

NiDI

**Nickel
Development
Institute**

Nickel stainless steels for marine environments, natural waters and brines

Guidelines for selection

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**Guidelines for
selection of
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Introduction

Data on the performance of nickel stainless steels in marine environments have been summarized in Uhlig's "Corrosion Handbook" (1), by Reinhart and Jenkins in a series of publications on the "Corrosion of Materials in Hydrospace" (2), in Beavers, Koch, and Berry's "Corrosion of Metals in Marine Environments" (3), in LaQue's "Marine Corrosion" (4), and in Sedrik's "Corrosion Resistance of Austenitic Fe-Cr-Ni-Mo Alloys in Marine Environments" (5), as well as Tuthill's and Schillmoller's "Guidelines for the Selection of Marine Materials" (6). Additional data on the performance in marine, fresh and brackish waters and brines are drawn from the extensive published literature on this subject.

It is presupposed that the reader has a working knowledge of stainless steels and the fundamental principles

of corrosion. The "Corrosion Theory Section" of the "Corrosion Handbook"(1) is suggested for those who may wish to review these principles in some depth.

The engineer usually begins with a good idea of the alloys that will meet the stresses and mechanical requirements of the assembly under consideration. It is the purpose here to provide guideline type information that will allow the engineer to take the next step and make a reasonable preliminary estimate of the manner in which the environment is likely to affect the performance of the materials he is considering. The charts and summaries presented provide useful guideposts, but can never serve in place of specific experience, specific data or properly conducted evaluations so necessary to the most successful use of materials.

Water and Water Quality

The major constituents of sea water are given in Table 1. *Salinity* is defined as the total amount of solid material in grams contained in one kilogram of sea water. *Chlorinity* is defined as the total amount of chlorine, bromine and iodine, in grams contained in one kilogram of sea water, assuming the bromine and iodine have been replaced by chlorine.

Fresh and brackish waters are generally analyzed for the constituents shown in Table 2.

Distilled and high purity water used in hospitals, biological laboratories and nuclear power plants has about 1 part per million (ppm) TDS and a resistivity of a 10^6 ohm-cm. Fresh waters range from 50 to 250 ppm TDS. Ground waters range up to several thousand ppm TDS. Brackish waters in sounds, harbors, and large estuaries range from 0.5 to full strength sea water. Brackish waters in tidal rivers fluctuate between fresh during most of the year to 2000-4000 ppm Cl during the dry season. Brines reach several times the strength of sea water and are normally deaerated.

Table 1 The major constituents of sea water*
Chlorinity = 19.00 †/00‡

Ion	Parts per million	Equivalents per million	Parts per million per unit chlorinity
Chloride, Cl ⁻	18,980.0	535.3	998.90
Sulfate, SO ₄ ⁻⁻	2,649.0	55.1	139.40
Bicarbonate, HCO ₃ ⁻	139.7	2.3	7.35
Bromine, Br ⁻	64.6	0.8	3.40
Fluoride, F ⁻	1.3	0.1	0.07
Boric acid, H ₃ BO ₃	26.0	...‡	1.37
Total		593.6	
Sodium, Na ⁺	10,556.1	159.0	555.60
Magnesium, Mg ⁺⁺	1,272.0	104.6	66.95
Calcium, Ca ⁺⁺	400.1	20.0	21.06
Potassium, K ⁺	380.0	9.7	20.00
Strontium, Sr ⁺⁺	13.3	0.3	0.70
Total		593.6	

* H.U. Sverdrup, M.W. Johnson, and R.H. Fleming, *The Oceans*, Prentice-Hall, Inc., New York, 1942. J. Lyman and R.H. Fleming, *J. Marine Research*, 3, 134-146, 1940.

† †/00 is used to denote grams per kilogram or parts per thousand.

‡ Undissociated at usual pH.

Table 2 Constituents of fresh and brackish waters

Calcium (Ca)	as CaCO ₃	ppm
Magnesium (Mg)	as CaCO ₃	ppm
Total hardness (TH)	as CaCO ₃	ppm
Phenolphthalein alkalinity (PA)	as CaCO ₃	ppm
Methyl orange alkalinity (MOA)	as CaCO ₃	ppm
Chlorides	as Cl	ppm
Sulfates	as SO ₄	ppm
Silica	as SiO ₂	ppm
Iron	as Fe	ppm
Dissolved oxygen (DO)	as O	ppm
pH Normally	6-8	
Total dissolved solids (TDS)		ppm

We play and swim in river and sea water as well as swimming pools. It is difficult to think of water as corrosive to metals although carbon steels rust and copper-base alloys corrode slightly in water. Not even sea water with all its dissolved salts is aggressive enough to cause general breakdown of the highly protective chromium oxide film that forms on nickel stainless steels as numerous investigators have observed and as Kain has pointed out in his polarization studies (7).

Although water itself is not corrosive to stainless steel, it is a medium which

favors several corrosion processes that can result in localized corrosion of stainless steels. Attention must be focused on the galvanic, crevice corrosion, fatigue and other processes that the water environment favors, rather than water itself. The principal factors that influence the corrosion behavior of nickel stainless steels in waters are set forth in Table 3.

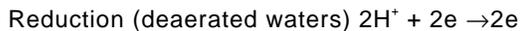
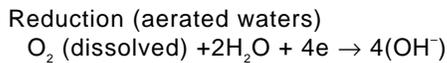
Table 3 Factors that influence the behavior of nickel stainless steels in water in the approximate order of their importance.

- Oxygen (and other oxidizing species)
- Chloride ion concentration
- Conductivity (galvanic effects)
- Crevices
- Sediment
- Scales and deposits
- Biological activity
- Chlorination practice
- Surface condition
- pH < 5
- Temperature

Oxygen and chloride concentration have a considerable influence on the effect of the other factors listed and exert the greatest influence on the behavior of stainless steels in water environments.

Galvanic Corrosion

Galvanic processes occur between different metals and between different areas of the same metal in the water environment. Water is an electrolyte, a poorly conductive one at the low dissolved solids content of fresh waters, and a highly conductive one at the high dissolved solids content of sea water. When two different metals are immersed in an electrolyte and connected through a metallic path, current will flow. Oxidation (corrosion) occurs at the anode, and reduction (normally oxygen reduction) occurs at the cathode. These reactions and the hydrogen reduction reaction that occurs in deaerated waters are represented in the usual form below.



The electrons flow through the metal path from the anode to the cathode. The circuit is completed by transport (migration) of the ionic species (OH^-) from the vicinity of the cathode to the vicinity of the anode. In the absence of other species, the rate at which these reactions occur, and consequently the rate at which the anode corrodes, is controlled by the rate at which oxygen can be reduced at the cathode. The rate of reduction of oxygen at the cathode in turn is determined primarily by the resistance to electron flow in the circuit, the cathodic surface area available for

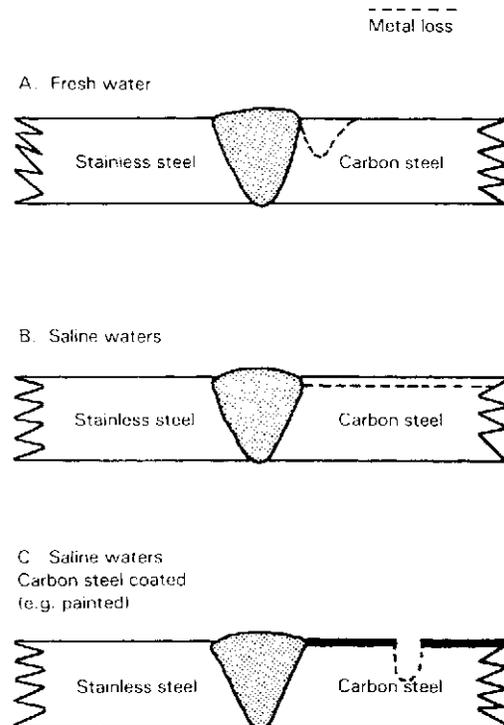
oxygen reduction and the amount of oxygen available at the cathodic area.

The galvanic current (corrosion) is directly proportional to the cathodic area when the cell is under cathodic control as it normally is in water.

$$I \text{ (galvanic current)} = c \text{ (constant)} \times A \text{ (cathodic area)}$$

Conductivity plays a major role by limiting galvanic corrosion to the immediate area of contact in low conductivity fresh water and by spreading the galvanic effect over rather large areas in highly conductive waters such as sea water, Figure 1.

Fig. 1 Pattern of metal loss on carbon steel welded to stainless steel



Painting the anode requires all of the anodic corrosion to occur in the very small areas where coating breakdown at scratches, welds, etc. occurs and exposes the steel. Painting the cathode reduces the area available for the rate-controlling oxygen reduction reaction and the amount of oxidation (corrosion) that can occur at the anode. Stainless steels are positioned towards the cathodic end of the galvanic series in sea water, Figure 2.

In Figure 2 the potential range shown for each alloy should be interpreted as the range within which the metal to sea water potential is likely to vary for each alloy, not as an indication that alloys close to each other in the series are likely to change position. This rarely happens. The second more anodic potential band for stainless steels should be interpreted as the potential that develops in a shielded area where crevice corrosion has initiated.

Lee and Tuthill (8) have developed quantitative guidelines for the amount of carbon steel or Ni-Resist required to suppress crevice corrosion of types 304 and 316 stainless steels in sea water, Table 4.

Table 4 Incidence of crevice corrosion of types 304 and 316 stainless steels (SS) coupled to carbon steel (CS) and Ni-Resist in sea water at 0.5 m/s for 28/30 days.

Area Ratio SS:CS	% of 120 crevice sites initiated		
	CS anode Temperature, °C		Ni-Resist anode Temperature, °C
Type 3041:0 (control)	14	28	28
10:1	6	35	-
50:1	0	0	-
100:1	0	3	6
	0	-	-
Type 3161:0 (control)	26	35	-
10:1	0	0	-
50:1	0	4	0
100:1	0	-	-

These data indicate that carbon steel is very effective in suppressing crevice corrosion of 304 and 316 stainless steel in up to 100:1 SS to CS area ratios at 14°C (57°F) in sea water. At 28°C (82°F) there is complete protection at 10:1 and a tenfold reduction in the percentage of sites where initiation occurs at 50:1 SS:CS area ratios. Ni-Resist (NR) is found to provide full protection for 316 and substantial protection for 304 at 50:1 SS: NR area ratios at temperatures up to 28°C (82°F).

The position of the copper alloys in the galvanic series suggests that copper alloys will not suppress crevice corrosion in stainless steels and, in fact, may accelerate crevice attack once it has started. Experience indicates copper alloys provide no useful galvanic protection for stainless steels.

Type 304 is the least noble of the nickel stainless steels and alloy 825 the most noble, being separated by about 0.05 volt. The various nickel stainless steels are generally coupled mechanically to each other and to nickel-base alloys without serious galvanic effects. There are two major qualifications, however.

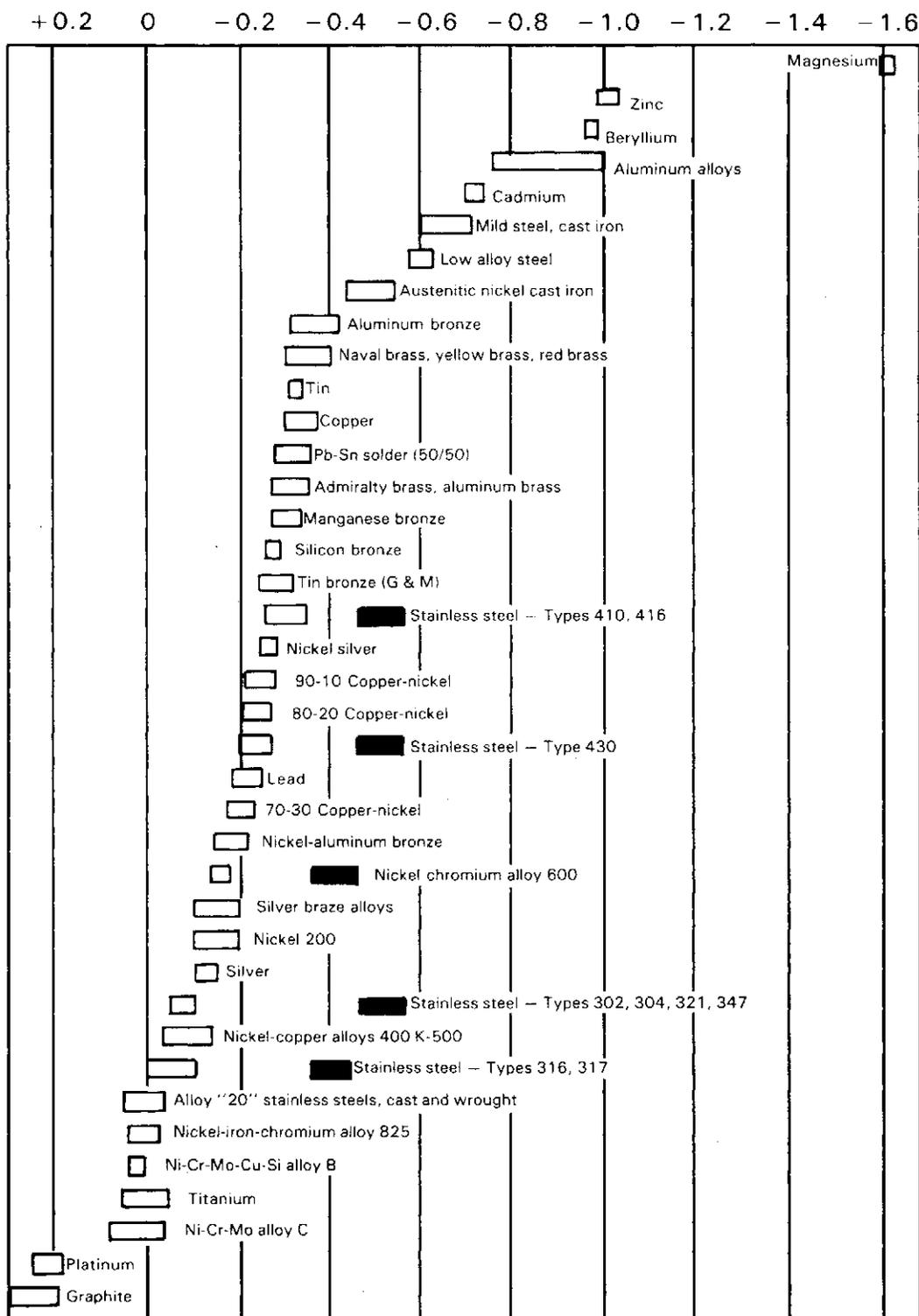
1. Should type 316L inadvertently be welded with type 308L filler metal instead of 316L, the weld metal will suffer severe localized corrosion. Hardfacing overlays for rotating seal faces and weld overlay of tailshafts are other applications where close attention must be given to the position of individual alloys with respect to each other in the galvanic series in order to avoid costly failures.
2. Both type 303 and 303Se suffer extraordinarily severe corrosion in sea water. The high density of manganese sulfide or selenide inclusion in these free-machining alloys create a surface with numerous built-in austenite-to-inclusion galvanic cells.

Carbon is 0.2-0.3 volt or more positive than the nickel stainless steels. Carbon

Fig. 2 Galvanic series

Corrosion potentials in flowing seawater, 8–13 ft/sec;
temp range; 50–80°F

Volts: saturated calomel half-cell reference electrode



Note: Alloys are listed in the order of the potential they exhibit in flowing seawater. Certain alloys indicated by the symbol: in low-velocity or poorly aerated water, and at shielded areas, may become active and exhibit a potential near -0.5 volts.

in the form of graphite-containing gaskets, packing and lubricants has been responsible for serious galvanic corrosion of stainless steels in sea water. Graphite in any form should never be used in contact with stainless steels in brackish or sea water. Carbon filled rubber O rings and gaskets are widely used in contact with stainless steels in sea water. The corrosion that occurs under O rings and black rubber gaskets is normally crevice corrosion. However, in some instances acids used for chemical cleaning have softened these carbon-filled rubbers sufficiently to release carbon and set up adverse galvanic cell action, greatly accelerating the crevice attack that occurs in these rubber-to-stainless crevices.

Galvanic corrosion is a two way street and the effect on the other material coupled to stainless steels must always be considered. Investigating why copper alloy tube sheets were being so severely corroded when copper alloy condensers were retubed with stainless steel and titanium tubes, Gehring, Kuester and Maurer(9) found that the whole inside surface area of the tube of the more noble alloys became effective as a cathode in copper alloy to stainless steel or titanium couples. Table 5 from their paper summarizes these findings.

Table 5 Effective length of condenser tube tending to galvanically corrode copper alloy tube sheets in sea water. (7/8 in. diameter tube)

AL-6X	40 ft
AL-29-4	40 ft
Ti-50A	40 ft
90-10CuNi	2 ft
Aluminum brass	2 ft

The more noble materials are so easily polarized that the cathodic area available for the reduction reaction (the rate controlling process) is multiplied far beyond the old two or four diameters rule of thumb which was based on copper alloy behavior. Later work by Gehring and Kyle (10) indicated that the

intensity of the galvanic effect decreased with salinity. The increasing resistance of the lower salinity waters limits the effective cathodic area.

Galvanic corrosion can occur between different constituents of the same metal as well as between different metals. Iron embedded in the surface of stainless steel, manganese sulfide stringers and less highly alloyed weld metal are common examples.

Table 6 Summary of galvanic corrosion of nickel stainless steels

- Galvanic corrosion occurs between weld metal and base metal, between different areas of the same metal and between different metals in water.
- The intensity of galvanic corrosion is determined by the conductivity, oxygen content and the effective anode-to-cathode area ratio.
- Galvanic effects are spread over a large area in brackish and sea water; are confined to the immediate area of the junction in fresh water; and are often negligible in deaerated brines.
- Steel, Ni-Resist, zinc and aluminum are very effective in suppressing crevice corrosion on stainless steels except types 303 and 303Se.
- Carbon, graphite-lubricated gaskets, packing, greases etc. are very effective in initiating severe corrosion of stainless steels.
- Galvanic effects can be significantly reduced by removing coatings from the anode and by coating the more noble (cathodic) material.
- Stainless steel (or titanium) tubing increases copper alloy tube sheet attack to the point where impressed current cathodic protection is normally required to control tube sheet corrosion.
- Galvanic corrosion between different grades of nickel stainless steels mechanically joined is rare, but can be severe when welded. Caution and exposure tests are suggested.
- Avoid use of types 303 and 303Se.

Crevice Corrosion

Although water itself is not aggressive enough to attack the protective film on nickel stainless steels, it is a medium in which localized breakdown of the chromium oxide film can and does occur in some crevices. Water favors processes that result in crevice corrosion although water itself is not the corroding agent.

Exposure Data

Corrosion data from the work of Reinhart and Jenkins(2) has been selected and shown in Table 7 as it represents carefully controlled and reported corrosion data on most of the older standard grades of stainless steel. Their exposure program also illustrates three major problems that arise in understanding and applying corrosion data on stainless steels in sea water.

1. "Corrosion rates calculated from weight losses are very misleading because they reflect a uniform thinning of the material" which does not occur with stainless steels in sea water. Corrosion rates have accordingly been omitted from Table 7. Corrosion rate data for stainless steels in saline waters are without meaning and should be ignored.
2. The average and maximum depth of attack outside the crevice formed by the nonmetallic insulator occurs under adherent biofouling attachments and with Jenkin's concurrence has been labeled "Under

Deposit Crevice Corrosion". Those familiar with sea water corrosion data know that the localized corrosion reported outside the crevice area occurs under biofouling and is another form of crevice corrosion. Those less familiar with sea water exposure data might suppose the salt water was aggressive enough to break down the protective film on stainless steel since the format in which the data are normally reported is interpreted in that manner for other environments. See Figure 1.

3. The tunneling attack reported on numerous specimens is a form of crevice corrosion which proceeds deep into the substrate more or less parallel to the manganese sulfide stringers in plate, sheet and wire. The point of attack where film breakdown occurred is frequently quite small. The unusually high incidence of tunneling reported is attributed to the shearing operation used in producing the specimens. Shearing leaves a network of tiny crevice-forming tears along the edges of sheared specimens.

Corrosion data from a later carefully controlled exposure program undertaken by Hack (11) have been selected and presented in Tables 8, 9 and 10. Great care was taken to prepare and expose the specimens so that all crevice sites were as uniform and as similar as careful preparation and planning could make them. The edges were machined

Table 7
Corrosion of stainless steels in near surface sea water

Alloy	Exposure, Days	Maximum depth of attack, mils		Tunneling
		Outside crevice under biofouling	In creviced area	
Basic 18 Cr - 8 Ni grades				
301	398	103(PR)	0	1150
301	588	103(PR)	50	1500
302	366	I	I	—
302	398	53(PR)	53(PR)	5400
302	588	52(PR)	52(PR)	5500
304	366	34	33	—
304	540	42	103	123
304	588	0	138	113
304(S)	366	50(PR)	50(PR)	—
304L	366	50(PR)	0	—
304L	398	115(PR)	0	1100
304L	540	115(PR)	115(PR)	1500
321	366	22	0	—
347	366	50(PR)	50(PR)	—
Mo Grades				
316	366	0	0	—
316	398	154	20	1350
316	540	0	63	70
316	588	0	130	1500(P R)
316(S)	366	50(PR)	50(PR)	—
316L	366	0	I	—
316L	398	0	0	—
317	366	0	I	—
Duplex				
329	366	0	I	—
Precipitation Hardening				
633	366	0	I	—
631 TH1050	398	125(PR)	125(PR)	2600
631 RH1100	398	125(PR)	125(PR)	750
Proprietary				
20 Cb	398	14	0	0
20 Cb	540	24	0	0
20 Cb	588	0	21	0
20 Cb-3	366	0	0	—

I - Insipient
PR - Penetrated
S - Sensitized

and ground carefully to minimize end grain attack and tunneling. Specimens were ground to a uniform 120 SiC grit finish. The crevice former was a serrated Delrin washer providing 20 identical crevice sites. Each panel had a Delrin washer on either side. A uniform 75in.-lb torque was used to tighten each assembly. Triplicate exposures were made in filtered sea water to eliminate biofouling and under-deposit crevice corrosion outside the Delrin washer area. Results are shown in Tables 8, 9, and 10.

Despite the precautions taken, Hack's data show that seldom were more than 50% of presumably identical crevice

sites attacked for the less resistant alloys. In many instances there was no attack at any of the 20 sites on one side and attack at only a few of the sites on the other side. The still large scatter, despite the care and precautions taken, indicates that there are factors influencing initiation of crevice attack that are beyond the ability of even the most skilled investigators to fully control. Although the exposure data in Tables 7 through 10 can be used by marine corrosion specialists to give reasonable estimates of relative performance, it is subject to considerable misinterpretation even by corrosion specialists familiar with other environments.

Table 8 Crevice corrosion results for austenitic alloys

Material	Chemical composition wt % (nominal)					No. of sites attacked		No. of sides attacked	Depth of attack, (mm)	Initiation time, (/h)
	Cr	Ni	Mo	Mn	Cu	per side	Total			
T316	17.5	10.7	2.4	1.6	0.3	1-13	33	6	0.29-1.93	24-102
34 LN	16.8	13.8	4.2	1.6	—	12-20	102	6	0.10-1.04*	36-102
T216	20.	6.	2.5	8.	—	7-10	50	6	0.10-0.64	51-77
Rex 734	21.3	9.4	2.7	3.8	—	2-9	39	6	0.01-1.00	51
T317L	18.9	12.2	3.6	1.7	—	7-20	91	6**	0.18-1.92	51-77
317LM	19.5	14.5	4.1	1.3	0.2	19-20	116	6	0.01-1.07	51-77
317L + 22-13-5	18.3	15.8	4.2	1.5	0.2	1-12	44	6***	0.18-1.09	51-479
	21.1	13.7	2.3	4.8	—	16-20	112	6	0.10-1.10	36-77
904L	20.5	24.7	4.7	1.5	1.6	0-13	36	5	0.14-0.74	51-365
4X	20.2	24.4	4.4	1.4	—	0-4	8	4	0.14-0.50	77-245
700	20.7	25.2	4.4	1.6	0.2	0-20	47	5	0.08-2.00	51-171
254 SLX	19.9	25.0	4.7	1.6	1.7	7-15	70	6	0.08-0.92	51-77
777	20.8	25.6	4.5	1.4	2.2	8-12	60	6	0.03-2.90	36-77
254 SMO	20.0	17.9	6.1	0.5	0.8	0-7	18	5	0.02-0.51	51-479
6X	20.4	24.6	6.4	1.4	—	0-3	11	4	0.01-0.62	51-365
20 Mod	21.6	25.5	5.0	0.9	—	0-5	6	2	0.12-0.46	51-365
20 Cb-3	19.4	33.2	2.2	0.4	3.2	0-15	49	5	0.14-3.10	51-171
20 Mo-6	23.9	33.4	5.6	0.4	3.3	0-6	13	3	<0.01-0.53	365-507
254SFER	29.4	22.2	2.1	1.7	0.1	0-3	11	5	0.34-0.90	102-221
825	22.0	44.0	2.7	0.4	1.7	413	37	6**	0.25-2.42	51-221
G	22.2	46.8	5.8	1.5	1.8	0-2	6	4	0.02-0.87	365-673†
G-3	22.8	43.7	7.0	0.8	1.8	0-2	2	1	0.06-0.21	102
625	22.3	61.0	8.5	0.1	—	0	0	0	—	—
C-276	15.5	54.7	15.5	0.5	0.1	0	0	0	—	—

* Specimen perforated.
 ** Gravity-assisted tunneling.
 *** Some attack initiating outside of crevice area.
 † Initiation not observed on some panels where attack occurred.

Table 9 Crevice corrosion results for duplex and ferritic alloys

Material	Chemical composition wt % (nominal)					No. of sites attacked		No. of sites attacked	Depth of attack, mm	Initiation time, h
	Cr	Ni	Mo	Mn	Cu	Per side	Total			
T329	27.0	4.2	1.4	0.3	0.1	9-15	73	6	0.02-1.29*	51-102
44LN	25.0	5.9	1.5	1.8	0.1	14-20	104	6	0.04-3.35	36-51
Ferrallium	26.2	5.6	3.2	0.8	1.8	0-1	2	2	0.03-0.08	365†
T439	17.7	0.3	–	0.3	–	1-17	58	6**	0.42-0.72*	24-77
T444	18.9	0.1	2.0	0.4	–	6-12	54	6	0.33-1.21*	51-245
26-1	25.9	0.1	1.0	–	–	0-5	10	4	0.15-0.46	51-107
26-1S	25.0	0.2	1.0	0.2	–	0-2	6	4	0.06-0.30	171-553
29-4	29.6	0.1	4.0	–	–	0	0	0	–	–
29-4C	28.8	0.8	3.8	0.2	–	0	0	0	–	–
29-4-2	29.5	2.2	4.0	–	–	0	0	0	–	–
SC-1	25.6	2.1	2.9	0.2	–	0-1	1	1	0.05	†
Monit	25.3	4.1	3.8	0.4	0.4	0	0	0	–	–

* Specimen perforated.
** Gravity-assisted tunneling; some attack initiating outside of crevice area.
† Initiation not observed on some panels where attack occurred.

Table 10 Crevice corrosion results for cast alloys

Material	Chemical composition wt % (nominal)					No. of sites attacked		No. of sites attacked	Depth of attack, mm	Initiation time, h
	Cr	Ni	Mo	Mn	Cu	Per Side	Total			
CA6N	12.4	8.0	–	0.2	–	15-20	111	6** ***	0.01-2.00	126-169†
CF8M	19.3	10.0	2.4	1.0	–	4-17	74	6	0.16-3.77	126†
IN-862	20.9	24.5	5.0	0.5	–	1-16	52	6	0.12-1.22	126-217†
CN7MS	19.4	22.1	2.9	1.0	1.6	14-20	102	6***	0.08-3.82	126
CN7M	20.0	28.2	2.5	0.2	3.1	13-18	99	6** ***	0.15-2.33	126†
625	20.6	63.7	8.5	–	–	0	0	0	–	–
CW 12M-2	18.1	62.8	17.6	0.5	0.1	0	0	0	–	–
Illum PD	24.6	5.4	2.0	0.9	–	3-20	73	6	0.08-4.53	48-126†
Ferrallium	25.2	5.2	2.5	1.0	3.2	0-14	37	4***	0.03-2.21	126-169

** Gravity-assisted tunneling.
*** Some attack initiating outside of crevice area.
† Initiation not observed on some panels where attack occurred.

Surface Condition

It is normal to assume in corrosion studies and in service that the surface is representative of the material, but the surface is frequently contaminated and is less resistant than the material itself. Surfaces are easily contaminated and the surface condition frequently has a profound effect on corrosion behavior. Mill scale, slivers and inclusions and any chromium-impooverished layers formed at elevated temperatures during mill processing are normally removed in the pickling operation. Pickling also removes embedded iron and other foreign matter from the surface leaving the surface clean and in a highly corrosion-resistant condition.

Unfortunately very little metal goes into service without further fabrication. Handling during shop fabrication frequently results in iron contamination and embedment in the surface. Welding results in heat tint, weld splatter and entrapment of slag from coated electrodes. Paint markings, grease and dirt add to surface contamination. Cleanup operations such as blasting and grinding, unless carefully controlled further deteriorate the surface. Most of the contamination during fabrication can be, and is, normally controlled, by experienced stainless steel fabricators. Nevertheless, surface contamination is the principal reason for poor performance of stainless steel in water environments.

A different type of surface condition can arise in the higher molybdenum (Mo) content stainless steels. Sedriks (5) has pointed out that sigma and chi phases can form directly from the melt, from transformation of delta ferrite or from the austenite in the high Mo content alloys. If chromium or molybdenum depletion occurs in the matrix sur-

rounding sigma or chi, the corrosion resistance can be reduced. Mill processing is normally controlled to minimize sigma and chi formation, the nitrogen addition being especially useful in this respect. Since these phase transformations are a function of time at elevated temperature, it is well to avoid unusually high heat inputs during welding of the higher Mo alloys.

Process of Crevice Corrosion

It has long been recognized that oxygen is depleted in well shielded crevices creating an oxygen concentration cell between the crevice and the area outside the crevice. It has also been recognized that acidic corrosion products and a low pH develop in some well shielded crevices. Oldfield and Sutton (12) developed a mathematical model of the processes taking place in the shielded area. Their model has greatly expanded our understanding of the mechanism of crevice attack. They identified four stages in crevice corrosion, but it is useful to add two more stages that emphasize special aspects of the process, Table 11.

Table 11 Six stages of crevice corrosion

1. Formation of a crevice by a crevice former
2. Oxygen depletion
3. Hydrolysis of metal ions and decrease in pH
4. Migration of chloride ion into the crevice
5. Initiation of crevice corrosion IF CRITICAL VALUES OF pH AND CHLORIDE ION CONCENTRATION ARE REACHED
6. Propagation

Crevice Formation

Crevices are formed in two ways, by man and by nature, Table 12.

Table 12 Crevice formers

Man made - Design	Man made - Oversight
Stationary O ring	Poor root pass of pipe
Gasket surfaces	weld
Sheared edge	Staggered instead of full length fillet weld
Tube-to-tube sheet joint	Paint
Bolted or riveted joint	Roughened surface
Rubber or plastic sleeve to metallic tube connection	
Natural - Organisms	Natural - Sediment and deposits
Adherent mussels, oysters, barnacles, Asiatic clams and other hard shelled micro and macro biofoulers	Sticky sediments
	Adherent precipitates
	Plastic and trash
Colonies of bacteria	
Sea weed strings	

Many crevices can be eliminated in design. There will remain, however, some crevices that can not reasonably be eliminated in design, such as stationary O ring seals and the gasket surfaces at flanged pipe joints. Crevices arising from oversights can be eliminated by inspection. Natural crevices under biofouling can be controlled by chlorination. Under-sediment and under-deposit crevices can be controlled by cleaning practice.

Oxygen Depletion

The very small amount of corrosion that occurs across the film soon consumes the oxygen within the crevice. The stainless steel remains passive with the oxide film intact. There is, however, no more oxygen for replenishment of defects in the film within the shielded

area and the film is weakened. The difference in oxygen concentration within the shielded area and outside in the bulk solution sets up an oxygen concentration cell which provides much of the driving force for the crevice reactions.

Hydrolysis of Metal Ions and Decrease in pH

The few metal ions entering the moist environment in the crevice hydrolyze, depleting hydroxyl ions. The pH decreases.

Migration of Chloride Ions Into the Shielded Area

Chloride ions from the bulk solution migrate into the crevice to balance the charge resulting from depletion of the hydroxyl ions.

Critical Crevice Solution

If pH decreases sufficiently and chloride ion concentration increases sufficiently to reach critical values, film breakdown and initiation will occur. If pH and chloride ion concentration *do not* reach critical values, there is no initiation. Oldfield and Sutton (13) have determined experimentally the pH and chloride ion concentration at which breakdown will occur under simulated crevice conditions for a number of nickel stainless steels, Table 13.

Table 13 Critical crevice solution

Alloy	pH	Chloride concentration		
		Molar	ppm	x SW*
Type 430	2.9	1	35,000	1.84
Type 304	2.1	2.5	88,750	4.68
Type 316	1.65	4.0	142,000	7.48
4.5% Mo alloy	1.25	4.0	142,000	7.48
6% Mo alloy	< 1.0	6.0	213,000	11.22
Alloy 625	0.0	6.0	213,000	11.22

*SW (sea water)

The chloride ion concentrations necessary for breakdown to occur (with no other species present) are considerably greater than the 18,980 ppm of chlorides found in full strength sea water. Achievement of such low pHs and such high chloride ion concentrations requires very tight, stable and fully shielded crevices. Table 13 provides a reasonably quantitative guide to the relative resistance of these alloys to crevice corrosion in saline waters in a format that is easier to apply and subject to less variation than the exposure data in Tables 7 through 10.

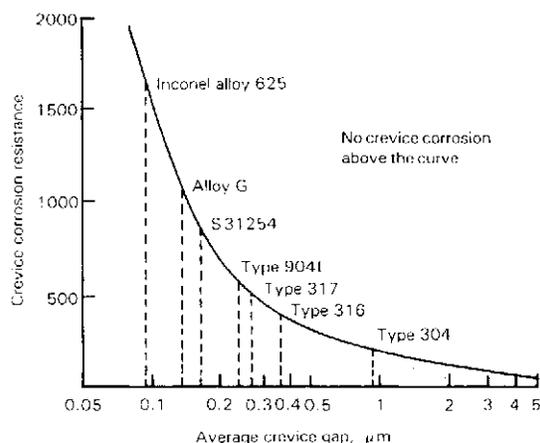
Propagation

If the critical crevice solution is reached, initiation occurs and propagation can proceed. The small shielded area is anodic to the large unshielded area outside the crevice. The galvanic effect favors deep penetration once initiation has occurred in normal saline waters. In deaerated waters, in the absence of other reducible species, hydrogen reduction becomes the rate controlling reaction. In such deaerated waters, propagation proceeds so slowly that crevice attack is seldom of practical significance.

Gap Dimension

Oldfield, Lee and Kain (14) have shown that the gap dimension of the crevice has a major influence on the development of a critical crevice solution within the crevice and initiation/no initiation in any given crevice. Oldfield and Sutton (13) have used the mathematical model of crevice corrosion to estimate the effect of 0.1 micrometre (μm) changes in the gap dimension on initiation for a number of stainless steels, Figure 3. The scale on the vertical axis is based on the experimentally determined critical crevice solution, Table 13. Smaller gaps are required to initiate crevice attack as alloy content increases.

Fig. 3 Effect of crevice gap on initiation of crevice corrosion in ambient temperature seawater



The 1 μm gap required to initiate crevice attack on type 304 is of the same order as a wringing fit. It is little wonder that investigators have had such difficulty in controlling uniformity of the gap dimension sufficiently to achieve consistent and reproducible crevice corrosion data. Oldfield's best estimate, after prolonged study and experimentation, is that the tightest gaps likely to be encountered in practice lie between 0.2 and 0.5 μm . Gaps of < 0.2 μm are almost impossible to achieve and are unlikely to be encountered in service.

Reinhart and Jenkin's (2) data for 316/316L in Table 7 show no crevice attack on 3 specimens, crevice attack on three and under-deposit attack on one. Hack's (11) data in Table 8 show attack at only 33 of 120 presumably identical sites on 316. The mathematical model indicates a gap of 0.4 μm is required before crevice attack will occur on 316/316L in sea water. It seems that gaps tight enough to result in initiation of crevice attack on 316/316L in sea water are likely to occur in some, but seldom all, of even the most carefully prepared "identical" crevices.

The very large tonnages of 316 used in marine service, of the order of 30,000 tons/year, suggests that the incidence of crevice attack is likely to be within the range of tolerable maintenance for many items of fabricated equipment,

especially when some galvanic protection is provided by less resistant materials in the same assembly. At the same time the incidence of crevice attack is far too high for useful service as condenser and heat exchanger tubing and piping except for emergency or temporary service (15).

Bulk Environment

Low pH in the water outside the shielded area will increase the incidence and severity of crevice attack on stainless steel, Table 14 (16).

Table 14 Effect of pH on crevice attack, max.% of crevice area corroded/ maximum depth in mm

pH	1000 ppm Chlorides		10,000 ppm Chlorides	
	304	316	304	316
6	20/0.02	0/0	30/0.04	10/0.01
3	40/0.08	15/0.10	35/0.28	50/0.08

Flint (17) also reports severe crevice attack on both 304 and 316 at pH 1.5 in acid mine and other low pH waters.

Deaeration

Depletion of oxygen in the waters out-

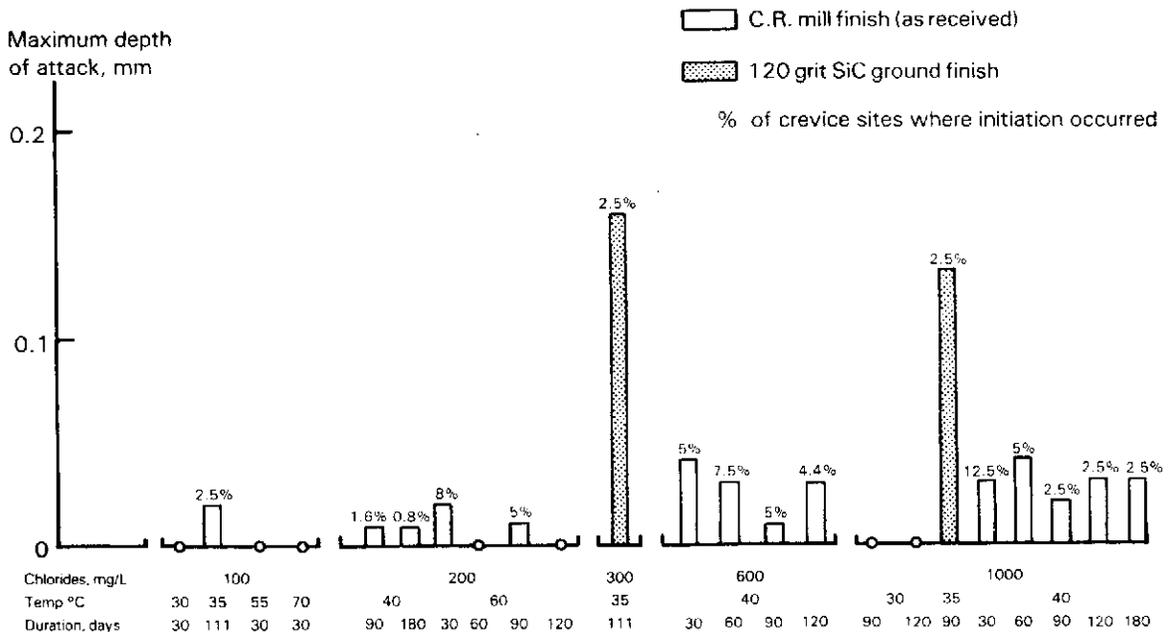
side the crevice has such a profound effect on propagation that in practice crevice corrosion is not a problem in either natural or artificially deaerated waters. Type 316 has given almost trouble-free service in deaerated desalination brines, in deaerated ground waters in reverse osmosis (RO) plant piping and in the cast form as high pressure oil field waterflood type pumps. The cast duplex alloys have also given excellent service up to 11 years in pumps handling deaerated sea water for oil field injection. Sulfate-reducing bacteria in deep wells have caused corrosion of stainless steels in deaerated waters, but in their absence type 316/CF8M has suffered little, if any, corrosion in deaerated waters up to temperatures as high as 180°F - 220°F.

Chlorides

Flint (16) reported, "Type 304 is satisfactory for long term storage and transportation of cold and hot waters with less than 200 ppm chlorides and is marginally satisfactory up to 1000 ppm. Type 316 would be preferred for critical applications above 200 ppm."

Figure 4 shows laboratory data on the

Fig. 4 Crevice corrosion of Type 304 in natural waters (14)



resistance of type 304 to simulated Colorado River water with 100 to 1000 ppm chlorides (14), Type 316 resisted attack in the same exposures. These data suggest that type 304 is useful in waters with > 200 ppm up to 1000 ppm chlorides where crevice attack in 5-10% of the tightest crevices can be tolerated and handled as routine maintenance. Type 316 would be preferred for more critical applications.

Figure 5 shows data on the resistance of types 304 and 316 in full strength and diluted sea water (17). These data indicate that alloys more resistant than 316 are likely to be required for critical applications such as condenser tubing when > 1000 ppm chlorides are present. A guide for selection of the standard grades of stainless steels for service in waters of different chloride ion concentrations based on the mathematical model of crevice corrosion was developed by Oldfield and Todd (18). Their guide has been used as a basis for Figure 6. The scale on the vertical axis is based on the critical crevice solution, Table 13, as in Figure 3.

Exposure data from Figure 4 and from Flint's report indicate that crevice attack on type 304 is rare below 200 ppm chlorides. This compares quite well with the 300 ppm limit for normal service and the 200 ppm limit for critical service developed from mathematical modeling, Figure 6. Since fresh waters seldom have more than 100 ppm chlorides these data agree well with the widespread successful use of type 304 in fresh waters in the United States, Europe and Japan.

The mathematical model suggests a 3000 ppm limit for type 316 for normal service and a 2000 ppm limit for critical service. Data from Figures 4 and 5 would suggest a somewhat lower limit for critical service for 316. The mathematical model suggests a limit of 5000 ppm for 904L for critical service. Reported experience with this alloy indicates good performance in saline waters with some crevice attack with

Fig. 5 Crevice corrosion diluted seawater Types 304 and 316 (15)
(120 grit SiC ground finish)

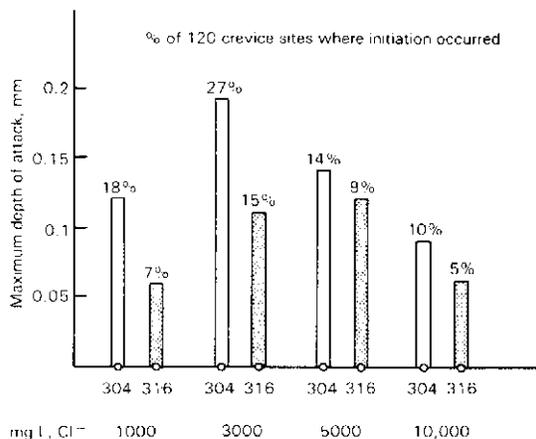
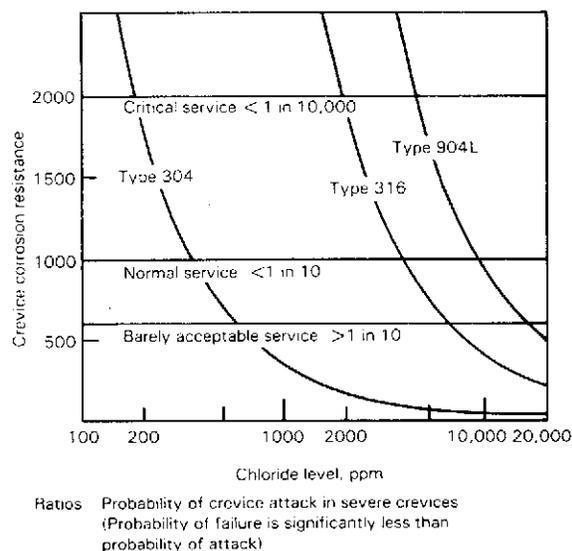


Fig. 6 Guide for selection of stainless steels for water



chlorides (See p. 34) < 4000 ppm. As for type 316, the model-suggested limit for critical service appears to be higher than actual experience would suggest for this alloy. On the other hand, the model-suggested limits for normal service for these alloys appear quite conservative compared to the wide usage of type 316 and significant usage of 904L at higher chloride concentrations with failure rates that users find quite tolerable for normal service.

Considering the wide scatter in crevice corrosion data the agreement between the model-suggested limits and actual experience is quite good. The model-suggested limits provide a good starting point that can be modified as the severity of the service requires.

Caution: This guide is based on the chloride ion concentration in the bulk environment. Both bacteria and evaporation are able to concentrate chlorides from very dilute solutions to damaging concentrations.

Temperature

Increasing temperature which normally increases corrosion processes also decreases the solubility of oxygen. Propagation rates for crevice corrosion, which are largely controlled by oxygen reduction on the cathodic area outside the crevice, do not increase as expected with temperature and actually decrease as temperatures approach the boiling point where virtually all of the oxygen is driven off.

Under Deposit Corrosion – Biofouling

Both micro-and macro-biofouling organisms attach themselves to stainless steels in brackish and saline waters. The area beneath attached organisms is an ideal crevice; very tight, stable and well shielded. Crevice corrosion develops in the manner previously described.

Chlorination Practice

Chlorine is widely used to control microfouling in condensers and heat exchangers. Residual chlorine concentrations of about 0.2 ppm at the outfall, when maintained continuously, will control microfouling. There is varying success with intermittent injection of

chlorine.

Up to 2 ppm of chlorine does not appear to be detrimental to stainless steel in saline or fresh waters. Most swimming pools have 1-2 ppm residual chlorine which does not initiate corrosion on the stainless steel ladders and other swimming pool hardware.

Overchlorination, however, can be serious and has caused corrosion of stainless steels in fresh as well as saline waters and must be guarded against. The amount of chlorine that stainless steels will tolerate has not been fully established, but experience suggests that chlorine injection practices that result in > 2 ppm should be evaluated carefully for their effect on the resistance of stainless steels in fresh and saline waters. Ashbaugh (19) reports failure of type 321 potable water tanks where sodium hypochlorite sterilizing solution was incompletely drained from the tanks and left for hours in this condition. In the Middle East extensive failures of stainless steel have been experienced in a water distribution system when sodium hypochlorite was added to the water used for hydrotesting and was not flushed and drained from the system.

Under Deposit Corrosion – Sediment and Precipitates

Sediment and precipitates sometimes shield portions of the surface from oxygen. If the sediment remains undisturbed and consolidates or if the precipitates are sticky, they can form tight stable crevices where crevice attack can occur in saline waters. Loose sediments that do not completely exclude oxygen from the surface and many precipitated films are benign. Thorough cleaning to bright metal on a regular schedule is the best practice.

Precipitates are less of a problem than sediments unless they are sticky and adhere tightly to the surface. Scheduled cleaning is the best remedial measure.

Effect of Velocity

High velocities prevent sediment build-up, reduce biofouling attachment, bacteria colony formation and generally help in keeping the surface clean. The chromium oxide film is tough, adherent and unaffected by the high velocities and turbulence associated with pump impellers, ship propellers and hydrofoils.

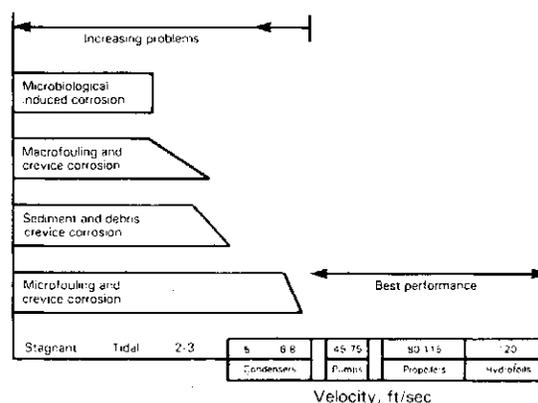
At low velocities and under stagnant condition, micro- and macro-foulers and sediment form crevices where crevice attack can occur. Stagnant conditions and sediments favor microbiological induced corrosion (MIC). Figure 7 illustrates the effect of velocity on the corrosion resistance of stainless steels.

Stagnant conditions and sediments are ideal for MIC and are the most difficult for all grades of stainless steels.

Macrofouling is responsible for most of the corrosion that occurs on the surface of stainless steels in saline waters. Crevice attack occurs in the area where the macrofoulers have attached to the surface. Above 2-3 fps, the free swimming larvae of the macrofoulers have increasing difficulty in attaching to the surface except during down time. Once attached during a down period, a return to operating velocities does not dislodge them, but does bring more nutrients to them enhancing growth. Continuous chlorination is effective in controlling biofoulers. Many hard shelled biofoulers are able to retreat into their shells at the first sign of a biocide and remain until the biocide has dispersed, making intermittent chlorination considerably less effective or ineffective.

Microfoulers are found attached to the inside of stainless steel and titanium condenser tubing operating in the normal 6-8 fps range. They seem able to attach and grow at somewhat higher velocities than the macrofoulers. These microfoulers form a multitude of tiny crevice sites which are primarily responsible for the corrosion failures of type 304 and 316 tubing in coastal condensers and of

Fig. 7 Effect of velocity on corrosion of stainless steels



duplex stainless steel tubing used in ships.

Much of the sediment entrained in cooling waters deposits out in the bottom of condenser and heat exchanger tubing at velocities below about 3fps and during shutdowns. Since there is a range of velocities in individual tubes above and below the nominal design velocity, the minimum practical design velocity for heat exchangers and condensers is at least 5 fps and preferably 6 fps. Any unit designed or operated at lower velocities is a prime candidate for under sediment crevice attack, MIC or both.

Above 8 fps to at least 120 fps nickel stainless steels are fully resistant to corrosion in sea water as would be expected, since the water itself does not corrode nickel stainless steels. Above 120 fps there is increasing likelihood of cavitation, however velocities > 120 fps are rarely encountered.

Nickel stainless steels are among the materials most resistant to cavitation when conditions are such that cavitation can occur, Table 15 (6).

Stagnant Waters

Numerous failures of stainless steels have been reported in both fresh and saline waters left standing in type 304 and 316 tubing, piping and storage

Table 15 Order of resistance to cavitation damage in sea water

(At normal cavitation erosion intensities where inherent corrosion resistance influences resistance to cavitation)

Resistance to cavitation damage rating	Metals
Group I —Most resistant. Little or no damage. Useful under supercavitating conditions.	Cobalt base hard facing alloy Titanium alloys Austenitic (series 300) and precipitation-hardened stainless steels Nickel-chromium alloys such as alloy 625 and alloy 718 Nickel-molybdenum-chromium alloy C
Group II —These metals are commonly utilized where a high order of resistance to cavitation damage is required but are subject to some metal loss under the most severe conditions of cavitation.	Nickel-copper-aluminum alloy K-500 Nickel-copper alloy 400 Nickel-aluminum bronze Nickel-aluminum-manganese bronze
Group III —These metals have some degree of cavitation resistance but are generally limited to low speed, low performance type applications.	70/30 copper-nickel alloy Manganese bronze G Bronze and M Bronze Austenitic nickel cast irons
Group IV —These metals are normally not used in applications where cavitation damage may occur unless heavily protected.	Carbon and low alloy steels Cast irons Aluminum and aluminum alloys

tanks in periods as short as 30 days. Failures of types 304, 316 and more highly alloyed stainless steel heat exchanger tubing also are reported when cooling water (fresh, brackish or salt water) is used on the shell side instead of the inside of the tubing as is the normal and much preferred practice. Few of these failures are well documented. Overchlorination and under-sediment crevice attack account for a number of these failures. In the last several years it has been increasingly recognized that bacteria are responsible for much of the corrosion that occurs in stagnant waters.

Microbiological Induced Corrosion

Microbiological induced corrosion (MIC) refers to the acceleration of crevice and other forms of corrosion by

micro-organisms. Bacteria are found in all natural waters. Some thrive on organic nutrients found in most waters. Others can survive quite well on hydrogen and CO₂ alone in the absence of organic matter. Under favorable conditions, bacteria colonize and multiply quite rapidly, creating slime layers that form on metals and other surfaces, Table 16.

Table 16 Conditions favoring MIC

- Natural waters
- Stagnant conditions
- Long duration of stagnant conditions
- Organic nutrients in water
- Sediment
- Absence or neglect of chlorination practice
- Chlorides and sulfates

It has been recognized that anaerobic sulfate reducing bacteria (SRB) such as

desulfovibrio desulfuricans can be responsible for corrosion that occurs in the absence of oxygen. Table 17 shows these and other strains that have been identified with metallic corrosion by Pope and coworkers (20).

Table 17 Bacteria and corrosion

Bacteria	Corrosive effect
Slime formers	Create sites where MIC can occur
SRB	Facilitate corrosion in absence of oxygen
Thiobacillus thiooxidans	Produces H_2SO_4
Nitrosomonas	Oxidizes NH_3 to NO_2
Nitrobacter	Oxidizes NO_2 to NO_3
Many species	Produces organic acids (formic, succinic)
Gallionella, Sphaerotilus	Oxidize ferrous (chloride) to ferric
Mn-oxidizing strains	Oxidize manganous (chloride) to manganic

Of these bacterial strains, SRB's and the iron and manganese types are the most troublesome for stainless steel. Colonies develop at preferred locations in stagnant waters or under sediments in slowly moving waters. The colonies create crevices excluding oxygen from the surface. The iron and manganese oxidizers have the ability to concentrate chlorides and to convert ferrous and manganous chlorides to ferric and manganic chloride. Both are strong oxidizers and well known pitting agents for stainless steels. The protective oxide film, already weakened by exclusion of oxygen, breaks down and deep pitting follows.

The mechanisms for SRB-induced corrosion are different. In the presence of SRB's the metallic corrosion product is normally a metal sulfide. It is thought that some SRB's use hydrogen, depolarizing the cathodic surface and

accelerating attack at the crevice site. SRB-induced corrosion is characterized by an encrusted deposit over a deep pit with a black powdery sulfide corrosion product beneath. SRB's occur in stagnant sea water and frequently in the deaerated waters from ground wells. SRB's are also found in the anaerobic lower section of biofilms that form under aerobic conditions. Attack by manganese oxidizers is also characterized by encrusted deposits. It has been reported on type 304 tubing in very low chloride content fresh water cooling systems and in clean waters used for hydrotesting. Figure 8 shows the type of corrosion caused by sulfate-reducing bacteria on a pump shaft coupling from a fresh water well in Louisiana.

Figure 9 shows pitting type corrosion of a horizontal weld seam in a type 316L tank that occurred when a clean low chloride water used for hydrotesting was left standing in the tank for 30 days instead of being drained as intended.

Pitting type failures of stainless steel piping systems, heat exchanger and condenser tubing and desalination plant chamber floors caused by water left in or incompletely drained from such systems is reported with depressing regularity. Stagnant water is ideal for MIC and for under-sediment crevice attack or both and should be avoided.

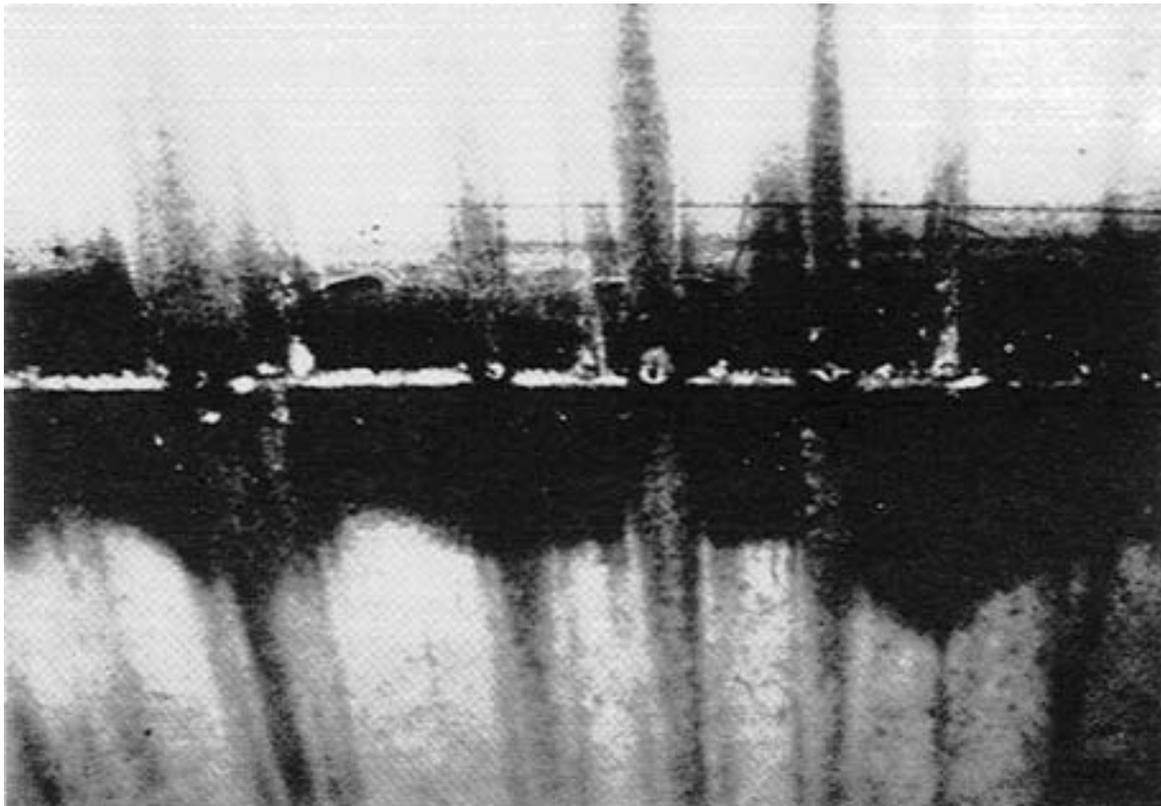
Remedial measures include:

1. Design flow rates of at least 5 fps.
2. Schedule cleanings to remove sediment.
3. Chlorinate or add biocides to hydrotest and cooling water (Do not overchlorinate)
4. Drain waters used for hydrotesting promptly and completely.
5. Drain cooling water systems for extended shutdown or standby. Blow drying of tubing and piping is best.
6. Maintain good housekeeping, general cleanliness.
7. Avoid stagnant conditions

Fig. 8 Sulfate-reducing bacteria attack on a type 410 stainless steel deep well pump coupling.



Fig. 9 Pitting in horizontal weld seam of type 316 tank - MIC (Kobrin)



Corrosion Fatigue

The endurance limit for annealed type 304 in air is of the order of 35,000 psi and for type 316 about 40,000 psi. The endurance limit increases with cold work. For type 304 cold drawn to 210,000 psi the endurance limit is of the order of 100,000 psi.

In sea water there is no true endurance limit as fatigue strength continues to decrease as the number of cycles increases. Lacking a true endurance limit, corrosion fatigue strength (CFS) has been defined as the maximum stress at which failure will not occur in 10^8 cycles in sea water. Corrosion fatigue strength is usually measured in a rotating beam test in the arrangement shown in Figure 10. The rate of cycling is normally adjusted to reach 10^8 cycles in 50-60 days. Shorter test times, that many investigators use to develop more data in less time, do not give adequate weight to the corrosion factor.

Table 18 shows the 48 day corrosion fatigue strengths at 10^8 cycles in sea water for a range of materials (21). For 304 the corrosion fatigue strength is 15 ksi as compared to 35 ksi in air. Why there should be such a drastic reduction in an environment that does not appreciably corrode the surface is not known but the reduction is real.

Figure 11, a plot of corrosion fatigue strength against tensile strength, indicates that CFS increases with strength for different stainless type alloys (21).

Despite the low corrosion fatigue strength, CF3 (the cast counterpart to type 304, previously designated CF4 to

reflect an earlier 0.04% carbon content) workboat propellers have been successfully used on workboats since 1952. CF3 is now an industry standard for 6-15

Fig. 10 Corrosion fatigue test arrangement

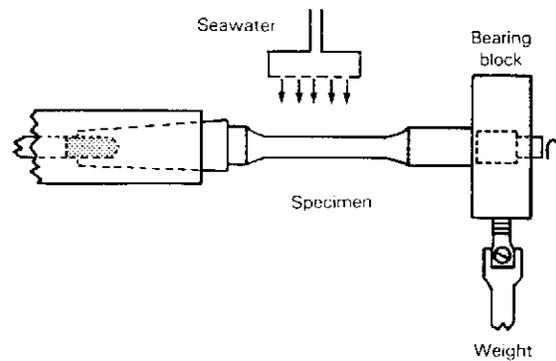
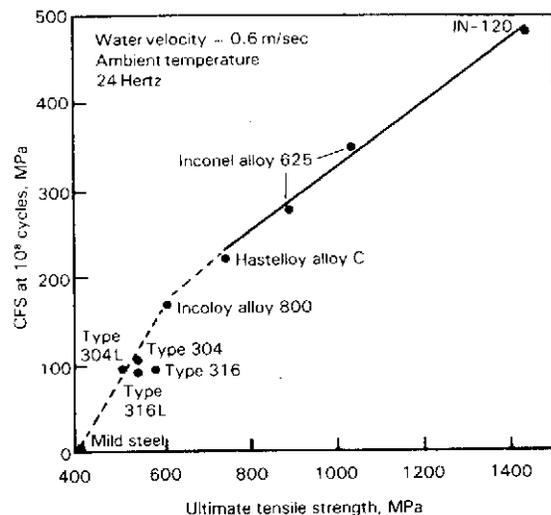


Fig. 11 Variation of corrosion fatigue strength with ultimate tensile strength of rotating bend specimens of various alloys in seawater



foot diameter propellers for workboats, controllable pitch propellers and bow thrusters. The steel hull and its cathodic protection system suppress crevice corrosion at anchor. Underway, with the

propeller in motion, stainless steel is resistant to sea water corrosion. The CFS of CF4 can be increased to 20,000 psi by cathodically protecting CF4 to -0.85 V (5).

Table 18 Corrosion fatigue strength in sea water

Forty-eight day corrosion fatigue strength (CFS) at 10^8 cycles of various materials in sea water					
Material	Chemical composition, weight % (nominal)	Ultimate tensile strength		CFS at 100 megacycles in sea water	
		Ksi	Kgf/mm ²	Ksi	Kgf/mm ²
IN-120 (Experimental alloy)	Ni-21Cr-14Co-4Mo-2.5Ti-2(Cb + Ta)	205	144	70	49.2
INCONEL* alloy 718 (Grain size = 0.01 mm)	Ni-19Cr-17Fe-5Cb-3Mo-0.8Ti-0.6Al	189	133	60	42.2
INCONEL alloy 625	Ni-21Cr-9Mo-3.6(Ta + Cb)-2.5Fe	149	105	50	35.1
INCONEL alloy 718 (Grain size = 0.068 mm)	Ni-19Cr-17Fe-5Cb-3Mo-0.8Ti-0.6Al	189	133	40	28.2
INCONEL alloy 625	Ni-21Cr-9Mo-3.6(Ta + Cb)-2.5Fe	129	91	40	28.2
INCONEL alloy 718 (Grain size = 0.152 mm)	Ni-19Cr-17Fe-5Cb-3Mo-0.8Ti-0.6Al	–	–	32	22.5
HASTELLOY** alloy C	Ni-16Cr-16Mo-5Fe-4W	108	76	32	22.5
MONEL* alloy K-500	Ni-29Cu-3Al-1Fe-0.7Mn-0.6Ti	176	124	26	18.3
INCOLOY* alloy 800	Fe-32Ni-21Cr-0.4Ti-0.4Al	89	63	24	16.9
18%Ni maraging steel (0.25mm mild steel coating)	Fe-18Ni-7Co-5Mo-0.4Ti	250	176	23	16.2
18%Ni maraging steel (cathodic prot. at -0.85V)	Fe-18Ni-7Co-5Mo-0.4Ti	250	176	15	10.6
Ni-Al Bronze, CA 955HT (Cast)	Cu-11Al-4Ni-4Fe	115	81	15	10.6
AISI Type 304 stainless steel	Fe-19Cr-10Ni-2Mn-0.08C	79	56	15	10.6
AISI Type 316 stainless steel	Fe-18Cr-12Ni-2Mn-2.5Mo-0.08C	85	60	14	9.8
AISI Type 304L stainless steel	Fe-19Cr-10Ni-2Mn-0.03C	75	53	14	9.8
AISI Type 316L stainless steel	Fe-18Cr-12Ni-2Mn-2.5Mo-0.03C	79	56	13	9.1
Ni-Al Bronze (Cast) CA 955	Cu-10Al-5Ni-5Fe-1.5Mn	87	61	12.5	8.8
Mn-Ni-Al Bronze (Cast) CA 957	Cu-12Mn-8Al-3Fe-2Ni	100	70	9	6.3
Mn Bronze (Cast) CA 865	Cu-40Zn-2Mn	73	51	8	5.5
18% Ni maraging steel (Unprotected)	Fe-18Ni-7Co-5Mo-0.4Ti	250	176	5	3.5
Mild steel	–	60	42	2	1.4
* Trademark of the INCO family of companies					
** Trademark of Cabot Corp.					

Stress Corrosion Cracking

Stress corrosion rarely occurs in natural waters, even sea water, at temperatures up to boiling, except in certain of the small vertical condensers used in the chemical industry where the cooling water is on the shell side. Remedial measures include venting the non-condensable gases through the top tube sheet in order to prevent evaporation and chloride salt build-up on the outside of the tubes in the vapor space or upgrading to higher nickel alloys such as Carpenter 20Cb3, Incoloy 825, and the newer 4.5 and 6% Mo austenitic and duplex alloys. Using lower chloride waters, for example fresh instead of saline water, is ineffective as waters as low as 12 ppm chlorides have stress

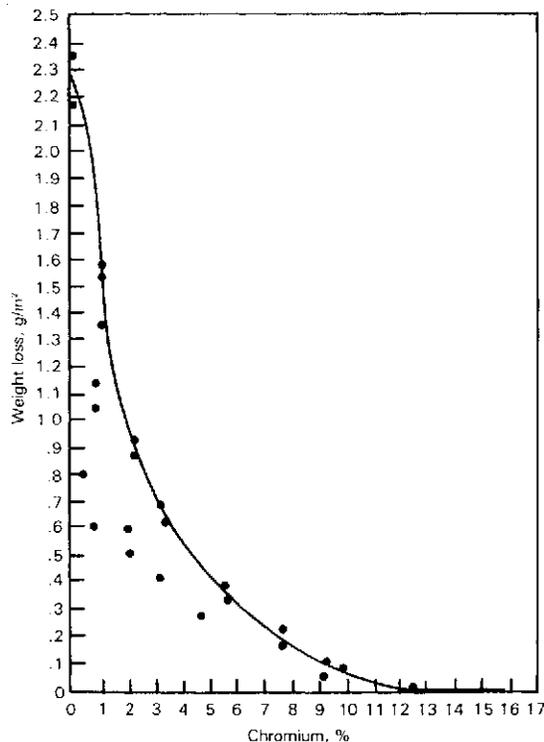
cracked type 304. Even such low chloride ion concentrations can be concentrated by evaporation.

Stress corrosion cracking (SCC) has not, as originally feared, been a problem for nickel stainless steel tubing or chamber wall linings in desalination plants up to about 220°F. Oxygen seldom exceeds 25 ppb. U-bend specimens are resistant to SCC in boiling sea water although there are reports of SCC of U-bend specimens exposed in the vapor space above boiling sea water (5). SCC has not been a problem in type 316 demisters in desalination plants where the demisters are stripping droplets from boiling sea water.

Nickel Stainless Steels in Marine Atmospheres

Nickel stainless steels are so resistant to corrosion in marine atmospheres that weight loss and corrosion rate are not very useful in determining relative resistance. Faulring's (22) plot of weight loss versus chromium content, Figure 12, shows weight loss decreases as chromium increases, approaching zero at 12% Cr and is virtually zero at 18% Cr (type 430).

Fig. 12 Weight loss versus chromium content for samples exposed 25.1 years



Baker and Lee (23) report that after 26 years exposure in the 25- and 250-meter test lots at Kure Beach, NC pitting was insignificant, less than 0.01 mm on the boldly exposed surface of all of the stainless steels shown in Figures 13 and 14, except type 410 where pit depths up to 0.06 mm were found. Although pits were shallow, they were numerous. The pit density per ASTM B 537, the percentage of the area stained, and the percentage of the area rusted are displayed in bar charts. Staining is discoloration. Rusting is defined as build-up of corrosion product visible at $7\times$ magnification with a measurable thickness of at least 0.05 mm.

Distance from the ocean is a major variable. The environment in the 25 meter lot is an order of magnitude more severe than in the 250 meter lot. These data indicate some advantage for type 316 over 304, but it is not as great as actual experience on offshore oil platforms and coastal structures would suggest. The nickel stainless steel grades are found to be significantly more resistant than the ferritic grades. Distinguishing relative performance for the nickel-containing grades is shown to be difficult because of the inherently high resistance of stainless steels to marine atmospheric corrosion.

Surface cleanliness is paramount to minimize staining. Electropolishing minimizes the staining on all grades.

Grinding, even wet grinding with clean belts and discs, markedly increases the staining over the whole surface on both 304 and 316.

Of somewhat greater concern is the resistance of stainless steels to SCC in the heat of midsummer sun. Careful measurements by Money and Kirk (24) indicate that stainless steel panels reach 50°C at Kure Beach, NC in the midday sun. They found the standard 300 series nickel stainless steels resistant to SCC in the annealed, ¼ hard and as-welded condition except for type 301 as-welded, which cracked. Furnace-sensitized 201, 301, 302, 304, 309 and 316 suffered SCC. Furnace sensitization results in a substantially greater degree of carbide precipitation than welding of the regular 0.08% carbon grades. Type 304L, 0.03% carbon max., did not crack in the furnace-sensitized

condition. There have been reports of SCC of 304 and 316 valve bolting during summer in some Gulf Coast plants.

Insulated stainless steel piping and pressure vessels have suffered SCC under the insulation in marine and other atmospheric exposures even when low chloride insulation has been used. Wetting of the insulation by rain, or indoors, by drips and leaks, allows the chlorides to concentrate by evaporation. Pitting and SCC follow, preferring those areas where the insulation has stuck to the surface after being wet at some point. Just as in the case of the vertical condensers, even very low atmospheric chloride concentrations some distance inland can be concentrated by evaporation sufficiently to cause SCC. Painting the stainless steel and minimizing wetting are the primary countermeasures that have proven successful.

Fig. 13 Relative performance of stainless steels exposed 25 meters from ocean for 26 years

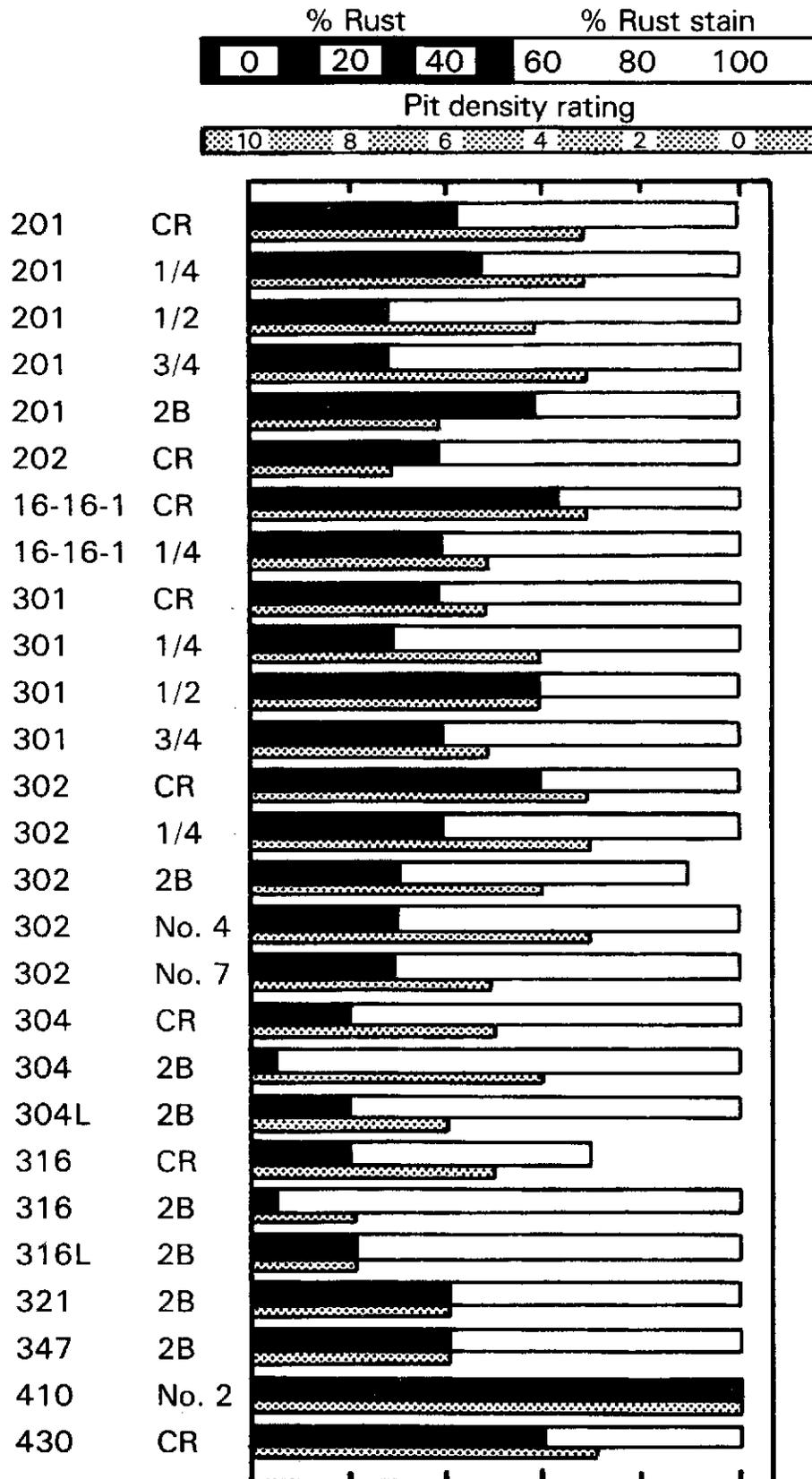
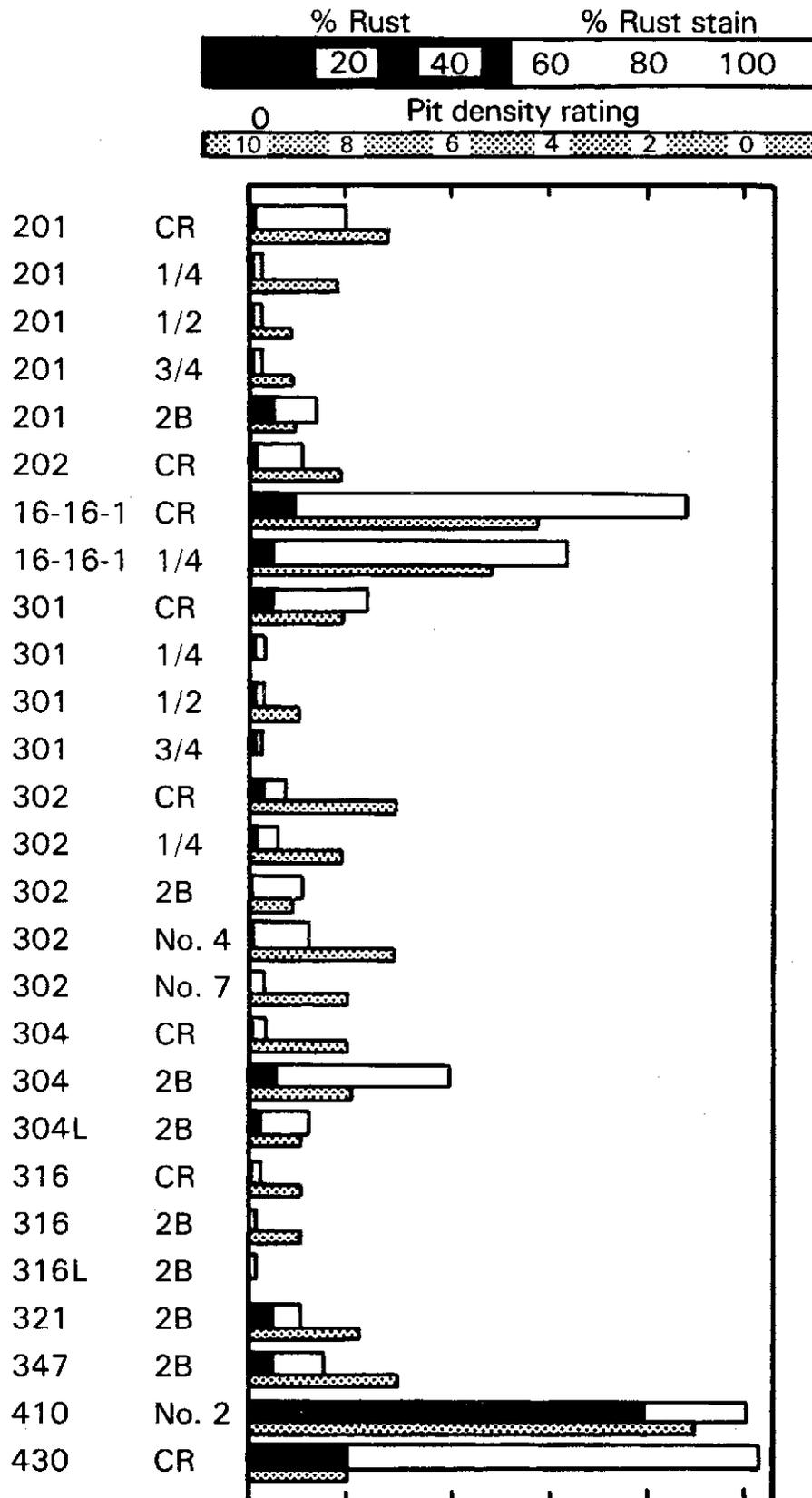


Fig. 14 Relative performance of stainless steels exposed 250 meters from ocean for 26 years



Appendix

Summary of Usage and Performance of Nickel Stainless Steels in Saline and Natural Waters and Brines

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Foreword

Actual user experience with stainless steels in natural waters and brines as reported in interviews with the responsible corrosion personnel in some 80 industrial plants in the U.S., Europe and the Mideast is summarized by alloy group and product form. By far the largest tonnage is in types 316/316L. Tubing is the product form in which most of the more highly alloyed materials are used and can best be compared.

Interviews were conducted with coastal, estuarine and riverside power and chemical plants, refineries, offshore oil and geothermal steam plants. Information from earlier surveys of stainless steels in desalination plants and marine service are also included.

It was found that nearly all coastal chemical plants, and many refineries, avoid the use of saline cooling water in contact with stainless steel equipment. The most common practice is to bring the saline cooling water to a central copper alloy heat exchanger, and provide closed loop cooling water systems to service stainless steel process units. Other plants use local ground waters, or recirculated cooling tower systems, to avoid the use of saline waters in stainless steel equipment.

A considerable number of power plants, sulfuric acid plants, desalination plants, geothermal steam plants, offshore oil, a few refineries and a miscellany of small chemical plants, do use saline waters in stainless steel tubed condensers and coolers. The Navy, where the CRES (corrosion resistant

steel) call out on the bill of materials is still common, and the marine industry are large tonnage users of the standard, and, to lesser extent, the newer more highly alloyed grades of stainless steel.

Users interviewed generally had some relevant experience with types 316/316L/CF3M/CF8M and one or two of the more highly alloyed grades. In most instances, they were also able to furnish some information on the important influence of other factors, such as tube sheet material, cathodic protection, biofouling and chlorination practice on alloy performance. The influence of these factors has been included to the extent available.

It became evident in the survey that the more highly alloyed stainless steels are just coming into widespread use, and primarily in those particular applications where type 316/316L's performance falls short of the users' demands. The rather recent entry of many of the more highly alloyed materials into saline water service does reduce the historical data base for these materials as compared to the older standard grades, but this is only natural, and is duly noted in the summaries.

The information on usage is presented for each alloy or alloy group separately as indicated in the preceding index.

A summary table of nickel stainless steel usage in chloride-bearing waters based on the information developed in the survey of user experience is also presented. The principal alloys and nor-

mal usage are shown in the "Preferred" column for several chloride-bearing waters. Other alloys, for the most part more highly alloyed materials, for which successful use was reported are shown in the second column under "Used Successfully". Omission of an alloy from this column does not mean the alloy might not be used successfully, just that there were no reports of such usage developed in the survey. The third column reports alloys reported to have suffered substantial under-deposit corrosion or other forms of crevice corrosion in these waters.

Summary of Experience - Austenitic Alloys

Types 303/304/304L/CF3
UNS S30300/S30400/S30403/J92500

Condenser tubing:
1 condenser, type 304, 600-700 ppm chlorides. 22 years OK, < 1% plugged.

Condenser tubing:
8 condensers, type 304, up to 160 ppm chlorides. Up to 19 years, good condition. Tube failures reported when manganese was high and chlorination in use. Sediment and incomplete drainage during standby periods also have led to corrosion failures. One retubing.

Propeller, workboat:
CF3, coastal waters and harbors. Up to 33 years OK with welded repairs to nicked blades and restraightening as required. The steel hull and its cathodic protection system protect the propeller during idle periods. Occasional blade breakage is reported. Replacement tips are cast and welded on.

Propellers, controllable pitch:
CF3. Up to 15 years OK.

Bow thrusters:
CF3. Up to 20 years OK.

Wire rope:
Type 304. 0.5-2 years submerged or spooled on winches. Sailboat stays, 1-5 years or more. Push pull cables for pleasure craft.

Pump impellers:
CF3. > 20 years with internal galvanic protection.

Cast and wrought deck fittings, stanchions, and other deck hardware:
Types 304/304L/CF3. > 10 years.

Deck and coastal plant handrails:
Type 304. > 10 years.

Instrument cabinets and control panels, weather deck:
Types 304/304L. > 10 years with some staining and crevice corrosion. Types 316/316L. > 10 years with less staining and crevice corrosion.

Fasteners:
Type 303, < 6 months. Type 304, good service in steel or aluminum. It is reported to be more difficult to galvanically protect 304 fasteners galvanically than 316.

Guidelines

While types 303/304/304L/CF3 are not generally thought of as marine materials, the cast CF3 alloy has earned its place as the standard propeller material for workboats, controllable pitch propellers, and bow thrusters. Type 304 wire rope is the standard material used for marine wire rope, despite its rather short service life, because it has a higher strength-to-weight ratio than can be achieved with more highly alloyed materials. Left wet and spooled on winches, 304 wire rope will be destroyed by crevice corrosion in less than 6 months.

Fasteners of type 304 give reasonably good service when used to fasten steel or aluminum. Type 303, the free machining modification, has its own built-in crevices from the stringers that contribute to its improved machinability. Type 303 fasteners fail by severe crevice corrosion in 6 months or less, even with steel or aluminum in the assembly.

Types 316/316L/CF8M/CF3M
UNS S31600/S31603/J92900/J92800

Condenser tubing:

20 condensers, type 316, 0.5-0.8 × strength sea water. 17 retubed after premature and sudden failures. 3 still in operation after 20 years, opened and cleaned weekly; flushed, drained and blown dry for standby.

Heat exchangers and cooling coils:

Sea water. About 5 years. Saline water left standing in idle units has resulted in several disastrous failures in only a few weeks.

Condenser tubing:

4 condensers, type 316, 2000-3000 ppm chlorides. Up to 10 years OK. These condensers use continuous rubber ball cleaning. No evidence of corrosion.

Vertical condensers:

Type 316, down to 14 ppm chlorides. SCC occurs beneath the top tube sheet unless the noncondensables are completely vented through the top tube sheet. (Cooling water is on the shell side.)

Tube sheets:

Type 316, 0.5-0.8 × strength sea water. Up to 20 years with organic coatings and/or cathodic protection to arrest under-deposit and under-gasket crevice corrosion.

Waterbox:

Type 316L welded, 0.5-0.8 ×

strength sea water. Up to 16 years OK with strict quality control of welding. Massive undermining type corrosion reported at weld defects.

Piping:

Type 316L welded, 0.5-0.8 × strength sea water. Up to 18 years OK as large diameter power plant condenser inlet piping. 15 years OK as 1½ - 6 in. diameter distribution piping, sloped so as to drain free on shut down, and properly welded.

Numerous failures reported when horizontal runs are not sloped so as to drain completely. Pinhole corrosion in root bead defects also reported.

Type 316L welded, desalination brines. Severe corrosion at defects in root bead in hot brine. Deep pitting in horizontal runs.

Type 316L welded, reverse osmosis deaerated brines. Satisfactory service reported.

Type 316L welded, reverse osmosis sea water. Multiple failures reported.

Instrument tubing:

Type 316/316L, marine atmosphere. Indefinite service in coastal plants, on weather deck of ships, and offshore platforms. Occasional problems reported when protective encasement retains sea water in contact with the outside.

Cooling water system strainers:

Type 316/316L, brackish and sea water. No significant corrosion reported.

Submarine masts, electrical connectors and hull-mounted equipment:

Type 316/316L/CF3M, sea water. Good service reported. The steel hull and its cathodic protection system afford considerable protection to most stainless steel components.

Oceanographic instrument housings:

Type 316L, sea water. Indefinite service reported.

Fasteners:

Type 316, marine service. Standard construction. Good service above and below waterline with steel and aluminum. Subject to substantial crevice corrosion below waterline in wood and nonmetallic hulls. SCC reported as valve body bolting in Gulf Coast plant during hot summer months.

Pump shafting:

Type 316, saline waters. Standard construction. Good service to more than 30 years in vertical turbine intake pumps with Ni-Resist case. Good service in centrifugal pumps fitted with steel inlet or outlet waster spools. Subject to significant crevice corrosion in all stainless steel pumps during out of service periods in the absence of galvanic protection.

Pump impellers:

CF3M/CF8M, saline waters. Standard construction. Good service over past 30 years when galvanically protected by case.

Valve stems and trim:

Type 316, saline waters. Widely used. No service data developed in survey.

Instrument components:

Types 316/316L/CF8M, sea water. Standard construction for a large variety of shipboard and oceanographic instruments handling, or immersed in, sea water. Generally satisfactory service, although crevice corrosion is sometimes a problem in initial usage until adjustments are made to prevent or compensate for it.

Desalination flash chamber linings:

Type 316L welded, desalination brines. Up to 20 years at temperatures up to 190°F as partial and complete chamber wall lining. Pin hole pitting in linings and welds has occurred in the floors of several type 316L lined chambers where sea

water or brine was left standing during shutdown periods. No evidence of SCC reported.

Guidelines

Types 316/316L/CF3M/CF8M are the workhorse alloys for marine and marine-related services. Ready availability world wide and general familiarity lead to their usage in all waters where types 304/304L/CF3 have experienced substantial corrosion and in new applications where the Mo-free grades are expected to perform poorly. Experience has shown that cleanliness and weld quality are far more critical to successful performance than chloride ion concentration. Horizontal runs of piping, tubing and desalination flash chamber floors are prone to corrosion, and costly failures, unless water is completely drained during shutdown or standby periods. In many applications galvanic protection from aluminum, steel or Ni-Resist in the same assembly is responsible for the excellent long term performance. In other applications, some degree of crevice attack is tolerated as long as the resulting maintenance is within limits the user considers acceptable. Type 316 is not suitable for vertically tubed chemical industry condensers unless noncondensables are completely vented through the top tube sheet.

17-4 PH
UNS S17400

17-4 PH H1100 pleasure craft and workboat propeller shafting, pump shafting, valve stems, hydrofoil struts, special fasteners, pins, swivels, oceanographic instruments and subsurface oilfield equipment components are some of the applications where the marine industry utilizes the higher strength available in the precipitation-hardening grades. Only boat shafting has been followed closely. Overall experience approaches 20 years.

Guidelines

The precipitation-hardening grades in both the cast and wrought form are widely used in marine equipment wherever their higher strength is required in a component. These grades suffer crevice attack to about the same degree as type 304 and require cathodic protection. Zinc collars provide the necessary protection for boat shafting especially on fiberglass hulls and aluminum hulls. Less noble materials such as aluminum, carbon steel and Ni-Resist provide protection to the PH stainless steel component in many of the assemblies where strength requires the PH grade. The slightly overaged condition, H1100 or H1150 is preferred for better resistance to SCC.

Carpenter 20Cb3/CN7M
UNS N08020/J95150

Condenser tubing:

Carpenter 20Cb3, desalination brines, test unit, 110-200°F. OK 3 years. At 250°F, incipient pitting 3 years.

Sulfuric acid cooler tubing:

Carpenter 20Cb3, sea water, 1 unit, 130°F: 5 years to replacement.

Vertical condenser:

Carpenter 20Cb3, fresh and brackish waters, is the standard replacement for types 304 and 316 which fail by stress corrosion cracking in vertical condenser service. 20 plus years good performance. See Vertical Condenser Tubing Tests (p. 40)

Pump shafting:

Carpenter 20Cb3, sea water. Standard material for navy firefighting pumps past 18 years. Some crevice corrosion under O rings reported. These areas are overlaid with alloy 625, excellent overall performance. Substantial pitting in several all alloy

Mideast desalination pumps after 9 months standby in sea water. Replaced.

Pump case and impeller:

CN7M, sea water. Standard material for navy firefighting pumps past 18 years, excellent resistance to erosion corrosion. Some crevice attack under O rings and on flanges. Pitting reported in several all alloy Mideast desalination pumps after 9 months standby in sea water. Repaired and returned to service.

Guidelines

While Carpenter 20Cb3 and CN7M are not usually considered for seawater service, under the right conditions these alloys have given outstanding performance, as in the navy pumps.

Firefighting pumps are in continuous operation at sea and in harbor. Operation keeps the surfaces clean. Crevice attack will occur in prolonged standby service, as happened in the Mideast, and under O rings and gaskets. Avoid horizontal runs and standby service without cathodic protection.

Nitronic 50
UNS S20910

Nitronic 50 pleasure craft and workboat propeller shafting, sailboat rigging, valve stems, and pump shafting:

Only boat shafting has been followed closely. Cathodic protection is less necessary than for 17-4 PH but is still required for best service. Overall experience is about 12 years for boat shafting and 14 years for other applications.

Guidelines

Nitronic 50 is useful as pleasure craft and workboat shafting, valve stems and pump shafts. Galvanic protection is desirable for best performance.

Sanicro 28
UNS N08028

water, low salinity, 305°F condensing fluid inlet temperature. 0.5 years OK.

Cooler tubing (66,000 ft):
Compressors, offshore oil platform, sea water. No other information available.

Isobutane boiler:
904L tube sheet, geothermal brine, 338°F. 0.5 years OK.

Ammonia cooler tubing:
Installed 1980, sea water. No other information available.

Heat exchanger:
JS700 tube sheet, 25% NaCl brine, 140°F shell side, 50% caustic tube side. 4.5 years OK.

Butadiene condenser tubing:
Refinery, sea water. Installed 1981. No other information available.

Piping:
904L, 1000-4000 ppm chlorides. Crevice corrosion of flange face required weld overlay with alloy 625. 5 years.

Piping, product transfer line to tanker:
Partially submerged in sea water. Installed in 1981. No other information available.

Guidelines

Guidelines

Sanicro 28 has been used for both pipe and tubing, but no information on performance was available. Based on sea water tests, galvanic protection would be required to avoid crevice attack.

The 4.5% Mo austenitic alloys have demonstrated sufficient resistance to corrosion in sea water to perform reasonably well as tubing. Chlorination to control microfouling appears necessary to minimize under-deposit corrosion. Flange faces and gasketed surfaces are subject to crevice corrosion in brackish as well as sea water. These alloys are good candidates for brine service.

Types 904L/Ciramet/254SLX/JS700
UNS N08904/N08700

AL6X/A16XN
UNS N08366/N08367

Sulfuric acid cooler tubing:
Ciramet (904L), 12 units, sea water. Up to 10 years. Some corrosion failures reported in tubes where biofouling related plugging had reduced flow: Other failures have occurred during seasons when low flow resulted in boiling in some tubes. Overall performance to date, Satisfactory.

Condenser tubing:
30 power plant condensers, coastal waters 0.5 to full strength sea water. Up to 12 years service. No evidence of corrosion in 26 condensers. Some corrosion failures in 4 condensers. Overall failures from corrosion 0.046% for the 12 year period during which condensers have been tubed with this alloy. Internal corrosion occurred in one condenser about 12 ft from the inlet end. Corrosion was confined to an area of the tubing between two support plates where the high temperature steam dump had impinged on the tubing due to failure

Vertical condenser:
904L, 254SLX, 50-1500 ppm chlorides, test unit, 180°F. Rated Useful. Refer to Vertical Condenser Tubing Tests (p. 40) program for more information.

Isobutane condenser:
904L tube sheet, irrigation waste

of a baffle plate. It was estimated that tubes may have reached wall temperatures as high as 400-700°F boiling the cooling water in this section.

Internal corrosion also has been found in two condensers at one location; tube failure rate, 0.017%/yr. And in two condensers at a second location; tube failure rate, 0.12%/yr. The corrosion at both locations is in the form of multiple shallow pits that progress slowly with time. This attack does not appear to be associated with microfouling or other deposits. As of this date the producer has been unable to determine the reason for the pitting attack in these condensers, but has recently introduced a nitrogen-bearing version of the alloy AL6XN.

Because of the corrosion that has occurred in these units, other condensers with AL6X tubes have been subject to frequent and detailed inspection. No evidence of significant corrosion in the other 26 condensers has been found other than 2-4 tubes that failed in one condenser where superheated steam was allowed to impinge directly on the exterior of these particular tubes due to an improperly installed drain.

Exposure tests, as well as operating experience, indicate AL6X is resistant to crevice corrosion in sea water under metallic and non-metallic crevice formers and to crevice corrosion under micro-and macro-biofouling deposits. Sedriks (5) has pointed out that if sigma and chi formation are accompanied by severe chromium or molybdenum depletion, it is possible that attack might occur. See also Surface Condition, p. 11. Since nitrogen retards sigma and chi formation, its addition would seem to be quite beneficial to the sea water corrosion resistance of this high Mo stainless steel.

Refinery coolers, di-glycol amine:
4 units, 2170 tubes, 180°F process side inlet temperature, sea water. 4.5 years. No evidence of corrosion found in yearly inspections. Monel waterboxes pitted and required cathodic protection.

Cooling coil:
1 unit, sea water. New installation.

Tubesheet:
AL6XN, chemical plant heat exchanger, AL29-4 tubes. New installation.
AL6XN, power plant AL6X tubes. New installation.

After condenser:
1 unit, brackish water. Colorado River water, 700-800 ppm chlorides. 5.5 years, OK.

Fan coolers, power plant:
2 sets, brackish water, up to 4000 ppm chlorides. 4 years, no corrosion.
2 sets, new.

Auxiliary coolers, power plant:
Four units, fresh water, low chlorides.
1 year, OK.

Condenser tubing:
Test unit at 110-200°F, desalination brines. 2 years, OK. At 250°F, 2 years, shallow pitting.

Heat exchangers:
Five units, 25% NaCl salt brines at 70-140°F tube side, 50% caustic shell side, JS 700 tube sheet. 5 years, OK.

Guidelines

AL6X has been fully resistant to corrosion in 26 of 30 coastal condensers and in refinery streams at temperatures up to 180°F. In the four condensers where surface pitting attack, as distinguished from crevice corrosion, has occurred, tube failure rates ranged from 0.017% to

0.12%/yr. AL6X has proven resistant to crevice corrosion in sea water. The recent nitrogen addition, AL6XN, is expected to further improve the sea water corrosion performance of this 6% Mo alloy.

254SMO
UNS S31254

Condenser tubing:

4 power plant condensers, copper alloy tube sheet. Baltic Sea water. OK after 4 years.
1 power plant condenser, type 321 tube sheet, new installation.

Heat exchangers:

6 units, 1 power plant, brackish water.
1 unit geothermal
3 coastal chemical plants

Heat pumps:

6 units, evaporator panels and pipes, 400 tons.

Tube sheet:

1 power plant, titanium tubes. Inspected for crevice corrosion at tube to tube sheet joint after 4 years. OK.

Piping:

5 RO desalination units, brackish ground water (500-2000 ppm chlorides) to sea water, Mideast. 1-2 years, no reports. Several RO plant manufacturers and users are currently replacing type 316 piping with 254SMO on RO plants with sea water feed.

21 offshore oil platforms, North Sea, salt water. Evaporators, fire mains, exhaust gas, storage-ballast and water flood injection, 6000 tons: Up to 5 years; no inspection reports. Usage increasing.
2 CPI cooling water systems
2 Power plant cooling water systems.

Valves and fittings:

Cast counterpart developed for

storage ballast system. New installation.

Exchangers and coolers:

4 coastal CPI plants.

Vent condensers:

5 MSF desalination plants,
Laboratory examination report on tubing from one vent condenser after 1 year – No evidence of internal or external corrosion. Vent condensers are sea water cooled and have CO₂, H₂S, chlorine and bromine gases on shell side. Copper alloy and type 316 fail from external corrosion.

Guidelines

Although service life is less than 5 years, there is growing evidence that 254SMO is resistant to crevice corrosion in sea water as condenser tubing and as piping in a variety of sea water services. The older installations have seen about 5 years service with no reports of significant corrosion to date. Condenser installations have been inspected, but reports on piping performance are not yet available. Development of a cast counterpart for valves and pumps and establishment of fabricators of fittings are positioning this alloy for further growth in sea water piping applications.

**Summary of Experience–
Duplex Alloys**

Type 329 – Duplex
UNS 32900

Condenser tubing:

NTK R-4 (Type 329), 65 ships, sea water. Up to 14 years service. Some under microfouling corrosion reported prior to installation of on board chlorine generators. Severe crevice corrosion reported in tube to tube sheet joint of one condenser.

Condenser tubing:

Type 329, peripheral tubes 1 unit, 200-2000 ppm chlorides. 22 years to replacement.

Condenser tubing:

Type 329, desalination brines, test unit, OK 3 years at 110-200°F; shallow pitting 3 years at 250°F.

Shipboard experience:

IHI tubed the main condensers of 65 tankers and cargo vessels with NTK R-4 (type 329) in the 1971-1980 period. Ship owners reported significant corrosion after the first several years of operation. Laboratory examination revealed that corrosion occurred beneath hard shelled microfouling growths within the tubing. On board chlorine generators were developed and installed. Chlorine was controlled at 0.2-0.3 ppm residual at the condenser exit. Under microfouling corrosion was reduced to limits that were tolerable for the ship owner. Severe crevice corrosion between the NTK R-4 tubes and NTK R-4 tube sheet with extensive retubing has also been reported. With the return to diesel power instead of steam, no ships have been fitted with NTK R-4 tubing by IHI since 1980.

Guidelines

Type 329 has demonstrated good resistance to brackish waters. Type 329 has suffered under microfouling type crevice attack, which can be controlled by chlorination, and severe tube-to-tube sheet crevice attack in sea water. Type 329 appears to have marginal resistance for sea water in the more critical services, but appears to be a good candidate for brine service.

Alloy 3RE60**Cooler, HNO₃:**

1 unit, 3000 ppm chlorides. Inlet

temperature of HNO₃ gas 100°F. > 7 years OK. Replaced 316 which failed by SCC in 2.5 years.

Cooler, margarine:

1 unit, 3000 ppm chlorides, flow restricted. Outlet water temperature is near boiling (180°F +). > 10 years OK.

Guidelines

Limited experience indicates good resistance to brackish waters.

Alloy 2205**Piping, sea floor:**

Sweet gas gathering lines, 5 offshore oil platforms, North Sea, 1600 tons. Up to 6 years, some startup corrosion problems. No service failures reported.

Corrosion reported at weld defects and from water left standing for extended periods in line during construction period. External crevice corrosion also reported. Some, possibly all, lines are both coated and cathodically protected. Selection was based on resistance to sweet gas (CO₂) corrosion.

Piping, sea water to process plant:

Installed 1980. No other information available.

Piping, sea water to offshore oil platform:

1 line. Installed 1980. No other information available.

Instrument tubing, sea floor wells:

2 installations, 10,000 ft Installed 1980-81. The instrument tubing is around an inner flexible pipe carrying crude/gas. This whole assembly is protected by a heavy outer protective wrap. No performance information available.

Air cooler tubing, offshore oil platform:

2 installations, 1980-81. No other

information available.

Guidelines

Experience shows that 2205, like the standard grades of stainless steel, is subject to corrosion when water is left standing for extended periods in the lines. Strict control of weld quality is also required. Coating and cathodic protection are certainly helpful and probably necessary on free runs of instrument piping that are not in contact with the bottom or subject to biofouling. Crevice corrosion seems likely to be a problem at connections and under biofouling.

Cast Duplex Stainless Steels

The cast duplex stainless steels used in pumps contain about 25Cr 5-6Ni 2-3Mo and sometimes Cu and/or N. As cast they contain > 50% ferrite. Heat treatments are designed to achieve a roughly 50% austenite 50% ferrite composition balance. The N addition is particularly helpful in improving corrosion resistance. PWHT after weld repairs is specific for each composition. Producers recommendations should be followed carefully.

Ferralium:	25Cr 5Ni 3Mo + N + Cu
Zeron 25:	25Cr 6Ni 2Mo + N
Zeron 100:	25Cr 6Ni 3Mo + N

Pumps, high pressure, oil field injection: > 54 installations, deaerated sea water. Up to 11 years service OK. A typical injection pump would have 20,000 hp and deliver 9000 gpm at 2800 psi. Typical constructions:

Case:	Duplex or CF8M
Impellers:	Duplex or CF8M
Wear rings:	Duplex, Stellite 6
Shaft:	K Monel, Alloy 625, UHB44
O rings:	Alloy 625 overlay in seal areas when standby periods are anticipated.

Few problems have been reported. Time between overhauls currently being extended from 20,000 to 40,000 hours. The cast duplex alloys have an excellent track record in these oil field injection pumps.

Pump impellers, offshore oil, sea water lift:

Duplex is being used as an alternative to CF8M in some lift pumps. The case is Ni-Resist.

Pumps, intake supplying sea water for fire fighting at large Mideast refinery:

Up to 4 years OK with occasional weld repairs.

Ni-Resist replaced CA6NM cases on these fire fighting pumps in 1979 due to severe corrosion and failures of CA6NM. Problems in procurement of quality Ni-Resist castings and weld repair of foundry defects, led to trial of Ferralium and Zeron 25 cases starting in 1982. As of 1985, cast duplex has replaced Ni-Resist for the cases, and is an accepted alternate for the impellers in these, and other sea water intake pumps at this refinery.

Guidelines

The high strength of the cast duplex alloys, the ability to weld repair efficiently, and good corrosion resistance has given them a leading position in high pressure oil field injection pumps, especially on offshore platforms where topside weight is an increasingly important consideration. The deaerated sea water used for injection is not corrosive to steel at low velocities. Initial use of these duplex alloys in pumps handling raw sea water is promising, but needs confirmation in further operation. Replacement of the Ni-Resist case with a duplex stainless steel deprives the impeller and shaft of the protection needed during idle or standby periods.

Summary of Experience – Ferritic Alloys

Sea-Cure
UNS S44660

Condenser tubing:

15 coastal power plants, 5 inland power plants on fresh water, 2 geothermal condensers: Up to 6 years service. No evidence of corrosion, except for 6 tube failures from internal corrosion in 1 of the 13 coastal condensers.

Experience, excellent. Overall failures from corrosion in coastal condensers 0.002% for the 6 year period this alloy has been in use. The corrosion reported on 6 tubes in one plant prompted an extensive evaluation program which resulted in increasing the Cr content from 26 to 27.5% and Mo from 3 to 3.4%. Two instances of hydrogen embrittlement from overprotection of the water box have been reported. Ferritic alloys are subject to hydrogen embrittlement when overprotected.

One coastal plant, which is forbidden to chlorinate, reports such severe internal microfouling that weekly cleanings are required year round, and almost daily in the summer months, to maintain heat transfer. Other plants with a variety of chlorination practices report good or better heat transfer as compared to the materials replaced.

Feedwater heater tubing:

Three low pressure and five high pressure feedwater heaters have been retubed with Sea-Cure starting in 1984.

Guidelines

Sea-Cure is a proven material for all saline waters and should be a good candidate for brine service. There has been

no corrosion under microfouling in the current 27.5% Cr, 3.4% Mo updated analysis. Overprotection should be guarded against. Sea-Cure is a promising candidate for feed water heater tubing, geothermal and other brine services.

Monit
UNS S44635

Condenser tubing:

Trial tubes in 1 condenser, fresh water, 200 ppm chlorides. Up to 6 years, no evidence of corrosion.

Trial tubes in 1 condenser, saline water, 0.8 × sea water. Up to 7 years no evidence of corrosion.

Auxiliary cooler:

Saline water, 0.3 × full strength sea water. Up to 7 years. Some superficial crevice attack noted under epoxy coating at inlet end. The water-box and tubesheet were epoxy coated and some of the coating adhered to the inside diameter at the inlet end. Otherwise, no evidence of corrosion. General condition OK.

Guidelines

Experience is limited. Information indicates Monit is a promising candidate material for saline water service, but may suffer some crevice corrosion beneath deposits.

CA6NM
UNS J91540

Propellers, ice breakers:

Sea water and ice. Up to 15 years. Good service.

The good low temperature impact strength of this composition has resulted in a distinct improvement in blade damage and breakage as compared to CA15 and other cast compositions previously used for icebreaker propellers.

Pumps, sea water intake pumps:
Severe corrosion and failures. Use discontinued.

Pumps, transfer, deaerated sea water for oil field injection:
9 large pumps. 7 years OK

Guidelines

The CA6NM alloy has given good service as propellers on ice breakers, despite the poor performance in sea water intake pumps. Propellers receive some degree of cathodic protection from the steel hull. In deaerated sea water service, CA6NM has given excellent service.

Summary of Experience – Vertical Condenser Tubing Tests

The results of a series of tests of alloy tubing in two vertical condensers at DuPont's Chambers Works over the 1966-1983 period were reported at a regional NACE conference on Corrosion Resistant Piping in the spring of 1985. Results from these tests are summarized below.

Shell side:

Delaware River water, 50-1500 ppm chlorides with excursions to 4000 ppm; pH 6.7-7.0. Oxygen, sufficient to support aquatic life (> 4ppm). Chlorinated. Flow controlled so that outlet water temperature was near boiling (> 180°F).

Tube side:

15 to 50 psi condensing steam

Duration:

80 days originally, later extended to 1 year

Evaluation:

Visual examination for corrosion and depth of attack after removal and cleaning.

Conclusions:

The alloys were ranked in three groups based on "severity of service" which referred primarily to the process inlet temperature. The criteria for rejection was whether or not an alloy would corrode.

Severe service (highest inlet temperatures):

- *Alloy C-276
- *Titanium (all grades)

Normally acceptable service

- *Inhibited Admiralty Brass
- *Alloy 825 (Identified as new standard tubing material)
- *Carpenter 20MO6

Alloy G3

*Monel

Alloy 625

Zirconium

Conditional service (Indications of possible weld corrosion)

- *Carpenter 20Cb3

AL6X

904L

2RK65

254SLX

* Alloys in current use at Chambers Works, Five other stainless steel tube alloys were rejected primarily for weld metal corrosion.

Guidelines

All alloys tested resisted SCC under conditions where type 316 frequently fails by SCC. The criteria used for selecting acceptable materials in each group, "No significant corrosion", is not quantitative, and is subject to somewhat different interpretation by the several different investigators that examined the tubing at different times during the 7 year test period. Restricting the flow to near boiling added to the severity of the test conditions. Nevertheless, useful information can be extracted from these rankings although the rankings do seem

ultraconservative. Note that Incoloy 825, although in the second group, is identified as the new standard tubing material for Chambers Works based on

these test results. Carpenter 20Cb3 has been a standard material for vertical tubed condensers at this plant for many years.

Table 19 Summary of Usage of Nickel Stainless Steels in Saline and Natural Waters and Brines

	Preferred	Useful	CC Reported
Fresh water < 200 ppm Cl	304	304L, 316, 316L & HA	Rare to none
Brackish waters < 1000 ppm Cl	304L/316L	HA, ferritic	304/304L
Brackish waters > 1000 ppm Cl	HA	316/316L, duplex, ferritic	316, 4.5% Mo
Vertical condensers fresh & brackish waters	Carp 20Cb3 Incoloy 825	304, 316, HA, duplex, ferritic	304/316 SCC (1)
Sea water w GP	316/316L	Duplex, CF3, CF8M 17-4 PH, Nitronic 50 CA6NM	Distance limited See Table 4
Sea water w/o GP	6% Mo + N (2) Sea-Cure	4.5% Mo, CN7M, duplex (3) ferritic	316/316L 4.5% Mo Duplex (3) CN7M 17-4 PH Nitronic 50 CA6NM
Brines, deaerated	316/316L CF8M Duplex		

Footnotes:

CC - Crevice corrosion

SCC - Stress corrosion cracking

HA - More highly alloyed nickel stainless steels.

GP - Galvanic, or impressed current, protection

4.5% Mo, 6% Mo + N, ferritic and duplex categories include several proprietary compositions.

(1) Types 304 and 316 fail from stress corrosion cracking underneath the top tube sheet in vertically tubed condensers.

(2). Alloys of this composition are resistant to under deposit and other forms of crevice corrosion in saline waters. Some pitting type failures have occurred in tubing of a N free composition.

(3) Duplex alloys appear more resistant to crevice corrosion than 316/316L, but show some susceptibility to under biofouling, under-deposit crevice attack in saline waters.

Table 20 Nominal composition of alloys

	C	Cr	Ni	Mo	Cu	
Type 303	0.15	18	9	-	-	0.2 P 0.15 S
304	0.08	18	9	-	-	
304L	0.03	18	9	-	-	
CF3	0.03	19	10	-	-	
316	0.08	17	12	2.5	-	
316L	0.03	17	12	2.5	-	
CF8M	0.08	19.5	10.5	2.5	-	
CF3M	0.03	19	11	2.5	-	
17-4 PH*	-	16.5	4	-	4	Cb + Ta = 0.3
Carp	0.06	20	34	2.5	3.5	Cb + Ta = 8 × C Min.
20Cb3*	0.07	20.5	29	2.5	3.5	
CN7M	0.03	21	12	2	-	5 Mn 0.15Cb 0.2N
Nitronic 50*	0.02	27	31	3.5	1	
Sanicro 28*	0.03	22	41	3.5	1.75	1 Ti 0.08Al
Incoloy 825*	0.03	20	25	4.5	1.5	0.06N
904L	0.03	21	25	4.5	-	0.04N
JS700*	0.03	20	25	6	-	
AL6X *	0.02	20	18	6	0.7	0.2N
254SMO*	-	25	5	1.5		
329		19	5	3		
3RE60*		22	5	3		
2205	0.04	26	5	3	1.7	0.17N
Ferralium *		25	6	2		
Zeron 25*		25	6	3		
Zeron 100*	0.02	27	3.5	3		
Sea-Cure*	0.03	25	4	4		
Monit*	0.06	12	4	0.7		
CA6NM						

* Trademarked product

17-4 PH	Armco Inc.
Carp 20Cb3	Carpenter Technology Corp.
Nitronic 50	Armco Inc.
Sanicro 28	Sandvik Steel Company
Incoloy 825	Inco Alloys International
JS700	Jessop Steel Co.
AL6X	Allegheny Ludlum Steel Corp.
254SMO	Avesta Jernverks AB
3RE60	Sanvik Steel Company
Ferralium	Haynes Intl.
Ferralium	Bonar Langley
Zeron 25	Mather & Prat
Zeron 100	Mather & Prat
Sea-Cure	Colt Industries
Monit	Uddeholm Co.

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