Focus on Seawater Corrosion

Guidelines for the use of copper alloys in seawater☆

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> *Users and designers have found the charts and data summaries in an earlier work, "Guidelines for Selection of Marine Materials," helpful in selecting materials for marine service. This review updates and extends those summaries for copper-base alloys, many of which were not included in the earlier work.*

Introduction

THE ENGINEER USUALLY BEGINS WITH a good idea of alloys that will meet the stresses and mechanical requirements of the assembly under consideration. The author's purpose is to provide guidelines that will allow the engineer to make a reasonable estimate of the effect of the environment on the performance of copper alloys. The charts and summaries provide useful guideposts, but they can never replace the experience, specific data, or properly conducted evaluations so necessary to the successful use of materials. Temperature and pH values that are normal for the waters and usage under consideration are assumed.

The principal constituents of water that affect the performance of copper alloys are dissolved oxygen, nutrients, bacteria, biofouling, organisms, sediment, trash, debris, and residual chlorine from the chlorination practice. Dissolved oxygen is usually reported in standard water analyses. Although the nature of sediments, bacteria, nutrients, biofouling organisms, debris, or chlorine present are often critical to performance, information on these important constituents is seldom included in water analyses and must be sought elsewhere.

Protective film formation

The corrosion resistance of copper and copper-base alloys in seawater is determined by the nature of the naturally occurring and protective corrosion product film. North and Pryor found the film to be largely cuprous oxide (Cu_2O), with cuprous hydroxychloride [$Cu_2(OH)_3Cl$] and cupric oxide (CuO) being present in significant amounts on occasion.[1] These studies indicated corrosion product film thicknesses to range from 2800 Å for copper to 4400 Å for Alloy C70600 (90:10 copper-nickel). The film is adherent, protective, and generally brown or greenish-brown in color.

The corrosion product film forms very quickly when clean; unfilmed copper or copper alloys are first wetted by seawater. The

rate of film formation is indicated as the rate of copper reduction in the effluent (Figure 1). Total copper decreases tenfold within 10 min and 100-fold in the first hour. In three months, copper in the effluent is seen to be virtually at the level of the copper in the intake water.

Weight loss corrosion studies show that the protective film continues to improve, with the corrosion rate dropping to 0.5 mpy (0.012 mm/y) in ~1 y, and a long-term, steady-state rate of ~0.05 mpy (0.001 mm/y) in 3 to 7 y in quiet, tidal, and flowing seawater (Figure 2).[2] Alloy C71500 (70:30 copper-nickel) exhibits the same pattern of decreasing corrosion rate with time.

Reinhart found that copper and its alloys of aluminum, silicon, tin, beryllium, and nickel had significantly *lower* long-term corrosion rates after 18 months compared to those specimens measured after only 6 months of exposure to seawater (Figure 3).[3] The only exception was Alloy C28000, Muntz metal, which exhibited a slightly higher corrosion rate after 18 months as compared to 6 months. Alloy C44300, Admiralty, was in the group characterized by a decreasing corrosion rate with time. The long-term, steady-state corrosion rate for copper and copper alloys, except for Muntz metal, is on the order of 1 mpy (0.025 mm/y) or less, and for the copper-nickel alloys on the order of 0.05 mpy (0.001 mm/y), within those velocities that each alloy can tolerate without damage to the protective corrosion product film.

Data from short-term (less than 1 y) corrosion tests on copper alloys in seawater, while useful for certain alloy-to-alloy comparisons in research investigations, can be very misleading if they are used to estimate service life. Short-term data tend to underestimate long-term durability. *Only the long-term, steady-state corrosion rate can be used to provide reasonable service life projections for copper alloys.* Table 1 lists the copper-base alloys commonly used in marine service.

Effects of velocity

Seawater moving over a surface creates a shear stress between that surface and the layer of seawater closest to the metal surface. As velocity increases, the shear stress increases until it strips away the protective film on copper and copper alloys.

Efird studied and estimated the critical shear stress for C12200, C68700, C70600, C71500, and C72200 (Table 2).[4] Figure 4 shows how the critical shear stress varies with velocity and pipe (or tube) diameter. The shear stress in 1-in. (25-mm) diameter pipe at 10 fps (3 m/s) is no greater than that in 12-in. (305-mm) diameter pipe at 12 fps (3.7 m/s) or that in 10-ft (3-m) diameter pipe at 16 fps (4.9 m/s). As the diameter increases, copper-base alloys will tolerate higher nominal velocities in the piping system.

Sato and Nagata showed that the shear stress at the inlet end condenser tube is about double that further down the tube (Figure
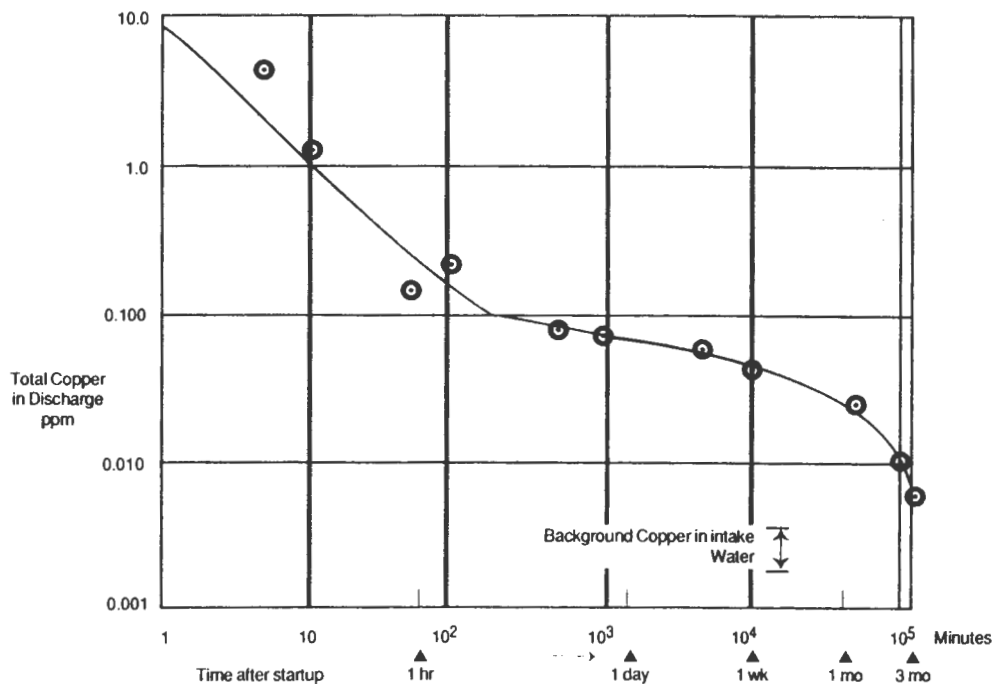
FIGURE 1—Formation rate of corrosion product film on Alloy C70600 in seawater.
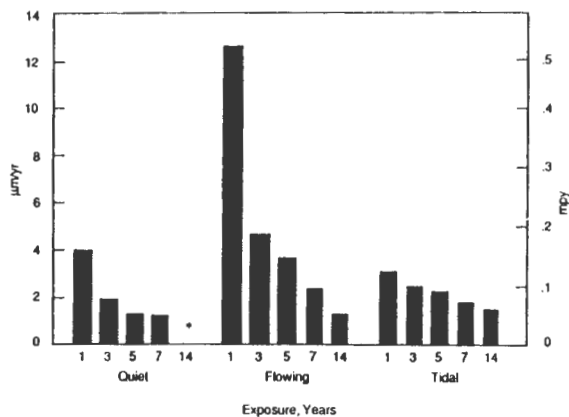

FIGURE 2—Corrosion rates for Alloy C70600 for long-term seawater exposures.

5).[5] These data explain why inlet-end erosion/corrosion is such a common occurrence and also explain the preference for the copper-nickel that have been developed because of their greater velocity tolerance. Sato and Nagata also showed that water velocity passing a partial obstruction in the bore of a condenser tube can reach 26 fps (8 m/s), even though the overall velocity remains in the normal 6.6 fps (2 m/s) range. This explains the occurrence of tube failures downstream of lodgements in condenser tubes when using debris-laden water.

Ferrara and Gudas studied the effect of velocity by mounting flat bars on a rotating disc.[6] When tested in this manner, C70600 exhibited a significantly lower corrosion rate than C71500 at peripheral velocities of 26 to 29 fps (7.9 to 8.8 m/s). Ferrara and Gudas found similar relationships in other tests in which high-velocity seawater was allowed to flow over the top and bottom surfaces of flat specimens, a *parallel flow test*. Although the 70:30 copper-nickel alloy has somewhat greater resistance to inlet-end erosion/corrosion

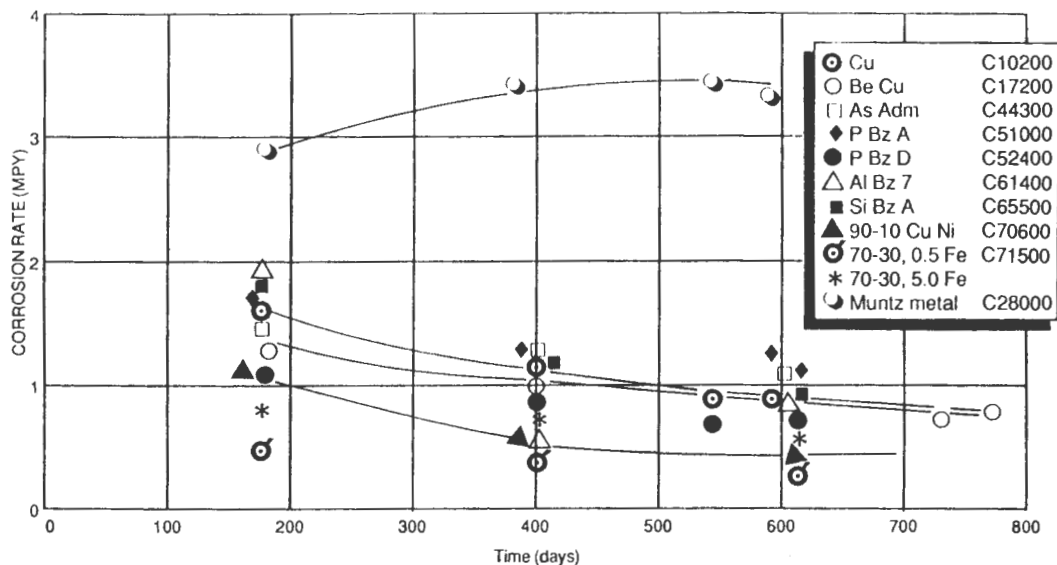|		
⊙ Cu	C10200
○ Be Cu	C17200
⊓ As Adm	C44300
♦ P Bz A	C51000
● P Bz D	C52400
△ Al Bz 7	C61400
■ Si Bz A	C65500
▲ 90-10 Cu Ni	C70600
♂ 70-30, 0.5 Fe	C71500
✳ 70-30, 5.0 Fe	
☾ Muntz metal	C28000

FIGURE 3—Corrosion rates for copper alloys for up to 800-day seawater exposures.

TABLE 1 — Principal copper alloys used in substantial tonnages in marine and marine-related service

Wrought

Copper alloy	Number	Principal uses
DHP copper	C1220	Hull sheathing. piping
PDO copper	C14200	Hull sheathing. piping
Beryllium copper	C17000	Undersea telephone cable repeater housings
Cartridge or 70:30 brass	C26000	Hardware components
Muntz metal	C28000	Tubesheets
Admiralty, arsenical	C44300	Heat exchanger tubing
Naval brass, arsenical	C46500	Tubesheets
Phosphor bronze	C51000	Bolting, boat shafting, marine wire rope, naval ordnance
Phosphor bronze	C52400	Naval ordnance
Aluminum bronze	C61400	Power plant and offshore oil piping
	C61300	and waterboxes
NiAl bronze	C63000	Pump shafts, valve stems (Navy)
	C63200	
Silicon bronze	C65500	Bolting
Aluminum brass	C68700	Condenser and heat exchanger tubing
Copper-nickel	C70600	Condenser and heat exchanger tubing. piping and waterboxes—shipboard. power, industrial and desalination plants, waterflood and offshore oil
Copper-nickel	C71500	Condenser and heat exchanger tubing. piping and waterboxes—shipboard. power, industrial and desalination plants, waterflood and offshore oil
Copper-nickel	C72200	Condenser and heat exchanger tubing

Cast alloys

Ounze metal	C83600	Plumbing fittings
Manganese bronze	C86500	Ship propellers
G Bronze	C90300	Pumps, valves, naval ordnance, Tailshaft sleeves
M bronze	C92200	Pumps, valves
Al bronze	C95200	Waterflood and seawater pumps
NiAl bronze	C95500	Propellers
NiAlMn bronze	C95700	Propellers
NiAl bronze	C95800	Pump, valves and fittings. ship propellers
Copper-nickel (80:20)	C96300	Tailshaft sleeves for ships
Copper-nickel (70:30)	C96400	Pumps. valves, fittings

TABLE 2 — Critical shear stress for copper-base alloys in seawater—Efird[4]

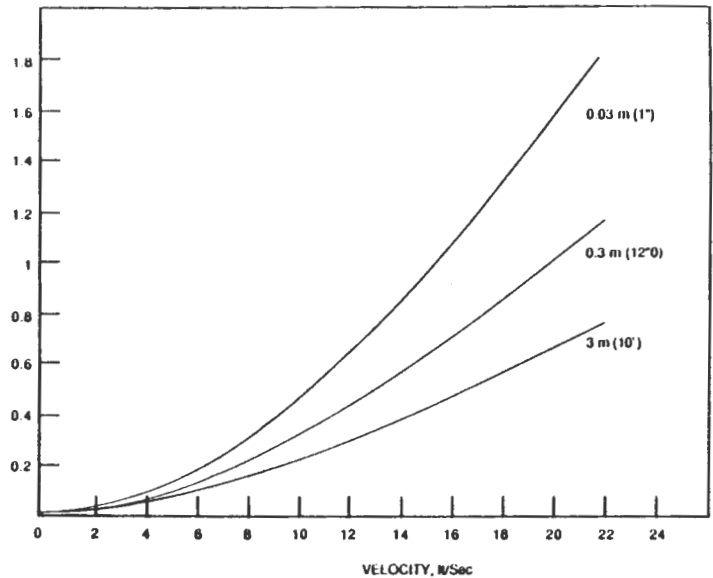| Alloy	Critical shear stress N/m² (lbf/ft²)
CA 122	9.6 (0.2)
CA 687	19.2 (0.4)
CA 706	43.1 (0.9)
CA 715	47.9 (1.0)
CA 722	296.9 (6.2)

FIGURE 4—Variation in shear stress between the flowing seawater and metal wall with the nominal velocity in the pipe and diameter of the pipe.
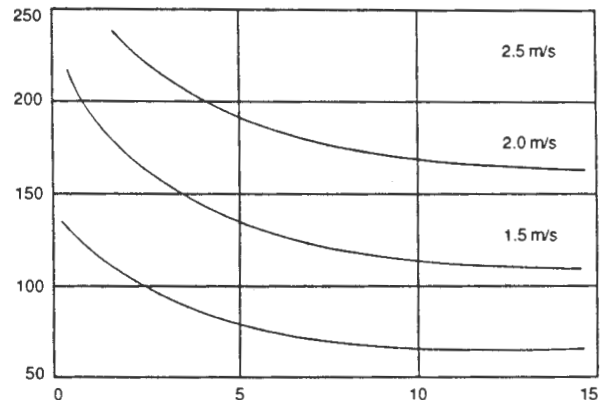

FIGURE 5—Variation of shear stress between the flowing seawater and metal wall with the distance from the inlet end.

based on alloy resistance to flow as indicated by velocity test data and service experience.

in condensers and heat exchangers, 90:10 copper-nickel is more resistant at the higher velocities encountered by ship hulls.

The British Nonferrous Metals Research Association impingement test uses a jet of highly aerated seawater directed normal to the specimen surface and has been widely used to study velocity effects and to rank the velocity resistance of materials. The results are expressed in terms of weight loss and as maximum depth of impingement attack. The results of a 60-day test at a jet velocity of 25 fps (7.6 m/s) are shown in Figure 6.[6] In this test, 90:10 copper-nickel had a lower weight loss and less depth of penetration than 70:30 copper-nickel.

The results of these different testing methods, while useful for ranking alloys, are difficult to apply directly to pumps, propellers, and piping. Table 3 has been prepared to assist designers in selecting copper alloys for condensers, heat exchangers, and piping applications. Table 4 can be used in selecting pump and propeller materials

Cavitation

With the high flow velocities found in some high-speed pumps and at the periphery of large ship propellers, pressure differentials sufficient to create momentary cavities in the seawater between leading and trailing surfaces are sometimes encountered. These cavities collapse, setting up a hammering action and fatigue stresses in the surface of the metal on the trailing or low-pressure side. The occurrence of cavitation is strongly influenced by the manner in which the flow is directed over the leading and trailing surfaces, by slight changes in the contour of the surfaces, and by the direction of water flow and velocity.

Cavitation tests are valuable for the specific condition under investigation, but are difficult to apply to other applications. Table 5 from Tuthill and Schillmoller groups a number of alloys in terms of their relative resistance to cavitation damage in seawater.[7] The more resistant copper alloys are in Group 2 and the less resistant in Group 3.

TABLE 3 — Velocity guidelines for copper alloys in seawater

Condensers and heat exchangers
Minimum velocity—any tube, any alloy, 3 fps (0.9 m/s)

Comment: It is necessary to keep the minimum velocity in any tube above 3 fps (0.9 m/s) at the lowest heat transfer demand anticipated so that sediment and particulate matter will be swept through and not deposited in the tube. Unremoved sediment reduces heat transfer and in time can lead to under sediment corrosion.

Maximum velocity—fps (m/s), average

	CA68700	CA70600	CA71500	CA72200
Once through	6.5 (2.0)	7.5 (2.3)	9.5 (2.9)	10 (3.1)
Two pass	5.5 (1.7)	6.5 (2.0)	8 (2.4)	10 (3.1)

Comment: Once the corrosion product film is fully formed (2 to 4 weeks), somewhat higher velocities can be tolerated for short periods not exceeding 15% of total operating time.

The water box and the return head of two pass units must be designed so that the flow in any tube is within 25% of the average flow for the unit. In smaller heat exchangers, the waterbox and return head may require extra volume to provide good flow distribution to all tubes.

Piping
Nominal velocity—fps (m/s)

	CA70600	CA71500
3-in. (76-mm) diameter and smaller	5 (1.5)	6 (1.8)
4- to 8-in. (101- to 203-mm) diameter with short radius bends	6.5 (2.0)	7.5 (2.3)
4-in. (101 mm) and larger with long radius bends and 8 in. (203 mm)	11 (3.35)	12 (3.7)

Note: Higher velocities can be tolerated in fresh waters, but the minimum remains the same.

Stagnant water

Avoid stagnant conditions. Flush, drain, and blow dry for extended standby. Circulate frequently if full.

TABLE 4 — Velocity guidelines for copper alloys in pumps and propellers—seawater

Peripheral velocity—fps (m/s)	Copper alloys
30 (9.1)	C83600 C87600
35 (10.7)	C90300 C92200
50 (15.2)	C95200 C86500
775 (22.9)	C95500 C95700 C95800

TABLE 5 — Order of resistance to cavitation damage in seawater—Tuthill and Schillmöller[7] [1]

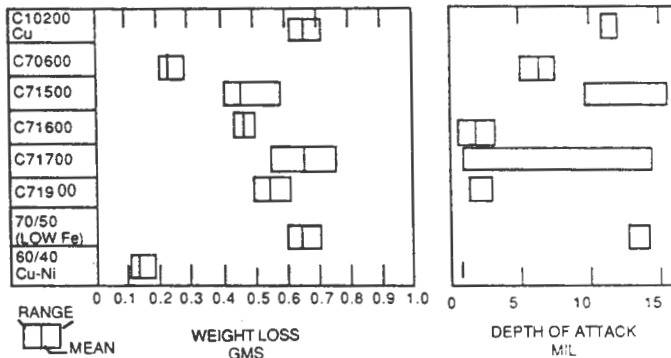| Resistance to cavitation damage rating	Metals
Group 1—Most resistant. Little or no damage. Useful under supercavitating conditions.	Cobalt-base hard facing alloy Titanium alloys Austenitic (AISI series 300) and precipitation-hardened SSs Nickel-chromium alloys such as Alloys 625 and 718 Nickel-molybdenum-chromium Alloy C
Group 2—These metals are commonly used 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 3—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 4—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

[1] At normal cavitation erosion intensities where inherent corrosion resistance influences resistance to cavitation.

Aluminum bronze and nickel-aluminum bronze alloys display outstanding resistance to cavitation, especially Alloy C95500 (Mil B 21230[1] Alloy 1), the principal, high-performance, propeller alloy for naval and merchant ships. Although the aluminum bronzes fall into Group 2 in Table 5, they closely approach the cavitation resistance of the alloys in Group 1. The Group 3 alloys, while still useful in applications in which cavitation may be encountered, do suffer substantial damage if cavitation prevails.

Corrosion fatigue

Corrosion fatigue strength (CFS) is commonly defined as the

FIGURE 6—Weight loss and depth of attack on copper alloys in BNRMRA jet impingement tests.

[1] Military specification.

TABLE 6 — Corrosion fatigue strength of propeller alloys in seawater— Metals Properties Council—Prager[8]

| Cast alloy | Corrosion fatigue strength[1] | |
	(psi)	(MPa)
C86500 ABS Type 2	9000 + 20%	62 + 20%
C95500 ABS Type 4	14,000 + 20%	96 + 20%
C95700 ABS Type 5	12,000 + 20%	83 + 20%

[1]These corrosion fatigue strengths were measured at 10^8 cycles and zero mean stress and must be reduced when mean tensile stresses are substantial.

fatigue strength at 10^8 cycles at zero mean stress. CFS should not be regarded as a true endurance limit, since failure may occur at lower stresses at greater than 10^8 cycles. Ship propellers, deep diving submersibles, undersea equipment, and certain pumps are subject to corrosion fatigue.

Ship propeller alloys

The thickness of large ship propeller blades at one-fourth to one-third the distance to the tip is 10 to 16 in. (254 to 406 mm) and is where fatigue loadings are greatest. Castings of this thickness generally cool very slowly, resulting in larger grain sizes and lower tensile properties than the smaller separately cast *test keel blocks* used for mechanical property determinations. Thus, the properties determined on keel blocks cannot be used directly for design purposes.

The outer surface layers of the propeller blade, which cool faster and have somewhat better properties than the interior, are removed in the grinding and polishing operations essential to obtaining requisite propeller surface finish. Porosity and other casting defects uncovered in the grinding and polishing operation must be held to a minimum, but they still contribute to some of the variations in measurement of the CFSs and in propeller performance. The CFSs of large, slowly cooled propeller alloy castings were determined in a Metals Properties Council program and are given in Table 6.[8] Since these CFSs were measured at zero mean stress, they must be adjusted downward when the mean tensile stresses are substantial.

Pump, piping, and heat exchanger alloys

CFS is an important characteristic of both cast and wrought alloys used in pumps, piping, and heat exchangers in deep diving submersibles, undersea equipment, and certain oil production activities. Much of this equipment is subject to low-cycle fatigue that can occur with repeated deep dives or repeated lowering of instruments to great depths, as well as to high-cycle fatigue associated with rotating machinery. Unlike propellers, this equipment is fabricated from wrought alloys as well as cast materials. Low-cycle fatigue strengths for copper alloys from the work of Czyryca and Gross are plotted in Figure 7.[9] Unlike high-cycle fatigue, in which seawater reduces the fatigue strength as measured in air, no significant difference in low-cycle fatigue behavior between air or seawater was found.

Galvanic behavior of copper and copper-base alloys

Copper and copper-base alloys occupy a useful mid-position in the galvanic series—more noble than steel, cast iron, NiResist, aluminum, and zinc; and less noble than stainless steel (SS), titanium, and nickel-base alloys. The corrosion potential of copper in flowing seawater is ~-0.33 V; nickel-aluminum bronze (the most noble) is -0.18 V; and aluminum bronze (the least noble) is -0.36 V SCE (saturated calomel electrode).

In addition to the corrosion potential, the effective cathode-to-anode area ratio and the amount of oxygen available at the cathodic surface have a pronounced effect on galvanic corrosion. The larger the effective cathode-to-anode area ratio and the more oxygen available at the cathode, the greater the galvanic effect will be. To a lesser extent, temperature and other chemical species present also effect galvanic behavior.

Scholes and Rowland reported the acceleration in corrosion resulting from galvanic coupling of a variety of materials.[10] The portion of their chart dealing with copper-base alloys is shown as Table 7. Most copper alloys can be coupled to each other without greatly accelerating the corrosion that would otherwise occur in the absence of coupling. Nevertheless, better performance and longer service life will be obtained if the copper alloy condenser tubing is more noble than the tubesheet and waterbox, if pump impellers are more noble than the case, and if valve seats are more noble than the body.

Some condensers have been retubed with highly alloyed SS or titanium tubing while still retaining the original copper alloy tubesheet. Other new condensers have used aluminum bronze tubesheets with titanium tubes. The severe tubesheet corrosion that followed led to studies that showed that the effective cathodic area was many times larger than had been supposed, approaching a 1000:1 cathode-to-anode ratio.[11] Copper alloy tubesheets require a carefully designed cathodic protection system when using titanium or SS tubes.

It has been the practice in the US to use C83600, C90300, and C90500 pumps and valves in C70600 piping systems because of their wide availability. Although these materials are less noble than the C70600 piping, they perform reasonably well. SS or titanium pumps and valves may be used in copper alloy piping systems since the cathodic area is small in relation to the piping. Although metal loss will increase somewhat in the piping, this has generally been tolerable. Copper alloy pumps and valves in SS or titanium piping systems would have difficulty in forming a good protective film and are not suggested for such service.

Effect of sulfides

In considering the effect of sulfides, it is useful to distinguish several conditions: (1) exposure to polluted sulfide waters during ship outfitting and extended power plant start-up periods; (2) exposure to sulfides in well-aerated waters in which sulfides may occur temporarily during dredging, red tides, or other transitory, nonequilibrium conditions; (3) exposure to sulfides generated by sulfate-reducing bacteria beneath sediment and other deposits that are allowed to remain unremoved in tubing; (4) long-term presence of sulfides in polluted waters; and (5) alternate exposure to aerated and sulfide-containing waters as occurs with each change of tide at some power plants.

Syrett noted that sulfides in saline waters are not particularly detrimental to copper alloys unless dissolved oxygen is also present or unless exposure to oxygen-free, sulfide-polluted waters is followed by exposure to aerated, unpolluted waters. The author found that in the complete absence of oxygen, corrosion rates remained low up to sulfide concentrations as high as 55 g/m^3 and at flow velocities up to 5 m/s. The corrosion rate remains low in the absence of oxygen, despite the more active potential, since the only cathodic reaction is hydrogen reduction (Point 1, Figure 8). In polluted waters with both oxygen and sulfide present, the cathodic reaction reverts to oxygen reduction with a much higher corrosion rate, as indicated by the large increase in current despite the more noble potential (Point 2, Figure 8). The potential at Point 2 is somewhat below that at which a stable cuprous oxide film can form, thus permitting the high corrosion rate to persist until either the oxygen or sulfide is consumed in the corrosion process.

Syrett also showed that the typical black sulfide film that forms during exposure to sulfide-polluted seawater will eventually be replaced by a normal oxide film when the sulfide-polluted seawater is replaced by clean, aerated seawater. However, substantially higher corrosion rates persist for some time during the transition period. These conditions commonly arise when vessels are fitted out in polluted harbors and later operate in the open sea. Experience indicates that once the vessel begins regular operation, the normal

TABLE 7 — Acceleration of the uncoupled corrosion rate of the anodic material for copper or carbon steel coupled to material "M" in flowing seawater after 1-y immersion—Scholes and Rowland[10]

Coupled material (M)	Uncoupled corrosion rate—1 y (mm/y)	Acceleration factors					
		Copper (Cu)			Mild steel		
		10:1 M	1:1 M	1:10 M	10:1 M	1:1 M	1:10 M
Zinc	0.05	20	10	3	20	10	3
N34 aluminum	0.01	100	20	2	80	20	2
Mild steel	0.13	7	3	1	1	1	1
HY80	0.10	7	3	1	1 MS	2 MS	3 MS
Ni-Resist Type D2[1]	0.15	7	3	1	1 MS	2 MS	3 MS
Tin	0.03	3	2	1	1 MS	2 MS	3 MS
Lead	0.01	25	8	1[2]	1 MS	2 MS	3 MS
Naval brass[3] C46500	0.04	2	2	1	1 MS	3 MS	7 MS
Aluminum brass C61400	0.01	2	2	1	1 MS	3 MS	7 MS
Aluminum bronze[3] (10% Al) C61800	0.02	2	2	1 CU	1 MS	3 MS	7 MS
Silicon aluminum bronze[3]	0.015	1	1	1	1 MS	3 MS	7 MS
Nickel aluminum bronze[3] C95800	0.015	1 CU	2 CU	1 CU	1 MS	3 MS	7 MS
Silicon bronze C6550	0.035	1 CU	1 CU	1 CU	1 MS	3 MS	7 MS
Copper C11000	0.03	1	1	1	1 MS	3 MS	7 MS
Phosphor bronze (3% Sn) C51000	0.02	1 CU	2 CU	1 CU	1 MS	3 MS	7 MS
Phosphor bronze (10% Sn) C52400	0.02	1 CU	2 CU	1 CU	1 MS	3 MS	7 MS
Gun Metal C90300	0.035	1 CU	1 CU	1 CU	1 MS	3 MS	7 MS
90:10 Cupro-nickel (1% Fe) C70600	0.02	2	2	2	1 MS	3 MS	7 MS
70:30 Cupro-nickel (1% Fe) C71500	0.02	1 CU	1 CU	2 CU	1 MS	3 MS	7 MS
TN732 Cupro-nickel C71900	0.02	1 CU	1 CU	2 CU	1 MS	3 MS	7 MS
Inconel 625	0.005	1 CU	1 CU	10 CU	1 MS	3 MS	7 MS
Monel 400[4]	0.003	1 CU	1 CU	10 CU	1 MS	3 MS	7 MS
AISI 316 SS[4]	0.005	1 CU	2 CU	10 CU	1 MS	3 MS	7 MS
Titanium	0.001	1 CU	5 CU	10 CU	1 MS	2 MS	5 MS
Carbon	—	1 CU	8 CU	40 CU	2 MS	4 MS	10 MS

[1]Materials in wrought form except cast form.
[2]Results based on 100-h tests for materials that can undergo polarity reversals.
[3]Acceleration factors subject to changes resulting from variable complex microstructure. CU and MS indicate that coupling with M accelerates corrosion of copper (CU) or mild steel (MS) rather than material (M).
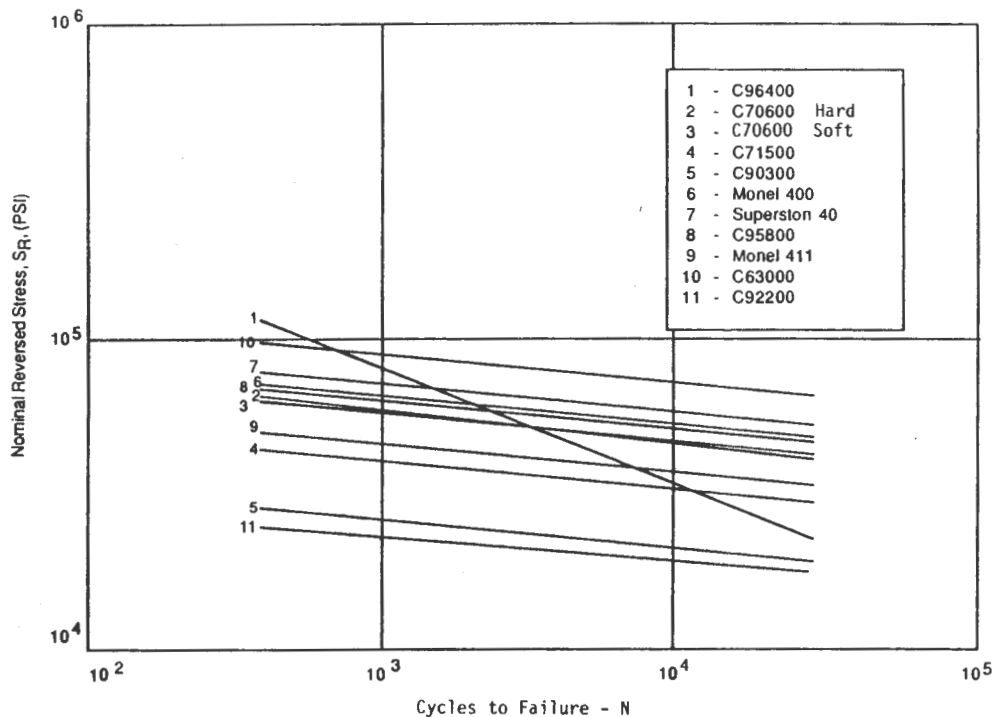[4]These materials are subject to crevice corrosion.

FIGURE 7—Low-cycle fatigue of nonferrous alloys.

$Cu \rightarrow Cu^{++}_{sol} + 2e^-$

$(O)_2 + H_2O + 2e^- \rightarrow 2OH^-$
$(O)1 + H_2O + 2e^- \rightarrow 2OH^-$

$Cu \rightarrow Cu^+$ (oxide) $+ e^-$

$Cu \rightarrow (Cu^+_{sol})_2 + e^-$

$Cu \rightarrow (Cu^+_{sol})_1 + e^-$
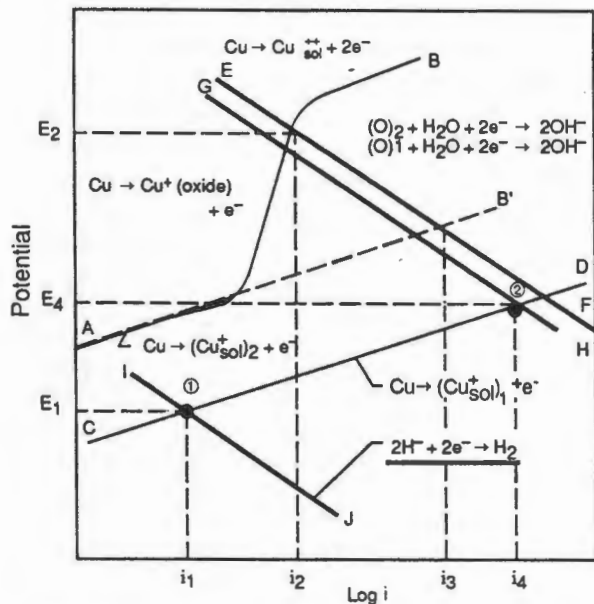
$2H^- + 2e^- \rightarrow H_2$

Potential

Log i

FIGURE 8—Influence of sulfide and oxygen on the corrosion current in a copper-nickel alloy exposed to flowing seawater.

protective film forms and persists during subsequent harbor visits. Syrett found that the normal protective film replaced the sulfide film in ~9 days.

Some coastal power plants have encountered sulfide corrosion problems during extended start-up periods when little or no attention was given to condenser lay-up procedures when the unit went down. Once the condenser was again placed in operation, a normal film gradually replaced the sulfide film. When properly done, chemical cleaning with inhibited hydrochloric acid removes the sulfide film and expedites formation of the protective film.

Coping with sulfides

Start-up periods: Keep the seawater circulating. Aerate and keep the pH neutral or above. Drain and air-blow dry for standby periods of more than 3 to 4 days.

Transitory sulfides in normally aerated waters: Eliminate the source of sulfides. Return to normal clean water operation as soon as possible. Normal vessel turnaround times in polluted harbors are routine and have seldom led to significant corrosion problems.

Unremoved deposits: Clean on a regular schedule by water flushing, water lacing, and/or shooting with nonmetallic brushes to remove deposits, restore heat transfer, and prevent corrosion under the sediment. Cleaning intervals of 2 to 6 months are normal.

Long-term exposure to deaerated sulfide-containing waters: Not generally recommended.

Alternate exposure to sulfide-polluted and aerated waters: Where occurring daily with tide changes, copper alloys are not recommended. Where alternative exposure seldom occurs, the film formed on the tubes during normal operation provides adequate protection to all but the most prolonged exposures.

Marine biofouling

Biological organisms abound in the open sea, coastal estuaries, and rivers. They are found on piers and pilings, boat hulls, offshore oil platforms, other marine structures, and within piping and condensers. Copper and copper alloys are more resistant to the attachment of biofouling organisms than steel and most of the other common materials of construction. Efird documented the resistance of C70600 to biofouling in quiet seawater over an 18-month period, as shown in Figure 9.[13] In the absence of wave action or velocities above 0.5 fps (0.15 m/s), the slime layer gradually thickens to the point at which biofoulers begin to attach to the thick slime layer after ~18 months. With the wave action on offshore platforms or with normal flow velocities in cooling water systems, the slime layer never reaches a thickness that permits biofouler attachment.

The normal condition of copper alloy surfaces in seawater is illustrated by the clean condition of the C70600 hull of the copper mariner after 52 months of sea time, as shown in Figure 10. A few pin head-size barnacles have been able to attach, but most have been removed by wave action underway. Those remaining could be removed easily by finger pressure. Operation had kept the hull almost as clean and smooth as it was originally. It is both the inherent resistance to biofouler attachment and the poor adherence of the occasional biofouler able to attach that made copper so useful as hull sheathing for sailing vessels and copper-nickel so useful for the piping, water boxes, and other components of marine cooling water systems.
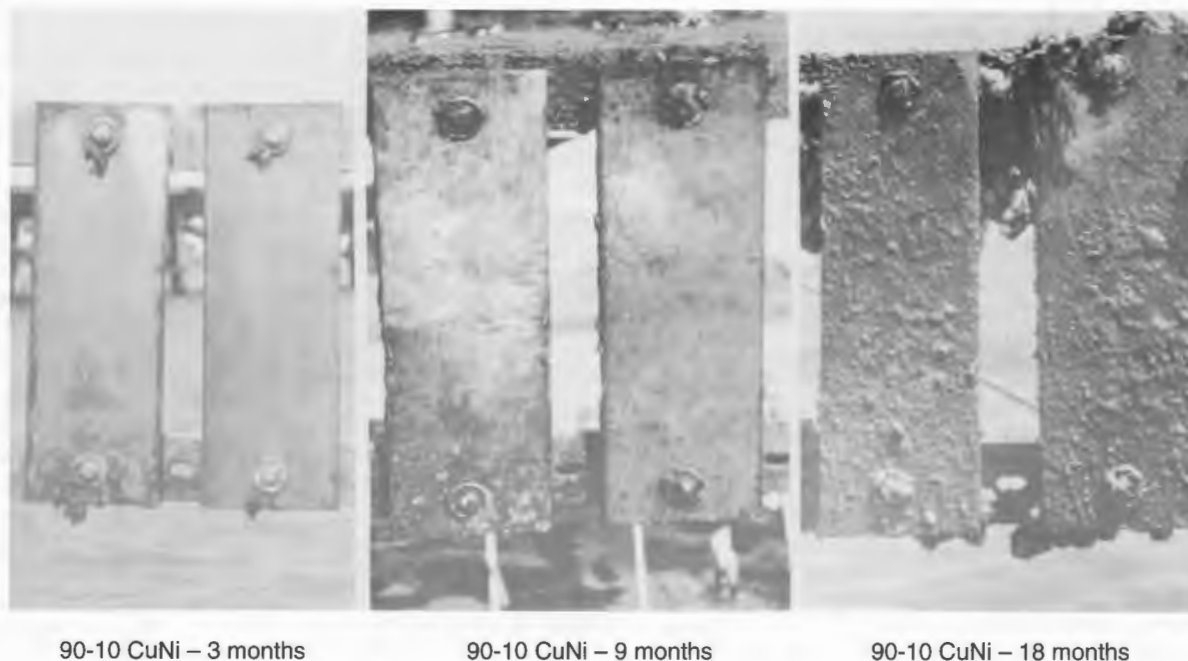

90-10 CuNi – 3 months   90-10 CuNi – 9 months   90-10 CuNi – 18 months

FIGURE 9—Progression of biofouling from 3 to 18 months on Alloy C70600 in seawater.

FIGURE 10—Small barnacles at the waterline on the bow area of Copper Mariner after 52 months of sea time.

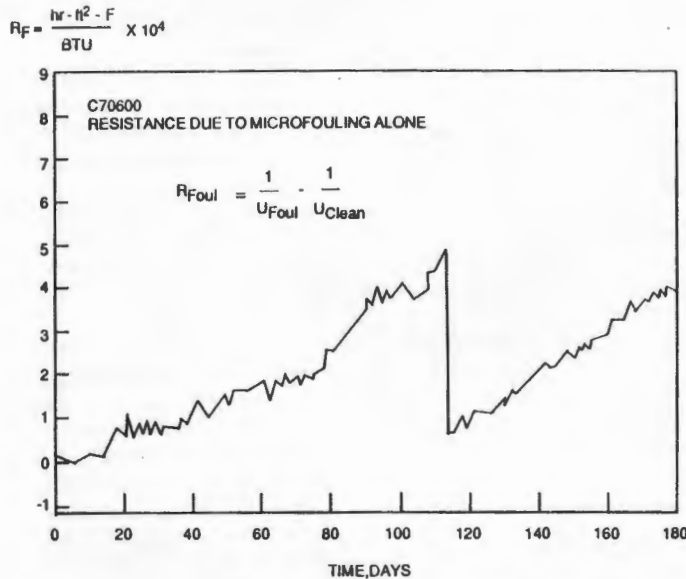$$R_F = \frac{hr \cdot ft^2 \cdot F}{BTU} \times 10^4$$

FIGURE 11—Resistance of Alloy C70600 to heat transfer resulting from the growth of a microfouling film on the inside wall of tube in clean seawater.

Copper alloys are also resistant to the microfouling that occurs within condenser and heat exchanger tubing. Lewis measured the time required for microfouling to significantly reduce the heat transfer of C70600 tubing in clean seawater at 6 to 8 fps (1.8 to 2.4 m/s) over a 180-day period (Figure 11).[14] While not immune to microfouling, the indicated 90- to 110-day interval between cleaning for C70600 is an order of magnitude greater than the 10-day cleaning interval found necessary for other than copper alloy condenser tubing in this study.

The resistance to biofouling is an inherent characteristic of copper alloys and appears to be associated with copper ion formation within the corrosion product film. Coupling to steel or less noble materials or cathodic protection, which suppresses copper ion formation, allows biofouling to occur on copper alloys as readily as on other materials.

Biocides

Chlorine is a widely used and effective biocide when injected continuously so that a 0.2 to 0.5 ppm residual is maintained at the outlet tubesheet of a power plant condenser. Intermittent injection, as usually practiced, is only partially effective at best. Barnacles, mussels, and other hard-shelled organisms possess the ability to tightly close their shells when first sensing a toxic substance such as chlorine in the water, to remain closed until it passes, and then to reopen and resume feeding. Copper alloy tubing is resistant to chlorination at concentrations required to control biofouling. Over-chlorination can damage copper alloy tubing, however.

Parting corrosion

Dezincification

Brass alloys with more than 15% zinc, such as Admiralty, aluminum brass, Muntz metal, naval brass, and manganese bronze, were susceptible to a specific form of corrosion in seawater termed dezincification (or parting corrosion). A porous, spongy layer or plug of copper devoid of zinc developed on the metal surface when in seawater service or stagnant environments. In some cases, the layer was superficial in depth; in others, it extended completely through the wall.

Dezincification is rarely encountered today except in the case of yellow brass, which is not normally produced with an inhibitor. The addition of 1% tin to Admiralty, naval brass, and manganese bronze reduces the tendency toward dezincification. The further addition of a few hundredths of a percent of arsenic effectively prevents dezincification in high-zinc alloys, such as C44300, C68700, C36600, and C46500. Antimony and phosphorus are also effective as dezincification inhibitors but are less commonly used. Other than the 1% tin content, which is not fully effective alone, the cast manganese bronze propeller Alloy C86500 is produced without an inhibitor. The steel hull and its cathodic protection system provide considerable protection for the propeller except at the outer portion of the blades, where velocity is highest.

Dealuminification

Dealuminification in the 5 to 8% aluminum bronzes is occasionally reported, but it is not a significant problem until aluminum reaches the 9 to 11% range. The cast aluminum bronzes containing 1 to 5% nickel have been widely used as pumps, valves, and propellers in marine service, with varying degrees of dealuminification-related problems. Ferrara and Caton reported on an extensive Navy study of aluminum bronze components from Naval vessels.[15] The authors concluded, "Dealloying in NAB (nickel-aluminum bronze) castings containing 4% minimum nickel appears to be limited to approximately 6 mm (1/4 in.) for service times up to 15 years." The composition of Alloy C95800 has been adjusted in accordance with their findings. The Navy specification for C95800 pump and valve components (MIL-B-24480) requires a 6-h final anneal at 1250 F (677 C). The C95500 composition changes and the 1250 F (677 C) anneal are designed to minimize dealuminification. The propeller alloy (C95500) and the Navy specification Mil-B-21230 remained unchanged. Weld repairs are permitted and routinely made on the nickel-aluminum bronze propeller alloy without sensitizing the alloy to stress cracking or dealuminification in later service.

Denickelification

Denickelification is occasionally reported in the higher-nickel content copper-nickel alloys in refinery overhead-condenser service, where hydrocarbon streams condense at temperatures above 300 F (149 C). The problem appears to be associated with hot spots that develop in the tubing as a result of fouling and thermogalvanic differences that arise. Although extensive studies have not been undertaken, the solution is more frequent cleaning to remove deposits that could lead to hot spots and/or increasing flow rate to avoid deposits.

Stress corrosion cracking

The higher-zinc content brasses are subject to stress corrosion in the presence of air (oxygen), water vapor, and traces of ammonia if the alloy is in the stressed (tempered) condition. These conditions can arise in marine atmospheres, in storage (the ammonia coming from such sources as rat and sea gull waste), as well as from operations. While it is rarely encountered in feedwater heaters and condensers because of their low oxygen content, air inleakage during downtime periods should be minimized.

TABLE 8 — Ammoniacal stress corrosion resistance of brasses, aluminum bronzes, and copper-nickel alloys—Thompson[15]

Alloy	Time to 50% relaxation (h)
C44300	0.30
C2800	0.35
C46500	0.50
C26000	0.51
C68700	0.60
C60600	4.08
C61400	5.94
C70600	234
C14200 PDO copper	312
C71500	2000

TABLE 9 — Galling resistance of silicon bronze and SS—Schumacher[17]

Metals in contact	Bhn	Threshold galling stress, psi (kg/cm^2)
Silicon bronze (C65500)	200	4000 (280)
AISI 304	140	2000 (140)
AISI 316	150	2000 (140)
Silicon bronze (C65500)	200	
on AISI 304	140	44,000 (3093)

FIGURE 12—Resistance to seizing at 150 C as a function of alloying elements.

Thompson studied the resistance of copper-base alloys to stress corrosion cracking (SCC).[16] Table 8 from his work shows the relative resistance of copper-base alloys to ammonia SCC. The aluminum bronze alloys exhibit a resistance greater by an order of magnitude. Copper and copper-nickel alloys are practically immune in service. There are some reports of the stress corrosion of copper-base alloys by sulfur dioxide, sulfamic and nitric acids, copper nitrate, industrial atmospheres, mercury, and other media, but the principal causative agents, if the other prerequisites are present, are ammonia or mercury.

Although aluminum bronze is resistant to ammoniacal SCC, it is susceptible in steam or hot water. The 0.2 to 0.5 tin addition in Alloy C61300 is sufficient to suppress the SCC tendency in steam. Some investigators believe that the tin addition also improves the resistance to ammoniacal SCC, but this has not been well established, probably because the inherent resistance is adequate for most applications.

When welded with a matching filler metal, aluminum bronze becomes susceptible to SCC in marine and desalination environments. Microfissuring of both the weld metal and heat-affected zones leaves these areas prone to parting corrosion and SCC. The remedy is to weld with a higher-aluminum content (10%) duplex filler metal. The final pass is made with nickel-aluminum bronze to minimize the possibility of galvanic corrosion of the higher-aluminum content filler metal.[16]

Nickel-aluminum bronze propellers are routinely and successfully welded with nickel-aluminum bronze filler metal without increasing the SCC susceptibility in service. Manganese bronze propellers are stress relief annealed after weld repair to reduce the possibility of SCC.

Galling and seizing resistance

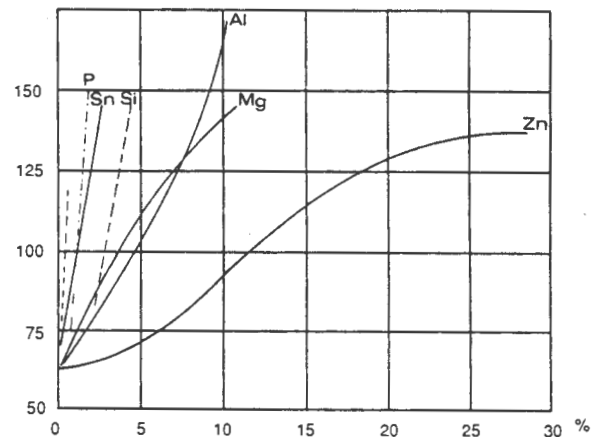Copper-base alloys are well known for their wear resistance, but less known for their outstanding resistance to galling and seizing. The tin bronzes have been used for components in the sliding mechanisms of naval ordnance, field artillery, and machine guns, which must resist galling and seizing under the extreme impact loadings of recoil. Lubrication is often marginal or nonexistent.

One popular galling test is made in a Brinell hardness tester. A small polished button of one material is slowly rotated 360 degrees against a flat polished plate of the second under increasing deadweight loads. The threshold galling stress is defined as the maximum load before a distinct weld junction can be observed at 10 times magnification. This usually occurs at the end of a wear track. This test method provides a relative rating (in psi) for the two materials in contact. The test has been used to develop ratings for SSs, nickel-base alloys, several steel alloys, and silicon bronze.[18] The data are given in Table 9.

While the threshold galling stress is low for both silicon bronze and AISI 304 SS when tested against themselves, there is an order of magnitude improvement when silicon bronze is run against AISI 304 SS. The applicability of these test data is probably limited to slowly moving, heavily loaded, poorly lubricated components.

Semenov studied and defined the resistance of copper-base alloys to galling and seizing as a function of their composition.[19] Figure 12 shows the relative resistance to galling of copper alloys with varying amounts of Zn, Mg, Al, Si, Sn, and P at 25 and 150 C. Small additions of P and Sn effect the greatest improvement, closely followed by Si, then Al and Mg, and finally Zn. Semenov's relative ratings indicate why the tin bronzes are so widely used in ordnance and appear to be in agreement with general experience.

Table 10 lists some of the principal applications for copper-base alloys in which resistance to galling and seizing in seawater is a principal consideration.

Desalination environments

Copper alloy tubing has made desalination economical and practical in the arid areas of the world. Distillation processes predominate, but there is an increasing usage of reverse osmosis, especially with brackish waters. In the distillation processes, raw seawater is pumped through the heat reject section, where it is warmed to 105 to 110 F (40 to 43 C) for easier deaeration. The heat reject section of the plant is similar to a power plant condenser and requires ~10% of the total tubing. Tubing performance has been similar to that in coastal power plant condensers, except in those desalination plants that draw their intake water from shore side wells rather than the open ocean. Water from shore side wells lacks oxygen and contains hydrogen sulfide, with 5 to 20 ppm being typical. Copper alloy tubing can be used successfully in sulfide-bearing waters free of oxygen, provided that care is taken to remove all debris and sediment that would damage the protective sulfide film. However, in practice, operations have not been up to the control and skill level required. Thus, titanium and SSs have been preferred for plants

TABLE 10 — Marine applications requiring high resistance to galling and seizing

Application	Alloy
Sliding mechanisms of naval ordnance and machine gun	C52100 C52400
Valve seats	C83600 C90300 C92200 C95200 C95800
Boat propeller shafting	C51000
Ships stern tube bearings	C96300
Wear rings	C95800[1]

[1]Other cast copper alloys are widely used for wear rings and have high resistance to galling, but C95800 alloy is more cathodic and tends to be protected by the pump case.
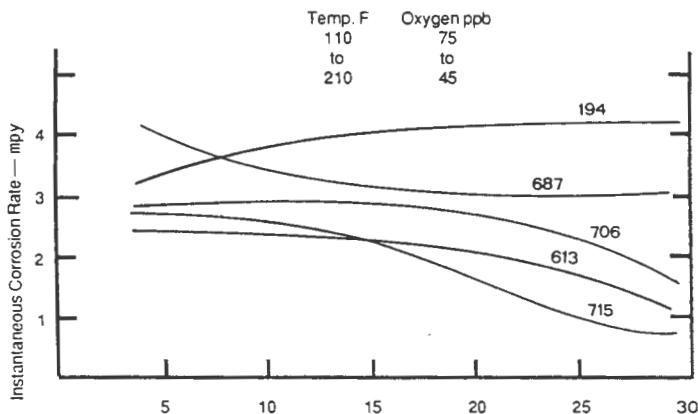
FIGURE 13—Variation in corrosion rate for copper alloys from 5 to 30 months in the heat recovery section of an experimental desalination plant.
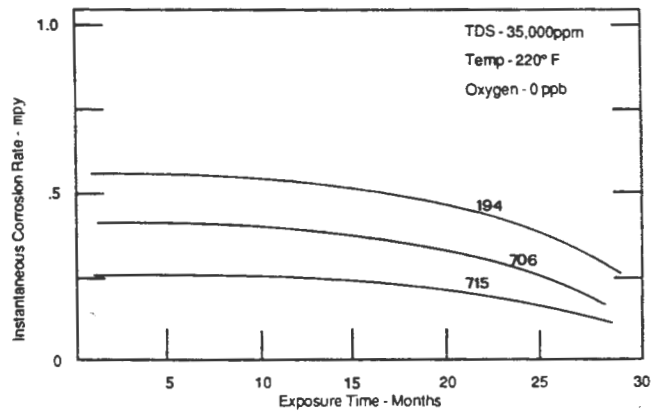
FIGURE 14—Variation in corrosion rate for copper alloys from 5 to 30 months in the brine heater section of an experimental desalination plant.
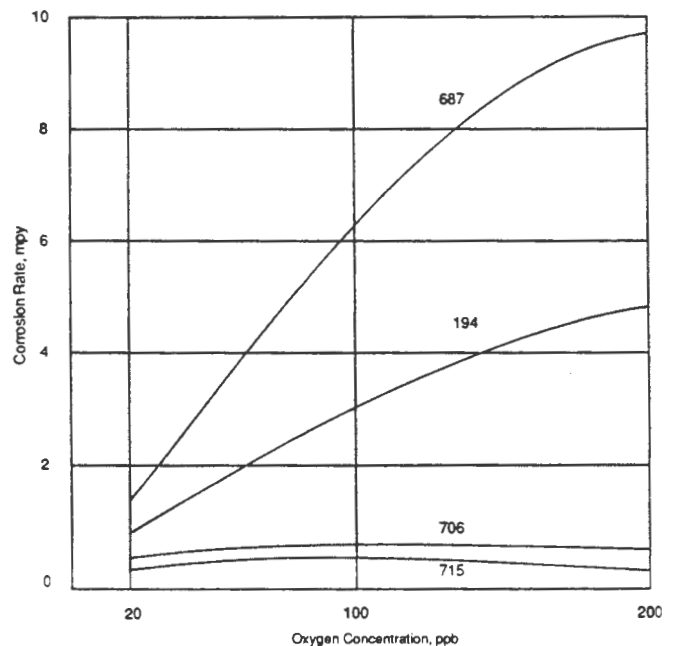
FIGURE 15—Corrosion rate as a function of low oxygen concentrations at 220 F (104 C) in an experimental desalination plant.

that are fed from shore side wells or are otherwise laden with hydrogen sulfide in the incoming seawater.

After deaeration, the seawater is fed through tubing in the heat recovery section, where it is gradually heated in a series of stages to either 180 F (82 C) in the plants using polyphosphates or 220 to 230 F (104 to 110 C) in the plants using acid or chemical additives. This section of the plant requires ~87% of the total tubing. Oxygen contents range from 20 to 100 ppb, and corrosion rates are low. Alloys C68700 and C70600 are used in the heat recovery section of the plant with outstanding success. Figure 13 illustrates the continuing downward trend of the corrosion rate of Alloy C70600 with time as compared to the more constant corrosion rate of C68700.[20] The tendency for the corrosion rate of Alloy C70600 to decrease with time as it does in seawater partly accounts for its increasing preference for use in the heat recovery section.

From the heat recovery section, the seawater is fed to the brine heater, where it is heated approximately another 10 F (6 C) before being fed to the first flash chamber. The brine heater requires ~3% of the total tubing. The principal problem in the brine heater is the precipitation of calcium carbonate and/or calcium sulfate. Scale formation occurs from overheating and/or inadequate polyphosphate, acid, or additive treatment. Even in well-operated units, it is often necessary to *rod* the tubes using a power-driven rotating tool. Since the tube walls must be scraped in this manner, both the

protective film and possibly some metal are lost. For this reason, somewhat heavier-wall 16-gage tubing is preferred in the brine heater. Figure 14 shows the same decreasing corrosion rate with time for C19400, C70600, and C71500 under brine heater service conditions that characterized C70600, C71500, and C61300 under heat recovery service conditions.[20] Although both C70600 and C71500 are used in brine heater service successfully, Alloy C71500 seems to be preferred.

Oxygen content affects copper alloys differently, as shown in Figure 15.[20] The corrosion rates of C70600 and C71500 remain low in the 20 to 200 ppb oxygen range, whereas those of C68700 and C19400 increase significantly as oxygen content increases. The lower rates maintained by C70600 and C71500 account for the preference of these alloys in desalination applications.

After the hot seawater leaves the brine heater, it is fed to the first flash chamber, where pure water is removed as steam. Above the demisters that gather and return water droplets, the steam is condensed on the outside of the tubing, also heating the incoming seawater. Provided that the noncondensible gases are properly vented from the flash chambers, the condensing steam has no effect on the outside of the tubing, which remains bright and clean.

The flash chamber floor, walls, and overhead must be protected

from the more corrosive brine. The first several chambers are lined with Alloy C70600 or constructed from C70600 clad material. Organic linings and coatings are often used as an alternate to C70600 linings in the subsequent lower-temperature flash chambers to reduce initial cost. The maintenance of organic linings varies widely. Little or no maintenance is reported on C70600-lined flash chambers. AISI 316L SS linings are also used as an alternate to C70600, but have suffered from corrosion during shutdown and standby periods.

Waterboxes are normally constructed of C70600. Brine heater piping is also normally C70600. While some plants use C70600 piping throughout the heat recovery section, others use fiber-reinforced plastic and coated steel below 168 to 180 F (76 to 82 C) with varying degrees of success.

More detailed data are available in a Dow Chemical Company report,[20] from which Figures 13 through 15 were taken, as well as the A.D. Little survey of performance reports.[21]

Summary

1. The initial unfilmed corrosion rate of copper alloys in seawater decreases ~100 times in the first hour of exposure at 60 F (16 C) and continues to decrease during the first several years of exposure.

2. Long-term steady-state corrosion rates for most copper alloys in seawater range between 0.5 and 1.0 mpy (0.01 and 0.025 mm/y); for copper-nickel, the most resistant alloys approach 0.05 mpy (0.001 mm/y).

3. Copper alloys vary widely in their resistance to velocity, with C95500 being the most resistant of the cast alloys, C72200 the most resistant of the condenser and heat exchanger alloys, and C70600 the most resistant of the ship hull plate alloys.

4. Copper alloys have an inherent resistance to biofouling that makes a major contribution to their usefulness as condenser tubing, piping, and other components of seawater cooling systems.

5. Although copper alloys generally may be coupled to each other without serious acceleration of galvanic corrosion, close attention to galvanic effects will considerably enhance performance. The use of SS or titanium tubes in copper alloy systems will generally require cathodic protection to prevent the accelerated corrosion of copper alloys that would otherwise occur.

6. Copper alloys are resistant to occasional excursions into polluted waters, but they are not recommended for frequent or continuous exposure to polluted, sulfide-bearing waters.

7. Parting corrosion has been largely overcome in high-zinc alloys by alloying and in the aluminum bronzes by proper welding techniques and heat treatment.

8. Copper-nickel alloys exhibit outstanding resistance to the ammoniacal SCC that occurs in the high-zinc alloys and to a lesser extent in aluminum bronze alloys.

9. Copper alloys exhibit outstanding resistance to seizing and galling under impact and rotating loadings.

10. Copper alloys have made modern desalination plants possible and practical for arid areas of the world.

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