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Alloy selection for service in chlorine, hydrogen chloride and hydrochloric acid

A GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS



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Introduction

Gaseous chlorine at low temperatures and in the absence of moisture is not particularly corrosive and is commonly handled in carbon steel. If any water is present, however, chlorine becomes aggressive to many metals.

Similarly, dry hydrogen chloride (HCl) is not corrosive to most metals. Once it is dissolved in water hydrochloric acid is

formed and this is corrosive to many metals and alloys.

Each of these three substances, chlorine, hydrogen chloride and hydrochloric acid is discussed under various conditions. Materials considered include steels, stainless steels, nickel-base alloys, copper-base alloys, titanium, zirconium and tantalum. *Table 1* lists some nickel-containing alloys commonly in use, and their UNS number.

<i>Table 1</i> Nominal composition of nickel-containing alloys used in Chlorine, Hydrogen Chloride and Hydrochloric Acid systems.									
		Nominal composition, %						ASTM Spec. ^b	
Alloy	UNS Number ^a	Ni	C	Cr	Мо	Cu	Fe	Plate	Seamless tube and pipe
Group I - C.P. Nickel and nickel-copper alloys									
200	N02200	99.5	0.08	-	-	-	0.2	B162	B161
201	N02201	99.5	0.01	-	-	-	0.2	B162	B161
400	N04400	66.5	0.2	-	-	-	1.2	B127	B165
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
G-30	N06030	42	0.01	29.5	5	1.8	15	B582	B622
G-35	N06035	55	0.02	33	8	-	2	B575	B622
C-22/622	N06022	56	0.01	21.5	13.5	-	4	B575	B622
C-4	N06455	66	0.01	16	15	-	5.5	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
Group III - Nickel-molybdenum alloys									
B-2	N10665	70.5	0.01		28	-	-	B333	B622
B-3	N10675	63	0.005	2	30	-	2	B333	B622
B-4	N10629	66	0.01	1	28	-	4	B333	B622

Table 1 con't Nominal composition of nickel-containing alloys used in Chlorine, Hydrogen Chloride and Hydrochloric Acid systems.									
		Nominal composition, %						ASTM Spec. ^b	
Alloy	UNS Number ^a	Ni	C	Cr	Мо	Cu	Fe	Plate	Seamless tube and pipe
Austenitic Stainless Steels									
304L	S30403	8	0.02	18	-	-	Bal	A240	A312
316L	S31603	10	0.02	16.5	2.1	-	Bal	A240	A312
800	N08800	33	0.07	21	-	-	Bal	A240	B407
20	N08020	33	0.02	19.5	2.2	3.2	Bal	A240	B729
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
Duplex Stainless Steel									
2205	S32205	5	0.02	22	3.2	-	Bal	A240	A790

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 800 and 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.

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. Various methods, such as graphs or tables, have been used to present corrosion data in concise, summary form. It is dangerous to use such published summaries, tables and graphs alone to select materials for industrial applications. They are of use in indicating which materials should not be exposed to a particular, potentially corrosive environment. Concise and condensed information is valuable in that it presents an overall view of the situation. It can be used for screening purposes, thus minimizing the number of materials to be tested or considered. Summary figures of this type are presented in this publication to provide such overviews.

In the chemical process industries, the common design parameter for tubing, valve trim and internals is about 0.1 mm/y (4 or 5 mpy) maximum corrosion rate. For heavierwall vessels and pipe, if the anticipated corrosion is expected to be uniform, an upper corrosion rate of 0.50 mm/y (20 mpy) may be acceptable. If a corrosion allowance of 3 to 6 mm (0.12"- 0.24") is applied under these circumstances a safe life of six to ten years can be expected. When corrosion of a localized nature is anticipated, e.g., pitting, crevice corrosion and stress corrosion cracking (SCC) characteristic of halide effects on many alloys, a corrosion allowance is inappropriate. A more detailed discussion of all aspects of materials selection for chlorine, HCl and hydrochloric acid is available elsewhere.

PRODUCTION OF CHLORINE

Commercial chlorine is co-produced with caustic soda (NaOH) by the electrolysis of a sodium chloride solution. Sodium hydroxide is produced at the cathode, while chlorine is evolved at the anode.

Mercury Cells

Production of chlorine and caustic soda using mercury cells is rarely used now, largely because of environmental concerns. Rubber-lined carbon steel was the conventional material of construction for mercury cell caustic. A fresh feed of about 25.5% sodium chloride brine diminishes to about 21% during electrolysis and is recycled to the cell for continued electrolysis. Chlorine is produced at the carbon or titanium anodes while the mercury at the cathode forms an amalgam (Na/Hg). In a separate vessel, the denuder, the amalgam is reacted with demineralized water to obtain 50% NaOH of very high purity.

For the brine heaters, both Alloy 400 (UNS N04400) and titanium or its variants, have been used. Titanium alloys are preferred, because of the problem of liquid-metal cracking (LME) of the nickel-base alloy by entrained mercury, as well as corrosion by small amounts of chlorine or hypochlorites.

Diaphragm Cells

In diaphragm cell electrolysis, an asbestos (or polymer-fibre) diaphragm separates a cathode and an anode, preventing the chlorine forming at the anode from re-mixing with the sodium hydroxide and the hydrogen formed at the cathode. The salt solution (brine) is continuously fed to the anode compartment and flows through the diaphragm to the cathode compartment, where the caustic alkali is produced and the brine is partially depleted. As a result, diaphragm methods produce alkali that is quite dilute (about 12%) and of lower purity than do mercury cell methods.

Membrane Cells

The membrane cell is analogous to the diaphragm cell except that the feed brine is more highly purified and the perfluorosulfone membrane has lower permeability than a diaphragm. This method is more efficient than the diaphragm cell and produces very pure caustic but requires very pure brine.

CORROSION BEHAVIOUR – CHLORINE

The chlorine as produced is wet and is thoroughly dried, by contact with 98% sulphuric acid, and is then essentially non-corrosive at ambient temperature. Chlorine reacts with moisture to form a stoichiometric amount of hydrochloric and hypochlorous acid.

Cl₂ + H₂O ----> HCl + HOCl

These by-product acids are responsible for the unanticipated corrosion in many plant operations, occasioned by ingress of moisture.

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 corrosion rates are based on relatively short-term tests and should be considered to be very conservative.

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

Carbon steel

Dry chlorine (Cl₂) at ambient temperatures is normally handled and shipped in carbon steel and corrosion is negligible. Usually, a more resistant alloy such as Alloy 400 or Alloy C-276 (UNS N10276) is specified for critical parts, such as valve trim, instrumentation and orifice plates in chlorine pipelines. In contrast, wet chlorine is extremely corrosive to steel and many nickel alloys, and requires Alloy C-276 or titanium.

Carbon steel resists dry chlorine and traces of moisture merely leave a film of ferric chloride. Chlorine is a powerful oxidant, however, and steel can ignite in dry chlorine, depending upon form and temperature. For example, steel wool or wire can ignite at as low as 50 °C (122 °F). Steel compressors are not specified above 110 °C (230 °F) since surfaces rubbing together can trigger ignition. Steel vessels are limited to a wall temperature of about 120 °C (250 °F) to 150 °C (300 °F) depending on specific application and company policy.

Carbon steel can be used up to 150 °C (300 °F) or even higher, up to about 200 °C (390 °F) if equipment is properly cleaned first. Traces of chlorinated solvent contaminants can accelerate corrosion and increase the chance of ignition. Grease tends to react exothermically with chlorine and can increase corrosion rate. When chlorine equipment is not in operation, proper shutdown procedures should be in place to keep the units dry, or free from chlorine, so as to prevent attack by wet residual chlorine on the steel.

Example of use

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 (UNS N02200) or Alloy 400 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.

Stainless steels

As indicated in *Figure 1*, conventional 300 series austenitic stainless steels are inherently more resistant than carbon steels to dry chlorine. Stainless steels can be used up to 350 °C (660 °F) but are not often employed because possible ingress of moisture during shutdown can lead to chloride stress-corrosion cracking (SCC) or pitting corrosion.

Duplex stainless steels, such as Alloy 2205 (UNS S32205), resist dry chlorine but the ferrite phase is preferentially attacked by HCl should ingress of moisture occur.

Alloy 20 (UNS N08020) or the cast version CN7M valves are used in refrigerated, liquid chlorine equipment to resist corrosion in the moist chlorine gas that can form under ice on the metal surface. The bolting on valves for liquid chlorine is usually Alloy C-276.

Nickel and its alloys

Non-chromium containing alloys, such as Alloys 200, 201 (UNS N02201), 400 and B-2 (UNS N10665) resist dry chlorine but are severely attacked if ingress of moisture occurs.





Alloy 400 is commonly used as valve trim but problems can ensue in refrigerated systems. Any water present below the dew point is corrosive to Alloy 400 and other nickel alloys.

Chromium-bearing grades such as Alloy 600 (UNS N06600) and Alloy C-276 (or its variants) are much better if contact with moisture is likely. Alloy C-276 is the standard valve stem material in carbon steel lines carrying dry chlorine since the stems can be in contact with humid air. Its more highly alloyed variants are not required but are equally resistant.

Alloy 200 and Alloy 600 are the alloys most commonly used for reactors, coils, agitators and piping in the 250-500 °C (480-930 °F) range. A temperature of 500 °C (930 °F) is a prudent upper limit for nickel in dry chlorine. Alloy 600 is stronger than Alloy 201 and may be substituted.

Copper and its alloys

Copper alloys are not usually employed since they are very rapidly attacked by acidic conditions should moisture contamination occur. Copper and its alloys will resist dry chlorine to about 200 °C (390 °F). Flexible, annealed copper tubing has been used for gas connections in some applications but must be replaced periodically for mechanical reasons.

Other metals

Titanium and its alloys will ignite and burn at temperatures as low as -18 °C (-0.4 °F) in dry chlorine and should never be exposed to liquid chlorine. Small amounts of water can passivate titanium, the amount needed to prevent attack varying with temperature. At room temperature 0.2% is adequate, rising to 1% at 175 °C (347 °F). With water present, titanium is resistant and has been used for impellers introducing chlorine to organic syntheses. It has also been used in butterfly valves in non-metallic lines handling wet chlorine at ambient temperature. In crevices, the balance between HCl and HOCl, from the presence of moisture, may not be maintained and severe corrosion may ensue.

Zirconium is resistant to dry chlorine at ambient temperatures but is corroded rapidly if water is present. It can corrode at rates of >1.3 mm/y (>50 mpy) in chlorine containing as little as 0.3% water at room temperature.

Tantalum resists both wet and dry chlorine up to about $250 \degree C$ (480 °F), with rates of 0 to 0.05 mm/y (0 to 2 mpy). Breakaway

corrosion occurs at higher temperatures, with rates of about 1.7 mm/y (66 mpy) at 300 °C (570 °F) and further increases in attack at only slightly higher temperatures.

CORROSION BEHAVIOUR – HYDROGEN CHLORIDE GAS

A guide to the selection of various alloys in dry HCl gas is provided in *Figure 2*. Upper corrosion limits of 0.075 and 0.50 mm/y (3 – 20 mpy) are shown as design parameters for certain components and these are conservative limits. (For example, some tests of 650 hours duration showed a rate of only 0.25 mm/y (10 mpy) at 590 °C [1,090 °F]). In operations above the dew point, the presence of moisture does not appreciably increase the corrosion rates. At lower temperatures where moisture condenses, the hydrochloric acid formed by reaction with water will be highly corrosive.

It must be pointed out that there are many variables, and that even small amounts of additives (e.g., agents to control catalyst activity) may exert an influence on the tenacity and vapour pressure of the protective corrosion scales.

Carbon steel

Carbon steel behaves in dry hydrogen chloride (HCl) in a manner similar to that in dry Cl_2 . It is usable up to about 250 °C (480 °F) above which another alloy, such as Alloy 200 is usually specified.



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

Stainless steels

Types 304L (UNS S30403) and 316L (UNS S31603) stainless steels are subject to chloride stress corrosion cracking (CSCC) below the dew point and during shutdown, even at ambient temperature. This can only be prevented if extreme precautions are taken to ensure a bone-dry feed to the unit and to maintain shutdown and start up precautions of gasblanketing and keeping the unit dry.

Nickel and its alloys

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 (UNS N08825) offer good all-around resistance. Alloy 800 (UNS N08800) and Alloy 825 resist the CSCC phenomenon and have been used, respectively, for EDC pyrolysis furnace tubing and fluid-bed oxy-chlorination reactor internals.

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 by-product formation and deactivation of the catalyst above 325 °C (615 °F). Alloy 200 has an upper-temperature limit of 550 °C (1,020 °F) and with localized hot spots, of say 750 °C (1,380 °F) catastrophic rates of corrosion and tube failure will occur.

Other metals

Titanium is resistant to dry hydrogen chloride gas at temperatures >150 °C (300 °F) due to the presence of a protective oxide film. Moisture present will cause corrosion and may produce hydrogen embrittlement.

Tantalum is resistant to dry hydrogen chloride gas up to at least 150 °C (300 °F). The metal is reportedly inert to hydrogen chloride gas containing water vapour to even higher temperatures.

CORROSION BEHAVIOUR -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 used in more than 100 chemical manufacturing processes. It is sold in four concentrations, ranging from 27 to 37%. Pure acid is produced by reacting hydrogen and chlorine, the resulting hydrogen chloride being absorbed in water. It should be noted, however, that the majority of commercial acid is recovered as a by-product from organic syntheses and may have significant contaminants unless otherwise specified.

Hydrochloric acid is a typical reducing acid. It has a powerful inclination to form the azeotrope (or constant boiling mixture, CBM) with water. Exposed to the atmosphere, the concentrated acid tends to lose hydrogen chloride (while dilute acid loses water vapour) to become the CBM, 20.2% HCl.

Since hydrochloric acid is a reducing acid, the cathodic reaction is hydrogen evolution upon contact with metals below hydrogen in the electromotive series. Dissolved oxygen or stronger oxidants promote corrosion of many nonferrous metals above hydrogen as well. *Figure 3* shows a general picture of appropriate alloy selection and immediately delineates the conditions suitable for handling with Alloy 400 and those where Alloy B-2 is required.

Carbon steels and cast irons

Over its entire concentration range, hydrochloric acid is severely corrosive to steel. Specific commercial inhibitors can reduce the rate sufficiently to permit acid cleaning of process equipment (e.g., of rust or calcareous deposits) with 10-15% HCl.

Grey cast irons are also severely attacked, suffering graphitic corrosion, and are not amenable to inhibition. The austenitic nickel cast irons are more resistant and certain high-silicon cast irons (e.g., 14.5% Si) even more so.

Example

In a distillation process, entrained water forms dilute hydrochloric acid by the hydrolysis of chlorinated solvents when the stream is cooled below 125 °C (255 °F). Excessive corrosion will then occur 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 at 0.25 to 4.0 mm/y (10 mpy to 160 mpy). 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.

Stainless steels

All kinds and varieties of stainless steels become active and are attacked by hydrochloric acid. In very low concentrations, the acid can cause pitting, crevice corrosion or CSCC. With duplex grades, the tendency is to attack the ferrite phase preferentially. This phenomenon is also observed in weldments in some cases.

Alloy 825 and Alloy 20 resist corrosion at all concentrations at temperatures <40 $^{\circ}$ C (100 $^{\circ}$ F).





The 6% Mo superaustenitic stainless steels, such as UNS S31254, UNS N08367, and UNS N08926, can be used in some applications in hydrochloric acid concentrations < 3 wt%. The 7% Mo superaustenitic stainless steel UNS S32654 with nominal 7.3% Mo can be used up to about 8% acid at room temperature.

Nickel and its alloys

The chromium-free nickel Alloy 200 and Alloy 400 (and variants thereof) are attacked by hydrochloric acid, only in the presence of dissolved oxygen or stronger oxidants. Cupric ions are also formed from the Alloy 400 to further aggravate attack. An exception is the use of Alloy 400 in steel pickling operations in which the evolution of hydrogen keeps all cations in the reduced state. Alloy 400 has been used at ambient temperature in reducing air-free systems up to 20% (see *Figure 3*).

The 30% Mo materials, i.e., Alloy B-2, Alloy B-3 (UNS N10675) and Alloy B-4 (UNS N10629), were developed specifically for this service and resist all concentrations of HCl to the atmospheric boiling point. Dissolved oxygen is a mild accelerant, however, and oxidizing contaminants (usually ferric ions which are often derived from handling and storage) cause very severe corrosion.

Of the chromium-bearing grades, Alloy 600 is basically non-resistant, suffering severe pitting as well as general corrosion. Those alloys which also contain molybdenum as well as chromium, such as Alloy 625 (UNS N06625) and Alloy C-276 (and derivative compositions) are much more resistant in the presence of oxidizing contaminants than the Ni-Mo alloys but only at relatively low temperatures and concentrations. Alloy C-276 for example, has excellent resistance to all concentrations at room temperature, and good resistance <0.5 mm/y (<20 mpy) in all concentrations up to 50 °C (120 °F). Alloy G-30 (UNS N06030) and Alloy G-35 (UNS N06035) have reasonable resistance at ambient temperatures and are especially resistant to oxidizing chloride solutions so are resistant in hydrochloric acid contaminated with oxidizing salts.

Emission-control equipment is now becoming standard for

the removal of HCl from various industrial gases. Corrosion in parts of this type of equipment can be very severe, and the rate of attack is not always predictable. Alloys such as C-276 and high-chromium, low-iron variants such as C-2000 (UNS N06200) will find increasingly wider application. In some cases such alloys can be applied as thin sheet 'wallpaper' to a structural steel duct or scrubber, providing effective resistance at reduced cost.

Copper and its alloys

Theoretically, copper alloys (with the exception of high-zinc brasses) should resist corrosion by HCl because they do not liberate hydrogen. In practice, dissolved oxygen produces cupric ions, which are themselves oxidizing contaminants, and corrosion becomes autocatalytic. Unless the complete absence of oxygen or oxidizing agents can be guaranteed, copper and its alloys should not be used.

Other metals

For all practical purposes, titanium alloys are not suitable for this service, although some grades (e.g., Ti-.15% Pd) are slightly more resistant than the unalloyed material. Even with very low corrosion rates, this metal tends to become embrittled by hydrogen absorption at cathodic sites.

Zirconium (e.g., R60702) tends to resist the liquid acid to well above its atmospheric boiling point (the CBM boils at about 110 °C [230 °F]) but vapour-phase attack can occur. Also, there must be insignificant amounts of oxidizing contaminants (<50 ppm). Oxidizing contaminants can form pyrophoric corrosion products. Zirconium can resist pure HCl at 120 °C (250 °F) under pressure. Corrosion resistance can be reduced by the presence of cold work and by grain boundary precipitates associated with welds.

Of the reactive metals, tantalum is the most resistant to hydrochloric acid. In addition to unalloyed tantalum specific tantalum alloys have been developed for improved strength and, in some applications, reduced cost.

Fluorides may be present in hydrochloric acid from some sources and this will greatly increase corrosion rates in these metals. Zirconium will tolerate <10 ppm while tantalum may tolerate 10 ppm or more.

Summary of alloys for use in Hydrochloric Acid

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A chart showing the indicated areas of use of various alloys is shown in *Figure 4*. This chart indicates where corrosion rates should be acceptable or excessive and is based on field experience using commercial acid. It does not take any account of economic factors or strength requirements for different applications. It is, however, useful as a first indicator of likely candidate materials to test or to avoid.



Figure 4 Metals with reported corrosion rates of <0.5 mm/y (<20 mpy)

	UNS Number				
Zone 1					
CN-7M Alloy 400 Copper Nickel 200 Silicon Bronze Silicon Cast Iron Tungsten Titanium (Gr. 7) Titanium (Gr. 2)	J95150 (1) (3) (6) N04400 (2) (3) (6) C11000 (2) (3) (6) N02200 (2) (3) (6) C65500 (2) (3) (6) F47003 (7) R07003 R52400 R50400 (4)				
Zone 2					
Silicon Bronze Silicon Cast Iron	C65500 (2) (6) F47003 (7)				
Zone 3					
Silicon Cast Iron	F47003 (7)				
Zone 4					
Alloy 400 Tungsten Titanium (Gr. 7)	N04400 (2) (3) (8) R07030 R52400 (5)				
All Zones (including 5)					
Platinum Tantalum Silver Zirconium Alloy B-2 Molybdenum	P04995 R05200 P07015 (3) (6) R60702 (3) (6) N10655 (3) (6) R03600 (3) (6)				
NOTES: 1. <2% at 25 °C (75 °F) 2. No air 3. No FeCl3 or CuCl2 4. <10% at 25 °C (75 °F) 5. <5% at B.P. 6. No Chlorine 7. Mo-Ni Alloy 8. <0.05% Concentration					

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