bed reactor to produce ethylene dichloride (EDC). The temperature is 275°C (525°F) and the pressure is 10 atmospheres. The process is exothermic; reaction heat is removed by the generation of steam on the shell side of the reactor.

Figure 2 indicates that stainless steel, Alloy 200 and Alloy 600 are candidate materials, and resist dry and even moist hydrogen chloride. Usually, Alloy 200 is used for the reactor tubes; the tubesheets and heads of the reactor are clad with nickel on steel; and the interconnecting piping between the reactors is made of Alloy 200. Temperatures should be carefully controlled in this exothermic reaction because of byproduct formation and deactivation of the catalyst above 325°C (615°F). Alloy 200 has an upper-temperature limit of 550°C (1020°F) and with localized hot spots, of say 750°C (1380°F), catastrophic rates of corrosion and tube failure will occur.

Types 304 and 316 stainless steels are subject to chloride stress corrosion cracking (CSCC) below the dewpoint and during shutdown, unless extreme precautions are taken to ensure a bone-dry feed to the unit and to maintain shutdown and startup precautions of gas-blanketing and keeping the unit dry. Alloys 800 and 825 resist the CSCC phenomenon and have been used, respectively, for EDC-pyrolysis furnace tubing and fluid-bed oxychlorination reactor internals.

HYDROCHLORIC ACID

Hydrochloric acid is an important mineral acid with many uses, including acid pickling of steel, acid treatment of oil wells, chemical cleaning and chemical processing. It is sold in four concentrations, ranging from 27 to 37%.

Hydrochloric acid is a typical reducing acid over its entire concentration range. Its strongly acidic character is harmful to steel. Nickel 200 and Alloy 400 behave similarly and find application at ambient temperatures up to 20% concentration, and at higher temperatures below 5% concentration. Figure 3 shows iso-corrosion lines for 0.050 mm/yr (.020 in/yr), which generally is considered the upper design limit of an alloy selection. The graph immediately delineates the conditions suitable for handling with Alloy 400, and those where Alloy B-2 is required.

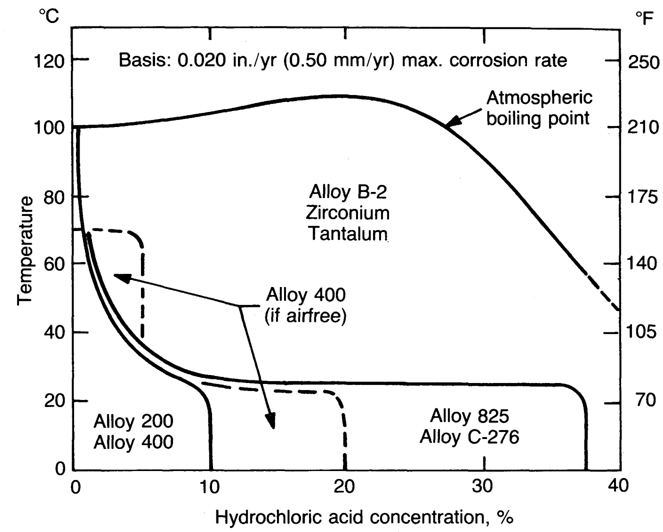

Figure 3
Hydrochloric acid—alloy selection guide.

At ambient temperature, Alloy 825 and Alloy C-276 can be used over the full range of acid concentration. These alloys are also selected to resist chloride stress corrosion cracking. Also, Alloy G and Alloy 625 perform well under these conditions.

The presence of impurities such as fluorides, ferric ions and cupric ions have a profound effect on the corrosion of many metals. Fluorides attack glass-lined steel and the refractory metals such as zirconium and tantalum. Ferric chlorides attack the nickel alloys, including Alloy B-2, and zirconium. Cupric salts have an accelerating effect similar to the ferric ions; both cause pitting and stress cracking. While the acid specification may be low in iron, the acid can easily become contaminated during shipment and handling, and from corrosion on steel in process vessels. Under such conditions, in the presence of oxidizing ferric chlorides, titanium and Alloy C-276 have given good performance and resist the pitting type of attack.

A more complete overview of candidate metals and alloys for hydrochloric acid service is presented in Figure 4, taken from NACE "Corrosion Data Survey". While very complete, it ignores economic factors and places emphasis on basing the choice on corrosion testing or field experience, using the grade of acid that will be available. In recent years, titanium and zirconium have been increasingly used as their price structure in tubular components has become competitive with the high-nickel alloys. Tantalum's application is limited by high cost, and it is chiefly used for the sheathing of certain critical components, such as thermocouples.

Example

In the distillation process, entrained water is carried along, and dilute hydrochloric acid is formed by the hydrolysis of organic acids, when the stream is cooled below 125°C (255°F). Excessive corrosion occurs on carbon steel condenser tubing, piping and in the bottom of the accumulator.

Depending on temperature and hydrochloric acid concentration, corrosion rates on carbon steel frequently run 0.25 to 4.0 mm/yr. It is extremely difficult to ensure a bone-dry system without inadvertent moisture pickup at flanges and seals, or to prevent entrainment of water. It should be noted that acid concentrations in such cases are mostly less than 0.5%, and that, as Figure 3 shows, Alloy 400 can withstand such conditions satisfactorily.

Alloy 400 has been used at ambient temperature in reducing air-free systems up to 20% hydrochloric acid concentration. Alloy B-2 and zirconium can resist the full range of concentration and temperature.

TECHNOLOGY TRENDS

No major changes in the use of established alloys of construction are foreseen except for the wider application of Alloy 400 and of Alloy C-276, and the utilization of titanium and zirconium in tubular components. At higher temperatures in chlorination processes, there is a trend toward specifying special liners on Alloy 200 and Alloy 600 to raise the upper limit of usefulness beyond 550°C (1020°F).

Emission-control standards are becoming more severe, necessitating the scrubbing and neutralization of HCl, the use of wastewater strippers to remove volatile organics, and the enclosing and collecting of emissions for incineration. Corrosion in parts of this equipment can be very severe, and the rate of attack is not always predictable. Some of the previously mentioned alloy-selection guidelines do apply, and new high-chromium, high-molybdenum, nickel-base alloys will find increasingly wider application.

First-cost considerations will continue to favor the use of plastic coatings and rubber liners for various equipment and piping, in addition to glass-lined equipment, even though special care is required to maintain such coatings and prevent damage at joints.

In chemical and process systems the alloy selection that gives equipment 10 years reliability of operation, minimum maintenance and continuity of production is generally the correct economical selection.

Additional information is contained in the references.

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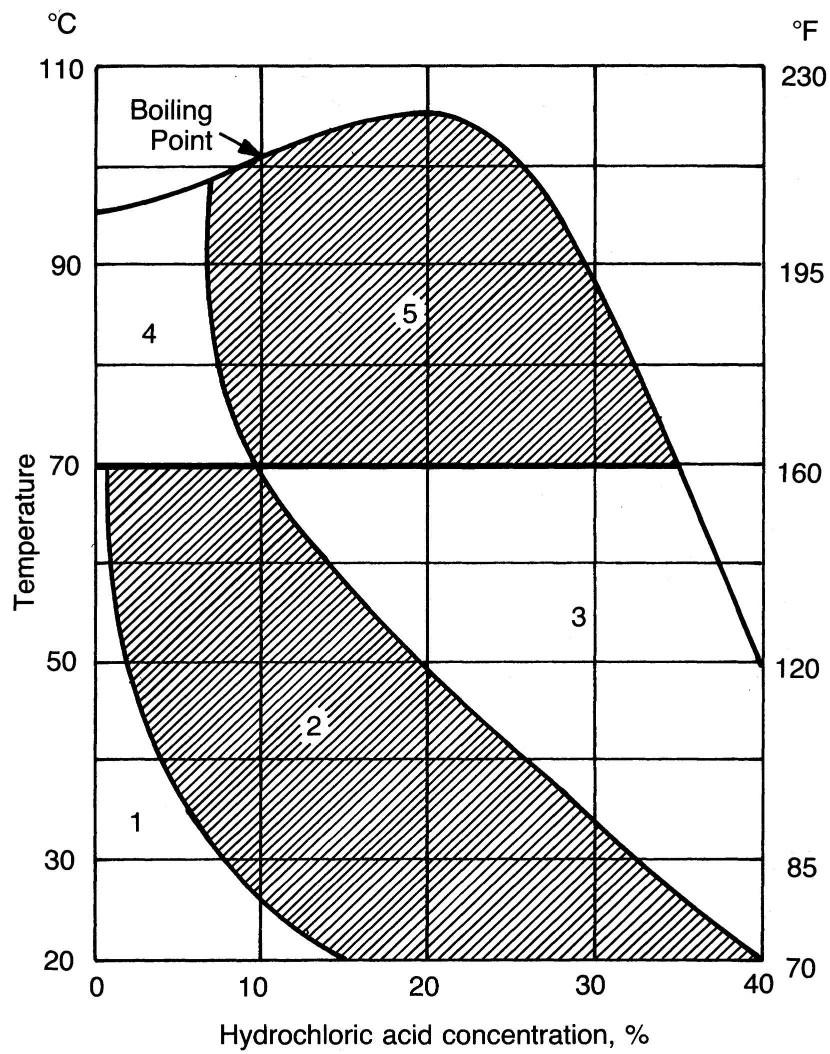

Figure 4
Alloys for hydrochloric acid service (Ref. 8; Ref. 2).

Metals With Reported Corrosion Rates of <20 MPY

Zone 1	**UNS NUMBER**
CN-7M	J95150 (1) (3) (6)
Alloy 400	N04400 (2) (3) (6)
Copper	C11000 (2) (3) (6)
Nickel 200	N02200 (2) (3) (6)
Silicon Bronze	C65500 (2) (3) (6)
Silicon Cast Iron	F47003 (7)
Tungsten	R07030
Titanium (Gr. 7)	R52400
Titanium (Gr. 2)	R50400 (4)
Zone 2	
Silicon Bronze	C65500 (2) (6)
Silicon Cast Iron	F47003 (7)
Zone 3	
Silicon Cast Iron	F47003 (7)
Zone 4	
Alloy 400	N04400 (2) (3) (8)
Tungsten	R07030
Titanium (Gr. 7)	R52400 (5)
All Zones (including 5)	
Platinum	P04995
Tantalum	R05200
Silver	P07015 (3) (6)
Zirconium	R60702 (3) (6)
Alloy B-2	N10665 (3) (6)
Molybdenum	R03600 (3) (6)

NOTES:

1. <2% at 25°C (75°F)
2. No Air
3. No $FeCl_3$ or $CuCl_2$
4. <10% at 25°C (75°F)
5. <5% at B.P.
6. No Chlorine
7. Mo-Ni Alloy
8. <0.05% Concentration

The Nickel Development Institute is an international nonprofit organization to serve the needs of people interested in nickel.

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