SPECIAL METALS

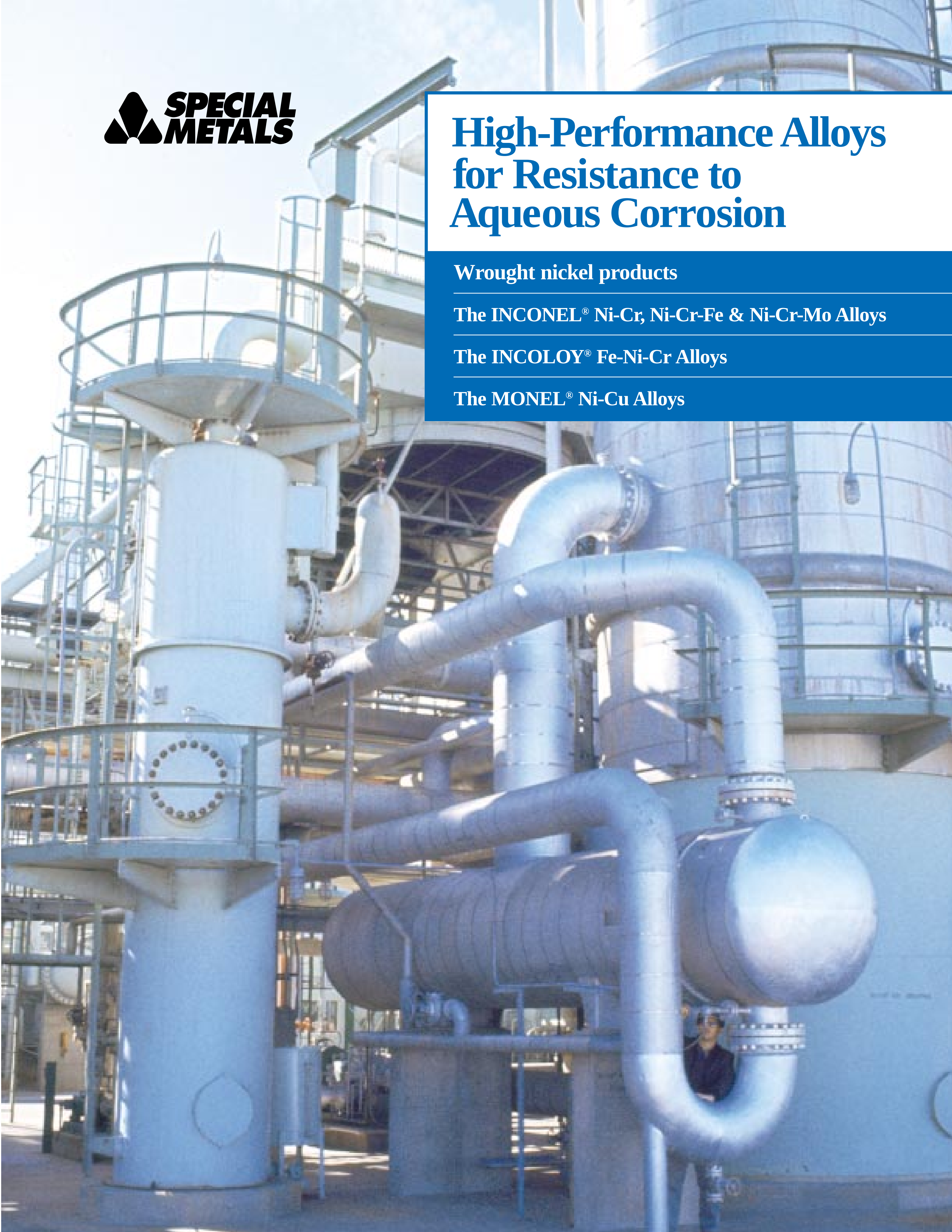
High-Performance Alloys for Resistance to Aqueous Corrosion

Wrought nickel products

The INCONEL® Ni-Cr, Ni-Cr-Fe & Ni-Cr-Mo Alloys

The INCOLOY® Fe-Ni-Cr Alloys

The MONEL® Ni-Cu Alloys



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Corrosion Problems and Alloy Solutions

Due to their excellent corrosion resistance and good mechanical properties, the Special Metals nickel-based alloys are used for a broad range of applications in an equally broad range of industries, including chemical and petrochemical processing, pollution control, oil and gas extraction, marine engineering, power generation, and pulp and paper manufacture. The alloys' versatility and reliability make them the prime materials of choice for construction of process vessels, piping systems, pumps, valves and many other applications designed for service in aqueous and high-temperature environments.

Many variables influence the performance of a specific material in a specific environment. These include concentration, temperature, aeration, liquid or gaseous flow rates, impurities, abrasives, and cycling process conditions. While every attempt has been made to present a broad base of information, more detailed data will often be needed for individual applications and environments. The reader is encouraged to contact Special Metals marketing and technical staff for more specific alloy properties and a wealth of experience of applications and alloy service and performance.

Corrosion problems can be found in many forms.

Metallic corrosion under aqueous conditions can take place by many mechanisms with quite varied results. A brief general description of each type of corrosion is presented here as an introduction. More detail of the mechanics of the various types of corrosion is presented later in this publication under “Corrosion Science and Electrochemistry”.

General Corrosion – General corrosion is a uniform attack and is the most commonly encountered type of corrosion. It is characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface area. The metal becomes thinner and eventually fails.

Localized Corrosion – Conditions may exist that cause corrosive attack in a very specific location or under a specific set of conditions. Such attack is normally referred to as localized. This type of corrosion takes several forms. Pitting, crevice attack, and microbially influenced corrosion (MIC) are all types of localized corrosion.

Pitting – Pitting is a form of very localized attack that results in the formation of holes in the metal. While the holes formed are generally small they can propagate very quickly leading to material perforation and failure in a very short period of time. The micro-environment within the pit itself can be autocatalytic making this a particularly dangerous form of attack.

Crevice Corrosion – Crevice attack usually takes place in a very tight gap between two surfaces (e.g. as with gaskets or fasteners or under mineral deposits). As with pitting, the micro-environment within the crevice can greatly differ from the general medium. Concentration cells can cause this type of corrosion to progress at a very rapid rate.

Microbially Influenced Corrosion (MIC) – MIC is a recently identified form of crevice attack. Certain types of bacteria form dome-shaped colonies on the metallic surface. The inside of the structure is sealed from the outside. The life cycle of the bacteria produces a corrosive environment within the colony which causes a crevice attack of the metal. While MIC usually takes place on components exposed to natural water (either fresh or brackish), it has also been encountered in process water in industrial systems.

Environmentally Assisted Cracking – Some types of corrosion take place as a result of chemical conditions within the environment and the mechanical condition of the metal itself. Both conditions must be present for this type of corrosion to take place. Corrosion fatigue, stress corrosion cracking, liquid metal cracking, and hydrogen embrittlement are all forms of environmentally assisted cracking.

Corrosion Fatigue – Corrosion fatigue failure takes place due to the reduction of fatigue resistance of the metal with the presence of a corrosive medium. Thus it is normally encountered not as a visible degradation of the metal but as a premature failure of a component under cyclic conditions. The stress under which the material fails would not normally be considered sufficient to cause failure.

Stress Corrosion Cracking – This refers to the cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. During this type of cracking, the metal is virtually unattacked over most of the surface while fine cracks progress through it at the attack site. Chloride stress cracking of stainless steels and ammonia stress cracking of nickel-copper alloys are examples of this type of attack.

Liquid Metal Cracking – Liquid metal cracking is a specialized form of stress corrosion. The susceptible metal (usually due to residual tensile stresses from fabrication) is attacked (cracked) by a low-melting liquid metal. An example is the cracking of aged Ni-Cr-Fe alloys by silver-base braze alloys.

Hydrogen Embrittlement – Hydrogen embrittlement takes place due to the penetration of the surface of susceptible metals by elemental hydrogen. This can result from the formation of metallic hydride compounds in some materials while in others it takes place by the interaction of dissolved hydrogen atoms. Regardless of the mechanism, the attack results in the formation and propagation of fine cracks and voids in the metallic structure.

Intergranular Corrosion – Intergranular corrosion, as the name implies, is the selective attack of a metallic component at the grain boundaries by a corrosive medium. Several conditions can lead to a material being susceptible to intergranular corrosion. In some environments the grain boundary of a metal simply exhibits the most reactive nature. Because of thermal mechanical processing, metallic compounds may tend to precipitate and migrate to the grain boundaries. If these are more reactive than the metallic matrix, they can be selectively attacked. Metallic reactions can cause areas adjacent to the grain boundary to be depleted of some element, rendering this zone less resistant to attack. A commonly encountered form of intergranular corrosion is the attack of non-stabilized austenitic stainless steels due to the formation of chromium carbide precipitates and the subsequent depletion of chromium.

Erosion Corrosion – Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive medium and the metal surface. Generally the movement is rapid and the effects of mechanical wear or abrasion are involved. Metal is removed from the surface as dissolved ions or corrosion products are mechanically swept away from the metal surface.

Galvanic Corrosion – Galvanic corrosion results from the electrical coupling of two dissimilar metals in a corrosive medium resulting in the attack of the less resistant metal. The metallic differences may be due to metallic structure as well as composition. The less noble material becomes anodic while the more noble becomes cathodic. The anodic material actually protects the cathodic leading to its own accelerated decay. Ranking of materials in an electromotive force (EMF) or galvanic series in a specific media will help determine the propensity of two materials for this type of corrosion. The farther apart the materials are in the series, the greater is the likelihood of attack of the less noble material.

Dealloying – Dealloying (also referred to as selective leaching) is the selective removal of one element of a solid alloy by a corrosion process. A corrosive medium specifically attacks one component of the alloy. A common example of this type of corrosion is the selective removal of zinc from brass (dezincification).

The solutions to the problems can be found in nickel and its alloying elements.

Nickel retains an austenitic, face-centered-cubic (fcc) crystal structure up to its melting point, providing freedom from ductile-to-brittle transitions and minimizing the fabrication problems that can be encountered with other metals. In the electrochemical series, nickel is more noble than iron but more active than copper. Thus, in reducing environments, nickel is more corrosion resistant than iron, but not as resistant as copper. Alloying with chromium provides resistance to oxidation thus providing a broad spectrum of alloys for optimum corrosion resistance in both reducing and oxidizing environments. Nickel-based alloys have a higher tolerance for alloying elements in solid solution than stainless steels and other iron-based alloys but maintain good metallurgical stability. These factors have prompted development of nickel-based alloys with multiple alloying additions to provide resistance to a wide variety of corrosive environments.

Nickel – Provides metallurgical stability, improves thermal stability and weldability, improves resistance to reducing acids and caustics, and increases resistance to stress corrosion cracking particularly in chlorides and caustics.

Chromium – Improves resistance to oxidizing corrosives and to high-temperature oxidation and sulfidation, and enhances resistance to pitting and crevice corrosion.

Molybdenum – Improves resistance to reducing acids, and to pitting and crevice corrosion in aqueous chloride containing environments. It contributes to increased high-temperature strength.

Iron – Improves resistance to high-temperature carburizing environments, reduces alloy costs, and controls thermal expansion.

Copper – Improves resistance to reducing acids (particularly non-aerated sulfuric and hydrofluoric) and to salts. Copper additions to nickel-chromium-molybdenum-iron alloys provide improved resistance to hydrochloric, phosphoric and sulfuric acids.

Aluminum – Improves resistance to oxidation at elevated temperatures and promotes age hardening.

Titanium – Combines with carbon to reduce susceptibility to intergranular corrosion due to chromium carbide precipitation resulting from heat treatments, and enhances age hardening.

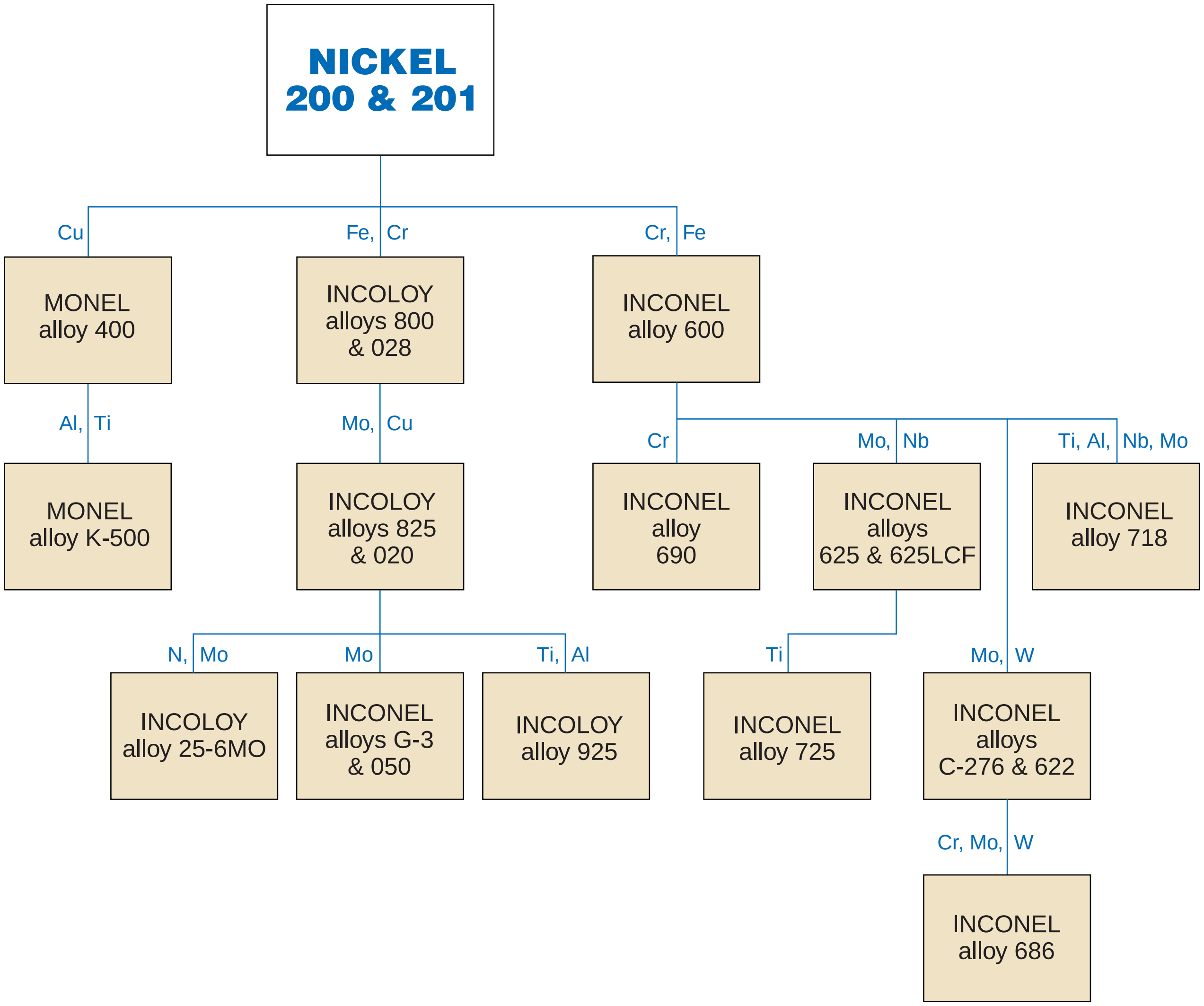
Niobium (Columbium) – Combines with carbon to reduce susceptibility to intergranular corrosion due to chromium carbide precipitation resulting from heat treatments, improves resistance to pitting and crevice corrosion, and increases high temperature strength.

Tungsten – Improves resistance to reducing acids and to localized corrosion, and enhances both strength and weldability.

Nitrogen – Enhances metallurgical stability, improves pitting and crevice corrosion resistance, and increases strength.

Cobalt – Provides increased high-temperature strength, and resistance to carburization and sulfidation.

Many of these alloying elements can be combined with nickel in single phase solid solutions over a broad composition range to provide alloys with useful corrosion resistance in a wide variety of environments. These alloys, in turn, provide useful engineering properties in the fully annealed condition without fear of deleterious metallurgical changes resulting from fabrication or thermal processing. Many of the high-nickel alloys can be strengthened by solid solution hardening, carbide precipitation, precipitation (age) hardening and by dispersion strengthened powder metallurgy.



The Special Metals Alloy Products

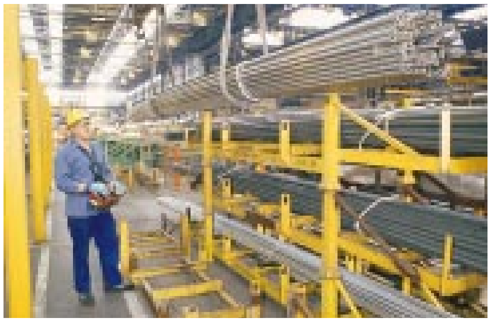
A world leader in the development and production of high-performance, mainly nickel-based, alloys, Special Metals has manufacturing facilities in the USA and Europe, and sales and service locations in North America, Europe and Asia. Serving markets ranging from aerospace to sub-sea oil and gas extraction, the company's production facilities include air melting and AOD refining, vacuum melting and remelting, electroslag remelting, alloy powder metallurgy, forging, extrusion, hot and cold rolling, and cold drawing. Product forms available from Special Metals include billet, bar, rod, plate, sheet, strip, seamless tubing, wire and welding consumables.

Nickel and the INCONEL®, INCOLOY® and MONEL® Corrosion-Resistant Alloys

Nickel 200 – Commercially pure wrought nickel with good mechanical properties and aqueous corrosion-resistance. Used for chemical and process plants such as caustic soda and synthetic fiber production, and for food handling. Available as rod and bar, flat products, seamless tubing and wire. Age-hardenable DURANICKEL® alloy 301 is also available as rod, bar and wire.

Nickel 201 – Similar to Nickel 200 but with low carbon controlled to prevent intergranular embrittlement at above 600˚F (315˚C). Used for chemical and process plants. Available as rod and bar, flat products, seamless tubing and wire.

MONEL® alloy 400 – A Ni-Cu alloy with high strength and excellent resistance to a range of media including seawater, dilute hydrofluoric and sulfuric acids, and alkalies. Used in marine and offshore engineering, salt production, feedwater heaters, and chemical and hydrocarbon processing. Available as billet, rod and bar, flat products, seamless tubing and wire. MONEL® alloy R-405 with controlled sulfur to improve its machining properties is also available as billet, rod and bar, and wire.



MONEL® alloy K-500 – Similar to MONEL alloy 400 but age-hardenable for higher strength and hardness. Used for pump shafts, oil well tools, doctor blades, springs, fasteners and marine propeller shafts. Available as billet, rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 600 – A Ni-Cr-Fe alloy with resistance to stress-corrosion cracking and caustic corrosion, and with high-temperature strength and oxidation-resistance. Used for chemical and petrochemical processing, nuclear and automobile engineering and thermal processing. Available as billet, rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 622 – Resistant to corrosion in a range of reducing and oxidizing media, and to localized corrosion and stress-corrosion cracking. Used in chemical processing and pollution control. Available as rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 625 – A Ni-Cr-Mo Nb-stabilized alloy with resistance to aggressive media, particularly to crevice corrosion, pitting and high-temperature oxidation. Used in aerospace, chemical processing, oil and gas extraction, pollution control, and marine and nuclear engineering. Available as billet, rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 625LCF® – Similar to INCONEL alloy 625 but with composition and processing controlled for optimum resistance to mechanical and thermal fatigue up to 1200˚F (650˚C). Widely used for bellows expansion joints. Available as flat products, notably as sheet and strip.

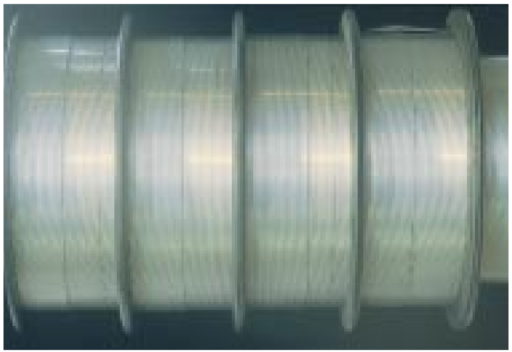
INCONEL® alloy 686 – Offers optimum resistance to localized corrosion in acid chloride environments, and excellent resistance to oxidizing, reducing and mixed acids. Used in pollution control, waste processing and process industry applications. Available as rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 690 – An alloy with excellent high-temperature corrosion-resistance for applications including nuclear steam generators, petrochemical processing, coal gasification, and sulfuric, nitric and nitric/hydrofluoric acid processing. Available as billet, rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 718 – An age-hardenable alloy combining strength up to 1300˚F (700˚C) with corrosion-resistance and weldability. Available as billet, rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 725™ – An alloy with corrosion-resistance comparable with that of INCONEL alloy 625 but with higher strength obtainable by age-hardening. Available as billet, rod and bar, seamless tubing and wire.

INCONEL® alloy C-276 – Offers resistance to reducing and mildly oxidizing environments, and is resistant to localized attack and to stress-corrosion cracking. Used widely in the chemical and process industries and for aggressive environments in the pollution control industry. Available as rod and bar, flat products, seamless tubing and wire.



INCONEL® alloy G-3 – Readily weldable and resistant to intergranular corrosion in the welded condition. Used for oil and gas well downhole tubulars, and for handling phosphoric and sulfuric acids. Available as rod and bar, flat products, seamless tubing and wire.

INCONEL® alloy 050 – An alloy with excellent resistance to stress-corrosion cracking, particularly in sour gas environments, used for downhole tubing in oil and gas extraction. Available as seamless tubing.

INCOLOY® alloy 800 – An alloy with strength and corrosion-resistance for use in chemical, petrochemical and food processing, for nuclear engineering and for the sheathing of electrical heating elements. For use, generally, at temperatures below 1200˚F (650˚C). Available as rod and bar, flat products, seamless tubing and wire.

INCOLOY® alloy 825 – A Ni-Fe-Cr-Mo Ti-stabilized alloy with excellent resistance to sulfuric and phosphoric acids. Resistant to reducing and oxidizing acids, pitting, stress-corrosion cracking and intergranular corrosion, it is used in chemical and petrochemical processing, oil and gas extraction, pollution control, waste processing and pickling applications. Available as billet, rod and bar, flat products, seamless tubing and wire.

INCOLOY® alloy 864™ – An alloy with excellent fatigue resistance, thermal stability and resistance to hot salt corrosion, pitting and chloride stress-corrosion cracking. Developed for automotive exhaust system flexible couplings, EGR systems, manifolds and tailpipes. Available as flat products and wire.

INCOLOY® alloy 925™ – With corrosion-resistance comparable with that of INCOLOY alloy 825 but with higher strength obtainable by age-hardening. Used in the oil, gas and marine industries for applications calling for high strength and resistance to general corrosion and pitting. Available as billet, rod and bar, seamless tubing and wire.

INCOLOY® alloy 020 – A Ni-Fe-Cr-Mo Nb-stabilized alloy resistant to general corrosion, pitting and crevice corrosion in media containing chlorides, and sulfuric, phosphoric and nitric acids. Available as billet, rod and bar, flat products, seamless tubing and wire.

INCOLOY® alloy 028 – A corrosion-resistant austenitic stainless steel used for downhole tubing in oil and gas extraction operations. Available as seamless tubing.

INCOLOY® alloy 25-6MO – A 6% molybdenum, nitrogen-bearing super-austenitic stainless steel resistant to pitting and crevice corrosion in media containing chlorides and other halides. Used for handling sulfuric and phosphoric acids, chemical plant, marine and offshore engineering, pulp and paper production, pollution control and nuclear service water piping. Available as rod and bar, flat products, seamless tubing and wire.

Table 1 – Nominal chemical compositions (% by weight)

Designation	UNS	Werkstoff	Ni	Cr	Mo	Fe	Cu	Other
Nickel 200	N02200	2.4060	99.6					C 0.04
Nickel 201	N02201	2.4061	99.6					C 0.02 max.
MONEL alloy 400	N04400	2.4360	65.1			1.6	32.0	Mn 1.1
MONEL alloy K-500	N05500	2.4375	64.7			1.0	30.2	Al 2.7, Ti 0.6
INCONEL alloy 600	N06600	2.4816	76.0	15.0		8.0		
INCONEL alloy 622	N06022	2.4602	59.0	20.5	14.2	2.3		W 3.2
INCONEL alloys 625 and 625LCF	N06625 N06626	2.4856	61.0	21.5	9.0	2.5		Nb 3.6
INCONEL alloy 686	N06686	2.4606	58.0	20.5	16.3	<1.0		W 3.8
INCONEL alloy 690	N06690	2.4642	61.5	29.0		9.0		
INCONEL alloy 718	N07718	2.4668	54.0	18.0	3.0	18.5		Nb 5.0, Ti 1.0
INCONEL alloy 725	N07725		57.0	21.0	8.0	7.5		Nb 3.5, Ti 1.5, Al 0.3
INCONEL alloy C-276	N10276	2.4819	57.0	16.0	16.0	5.5		W 4.0
INCONEL alloy G-3	N06985	2.4619	44.0	22.0	7.0	19.5	2.0	
INCONEL alloy 050	N06950		50.0	20.0	9.0	17.0		
INCOLOY alloy 800	N08800	1.4876	32.5	21.0		46.0		C 0.05
INCOLOY alloy 825	N08825	2.4858	42.0	21.5	3.0	28.0	2.0	
INCOLOY alloy 864	S35135		34.0	21.0	4.2	39.0		Si 0.8, Ti 0.6
INCOLOY alloy 925	N09925		44.0	21.0	3.0	28.0	1.8	Ti 2.1, Al 0.3
INCOLOY alloy 020	N08020	2.4660	35.0	20.0	2.5	37.0	3.5	Nb 0.6
INCOLOY alloy 028	N08028	1.4563	32.0	27.0	3.5		1.0	Mn 2.0
INCOLOY alloy 25-6MO	N08926	1.4529	25.0	20.0	6.5	47.0	0.9	N 0.20

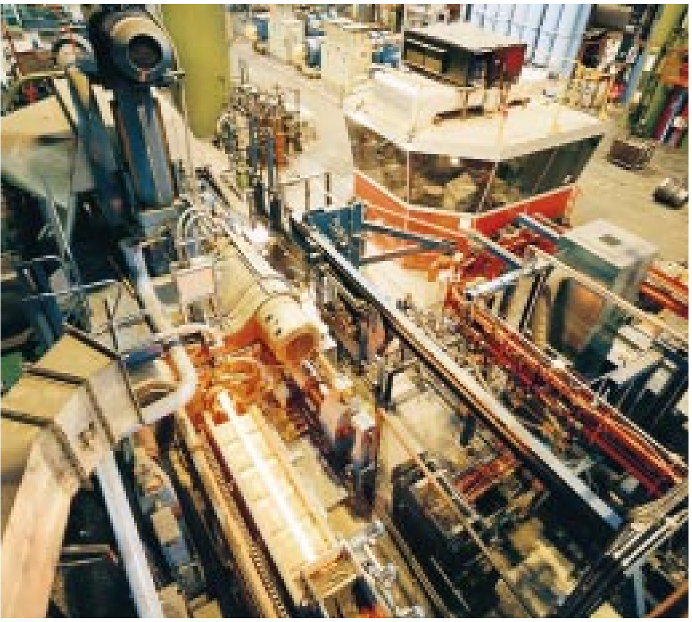


Table 2 – Typical physical and mechanical properties of corrosion-resistant alloys (Typical data, not suitable for design or specifications)

Alloy	Density		Nominal room-temperature mechanical properties (Annealed material unless noted)					
			Tensile strength		0.2% yield strength		Elongation	Hardness
	lb/in^3	g/cm^3	ksi	MPa	ksi	MPa	%	Brinel
Nickel 200	0.321	8.89	65	448	30	207	45	110
Nickel 201	0.321	8.89	60	414	35	241	50	100
DURANICKEL® alloy 301 (aged)	0.296	8.19	160	1100	125	860	25	340
MONEL® alloy 400	0.318	8.80	80	552	40	276	45	140
MONEL® alloy R-405 (stress-relieved)	0.318	8.80	95	655	85	586	25	205
MONEL® alloy K-500 (aged)	0.305	8.44	155	1069	100	689	25	310
INCONEL® alloy 600	0.306	8.47	100	689	50	345	40	170
INCONEL® alloy 622	0.311	8.61	115	793	55	379	60	170
INCONEL® alloy 625	0.305	8.44	125	862	65	448	50	200
INCONEL® alloy 625LCF®	0.305	8.44	130	896	70	483	50	255
INCONEL® alloy 686	0.315	8.73	110	758	55	379	60	180
INCONEL® alloy 690	0.296	8.19	100	689	50	345	45	170
INCONEL® alloy 718 (aged)	0.296	8.19	205	1413	165	1138	20	425
INCONEL® alloy 725™ (aged)	0.300	8.30	185	1276	130	896	30	355
INCONEL® alloy C-276	0.321	8.89	110	758	50	345	60	180
INCONEL® alloy G-3	0.294	8.14	105	724	55	379	40	140
INCONEL® alloy 050 (as drawn)	0.303	8.39	130	896	125	862	13	326
INCOLOY® alloy 800	0.287	7.94	90	621	50	345	40	165
INCOLOY® alloy 825	0.294	8.14	95	655	45	310	45	155
INCOLOY® alloy 864™	0.290	8.02	95	655	40	276	45	150
INCOLOY® alloy 925™ (aged)	0.292	8.08	170	1172	120	827	25	320
INCOLOY® alloy 020	0.292	8.08	95	655	60	414	35	180
INCOLOY® alloy 25-6MO	0.290	8.03	110	758	55	379	45	180
INCOLOY® alloy 028	0.290	8.03	90	621	40	276	40	160

A Guide to Aqueous Corrosion-Resistance

(All alloys listed are resistant to chloride cracking)

★ = Good to excellent
☆ = Acceptable
– = Not suitable

	Sulfuric Acid	Hydrochloric Acid	Hydrofluoric Acid	Phosphoric Acid	Nitric Acid	Organic Acids	Alkalines & Salts	Seawater
Nickel 200	☆	☆	★	☆	–	★	★	☆
Nickel 201	☆	☆	★	☆	–	★	★	☆
DURANICKEL® alloy 301	☆	☆	★	☆	–	★	★	☆
MONEL® alloy 400	★	☆	★	★	–	★	★	★
MONEL® alloy R-405	★	☆	★	★	–	★	★	★
MONEL® alloy K-500	★	☆	★	★	–	★	★	★
INCONEL® alloy 600	☆	–	☆	☆	–	★	★	☆
INCONEL® alloy 622	★	★	★	★	★	★	★	★
INCONEL® alloy 625	★	★	★	★	★	★	★	★
INCONEL® alloy 625LCF®	★	★	★	★	★	★	★	★
INCONEL® alloy 686	★	★	★	★	★	★	★	★
INCONEL® alloy 690	☆	☆	★	★	★	★	★	☆
INCONEL® alloy 718	☆	☆	☆	☆	☆	★	★	★
INCONEL® alloy 725™	★	★	★	★	★	★	★	★
INCONEL® alloy C-276	★	★	★	★	☆	★	★	★
INCONEL® alloy G-3	★	★	★	★	★	★	★	★
INCONEL® alloy 050	★	★	★	★	★	★	★	★
INCOLOY® alloy 800	☆	☆	–	☆	★	★	☆	☆
INCOLOY® alloy 825	★	★	★	★	★	★	★	★
INCOLOY® alloy 864™	☆	☆	☆	☆	★	★	★	★
INCOLOY® alloy 925™	★	★	★	★	★	★	★	★
INCOLOY® alloy 020	★	★	★	★	★	★	★	★
INCOLOY® alloy 25-6MO	★	★	☆	★	★	★	★	★
INCOLOY® alloy 028	☆	★	☆	☆	★	★	★	★

Corrosion by Acids

Acids can be either oxidizing or reducing in nature. Some metals are resistant to oxidizing acids (e.g. nitric) while others are resistant to reducing acids (e.g. hydrochloric or sulfuric). By alloying such metals it is possible to produce materials that resist corrosion in both media. Data are presented in this section of the publication describing the performance of various nickel alloys in the acid environments in which they are most often used. The choice of an alloy for a specific environment will depend on the acid or the mixture of acids present, on concentration, temperature, aeration, contaminants, flow characteristics, the presence and tightness of crevices, other material in the system, and many other environmental conditions.

The iso-corrosion charts and much of the tabular data presented were generated from laboratory testing of material in pure or mixed acids. Field data generated from the actual exposure to specific process environments are also presented. While these data may be used as guidelines for material selection, the reader is cautioned to consider that variations or the presence or absence of any of the environmental conditions described can significantly alter the performance of an alloy in any environment. A complete and accurate definition of the environment to which the material will be exposed is necessary if a proper alloy selection is to be made.

Sulfuric Acid

Sulfuric acid is often encountered in industrial environments because it is used extensively in a variety of chemical processes. It is reducing in concentrations up to about 25%. At greater concentrations, it begins to take on oxidizing characteristics. Concentrated acid (above 87% by weight) at room temperature is the most commonly encountered commercial product and is oxidizing in nature. Thus, dilute and intermediate strengths of the acid can be contained by materials resistant to reducing conditions while stronger concentrations require materials resistant to oxidizing media.

Selection of a metal or alloy for a particular process depends primarily on the reducing or oxidizing nature of the solution as determined by acid concentration, aeration, temperature and nature of impurities. Selection depends on factors such as velocity, film formation, continuity of exposure, allowable metallic content of the solution, and physical properties of the alloy.

The most commonly used nickel alloys in processes containing dilute sulfuric acid are INCOLOY alloys 25-6MO, 825 and 020, and INCONEL alloy G-3. For aggressive, hot, sulfuric acid environments, INCONEL alloys 625, 622, C-276 and 686 are most often selected.

Nickel 200

Nickel 200 can be used with sulfuric acid solutions at low or moderate temperatures. Aeration increases corrosion rates, particularly in dilute acids. In concentrated acids, aeration decreases corrosion rates, possibly because of the formation of a passive film, but Nickel 200 is seldom used in this service because other, more resistant materials are adequate.

MONEL alloy 400

MONEL alloy 400 is used for handling sulfuric acid solutions under reducing conditions. Figure 1 shows the effects of aeration in 5-6% acid concentration on the corrosion rate of MONEL alloy 400 at various temperatures. In air-free solutions the rate is very low at all temperatures. As with Nickel 200, but to a lesser degree, aeration increases the corrosion rate for MONEL alloy 400.

At higher temperatures in aerated acid, the rate decreases until the boiling point is reached, when the corrosion rate is the same as in air-free acid. Above 85%, the acid becomes oxidizing, and the corrosion rate undergoes a sharp increase which is only slightly affected by aeration. Boiling 25% acid also attacks MONEL alloy 400, the reduction of the cation releasing hydrogen sulfide, sulfur dioxide and attendant sulfur from their interaction. MONEL alloy 400 has shown suitable resistance to boiling sulfuric acid solutions up to about 15% concentration.

In practice, MONEL alloy 400 has shown satisfactory resistance in the storage of 80% acid at room temperature, but should not be used continuously with pure acid of higher concentration without preliminary tests.

At elevated temperatures, the maximum concentration for the use of MONEL alloy 400 in pure acid solutions is reduced to about 65%. In some organic processes, concentrated acid (93 to 98%) is added to large proportions of organic materials and is progressively diluted to lower

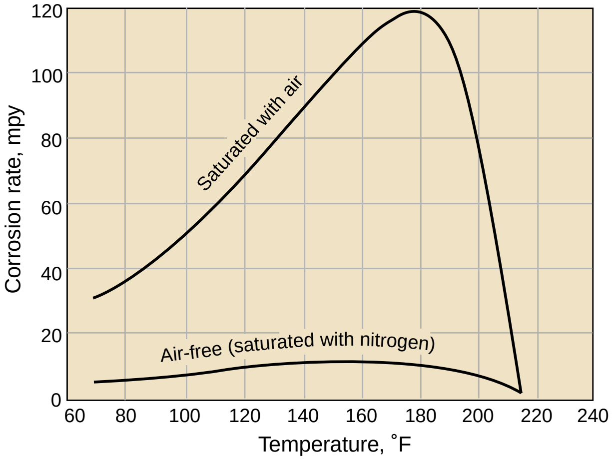


Figure 1 – Effect of temperature on corrosion of MONEL alloy 400 in sulfuric acid. Acid concentration, 5-6%. Velocity, 15.5-16.5 ft/min.

concentrations. In such cases MONEL alloy 400 frequently has good resistance because of dispersion of the acid and the film-forming or inhibiting action of some organic materials.

In most sulfuric acid applications, the actual corrosion rate of MONEL alloy 400 will be close to the air-free rate because continuous air saturation is uncommon. A high degree of aeration would be expected only when air is bubbled continuously through the solution or when the solution is sprayed or poured through the air or churned up with considerable air in pumping. The rate at which air may be replenished at a quiet solution-air interface is small compared to the rate at which oxygen can be removed by corrosion. Consequently, a high degree of aeration would be expected only at the liquid line and, if this level is constant, corrosion would be accelerated at this line. The presence of organic materials, such as foods, fats and sugars, will limit the degree of aeration because these materials will react with dissolved oxygen and remove it from solution.

The presence of oxidizing salts (such as ferric sulfate, chromates, dichromates, nitrates, nitrites, peroxides, and cupric salts) may make sulfuric acid solutions very corrosive to MONEL alloy 400. Note that recirculation of, or long residence time in, intermediate concentrations of acid results in autocatalytic corrosion due to the accumulation of cupric ions in the acid from the corrosion of this nickel-copper alloy.

The usual effect of increasing velocity between metal and liquid is an increase in corrosion rate. This motion brings fresh acid and oxygen, if present, to the metal surface, removes spent acid, and thins the diffusion film through which reactants and products must pass. For MONEL alloy 400, velocity effects are most pronounced in aerated acid solutions. Abnormally high velocities, especially when abrasive solids are suspended in solution, should be avoided.

Experience with MONEL alloy 400 indicates that it is not susceptible to stress-corrosion cracking in sulfuric acid solutions, except those containing mercury salts or considerable amounts of hydrofluoric or fluorosilicic acid. In these cases the possibility of stress-corrosion cracking can be avoided by giving the fabricated MONEL alloy 400 equipment a stress-relieving heat treatment, 1000-1200˚F (538-648˚C)/1 hour/slow cool, before placing it in service.

INCONEL alloy 600

Because of its chromium content, INCONEL alloy 600 offers better resistance to sulfuric acid under oxidizing conditions than either Nickel 200 or MONEL alloy 400. INCONEL alloy 600 usually has adequate resistance to corrosion by cold, non-aerated sulfuric acid solutions up to about 70% concentration although its resistance is not as good as that of MONEL alloy 400. The oxidizing power of dissolved air is not sufficient to maintain passivity except in concentrated acid. Consequently, corrosion rates are increased by aeration in pure, dilute solutions (Table 3). INCONEL alloy 600, which is more corrosion sensitive to temperature increases than is MONEL alloy 400, should not be subjected to hot sulfuric acid solutions except at low concentrations. When aeration is combined with elevated temperatures, corrosion rates are usually high.

The addition of oxidizing salts to sulfuric acid tends to passivate INCONEL alloy 600 which, in contrast with MONEL alloy 400, can be used with acid mine waters or brass pickling solutions. However, in very hot solutions

Table 3 – Corrosion-resistance of INCONEL alloy 600 in sulfuric acid solutions

Acid concentration, % by wt	Temperature, ˚F (˚C)	Duration of test, h	Velocity, ft/min (m/min)	Corrosion rate, mpy (mm/a)*	
				Non-aerated	Air saturated
0.16	212 (100)	–	–	3.7 (0.09)	–
1	86 (30)	120	15.5 (4.72)	–	49 (1.24)
1	172 (78)	22	15.5 (4.72)	–	110 (2.79)
5	65 (18)	100	None	2.4 (0.06)	–
5	86 (30)	20	15.5 (4.72)	9 (0.23)	–
5	86 (30)	23	16.0 (4.88)	–	78 (1.98)
5	140 (60)	100	None	10 (0.25)	–
5	176 (80)	20	16.0 (4.88)	30 (0.76)	150 (3.81)
10	–	24	None	4.2 (0.11)	–
70	86 (30)	20	15.5 (4.72)	46 (1.17)	–
93	86 (30)	20	15.5 (4.72)	270 (6.86)	10 (0.25)

*mpy= .001 inches per year, mm/a= millimeters per annum this passivation may not occur. It should also be remembered that it is difficult to maintain passivation in crevices (e.g. bolting, threaded connections, and flange faces) because the oxidizing ions are not replenished therein.

INCOLOY alloy 800

INCOLOY alloy 800 has little application in strong sulfuric acid.

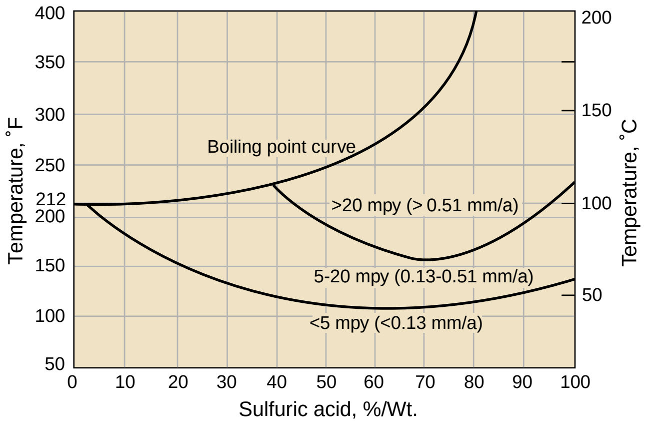


Figure 2 – Iso-corrosion chart for INCOLOY alloy 825 in sulfuric acid.

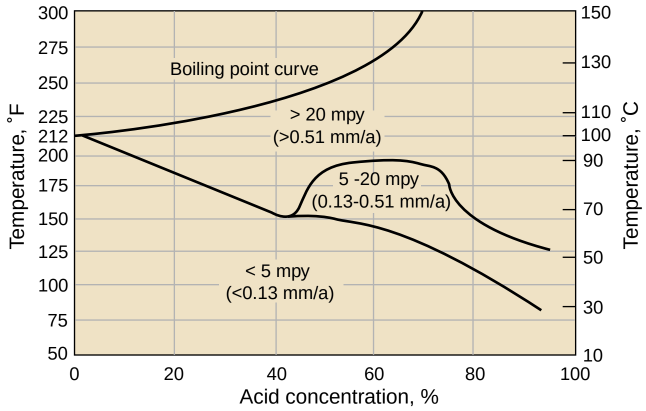


Figure 3 – Iso-corrosion chart for INCOLOY alloy 25-6MO in sulfuric acid.

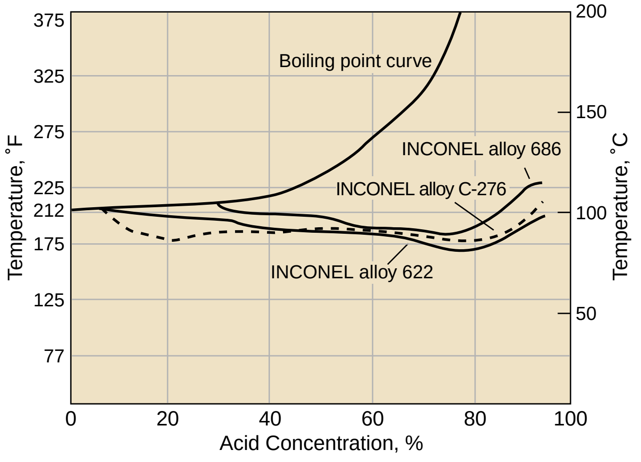


Figure 4 – Comparative behavior of Ni-Cr-Mo alloys in sulfuric acid. The iso-corrosion lines indicate a corrosion rate of 20 mpy (0.51 mm/a).

INCOLOY alloys 825, 020 and 25-6MO

INCOLOY alloy 825 has excellent resistance to sulfuric acid at intermediate concentrations. Field test results in plant sulfuric acid mixtures are shown in Table 4. Based on test results and service experience, INCOLOY alloy 825 should have very good resistance, i.e. <5 mpy (<0.13 mm/a) to corrosion in sulfuric acid solutions between 40 and 80% concentration by weight at 120˚F (50˚C).

The general resistance of INCOLOY alloy 825 is summarized in the iso-corrosion chart shown in Figure 2. Severe digressions from this behavior can occur in the presence of contaminants, which are notorious in intermediate strengths of acid in chemical processes.

A comparison of these corrosion rates with those for MONEL alloy 400 will show that INCOLOY alloy 825 has greater resistance to low concentrations of sulfuric acid at higher temperatures; that its resistance extends throughout the high concentrations where the acid is oxidizing; and that the presence of oxidizing salts (other than chloride) is actually beneficial. Also, in applications where chlorides are present, such as rock salt additions to sulfuric pickling baths, INCOLOY alloy 825 has provided excellent service. A number of mixtures containing oxidizing salts and the resultant corrosion rates are shown in Table 4. In applications where the exposure is continuously submerged in chloride-contaminated applications, the higher molybdenum alloys, such as INCONEL alloys C-276, 622, 625, or 686 are required.

Due to similarities in chemical compositions, INCOLOY alloy 020 performs in a like manner to alloy 825 in sulfuric acid service and, thus, is used in similar applications.

INCOLOY alloy 25-6MO, with a molybdenum content of 6%, as opposed to 3% for INCOLOY alloy 825, has useful resistance to corrosion in sulfuric acid solutions less than 10% concentration by weight at boiling temperatures, at up to 50% concentration at 140˚F (60˚C), and in all concentrations up to 120˚F (50˚C). The general resistance of INCOLOY alloy 25-6MO is summarized in the iso-corrosion chart shown in Figure 3. It is a contender for intermediate strength acid contaminated with chlorides.

The 20 mpy (0.51 mm/a) iso-corrosion diagrams for the Ni-Cr-Mo alloys in non-deaerated sulfuric acid discussed above are summarized in Figure 4. The relative sulfuric acid corrosion-resistance of these alloys varies with acid concentration. In dilute acid (<50%) the relative order of corrosion-resistance, in descending order, would be:

INCOLOY alloy 825/INCONEL alloy 686/INCONEL alloy G-3
INCONEL alloy 622
INCONEL alloy 625
INCONEL alloy C-276
INCOLOY alloy 25-6MO

In concentrated sulfuric acid (>50%) the descending order would be:

INCONEL alloy 686
INCONEL alloy C-276
INCONEL alloy 622
INCOLOY alloy 825
INCONEL alloy 625
INCONEL alloy G-3
INCOLOY alloy 25-6MO

Table 4 – Plant corrosion tests of INCOLOY alloy 825 in sulfuric and mixed acid solutions

Test conditions	Temperature ˚F (˚C)	Duration of test, days	Corrosion rate, mpy (mm/a)
Aqueous solution containing 0.5% sulfuric acid.	210 (99)	12	2 (0.05)
1-4% sulfuric acid, 20-25% ammonium sulfate, and 10-15% sodium sulfate. Immersed in tank.	95-104 (35-40)	–	0.1 (0.003)
Spent acid liquor from tall oil splitting. Contains 1% sulfuric acid by weight and 1% tall oil and 2-3% lignin by volume. Acid discharge line from centrifuge.	250 (121)	33	0.1 (0.003)
25-50 gm/l sulfuric acid, 25-100 gm/l manganese sulfate, 1-3 gm/l ferric sulfate. Immersed in sump manganese dioxide electrolysis circuit. Flow, 100 gal/min (379 l/min).	200 (93)	19	2.8 (0.07)
In uranium ore leach tank in mixture containing 60% solids, 28-55 gm/l sulfuric acid, 5-10 gm/l ferric ion, some ferrous ion, 0.1% sodium chlorate.	113 (45)	41	0.1 (0.003)
100-200 gm/l sulfuric acid, 40-100 gm/l selenious acid, small amounts of sulfurous acid.	70-80 (21-27)	90	Nil
Mixture of sulfuric acid and sebacic acid, pH1.	Room	30	0.1 (0.003)
5-10% sulfuric acid plus 0.25% copper sulfate in pickling of brass. Immersed 1 ft (0.30 m) below surface in continuous strip pickler.	100-200 (38-93)	162	0.1 (0.003)
5% sulfuric acid plus 10-300 mesh ore of manganese dioxide and manganese oxide. Attached to steam coil in leaching tanks.	180 (82)	245	0.5 (0.01)
Evaporation of aluminum sulfate solution from 28.2 to 58.7% aluminum sulfate containing 0.1% ferric oxide, 0.3% ferrous oxide, and traces of chromium oxide and alumina.	195-250 (91-121)	44	0.8 (0.02)
9% sulfuric acid, 1% hydrofluoric acid, 3% sodium sulfate, 1% silica, 0.5% sodium fluosilicate, and balance water. Immersed in tank near entrance.	80-120 (27-49)	62	1 (0.03)
12% sulfuric acid pickling solution containing copper sulfate up to 11.2%. Immersed inside tank of Mesta pickler.	180 (82)	26	0.2 (0.005)
20% sulfuric acid plus 4% sodium dichromate. Immersed in cleaning solution for aluminum.	150-160 (66-71)	77	19 (0.48)
Up to 20% sulfuric acid, 100 gm/l cupric sulfate, 10 gm/l nickel sulfate, and traces of chloride. Treatment of copper residue in nickel refining. Immersed in concentration plant air blowers.	195 (91)	7	5 (0.13)
In sulfuric acid solutions of various concentrations in vacuum evaporator. Recovery of sulfuric acid in paper making:			
39% sulfuric acid	120 (49)	120	Nil
42% sulfuric acid	135 (57)	120	0.3 (.008)
55% sulfuric acid	160 (71)	120	4 (0.10)
50% sulfuric acid, 22% nitric acid, and 19% water. Immersed in laboratory tests.	150 (66) 182 (83)	6 5	0.5 (.01) 4.3 (0.011)
67% sulfuric acid plus gas mixture containing 44% propylene and 56% propane. In outlet piping from second stage reactor circulating pumps, pressure 400 psi (28.1 kg/cm^2).	125 (52)	170	0.2 (.005)
In 78% sulfuric acid with traces of benzene sulfonic acid in bottom of acid settling tank.	100-130 (38-54)	8	5 (0.13)
78% sulfuric acid containing 3.5% hydrogen peroxide plus various salts of iron, manganese, chromium, and nickel in holding tank.	100-300 (38-149)	8	5 (0.13)
79-93% sulfuric acid containing small amounts of phosphine, ammonia, and hydrogen sulfate. In exit of packed tower in falling acid stream.	50-90 (10-32)	189	2.2 (0.056)
91.6% benzene sulfonic acid, 3.5% sulfuric acid. Immersed in glass-lined vessel.	140 (60)	7	45 (1.14)
36% sulfuric acid, 28% oxalic acid, 32% water, and 4% ash. On agitator support in vacuum evaporation pan. Alternately immersed and exposed.	140 (60)	171	2.4 (0.061)

INCONEL alloy G-3

INCONEL alloy G-3 has good-to-excellent resistance to sulfuric acid because of its chromium and molybdenum contents, and a small addition of copper. It has useful resistance to corrosion, i.e. <5 mpy (<0.13 mm/a) in sulfuric acid solutions up to 5% concentration by weight at boiling temperatures, up to 75% concentration at 120˚F (50˚C), and in all concentrations up to 100˚F (38˚C). The general resistance of INCONEL alloy G-3 is summarized in the iso-corrosion chart shown in Figure 5.

INCONEL alloy C-276

INCONEL alloy C-276 has excellent resistance to sulfuric acid because of its very high molybdenum content, as well as a small addition of tungsten. Based on test results and service experience, it should have useful resistance to corrosion in sulfuric acid solutions up to 10% concentration by weight at boiling temperatures, and in all concentrations up to about 175˚F (80˚C). Its general resistance is summarized in the iso-corrosion chart shown in Figure 6. Chloride contamination in sulfuric acid environments will lower its resistance; a trend observed for all nickel alloys.

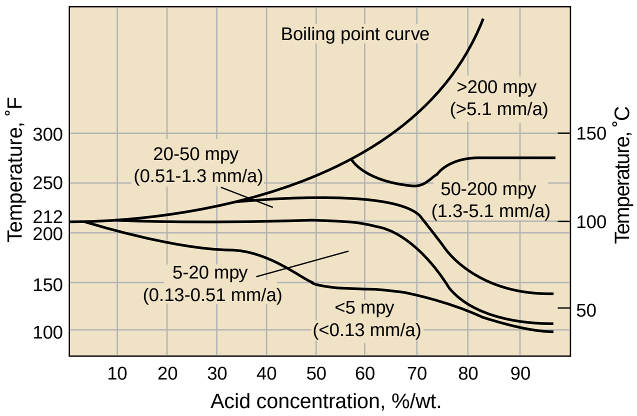


Figure 5 – Iso-corrosion chart for INCONEL alloy G-3 in sulfuric acid.

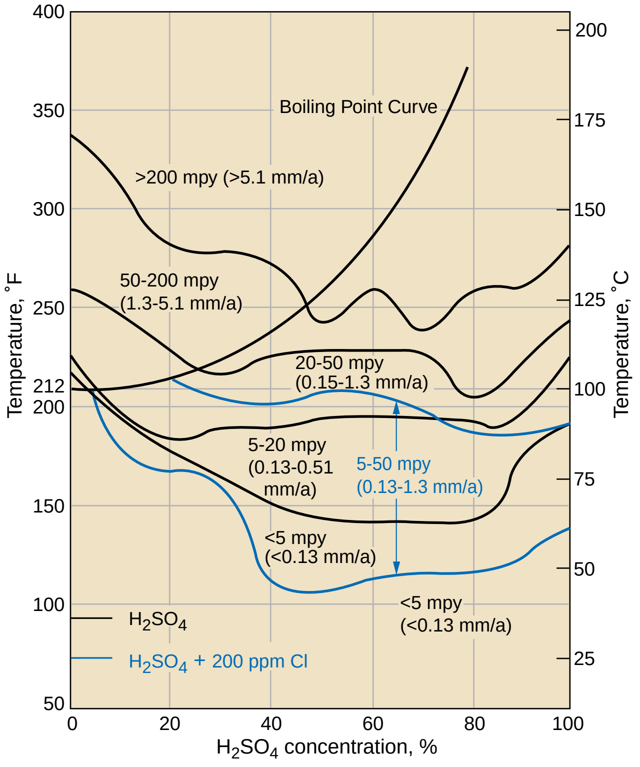


Figure 6 – Iso-corrosion chart for INCONEL alloy C-276 in sulfuric acid.

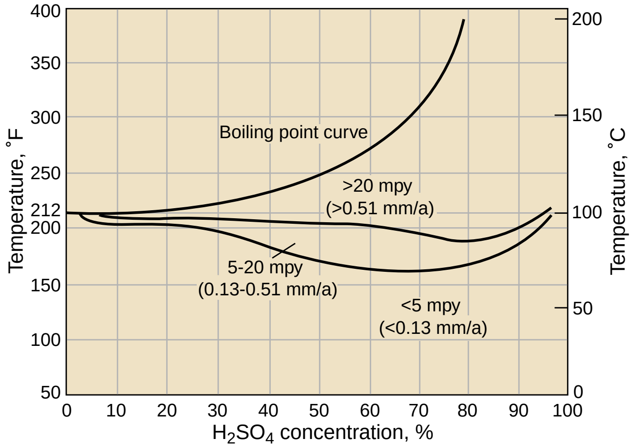


Figure 7 – Iso-corrosion chart for INCONEL alloy 622 in sulfuric acid.

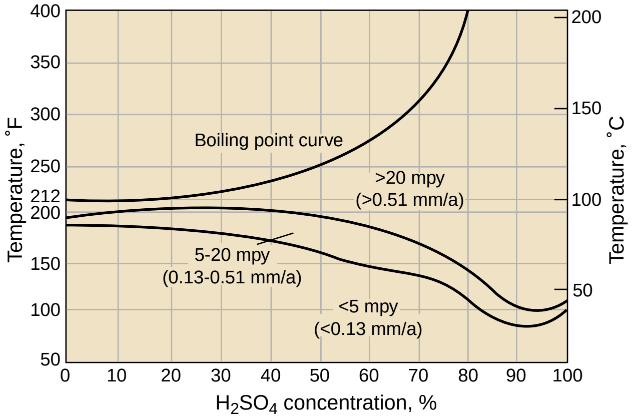


Figure 8 – Iso-corrosion chart for INCONEL alloy 625 in sulfuric acid.

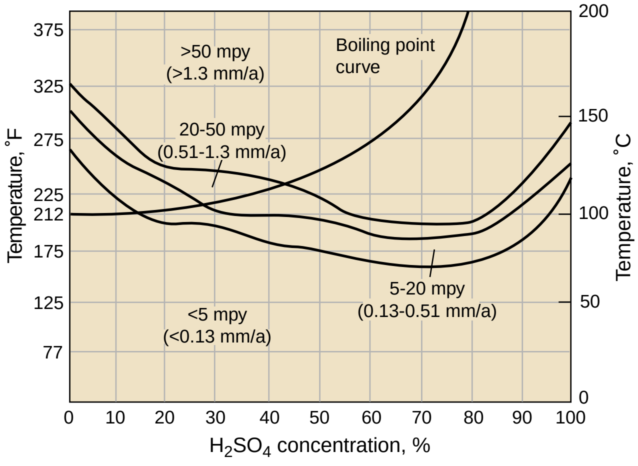


Figure 9 – Iso-corrosion chart for INCONEL alloy 686 in sulfuric acid.

INCONEL alloys 622, 625 and 686

Ni-Cr-Mo alloys such as INCONEL alloys 622, 625 and 686 show excellent resistance to sulfuric acid. The alloys' resistances are due to their high molybdenum and chromium contents, as well as additions of niobium (alloy 625) or tungsten (alloys 622 and 686). In general, they offer resistance similar to that of INCONEL alloy C-276. However, by virtue of their higher chromium contents, they offer good resistance to more concentrated acid solutions. The general resistance of INCONEL alloys 622, 625 and 686 are summarized in the iso-corrosion charts shown in Figures 7, 8 and 9. A comparison of these alloys shows that a ranked order of resistance in sulfuric acid would be:

INCONEL alloy 686
INCONEL alloy 622
INCONEL alloy 625.

Hydrochloric Acid

Hydrochloric is a typical reducing acid across its entire concentration range. Its strongly acidic character and the harmful effect of the chloride ion combine to make it a very severe corrosive. The high-nickel alloys are among the few metallic materials with useful resistance to hydrochloric acid solutions.

The presence of oxidizing contaminants (e.g. ferric or cupric ions) can drastically change the corrosivity and corrosive characteristics of a hydrochloric acid environment and the presence of such species must be considered in material selection. The most commonly used nickel alloys in processes containing dilute hydrochloric acid are INCOLOY alloys 25-6MO, 825 and 020, and INCONEL alloy G-3. For aggressive, hot hydrochloric acid environments, INCONEL alloys 625, 622, C-276 and 686 are more often selected.

Nickel 200 and MONEL alloy 400

Nickel 200 and MONEL alloy 400 are similar in their resistance to hydrochloric acid. As nickel does not readily liberate hydrogen from acid solutions, however, aeration changes the cathodic reaction to oxygen reduction and allows a higher rate of corrosion. Figure 10 shows the effects of acid concentrations and aeration on the corrosion rates of Nickel 200 and MONEL alloy 400 at 86˚F (30˚C). At up to 10% concentration both materials behave similarly, with corrosion rates in air-free solutions less than 10 mpy (0.25 mm/a).

Above 15% acid concentration, the corrosion rates of MONEL alloy 400 increase sharply and limit its normal applications at room temperature to concentrations under 10% in aerated solutions and under 20% in air-free solutions.

Nickel 200 may be used for applications in acid concentrations up to 30%, either aerated or non-aerated at room temperature. Since the performance of nickel in concentrated hydrochloric acid may be influenced by the relatively low solubility of its corrosion products, caution should be used in applying these data to service at high velocities.

Figure 11 shows that increasing temperature affects the corrosion rate of Nickel 200 more than that of MONEL alloy 400 in 5% acid. Both materials, but particularly MONEL alloy 400, are commonly used in acids of lower concentrations at higher temperatures. In most processes in which hydrochloric acid is formed as a result of

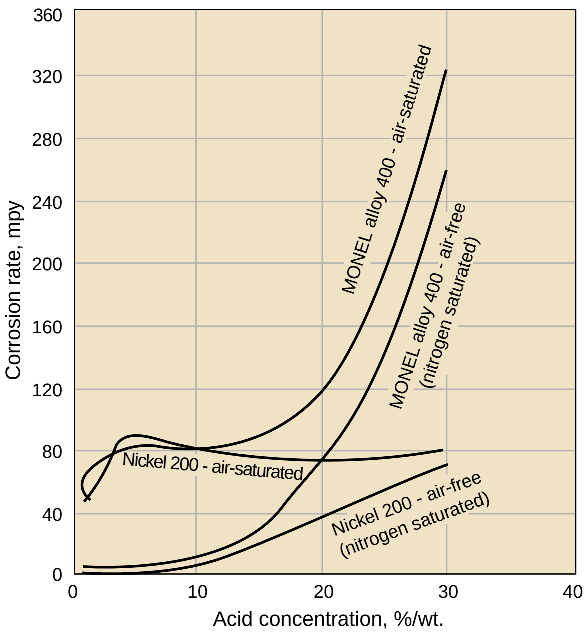


Figure 10 – Corrosion of Nickel 200 and MONEL alloy 400 in hydrochloric acid solutions at 86˚F (30˚C).

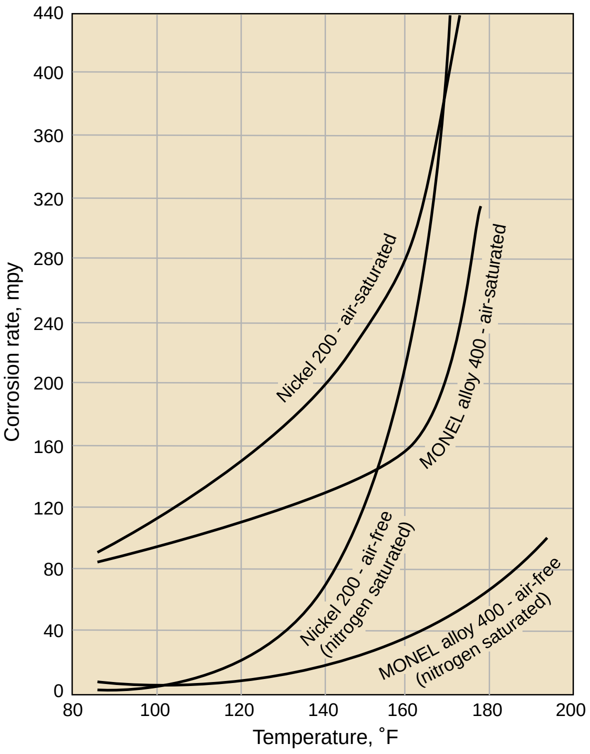


Figure 11 – Effect of temperature on corrosion of Nickel 200 and MONEL alloy 400 in 5% hydrochloric acid.

hydrolysis of chlorides or chlorinated solvents, acid concentrations are less than 0.5%. Nickel 200 and MONEL alloy 400 can withstand these concentrations satisfactorily at temperatures up to 300 or 400˚F (149 or 204˚C).

Applications for MONEL alloy 400 and Nickel 200 in air-saturated hydrochloric acid above room temperature are usually limited to concentrations under 3 or 4%. MONEL alloy 400 has been used to handle aerated acid of 2% concentration at 120˚F (49˚C) and of 1% at 180˚F (82˚C).

INCONEL alloy 600

Although INCONEL alloy 600 has fair resistance to dilute hydrochloric acid solutions, its performance (influenced by chromium content) is not as good as that of MONEL alloy 400 or Nickel 200. It has demonstrated good resistance to cold aerated acid below 2% concentration and satisfactory resistance at room temperature to concentrations up to 20%.

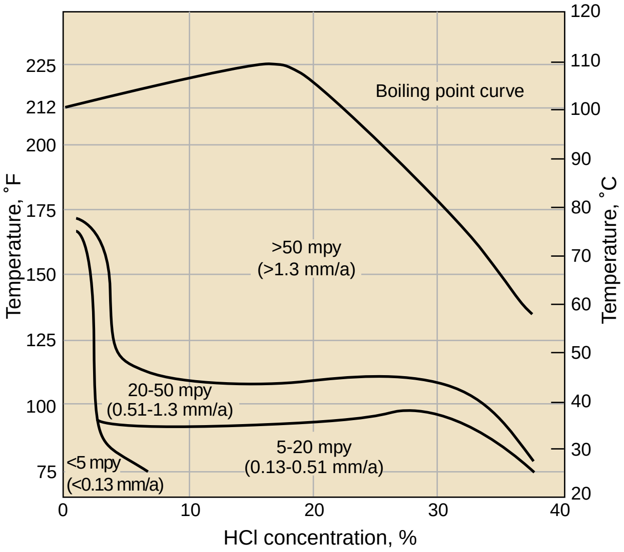


Figure 12 – Iso-corrosion chart for INCOLOY alloy 25-6MO in hydrochloric acid.

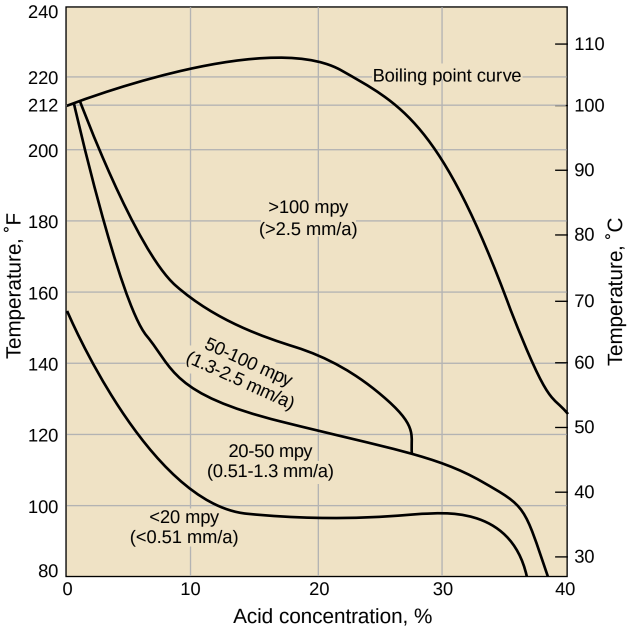


Figure 13 – Iso-corrosion chart for INCOLOY alloy 825 in hydrochloric acid.

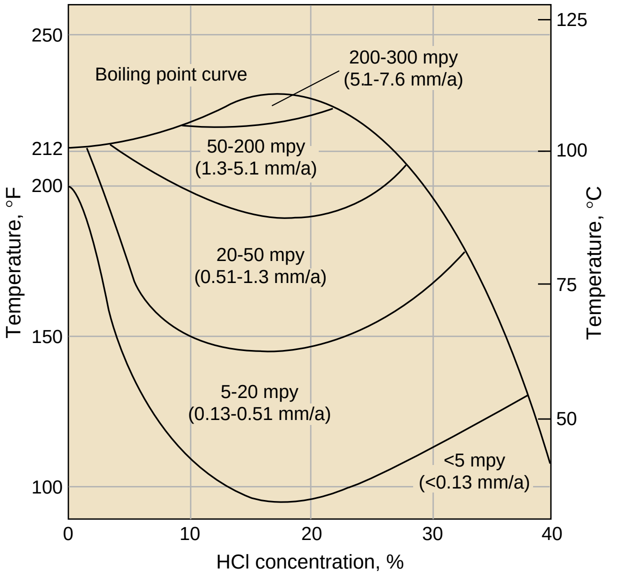


Figure 14 – Iso-corrosion chart for INCONEL alloy C-276 in hydrochloric acid.

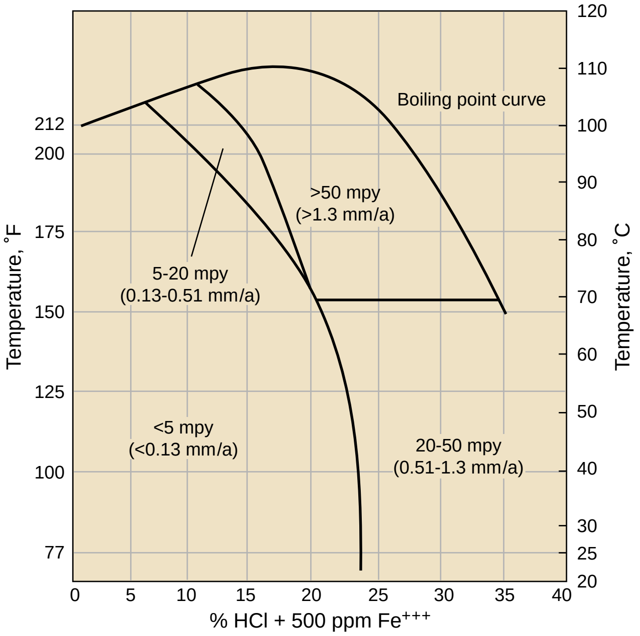


Figure 15 – Iso-corrosion chart for INCONEL alloy 686 in hydrochloric acid + 500 ppm Fe^{+++}.

INCOLOY alloys 825, 020 and 25-6MO

INCOLOY alloys 825, 020 and 25-6MO have good resistance to corrosion in hydrochloric acid solutions. The general resistance of INCOLOY alloy 25-6MO is summarized in the iso-corrosion chart shown in Figure 12. Resistance to corrosion by hydrochloric acid is greatly improved by the addition of copper and molybdenum as well as by the higher nickel content in INCOLOY alloys 825 and 020. The general resistance of INCOLOY alloy 825 is summarized in the iso-corrosion chart shown in Figure 13.

INCONEL alloys 622, 625, C-276 and 686

INCONEL alloy C-276 has excellent resistance to hydrochloric acid because of its very high molybdenum content, as well as a small addition of tungsten. Based on test results and service experience, INCONEL alloy C-276 should have useful resistance to corrosion in hydrochloric acid solutions up to 3% at boiling temperatures, up to 5% at 176˚F (80˚C) and in all concentrations up to about 150˚F (66˚C). Its general resistance is summarized in the iso-corrosion chart shown in Figure 14.

INCONEL alloys 622 and 686, because of their high molybdenum contents, have very good resistance to hydrochloric acid, particularly in strong concentrations or oxidizing conditions. These alloys are more resistant than Nickel 200 or MONEL alloy 400, especially when the acid is contaminated with oxidizing species, e.g. cupric, ferric, or oxygen. An iso-corrosion chart for INCONEL alloy 686 in hydrochloric acid containing 500 ppm ferric ions is shown in Figure 15. Comparing these data with those from exposure to pure hydrochloric acid, it is apparent that the addition of oxidizing species can actually decrease the corrosion rate of Ni-Cr-Mo alloys. Conversely, the corrosion rate of Ni-Mo alloys is increased. With an absence of chromium, Ni-Mo alloys have no resistance to environments containing oxidizing species.

INCONEL alloy 625 has good resistance to dilute hydrochloric acid by virtue of its 9% molybdenum content. The general resistance of INCONEL alloys 622, 625 and 686 is summarized in Figures 16, 17 and 18.

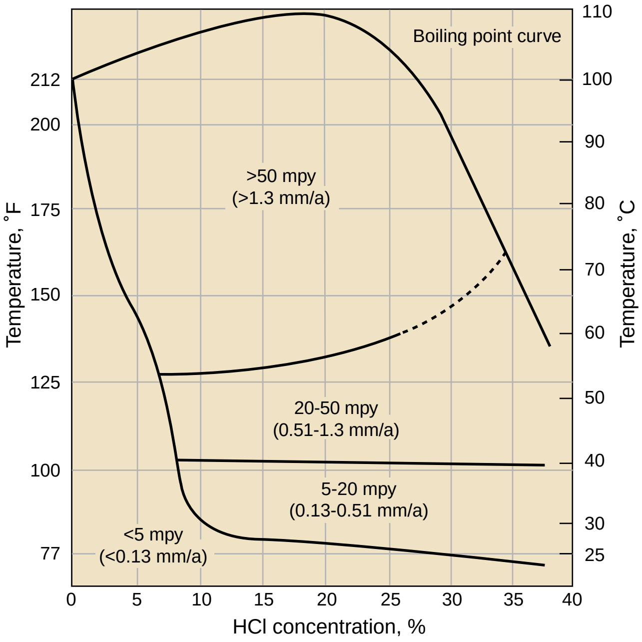


Figure 17 – Iso-corrosion chart for INCONEL alloy 625 in hydrochloric acid.

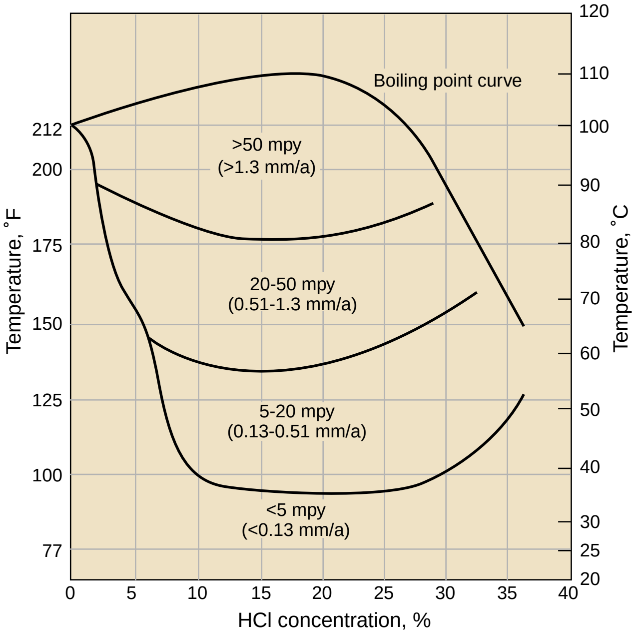


Figure 16 – Iso-corrosion chart for INCONEL alloy 622 in hydrochloric acid.

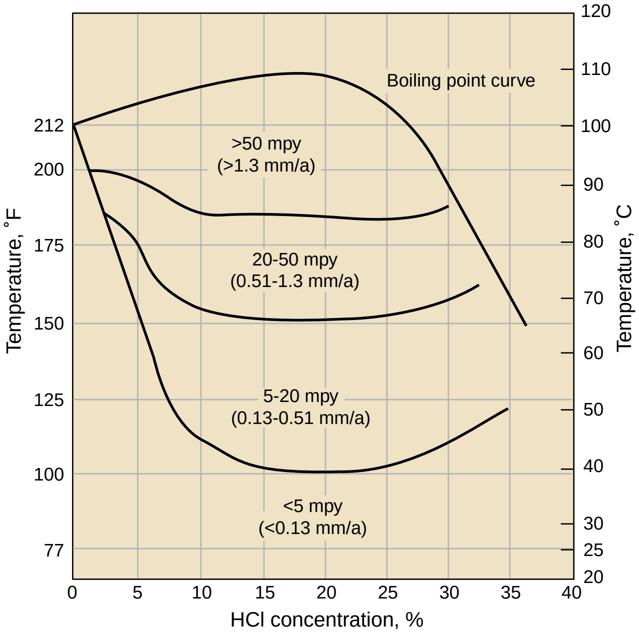


Figure 18 – Iso-corrosion chart for INCONEL alloy 686 in hydrochloric acid.

A comparison of the corrosion-resistance of the various alloys discussed for use in hydrochloric acid is shown in Figure 19. In this figure, the 20 mpy (0.51 mm/a) iso-corrosion lines show the overall relative order of resistance to be, in descending order:

INCONEL alloy 686/INCONEL alloy C-276
INCONEL alloy 622
INCONEL alloy 625
INCOLOY alloy 825
INCOLOY alloy 25-6MO

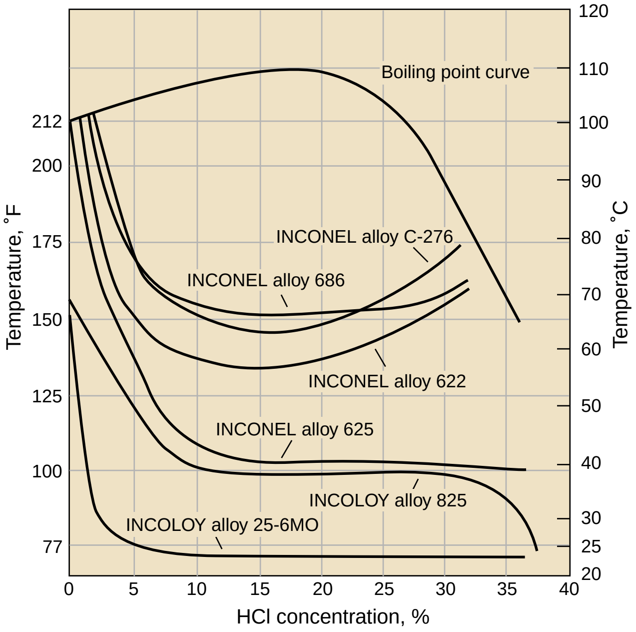


Figure 19 – Comparative behavior of nickel-based alloys in hydrochloric acid. The iso-corrosion lines indicate a corrosion rate of 20 mpy (0.51 mm/a).

Hydrofluoric Acid

Although it is chemically classified as a weaker acid than hydrochloric or sulfuric, few compounds are more corrosive than hydrofluoric acid. Only gold and platinum are completely resistant to attack in aqueous solutions. The engineering materials that are useful in hydrofluoric acid owe their corrosion-resistance to the formation of fluoride films.

Table 5 – Plant corrosion tests in the storage of commercial 60-65% hydrofluoric acid[a]

Material	Corrosion rate, mpy (mm/a)
MONEL alloy 400	22 (0.56)
Nickel 200	>200 (>5.08)[b]
INCONEL alloy 600	150 (3.81)
AISI 304 stainless steel	>210 (>5.33)[b]
AISI 316 stainless steel	>190 (>4.83)[b]
Mild Steel	170 (4.32)

(a) Acid contains 1.5-2.5% fluosilicic acid, 0.3-1.25% sulfuric acid, and 0.01-0.03% iron. Test specimens immersed in solution in storage tank. Temperature, 60-80°F (15-27°C); duration of test, 28 days.

(b) Specimen completely destroyed during test.

Table 6 – Plant corrosion tests in impure 12% hydrofluoric acid[a]

Material	Corrosion rate, mpy (mm/a)
MONEL alloy 400	22 (0.30)
Nickel 200	4 (0.10)
INCONEL alloy 600	9 (0.23)
AISI 302 stainless steel	160 (4.06)[b]
AISI 316 stainless steel	700 (17.8)[b]

(a) Acid contains approximately 12% hydrofluoric acid, 0.2% fluosilicic acid, and 1 gm/l of ferric oxide as ferric salts. Test specimens immersed in solution resulting from water absorption of fluorine from chemical process. Velocity, 3.2 ft/min (9.8 m/s); ave. temperature, 182°F (83°C); time 7 days.

(b) Specimens perforated by cracking due to stress-corrosion at machined edges and code-letter stamping.

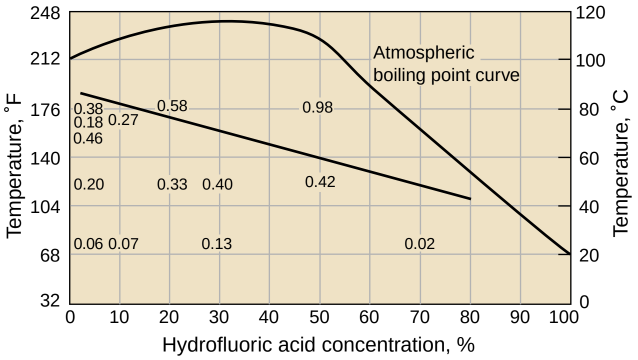


Figure 20 – Corrosion data for Nickel 200 in hydrofluoric acid. Corrosion rates are shown in mm/a.

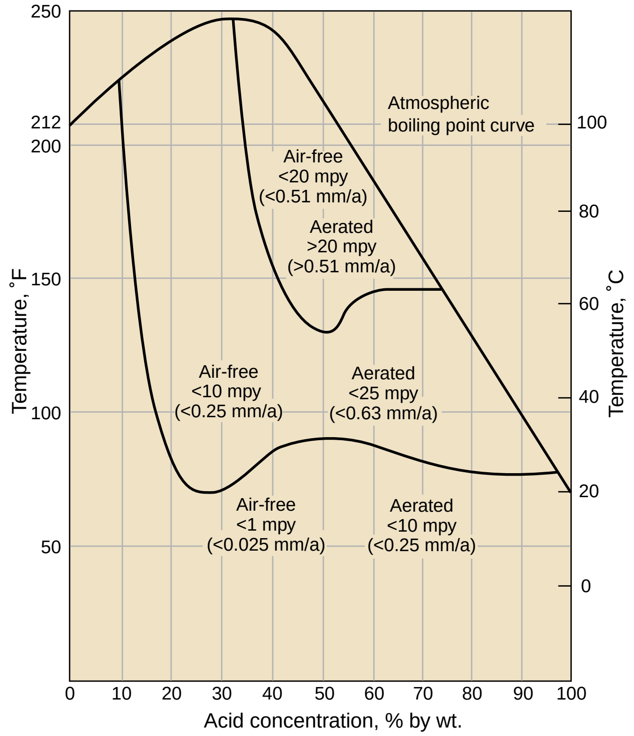


Figure 21 – Iso-corrosion chart for MONEL alloy 400 in hydrofluoric acid.

The choice of a material for handling hydrofluoric acid should be based on the concentration, temperature, velocity and degree of aeration of the acid, and on the presence of impurities. As with other non-oxidizing acids, aeration or the presence of oxidizing chemicals in hydrofluoric acid increases its corrosive attack on most metals. Results of plant corrosion tests of nickel alloys and other materials in hydrofluoric acid solutions are shown in Tables 5-7. The most commonly used nickel alloy in processes containing hydrofluoric acid is MONEL alloy 400. Nickel 200 and INCONEL alloy 600 are used for some applications.

Nickel 200

While Nickel 200 shows excellent resistance to anhydrous hydrogen fluoride, even at elevated temperatures, its use in aqueous solutions of hydrofluoric acid is usually limited to temperatures below 180˚F (82˚C). Severe corrosion has occurred on material exposed at room temperature to commercial acid of 60-65% concentration. The general resistance of Nickel 200 is summarized in the iso-corrosion chart shown in Figure 20.

MONEL alloy 400

MONEL alloy 400 is an outstanding material of construction for hydrofluoric acid service. Figure 21 is an iso-corrosion chart showing resistance to attack in air-free and aerated acid. Again, aeration, or the presence of oxidizing salts, increases the corrosion rate, but in non-aerated acid (open to the atmosphere with no attempt to deaerate or aerate), MONEL alloy 400 resists all concentrations, up to the boiling point (Figure 22). The presence of small

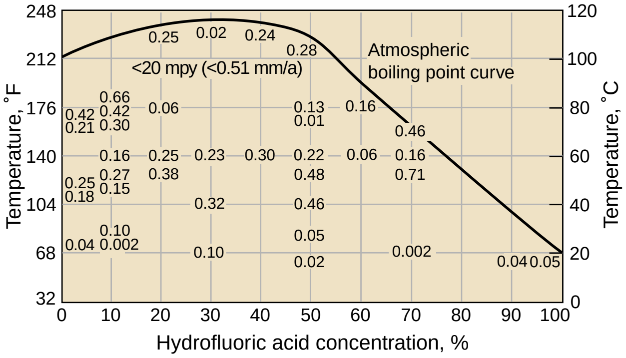


Figure 22 – Corrosion data for MONEL alloy 400 in hydrofluoric acid. Corrosion rates are shown in mm/a.

Table 7 – Corrosion tests in hydrofluoric acid alkylation plants

	Test conditions
Test 1.	Inlet side of preheater channel. Liquid composition: 79-92% hydrofluoric acid, 0.8-2.5% water, remainder isobutane and acid-soluble oil. Temperature: average, 120˚F (49˚C); max., 135˚F (57˚C). Duration of test, 111 days.
Test 2.	Outlet side of preheater channel. Composition same as Test 1. Temperature: average, 235˚F (113˚C); max., 260˚F (127˚C). Duration of test, 111 days.
Test 3.	Top of regeneration column just below vapor outlet. Composition: 90-95% hydrofluoric acid and 5-10% isobutane. Acid phase: 90-95% hydrofluoric acid, 0.5-2.5% water, 1.0-5.0% oil. Temperature: average, 275˚F (135˚C); max., 300˚F (149˚C). Pressure, 120-150 psi (8.44-10.5 kg/cm^2). Duration of test, 70 days.
Test 4.	Top of regeneration column. Composition: equal parts of 93% hydrofluoric acid and isobutane vapor. Temperature: average, 215˚F (102˚C) ; max., 220˚F (104˚C). Duration of test, 49 days.
Test 5.	Bottom of regeneration column in acid tar containing 1-10% hydrofluoric acid- 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% hydrofluoric acid, 1.6% water and oils. Test made beneath grid plate of column. Feed, 194 bbl per day. Temperature: average, 220˚F (104˚C); max., 250˚F (121˚C). Duration of test, 45 days.
Test 7.	Bottom of dehydrator column beneath bottom plate. Feed contains 89.3% hydrofluoric acid and 1.6% water. Feed rate, 15 bbl per day. Temperature: average, 225˚F (107˚C); max., 250˚F (121˚C). Duration of test, 45 days.
Test 8.	Top of hydrofluoric acid stripper column above top tray. Composition of vapor 10% hydrofluoric acid and 90% light hydrocarbons. Temperature: average, 110˚F (43˚C); max., 150˚F (66˚C). Duration of test, 117 days.

	Corrosion rate, mpy (mm/a)							
Material	**Test 1**	**Test 2**	**Test 3**	**Test 4**	**Test 5**	**Test 6**	**Test 7**	**Test 8**
MONEL alloy 400	0.3 (0.008)	0.5 (0.01)	0.5 (0.01)	0.5 (0.01)	7.5 (0.19)	7.1 (0.18)	22 (0.56)	0.7 (0.02)
Nickel 200	1.1 (0.03)	3.5 (0.09)	13 (0.33)	14 (0.36)	11 (0.28)	18 (0.46)	68 (1.73)	0.7 (0.02)
INCONEL alloy 600	0.8 (0.02)	19 (0.48)	0.7 (0.02)	25 (0.64)	23 (0.58)	25 (0.64)	>130[a] (>3.30)	0.5 (0.01)
AISI 302 stainless steel	–	–	–	>110[a] (>2.79)	36 (0.91)	–	–	–
AISI 304 stainless steel	–	–	–	63[b] (1.60)	45 (1.14)	11 (0.28)	>120[a] (>3.05)	–
AISI 316 stainless steel	–	–	–	1 (0.03)	1.5 (0.04)	–	–	–

(a) Completely corroded away. Original thickness was 0.032 in (0.81 mm).

(b) Perforated by pitting. Original thickness was 0.032 in (0.81 mm).

amounts of reducing sulfur compounds or sulfuric acid is not detrimental. The alloy is also comparatively insensitive to velocity effects and is widely used for critical components such as bubble caps or valves in contact with flowing acid. It is more resistant to general corrosion in non-deaerated acid than many more highly alloyed materials.

In common with some other high-nickel alloys, MONEL alloy 400 is subject to stress-corrosion cracking in moist, aerated hydrofluoric or hydrofluosilicic acid vapor. Cracking is unlikely, however, if the metal is completely immersed in the acid. Avoiding aeration is also beneficial. It is well known that stress-corrosion cracking can be prevented by eliminating tensile stresses on the metal. For most metals a full anneal is employed, but for MONEL alloy 400 heating for one hour between 1000 and 1200˚F (538 and 648˚C), followed by slow cooling, is usually sufficient.

INCONEL alloys 600 and 690

INCONEL alloy 600 is resistant to dilute non-deaerated hydrofluoric acid solutions up to 70˚C (158˚F). The presence of oxidizing salts usually improves corrosion resistance. Selective corrosion of weldments will occur if they contain significant amounts of niobium (e.g. INCONEL filler metal 82 and INCONEL welding electrode 182). Figure 23 shows the general corrosion-resistance of INCONEL alloy 600 in hydrofluoric acid. The relative corrosion resistance of INCONEL alloys 600 and 690 is shown in Figure 24.

INCOLOY alloys 800, 825, 020 and 25-6MO

INCOLOY alloy 800 is less resistant to anhydrous hydrofluoric acid than the molybdenum-bearing INCOLOY alloys. However, they are not nearly as resistant as MONEL alloy 400 to hydrofluoric acid solutions. For equipment which cannot be stress-relieved, INCOLOY alloy 825 is occasionally used because of its high resistance to stress-corrosion cracking. Aeration, or the presence of oxidizing salts, is beneficial. In general, these alloys are not used in hydrofluoric acid service.

INCONEL alloys 622, 625, C-276 and 686

These Ni-Cr-Mo alloys do not offer the dramatically improved corrosion-resistance that they do in some other media and are not as resistant as Nickel 200 or MONEL alloy 400 in aqueous hydrofluoric acid.

A comparison of the corrosion resistance of the various alloys discussed in non-deaerated hydrofluoric acid is shown in Figure 24. In this figure, the 20 mpy (0.51 mm/a) iso-corrosion lines show the overall relative order of resistance to be, in descending order:

MONEL alloy 400
INCONEL alloys 686, 622 & C-276/Nickel 200
INCONEL alloy 600/INCONEL alloy 690
INCOLOY alloy 825
INCONEL alloy 625

in most commercial concentrations (<50%).

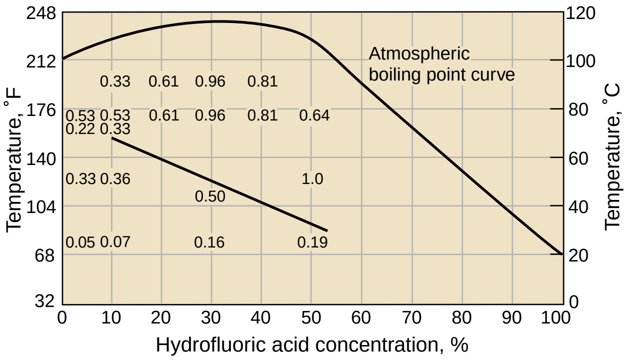


Figure 23 – Corrosion data for INCONEL alloy 600 in hydrofluoric acid. Corrosion rates are shown in mm/a.

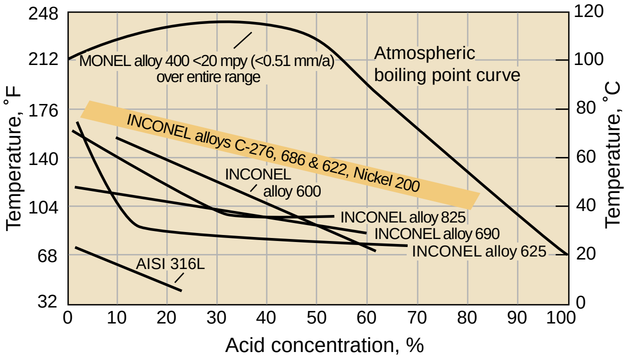


Figure 24 – A summary iso-corrosion chart for 20 mpy (0.51 mm/a) data in hydrofluoric acid.

Phosphoric Acid

Pure phosphoric acid has no effective oxidizing power and is classified as a non-oxidizing acid, much like dilute sulfuric. Commercial phosphoric acid, however, usually contains impurities such as fluorides and chlorides that markedly increase its corrosivity. Oxidizing compounds, such as ferric salts, may also be present to influence corrosion. Possibly because of variations in impurity contents of acids studied, published corrosion rates do not always agree. The most commonly used nickel alloys in processes containing pure phosphoric acid are INCOLOY alloys 825, 020 and 25-6MO, and INCONEL alloy G-3. For aggressive, hot phosphoric acid environments, especially those contaminated with halides, INCONEL alloys 625, 622, C-276 and 686 are selected.

Nickel 200

Nickel 200 has limited usefulness in phosphoric acid. In pure, unaerated acid, corrosion rates are low for all concentrations at atmospheric temperatures. In hot or concentrated acid, rates are usually too high for the use of commercially pure nickel.

MONEL alloy 400

MONEL alloy 400 has useful resistance to pure phosphoric acid. Rates are below 10 mpy (0.25 mm/a) for all concentrations at temperatures up to 176˚F (80˚C). Higher temperatures and aeration can significantly increase corrosion rates (Figure 25). Corrosion rates in crude phosphoric acid are likely to be high because oxidizing salts may be present. As little as 0.4% ferric ion may increase the corrosion rate of an alloy by an order of magnitude.

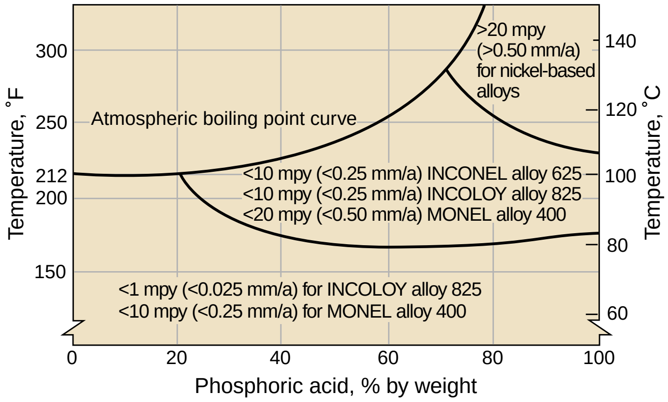


Figure 25 – Material selection chart for nickel alloys in pure phosphoric acid.

INCOLOY alloys 020, 825 and 25-6MO

INCOLOY alloy 825 has excellent resistance to pure phosphoric acid at all concentrations and temperatures up to and including boiling 85% acid. Laboratory and plant corrosion test results are shown in Table 8. In commercial grade phosphoric acid environments, significant pitting or crevice corrosion would limit the application of INCOLOY alloy 825.

INCOLOY alloys 020 and 25-6MO normally offer less resistance to corrosion by phosphoric acid than alloy 825, and alloy 25-6MO is generally less resistant than alloy 020.

INCONEL alloy 600

INCONEL alloy 600 is resistant to all phosphoric acid concentrations at room temperature. However, corrosion rates increase rapidly with temperature so the alloy is not suitable for use in hot acid.

INCONEL alloys G-3, 622, 625, C-276 and 686

By virtue of their high chromium and molybdenum contents, as well as small additions of niobium or tungsten, INCONEL alloys G-3, 622, 625, C-276 and 686 have excellent resistance to phosphoric acid. In pure, concentrated, boiling acid, these alloys are not better than INCOLOY alloy 825. However, they show superior resistance in the presence of appreciable amounts of chlorides and fluorides, which may cause pitting of alloy 825. Wet process acid evaporators are examples of such an environment. In a solution of 25% phosphoric and 2% hydrofluoric acid at boiling temperature, INCONEL alloy 625 corroded at 2 mpy (0.05 mm/a) in a 48-hour test. Longer tests in actual service have shown very low rates and no localized attack in evaporating wet-process

Table 8 – Laboratory corrosion tests of INCOLOY alloy 825 in pure phosphoric acid solutions

Concentration, % by wt	Test conditions	Temperature, ˚F (˚C)	Duration of test, days	Corrosion rate, mpy (mm/a)
45	Half immersed in liquid and vapor while boiling in open beaker. Concentration varied with evaporation and addition of water.	145-155 (63-68)	30	0.6 (0.02)
60	Immersed in boiling solution in flask equipped with reflux condenser. Average of three 20-h tests.	Boiling	0.8	6.8 (0.17)
70	Immersed in boiling solution in flask equipped with reflux condenser.	Boiling	1	8.6 (0.22)
70	Immersed in boiling solution in flask equipped with reflux condenser. Average of four 20-h tests.	Boiling	0.8	7.1 (0.18)
75	Immersed in solution of commercial acid. Velocity, 800-1000 ft/min (244-305 m/min).	172 (78) 185 (85) 194 (90) 203 (95) 221 (105)	30 30 30 30 30	0.2 (0.005) 0.3 (0.008) 0.3 (0.008) 0.5 (0.013) 1.3 (0.03)
75	Half immersed in liquid and vapor while boiling in open beaker. Concentration varied with evaporation and addition of water.	240-260 (115-127)	30	3.9 (0.10)
85	Immersed in boiling solution in flask equipped with reflux condenser. Average of three 24-h tests.	Boiling	1	36 (0.91)
85	Immersed in boiling solution in flask equipped with reflux condenser. Average of four 24-h tests.	Boiling	0.8	50 (1.27)

phosphoric acid. Results of other plant exposures for INCONEL alloy 625 are shown in Table 9. The general resistance of INCONEL alloys G-3 and C-276 is summarized in the iso-corrosion charts shown in Figures 26 and 27.

A comparison of the Special Metals alloys ranks the order of corrosion resistance in commercially pure phosphoric acid, in descending order, as:

INCONEL alloy 686
INCONEL alloy C-276
INCONEL alloy 625
INCONEL alloy G-3
INCOLOY alloy 825
MONEL alloy 400

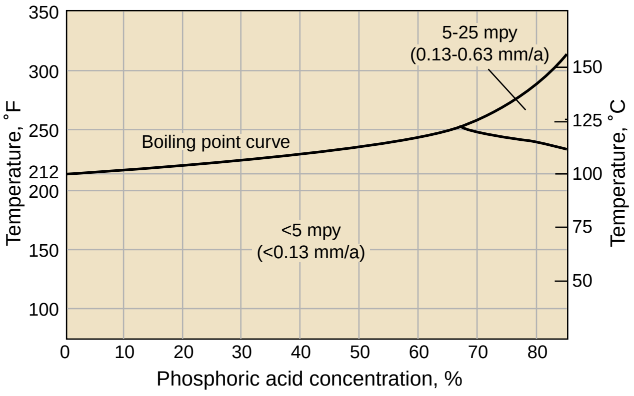


Figure 26 – Iso-corrosion chart for INCONEL alloy C-276 in phosphoric acid.

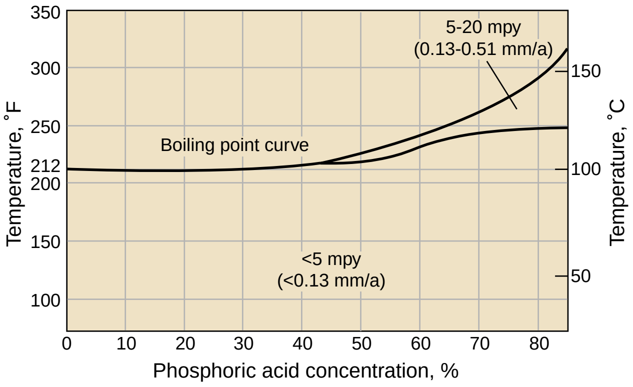


Figure 27 – Iso-corrosion chart for INCONEL alloy G-3 in phosphoric acid.

Table 9 – Corrosion tests of INCONEL alloy 625 in phosphoric acid environments

Test conditions	Temperature, °F (°C)	Duration of test	Corrosion rate, mpy (mm/a)
28% wet process phosphoric acid (20% P_2O_5) 20-22% sulfuric acid, about 1-1.5% fluoride probably as fluosilicic acid. Aeration, moderate. Agitation, natural convection only.	180-230 (82-110)	42 days	1.4 (0.04)
55% wet process phosphoric acid (40% P_2O_5 equivalent) containing 3% sulfuric acid and suspended calcium sulfate; slurry. Gases containing water and fluorine compounds are evolved at the exposure area. Aeration, none. Agitation, 50 ft/min (15 m/min).	230-234 (110-112)	112 hours	59 (1.50)
99% wet process phosphoric acid (72% P_2O_5), 3.7% sulfuric acid (3% SO_3), 0.5% fluoride. Aeration, moderate. Agitation, only sufficient to break up foam.	60-600 (15-315)	20.8 days	14.8 (0.38)
Exhaust gases from evaporator, entrained phosphoric acid, sulfuric acid vapor, sulfur trioxide, nitrous acid, silicon tetrafluoride, water vapor; sprayed with water containing 0.1% phosphoric acid, 0.06% sulfuric acid, 0.1% combined fluoride. Aeration, extensive. Agitation, constantly sprayed with water.	50-355 (10-180)	20.8 days	12.9 (0.33)
Gases containing hydrofluoric acid, silicon fluoride, sulfur dioxide with entrained phosphoric acid (72% P_2O_5), 3.7% sulfuric acid (3% SO_3). Aeration, extensive. Agitation, fast-moving gas stream.	60-650 (15-343)	20.8 days	2.1 (0.05)

Nitric Acid

Nitric acid is strongly oxidizing and, because of this, alloys with the best resistance are those that form passive oxide films. Thus, alloys with significant chromium contents offer much greater resistance than those with lesser amounts. While nickel alloys offer good resistance to pure nitric acid, they are particularly effective in mixed acid media (e.g. nitric with reducing acids such as sulfuric or phosphoric). When small amounts of chlorides or fluorides are present, Ni-Cr-Mo alloys show superior resistance.

Nickel 200 and MONEL alloy 400

Nitric acid of greater than 0.5% concentration rapidly attacks both Nickel 200 and MONEL alloy 400.

INCOLOY alloy 800

Because of its chromium content, INCOLOY alloy 800 offers excellent resistance to nitric acid. It also offers stress-corrosion resistance significantly superior to austenitic stainless steels. However, like INCONEL alloy 600 and non-stabilized stainless steels, it can be sensitized and made subject to intergranular attack by prolonged heating in the 1000-1400˚F (538-760˚C) temperature range.

INCOLOY alloy 825

Because of its high chromium, INCOLOY alloy 825 has excellent resistance to nitric acid solutions at all concentrations and temperatures up to and including boiling 65%. The alloy is stabilized against sensitization by its addition of titanium. Thus, exposure to intermediate temperatures during welding or stress relieving are not detrimental. Post-weld heat treatment before use in oxidizing acid media is not normally required.

INCONEL alloys 600 and C-276

These alloys, containing approximately 16% chromium, are resistant to nitric acid in concentrations over 20% at room temperature. In 10% boiling acid, INCONEL alloy 600 is excellent (Figure 28). However, it can be sensitized and show high intergranular corrosion rates in hot acid. Exposure to intermediate temperatures can sensitize the alloys, resulting in susceptibility to intergranular corrosion.

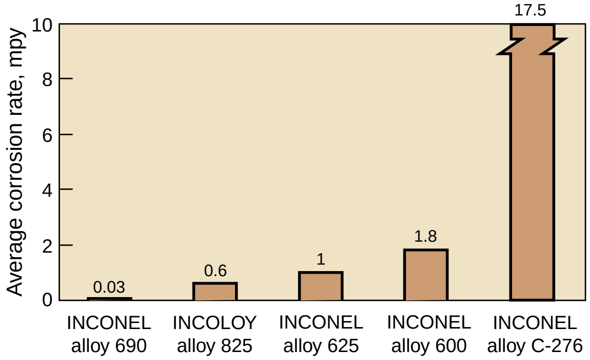


Figure 28 – Average corrosion rates for nickel alloys in 10% nitric acid at boiling temperatures.

INCONEL alloy 690

With its higher chromium content (30% versus 16%), INCONEL alloy 690 offers significantly improved resistance to nitric acid in comparison to alloy 600. INCONEL alloy 690 exhibits lower corrosion rates than INCONEL alloy 625 in mixed nitric/hydrofluoric acid media as illustrated in Table 10.

INCONEL alloy 625

INCONEL alloy 625 has good resistance to nitric acid. A corrosion rate of 30 mpy (0.76 mm/a) in boiling 65% acid is typical. It is stabilized against sensitization and does not require post-weld heat treatments before use in oxidizing acids. In a boiling 15% nitric/3% hydrofluoric acid solution, where AISI 316 stainless steel corroded at 236 mpy (5.99 mm/a), INCONEL alloy 625 corroded at only 34 mpy (0.86 mm/a).

Table 10 – Isothermal corrosion rates at 203˚F (95˚C) in nitric-hydrofluoric acid. Coupons tested for 120 h at 30 ml/cm². Solutions changed three times.

Alloy	Penetration rate, mpy (mm/a)		
	Matrix wrought alloy		Welded alloy
	10M HNO_3 - 0.01M HF	10M HNO_3 - 0.1M HF	10M HNO_3 - 0.1M HF
INCONEL alloy 690	9 (0.23)	63 (1.60)	68 (1.73)
INCONEL alloy 625	18 (0.46)	147 (3.73)	170 (4.32)
INCOLOY alloy 825	28 (0.71)	206 (5.23)	230 (5.84)
AISI 304	21 (0.53)	248 (6.30)	190 (4.83)
INCONEL alloy C-276	134 (3.40)	841 (21.36)	760 (19.3)

Organic Acids

With few exceptions, organic acids are weak and non-oxidizing. Those most commonly encountered are the monocarboxylic acids – formic, acetic, propionic, and butyric. In general, the corrosivity of these acids becomes weaker as the length of their carbon chain becomes longer. Thus, formic is most corrosive, followed by acetic, etc. As with other non-oxidizing acids, aeration and temperature usually increase corrosion.

Nickel 200

Nickel 200 has excellent resistance to organic acids of all concentrations if little dissolved oxygen is present. However, corrosion rates in aerated media can be high. For example, in 85% acetic acid saturated with air at ambient temperatures, a corrosion rate of 400 mpy (10.2 mm/a) has been observed. In similar tests, Nickel 200 in acetic acid of 0.1% concentration corroded at 10 mpy (0.25 mm/a) and in 5% acid, at 40 mpy (1.02 mm/a). Table 11 shows the resistance of Nickel 200 to corrosion by acetic and other organic acids under various conditions.

MONEL alloy 400

MONEL alloy 400 is generally not as resistant as the other nickel-based alloys to most organic acids. In air-free acetic acid at room temperature, rates are less than 4 mpy (0.10 mm/a) for all concentrations. Aeration and temperature tend to increase rates, however, and the gradual accretion of cupric ions as corrosion products aggravates attack in an autocatalytic manner. In acetic acid of more than 50% concentration, the rates begin to fall and in a test in glacial acid at 230˚F (110˚C) the rate was only 13 mpy (0.33 mm/a). MONEL alloy 400 has been used for distillation of fatty acids at temperatures up to 500˚F (260˚C).

INCOLOY alloys 800, 825, 020 and 25-6MO

INCOLOY alloy 800 behaves quite similarly to austenitic stainless steels when exposed to organic acids. Although laboratory data may suggest an appropriate corrosion resistance, actual practice is to employ a molybdenum bearing alloy instead. The presence of molybdenum in INCOLOY alloys 825, 020 and 25-6MO greatly enhances

Table 11 – Corrosion-resistance of Nickel 200 in organic acids

Acid	Conditions	Temperature ˚F (˚C)	Duration of test, days	Corrosion rate, mpy (mm/a)
Acetic anhydride 99%, plus acetic acid 1%	In a still	310 (154)	638	0.2 (0.01)
Acetic anhydride 60%, plus acetic acid 40%	In a still	284 (140)	–	0.6 (0.02)
Butyric acid	Distillation, liquid Distillation, vapor	230-265 (110-130) 212-250 (100-121)	32 7	36 (0.91) 9 (0.23)
2% Butyric acid	Liquid Liquid	Room 160 (71)	7 10	2.3 (0.06) 5.4 (0.14)
2% Citric acid	Lab. immersed Lab. immersed Lab. aerated	Room 160 (71) 180 (82)	5 10 3	0.8 (0.02) 5.5 (0.14) 34 (0.86)
5% Citric acid	Lab. immersed Lab. aerated Lab. immersed	86 (30) 86 (30) 140 (60)	7 7 7	5 (0.13) 15 (0.38) 20 (0.51)
58% Citric acid	Lab. immersed	Boiling	7	17 (0.43)
90% Formic acid	Storage tank, liquid Storage tank, vapor In still, liquid In still, vapor	Atm Atm 212 (100) 212 (100)	14 7 8 27	4 (0.10) 7 (0.18) 18 (0.46) 7 (0.18)
50% Hydroxyacetic acid	Lab. immersed Lab. immersed	86 (30) Boiling	7 7	0.3 (0.01) 7.6 (0.19)
2% Lactic acid	Lab. immersed Lab. immersed	Room 160 (71)	7 7	2.1 (0.05) 3.4 (0.09)
10-22% Lactic acid	Vac. evaporator	130 (54)	15	51 (1.30)
85% Lactic acid	Lab. immersed	Room	7	2.7 (0.07)
Up to 85% Lactic acid	Vac. evaporator, liquid Vac. evaporator, vapor	120-180 (49-82) 120-180 (49-82)	120 120	10 (0.25) 11 (0.28)
66% Propionic, 17% Iso-butyric, 17% n-butyric acids	Reboiler liquid	300 (149)	21	24 (0.61)
57% Tartaric acid	Vac. evaporating pan	130 (54)	10	7.5 (0.19)

the resistance of these alloys to corrosion by organic acids. They are highly resistant even to boiling concentrated acetic acid, acetic-formic acid mixtures, and maleic and phthalic acids. Data from laboratory corrosion tests for INCOLOY alloy 825 are shown in Table 12.

INCONEL alloy 600

INCONEL alloy 600 has satisfactory resistance to hot, concentrated organic acids such as formic or acetic. It has outstanding resistance to ambient temperature acetic acid and to hot, fatty acids such as stearic, oleic, linoleic and abietic.

INCONEL alloys G-3, 625, C-276 and 686

INCONEL alloy 625 has excellent resistance to organic acids. Results from 48-h laboratory tests in boiling acid solutions are glacial acetic – <1 mpy (<0.03 mm/a), 1:1 acetic-acetic anhydride – 4 mpy (0.10 mm/a), 10% acetic + 2% formic – 1 mpy (0.03 mm/a), and 5% formic – 3 mpy (0.08 mm/a). INCONEL alloys G-3 and C-276 are also resistant to organic acids. Tables 13 and 14 show their resistance to boiling formic and acetic acid solutions. INCONEL alloy C-276 is preferred for the more severe services, such as acid evaporators or reboilers.

Table 12 – Corrosion-resistance of INCOLOY alloy 825 in 20-hour tests in boiling 10% organic acid solutions

Acid	Corrosion rate, mpy (mm/a)
Acetic	<0.1 (<0.003)
Formic	2.5 (0.06)
Lactic	0.3 (0.008)
Maleic	0.1 (0.003)
Phthalic	<0.1 (<0.003)
Oxalic	20 (0.51)

Table 13 – Corrosion-resistance of nickel alloys in 24-hour tests in boiling 40% formic acid

Alloy	Corrosion rate	
	mpy	mm/a
INCOLOY alloy 825	7.9	0.2
Nickel 200	10.3-10.5	0.26-0.27
MONEL alloy 400	1.5-2.7	0.038-0.068
INCONEL alloy 600	10.0	0.25
INCONEL alloy G-3	1.8-2.1	0.046-0.05
INCONEL alloy 625	6.8-7.8	0.17-0.19
INCONEL alloy C-276	2.8-2.9	0.07-0.074

Table 14 – Corrosion-resistance of nickel alloys in four 24-hour tests in boiling acetic acid

Alloy	Acetic acid concentration	Corrosion rate	
		mpy	mm/a
INCOLOY alloy 825	10%	0.60-0.63	0.0152-0.0160
INCONEL alloy 625	10%	0.39-0.77	0.01-0.019
INCONEL alloy C-276	10%	0.41-0.45	0.011-0.0114
INCONEL alloy 686	80%	<0.1*	<0.01*

*Test was run according to MTI procedure.

Corrosion by Alkalies

Corrosion rates in chemical processing media usually decrease as the pH increases. In alkaline solutions, the hydrogen ion is present in very low concentrations. However, many metals pass through a minimum corrosion rate at some pH, usually basic, and then suffer increased corrosion as pH continues to rise. Quite often corrosion by alkalies leads to pitting and other localized attack because they tend to form cathodic films, and attack is concentrated at susceptible anodic areas. Austenitic stainless steels and other low nickel materials may suffer either stress-corrosion cracking or general corrosion in hot concentrated caustic.

Resistance to attack by alkalies generally improves with increasing nickel content. Results of both plant and laboratory tests, some of which are shown in Tables 15, 16 and 17, show that Nickel 200 and high-nickel alloys are highly satisfactory for handling these materials. The most commonly used nickel alloys in alkali process media are Nickel 200, MONEL alloy 400, and INCONEL alloys 600 and 625.

Nickel 200

The outstanding corrosion characteristic of Nickel 200 is its resistance to caustic soda and other alkalies (ammonium hydroxide is an exception). Nickel 200 is not attacked by anhydrous ammonia or ammonium hydroxide in concentrations of 1%. Stronger concentrations can cause rapid attack in the presence of dissolved oxygen.

Nickel 200 shows excellent resistance to all concentrations of caustic soda (sodium hydroxide) at temperatures up to and including the molten state. Below 50% concentration, corrosion rates are negligible, being usually less than 0.1 mpy (0.003 mm/a) even in boiling solutions. As concentrations and temperatures increase, corrosion rates increase very slowly. The general resistance of Nickel 200 is summarized in the iso-corrosion chart shown in Figure 29.

The chief factor influencing the behavior of nickel in highly concentrated caustic soda is the nature of the film formed during exposure to the caustic. Under most conditions, a protective film of black nickel oxide is formed that results in a marked decrease in corrosion rates over long exposure. For example, specimens of Nickel 201 were exposed to a caustic solution made by adding 500 cc of water to 2 kg of technical grade flake caustic followed by heating in a Nickel 201 pot at a temperature of 790-830˚F (412-443˚C). The corrosion rate during the first 24 hours averaged 21 mpy (0.53 mm/a). The specimens were put back into test without removal of their oxide coating. At the end of a week, the overall corrosion rates had dropped to an average of 2.8 mpy (0.07 mm/a). The test was continued for another week with the same specimens. The average rate of corrosion, 2.8 mpy (0.07 mm/a), was maintained.

The presence of chlorates in caustic soda solutions increases the corrosion rates of Nickel 200 considerably

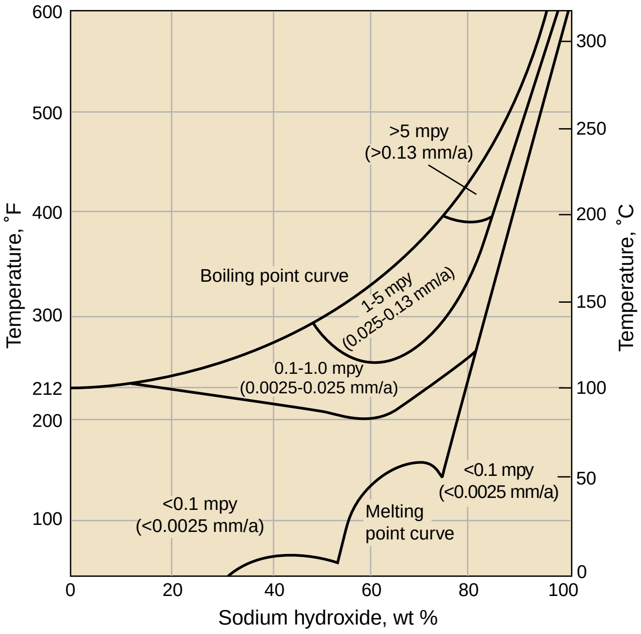


Figure 29 – Iso-corrosion chart for Nickel 200 and 201 in sodium hydroxide.

Table 15 – Plant tests in 23% caustic soda in tank receiving liquor from evaporator. Average temperature, 220°F (104°C)

Material	Corrosion rate, mpy (mm/a)
Nickel 200	0.16 (0.004)
MONEL alloy 400	0.20 (0.005)
INCONEL alloy 600	0.17 (0.004)

(Table 18). In view of these harmful effects, it is advisable to remove chlorates as thoroughly as possible before evaporation in the high-temperature range in the presence of nickel.

It is also known that the presence of oxidizable sulfur compounds tends to increase the corrosiveness of caustic toward nickel. This effect is noted primarily with the sulfides such as hydrogen sulfide, mercaptans, or sodium sulfide and to a much lesser extent with partially oxidized compounds such as thiosulfates and sulfites (Table 19).

It has been found that the effect of oxidizable sulfur compounds can be avoided by the addition to the caustic solution of sufficient sodium peroxide to oxidize them to sulfates. An excess of peroxide does not seem to alter the corrosiveness of caustic soda toward nickel.

As in other environments, when nickel is to be used above 600˚F (315˚C), the preferred material is the low-carbon grade, Nickel 201.

MONEL alloy 400

Because of its high nickel content, MONEL alloy 400 is nearly as resistant as Nickel 200 to caustic soda through most of the concentration range, although subject to stress-corrosion cracking in strong alkalis at elevated temperatures. The corrosion rates of MONEL alloy 400 are higher in highly concentrated caustic soda and caustic potash at high temperatures. MONEL alloy 400 is resistant to anhydrous ammonia and to ammonium hydroxide solutions of up to 3% concentration in the absence of dissolved oxygen.

INCOLOY alloys 800, 825, 020 and 25-6MO

While these alloys have excellent resistance to alkaline solutions, with a corrosion rate of 0.5 mpy (0.01 mm/a) in boiling 50% sodium hydroxide, they are not as resistant as Nickel 200 and are seldom used in alkaline environments unless other corrosives are involved. They also can

Table 16 – Laboratory corrosion tests, mpy (mm/a), in boiling 30 and 47% caustic potash for 26 days

Material	30% KOH saturated with KCl 0.05% $KClO_3$		47% KOH saturated with KCl 0.078% $KClO_3$	
	Liquid	Vapor	Liquid	Vapor
Nickel 200	0.2 (0.005)	0.1 (0.003)	0.1 (0.003)	0.3 (0.008)
INCONEL alloy 600	0.1 (0.003)	0.1 (0.003)	0.4 (0.010)	0.1 (0.003)

Table 17 – Laboratory corrosion tests of Nickel 200 in 75% caustic soda

Caustic concentration, %	Temperature, °F (°C)	Duration of test, h	Corrosion rate, mpy (mm/a)
75	250 (121)	20	1.0 (0.025)
75	400 (204)	48	0.8 (0.020)

Table 18 – Laboratory corrosion tests in evaporation of caustic soda from 73-96%, with and without chlorate

Material	Corrosion rate, mpy (mm/a)	
	Without chlorate	With 0.30% chlorate
Nickel 200	1.5 (0.038)	260 (6.60)
INCONEL alloy 600	2.2 (0.056)	380 (9.65)

Temperatures, 360-840˚F (182-449°C). Duration of tests, 24 hours.

Table 19 – Effect of oxidizable sulfur compounds on corrosion of Nickel 200 in caustic soda

Corrosive	Corrosion rate, mpy (mm/a)
Commercial sodium hydroxide being concentrated from 50 to 75% NaOH (sulfur content at start, calculated as H_2S, 0.009%)	1.7 (0.04)
75% chemically pure sodium hydroxide	0.6 (0.015)
75% chemically pure sodium hydroxide plus 0.75% sodium sulfide	22.8 (0.58)
75% chemically pure sodium hydroxide plus 0.75% sodium thiosulfate	7.9 (0.20)
75% chemically pure sodium hydroxide plus 0.75% sodium sulfite	5.2 (0.13)
75% chemically pure sodium hydroxide plus 0.75% sodium sulfate	0.6 (0.015)

Temperatures, 226 ± 9°F (108 ± 5°C). Duration of tests, 19-22 hours.

suffer stress-corrosion cracking in hot concentrated alkalis. These alloys are resistant to ammonia and ammonium hydroxide solutions under most service conditions.

INCONEL alloy 600

For high-temperature caustic applications in which sulfur is present, INCONEL alloy 600 is preferred to Nickel 201. However, alloy 600 can suffer stress-corrosion cracking in some alkali environments. For this reason, alloy 600 components should be stress relieved prior to use and operating stresses should be kept to a minimum. INCONEL alloy 600 resists sodium hydroxide at boiling temperatures in concentrations through 80%. Test results in sodium hydroxide at 572˚F (300˚C) are shown in Table 20.

As with Nickel 200, the presence of chlorates in caustic soda increases corrosion rates. Because of its chromium content, INCONEL alloy 600 is almost entirely resistant to attack by solutions of ammonia over a complete range of concentrations and temperatures.

INCONEL alloys 622, 625, C-276 and 686

While they offer excellent corrosion resistance, Ni-Cr-Mo alloys are not normally required for service in uncontaminated caustic environments. They can offer some advantages in halide-contaminated environments.

Table 20 – Performance of nickel alloys in boiling caustic solutions (Average of duplicates)

Alloy	NaOH concentration	Test period, h	Corrosion rate, mpy (mm/a)
Nickel 200	50%	720	<1 (<0.025)
MONEL alloy 400	50%	720	<1 (<0.025)
INCONEL alloy 600	50%	720	<1 (<0.025)
INCOLOY alloy 825	50%	720	<1 (<0.025)
INCONEL alloy 625	50%	720	<1 (<0.025)
INCONEL alloy C-276	50%	720	<1 (<0.025)
INCONEL alloy 600	10%	504	Nil
INCONEL alloy 600	20%	504	Nil
INCONEL alloy 600	30%	504	<1 (<0.025)
INCONEL alloy 600	40%	504	<1 (<0.025)
INCONEL alloy 600	50%	504	<1 (<0.025)
INCONEL alloy 600	60%	504	4.1 (0.10)
INCONEL alloy 600	70%	504	2.7 (0.07)
INCONEL alloy 600	80%	504	<1 (<0.025)

Corrosion by Salts

When dissolved in water, salts increase their conductivity and thereby are able to carry higher corrosion currents. Therefore, galvanic effects are more pronounced in salt solutions than in pure water. Salts may be categorized and their corrosive characteristics defined and ranked (Table 21).

The most commonly used nickel alloys in process environments containing sulfate salts are INCOLOY alloys 25-6MO, 825 and 020 and INCONEL alloys G-3, 625, 622, C-276 and 686. For processes using chloride salts, the most commonly used materials are MONEL alloy 400 (for reducing conditions), INCOLOY alloys 25-6MO, 825 and 020, and INCONEL alloys G-3, 625, 622, C-276 and 686.

Nickel 200 and MONEL alloy 400

Nickel 200 and MONEL alloy 400 are not subject to stress-corrosion cracking in any of the chloride salts and have excellent general resistance to all of the non-oxidizing halides. This behavior is illustrated by tests conducted in a potash liquor at 235˚F (113˚C) consisting of 21% KCl, 14% NaCl, 1.0% $CaCl_2$, 0.1% $CaSO_4$ and 2.5% $MgCl_2$ with a pH of 7.1. After 1000 hours, MONEL alloy 400 and Cu-Ni alloys corroded generally at low, measurable rates. No general attack occurred on the Ni-Fe-Cr and iron-based alloys. Ni-Fe-Cr alloys with less than 6% molybdenum suffered pitting or crevice corrosion. Alloys with lower nickel content failed by stress-corrosion cracking. Grade 12 titanium experienced crevice corrosion underneath a Teflon washer (Table 22).

Table 21 – Classification of salts by corrosive characteristics

Characteristic pH	Halide	Non-halide
Neutral	Sodium chloride Potassium chloride	Sodium sulfate Potassium sulfate
Neutral and Alkaline-Oxidizing	Sodium hypochlorite Calcium hypochlorite	Sodium nitrate Sodium nitrite Potassium permanganate
Acid	Magnesium chloride	Potassium bisulfate Ammonium sulfate Aluminum sulfate
Acid-Oxidizing	Cupric, ferric, mercuric, stannic chloride	Cupric, ferric, mercuric, nitrate, or sulfate
Alkaline	Potassium fluoride	Sodium and potassium phosphates, carbonates

Table 22 – Corrosion test results for various alloys in potash liquor at 235°F (113°C). Duplicate U-bent stress-corrosion cracking specimens with PTFE insulators tested for 1000 h

Alloy	Corrosion rate, mpy (mm/a)	Pitting	Crevice corrosion*	SCC
MONEL alloy 400	0.5 (0.01) 0.6 (0.02)	No No	No No	No No
INCONEL alloy 800	<1 (<0.025) –	Yes Yes	No Yes	No No
INCOLOY alloy 825	<1 (<0.025) –	Yes Yes	No No	No No
70-30 Cu-Ni	0.5 (0.01) 0.5 (0.01)	No No	No No	No No
90-10 Cu-Ni	0.4 (0.01) 0.4 (0.01)	No No	No No	No No
Ti-12	<1 (<0.025) –	No No	Yes Yes	No No

*Crevice corrosion under PTFE U-bent bolt insulator.

The oxidizing acid chlorides such as ferric, cupric and mercuric are very corrosive and should not be used unless their concentration is very low. Mercuric salts cause liquid metal cracking because of electrochemical reduction of mercuric ions to metallic mercury at cathodic sites. Stannic chloride is less strongly oxidizing and Nickel 200 can withstand dilute solutions at room temperature.

The oxidizing alkaline chlorides can cause pitting if the maximum safe limit (500 ppm available chlorine for continuous exposure) is exceeded. The corrosion of Nickel 200 in sodium hypochlorite sterilizing solutions at 77˚F (25˚C) was 0.1 mpy (0.003 mm/a) at 35 ppm available chlorine, 0.3 mpy (0.008 mm/a) at 100 ppm, and 0.8 mpy (0.02 mm/a) at 500 ppm. For intermittent exposure, as in textile bleaching followed by rinsing and scouring, concentrations up to 3 g/l of available chlorine can be handled. As little as 0.5 ml of 1.4 specific gravity sodium silicate per liter of bleach is an effective inhibitor.

A mixed group of very reactive and corrosive chlorides – phosphorus oxychloride, phosphorus trichloride, nitrosyl chloride, benzyl chloride, and benzoyl chloride – are commonly contained in Nickel 200.

Nickel 200 has excellent resistance to neutral and alkaline salt solutions. Even under severe exposure conditions, rates are usually less than 5 mpy (0.13 mm/a), Table 23. In acid salts, corrosion rates may vary considerably, as shown in Table 24.

INCOLOY alloys 800, 825, 020 and 25-6MO

INCOLOY alloy 800 does not have the same degree of resistance to strong chloride solutions as do Nickel 200, INCONEL alloy 600 or MONEL alloy 400. It is subject to pitting in strong neutral and acid chlorides. However, it is resistant to stress-corrosion cracking in these media. In salts other than the halides, INCOLOY alloy 800 exhibits excellent resistance to a wide variety of both oxidizing and non-oxidizing salts.

Because of their molybdenum contents, INCOLOY alloys 825, 020 and 25-6MO are much more resistant to pitting and crevice corrosion in chloride solutions than alloy 800. Again, appreciable amounts of oxidizing acid chlorides will lead to pitting/crevice corrosion and only very dilute solutions can be handled. INCOLOY alloys 825 and 020 are highly resistant to stress-corrosion cracking in chloride media. Because of its lower nickel content, INCOLOY alloy 25-6MO is not as resistant to chloride stress-corrosion cracking as the alloys with higher nickel content. All these alloys exhibit resistance to stress-corrosion cracking vastly superior to that of austenitic stainless steels.

INCOLOY alloys 825 and 25-6MO are resistant to all classes of salts except the oxidizing halides.

INCONEL alloy 625LCF and INCOLOY alloy 864

In some applications (e.g. automotive components), resistance to salts under alternating wet and dry conditions (cycling from cool to elevated temperature and splashing on hot components) is required. In such cases aqueous chloride stress-corrosion cracking and pitting as well as oxidation and intergranular salt attack at high temperature are possible failure mechanisms. INCONEL alloy 625LCF and INCOLOY alloy 864 have shown excellent resistance to these failure mechanisms.

Table 23 – Corrosion-resistance of Nickel 200 in neutral and alkaline salt solutions

Corrosive	Exposure condition	Corrosion rate, mpy (mm/a)
Cobalt acetate	In evaporator at 225°F (107°C) for 950 h.	4 (0.10)
Sodium metasilicate	In evaporator concentrating solution to 50% at 230°F (110°C) for 42 days.	0.02 (0.001)
Sodium sulfate	Saturated solution at 170°F (77°C), pH 9-10, in slurry tank for 48 days.	0.8 (0.02)
Sodium hydrosulfide	45% solution in storage tank at 120°F (49°C) for 367 days.	0.1 (0.003)

Table 24 – Corrosion-resistance of Nickel 200 in acid salt solutions

Corrosive	Exposure condition	Corrosion rate, mpy (mm/a)
Aluminum sulfate	Quiet immersion in 25% solution in storage tank at 95°F (35°C) for 112 days.	0.6 (0.02)
	In evaporator concentrating solution to 57% at 240°F (115°C) for 44 days.	59 (1.50)
Ammonium chloride	In evaporator concentrating 28 to 40% at 216°F (102°C) for 32 days.	8.4 (0.21)
Ammonium sulfate plus sulfuric acid	In saturated solution containing 5% sulfuric acid in suspension tank during crystallization at 106°F (41°C) for 33 days.	3.0 (0.08)
Manganese chloride plus some free hydrochloric acid	Immersed in boiling 11.5% solution in flask equipped with reflux condenser at 214°F (101°C) for 48 h.	8.7 (0.22)
Manganese sulfate	In evaporator concentrating 1.25-1.35 specific gravity at 235°F (113°C) for 11 days.	2.9 (0.07)
Zinc chloride	In evaporator concentrating 7.9 to 21% at 100°F (38˚C) under 26-28 in (66-71 cm) vacuum for 210 days.	4.6 (0.12)
	In evaporator concentrating 21 to 69% at 240°F (115°C) under 15-18 in (38-46 cm) vacuum for 90 days.	40 (1.02)
Zinc sulfate	Saturated solution containing trace of sulfuric acid in evaporating pan at 225°F (107°C) for 35 days with vigorous stirring.	25 (0.64)

INCONEL alloy 600

The comments made for Nickel 200 and MONEL alloy 400 are generally applicable to INCONEL alloy 600 as well. However, in oxidizing acid salts INCONEL alloy 600 is superior. This resistance does not extend to solutions containing oxidizing acid chlorides. INCONEL alloy 600 is practically unaffected by silver nitrate solutions and is used extensively in the manufacture of photographic materials containing silver salts.

The alloy is one of the few materials suitable for use with strong, hot solutions of magnesium chloride. In addition to the advantage of its low rate of corrosion, less than 1 mpy (0.03 mm/a), it shows no tendency to suffer stress-corrosion cracking. At liquid-air interfaces, pitting may occur. In nitrosyl chloride over 110˚F (43˚C), INCONEL alloy 600 is preferred to Nickel 200.

INCONEL alloys 622, 625, C-276 and 686

Because of their high molybdenum contents, these Ni-Cr-Mo alloys are very resistant to pitting and crevice corrosion. U-bent specimens subjected to 45% magnesium chloride for various exposure periods showed no evidence of cracking. The Ni-Cr-Mo alloys are very resistant to all classes of salts. Table 25 shows results for INCONEL alloy 625 in various salt environments.

Table 25 – Corrosion testing of INCONEL alloy 625 in salt-containing media

Test conditions	Temperature, °F (°C)	Duration of test	Corrosion rate, mpy (mm/a)	Max. pitting depth, mil (mm)
Five solutions, each singly; 40% calcium chloride, pH 2, 35% of time; 40% zinc sulfate, pH 1.8, 35% of time; 3-30% aluminum sulfate, pH 3, 15% of time; 40% magnesium sulfate pH 3, 10% of time; 40% zinc chloride, pH 1.8, 5% of time. Aeration, moderate. Agitation, lightnin' mixer.	70-200 (21-93)	73 days	0.1 (0.003)	1 (0.03)
Cuprous chloride, cuprous cyanide, p-chlorophenol-N-methyl pyrolidone, p-cyanophenol. Aeration, none. Agitation, by boiling only.	455 (235)	43 h	0.5 (0.013)	–
5-20% cyanuric chloride in carbon tetrachloride or toluene, 0.5% chlorine, 0.3% cyanogen chloride, hydrogen chloride and phosgene.	–	–	0.5 (0.013)	1 (0.03)
Zinc chloride up to 71% (72° Be). Aeration, none; under 28 in. (71 cm) vacuum. Agitation.	225 (107)	35 days	0.3 (0.008)	3 (0.08)
51% magnesium chloride, 1% sodium chloride, 1% potassium chloride, 2% lithium chloride as concentrated from natural Bonneville brines of 33% solubles. Aeration, little. Agitation, moderate.		100 h with brine only, 20 h with 0.2% fluosilicic acid and 0.1% HF		
Liquid phase	330-335 (165-168)		2 (0.05)	–
Vapor phase	330-355 (165-180)		3 (0.08)	–
53% magnesium chloride, 1% sodium chloride, 1% potassium chloride, 2% lithium chloride as concentrated from natural Bonneville brines of 33% solubles. Aeration, little. Agitation, moderate to considerable.	335-355 (168-180)	200 h	0.5 (0.013)	–
Vapor phase above 53% magnesium chloride with 8,000-10,000 ppm hydrochloric acid in condensate. Aeration, air-free after start-up.	335-345 (168-174)	200 h	4 (0.10)	–
Vapors over 50% magnesium chloride with 500-4000 ppm hydrochloric acid in condensate and 1000 ppm magnesium chloride. Aeration, moderate after start-up. Agitation.	310 (154)	45 h	2 (0.05)	Scattered pits
50% magnesium chloride solution plus 1% sodium chloride, 1% potassium chloride, 2% lithium chloride, concentrating natural Bonneville brine from 33% soluables to 50%. Aeration, little. Agitation, moderate.	310 (154)	45 h	0.8 (0.020)	Scattered pits

High contents of molybdenum and chromium along with lesser contents of some minor alloying elements (e.g. tungsten or niobium) increase the resistance of nickel-based alloys to acid chlorides. INCONEL alloys 686, 622 and C-276 show the highest resistance, followed by INCONEL alloy 625, down to INCOLOY alloy 25-6MO, down to INCOLOY alloy 825, down to AISI 316 stainless steel. In extreme crevice corrosion conditions (low pH, oxidizing halides and high-temperature), the rank order of the Special Metals alloys, see Figure 30, would be, in descending order:

INCONEL alloy 686
INCONEL alloy 622
INCONEL alloy C-276

Though molybdenum is the prime alloying ingredient used to prevent pitting and crevice corrosion, tungsten also has a significant effect. In Figure 30, UNS N06455, which contains no tungsten, experiences much greater attack than INCONEL alloy C-276 which contains 4% tungsten. The same effect is seen when comparing UNS N06059, which contains no tungsten, with INCONEL alloy 686 which contains 4%.

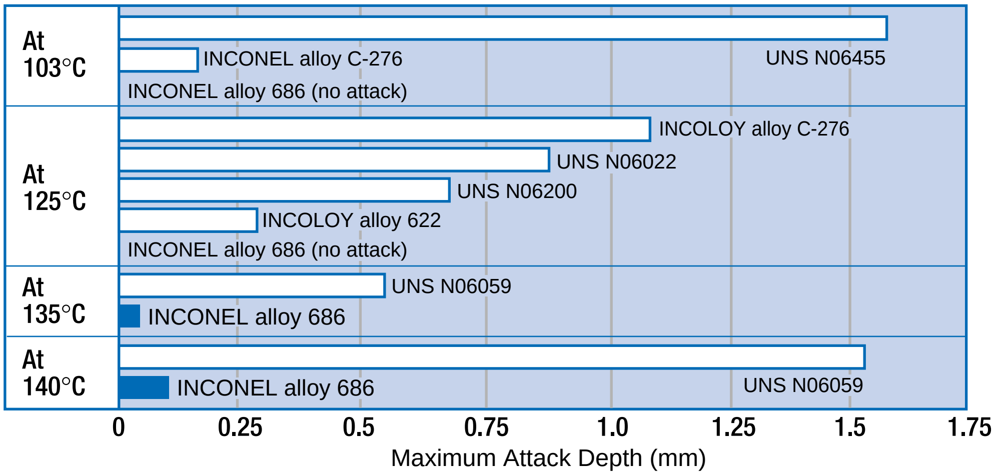


Figure 30 – Relative resistance of nickel-based alloys to crevice corrosion as a function of temperature in 11.9% H_2SO_4 + 1.3% HCl + 1% $FeCl_3$ + 1% $CuCl_2$.

Atmospheric Corrosion

Many variables influence the corrosion characteristics of an atmosphere. Diverse factors (e.g. relative humidity, temperature, sulfur dioxide content, hydrogen sulfide content, chloride content, amount of rainfall, dust) and even orientation of the exposed metal, all can effect marked influences in corrosion behavior. In an arid atmosphere, free of contaminants, only negligible corrosion would be expected.

A common practice is to classify atmospheres into categories, e.g. rural, industrial and marine. There are also possible further sub-divisions, such as tropic or polar, wet or dry. In most cases, however, the prime three provide adequate classification.

In an industrial atmosphere, many types of contaminants can be expected, but contamination by sulfur (in the form of sulfur dioxide, sulfur trioxide or hydrogen sulfide) is usually the most important. The burning of fossil fuels generates large amounts of sulfur dioxide, which is converted to sulfurous acid and oxidized to sulfur trioxide (forming sulfuric acid) in the presence of air and moisture. The corrosivity of an industrial atmosphere diminishes with distance from a city because the degree of sulfur dioxide concentration decreases.

Marine atmospheres severely corrode many metals. The atmospheric test laboratory at Kure Beach in North Carolina shows that steels exposed 80 feet (25 meters) from the ocean corrode ten to fifteen times faster than steels exposed at a distance of 800 feet (250 meters).

Rural atmospheres, with their low content of industrial gases and dusts and lack of chlorides, are the least aggressive of the atmospheres commonly considered.

Nickel 200

When exposed indoors, Nickel 200 will remain reasonably bright and free of tarnish, being superior to silver, copper, and brass in this respect. Outdoors, it becomes dull, acquiring a thin adherent corrosion film (which is usually a sulfate). The rate of corrosion is extremely slow, although corrosion rate does increase with increases in the sulfur dioxide content of the atmosphere. Marine atmospheres and rural atmospheres are comparable in their effects on Nickel 200, both resulting in very low corrosion rates. Marine atmospheric corrosion rates for Nickel 200 and other nickel alloys are shown in Table 26.

Table 26 – Corrosion-resistance of nickel alloys to marine atmosphere at Kure Beach, North Carolina

Alloy	Test lot	Time, y	Ave. corrosion rate mpy (mm/a)	Pitting attack, mils (mm)
Nickel 200	80 ft (25 m)	20	<0.1 (<0.0025)	Nil
Nickel 200	800 ft (250 m)	36	<0.1 (<0.0025)	0
MONEL alloy 400	80 ft (25 m)	20	<0.1 (<0.0025)	<1 (<0.025)
MONEL alloy 400	800 ft (250 m)	36	<0.1 (<0.0025)	<4 (<0.1)
MONEL alloy K-500	800 ft (250 m)	36	0.008 (0.0002)	8 (0.2)
INCONEL alloy 600	80 ft (25 m)	20	<0.01 (<0.00025)	Nil
INCONEL alloy 600	800 ft (250 m)	36	<0.01 (<0.00025)	4 (0.1)
INCOLOY alloy 800	80 ft (25 m)	20	<0.01 (<0.00025)	<1 (<0.025)
INCOLOY alloy 825	80 ft (25 m)	20	<0.01 (<0.00025)	<1 (<0.025)
INCONEL alloy 625	80 ft (25 m)	21	0.04 (0.001)	–
INCONEL alloy 625	800 ft (250 m)	21	0.04 (0.001)	–
INCONEL alloy C-276	800 ft (250 m)	56	Nil - bright mirror finish	–

MONEL alloy 400

Corrosion of MONEL alloy 400 is negligible in all types of atmospheres. Indoor exposure produces a very light tarnish that is easily removed by occasional wiping. Outdoor surfaces that are exposed to rain develop a thin gray-green patina. In sulfurous atmospheres, a smooth, brown, adherent film forms. Because of its low corrosion rate and the pleasing patina which develops, MONEL alloy 400 is used for architectural service as roofs, gutters, and flashings.

INCONEL alloy 600 and INCOLOY alloy 800

INCONEL alloy 600 and INCOLOY alloy 800 will remain bright indefinitely in indoor atmospheres, even in damp sulfurous atmospheres that may fog Nickel 200 and MONEL alloy 400. Outdoors, in rural atmospheres, the alloys will stay bright for many years but may develop a slight tarnish in industrial, sulfur-bearing atmospheres. Free exposure to the atmosphere is more favorable than sheltered exposure in which the beneficial effects of rain in washing the surface and sun and wind in drying cannot occur. INCOLOY alloy 800 may develop a very thin oxide film and very slight pitting after prolonged exposure to marine environments.

INCOLOY alloys 825, 020 and 25-6MO
INCONEL alloys G-3, 622, 625, C-276 and 686

These Fe-Ni-Cr-Mo and Ni-Cr-Mo alloys remain bright and tarnish-free in rural and industrial environments. They also remain bright in marine environments (Table 26).

Corrosion by Waters

To review this subject meaningfully, the chemistry (i.e. the amount and type of impurities present) must be defined. It is probably easiest to divide potentially corrosive water into three main classifications – distilled and high purity water, fresh water, and seawater. Of these, distilled and high purity waters are the least corrosive because dissolved gases and solids are at a minimum. In general, fresh waters (e.g. potable or "tap" water) are intermediate, and seawater is the most severe.

Many common engineering alloys show good resistance to general corrosion by waters. However, the three major problems in the industrial use of water are pitting, crevice corrosion and stress-corrosion cracking. Nickel and nickel-based alloys are resistant to most waters. The molybdenum containing nickel-based alloys are also very resistant to the effects of macrobiological and microbiological organisms that are often found in fresh and waste waters.

Fresh and Process Waters

Nickel 200

The resistance of Nickel 200 to corrosion by distilled and natural waters is excellent. Analysis of distilled water from a nickel storage tank indicated a rate of corrosion of 0.001 mpy (0.00003 mm/a). Similarly, tests in domestic hot water up to 200˚F (93˚C) normally show rates of less than 0.02 mpy (0.0005 mm/a) and occasionally as high as 0.2 mpy (0.005 mm/a). Nickel 200 is especially resistant to water containing hydrogen sulfide or carbon dioxide. In distilled water saturated with 50:50 carbon dioxide and air at 160˚F (71˚C), the corrosion rate was less than 1 mpy (0.03 mm/a). However, in steam condensate at elevated pressure, e.g. 35 psi (0.24 MPa), high rates of attack occur when there is 55-90% carbon dioxide in the non-condensable gases.

MONEL alloys 400 and K-500

MONEL alloys 400 and K-500 have excellent resistance to distilled and both hard and soft fresh waters. Rates of corrosion are usually less than 1 mpy (0.03 mm/a) under the most severe conditions of temperature and aeration. In acid-mine waters that contain oxidizing salts, attack is accelerated.

Like Nickel 200, MONEL alloy 400 had a high corrosion rate of 60 mpy (1.52 mm/a) in a short-time test in steam condensate at 160˚F (71˚C) where the vapor phase contained 70% carbon dioxide and 30% air at 85 psi (0.59 MPa) as non-condensable gases. The corrosion rate was lower for other ratios of carbon dioxide and air. Deaeration of the feed, or venting of the non-condensable gases will prevent this attack.

INCONEL alloys 600 and 690

INCONEL alloys 600 and 690 are essentially immune to general corrosion by fresh waters, including the most corrosive of natural waters containing free carbon dioxide, iron compounds, and dissolved air. Although subject to pitting in chloride-bearing fresh water, they remain free from stress-corrosion cracking.

INCONEL alloys 600 and 690 are resistant to all mixtures of steam, air, and carbon dioxide and are particularly useful in contact with steam at high temperatures. Alloy 690 offers improved resistance to stress-corrosion cracking in some of the most demanding environments (e.g. nuclear steam generator tubes and components).

INCONEL alloys G-3, 622, 625, 725, C-276 and 686

In fresh and distilled water, corrosion rates for these nickel-chromium-molybdenum INCONEL alloys are essentially zero.

INCOLOY alloys 800, 825, 925, 020 and 25-6MO

INCOLOY alloys 800 shows negligible rates of attack in fresh and distilled water. In addition to exhibiting low corrosion rates, it is highly resistant to stress-corrosion cracking and is often used to replace the austenitic stainless steels in chloride-containing waters.

The molybdenum-bearing INCOLOY alloys 825, 020, 925 and 25-6MO exhibit excellent resistance to fresh and distilled waters including resistance to chloride stress-corrosion cracking.

Seawater and Marine Environments

Nickel 200

Nickel 200 is susceptible to severe localized attack in stagnant or very low-velocity seawater, which can occur under fouling organisms or other deposits. For these reasons, it is not generally used in seawater applications, especially under conditions of impingement (Table 27). In general, Nickel 200 finds application in water-cooled heat exchangers only where it is required for the process-side chemical.

MONEL alloys 400 and K-500

In seawater or brackish water, MONEL alloys 400 and K-500 give excellent service in moderate or high-velocity systems, as do most nickel alloys (Table 27). They have excellent resistance to cavitation and erosion corrosion, and rates in flowing seawater are usually less than 1 mpy (0.03 mm/a). MONEL alloy K-500 has very good corrosion fatigue strength of 26 ksi (179 MPa) at 10^8 cycles. In stagnant or slow moving seawater, fouling may occur followed by pitting. Such pitting tends to slow down after a fairly rapid initial attack and rarely exceeds 50 mils (1.3 mm) in depth, even after exposure for several years.

Table 27 – Resistance of nickel alloys to impingement attack by seawater at 150 ft/sec (45.7 m/s)

Alloy	Corrosion/Erosion rate	
	mpy	mm/a
INCONEL alloy 625	Nil	Nil
INCOLOY alloy 825	0.3	0.008
MONEL alloy K-500	0.4	0.01
MONEL alloy 400	0.4	0.01
Nickel 200	40	1.0

Table 28 – Crevice corrosion-resistance of nickel alloys exposed to seawater at ambient temperatures

Alloy	% Mo	PRE[a]	Crevice test type	Exposure, days	Max. depth of attack, mils (mm)
Nickel 200	0	—	Washers	30	63 (1.60)
INCONEL alloy 600	0	16	Washers	30	34 (0.86)
INCONEL alloy 718	3.0	22.5	Washers	30[e]	16 (0.41)[e]
INCONEL alloy 718	3.0	22.5	PTFE[f]	180	32 (0.82)
INCOLOY alloy 825	3.2	26.0	Washers	30	10 (0.25)
INCOLOY alloy 925	0	26.0	PTFE	180	114 (2.90)
INCOLOY alloy 25-6MO	6.5	35.8	Vinyl Sleeve[b]	60	5 (0.13)
INCONEL alloy G-3	7	32.5	Washers	30	3 (0.07)
INCONEL alloy 625	9	40.8	MCA[c]	90	0
INCONEL alloy 625	9	40.8	PTFE	180	4 (0.11)
INCONEL alloy 725	9	40.8	Washers	30	0
INCONEL alloy C-276	16	45.2	PCA[d]	60	0
INCONEL alloy C-276	16	45.2	PTFE	180	4 (0.12)
INCONEL alloy 686	16	50.8	PCA	60	0
INCONEL alloy 686	16	50.8	PTFE	180	0
MONEL alloy 400	0	—	PTFE	180	27 (0.68)
MONEL alloy K-500	0	—	PTFE	180	49 (1.24)

(a) Based on typical alloy compositions. PRE = % Cr + 1.5 (% Mo + % W + % Nb) + 30 (% N).
(b) Tube specimen inserted into vinyl tubing to form tight crevice on OD of metal tube.
(c) Surface finish ground, with Delrin crevice assemblies.
(d) Surface finish ground and pickled, with Perplex crevice assemblies.
(e) Estimated.
(f) Surface ground, with PTFE crevice assemblies.

INCONEL alloy 600 and INCOLOY alloy 800

INCONEL alloy 600 and INCOLOY alloy 800 contain no molybdenum and, thus, are subject to severe crevice attack beneath deposits in seawater. They are not generally used in marine environments.

INCOLOY alloys 825, 020, 925 and 25-6MO

The molybdenum-bearing INCOLOY alloys offer good resistance to flowing seawater. INCOLOY alloys 825 and 925 are more susceptible to crevice attack due to biofouling (Table 28). Under crevice conditions, INCOLOY alloy 25-6MO is significantly more resistant to corrosion. By virtue of their higher nickel contents, INCOLOY alloys 825 and 925 offer excellent resistance to chloride stress-corrosion cracking.

INCONEL alloys 622, 625, 625LCF, C-276, 686, 718 and 725

Corrosion rates for these Ni-Cr-Mo and Fe-Ni-Cr-Mo alloys in marine environments are very low. In seawater, under both flowing and stagnant conditions, their weight losses are extremely low. All of these alloys are very resistant to stress-corrosion cracking in waters containing chlorides.

INCONEL alloys 625, 625LCF, 718 and 725 show excellent corrosion fatigue strength in seawater (Figure 31). However INCONEL alloy 718 is not as resistant to crevice corrosion as alloys 625, 625LCF and 725.

Table 28 compares the crevice corrosion resistance of nickel-based corrosion-resistant alloys in seawater. Nickel alloys with a PRE (Pitting Resistance Equivalent) number greater than 40 are very resistant to crevice corrosion in seawater. In very tight crevice conditions, INCONEL alloy 625 and materials of lesser alloy content, and similar or lower PRENs, can be severely attacked. Under such conditions, highly alloyed materials such as INCONEL alloys 622, C-276, and 686 are required. An example of this type of application is seawater-cooled plate-type heat exchangers, which have a multiplicity of crevices.

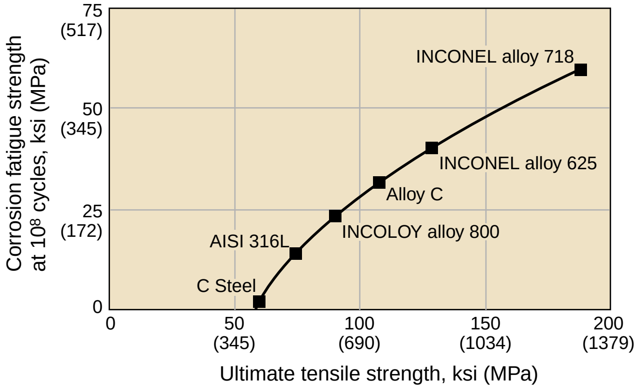


Figure 31 – Corrosion fatigue strength of nickel alloys in seawater.

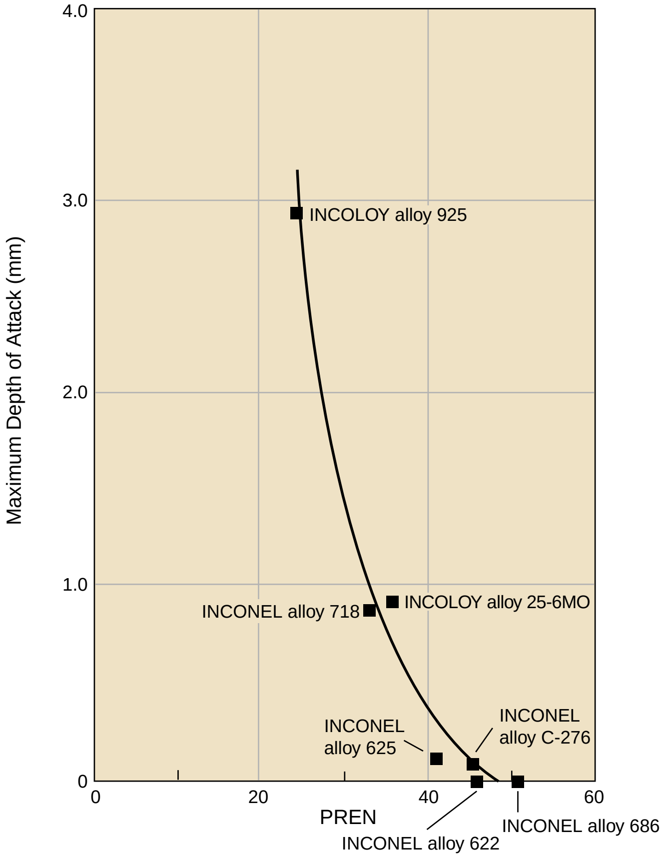


Figure 31A – Maximum depth of attack by crevice corrosion after exposure to quiescent seawater at 85˚F (29˚C) for 180 days as a function of PREN*.
***PREN = % Cr + 1.5 (% Mo + % W + % Nb) + 30 (% N)**

Fluorine and Hydrogen Fluoride

Fluorine, the most electronegative of the elements, is also the most reactive. Its oxidizing potential is so strong that it forms compounds with all common elements, even some of the "inert" gases. Combustible substances burst into flame and even asbestos becomes incandescent when held in a stream of fluorine.

Since all metals react directly with fluorine, metals which have useful resistance depend on the formation of a protective fluoride film. At room temperature, nickel, copper, magnesium and iron form protective films and are considered satisfactory for handling fluorine at low temperatures. At elevated temperatures, Nickel 201 and MONEL alloy 400 offer the best resistance. The most commonly used nickel alloys in processes containing fluorine are MONEL alloy 400 and INCONEL alloys 600, 625 and C-276.

Nickel 201, MONEL alloy 400 and INCONEL alloy 600 have excellent resistance to fluorine and hydrogen fluoride. At high temperatures, Nickel 201 and MONEL alloy 400 are preferred (see Tables 29, 30 and 31).

Table 29 – Corrosion-resistance of nickel alloys and other commercial materials to fluorine

Material	Corrosion rate, mpy (mm/a)					
	Temperature, °F (°C)					
	400 (752)	450 (842)	500 (932)	600 (1112)	650 (1202)	700 (1292)
Nickel 201	0.21 (8.4)	0.58 (22.8)	1.55 (61.2)	8.84 (348)	4.89 (192)	10.4 (408)
MONEL alloy 400	0.15 (6)	0.46 (18)	0.61 (24)	18.3 (720)	24.4 (960)	>1000 (>25.4)
INCONEL alloy 600	11.6 (456)	>25.4 (>1000)	18.9 (744)	>25.4 (>1000)	>25.4 (>1000)	>25.4 (>1000)
Deoxidized copper	>25.4 (>1000)	—	>25.4 (>1000)	>25.4 (>1000)	—	>25.4 (>1000)
AISI 430	23.8 (936)	—	—	—	—	—
AISI 347	>25.4 (>1000)	—	—	—	—	—
AISI 309-Cb	>25.4 (>1000)	—	—	—	—	—
AISI 310	>25.4 (>1000)	—	—	—	—	—
SAE 1020 (0.22% Si)	>25.4 (>1000)	>25.4 (>1000)	—	—	—	—

**Table 30 – Corrosion tests* in hydrogen fluoride gas.
Test duration, 36 hours. Temperature 930-1110˚F (500-600˚C)**

Material	Corrosion rate, mpy (mm/a)	Comments
INCONEL alloy C-276	0.3	Iridescent tarnish film
INCONEL alloy 600	0.7	Iridescent tarnish 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

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

Table 31 – Corrosion rate in hydrogen fluoride-steam mixture

Alloy	Corrosion rate, mpy (mm/a)				
	1022°F (550°C)	1112°F (600°C)	1202°F (650°C)	1292°F (700°C)	1382°F (750°C)
Nickel 200	31 (0.79)	72 (1.83)	108 (2.74)	144 (3.66)	120 (3.05)
MONEL alloy 400	—	24 (0.61)	60 (1.52)	156 (3.96)	204 (5.18)

Chlorine at Ambient Temperature

Dry chlorine is not particularly corrosive at ambient temperatures. Chlorine gas reacts with the water to form equal parts of hypochlorous and hydrochloric acid. Hypochlorous acid is an oxidizing acid and bleaching agent which is reduced to hydrochloric acid in the bleaching reaction. This combination of an oxidizing and a non-oxidizing acid is responsible for the corrosive effect of moist chlorine on metals.

Nickel 200, MONEL alloy 400, INCONEL alloys 600, 622, 625, C-276 and 686, and INCOLOY alloys 800, 825 and 020

All of these nickel-based alloys are resistant to dry chlorine. MONEL alloy 400 is a standard material for trim on chlorine cylinder and tank car valves, for orifice plates in chlorine pipe lines, and for various parts of chlorine-dispensing equipment. Wet chlorine at temperatures below the dew point, or aqueous solutions containing considerable amounts of free chlorine, are very corrosive to all of these alloys, except INCONEL alloy C-276 which is used for valve stems in MONEL alloy 400-seated valves to combat the effects of the ingress of moisture.

Chlorine and Hydrogen Chloride at High Temperatures

Nickel alloys are outstanding in their resistance to chlorine and hydrogen chloride at elevated temperatures. Although chlorine is a strong oxidizer and will combine directly with metals, at lower temperatures this reaction is so sluggish that dry chlorine can be shipped in steel. As the temperature is increased this reaction rate increases slowly, until a critical point (which varies with the metal under consideration) is reached. Above this critical temperature, corrosion rates increase rapidly and in some cases are roughly proportional to the vapor pressure of the particular metal chloride involved (Figure 32).

Vapor pressure is not always a reliable indicator of corrosion rates since some metal chlorides melt or decompose at temperatures at which the vapor pressure is still low. Such degradation of the metal chloride exposes fresh metal to the gas and causes increased attack. Some metals will actually ignite in chlorine above a certain temperature, thereby evolving heat which would raise both the metal temperature and rate of reaction.

Hydrogen chloride forms spontaneously and even explosively in sunlight or at high temperatures when hydrogen and chlorine are combined. When dry, this important industrial gas behaves toward metals much like chlorine. Wet hydrogen chloride at temperatures below the dew point behaves as a concentrated hydrochloric acid. At high temperatures, hydrogen chloride and chlorine are similar in their behavior except that platinum and gold are very resistant in hydrogen chloride but are readily attacked in chlorine because of its oxidizing nature.

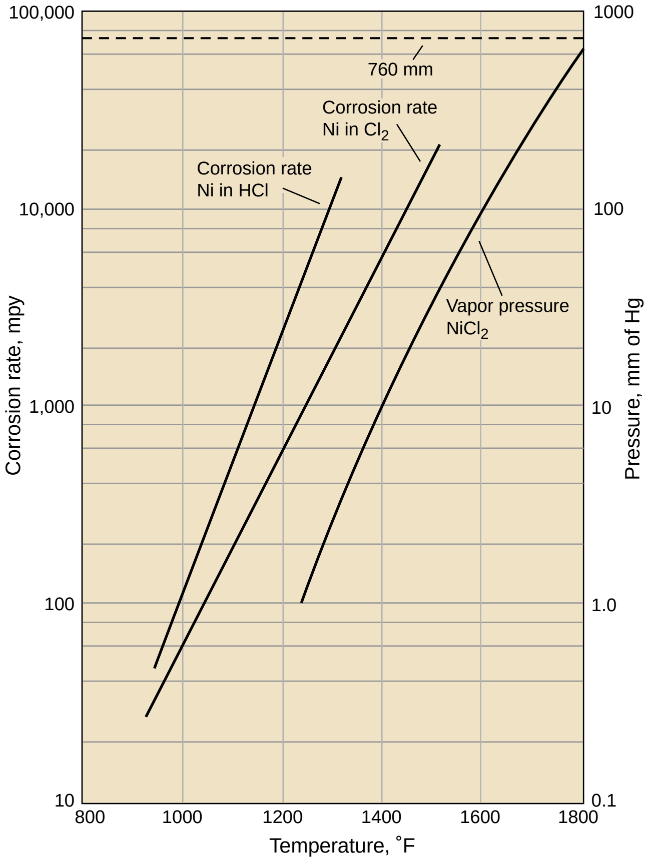


Figure 32 - Corrosion of nickel in dry chlorine and dry hydrogen chloride. Rates converted from inches per month.

Figure 33, for INCONEL alloy 600 in dry chlorine, shows that longer test runs yielded somewhat lower corrosion rates, probably due to the effect of time on the formation of protective films. From this study Tables 32 (chlorine) and 33 (hydrogen chloride) list temperatures at which various corrosion rates were exceeded, and suggest upper temperature limits for continuous service. Similar corrosion is observed in hydrogen chloride (Figure 34). These suggested temperature limits are believed to be conservative since longer testing periods are expected to give lower corrosion rates for many of the materials which develop protective chloride films.

Evidence that these temperature limitations may be on the conservative side is supported by the additional data in Table 34. Nickel 201 and INCONEL alloy 600 are the most practical alloys for service in chlorine and hydrogen chloride at elevated temperatures.

Where the major consideration is resistance to corrosion at temperatures below the dew point, but provision against high-temperature attack is also desired, the indicated order of preference for materials of construction would be platinum, followed by INCONEL alloy 686, INCONEL alloy C-276, INCONEL alloy 625, MONEL alloy 400, Nickel 200, INCONEL alloy 600, copper, and carbon steel. Nickel 201 and INCONEL alloy 600 would be rated above the Ni-Mo or Ni-Cr-Mo alloys in cases where the major requirement would be resistance to attack at temperatures from 850 to 1000˚F (454 to 538˚C).

In the selection of materials for high-temperature chlorine or hydrogen chloride service, particularly at temperatures above 700˚F (371˚C), not only the corrosion rate of the material, but the effect that the temperature may have on the mechanical properties of the material must be considered.

Table 32 – Corrosion-resistance of nickel alloys and other commercial materials in dry chlorine[a]

Material	Approximate temperature at which given corrosion rate is exceeded in short time tests in dry chlorine, °F (°C)			Suggested upper temperature limit for continuous service, °F (°C)
	30 mpy (0.76 mm/a)	60 mpy (1.52 mm/a)	120 mpy (3.05 mm/a)	
Nickel 201	950 (510)	1000 (538)	1100 (593)	1000 (538)
INCONEL alloy 600	950 (510)	1000 (538)	1050 (565)	1000 (538)
INCONEL alloy C-276	900 (482)	1000 (538)	1050 (565)	950 (510)
MONEL alloy 400	750 (399)	850 (454)	900 (482)	800 (426)
AISI 316 stainless steel	600 (315)	650 (343)	750 (399)	650 (343)
AISI 304 stainless steel	550 (288)	600 (315)	650 (343)	600 (315)
Deoxidized copper	350 (177)	450 (232)	500 (260)	400 (204)[b]
Carbon steel	250 (121)	350 (177)	400 (204)	400 (204)[c]
Aluminum	250 (121)	300 (149)	300 (149)	250 (121)[d]

(a) It is emphasized that these values are based on short-time laboratory tests under controlled conditions. They should be interpreted only as indicative of the limitations of the materials and should not be used for estimation of the service life of equipment.
(b) Ignites at about 600°F (315°C).
(c) Ignites at 450-500°F (232-260°C).
(d) Ignites at 400-450°F (204-232°C).

Table 33 – Corrosion-resistance of nickel alloys and other commercial materials in dry hydrogen chloride[a]

Material	Approximate temperature at which given corrosion rate is exceeded in short time tests in dry hydrogen chloride, °F (°C)			Suggested upper temperature limit for continuous service, °F (°C)
	30 mpy (0.76 mm/a)	60 mpy (1.52 mm/a)	120 mpy (3.05 mm/a)	
Nickel 201	850 (454)	950 (510)	1050 (565)	950 (510)
INCONEL alloy 600	800 (426)	900 (482)	1000 (538)	900 (482)
INCONEL alloy C-276	700 (371)	800 (426)	900 (482)	850 (454)
AISI 316 stainless steel	700 (371)	700 (371)	900 (482)	800 (426)
AISI 304 stainless steel	650 (343)	750 (399)	850 (454)	750 (399)
Carbon steel	500 (260)	600 (315)	750 (399)	500 (260)
Ni-Resist (Type 1)	500 (260)	600 (315)	700 (371)	500 (260)
MONEL alloy 400	450 (232)	500 (260)	650 (343)	450 (232)
Copper	200 (93)	300 (149)	400 (204)	200 (93)

(a) It is emphasized that these values are based on short-time laboratory tests under controlled conditions. They should be interpreted only as indicative of the limitations of the materials and should not be used for estimation of the service life of equipment.

The effect of moisture in hydrogen chloride at elevated temperature has been studied. It has been shown that 0.25% moisture in hydrogen chloride does not significantly alter the corrosion of Nickel 201 at 1000˚F (538˚C), Table 35.

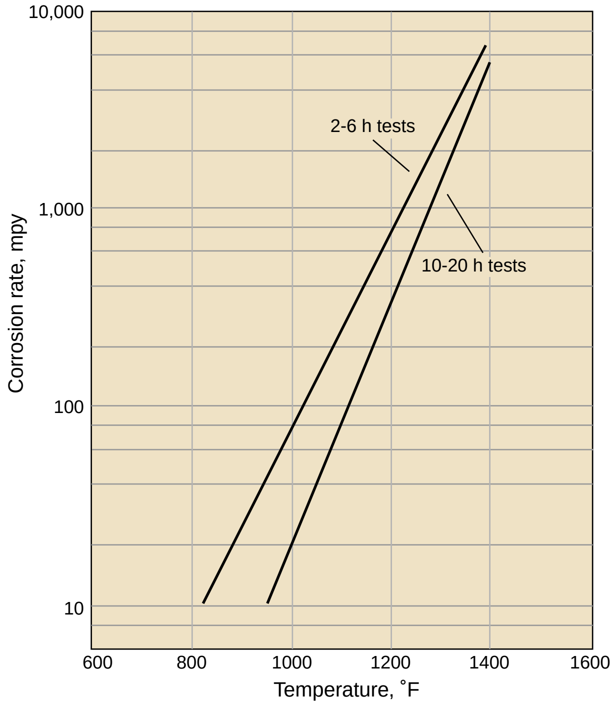


Figure 33 - Corrosion of INCONEL alloy 600 in dry chlorine gas. Rates converted from inches per month.

Table 34 – Laboratory corrosion tests in anhydrous hydrogen chloride gas. Temperature 930°F (498°C). Test duration, 500 h.

Material	Corrosion rate, mpy (mm/a)
Nickel 201	3 (0.08)
INCONEL alloy 600	3 (0.08)
AISI 304L stainless steel	11 (0.28)

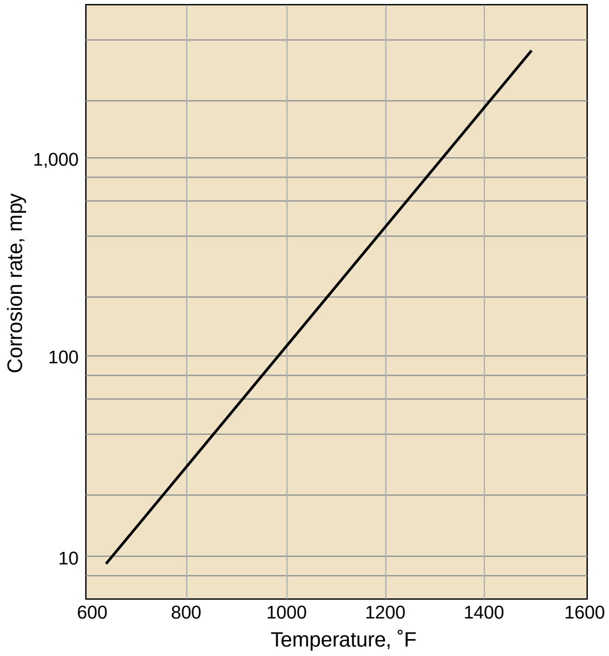


Figure 34 - Corrosion of INCONEL alloy 600 in dry hydrogen chloride gas. Rates converted from inches per month.

In the synthesis of hydrogen chloride from hydrogen and chlorine, the preferred combustion chamber design makes use of metal construction, with the temperature of the metal being controlled within proper limits by means of water jackets. In this connection, it appears that the danger of corrosion by condensed hydrochloric acid at some temperature near the dew point is greater than by dry hydrogen chloride at elevated temperatures.

The allowable temperature range for any metal or alloy may be contracted at its lower end by the hydroscopic nature of the chloride of the metal concerned; for example, iron should not be used at a temperature less than 54˚F (30˚C) above the $HCl\text{-}H_2O$ dew point, while copper may be used as long as the temperature is 9˚F (5˚C) above the dew point. In view of the hydroscopic nature of nickel chloride, it would be prudent to assume that hydrochloric acid might condense on a nickel surface at a temperature as much above the dew point as in the case of iron, i.e. 54˚F (30˚C).

Table 35 – Corrosion-resistance of nickel alloys in hydrogen chloride at 1000°F (538°C)

Material	Corrosion rate, mpy (mm/a)					Weight Loss, mg/dm^2 wet gas[a]			
	Wet gas[a]				Dry as, 20 hours				
	4 h	8 h	20 h	47 h		4 h	8 h	20 h	47 h
Nickel 201	120 (3.05)	70 (1.78)	28 (0.71)	–	37 (0.94)	126 (3.20)	143 (3.63)	140 (3.56)	–
MONEL alloy 400	–	–	–	49 (1.24)	–	124 (3.15)	165 (4.19)	–	600 (15.2)
INCONEL alloy 600	–	–	34 (0.86)	–	–	110 (2.79)	105 (2.67)	165 (4.19)	–

(a) Moisture content of gas about 0.25% by weight after bubbling through concentrated hydrochloric acid and before passing over the test specimens.

High-Temperature Considerations

In the selection of materials for high-temperature service, particularly at temperatures above 700˚F (371˚C), not only the corrosion rate of the material, but the effect that the temperature may have on the mechanical properties of the material must be considered.

The previous section of this publication has shown that commercially pure nickel products have useful corrosion resistance at temperatures up to around 1000˚F (538˚C). In considering the use of commercial nickel at elevated temperatures, it is necessary to consider two of its limitations. Nickel 200, having a nominal content of up to 0.10% C, is subject to embrittlement by *intergranularly* precipitated carbon or graphite when held at temperatures of 800-1400˚F (426-760˚C) for extended periods of time. Nickel 201 (low-carbon nickel), having a maximum carbon content of 0.02%, is not subject to such embrittlement, provided it is not in contact with carbonaceous materials.

Both Nickel 200 and 201 are subject to intergranular embrittlement by sulfur compounds at temperatures above about 600˚F (315˚C). In applications where carbon or sulfur compounds are present, or where high-temperature strength is required, INCONEL alloy 600 is frequently substituted for Nickel 200 or Nickel 201.

Exposure to High Temperatures During Fabrication

Nickel alloys are selected primarily for their corrosion resistance. Heat treatments (e.g. improper annealing, stress relief, etc.) and welding can cause corrosion of the alloy in some process environments. Corrosion may be due to sensitization of the base metal in heat-affected zones as described in the section on intergranular corrosion, formation of secondary phases, segregation in the weld metal, or residual stress. All these types of heating may result in intergranular attack, pitting, crevice corrosion, or stress-corrosion cracking in some materials.

Effects of Welding and Fabrication on Corrosion Resistance

Nickel alloys are readily weldable. The presence of welds in fabricated components introduces special corrosion considerations. The structure of a weldment is similar to that of a casting. Dendrite formation and growth occur first from the highest melting point constituents as the weld puddle solidifies. As dendrite growth continues, lower melting point materials are typically relegated to the inter-dendrite spaces, causing chemical segregation within the weld. This coarse dendritic structure, with chemical inhomogeneity, can cause the weld metal to become anodic to the base metal in corrosive environments. Thus, a relatively small anode (weld metal) and a large cathode (base metal) can lead to an unfavorable galvanic corrosion situation.

The weld metal characteristics can also lead to preferential general corrosion or pitting and crevice corrosion of the weld metal in environments where the corrosion resistance of an alloy is being pushed to its limit. Post-weld heat treatment is usually impractical and offers only limited improvement in the corrosion resistance of nickel alloy welds. A proven means of preventing preferential attack of as-welded structures is the use of a weld metal which is more noble than the base metal. When fabricating Ni-Cr-Mo alloys it is common to use a welding product with a higher level of molybdenum than the base metal. This is normally referred to as "overmatching". The use of more highly alloyed welding products will compensate for the elemental segregation inherent in the weld metal.

A common example of the practice of using overalloyed welding products is the use of 9 to 14% molybdenum containing INCONEL welding electrode 112/filler metal 625 or INCONEL welding electrode 122/filler metal 622 for welding 6% molybdenum super-austenitic alloys such as INCOLOY alloy 25-6MO. The same prac-

Table 36 – Critical pitting temperatures for nickel alloy filler metals weld-overlayed on carbon steel. Duplicate and triplicate tests in 11.9% H_2SO_4 + 1.3% HCl + 1% $CuCl_2$ + 1% $FeCl_3$

Welding process	Alloy filler metal	1st layer overlay temperature, °F (°C)			2nd layer overlay temperature, °F (°C)			3rd layer overlay temperature, °F (°C)		
GMAW	INCONEL C-276	167 (75)	167 (75)	–	203 (95)	203 (95)	–	203 (95)	203 (95)	–
GMAW	UNS N06022	167 (75)	158 (70)	–	212 (100)	212 (100)	–	212 (100)	212 (100)	–
GMAW	INCONEL 622	167 (75)	185 (85)	–	–	>212 (>100)	–	>212 (>100)	>212 (>100)	–
GMAW	INCO-WELD 686CPT	>212 (>100)	>212 (>100)	–	>212 (>100)	>212 (>100)	–	>212 (>100)	>212 (>100)	–
SAW	INCO-WELD 686CPT	176 (80)	167 (75)	185 (85)	212 (100)	212 (100)	212 (100)	–	–	–
ESW	INCO-WELD 686CPT	203 (95)	203 (95)	212 (100)	212 (100)	212 (100)	212 (100)	–	–	–

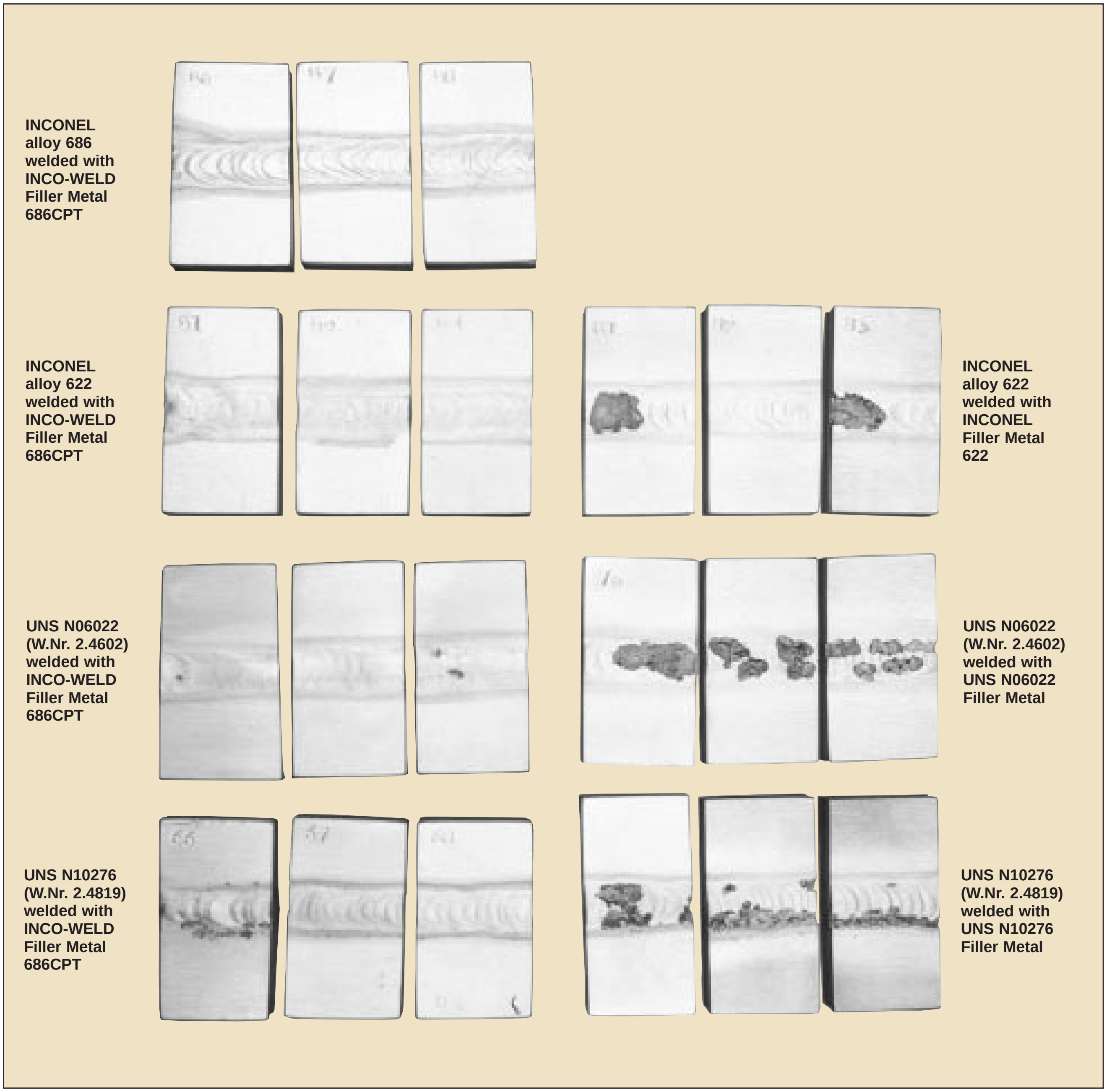


Figure 35 - Pitting-resistance of base metal/weld metal combinations.
Exposed for 3 days at 217˚F (103˚C) in 11.9% H_2SO_4 + 1.3% HCl + 1% $FeCl_3$ + 1% $CuCl_2$.

tice is applied to even more highly alloyed materials. As shown in Figure 35, matching composition welds in INCONEL alloys 686 and 622, alloy N06022, and alloy C-276 are preferentially attacked in a pitting environment relating to certain flue gas desulfurization conditions. The use of the overmatching INCO-WELD filler metal 686CPT to join these alloys prevents the attack. The higher alloy content of this filler metal offsets the effects of elemental segregation experienced with matching composition filler materials.

The corrosion seen in Figure 35 is preferential weld metal attack and should not be confused with intergranular heat-affected-zone (HAZ) attack. This attack of the base metal is due to base metal sensitization produced by heat from the welding process, and can be prevented by the use of a low carbon or stabilized base metal.

Iron dilution of the alloy weldment can be an important factor during weld overlaying on steel and joining alloy-clad steel components. Dilution of the weld deposit from filler metals such as INCONEL 622, 625 or C-276 with iron from the substrate can lower the weld metal corrosion resistance. This is illustrated by corrosion testing of weld overlays on carbon steel in Table 36 (page 45). The critical pitting temperature increases for alloys C-276, N06022 and 622 in successive weld metal layers as the iron dilution decreases. The use of INCO-WELD filler metal 686CPT provides excellent corrosion-resistance even in the first layer due to its high alloy content and very

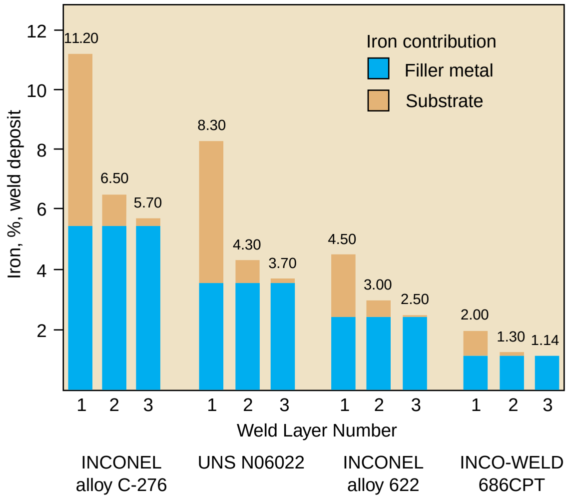


Figure 36 - Effect of filler metal composition on iron content for Ni-Cr-Mo alloys overlayed on steel by the GMAW process.

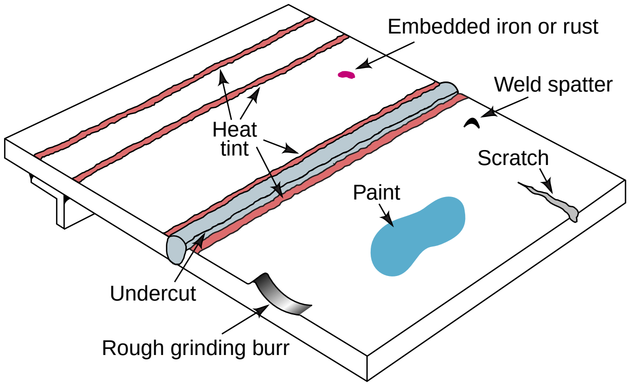


Figure 37 - Some post-fabrication surface conditions that call for attention and removal to avoid their possible effects on corrosion-resistance.

low initial iron content. The iron levels for one, two and three layer welds deposited on steel are shown in Figure 36. The amount of iron dilution from the steel substrate seems to be proportional to the initial iron content of the filler metal. Thus, in welding operations where iron pick-up should be minimized, selection of the appropriate filler metal is very important.

Post-Fabrication Cleaning

Cleaning the surface of a nickel alloy may be required to prevent process contamination or to ensure performance. Surface conditions that can effect corrosion resistance may be due to surface contamination (including embedded iron), to mechanical damage, and to welding related artifacts (Figure 37).

Some contaminants may be removed by degreasing. The use of a non-chlorinated solvent is effective. The use of a chlorinated solvent is not recommended as residual chlorides may remain in crevices and cause crevice corrosion or chloride stress-corrosion cracking of susceptible alloys.

During fabrication, metal products often come in contact with steel components and tools. Transportation, handling, forming, grinding and welding can all result in physical contact with iron-based structures. During such contact, iron may become embedded into the surface of an alloy component. When stainless steels (e.g. austenitic grades such as AISI 316, 317 and 904L) and super-austenitic grades (e.g. INCOLOY alloy 25-6MO) are exposed to aggressive acid and acid-halide environments, the embedded iron can accelerate localized attack such as crevice and/or pitting corrosion. Thus, parts fabricated from such grades should be cleaned prior to exposure to this type of service environment to optimize resistance to corrosion. Embedded iron has not been shown to affect the corrosion resistance of higher alloyed materials, such as INCONEL alloys 622, 625, C-276 and 686.

Passivation

Passivation is the formation of a thin, protective film on a metal which makes the metal passive (corrosion-resistant). While stainless steels require an acid treatment to passivate their surface, nickel and the high-nickel alloys become passive upon exposure to air. The film itself is a chromium-nickel-iron-molybdenum oxide for the chromium-bearing nickel alloys. Chromium is the key constituent giving the film its outstanding corrosion resistance.

The film formed in air at the mill is stable. However, during fabrication, the film may be damaged locally when iron, weld spatter, arc strikes and heat tint scale create local defect sites (i.e. local imperfections in an otherwise passive film). The undamaged surface remains passive throughout fabrication. Removal of defects, by pickling, electropolishing, or mechanical means, immediately restores the film and passivity so passivating by acid washing is not required.

Nitric acid cleaning/passivation treatments for stainless steels are described in ASTM A380. It should be noted that these treatments are not suitable for cleaning structures after fabrication. They are applicable only to passivating chromium-nickel stainless steels and are not applicable for cleaning nickel alloys after fabrication. As already stated, such treatments are not required to optimize the corrosion resistance of the nickel-based alloys.

Field Corrosion Testing

When new processes or systems are first proposed, there may be insufficient data available to make reliable alloy selections for the conditions involved. After a close study of the chemistry for a process, it is usually very difficult, if not impossible, to duplicate such conditions in the laboratory. A practical approach to obtaining corrosion data having some degree of relevancy and reliability is to expose corrosion test spools in pilot or full-scale operating plants. Pilot plants offer the first opportunity to conduct corrosion tests under actual process conditions. As systems are scaled up to full-size commercial plants, corrosion testing can be continued to verify earlier data and monitor corrosion of the equipment. In the case of a failure of a process component, corrosion data can be obtained by this procedure to assist in material replacement.

Field corrosion testing may be conducted in accordance with ASTM Standard Recommended Practice G-4 for Conducting Plant Corrosion Tests or NACE Standard RP0497-97. A typical corrosion test spool used is shown in Figure 38. PTFE is used as an insulator to avoid galvanic effects. Contact of the end face of the PTFE spacer with the specimen provides a crevice which assists in evaluating the susceptibility of the specimen to crevice corrosion in the environment. Duplicate samples of each alloy, located at non-adjacent positions, are exposed.

When the spools are returned after exposure, the specimens are cleaned, weighed and examined for localized attack. In the case of severe pitting, weight loss alone is considered to be of little value. More important is the depth of pitting recorded. When only shallow pits are present or pitting is incipient, <1 mil (<0.0254 mm), the weight loss is considered to be valid and corrosion rates are calculated. When crevice corrosion is observed, a record is made of the depth of the attack. Crevice corrosion is an indication of the susceptibility of an alloy to corrosion under scale deposits and in crevices built into the equipment design.

The importance of field testing cannot be over-emphasized. Sample materials are available from the marketing or technology departments of Special Metals Corporation at Huntington, WV, U.S.A. or Hereford, U.K.

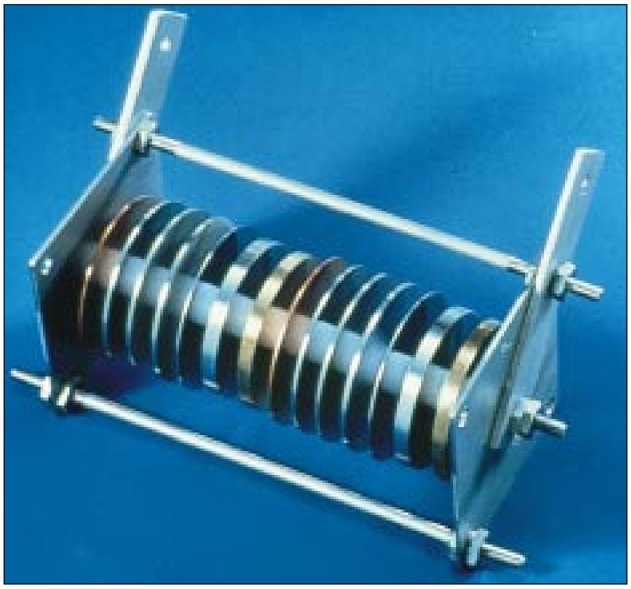


Figure 38 - A typical test coupon assembly for field corrosion testing.

High-Performance Alloys for Resistance to Aqueous Corrosion

Appendix

Corrosion Science and Electrochemistry

Corrosion is most often defined as the electrochemical deterioration of metallic materials by reaction with their environment. Since electrochemistry deals with the interaction of electricity and chemical change, corrosion is the destructive chemical change of a metal or alloy which either causes, or is caused by, the flow of direct electrical current (d.c.). For a current to flow, a complete electrical circuit is required. In a corroding system (Figure 39), this circuit is made up of four components:

1) The anode is the electrode of an electrolytic cell at which oxidation is the principal reaction. Electrons flow away from the anode in the external circuit. It is usually the electrode at which corrosion occurs and metal ions enter solution.
2) The electrolyte is a conductive liquid through which the current is conveyed by positively charged ions (cations) to the cathode. Negatively charged anions are simultaneously attracted to the anode.
3) The cathode is the electrode of an electrolytic cell at which reduction is the principal reaction. Electrons flow toward the cathode in the external circuit.
4) A metallic path is an external circuit to complete the connection between anode and cathode.

In the absence of an externally applied current, a potential difference or voltage must exist between the anode and cathode or no current will flow. This voltage is the driving force of the corrosion reaction.

The potential difference or driving force for corrosion is most evident in the case of bi-metallic junctions (see Galvanic Corrosion). It is somewhat more difficult to see why a single metal should display both anodic and cathodic areas. In practice, such differences are caused by many factors inherent in the metal such as inclusions, exposure of various crystallographic planes, variations in alloy content, or microscopic surface imperfections. Discrete anodes and cathodes can also be caused by variations in the electrolyte, such as temperature differences or concentration gradients of the solution, of ions in the solution, or of dissolved gases such as oxygen. In any event, the anodic reaction converts the metal (M^o) to its positive ion (e.g. M^{++}), releasing electrons through the metallic junction which comprises the external circuit.

As an example of these principles, iron immersed in water (Figure 40) exhibits discrete areas which are anodic to the rest of the metal surface. At these areas iron is oxidized according to the equation:

$$Fe \rightarrow Fe^{+2} + 2e$$

If the water is pure and contains no dissolved oxygen, the cathodic reaction is the reduction of ionic hydrogen (protons or "atomic" hydrogen):

$$2H^+ + 2e \rightarrow H_2$$

To maintain overall electrical neutrality these reactions must proceed in balance. Therefore, two hydrogen ions must be reduced for every iron atom which corrodes. In pure water only one water molecule in approximately 10 million dissociates to produce hydrogen and hydroxide ions so that the supply of hydrogen ions is quite limited. For this reason the cathodic reaction is quite slow and corrosion rates are very low. Cases in which the rate of attack is limited by the speed of the cathodic reaction are cathodically controlled reactions.

If, as is usually the case, dissolved oxygen is present in the water, another cathodic reaction can occur, the reduction of oxygen:

$$\tfrac{1}{2} O_2 + H_2O + 2e \rightarrow 2OH^-$$

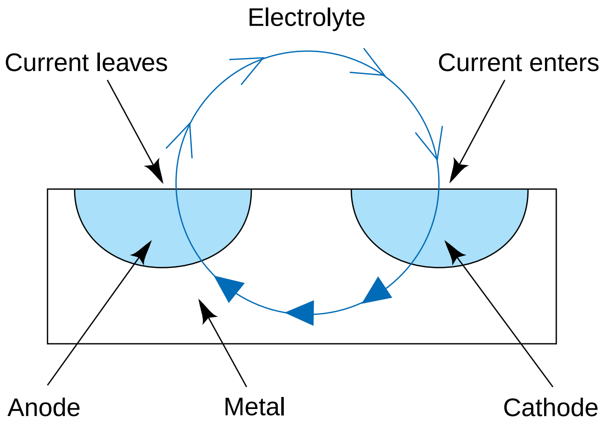


Figure 39 - A corroding system.

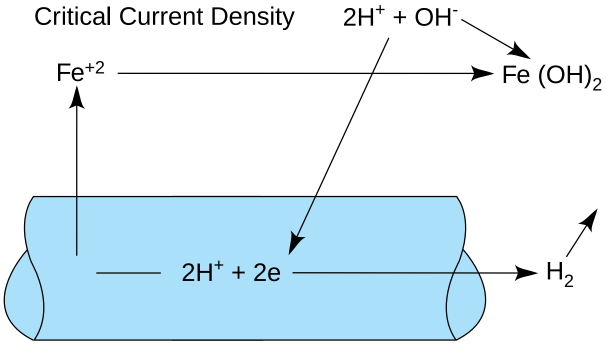


Figure 40 - Corrosion of iron in water.

This reaction will support a more rapid rate of attack since it depends only on the diffusion of oxygen to cathodic areas of the iron. As would be expected, increasing the amount of dissolved oxygen increases the corrosion rate of iron. However, at very high dissolved oxygen concentrations, the corrosion rate drops to a very low value. This surprising drop is the advent of the phenomenon called "passivity", a specific form of "polarization" as described below.

Polarization

In practice, a metal often shows a high initial rate of corrosion. However, in general, the rate often diminishes with time. This effect, known as polarization, might be defined as the change from open-circuit electrode potential as the result of the passage of current. Polarization may result from reactions at either the anode or the cathode.

Anodic polarization – In some corrosion reactions (e.g. iron in aerated water) the corrosion rate diminishes due to an accumulation of insoluble corrosion products which become somewhat protective of the iron anode. This phenomenon, anodic polarization, is defined as the change of the electrode potential in the noble (positive) direction due to current flow. Other examples of anodic polarization are iron or non-alloyed steel exposed to concentrated nitric, sulfuric and phosphoric acids.

Cathodic polarization – Conversely, polarization can result from reactions at the cathode. For example, when iron is immersed in non-aerated neutral water, the absence of dissolved oxygen permits development of an adsorbed film of hydrogen which likewise reduces the corrosion current. This is known as cathodic polarization and is defined as the change in the electrode potential in the active (negative) direction due to current flow.

Specific corrosion inhibitors may work on either the anodic or cathodic sites, their adsorption causing the same decrease of corrosion current. Strong anodic inhibitors (e.g. chromates, nitrites or even an excess of dissolved oxygen in water) result in the type of anodic polarization known as "passivity".

When no current flows between anode and cathode areas, the potential difference between them is at a maximum known as the "open-circuit potential". As soon as current begins to flow, this difference decreases. This decrease in potential is known as polarization. The decrease in anode potential is anodic polarization; in cathode potential, cathodic polarization.

Passivity

Chemists have long ranked materials according to their oxidation potentials or tendencies to be oxidized. Such a ranking, known as the electromotive force series, is a means of measuring chemical reactivity values of metals (Table 37). In this listing, metals such as gold and platinum have large positive values indicating little susceptibility to oxidation. Such corrosion-resisting metals are known as the noble metals and are found in nature in their pure metallic state. A metal which has a large negative value, like zinc, is called an active metal and is readily oxidized.

A metal active in the electromotive force series, or an alloy composed of such metals, is considered passive when its electrochemical behavior becomes that of an appreciably less active or noble metal. In other words, when iron, an active metal, begins corroding at a very low rate, it has become passive and behaves like a noble metal. Not all metals exhibit passivity, but the ones that do are among the most widely used corrosion-resisting materials. Nickel, chromium, titanium, and zirconium spontaneously passivate in air. Alloying iron with chromium above about 10% Cr produces characteristically passive stainless steels. Chromium additions to nickel-based alloys also generally enhance resistance, as described further below.

The usual explanation of passivity is that a thin invisible protective film – either metal oxide, insoluble salt or *chemisorbed* oxygen – forms on the surface of the metal, preventing further contact with the electrolyte. In the case of iron, when more oxygen reaches the metal surface than can be used in the cathodic reaction, a protective passive film is able to form. A temporary passive iron oxide film is also formed when iron is immersed in concentrated nitric acid. More permanent films are formed on aluminum, titanium and stainless steels and chromium-bearing nickel alloys.

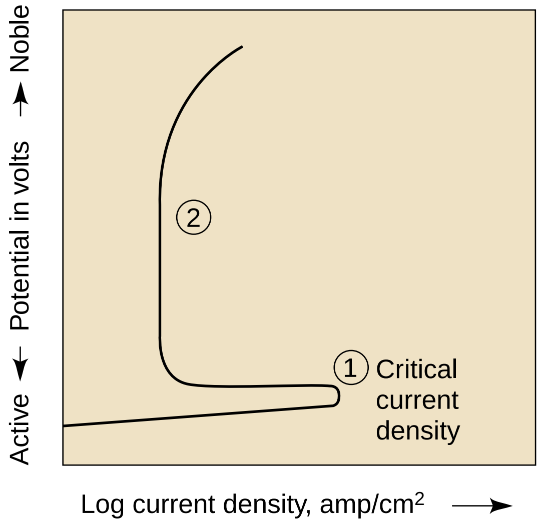


Figure 41 - Polarization curve for a passive metal anode. (1) maximum current and maximum corrosion. (2) passive state. Current at (2) can be hundreds or thousands of times smaller than (1).

If we now examine a polarization diagram for a passive metal anode, we can see that it does not polarize along a straight line as shown in an idealized diagram, but follows an S-shaped curve (Figure 41). The electrochemical behavior of most metals exhibiting active-passive transitions is illustrated by such curves. As the potential of the anode becomes increasingly noble, the current per unit area and the corrosion rate increase until a critical current density is reached. This value corresponds to the maximum corrosion rate. At more noble potentials, the current density falls by orders of magnitude and passivity is established. In the iron-water system, increases in oxygen content allow more current to flow until the critical density is reached. Further increases give rise to passivity.

Table 37 – Standard oxidation reduction potentials at 25°C (77°F). Volts vs normal hydrogen electrode*

Element	Electrode Reaction	Redox Potential
Gold	$Au = Au^{+3} + 3e$	+1.498
Oxygen (acid media)	$O_2 + 4H + 4e = 2H_2O$	+1.229
Platinum	$Pt = Pt^{+2} + 2e$	+1.2
Iron (ferric)	$Fe^{+2} = Fe^{+3} + e$	+0.771
Oxygen (neutral or alkaline media)	$O_2 + 2H_2O + 4e = 4OH$	+0.401
Copper	$Cu = Cu^{+2} + 2e$	+0.337
Hydrogen	$H_2 = 2H^+ + 2e$	0.000
Nickel	$Ni = Ni^{+2} + 2e$	–0.250
Iron (ferrous)	$Fe = Fe^{+2} + 2e$	–0.440
Chromium	$Cr = Cr^{+3} + 3e$	–0.744
Zinc	$Zn = Zn^{+2} + 2e$	–0.763

*Electrode potential values are given and are invariant, e.g. $Zn = Zn^{+2} + 2e$ and $Zn^{+2} + 2e = Zn$ are identical and represent zinc in equilibrium with its ions with a potential of -0.763 volts vs normal hydrogen electrode.

FORMS OF CORROSION

Corrosion can be categorized into several types. Each basic form and various sub-categories are discussed below, generally in relation to their effect on nickel-based alloys. It is noted that these types of corrosion can occur in other materials and may initiate and propagate by significantly different mechanisms.

General Corrosion

If corrosion proceeds uniformly over a metal surface, the attack is classified as general or uniform corrosion. This type of corrosion can often be predicted, permitting corrosion allowances to be used in equipment design, which is obtained from corrosion charts or laboratory tests.

In general corrosion, the anode areas on the metal surface shift to different positions until the entire metal surface has been anodic at some time or another. It is possible that, at a given point, corrosion occurs on a group of readily dissolved atoms until this group is depleted and then the point of attack moves to some other point. In this way the metal suffers a general thinning.

As with all types of corrosion, many factors influence the rate of attack. The corrosive medium is the most important factor governing corrosion. The acidity, temperature, concentration, motion relative to metal surface, degree of oxidizing power and aeration, and presence or absence of inhibitors or accelerators should always be considered. Most of these factors interact and often this interaction is very complex. For instance, in the discussion of the corrosion of iron in water, aeration was seen to play two roles. Oxygen can behave as a *depolarizer* and increase the rate of corrosion by speeding up the cathodic reaction. It also can act as a *passivator* because it promotes the formation of a stable, passive film. As a general rule, increases in temperature increase reaction rates, but increasing temperature also tends to drive dissolved gases out of solution so that a reaction that requires dissolved oxygen can often be slowed down by heating. In a general way, various types of metals and alloys can be classified according to their characteristic corrosion resistance in certain types of media. The environments themselves can be categorized as being of an oxidizing or reducing nature.

Atmospheric conditions are oxidizing in nature to the irons and steels utilized in many common applications. Under immersion conditions, an aqueous environment is usually oxidizing in nature due to the presence of dissolved oxygen unless specifically treated for its removal, and the cathodic reaction is usually reduction of water to form hydroxyl ions. Acidic waters liberate hydrogen gas and can be considered to be reducing in nature, as are most dilute acids.

Conversely, chemical environments in the absence of serious contamination can be loosely categorized as being of a specific type. As shown in Figure 42, oxidizing solutions comprise compounds such as chromic acid, nitric acid, concentrated sulfuric acid, peracetic acid and solutions of oxidizing salts (e.g. ferric or cupric salts, nitrites, chromates). Characteristically, in oxidizing environments, the cathodic reaction is reduction of the anion or of high valence cations, e.g. of ferric to ferrous. Reducing chemicals are those like dilute halogen or other mineral acids and alkalis. In reducing environments, the cathodic reaction is usually reduction of the hydrogen ions, generating atomic hydrogen initially.

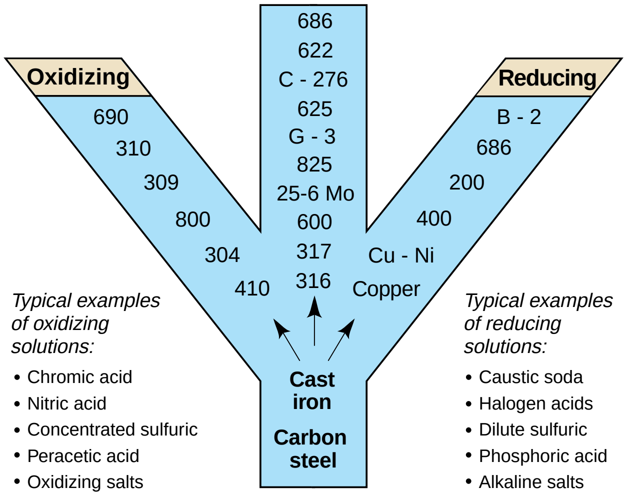


Figure 42 - The Y of corrosion. An alloy selection chart.

As the environments become more corrosive and irons and steels are unsatisfactory, corrosion resistance in oxidizing environments is improved with alloys of a passive nature. Alloys typically used (in order of increasing resistance) are chromium stainless steels, austenitic stainless steels, and nickel-chromium alloys (e.g. INCONEL alloy 690).

In reducing acid environments, materials commonly used (in order of resistance) include austenitic Cr-Ni stainless steels (e.g. AISI 316 and 317), super-austenitic stainless steels (e.g. INCOLOY alloy 25-6MO), and nickel-based alloys (INCOLOY alloy 825, INCONEL alloys G-3 and 625) with the ultimate corrosion resistance being offered by the advanced Ni-Cr-Mo alloys (e.g. INCONEL alloys C-276, 622 and 686) and Ni-Mo alloys.

The ideal materials are those which perform well in both types of environments. Ni-Cr-Mo alloys (INCOLOY alloy 825 and INCONEL alloys 625 and C-276) offer resistance to both oxidizing and reducing conditions. Of this family of alloys, INCONEL alloy 686 offers the greatest resistance to these conditions.

A practical method for determining corrosion rate is by measurement of mass loss per unit area and time. Either mils per year (mpy) or millimeters per annum (mm/a), an expression of thickness of metal removed per unit time or, more specifically, thickness of material lost over a period of time, assuming uniform corrosion, are preferred. 40 mpy equals about one mm/a.

The formula below can be used to calculate corrosion rates in various units using the constants listed.

Corrosion rate = (K x W)/(A x T x D) where
K = a constant (see table below)
T = time of exposure, hours (h), to the nearest 0.01 h
A = area, cm^2, to the nearest 0.01 cm^2
W = mass loss, g, to the nearest 0.001 g, and
D = density, g/cm^3.

Constant K in corrosion rate equation

Corrosion Rate Units Desired	K
mils per year (mpy)	3.45×10^6
inches per year (ipy)	3.45×10^3
inches per month (ipm)	2.87×10^2
millimeters per year (mm/a)	8.76×10^4
micrometers per year (µm/y)	8.76×10^7

A convenient rating for metals subject to uniform corrosion in a chemical media is based on:

1. Excellent – corrosion rate less than 2 mpy (0.05 mm/a). Metals in this category are suitable for making critical parts such as springs or valve seats.
2. Satisfactory – corrosion rate 2-20 mpy (0.05-0.51 mm/a). This rate indicates metals are generally suitable for non-critical parts where a higher rate of attack can be tolerated.
3. Acceptable – corrosion rate 20-50 mpy (0.51-1.3 mm/a). A rate tolerable for massive equipment with a generous corrosion allowance.
4. Usually unsatisfactory – corrosion rate over 50 mpy (1.3 mm/a).

Localized Corrosion

Localized attack is insidious because it precludes the concept of a corrosion allowance. Localized corrosion takes two common forms, open pitting of susceptible metals and alloys and crevice corrosion. Pitting, crevice corrosion, and microbially induced corrosion are all types of localized corrosion.

Pitting – Under certain conditions, anodic areas on a metal surface remain stationary rather than mobile. When this occurs corrosion takes the form of pits rather than general thinning. Although pitting can arise from various causes, certain chemicals – mainly halide salts and particularly chlorides – are well known pit producers.

The passive metals are particularly susceptible to pitting in chloride environments. It seems that the chloride ions accumulate at anodic areas and either penetrate or dissolve the passive film at these points (Figure 43).

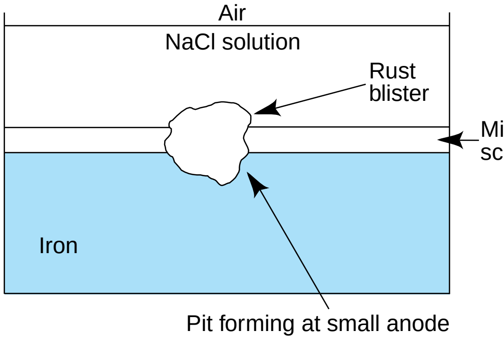


Figure 43 - Pitting at break in mill scale.

Since the chloride corrosion products are acid salts (e.g. ferric chloride), the acidity at the anode increases as more chloride migrates to the anode, and the corrosion rate increases with time. Self-accelerating reactions of this kind are described as autocatalytic reactions (Figure 44). In some cases, a "bottle-shaped" pit is formed, a distinct cavity existing below a much smaller aperture.

The oxidizing chlorides such as ferric, cupric, and mercuric chloride are the most aggressive pitting agents. The metallic cation is reduced at the cathode sites and dissolved air or oxygen is not a prerequisite for corrosion. With the non-oxidizing chlorides (e.g. NaCl), oxygen reduction is the cathodic reaction and pitting is normally slower because the rate of the cathodic reaction is controlled by the diffusion of oxygen to the cathode. Iron-based and nickel-based alloys containing chromium and molybdenum are usually more resistant to pitting corrosion.

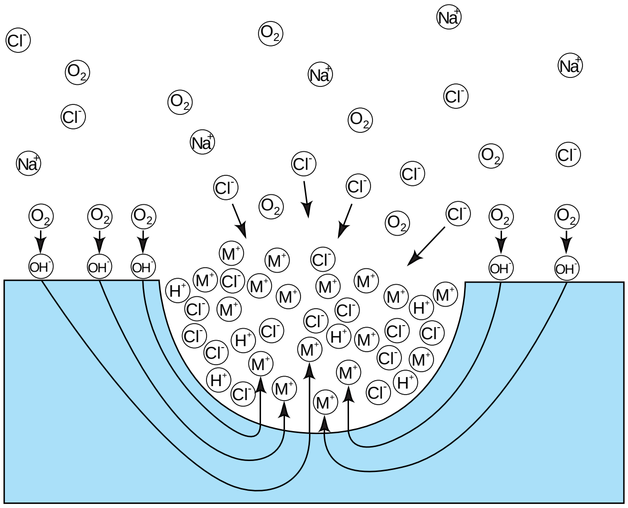


Figure 44 - Autocatalytic process occuring in a corrosion pit.

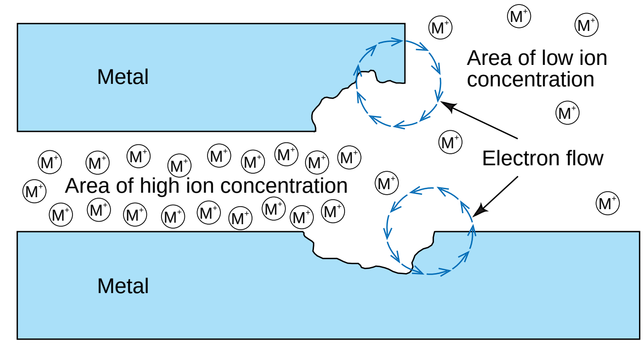


Figure 45 - Corrosion resulting from metal-ion concentration.

Crevice Corrosion – Crevice corrosion is another form of localized attack that as the name implies occurs within the crevices formed by overlapping sections of metal or under tightly adhering non-metallic structures. Like pitting, crevice corrosion of nickel-based alloys is usually promoted by halide salts, particularly chlorides and fluorides. There are two principal mechanisms which drive crevice corrosion, ion concentration cells and oxygen concentration cells. Both mechanisms normally depend upon the presence of chloride ions to propagate the attack.

Within a crevice, some metal may be dissolved and go into solution as metal ions. Outside the crevice, the same process will occur but the relative amounts of solution will result in a lower concentration outside the crevice than within. The metal just outside the crevice will begin to go into solution at a more rapid rate in an attempt to balance this concentration. In other words, the metal outside the crevice will be anodic to the metal within the crevice and this potential difference will support a current. If the solution is in motion, the ions will be carried away as they are produced, preventing equilibrium, and corrosion will continue (Figure 45). This situation constitutes a metal ion concentration cell, the crevice acting as cathode.

This type of corrosion may also occur due to differences in accessibility of dissolved oxygen. In such cases, the corrosion is due to an oxygen concentration cell. One of the most common forms of attack, it is also called crevice corrosion. A crevice acts as a diffusion barrier and corrosion occurs most often within a crevice or just outside.

Within a crevice, the oxygen concentration is usually lower than the oxygen concentration outside it. Since the cathodic reaction uses oxygen, the area outside becomes cathodic to the area within, which then suffers accelerated attack. Corrosion will proceed until the oxygen concentration is equalized or may continue until the metal is destroyed if oxygen continues to be supplied to the area outside the crevice.

Figure 46 shows a typical site for an oxygen cell. The lap crevice, by acting as a circulation barrier, leads to oxygen-cell attack by preventing equalization between inside and outside oxygen concentrations.

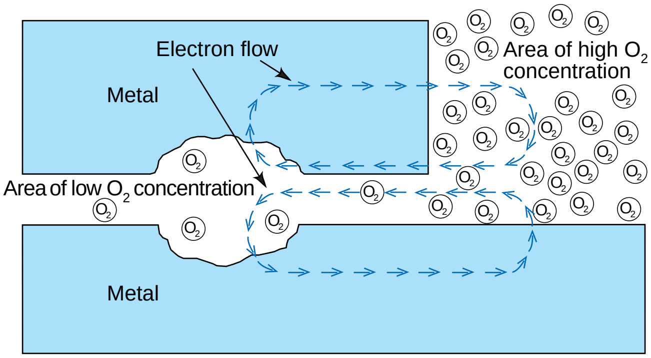


Figure 46 - Corrosion resulting from oxygen concentration.

In practice, both metal-ion and oxygen concentration cells can exist at the same time and in opposition to each other. The final location of the corrosive attack would then be determined by the cell which has the stronger potential. A tight, deep crevice is the most severe condition.

These active/passive cells, which may be considered as oxygen concentration cells of a particularly aggressive form, may develop, under favorable conditions, potentials as high as 500 my or more on materials like stainless steel. Pits result from the action of cells of this type. Similarly, crevices between overlapping metallic surfaces may become the sites of anodic areas with resulting severe corrosion in the crevices. For this reason, cracks or crevices should be avoided in the fabrication of corrosion-resisting equipment.

Oxygen concentration cells may initiate pitting in almost any metal or alloy, under loosely attached, porous materials which shield the underlying metal from free contact with a solution, especially if the main body of the solution is in motion. In such cases, the attack is known as under-deposit corrosion or poultice corrosion. Corrosion under wet insulation is an example of the latter; it can cause severe corrosion of steel or stress corrosion cracking of stainless steels (see further below).

Microbially Induced Corrosion – An interesting form of crevice corrosion is microbially induced corrosion sometimes referred to as microbiologically influenced corrosion (MIC). Bacteria recognized as the agents of MIC live, thrive and multiply at pits, grain boundaries, weld undercuts, and inside the tube walls of pipes, heat-exchanger tubing, and other metallic structures associated with water.

A number of different bacteria are known to induce MIC. However, the types generally fall into two main classifications – anaerobic or reducing type bacteria (sulfate reducing and manganese reducing), and pseudomonas (aerobic) or oxygen consuming. This latter category is probably the most familiar in that it is a recognizable slime.

MIC can occur in a wide range of applications, especially where stagnant water conditions are present, where pipe systems are not properly flushed, where normally moving water stagnates at plant shutdowns, etc. The standard treatment is the injection of biocides into the water, chiefly chlorine derivatives. But the presence of free chlorine and the means of controlling it are all subject to variables which lessen the effectiveness of the treatment. Operating conditions, water temperatures, the climate of the region where the plant is located, available nutrient levels, available oxygen, evaporation, etc.; all can affect a chemical treatment and lead to a loss of biocide capability.

The susceptibility of the AISI 300 series of stainless steels to MIC has been well documented. Results of a laboratory testing program showed that in low total inorganic carbon, low chloride water, a slight increase in chromium, nickel and molybdenum from 316L composition reduces the risk of MIC attack substantially. Further, iron-based alloys, notably the 6% Mo austenitic stainless grades, are more resistant to MIC than 316 stainless steel.

Additionally, in field testing of welded specimens in a fire protection system at a nuclear power plant, 304 and 316L stainless steels showed evidence of MIC after only 5 months of exposure. Attack was in the form of rust deposits on the weld, heat affected zone, and base metal. It was caused by iron oxidizing bacteria. INCOLOY alloy 25-6MO is resistant to the MIC and is used in the service water piping systems of many power plants. More highly alloyed corrosion-resistant nickel-based materials such as INCONEL alloys 622, 625, C-276 and 686 are essentially immune to MIC attack.

The Critical Crevice Temperature (CCT) test described below is a good screening test for selecting alloys for resistance to MIC (Table 38).

Ranking the resistance of alloys to localized corrosion

Resistance to pitting and crevice corrosion can be, to some extent, measured using comparison factors. Critical pitting temperatures (CPT), critical crevice temperatures (CCT), and pitting resistance equivalency numbers (PREN) are all used to rank the relative resistance of alloys to the forms of localized corrosion.

Pitting resistance equivalency number (PREN) – The corrosion resistance of pit-resistant stainless steels (e.g. AISI 316 and 317, and INCOLOY alloy 25-6MO) is largely determined by their composition. The PREN typically used to compare stainless steels is determined by a calculation based on their contents of chromium, molybdenum and nitrogen:

PREN = %Cr + 3.3 (%Mo) + 30 (%N)

As a general rule, the higher the PREN, the better the resistance to pitting. However, alloys having similar values may differ considerably in actual service. Those with values greater than 38 on the PREN scale offer more resistance than the 304 and 316 stainless steels. INCOLOY alloy 25-6MO, with a PREN of 47, offers a cost-effective means of avoiding aggressive chloride attack.

PRENs for nickel-based corrosion-resistant alloys (e.g. INCOLOY alloy 825 and INCONEL alloys G-3, 622, 625, 686 and C-276) are calculated by a somewhat different equation. For such alloys, molybdenum, chromium, tungsten and niobium are the most influential alloying elements.

PREN = %Cr + 1.5 (%Mo + %W + %Nb)

Table 38 – Critical pitting temperature (CPT) and critical crevice temperature (CCT) of nickel-base alloys as determined by ASTM G-48, methods C & D (acidified 10% $FeCl_3$)

Alloy	CPT, ˚F (˚C)	CCT, ˚F (˚C)
INCONEL alloy 686	>185 (>85)	>185 (>85)
INCONEL alloy 622	>185 (>85)	>185 (>85)
INCONEL alloy C-276	>185 (>85)	113 (45)
INCONEL alloy 625	>185 (>85)	95 (35)
INCONEL alloy 725	>185 (>85)	95 (35)
INCOLOY alloy 25-6MO	158 (70)	86 (30)
INCONEL alloy 718	113 (45)	41 (5)
INCOLOY alloy 825	86 (30)	41 (5)
INCOLOY alloy 925	86 (30)	<32 (<0)
AISI 316 stainless steel	68 (20)	<32 (<0)

Addition of the nitrogen factor to this equation as in Table 39 will allow calculation of PRENS for both iron-based and nickel-based alloys.

As with stainless steels, a higher PREN for a corrosion-resistant alloy is generally indicative of superior resistance to corrosion. A ranking of stainless steels and alloys by PREN is presented in Table 39.

Critical Pitting Temperature (CPT) – The CPT for an alloy is determined by conducting a test in accordance with ASTM Standard Test Method G-48, Method C. The test is conducted by exposing samples to acidified 6% ferric chloride solutions and raising the temperature by incremental amounts until the onset of pitting. New, unexposed test specimens and a fresh test solution are used at each test temperature. In accordance with the test method, the CPT may be estimated for both nickel- and iron-based alloys by the equation:

CPT (deg. C) = 2.5 (%Cr) + 7.6 (%Mo) + 31.9 (%N) - 41.0

The CPT required for a particular application will be determined by the service conditions and the requirements of that service. The minimum accepted temperature for North Sea offshore applications is 104˚F (40˚C), while in pulp and paper bleaching environments, this temperature would typically be 122˚F (50˚C). A ranking of alloys can be achieved as shown in Table 38.

Critical Crevice Temperature (CCT) – The CCT for an alloy is determined by conducting a test in accordance with ASTM Standard Test Method G-48, Method D. The test is conducted by exposing samples to the same test solution as used in the Method C test while using a multiple crevice device (TFE-fluorocarbon washer) attached to the surface of the specimen. In accordance with the test method, the CCT may be estimated for nickel-based alloys by the equation:

CCT (deg. C) = 1.5 (%Cr) + 1.9 (%Mo) + 4.9 (%Nb)
+ 8.6 (%W) - 36.2

or for iron-based alloys by the equation:

CCT (deg. C) = 3.2 (%Cr) + 7.6 (%Mo) + 10.5 (%N) - 81.0.

CCT test results are also shown in Table 38 with the temperature recorded indicating the onset of crevice corrosion.

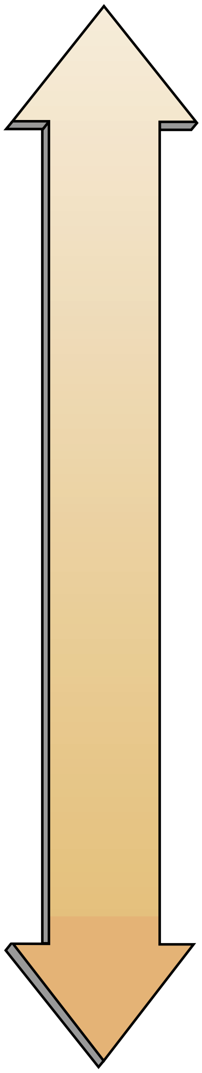
Galvanic Corrosion

When dissimilar metals are in electrical contact in an electrolyte, the less noble metal is attacked to a greater degree than if it were exposed alone. This attack is known as galvanic corrosion because the entire system behaves as a galvanic cell.

Although the electromotive force series (Table 37) gives a ranking of metals according to chemical reactivity, it does not take into account some of the factors which influence corrosion

Table 40 – Galvanic series in seawater

Active (anodic, or least noble)



Magnesium
Magnesium alloys
Zinc
Aluminum alloys
Mild steel
Ni-Resist cast iron
AISI 304 stainless steel (active)
AISI 316 stainless (active)
Manganese bronze
Nickel 200 (active)
INCONEL alloy 600 (active)
Admiralty brass
Aluminum brass
Copper
70-30 copper-nickel
Nickel 200 (passive)
INCONEL alloy 600 (passive)
MONEL alloy 400
AISI 304 stainless steel (passive)
AISI 316 stainless steel (passive)
INCOLOY alloys 825 and 925
INCOLOY alloy 25-6MO
INCONEL alloys 625 and 725
INCONEL alloy C-276 and 622
INCONEL alloy 686
Titanium
Graphite
Gold

Passive (cathodic, or most noble)

Table 39 – Pitting Resistance Equivalency Numbers (PREN) for corrosion-resistant alloys

Alloy	Ni	Cr	Mo	W	Nb	N	PREN
316 Stainless Steel	12	17	2.2	–	–	–	20.4
317 Stainless Steel	13	18	3.8	–	–	–	23.7
INCOLOY alloy 825	42	21.5	3	–	–	–	26.0
INCOLOY alloy 864	34	21	4.3	–	–	–	27.4
INCONEL alloy G-3	44	22	7	–	–	–	32.5
INCOLOY alloy 25-6MO	25	20	6.5	–	–	0.20	35.8
INCONEL alloy 625	62	22	9	–	3.5	–	40.8
INCONEL alloy C-276	58	16	16	3.5	–	–	45.2
INCONEL alloy 622	60	20.5	14	3.5	–	–	46.8
INCONEL alloy 686	58	20.5	16.3	3.5	–	–	50.8

PREN = %CR + 1.5 (%Mo + %W + %Nb) + 30 (%N) reactions. For this reason, another ranking known as "The Galvanic Series" is more often used (Table 40). This series gives an indication of the rate of corrosion between different metals or alloys when they are in contact in an electrolyte, specifically seawater but broadly applicable to waters in general.

The metal close to the active end of the chart will behave as an anode and corrode, and the metal closer to the noble end will act as a cathode and be protected. The distance between two metals in the chart is proportional to the potential difference which can be expected and is usually an indication of corrosion rate. In most cases, metals from one group may be coupled with other metals from the same group without causing severe galvanic corrosion. The reason that the chart is not completely predictive is that polarization effects vary from metal to metal and some couples, e.g. aluminum and stainless steel, corrode less than would be expected. Figure 47 is a graphic example of galvanic corrosion, occurring where the bolt material was more noble than the sheet metal.

Design is a major factor in preventing or minimizing galvanic corrosion. If dissimilar metals must be used, the use of insulation to prevent electrical contact is effective. Where this approach is not possible, the area of the more active material should be large in comparison to the noble material, otherwise, an unfavorably high current density at the anode will cause very rapid corrosion. For example, a copper rivet in a steel sheet suffers little attack, whereas a steel rivet in a copper plate suffers very rapid attack. Coating a steel or cast iron water-box in contact with a copper-bronze tubesheet assembly will cause severe localized corrosion at defects in the coating. Most often galvanic corrosion shows up as furrows or troughs on the corroded metal at its point of contact with the more noble metal.

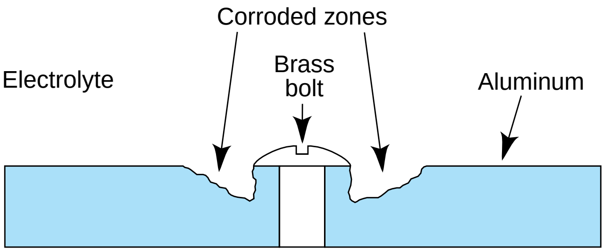


Figure 47 - Galvanic corrosion.

Environmentally Assisted Cracking

Stress-Corrosion Cracking – Stress-corrosion cracking (SCC) requires three simultaneous factors – surface tensile stress, susceptible alloy, and specific environment – the alteration or elimination of any one of them can prevent this attack. Where it is possible, the alteration of the environment or the choice of a different alloy is the best solution. In cases where neither the alloy nor environment can be changed, surface tensile stress must be eliminated.

Elimination of stress is usually attempted through heat treatment, but it is often difficult or impossible to completely eliminate stresses on complex fabricated equipment and the procedure is always costly. When this approach is taken, design of the equipment demands that operating stresses be kept as low as possible, hot spots be avoided, crevices or deposits that may lead to pits that act as stress concentration points be kept in mind, and frequent maintenance inspections be performed. Shot peening to induce compressive stress on the exposed surface has been found effective in some applications, provided the surface corrosion rate is very low.

Table 41 lists some of the common alloy systems and the specific media in which they are subject to this attack. Figures 48 and 49 are examples of transgranular and intergranular stress-corrosion cracking. In chloride environments, increasing nickel content of an alloy is used to prevent SCC. Figure 50 shows that alloys containing more than 45% nickel are highly resistant to chloride SCC. Nickel alloys are also used for their resistance to caustic, polythionic acids, and some deep sour gas well environments.

Liquid Metal Cracking – Liquid metal cracking is caused by penetration of highly stressed grain boundaries by liquid metals such as mercury or by molten metals. Zinc, lead, silver, and other low melting metals can crack susceptible nickel-based alloys. An example of this type of attack is that of highly stressed brass in mercuric salts, where the mercuric ion is reduced to metallic mercury at cathodic sites. Similarly, MONEL alloy 400 that is in a stressed condition may fail by intergranular cracking when exposed in mercury or mercury salts.

Hydrogen Embrittlement – Hydrogen embrittlement or hydrogen stress cracking occurs in hardened steels due to atomic hydrogen entering the metal at cathodic sites. This is often associated with hydrogen sulfide environments, when it is known specifically as sulfide stress cracking.

Table 41 – Environments which can induce stress-corrosion cracking of susceptible material

Alloy	Environment	Cracking
Al-Mg	Chlorides	Intergranular
Brass	Ammonia	Intergranular
Steel	Nitrate, hydroxides	Intergranular
AISI 300 series stainless steels	Chlorides, hydroxides	Transgranular (can be intergranular if sensitized)
MONEL alloy 400	Mercury, mercury salts, chromic acid, aerated hydrofluoric acid vapor, ammonia	Inter-and transgranular
INCONEL alloy 600	Fused caustic	Intergranular
Nickel 200 and 201	Molten metals	Intergranular
Ni-Cr-Mo alloys and MONEL alloy K-500	Sulfide brines	Transgranular (can be intergranular if age-hardened)

Figure 48 - Transgranular cracking in an austenitic stainless steel U-bend specimen exposed for 8 days to boiling 42% $MgCl_2$ vapors. Etchant, glyceregia. (70X)

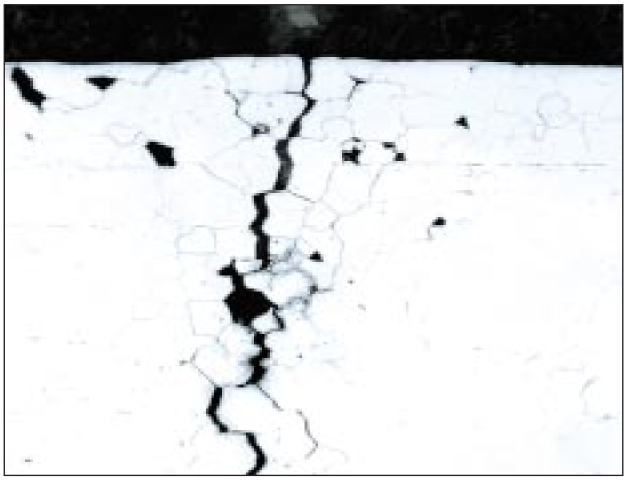


Figure 49 - Intergranular cracking in an austenitic stainless steel exposed to room temperature polythionic acid for 1 hour. (100X)

Corrosion Fatigue – Metals that fail as a result of being subjected to cyclic stress are said to suffer fatigue. Failure is by transgranular cracking and is usually only a single crack. High-temperature fatigue is intergranular since, above the equicohesive temperature, grain boundaries are weaker than the grains. A few metals such as lead and tin have low equicohesive temperatures and fail intergranularly even at room temperature.

Endurance limit and fatigue strength are measures of a metal's ability to withstand cyclic stressing in air. When the metal is cyclicly stressed in corrosive environments, the joint action of corrosion and fatigue greatly intensifies the damage, which is termed corrosion fatigue to distinguish it from the purely mechanical phenomenon. Cracking is again transgranular, but there are usually a number of cracks and they quite often begin at the base of a corrosion pit. Figure 51 shows a comparison between fatigue fracture surfaces of a metal exposed in air versus exposure in a corrosive.

Fatigue data determined in air are useless as a design criterion for a part to be placed in service in a severe corrosive environment. Unfortunately, corrosion fatigue data for environments other than water or sea water are almost totally lacking. Important considerations in selecting a metal for resistance to corrosion fatigue are the resistance of the metal to the corrosive environment and its strength.

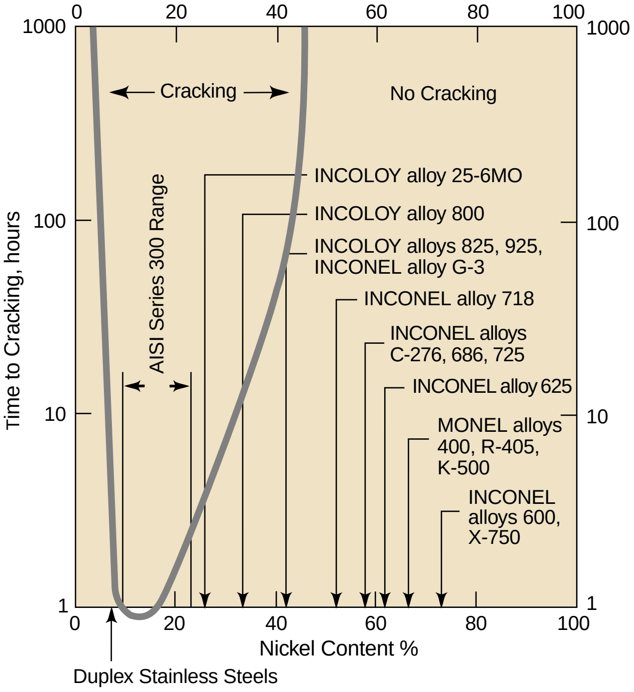


Figure 50 - The classic indicator of susceptibility to chloride-ion stress-corrosion cracking is the boiling 42% magnesium chloride test. The test has shown that alloys containing more than about 45% nickel are immune to chloride stress cracking.

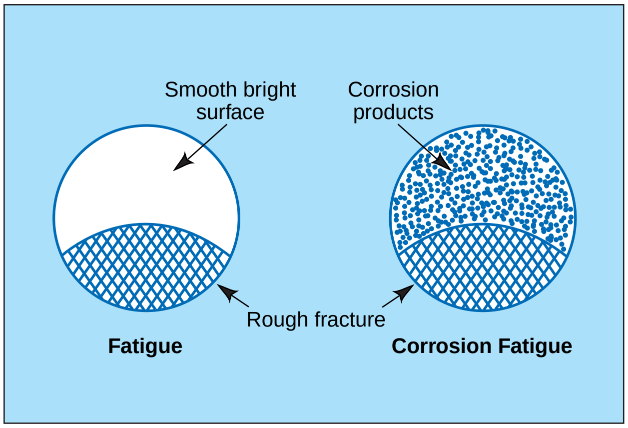


Figure 51 - Schematic illustration of fatigue and corrosion-fatigue failures.

Erosion Corrosion

Abrasion is simply mechanical removal of metal, as by sand or silt, and erosion is flow-induced wear. Cavitation is mechanical damage caused by the implosion of vapor bubbles on a rapidly moving surface such as a pump impeller. These mechanical problems are usually resolved by replacing the failed equipment with a harder, tougher metal.

Erosion-corrosion is an acceleration of corrosion caused by the removal of otherwise protective surface corrosion-product films by the flowing liquid. Typical examples are encountered with flow of concentrated sulfuric acid in steel pipe (whereas steel tanks may be entirely satisfactory) and inlet end attack of copper alloy heat-exchanger tubes in flowing waters. Typically, erosion-corrosion is avoided by the use of nickel-based alloys.

Intergranular Corrosion

Intergranular corrosion (IGC) is a localized attack along the grain boundaries of a metal or alloy. Corrosion can proceed to the point where whole grains of metal fall away and the metal loses its strength and metallic characteristics. Two examples of this type of corrosion are shown in Figures 52 and 53.

Intergranular corrosion is usually caused by an improper heat treatment or heat from welding that causes the precipitation of certain alloy components at the grain boundary. This precipitation causes a depletion of corrosion-resisting elements in the area surrounding the grain boundary, and this area becomes anodic to the remainder of the grain.

The austenitic stainless steels comprise the class of materials in which this form of attack is most common, although many nickel-based alloys may also display IGC. The precipitate is a chromium carbide or other precipitate that appears at the grain boundaries during heating between 800 and 1400˚F (426 and 760˚C). The depleted component is chromium and attack occurs in the chromium depleted areas. This condition is known as sensitization.

There are three methods of combating intergranular corrosion in cases where susceptible alloys may be heated in the sensitizing range. This exposure is inevitable in weldments, with their inherent gradient between the molten weld and the cool parent metal. The first method is to reheat the metal to a temperature high enough to *redissolve* the precipitated phase and then cool quickly enough to maintain this phase in solution (a "solution anneal"). The second method, called stabilization, is to add certain elements such as niobium and titanium in order to make use of their ability to combine more readily than chromium with carbon. In this way chromium is not depleted and the metal retains its corrosion resistance. This method is used with INCOLOY alloys 825 and 020, and INCONEL alloy 625. The third is to restrict the amount of one of the constituents of the precipitate – usually carbon – and thereby reduce the extent of the precipitation and resulting alloy depletion.

Corrosion acceptance tests are designed to determine if a material has been produced for optimum corrosion resistance; i.e., to make sure that corrosion resistance is not lowered during heating of the nickel alloy. If the corrosion rate of material is increased to more than the maximum acceptable rate, the material fails the test. Improper production or heat treatment is indicated. The typical rate (Table 42) is the result of mostly general corrosion and is a function of alloy composition. Corrosion rates beyond the typical rate are the result of accelerated intergranular attack caused by precipitation of secondary grain boundary phases.

Intergranular corrosion acceptance tests are used to confirm proper production of the material being tested. Such tests should not be used to compare materials for service in commercial environments. For example, INCONEL alloy C-276 is more resistant to corrosion than INCOLOY alloy 020 in most commercial applications. However, in the ASTM G-28-A test, the maximum corrosion rate for alloy C-276 is much higher than that for alloy 020.

Dealloying

With some alloys, a specific constituent may be selectively dissolved in certain environments. Sometimes called parting corrosion, the most common form is dezincification of yellow brass (i.e. copper alloys with >15% zinc) in aggressive waters. Attack can be minimized by modifications in alloy composition, as by additions of arsenic, antimony or zinc. Under more severe conditions, copper-nickels, aluminum bronzes and even MONEL alloy 400 can suffer a similar loss of an alloying constituent.

Figure 52 - Intergranular corrosion. (200X)

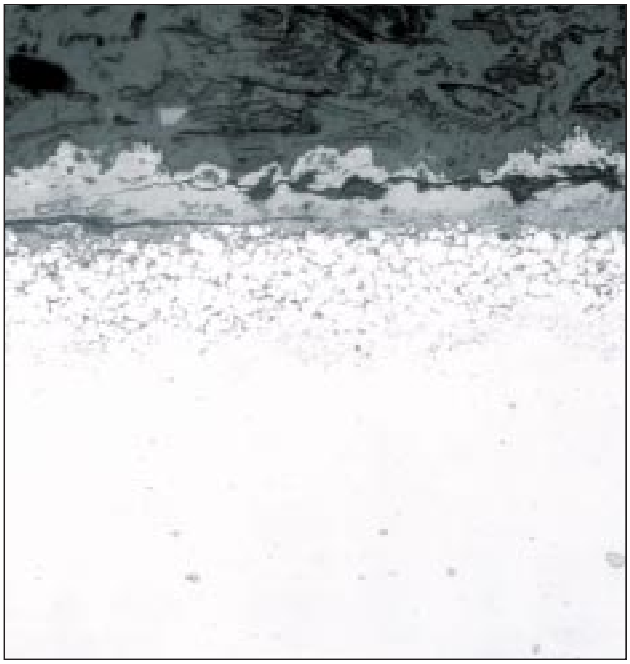


Figure 53 - Intergranular oxidation. (200X)

Table 42 – Acceptance tests and criteria for corrosion-resistant alloys

Alloy	Sensitization heat treatment	Applicable tests	Exposure time, h
INCOLOY alloy 020	1250°F (677°C)/1 h, AC	ASTM G-28-A ferric sulfate (Streicher)	120
INCOLOY alloy 825	1250°F (677°C)/1 h, AC	ASTM A-262-C 65% HNO_3 (Huey)	240
INCONEL alloy 690	None	ASTM A-262-B ferric sulfate (Streicher)	120
		ASTM A-262-C 65% HNO_3 (Huey)	240
INCONEL alloy 600	None	ASTM G-28-A ferric sulfate (Streicher)	24
INCONEL alloy 625	None	ASTM G-28-A ferric sulfate (Streicher)	120
INCONEL alloy 622	None	ASTM G-28-A ferric sulfate (Streicher)	24
	None	ASTM G-28-B ferric chloride cupric chloride (PEMT)	24
INCONEL alloy 686	None	ASTM G-28-A ferric sulfate (Streicher)	24
	None	ASTM G-28-B ferric chloride cupric chloride (PEMT)	24
INCONEL alloy C-276	None	ASTM G-28-A ferric sulfate (Streicher)	24
	None	ASTM G-28-B ferric chloride cupric chloride (PEMT)	24
INCOLOY alloy 25-6MO	None	ASTM G-48-A ferric chloride pitting test	72
		ASTM G-48-B ferric chloride crevice corrosion test	72
		ASTM G-48-C ferric chloride pitting test	72
		ASTM G-48-D ferric chloride crevice corrosion test	72

*mpy = .001 inches per year, mm/a = millimeters per annum

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