A Member

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.

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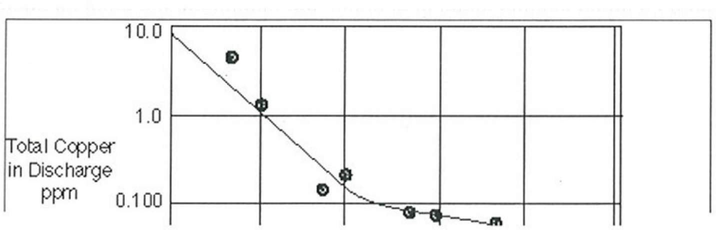
Protective Film Formation

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 A for copper to 4400 A 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.



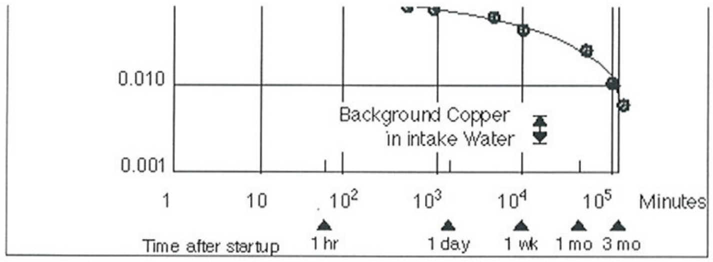


Figure 1. Formation rate of corrosion product film on Alloy C70600 in seawater.

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 ~0.0S 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.

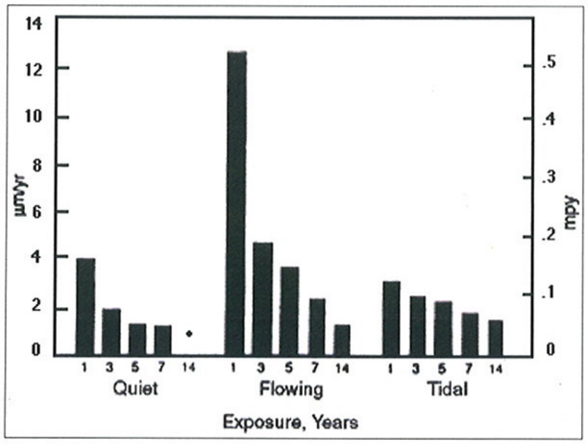


Figure 2. Corrosion rates for Alloy C70600 for long-term seawater exposures.

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.

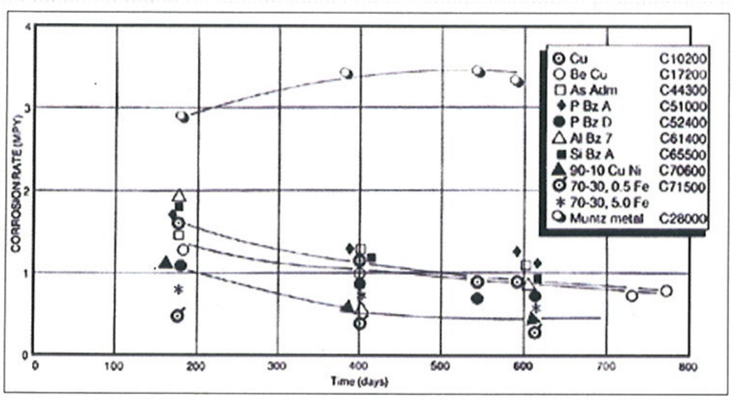


Figure 3. Corrosion rates for copper alloys for up to 800-day seawater exposures.

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.

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 C61300	Power plant and offshore oil piping and waterboxes
NiAl bronze	C63000 C63200	Pump shafts, valve stems (Navy)
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

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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.

Table 2. Critical shear stress for copper-base alloys in seawater-Efird[4]

Alloy	Critical Shear Stress N/m^2 (lbf/ft^2)
CA 122	9.6 (0.2)
CA 687	19.2 (0.4)

Alloy	Critical Shear Stress N/m² (lbf/ft²)
CA 706	43.1 (0.9)
CA 715	47.9 (1.0)
CA 722	296.9 (6.2)

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.

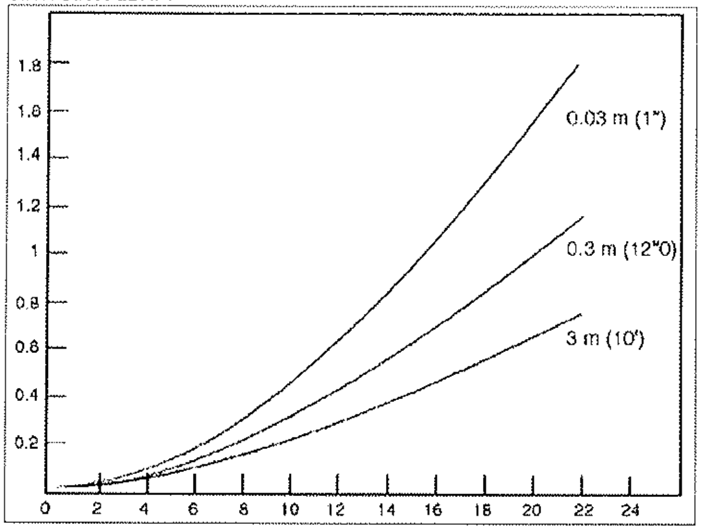

Figure 4. Variation in shear stress between the flowing seawater and metal wall with the nominal velocity in the pipe and diameter of the pipe.

Sato and Nagata showed that the shear stress at the inlet end condenser tube is about double that further down the tube (**Figure 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.

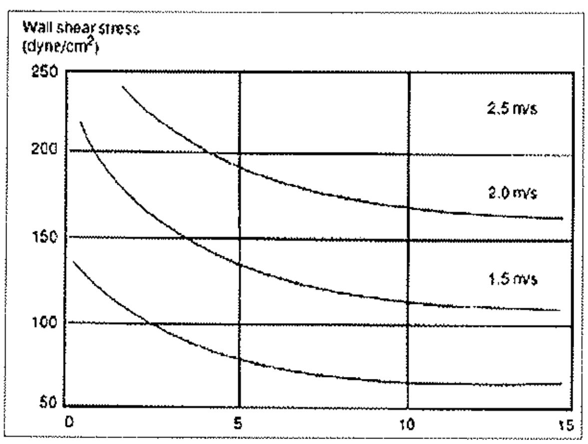

Figure 5. Variation of shear stress between the flowing seawater and metal wall with the distance from the inlet end.

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 C71 500 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 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.

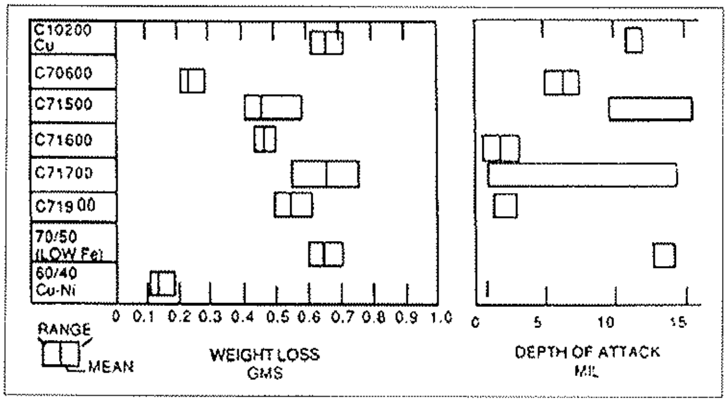

Figure 6. Weight loss and depth of attack on copper alloys in BNRMRA jet impingement tests.

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

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)

Note: 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)

Note: 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

Peripheral Velocity-fps (m/s)	Copper Alloys
	C87600
35 (10.7)	C90300 C92200
50 (15.2)	C95200 C86500
775 (22.9)	C95500 C95700 C95800

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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.

Aluminum bronze and nickel-aluminum bronze alloys display outstanding resistance to cavitation, especially Alloy C95500 (Mil B 21230 Alloy 1) (Military specification), 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.

Table 5. Order of resistance to cavitation damage in seawater-Tuthill and Schillmoller[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.

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Corrosion Fatigue

Corrosion fatigue strength (CFS) is commonly defined as the 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.

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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.

Table 6. Corrosion fatigue strength of propeller alloys in seawater- Metals Properties Council-Prager[8]

	Corrosion Fatigue Strength(1)	
Cast Alloy	(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 108 cycles and zero mean stress and must be reduced when mean tensile stresses are substantial

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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.

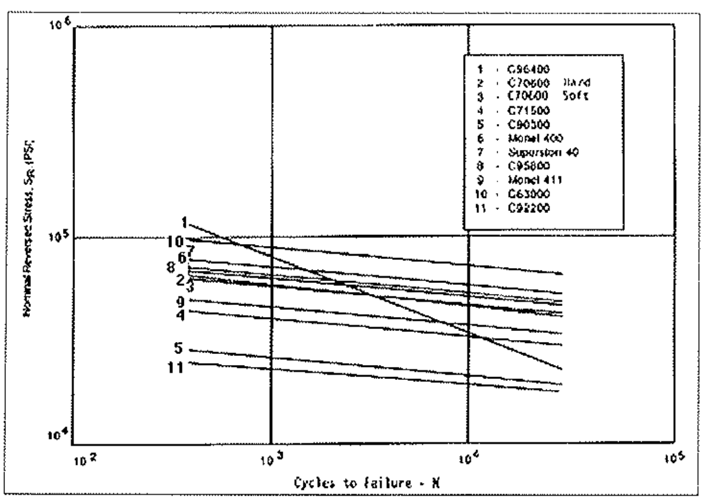

Figure 7. Low-cycle fatigue of nonferrous alloys.

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Galvanic Behavior of Copper and Copper-Base Alloys

Copper and copper-base alloys occupy a useful mid-position in the galvanic seriesmore 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.

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-1y (mm/y)	Acceleration factors Copper (Cu) 10:1 M	Copper (Cu) 1:1 M	Copper (Cu) 1:10 M	Mild Steel 10:1 M	Mild Steel 1:1 M	Mild Steel 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	2S	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 C61 400	0.01	2	2	1	1 MS	3 MS	7 MS
Aluminum bronze(3) (10o/o 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 C6S50	0.035	1 CU	1 CU	1 CU	1 MS	3 MS	7 MS
Copper C1100	1	1	1	1 MS	3 MS	7 MS	
Phosphor bronze (3% Sn) CS1000	0.02	1 CU	2 CU	1 CU	1 MS	3 MS	7 MS
Phosphor bronze (10% Sn) CS2400	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
Iconel 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

(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.

Coupled material (M)	Uncoupled corrosion rate-1y (mm/y)	Acceleration factors Copper (Cu) 10:1 M	Copper (Cu) 1:1 M	Copper (Cu) 1:10 M	Mild Steel 10:1 M	Mild Steel 1:1 M	Mild Steel 1:10 M
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.

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.

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Footnotes

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