## THE SUCCESSFUL USE OF AUSTENITIC STAINLESS STEELS IN SEAWATER

A PRACTICAL GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS Nº 1259

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### The Successful Use of Austenitic Stainless Steels in Sea Water

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#### ABSTRACT

Austenitic stainless steels are providing excellent trouble-/ree service in sea water for pumps, propellers, valves, and other marine equipment. Occasionally, a failure occurs as the result of deep localized pitting in a crevice.

Data are given showing that austenitic, ferritic, and martensitic stainless steels suffer pitting in crevices and under deposits in quiescent sea water.

Austenitic stainless steels remain free from attack in high-velocity sea water. Low-purity ferritic and the martensitic stainless steels frequently pit in high-velocity sea water.

Crevice corrosion can be controlled effectively with cathodic protection from iron, zinc, aluminum, or magnesium galvanic anodes or impressed current cathodic protection by polarization to -0.6 v vs Calomel. Austenitic stainless steel performs well in many situations because it is a component of a multi-alloy assembly utilizing iron or steel.

Examples from field experience are given.

#### INTRODUCTION

During the past decade, there has been a growing use of austenitic stainless steel in marine equipment. Most applications have been successful but an unexpected failure has been observed occasionally. It is the purpose of this paper to describe when and how to use austenitic stainless steel with success.

The selection of stainless steels appears to result from the engineering requirements of new, advanced, high-speed, high-reliability commercial, pleasure, and military craft. Ocean science and engineering, offshore oil production, fishing, and ocean mining are also contributing to the selection of stainless steels for sea-water applications.

The increasing use of stainless steel in the marine environment is found in work-boat propellers, pump components, bow thrusters, valves, shafting and shaft components, through-hull fittings, parts on data-gathering buoys, fasteners, and housings of oceanographic instruments. When austenitic stainless steel has given good, corrosion-free service, it is most often found to be used as a key component in a multicomponent, multi-alloy assembly or system receiving the benefit of built-in cathodic protection.

For example, in Fig. 1 a cast Type 304 (Alloy Casting Institute CF-4) propeller is being used on a steel seagoing tugboat with zinc anodes attached to the rudder. Fig. 2 shows a cast ACI CE- $30^{1,2}$  power-plant sea-water circulation-pump impeller free of any corrosion after 6 years of service that was used in combination with an austenitic cast-iron suction bell and diffuser.

#### BEHAVIOR OF THE STAINLESS STEELS IN SEA WATER

A brief review of the behavior of stainless steels in sea water is in order before discussing the



FIG. 1 — CAST TYPE 304 (ACI CF-4) TUGBOAT PROPELLER.

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FIG. 2 — CAST ACI CE-30 PUMP IMPELLER AFTER 6 YEARS' SERVICE.

criterion for successful use of stainless steels in marine applications.

The stainless steels are passive-active alloys. In the passive state, stainless steels are highly resistant to corrosion, showing little or no corrosion depending on the exposure. In the active state, when passivity is destroyed, these alloys display localized attack, with little total metal loss, in the form of serious pitting properly identified as crevice corrosion. The pitting localized mode of attack is associated with crevices in the equipment or under deposits of some foulant such as weld slag, mud, other inorganic solids, and/or attached marine growth.

Most investigators believe that passivity of stainless steels results from the presence of a thin, hydrous, chromium oxide film. In stainless steels, this corrosion barrier is the result of chromium. Additions of nickel and molybdenum stabilize the film on austenitic stainless steel. Passivity is maintained by an oxidizing agent or oxygen. It also can be maintained in many aqueous solutions as long as there is no significant difference in potential of the stainless from point



FIG. 3 — CAST TYPE 316 (ACI CF-8M) FLANGE — CREVICE CORROSION.

to point even if an oxidizing agent is not present (deaerated sea water).

The chloride ion, if sufficiently concentrated, is capable of destroying the passivity of austenitic stainless steels under specific chemical or physical circumstances. In sea water with about 19,000 ppm of chloride, passivity can be destroyed and localized attack in crevices or under deposits can occur. Fig. 3 shows crevice corrosion in a segment taken out of a 316 flange assembly that was a component of a sea-water filter. Flange assemblies, by the nature of design, have deep crevices.

Proposed mechanisms or theories of crevice corrosion are fully described by Fontana and Greene<sup>3</sup> and Uhlig.<sup>4</sup> The normal reaction of stainless steel in sea water in the absence of deposits or crevices is the extremely slow oxidation of metal at anodic sites. Reduction of oxygen occurs on the cathodic zones, forming hydroxyl ions. In crevices, there is a lack of diffusion of oxygen and a reduction in the formation of hydroxyl ions. Chloride ions are more mobile than hydroxyl ions. With a lack of hydroxyl ions, an excess of metal chloride is produced. The excess metal chloride reacts with water to form an insoluble metal hydroxide at the remote cathode and hydrochloric acid in the crevice or anode. The pH in crevices and at the bottom of pits has been measured as low as 1.0. The reaction is autocatalytic. Once it has started, it results in deep penetration or localized attack. The rate of localized

TABLE 1 --- CORROSION BEHAVIOR OF STAINLESS STEELS IN SEA WATER IN THE PANAMA CANAL ZONE (REF. 6)

Stainless Steel AISI Type	Nature	Corrosion Rate (mils/yr)			Average of 20 Deepest Pits (mils)*			Deepest Pits (mils)*		
	Exposure	1 Year	4 Years	8 Years	1 Year	4 Years	8 Years	1 Year	4 Years	8 Years
Type 410 13 Cr	Immersion	2.98	1.97	1.75	61(11)	148	161	260(p)	260(p)	259(p)
Type 302 18 Cr-8 Ni	Immersion	1.46	0.88	0.69	70(12)	107	140	261(p)	286(p)	236
Type 316 18Cr-13Ni-3Mo	Immersion	0.59	0.07	0.25	44 (7)	48	154	245(p)	93	<b>24</b> 5(p)
Type 321 17Cr-10Ni-Ti	Immersion	1.16	0.81	0.62	64 (8)	175	193	<b>270</b> (p)	273(p)	272(p)

\*Pit depths referred to the original surface of the metal either by measurement from an uncorroded surface or by calculation using the original and final average measured thickness of the sample. Average of 20 deepest pits represents average of the five deepest pits measured on each side of duplicate specimens. Area, 2.25 sq ft on immersed specimens; values in parentheses indicate total number averaged when less than 20 measurable pits. Perforation of plate by deepest pit is indicated by (p).

corrosion is accelerated by the small, active anodic areas with respect to the normally much larger passive cathodic areas.<sup>5,12</sup>

The foregoing points are illustrated by actual corrosion test data. Table 1 gives immersion test data for standard AISI stainless steels in quiescent sea water tested in the Panama Canal Zone.<sup>6</sup> The average calculated corrosion rates of all the alloys tested as derived from the weight loss and area exposed during the specified time are extremely low. With such low corrosion rates, the stainless steels would be acceptable for most services were it not for the fact that the whole weight loss occurs on a very small portion of the surface in pits from crevice corrosion. Average corrosion rates of stainless steels are very misleading in sea water and nearly useless in assessing stainless alloys because of localized corrosion.

Table 1 shows that pitting from crevice corrosion was very deep, with perforation in some instances, on all alloys exposed. The possibility and consequences of localized corrosion, and the prevention of such attack must be assessed in view of the mechanical requirements of equipment to obtain satisfactory service from stainless alloys in in the marine environment.

Table 2 gives additional sea-water test data from

TABLE 2	- CORROSION	BEHAVIOR OF	STAINLESS ST	EELS
	IN LOW-VELOC	ITY SEA WATE	R (REF. 1) <sup>a</sup>	

	<b>—</b> .		Depth of Pitting (mils)						
AISI Period		st Weight	Under D	eposits	Crevice				
Туре	(days)	(gm)	Maximum	Averageb	Maximum	Averageb			
405	755 <sup>c</sup>	135	100	59	187 <sup>d</sup>	103			
430	568 <sup>c</sup>	109	135	57	72 <sup>e</sup>	61			
304	320	12	35	22	36	24			
321	944		53 <sup>f</sup>	15	56	24			
347	755 <sup>c</sup>	26	148	59	61	46			
347	755°	30	79	54	47	38			
316	944		7						
			(1 pit)		10	3			
316	1,255	3	50	22	170	46			
317	1,075	5	23	12	45	27			
309	320	11	20	12	55 <sup>d</sup>	55 <sup>d</sup>			
310	320	4	6	3	24 <sup>d</sup>	24 <sup>d</sup>			
329	106	0	0	0	10	2 pits			

<sup>a</sup>Panels  $12 \times 12$  in. were completely immersed at Kure Beach, N. C., in sea water flowing 1 to 2 ft/sec.

<sup>b</sup>These values are averages of the 10 deepest pits.

 ${}^{\mbox{c}}\mbox{Specimens withdrawn from test because of failure in period indicated.}$ 

<sup>d</sup>Specimen became perforated.

<sup>e</sup>Local attack directly under washer; holes were greatly enlarged.

<sup>f</sup>One pit in weld, 0.125 in. deep.

TABLE 3 - EFFECT OF SEA-WATER VELOCITY ON PITTING OF
WELDED TYPES 316 AND 310 STAINLESS STEELS (1,257 Days in Test)
(BEE 7)

	In FI	ume at 4 F	t/Sec	In Ba	asin at 0 Ft/Sec		
Material	Number of Pits	Maximum Depth (mils)	Average Depth* (mils)	Number of Pits	Maximum Depth (mils)	Average Depth* (mils)	
Type 316 plate**	0	0	0	87	78	38	
Type 316 weld	0	0	0	47	130	76	
Type 310 plate	0	0	0	19	110	38	
Type 310 weld	0	0	0	23	> 250†	120	

\*Average of 10 deepest pits.

\*\* Test coupons — 12 in.  $\times$  8 in.  $\times$  ½-in.-thick with 11 lineal in. of SMA weldment in "t" pattern.

<sup>†</sup>Perforated from one side (thickness of specimen = 0.25 in.).

Kure Beach, N. C., at low velocities of 1 to 2  $ft/sec.^1$  In this test, a wide range of standard stainless steels was exposed, yet the results were similar to the Panama Canal results even at 2 ft/sec. That is, weight loss was low but local attack under deposits or in crevices was severe.

In high-velocity sea water, velocities above which inorganic deposits cannot accumulate and marine biofouling cannot attach to the metal surface, the austenitic stainless steels remain free of corrosion. The corrosion resistance of two austenitic stainless steels at a flow of 4 ft/sec is demonstrated in Table 3 in comparison with the same stainless steels at under-stagnant or no-flow conditions.<sup>7</sup> Fig. 4 is a photograph of a Type 316 (ACI CF-8M) pump case, a multistage, high-pressure, sea-water injection pump from a West Coast secondary oil recovery operation, that demonstrates the property of extreme corrosion resistance of austenitic stainless steel in the presence of high-velocity, turbulent sea water.

Although the primary purpose of this paper is to discuss the usage of Types 304 and 316 stainless steels in sea water, a brief reference to the AISI 400 stainless steels (ferritic and martensitic), the free-machining AISI 300 series, and the more highly alloyed proprietary materials is in order.

Fig. 5 shows the heavy, frequent pitting of an AISI 416 sea-water pump shaft after 10 years of service. This shaft was used in a large cast-iron pump with an ACI CF-8M impeller. Fig. 6 shows



FIG. 4 — CAST TYPE 316 (ACI CF-8M) PUMP CASE — NO LOCALIZED ATTACK.



FIG. 5 — WROUGHT AISI 416 PUMP SHAFT FROM POWER-PLANT SEA-WATER PUMP.

an AISI 303 sea-water pump shaft after 1 year of service. This pump had all cast-iron components except for the shafting. AISI 303 stainless steel has either sulfur or selenium additions to improve the malleability. However, these additions result in pit-initiating inclusions and significantly lower resistance to localized corrosion.<sup>8</sup>

Corrosion-rate data for Types 316, 304, 430, and 410 stainless steels at 13 ft/sec with crevices present are displayed in Fig. 7, showing the effect of temperature.<sup>1</sup> The extreme acceleration of corrosion of Type 410 in 75 °F sea water is evident. The pump shaft in Fig. 5 was in a pump handling 72 °F sea water.

The use of the AISI 400 series and 303 grade may not be advisable for immersion service in sea water.<sup>9,10</sup> On the other hand, the more highly alloyed proprietary stainless steels, those with more nickel, added copper, and molybdenum, show less frequent localized corrosion effects and to a lesser depth.<sup>11,12</sup> The proprietary nickel-chromiummolybdenum-iron alloys are essentially immune from localized corrosion in quiescent sea water.<sup>12</sup>

#### SUGGESTED GUIDELINES FOR APPLICATION OF AUSTENITIC STAINLESS STEELS IN SEA WATER

Crevice corrosion of all 300 series stainless steels, except the resulfurized varieties, can be



FIG. 6 — WROUGHT AISI 303 PUMP SHAFT FROM SEA-WATER PUMP — 1 YEAR.

suppressed by cathodic protection from iron or steel in other components of the same assembly in quiescent sea water. Or, austenitic stainless steels can be cathodically protected with zinc and aluminum anodes or with an impressed current system. A combination of less noble material and sacrificial protection is very effective, as illustrated in Fig. 1. It follows, then, that the localized-attack stainless steels displayed in low-velocity sea water in crevices or under deposits can be controlled effectively.

Lennox et  $al.^{13}$  demonstrated that cathodic protection using both iron and aluminum anodes reduced crevice corrosion to very low levels in tests of 490 and 649 days (Fig. 8). The area ratio of anode to cathode was 1:9. Lennox et al. reported



FIG. 7 — EFFECT OF SEA-WATER TEMPERATURE ON CORROSION OF STAINLESS STEEL.



STAINLESS STEEL, WITH AND WITHOUT CATHODIC PROTECTION.

current density requirements for polarizing stainless steel, carbon steel, and 6061-T6 aluminum with zinc anodes at an anode to cathode ratio of 1:38 (Table 4). The greatest current density was required for stainless steel in polarizing to -1.02 v with respect to an Ag/AgCl cell. This would indicate a shorter anode life for zinc in protecting stainless steel than in protecting carbon steel or aluminum.

However, Lennox *et al.* show that when stainless steel is protected by iron, it is only necessary to shift the stainless potential from -0.2 to -0.6 v. It is not necessary to polarize austenitic stainless steel to -1.02 v. Although current density data are lacking, it might appear that the current density required to protect stainless steel in quiet sea water is not particularly great, perhaps as low or lower than the current density required to protect steel. If this observation was true, with the knowledge that the driving potential to polarize to only -0.6 v instead of -0.85 v or lower for steel, an iron anode might conceivably have a long life even compared with a zinc anode.

The effectiveness of cathodic protection can be demonstrated with several successful applications. A hot-brine recirculation pump was operated by the Office of Saline Water at the Chula Vista, Calif., desalination demonstration plant for 4 years. This large, single-stage scroll-type pump is constructed entirely of CF-8M except for bearing material. After 4 years of service no significant corrosion was found. In the design, iron anodes were purposely placed on the four manholes and 12 blocks of iron were inset in the casing. The pump also had steel suction and discharge piping. The iron anodes were supplied to be a safeguard during shutdown periods to protect against crevice corrosion and to obviate draining the pump located at the bottom of a deep pit. The corrosion design was very effective. In a 4-year period, the anodes appeared to have lost only about one-third their original volume.

Figs. 9 through 11 illustrate a manhole anode, an insert block and the impeller discharge, and a block anode after service. Fig. 2, showing the cast ACI CE-30 pump impeller, illustrates a similar principle. The stainless casing and impeller of this power-plant pump performed without corrosion because of galvanic protection from austenitic cast-iron (Ni-Resist) components and a cast-iron pipe column; yet, with the area of the iron parts being substantially greater than the stainless surface area, the corrosion of the iron components

TABLE 4 — COMPARATIVE CURRENT REQUIREMENTS TO POLARIZE THREE STRUCTURAL METALS TO - 1.02 v\* (688 days' exposure, Key West, Fla.) (Ref. 13) Mean Current Density

Cathode Metal	to Cathode (milliamps/sq ft)**
Stainless steel	2.86 to 2.92
Carbon steel	1.88 to 2.57
6061-T6 aluminum	0.57 to 1.11

\*Ag/AgCl reference.

\*\*Based on zinc anode weight-loss data; 100-percent anode efficiency assumed and 17.5-sq-ft cathode area used in calculations. Anode-to-cathode area ratio 1:38. is not adversely affected. The pump has built-in protection during power-plant outage. Similarly, the tugboat propeller in Fig. 1 gives excellent corrosion-free service at high velocity while operating and receives cathodic protection from zinc anodes when idle.

These examples illustrate good performance of austenitic stainless steels using cathodic protection. In many marine applications, stainless steel performs very well because the very nature of the system involves steel, zinc, aluminum, or impressed current to protect the steel. In the case of the



FIG. 9 — CAST 316L (ACI CF-3M) BRINE RECIRCULA-TION PUMP WITH AN IRON ANODE ATTACHED TO MANHOLE COVER.



FIG. 10 — INSIDE OF BRINE RECIRCULATION PUMP. IRON ANODE IN UPPER CASE AND VIEW OF IMPELLER — DISCHARGE ZONE.



FIG. 11 — AN IRON ANODE FROM BRINE RECIRCULATION PUMP AFTER 3 YEARS' SERVICE.

power-plant pump, the surrounding pump components were selected in sea-water-resistant cast irons. This combination of corrosion-resistant metals in galvanic coupling provides built-in protection against localized attack of the stainless components.

It was mentioned earlier that the free-machining resulfurized stainless steels, AISI 303 and those containing selenium, 303 Se, are subject to heavy corrosion in sea water from inclusions. The AISI 400 grades, both ferritic and martensitic, also display heavy pitting in sea water, even in the absence of deposits or crevices. Field experience indicates that cathodic protection from iron components cannot be relied upon to protect these stainless steels. This observation is demonstrated in Fig. 5, showing a Type 416 stainless steel pump shaft from a cast iron pump, and in Fig. 6, showing a Type 303 shaft from a cast-iron pump.

Caution should be exercised in considering the Types 303 and 400 stainless steel for use in sea water. Some authorities do not favor their use.<sup>9,10</sup>

#### HIGH-VELOCITY SEA WATER

In high-velocity sea water, localized corrosion of the 300 series stainless steels ceases to be much of an engineering problem, even in the absence of cathodic protection. Exceptions rest with the free-machining 303 grades and the ferritic or martensitic 400 series stainless steels.

For example Table 3 shows that Types 316 and 310 stainless steels suffered no corrosion in a 1,257-day test at flow velocities of 4 ft/sec. In this test, the specimens remained free of deposits.

Several sources state<sup>1,9</sup> that stainless steels exposed to sea water at continuous flow velocities greater than 6 ft/sec will not suffer localized attack. At 6 ft/sec and greater, foreign deposits from marine growth or from inorganic sediment usually cannot attach or accumulate, so there is no opportunity for crevice corrosion.

These observations then lead to the next premise for the successful use of stainless steel in sea water. When an austentic stainless steel is used in a high-velocity, turbulent environment that maintains the surfaces free of deposits, austenitic stainless steel should remain free from corrosion. Demonstration of the ability of austenitic stainless steel to remain corrosion-free in high-velocity, turbulent salt water is shown by the excellent condition of the multistage pump case in Fig. 4.

There is some evidence that crevice attack even within mechanical crevices in fast-moving sea water may not be as much a problem as in quiescent sea water. For instance, a joint of Type 304 pipe of socket-weld construction tested at the Francis L. LaQue Corrosion Laboratory, Wrightsville Beach, N.C., test site with water flowing at 4.8 ft/sec displayed little evidence of crevice corrosion in 105 days. Possibly, the diffusion gradient of oxygen and hydroxyl ion becomes greater with the severity of turbulence and velocity, reducing the accumulation of low-pH chloride compositions within the crevice. At high velocities and turbulence, oxygen becomes more available everywhere because of a reduction in thickness of the diffusion boundary layer. The ability of turbulence to reduce or stop crevice corrosion is probably dependent on relative velocity and crevice geometry. This observation suggests the need for further laboratory study to establish the limits of crevice size in turbulent water beyond which localized attack might occur.

It might be pointed out that the pump case in Fig. 4 has a substantial number of crevices where wear rings and bushings were inset into the case, yet no localized attack was observed.

Another distinct virtue of the austenitic stainless steels is the resistance to erosion corrosion at higher velocities and to cavitation damage. Table 5 demonstrates the resistance of Types 304 and 316 steels compared with several other metals in high-velocity jet impingement tests performed at Wrightsville Beach. The test data indicate a distinct break in resistance of alloys between stainless and nickel-based alloys when compared with copper-based alloys, steels, and cast irons. The comparative results suggest why austenitic stainless steels and high-strength, precipitationhardening stainless steels are selected for durable centrifugal pumps, jet pumps, and hydrofoils.

Table 6 presents qualitative metal-loss data from cavitation tests recently performed in fresh water in Southern California.<sup>14</sup> In these experiments, water was discharged at 192 ft/sec directly at a square-edged blade of the test metal submerged in a test chamber. In this test chamber, true cavitation conditions were judged to exist because of the spongy appearance of nonresistant metals and the crackling noise generated in the cabinet. Although sea water has somewhat different characteristics than fresh water, Kerr<sup>15</sup> showed very little difference in cavitation damage of metals comparing fresh water with salt water. The austenitic stainless

TABLE 5 SUMMARY OF CORROSION DATA FOR MATERIALS TESTED IN HIGH-VELOCITY JET APPARATUS										
Francis L. LaQue Corrosion Laboratory The International Nickel Co., Inc.										
Duration of Tests: 30 days Exposed area of specimens: 3.5 sq in.										
Material	Weight Loss (gm)	Corrosion Rate (mils/yr)	Average Sea-Water Temperature (°C)	Sea-Water Velocity (ft/sec)						
Stellite 6B*	0.003	0.1	12	128						
Hastelloy C*	0.010	0.2	12	128						
AISI 304	800.0	0.2	10	142						
AISI 316	800.0	0.2	10	142						
Incoloy Alloy 825**	0.011	0.3	11	141						
17-4 PH 1	0.012	0.3	10	142						
Monel Alloy 400**	0.016	0.4	11	141						
Aluminum brass CA-687	0.815	21.0	20	128						
Nickel-aluminum-bronze CA-958	1.223	31.0	11	141						
Ni-Resist Type 2	0.923	27.0	10	129						
90-10 copper-nickel CA-706	1.157	26.0	16	131						
"G" bronze CA-905	1.251	30.0	20	125						
356-T6 cast aluminum	0.854	66.0	17	137						
Carbon steel	4.404	120.0	10	142						
Cast Iron	7.138	210.0	10	129						
Trade marks: *Stellite Div., 0 **Huntington All †Armco Steel Co	Cabot Co oys, Inc orp.	кр. •								

#### TABLE 6 - FRESH-WATER CAVITATION TEST (REF. 15)

Bars 7  $\times$  2  $\times$  ¼ in. immersed in raw Colorado River water. Water passes through a round edge orifice, ¼ in. In diameter with a pressure drop of 210 psi. Throat velocity is approximated at 192 ft/sec, impinging on ¼-in. dimension, which is square corner.

	Weight Loss (gm)			Other	
Alloy	14 Days	28 Days		Remarks	Nominal Composition
Type 17-4 PH*	0.20	0.42			
Type 410 hardened	0.18	0.45		Broke when dropped	
Type 316 stainless steel	0.20	0.60			
Type 304 stainless steel	0.42	0.77			
Type 409 stainless steel	0.46	1.12			
Type 430 stainless steel	0.40	1.07			
Type 410 annealed	0.49	1.26			
Monel 400**	0.68	1.31			
Ampco D-4 <sup>†</sup>	0.66	1.53		ASTM B-148 9D	10AI-5Fe-5Ni-Cu Bal.
Ampco 483	1.39	1.99		CDA 958	9AI-4Fe-4.5NI-1 Mn-Cu Bal,
Ampco 483	0.88	1.86		CDA 958	
Ampco 18	1.24	2.21		ASTM B-148 9C	10.5AI-4Fe-Bal, Cu
Ampco 66	1.52	4.63		ASTM B-147 8C	6AI-3Fe-3.5Mn-62Cu-Bal Zn
Ampco 71	0.67	9.97		ASTM B-143 2A	6Sn-1.5Pb-4.0Zn-Bal Cu
Ni-Resist	8.50				
Ni-Resist	11.40				
Carbon steel	13.80	38.53			
Ductile iron			105.6	9 days — taken out b	efore cut in two.
Grey cast iron			122.4	10 days — cut in two	
Trade marks: **Huntin *Armco †Ampco	gton Alloy Steel Corp Metals, In	s, Inc. c.			

steels rank very high in performance, being substantially superior to Monel Alloy 400 and the bronzes and far superior to steel and cast iron.

Mechanical engineers and equipment suppliers have observed the high degree of resistance of austenitic stainless steels to erosion-corrosion and cavitation damage, so they are making broad use of these materials for work-boat propellers, pump impellers and casings, throttling valves, and hydro-electric turbine runners.

#### STRESS CORROSION CRACKING

Austenitic stainless steels are susceptible to cracking in certain chloride environments when they contain residual stresses caused by welding, cold-forming, or shearing at elevated temperatures, especially where there is an opportunity for chlorides to concentrate by evaporation.

Although sea water is a strong chloride solution. there are few reported cases of stress corrosion cracking at ambient temperatures in fabricated, austenitic stainless-steel assemblies. This observation is supported by the multitude of successful applications of austenitic stainless steels in sea water at nonelevated temperatures. To a large degree, this position can be upheld by tests with cold-worked and stressed specimens of Types 301, 304, 321, and 310 stainless steels exposed at International Nickel Co.'s Kure Beach, N.C., test site. The 80-ft test lot, located 80 ft from the Atlantic Ocean, can be characterized as an aggressive sea-spray environment at ambient temperatures. Tests at this site by Phelps and Loginow<sup>16</sup> and Logan and McBee<sup>17</sup> for periods of 240 and 450 days, respectively, of specimens, including variations in stress following cold reductions, produced no stress corrosion cracking failures.

#### INTERGRANULAR CORROSION

Austenitic stainless steels such as AISI Types 302, 304, 316, 317, and 310 can become susceptible to an attack known as intergranular corrosion as a result of exposure to temperatures ranging from 800 to 1,650 °F (427 to 899 °C). This "sensitization" is generally attributed to the precipitation of chromium carbides at the grain boundaries, which lowers the effective chromium content and corrosion resistance near the grain boundaries. The degree of sensitization is related to time at temperature and carbon content of the stainless.

The phenomenon of sensitization and intergranular corrosion led to the development of the low-carbon ELC or L grades (304L and 316L) and to grades stabilized by columbium (347) or titanium (321).

Sensitization, as applicable to sea-water components, can come about by welding operations or slow cooling of stainless steel through the sensitizing range.

Although many aqueous environments do not cause intergranular attack of sensitized stainless steels, it has been shown by the Welding Research Council<sup>18</sup> that 300 series stainless steels, relatively high in carbon content as welded and stainless steels of medium carbon content heavily sensitized by furnace heat treatment, displayed intergranular corrosion in ambient sea-water exposures.

An occasional report is encountered of a cast component, such as a pump impeller, suffering surface roughening or intergranular fracture. These experiences are usually traced back to faulty solution annealing of the casting.

Figs. 12A and 12B show a pump impeller displaying surface corrosion and the corresponding pump case completely free of corrosion, both subject to the same ambient sea-water environment. The impeller and pump case were parts of the same



FIG. 12A — CASING AND END PLATE OF A TYPE 316 (ACI CF-8M) PUMP.

pump, both cast in Type 316 (CF-8M) steel. The impeller was found to have been sensitized.

The following are suggestions for avoiding the hazards of intergranular corrosion.

1. If welding is required in wrought product forms, select one of the low carbon grades such as 304L, 316L, and 317L or select the stabilized grades such as 347 and 321.

2. For castings, either restrict carbon to 0.04 percent (that is, CF-4M and CF-4) or solution anneal from above, 2,050 °F (1,120 °C).

Solution annealing refers to the recognized heat treatment given austenitic stainless steels whereby the stainless is heated to a temperature sufficient to solutionize all carbon and carbides. The heated item is quenched rapidly through the sensitizing range so that chromium carbides cannot migrate to the grain boundaries.

#### CORROSION FATIGUE

Corrosion fatigue is defined as the fracture of a metal under repeated cyclic stressing in the presence of a corrosive medium. The fatigue resistance of a metal is reduced, often to a large degree, by the presence of a corrosive environment when compared with the fatigue resistance as measured in air. In fact, metals do not show a true endurance limit in sea water or other corrosive media.

Corrosion fatique testing of various metals and alloys does produce numerical figures of cycles to failure at various alternating stress levels. Plots of stress level vs cycles to failure show tendencies for the curves to level out similar to S-N curves for metals tested in air, but corrosion fatigue curves never become asymptotic.

The lack of a true endurance limit in sea water has handicapped mechanical engineers and metallurgists alike in designing marine equipment subject to cyclic stress loading. Nevertheless, ship propellers and shafting that are subject to alternating stress patterns are being used successfully. Conservative designs are required for success.

Corrosion fatigue testing and analysis in sea water are complex and involve such variables as smooth test specimens vs notched, localized corrosion ten-



FIG. 12B — THE IMPELLER SHOWS INTERGRANULAR CORROSION.

dencies of the metals, grain size, cathodic protection, and relative tensile strengths. A more detailed discussion of this subject is found in a report by Sedriks and Money<sup>19</sup> and references listed therein.

In this work, corrosion fatigue strength (CFS) of various materials in sea water appears with testing concluded at 100 megacycles (see Table 7). These tests were run on smooth rotating bar samples.

The CFS for AISI Type 304 at 100 megacycles of 15 ksi is substantially lower than the published endurance limit in air of 35 ksi.

Table 7 does tend to indicate that corrosion resistance, small grain size, and cathodic protection are beneficial. Tensile strength cannot be related to corrosion fatigue because corrosion resistance is a factor.

Corrosion fatique properties of metals and alloys in sea water are distinctly lower than engineering fatigue as measured in air. The austenitic stainless steels can be very useful in cyclic operation, as proven by experience with work-boat propellers, but it is necessary to apply reasonable factors of safety.

#### SUMMARY

The AISI austenitic stainless steels, primarily Types 316 and 316L and the cast counterparts CF-8M and CF-4M, are being routinely used in submerged ambient sea-water applications. In selected situations, Types 304, 304L, and the precipitation-hardening grades, with cast counterparts, are also being used successfully.

The successful use of stainless steels in sea water is dependent on three primary factors; the selection of the correct grade; the presence of sufficient velocity or turbulence to keep the stainless clean; or the presence of sufficient cathodic protection from less noble materials to prevent crevice corrosion.

#### CONCLUSIONS

The degree of success in the use of austenitic stainless steels in sea water is dependent on the following conclusions, which may be considered as suggested guidelines.

TABLE 7 CORROSION FATIGUE STRENGTH (	CFS) OF	VARIOUS MATERIALS	IN SEA WATER
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Material	Nominal Compositions Major Alloying Constituents (weight percent)	Ultimate Tensile Strength (ksi)	CFS at 100 Megacycles in Sea Water (ksi)
Inconel* alloy 718 (grain size = 0.01 mm)	Ni-19Cr-17Fe-5Cb-3Mo-0.8Ti-0.6Al	189	60
Inconel allov 718 (grain size = $0.068$ mm)	NI-19Cr-17Fe-5Cb-3Mo-0.8TI-0.6AI	189	40
Inconel allov 625	NI-21Cr-9Mo-3.6(Ta+Cb)-2.5Fe	129	40
Inconel alloy 718 (grain size $= 0.152$ mm)	NI-19Cr-17Fe-5Cb-3Mo-0.8TI-0.6AI	-	32
Monel* alloy K-500	NI-29Cu-3AI-1Fe-0.7Mn-0.6TI	176	26
Incoloy* alloy 800	Fe-32NI-21Cr-0.4TI-0.4AI	89	24
18 percent Ni maraging steel (cathodic protection at -0.85 v)	Fe-18Ni-7Co-5Mo-0.4Ti	250	15
Ni-Al bronze, ASTM-955 (cast)	Cu-11AI-4Ni-4Fe	115	15
AISI Type 304 stainless steel	Fe-19Cr-10NI-2Mn-0.08C	79	15
AISI Type 316 stainless steel	Fe-18Cr-12NI-2Mn-2.5Mo-0.08C	85	14
AISI Type 304L stainless steel	Fe-19Cr-10NI-2Mn-0.03C	75	14
AISI Type 316L stainless steel	Fe-18Cr-12Ni-2Mn-2.5Mo-0.03C	79	13
Ni-Al bronze (cast)	Cu-10AI-5Ni-5Fe-1.5Mn	87	12.5
Mn-Ni-Al bronze (cast)	Cu-12Mn-8AI-3Fe-2Ni	100	9
Mn bronze (cast)	Cu-40Zn-2Mn	73	8
18 percent maraging steel (unprotected)	Fe-18NI-7Co-5Mo-0.4Ti	250	5
Mild steel		60	2
*Trademark of Huntington Alloys, Inc.			

1. The AISI 300 stainless steels may undergo deep localized crevice corrosion in mechanical crevices or under deposits in quiescent sea water. The difference in performance of the various grades of Type 300 stainless steels under these circumstances is not of practical significance.

2. In view of deep localized attack, published average corrosion-rate data calculated from weight loss, area, and time are very misleading.

3. The AISI 400 series stainless steels not only suffer deep crevice corrosion in quiescent sea water, but most often display pitting even in high-velocity sea water in the absence of deposits.

4. In quiescent sea water, the austenitic stainless steels can be cathodically protected very effectively with iron, zinc, aluminum, and magnesium anodes or by an impressed current system.

5. The iron or steel anode is very effective in reducing crevice-type corrosion of austenitic stainless steel. Research work in defining current density, velocity effects, geometry of crevices, and anode life for steel anodes would reduce the problem of over-design as is now the practice.

6. In quiescent sea water, when applications cannot rely on cathodic protection, the more highly alloyed stainless steels, containing higher levels of nickel, molybdenum, and/or copper or the nickelchromium-molybdenum alloys with very high levels of corrosion resistance, are indicated.

7. High-velocity, turbulent sea water with sufficient agitation to keep austenitic stainless steels free of deposits, either biological or inorganic, permit stainless steel to remain passive and corrosion-free.

8. Chloride stress corrosion cracking is not a problem in ambient temperature sea water.

9. Intergranular corrosion of sensitized austenitic stainless steels has been observed in sea water. The usual precautions of specifying low-carbon or stabilized grades for welding and adequate solution annealing for castings is advisable.

10. The corrosion fatigue properties of austenitic

stainless steels are only moderate.

Conservatism in design loads and reasonable attention to good mechanical design is suggested.

#### REFERENCES

- 1. Metals Handbook, 8th ed., American Society for Metals, Metals Park, Ohio (1961) Vol. 1, 432-443, 559.
- "Heat Resistant Castings Corrosion Resistant Castings," International Nickel Co., Inc., New York (1968).
- 3. Fontana, M. B. and Green, N. D.: Corrosion Engineering, McGraw-Hill Book Co., Inc., New York (1967) 39-44.
- 4. Uhlig, H. H.: Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering, John Wiley & Sons, Inc., New York (1963).
- 5. Ellis, O. B. and LaQue, F. L.: "Area Effects in Crevice Corrosion," Corrosion (Nov. 1951) 362.
- Alexander, A. L., Southwell, C. R., and Ferguson, B. W.: "Corrosion of Metals in Tropical Environments," *Corrosion* (July 1961) 345.
- "Corrosion Resistance of the Austenitic Chromium-Nickel Stainless Steels in Marine Environments," International Nickel Co., Inc., New York (1963).
- Henthorne, M.: "Corrosion of Resulfurized Free-Machining Stainless Steels," Corrosion (Dec. 1970).
- 9. Peterson, M. H. and Lennox, T. J., Jr.: "The Corrosion Behavior of Stainless Steels in Seawater," Naval Research Laboratory Memorandum Report (June 1967) 1795.
- Huston, K. M. and Teel, R. B.: "Some Observations of the Potentials of Stainless Steels in Flowing Seawater," Corrosion (July 1952).
- 11. Anderson, D. B.: "Statistical Aspects of Crevice Corrosion in Sea Water," *Proc.*, ASTM Symposium on Pitting Corrosion (Oct. 1974).
- 12. Tuthill, A. H. and Schillmoller, C. M.: "Guidelines for the Selection of Marine Materials," International Nickel Co., Inc., New York.
- Lennox, T. J., Jr., Peterson, M. H., and Groover, R. E.: "Marine Corrosion Studies," NRL Memorandum Report (1948).
- 14. Private communication: D. A. Reedy, Metropolitan Water District of Southern California.

- Kerr, S. L.: "Determination of the Relative Resistance to Cavitation Erosion by the Vibratory Method," *Trans.*, ASME (July 1937).
- Phelps, E. H. and Loginow, A. W.: "Stress Corrosion of Steels for Aircraft and Missiles," *Corrosion* (1960) 325.
- Logan, H. L. and McBee, M. J.: "Stress-Corrosion Cracking of Cold-Reduced Austenitic Stainless Steels," Materials and Res. Standards (Aug. 1963).
- 18. "Intergranular Corrosion of Chromium-Nickel Stain-

less Steels," Bull. 138, Welding Research Council (Feb. 1969).

- Sedriks, A. J. and Money, K. L.: "Corrosion Fatigue Properties of Nickel-Containing Materials in Sea Water," P-BL 240, International Nickel Co., Inc., New York.
- 20. "Selection of Metallic Materials to be Used in All Phases of Water Handling for Injection Into Oil-Bearing Formations," NACE Standard RP-04-75, National Association of Corrosion Engineers, Houston.

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