



Corrosion Behavior of Copper Alloys in Seawater with emphasis on UNC C97500

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Abstract: Copper based alloys are frequently used in marine water systems. They have indeed an attractive price and offer interesting mechanical characteristics associated to a relatively good resistance to corrosion in sea water. Nevertheless, they can suffer from certain forms of corrosion such as localized corrosion with sulphides pollution, crevice corrosion, or stress corrosion cracking in sea water more or less polluted with ammonia. 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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1. Introduction

Copper and copper alloys are widely used in a variety of products that enable and enhance our everyday lives. They have excellent electrical and thermal conductivities, exhibit good strength and formability, have outstanding resistance to corrosion and fatigue, and are generally nonmagnetic. They can be readily soldered and brazed, and many can be welded by various gas, arc and resistance methods. They can be polished and buffed to almost any desired texture and luster. Pure copper is used extensively for electrical wire and cable, electrical contacts and various other parts that are required to pass electrical current. Coppers and certain brasses, bronzes and copper nickels are used extensively for automotive radiators, heat exchangers, home heating systems, solar collectors, and various other applications requiring rapid conduction of heat across or along a metal section. Because of their outstanding ability to withstand corrosion, coppers, brasses, bronzes and copper nickels are also used for pipes, valves and fittings in systems carrying potable water, process water or other aqueous fluids, and industrial gases. Copper alloys are also ideally suited where it is important to minimize bacterial levels on touch surfaces. Because of their inherent ability to kill 99.9% of bacteria within two hours, more than 280 copper

alloys have been granted public health registration by the U.S. Environmental Protection Agency (EPA). This unprecedented registration recognizes copper's inherent ability to continually kill bacteria between regular cleanings, and aids in reducing infection-causing bacteria on touch surfaces in hospitals, schools, offices and other public establishments.

UNS C95700 is an Aluminum Bronze grade Cast Copper Alloy. It is composed of (in weight percentage) 75% Copper (Cu), 2% Nickel (Ni), 3% Iron (Fe), 8% Aluminum (Al), and 12% Manganese (Mn). Another common designation of UNS C95700 copper alloy is UNS C95700.

Copper is one of the most useful metals known to man, and it was one of the first to be utilized. Copper is a reddish-yellow material and is extremely ductile. Copper has a face-centered-cubic (fcc) crystal structure and has the second best electrical conductivity of the metals, second only to silver compared to which it has a conductivity of 97%. The thermal conductivity of copper is very high, falling in between silver and gold. There are almost 400 different copper alloys depending on the commercial product made; rods, plates, sheets, strips, tubes, pipes, extrusions, foils, forgings, wires, and castings from foundries.

The typical elastic modulus of copper alloys at room temperature (25°C) is about 117 GPa. The typical density of copper alloys is from 8.8 to 8.94 g/cm³. The typical tensile strength varies between 172 and 220 MPa. The wide range of ultimate tensile strength is largely due to different heat treatment conditions.

All metals and alloys undergo corrosion, which is defined as the destructive attack of a metal by the environment, by chemicals, or electrochemical processes. The driving force is the free energy of reaction of the metal to form a metal oxide (generally). Since corrosion reactions generally occur on the metal surface, they are called interfacial processes. The corrosion process takes place at the metal medium phase boundary and therefore is a heterogeneous reaction in which the structure and condition of the metal surface have a significant role (e.g., whether the surface is uncoated, coated with an adhesive, compact, or loose porous coating, or whether its properties have been changed by machining and processing). The corrosive medium must be transported to the surface and the corrosion products removed. Therefore, material transport phenomena, including free convection and diffusion into adjacent surface layers, must also be taken into account.⁽⁴⁾ Some metals, like sodium, undergo “corrosion” within minutes while other metals, like gold and mercury, undergo “corrosion” only after years of exposure. The same is true with alloys; some alloys undergo corrosion within days (e.g., low carbon steel and some types of stainless

steel) while other alloys (e.g., copper/nickel/zinc alloy) are relatively resistant and undergo corrosion only after years of exposure.

2. Material and Methods

2.1. Copper alloys

Copper and copper alloys are produced to conform with a wide variety of national and international specifications prepared to suit different conditions and requirements. They are ductile and may be manufactured by extrusion, forging, rolling, drawing, hot stamping and cold forming. They can also be cast by all of the traditional casting methods such as sand and die, and by continuous and centrifugal methods. Table 2 gives a selection of EN standards for copper and copper alloy product forms. It is clear that, by selection of the appropriate wrought or cast route, almost any shape can be obtained. For example, by the use of centrifugal casting, tubes in bronzes may be made which would either not be covered in the wrought specifications or be of non-standard sizes. For seawater systems, copper-nickel and aluminum bronze are often preferred, although other copper alloys are used in marine service and have their specific advantages. Copper alloys differ from other metals in that they have an inherent high resistance to bio-fouling, particularly macro-fouling, which can eliminate the need for antifouling coatings or water treatment.

Table 1: Alloy Groups

Alloy Group	Alloy Types
Coppers	Cu
Copper-nickels	90-10 Cu-Ni 70-30 Cu-Ni Cu-Ni-Cr Cu-Ni-Sn Cu-Ni-Al
Bronzes	Cu-Sn-P (phosphor bronze) Cu-Sn-Zn (gunmetal) Cu-Al (aluminum bronze/nickel aluminum bronze) Cu-Si (silicon bronze)
Brasses	Cu-Zn
Copper-beryllium	Cu-Be

Table 2: 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, Water flood and offshore oil
Copper-nickel	C71500	Condenser and heat exchanger tubing, piping and water boxes-shipboard. power, industrial and desalination plants, water flood 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	Water flood 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

2.2. Aluminum Bronzes

Aluminum bronze refers to a range of copper-aluminum alloys which combine high strength and corrosion resistance and are widely used in both cast and wrought forms. These alloys are basically copper with 4-12% Al. They have a thin, adherent surface film of copper oxides and aluminum oxides, which will heal very rapidly if damaged. Furthermore, they have good resistance to erosion and wear, as well as good corrosion fatigue properties.

For up to about 8% Al, the alloys are alpha phase and can be readily rolled and drawn. At 8-12% Al, a second phase, beta is formed and the alloys can be wrought or cast. Additions of iron, manganese, nickel or silicon can also be present. Generally, the corrosion resistance of the aluminum bronzes increases as the aluminum, and other alloying additions, increase. At 9-10% Al, additions of 4-5% iron and nickel produce alloys with both high strength and corrosion resistance in non-polluted waters. A derivation, aluminum silicon bronze CW302G, finds application notably where low magnetic permeability is required. It is also covered by Def Stan 02-834 which gives a maximum magnetic permeability value of 1.05. This aluminum bronze is typically used for chains and deck fittings on minesweepers.

The metallurgical structure of aluminum bronze alloys is very complex and described together with corrosion properties and applications in detail by Meigh and Campbell(13,14) and the implications are nicely summarized by Francis(6). Careful control of chemistry and processing is required to ensure the structure is maintained in an optimum condition and does not form less corrosion resistant phases which can promote selective phase attack. Nickel and iron provide increased ductility and improved castability and are also the two alloying additions which retard decomposition of beta phase in the structure or alter the decomposition to provide higher corrosion resistance. These alloys are known as the nickel aluminum bronzes or NABs. Those with 5% each of nickel and iron are widely used and exhibit useful precipitation hardening characteristics. The corrosion resistance can be improved by a heat treatment of $675\pm 25^\circ\text{C}$ for 4 to 6 hours followed by air cooling for castings and $725\pm 25^\circ\text{C}$ for wrought material and is particularly advantageous after welding(Francis, 2009; Meigh, 2000).

Aluminum bronze alloys have a high order of resistance to ammonia stress corrosion cracking and, although there have been some instances of failure in high pressure steam, extremely high resistance is found in marine environments. Selective phase attack has occasionally been observed at crevices and other shielded areas on NAB. This is due to a drop of pH within the crevice resulting in a normally cathodic phase in the structure called kappa III becoming galvanically less noble to the surrounding alpha phase. It is more pronounced when the NAB is coupled to more noble alloys in non-chlorinated systems. It can be avoided by ensuring exposure to aerated flowing seawater when going into service so the protective surface films in exposed surrounding areas become established, by galvanic coupling to less noble alloys in the system or cathodic protection (Francis, 2009).

Of the copper alloys, NAB has a very high resistance to cavitation and has become an established alloy for ship propellers.

Table 3: Resistance to General Corrosion, Crevice Corrosion and Corrosion- Erosion in Flowing Seawater of cast alloys

Alloys	Alloys General Corrosion Rate		Crevice Corrosion		Erosion-Corrosion Alloys Resistance	
	mil/yr	mm/yr	mil/yr	mm/yr	mil/yr	mm/yr
Leaded Red Brass	1.6	0.04	<1.6	<0.04	12	3.7
Red Brass (Gunmetal)	0.9	0.023	<0.9	<0.023	20	6.1
High tensile Brass	8.7	0.22	0.9	<0.074	8	2.4
Aluminum Bronze	2.9	0.074	<2.9	<0.51	15	4.6
Nickel aluminum Bronze	2.9	0.074	2	3.6	14	4.3
Manganese aluminum Bronzes	2.1	0.053	140	0	14	4.3
Austenitic cast iron (AUS 202)	2.7	0.069	0	0.23	>20	>6
Austenitic stainless steel 304	0.9	0.023	9	0.11	>30	>9

2.3. Corrosion resistance and Freedom from Oxide Flaking

The outstanding corrosion resistance of aluminum bronzes in marine and chemical processing environments is due to the formation of an intrinsic, thin but tough adherent film of aluminum oxide. This film is self-healing and once formed, prevents further oxidation and consequently eliminates flaking so often encountered with ferrous alloys. Furthermore, the

nickel-aluminum bronzes have excellent resistance to stress corrosion and corrosion fatigue. This freedom from oxide flaking combined with corrosion resistance, together with good creep and fatigue properties at elevated temperature, makes aluminum bronzes ideal for high temperature service. Special alloys with high aluminum content perform well as glass mould tooling where good thermal conductivity improves production speed. Unlike the high-tensile bronzes (manganese

bronzes) and other bronzes, nickel aluminum bronzes are highly resistant to stress corrosion cracking. They are also rarely, if at all, susceptible to pitting and are generally far more resistant to selective attack.

In view of the fact that their strength is comparable to many ferrous alloys, it is possible, without radical re-design, to substitute aluminum bronzes where even mild corrosion of ferrous components is a potential problem. This applies particularly in critical areas of plant operation such as pumps and valves. Table 2 gives a comparison of the resistance to corrosion of various ferrous and non-ferrous alloys. Aluminum bronzes are resistant to attack from a wide range of chemicals which are listed in Appendix Three. For further information on corrosion resistance see CDA, Publication No. 80.

The data in Table 2 is taken from Defence Standard 01/2 "Guide to Engineering Alloys Used in Naval Service: Data Sheets". The figures for general corrosion rate and crevice corrosion were determined using samples fully immersed beneath rafts in Langstone Harbour for one year. General corrosion results were provided by freely exposed specimens; crevice corrosion results by specimens held in Perspex jigs providing crevice conditions between the metal sample and the Perspex. The corrosion/erosion resistance tests were carried out using the Brownsdon and Bannister test, the specimens were fully immersed in natural sea water and supported at 60°C to a submerged jet, 0.4 mm diameter placed 1 - 2 mm away, through which air was forced at high velocity. From the minimum air jet velocity required to produce corrosion/erosion in a fourteen-day test, the minimum sea water velocity required to produce corrosion/erosion under service conditions was estimated on the basis of known service behavior of some of the materials.

2.4. Galvanic Behavior

Galvanic corrosion is the enhanced corrosion which occurs to the least noble metal within a mixed metal system, in electrical contact with the other metals and exposed to an electrolyte. The least noble alloy is called the anode and the nobler alloy the cathode. If the galvanic current is significant, the anode will corrode more than it normally would in an uncoupled situation and the cathode will corrode less. This forms the basis for cathodic protection, where less noble materials (e.g. zinc, aluminum or iron alloys) are connected intentionally as sacrificial anodes in order to protect other alloys in the system.

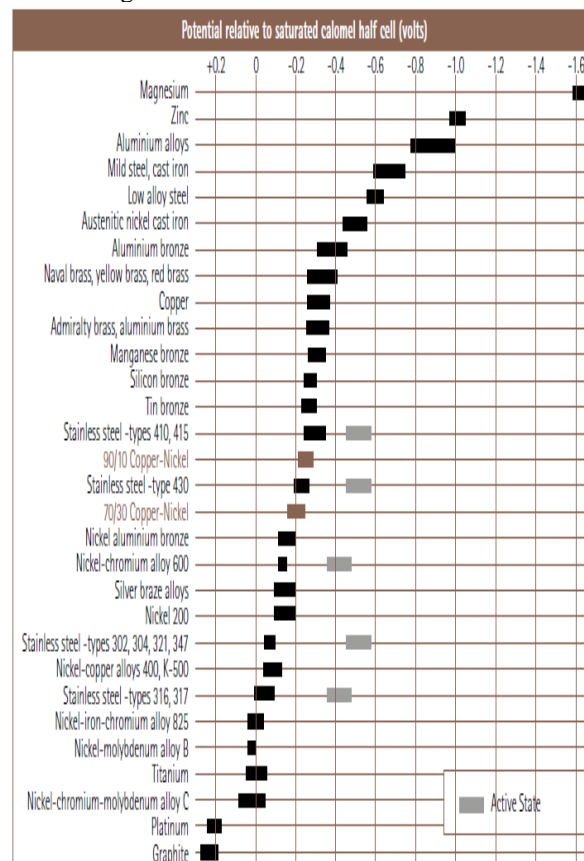
Where seawater is the electrolyte, a Galvanic Series can be used, such as that shown in Figure 3, in order to predict which of the metals in contact is the least noble and whether higher corrosion rates may occur than might otherwise be expected. The alloys nearer the top of the chart are less noble (more anodic) in

seawater than those towards the bottom and would be expected to corrode preferentially. The further apart in the series the coupled alloys are, the greater the potential difference between them and the more likely it is for corrosion to occur. It is seen that copper alloys are in the middle of the Series whereas steel; zinc and aluminum are appreciably less noble and would be expected to corrode preferentially when coupled to them in a system. Passive stainless steels, nickel alloys, titanium and graphite are all nobler than copper alloys, and the copper alloys would therefore risk galvanic corrosion.

However, other factors can play a part. The relative surface areas of the galvanically coupled metals, exposed to the seawater, have an important influence on the extent of corrosion. The surface area of the cathodic alloys exposed to seawater normally limits the galvanic current.

Therefore, a small cathodic area in contact with a large anodic area can have little effect on the overall corrosion rate of the less noble, anodic material. Alternatively, if the relative area of the nobler, cathodic area is high, then excessively high corrosion rates of the anode might be experienced.

Figure 1: Galvanic Series in seawater



2.5. Crevice Corrosion

Practically all metals and alloys suffer accelerated local corrosion either within or just outside crevices or "shielded areas" where two components or parts of the same component are in close contact with one another but a thin film of water can penetrate between them. The effect is greatest for stainless steels which depend upon free access of oxygen to the wetted surfaces to maintain the protective oxide film on which their corrosion resistance depends. Crevice corrosion of stainless steels usually takes the form of severe pitting within the crevice and this is a serious limitation on the uses to which these alloys may be put. Crevice corrosion of copper-nickel alloys takes a different form, resulting in a narrow trench of corrosion at the edge of the crevice often with some deposition of copper on the metal surface within the crevice. Most other copper alloys show similar crevice corrosion but to a greater or lesser extent. Crevice corrosion of aluminum bronzes tends to occur within the crevice and usually takes the form of selective phase attack and dealloying.

The effects are, therefore, related to the metallurgical structure of the particular aluminum bronze concerned and are least in the single phase alloys. None of the aluminum bronzes, however, is seriously affected by crevice corrosion in the way that stainless steels may be, since the attack does not produce pitting or serious roughening of the surface.

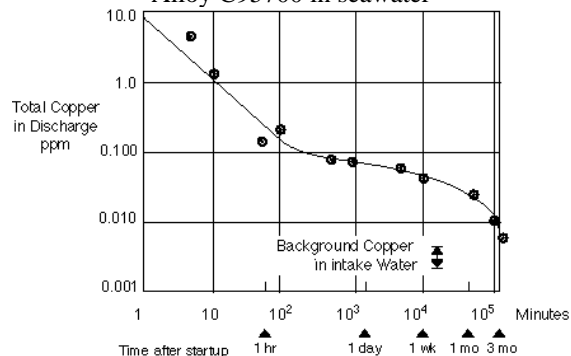
3. Results

3.1. 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 (Cu₂O), with cuprous hydroxychloride [Cu₂(OH)₃Cl] and cupric oxide (CuO) being present in significant amounts on occasion [North, Pryor, Corros. Sci., Vol. 10, p. 197, 1970]. These studies indicated corrosion product film thicknesses to for Alloy C795700. The film is adherent, protective, and generally brown or greenish-brown in color.

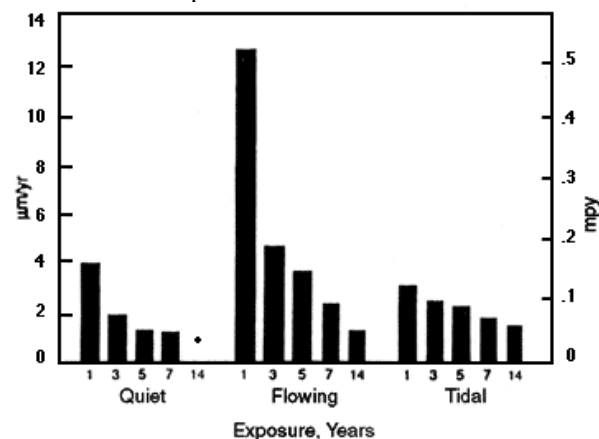
The corrosion product film forms very quickly when clean; un-filmed copper or copper alloys are first wetted by seawater. The rate of film formation is indicated as the rate of copper reduction in the effluent (Figure 2). Total copper decreases tenfold within 10 min and 100-fold in the first hour. In three months, copper in the effluent is seen to be virtually at the level of the copper in the intake water.

Figure 2: Formation rate of corrosion product film on Alloy C95700 in seawater



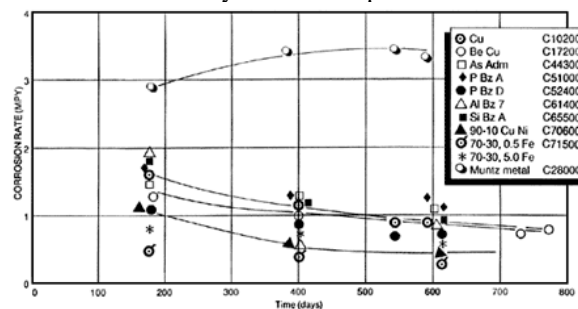
Weight loss corrosion studies show that the protective film continues to improve, with the corrosion rate dropping to 0.5 mpy (0.012 mm/y) in ~1 y, and a long-term, steady-state rate of ~0.05 mpy (0.001 mm/y) in 3 to 7 y in quiet, tidal, and flowing seawater (Figure 2) [INCO TP A-1222, 1975] Alloy 95700 exhibits the same pattern of decreasing corrosion rate with time.

Figure 3: Corrosion rates for Alloy C95700 for long-term seawater exposures



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).

Figure 4: Corrosion rates for copper alloys for up to 800-day seawater exposures



3.2. 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 [Ferrara, Gudas, 1972]. Since these CFSs were measured at zero mean stress, they must be adjusted downward when the mean tensile stresses are substantial.

Table 4: Corrosion fatigue strength of propeller alloys in seawater- Metals Properties Council-Prager

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 108 cycles and zero mean stress and must be reduced when mean tensile stresses are substantial.

3.3. 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. Efirid documented the resistance of C70600 to Biofouling in quiet seawater over an 18-month period, as shown in Figure 7. 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.

4. Discussions

The initial un-filmed 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.

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). 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.

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.

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. 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.

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

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