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Copper Alloys in Seawater: Avoidance of Corrosion

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Copper-nickel fittings for a seawater piping system (©KME Germany)

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Summary

Copper alloys have been widely used in seawater and related brines, such as in thermal desalination plants, for many years, generally with excellent results. They are commonly used for piping, valves, pumps and heat exchanger tubing, but have found many other applications. Figure 1 shows copper-nickel piping on a chemical tanker, while Figure 2 shows copper-nickel tubing in an oil cooler. Such oil coolers have been in use for 10 to 15 years without problems.



*Figure 1 - 90/10 copper-nickel piping on a marine chemical tanker
(Courtesy of Eucaro Buntmetall)*



Figure 2 - 90/10 copper-nickel tubing in an oil cooler

Occasionally there are failures due to corrosion, and in many cases these could be avoided by following some simple design recommendations, by selecting an alternative copper alloy, or by using a simple preventative strategy. This document covers the most common types of corrosion and shows simple methods to avoid them. If these are implemented at the design stage, it can save a large expenditure after a corrosion failure.

This guide has been written principally for marine, mechanical and other engineers who have to select materials of construction but do not have a corrosion background.

1.0 Alloys

The most commonly used copper alloys in seawater are copper-nickel alloys and nickel aluminium bronzes (NAB). The former are mainly used for piping, fittings and heat exchanger tubing, while NAB are commonly used for pumps and valves, although they can be used for other components, such as propellers and fasteners, where higher strength is required.

Other alloys are sometimes used in seawater, such as aluminium brass, the tin bronzes and the gunmetals. However, their use is more limited, although they have some applications and they are discussed at relevant places in the text. The nominal compositions of all the alloys discussed in the text are shown in Table 1. The compositions and mechanical properties are described in more detail in reference ⁽¹⁾ and the effects of composition on corrosion are discussed in references ⁽²⁾ and ⁽³⁾. The alloys will mostly be referred to by the common names listed in Table 1.

Table 1 – Nominal Composition of Copper Alloys Discussed in the Guide

Type	EN No (UNS No)	Common Name	Nominal Composition (wt %)								
			Cu	Ni	Fe	Mn	Al	Zn	Sn	Pb	Other
Wrought	CW352H (C70600)	90/10 Copper-nickel	Rem	10	1.7	1					
	CW354H (C70600)	70/30 Copper-nickel	Rem	30	0.7	0.7					
	CW353H (C71640)	66/30/2/2 Cu-Ni-Fe-Mn	Rem	30	2	2					
	CW702R (C68700)	Aluminium Brass	78				2	Rem			0.4 As
	CW712R (C46400)	Naval Brass	61					Rem	1		
	CW307G (C63200)	Nickel Aluminium Bronze	Rem	4.5	4		9				
Cast	CC333G (C95800)	Nickel Aluminium Bronze	Rem	4.5	4		9				
	CC482K (C92400)	Admiralty Gunmetal	Rem					2	10	1.5	
	CC480K (C90700)	Phosphor Bronze	Rem						10		0.2 P
	CC491K (C83600)	G2 Gunmetal	Rem					5	5	5	
	CC492K (C92410)	LG4 Gunmetal	Rem					2	7	3	

Rem = Remainder

2.0 Information

When designing any component or system that will be in contact with seawater, or brine, it is important to obtain information about the conditions, which will help in selecting the best alloy and any corrosion preventative measures that may be advisable. The information required when using copper alloys is described below.

- **Composition:**

The water composition is not required in detail. Copper alloys have been used successfully over a wide range of chloride concentrations from 1,000 mg/L or less to 50,000 mg/L (in MSF [multi-stage flash] desalination plants). The pH is important and copper alloys are best used in the range 6.5 to 9.1. The pH of seawater is typically in the range 7.8 to 8.2, but incursions of freshwater or chemical additions may drive the pH to unacceptably low values.

- **Temperature:**

The corrosion of copper alloys is not affected much by temperature and they have been used in seawater from 0 to 70°C. They have also been used to 110°C for brine heater tubes in MSF desalination plants ⁽³⁾.

- **Solids:**

If there are suspended solids in the seawater, the corrosion rate of all copper alloys can be increased. In general, the metal loss increases as the velocity, solids content and particle diameter increase. The severity of attack is also governed by the particle angularity and its angle of impact. Open seawater contains up to 50 mg/L solids with a diameter < 50 µm and does not cause any significant increase in corrosion of copper alloys. As the concentration increases, the corrosion rate increases slightly up to ~100 mg/L solids ⁽³⁾. At higher solids content, the particle diameter and velocity determine the corrosion rate ⁽³⁾.

Normally aluminium brass is the copper alloy most susceptible to erosion by solids, while 66/30/2/2 Cu-Ni-Fe-Mn is the most resistant. The issues for heat exchangers are discussed in more detail in reference ⁽³⁾ and an indication of satisfactory sand loadings and size for copper-nickel alloys is given in reference ⁽⁴⁾. For higher loadings, lower maximum flow rates are normally required ⁽²⁾. For complex cases, it is recommended that a corrosion specialist be consulted.

- **Pollutants:**

The main pollutants that affect the corrosion of copper alloys are sulphide and ammonia. These are not always measured in standard water analyses and it is important to check whether these can be present, either continually or intermittently. These pollutants occur in land-based plants and are rarely present in the open ocean. They can affect corrosion at very low concentrations, so it is important that analytical techniques with the required sensitivity are used. More details of the important concentrations are discussed in Section 5.0.

- **Additions:**

It is also important to know if there are to be any chemical additions to the seawater, as these may affect corrosion. A common one is chlorine/hypochlorite, which is often added to prevent fouling of seawater piping systems. The effect of chlorine on corrosion and safe levels are discussed in Sections 3.0, 5.0 and 6.0. Ferrous sulphate additions to prevent corrosion are discussed in more detail in Sections 3.0, 8.0 and the Appendix. Chemical additions may also be made to control scaling, aid flocculation during filtering or otherwise aid process control. Often such chemicals are added at low concentrations, but it is important to check with a corrosion engineer whether these additions might affect corrosion at the concentration at which they are to be added.

3.0 Velocity

It is well known that copper alloys can suffer erosion corrosion (also known as impingement attack) if the local water velocity or degree of turbulence is too high ⁽³⁾. When designing piping systems, there is a difference between large and small bore pipe, because the laminar boundary layer is thicker with large diameter pipe, and small irregularities in the surface, such as those due to deposits or prominent weld beads, will have a lesser effect on local turbulence. With small diameter pipe and tubing even quite small irregularities can disturb the flow and lead to local water velocity increases of 200 to 500% ⁽³⁾.

Table 2 suggests some safe velocity limits for wrought copper alloys used for piping and heat exchanger tube. It can be seen that the velocities for heat exchanger tube and pipe of NPS (nominal pipe size) ≤ 3 (80 mm DN) are the same. All of these velocities assume that it is clean, natural seawater. If there is chlorine/hypochlorite present, then the limits in Table 2 are still valid provided that the safe chlorine concentrations in Section 6.0 have not been exceeded.

Table 2 – Safe Velocities for Copper-nickel Tube and Pipe

Alloy	Maximum Velocity (m/s)		
	Heat Exchanger Tube	Pipe (\leq NPS 3) (DN \leq 80 mm)	Pipe ($>$ NPS 3) (DN $>$ 80 mm)
Aluminium Brass	1.5-2.0	1.5-2.0	2.0-2.5
90/10 Copper-nickel	2.0-3.0	2.0-3.0	3.0-3.5
70/30 Copper-nickel	2.5-3.5	2.5-3.5	3.5-4.0
66/30/2/2 Cu-Ni-Fe-Mn	3.0-3.5	3.0-3.5	3.5-4.5
Nickel Aluminium Bronze		2.5-3.5	2.5-3.5

If it proves necessary to use one of the alternative cast copper alloys in Table 1, then the safe velocity for admiralty gunmetal and phosphor bronze is about the same as that of NAB, but at the lower boundary. The safe velocities for the gunmetals are about 0.5 m/s less for LG4 and 1.0 m/s less for LG2, compared with phosphor bronze. This really applies to valves, as the flow in pumps is complex. Although the impeller tip speed may be 20 m/s or more, the water there is not stationary and it is the relative velocity that is important. Hence, velocities in pumps and safe use of materials are the responsibility of the pump supplier. Similarly internal materials within a valve are the valve manufacturer's responsibility.

It is important in design to avoid anything that can increase local turbulence, particularly if a system is running close to the upper velocity in Table 2. Hence, right angle bends should be avoided and bends at least of radii 1.5D are required, with 5D or 3D bends being even better if space allows. Additionally a straight length of pipe for a distance of 3D upstream and 5D downstream of pumps and valves can be beneficial.

When welding, it is important that the root bead does not over-penetrate and cause erosion corrosion due to localised increase in turbulence. The safe amount of penetration is variable depending on pipe diameter, as discussed earlier, but skilled welders usually do not have a problem when welding the copper-nickel alloys. The recommended maximum weld bead protrusions are shown in Table 3 ⁽⁵⁾, which allow for both weld bead penetration and alignment mismatch. More details about welding copper-nickel alloys are also in reference ⁽⁶⁾. Figure 3 shows severe erosion corrosion of 90/10 copper-nickel after the weld bead of a weld neck flange due to excessive water velocity.

Table 3 – Maximum Weld Bead Protrusion for Copper-nickel Piping ⁽⁵⁾

Nominal Pipe Diameter mm	Pipe Size Nominal Pipe Size	Maximum Protrusion mm
< 40	<1½	1.5
50-150	2 - 5	2.0
175-250	6 - 10	2.5
> 300	>12	3.0



Figure 3 - Erosion corrosion of 90/10 copper-nickel after the weld on a weld neck flange due to excessive flow velocity (Courtesy of KME)

There is one case where bulk water velocities in excess of those in Table 2 can be used, and that is when the flow is intermittent. A classic example of this is in firewater systems, either on or offshore. It is a common practice to use 90/10 copper-nickel small bore pipe with NAB or gunmetal sprinklers. The velocity when the seawater is flowing can be 5 to 10 m/s and, although a small amount of erosion corrosion may occur, it is trivial because these systems are usually only tested for about one hour per week and remain stagnant for the rest of the time. Any surfaces that have suffered erosion corrosion can then re-passivate. Copper-nickel firewater systems have been successful all over the world.

In addition to these maximum velocities, it is also advisable to ensure a minimum velocity in waters where there is mud or silt in suspension, as this can settle out at very low water velocities, where it will reduce the heat transfer coefficient. It may also give rise to some corrosion under deposits. Different authorities recommend various minimum flows from 0.5 to 1 m/s. The cleaner the water is, the lower the minimum flow to prevent deposit formation.

All of the above discussion has been concerned with flow in pipes. Copper-nickel cladding has been used on ships' hulls and on offshore platform steel legs⁽⁷⁾. The safe velocities in such applications can be higher and reference should be made to specialist publications such as references⁽⁷⁾ and⁽⁸⁾.

With heat exchangers that are high up, as in the case of many steam dump condensers, it is not uncommon to use the syphon effect to increase flow. The diagram in Figure 4 shows how air can be released under syphonic conditions and the turbulence from this can result in severe erosion corrosion⁽⁹⁾. Analyses of real condensers have shown that the inlet and outlet of the second pass are most susceptible to this form of attack⁽⁹⁾. Figure 5 shows severe erosion corrosion of 66/30/2/2 Cu-Ni-Fe-Mn tubing from a steam dump condenser due to syphonic air release. Attack due to syphonic air release can be prevented by maintaining a pressure in the tubing exceeding 0.6 bar⁽⁹⁾.

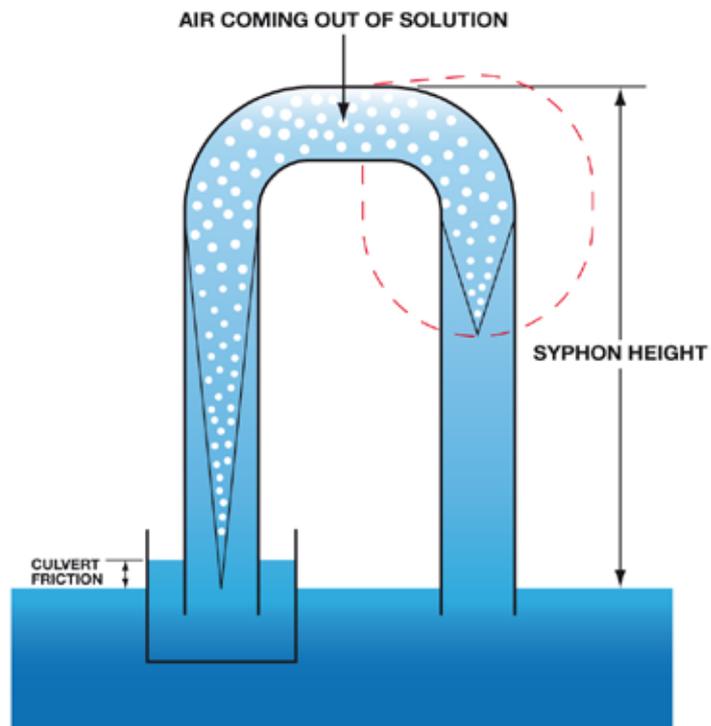


Figure 4 - Diagram showing syphonic air release

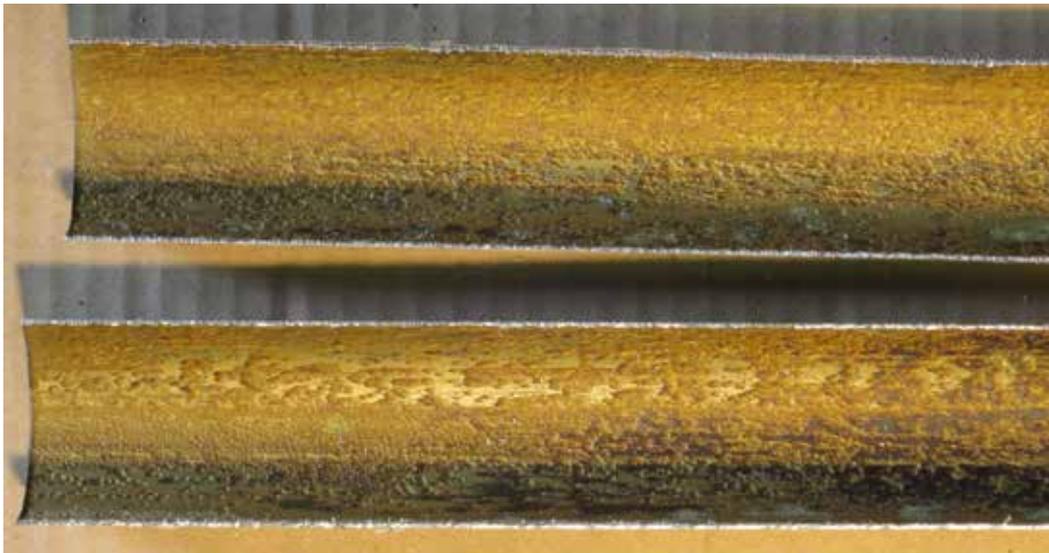


Figure 5 - Severe erosion corrosion of 25.4 mm OD 66/30/2/2 Cu-Ni-Fe-Mn in a dump condenser due to syphonic air release

4.0 Temperature

As stated earlier in Section 2.0, temperature has only a minor effect on the corrosion of the copper alloys in Table 1 when used in seawater. Stainless steels can suffer crevice corrosion in seawater and the upper temperature limit for superduplex and 6% Mo austenitic alloys is about 35 to 40°C. Although copper alloys can suffer crevice corrosion, the attack is outside the crevice rather than inside, as for stainless steels. In addition it is rarely deeper than 0.2 mm and the author knows of no service failures of copper-nickel due to crevice corrosion. This means that copper-nickel is ideal for seawater and firewater piping in installations in tropical climates, where exposure in the sun can lead to pipe wall temperatures of 60 to 70°C, especially under stagnant conditions. There are many examples of the successful use of copper alloys in tropical seawater systems, while there have been crevice corrosion failures of high alloy stainless steels due to crevice corrosion at temperatures > 40°C.

Although some of the copper-zinc alloys can suffer selective loss of zinc (dezincification) in some waters, particularly at elevated temperatures, none of the gunmetals or aluminium brass suffer from dezincification in seawater⁽³⁾.

Low alloy stainless steels, such as the 300 series austenitic alloys can suffer chloride stress corrosion cracking (SCC) at moderate temperatures, with concentrations of chloride less than that in seawater. The copper-nickel alloys, gunmetals and the bronzes are not susceptible to chloride SCC⁽³⁾.

5.0 Pollutants

There are two main pollutants that can cause corrosion of copper alloys in seawater – sulphide and ammonia. These will be dealt with separately in the following sections. There is little data on the effect of the two together, but what is known is discussed in the section on ammonia.

5.1 Sulphide

Sulphide is usually produced in seawater by anaerobic bacteria that reduce the sulphate to sulphide as part of their metabolic processes (Sulphate Reducing Bacteria [SRB]). Sulphide alone is not particularly corrosive to copper alloys but, when deaerated water containing sulphide mixes with aerated seawater, the mixture can be extremely corrosive. This can occur for example when deaerated bottom mud is stirred up by a seawater suction pipe close to the bottom. Sulphide is not usually a problem in the open ocean, but Figure 6 shows a failure of a 90/10 copper-nickel pipe handling seawater on an FPSO (floating production, storage and offloading) vessel. The sulphide was introduced because the sewage outfall was placed too close to the seawater intake.



Figure 6 - Pitting attack of 90/10 copper-nickel due to sulphide in the seawater (Courtesy of Intertek)

The attack takes the form of pitting, which is exacerbated the higher the seawater velocity. All copper alloys are susceptible to attack by sulphides, but NAB and 66/30/2/2 Cu-Ni-Fe-Mn are the most susceptible, with 70/30 copper-nickel being the most resistant. Admiralty gunmetal and phosphor bronze are better than NAB in sulphide polluted water and have been used for pumps in such waters ⁽³⁾.

When selecting copper alloys, it is important to not only know the sulphide content, but also whether it is continuously present or only intermittently. As little as 0.01 mg/L sulphide has caused serious corrosion of the most susceptible copper alloys and, if any sulphide is detected in the water, one of the methods to combat it, described in the following text, should be adopted.

Where the sulphide is present continuously, one option is to fit a redox probe near the beginning of the section with copper alloys and use it to control the redox potential with small doses of chlorine/hypochlorite. This solved problems of sulphide attack in some Belgian power stations and the method is described in more detail in reference ⁽¹⁰⁾. It is important that excess chlorine is NOT injected, as this will cause accelerated corrosion of many copper alloys in the presence of sulphide ⁽³⁾.

The same method can be adopted for intermittently polluted waters as well, as chlorine will only be dosed when the redox potential drops due to the presence of sulphide. However, there are other methods that can be used to prevent premature failure in the case of intermittent pollution.

One of these is to aid protective film formation during periods of non-pollution. While simply flowing clean seawater through the piping and heat exchangers is important, the corrosion resistance of the heat exchanger tubes can be increased by ferrous sulphate dosing. This is usually done by adding a concentrated solution of ferrous sulphate directly into the inlet water box, or into the pipe close to the water box, to give a concentration of 1 mg/L Fe²⁺ in the seawater for one hour per day. This can sometimes be discontinued after sixty days, when a protective film has formed on the tubes. The dosing must be done correctly and more details are given in Section 12.

Whether the pollution is continuous or intermittent, it is recommended that the copper alloys most resistant to sulphides be chosen to minimise the risk of a premature failure. For heat exchanger tubes the most resistant alloy is 70/30 copper-nickel, while for castings for pumps and valves, admiralty gunmetal is the best. It is preferred to phosphor bronze because it is difficult to make pressure-tight castings in this alloy, while, if the lead content of admiralty gunmetal is at the maximum, castings will be pressure-tight.

5.2 Ammonia

Ammonia is less well known as a problem pollutant in seawater, but it has caused a number of service failures and can arise from a number of causes⁽³⁾. These include discharges from adjacent fertiliser plants, the die-back of certain algae blooms and cargo ships washing out fertiliser storage tanks while close to shore. There are other causes, but most indicate that ammonia pollution is intermittent and coastal.

This means that water analyses for the site must cover various states of the tide and times of the year if possible. Ammonia concentrations of 1 to 2 mg/L can give rise to problems and higher concentrations will increase the risk of attack. Even if ammonia is only detected at 0.2 to 0.5 mg/L, it is advisable to take the precautions discussed below, as there may be higher concentration pollution incidents in the future. Heat transfer is required to initiate attack, and therefore it only affects heat exchanger tubing. 90/10 copper-nickel and 66/30/2/2 Cu-Ni-Fe-Mn are the most susceptible alloys, while aluminium brass is the most resistant. Attack due to ammonia takes the form of pitting at deposits or adjacent to crevices, but can also occur as pitting if the water flow velocity is very low. There is no minimum temperature for ammonia pitting, and as little as 10°C difference across a copper-nickel tube has caused pitting. Figure 7 shows corrosion of 90/10 copper-nickel due to ammonia in the as-received condition and after removing the corrosion products.

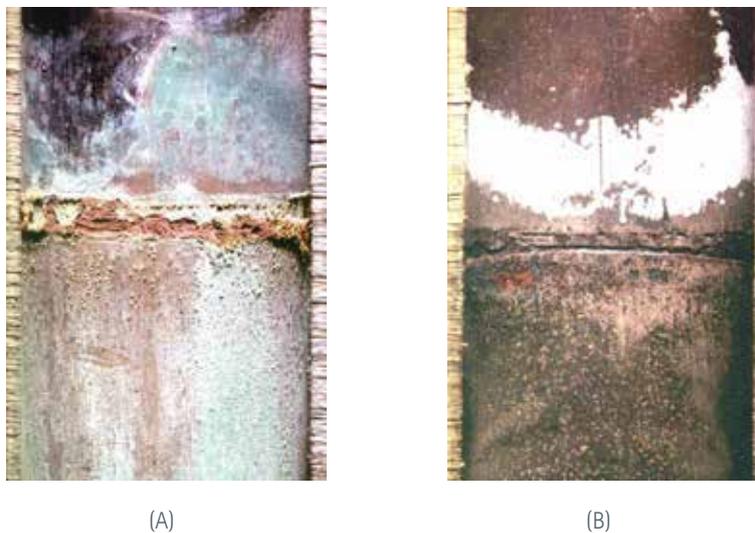


Figure 7 - Ammonia induced attack of 90/10 copper-nickel heat exchanger tube
(A) As-received (B) After cleaning in cold 10% sulphuric acid

The best way to resist ammonia pollution is to form protective films in clean seawater as quickly as possible. While flowing clean seawater through the heat exchangers will help, dosing with ferrous sulphate has proved to be extremely beneficial in several cases⁽³⁾, and the guidelines in the Appendix should be followed for dosing in the correct manner. As for sulphide pollution, it is often necessary to dose only for the first sixty days, while protective films form. Thereafter dosing can often be discontinued, or significantly reduced. It is important to do regular ammonia checks throughout the start-up period to ensure that high contamination levels are not occurring. During start-up, ammonia concentrations above 2 mg/L are best avoided by shutting down, if possible, until the pollution incident is over.

Although some copper alloys, particularly brasses containing $\geq 40\%$ zinc, are susceptible to SCC in the presence of ammonia, tests on copper-nickel and aluminium brass heat exchanger tubing showed no SCC of heavily cold-worked tubing after sixty days exposure to seawater with 2 mg/L ammonia⁽³⁾. Other testing showed no cracking of aluminium brass with 1,000 mg/L ammonia, but extensive cracking with 7,500 mg/L. No cracking occurred with 90/10 copper-nickel, even at the highest ammonia concentration⁽³⁾.

The presence of ammonia and sulphide together is rare but may occur in very polluted harbours with mixed waste, or downstream of a water inlet heavily fouled with zebra mussels. The latter can give off both sulphide and ammonia as part of their metabolic processes.

Accelerated corrosion by zebra mussels can be alleviated by their removal and the introduction of low level chlorination (0.3 to 0.5 mg/L continuously) to prevent their re-introduction. In the case of very polluted harbour water, the best solution is to adopt a low level chlorine dosing system with a redox probe, as for continuous sulphide pollution, described earlier, combined with ferrous sulphate dosing to aid film formation.

6.0 Fouling and Chlorination

It is well known that copper alloys have inherent low susceptibility to the attachment of marine organisms, such as shellfish and sea grasses ⁽²⁾. Even when it does attach, it sloughs off or detaches readily and does not generally cause a corrosion problem. However, micro-organisms (slimes) can adhere, although they do not generally cause a corrosion problem. If the copper alloy is connected to a less noble metal, such as steel or cast iron, or the alloy is cathodically protected, then this can make attachment of marine organisms more likely ⁽²⁾.

Attachment of micro-organisms can impede heat transfer and seawater systems with copper alloys are often dosed with chlorine/hypochlorite to optimise heat transfer. The dosing may be at a low, continuous level or it may be at higher concentrations intermittently. It has been shown that excessive chlorination exacerbates erosion corrosion with copper alloys ⁽¹¹⁾. Figure 8 shows a scratch on an aluminium brass tube that did not heal due to excessive chlorine. Similar scratches on tubes not dosed with chlorine did not show any attack.



Figure 8 - Erosion corrosion of a scratch on an aluminium brass condenser tube due to excessive chlorination

The study of Francis ⁽¹¹⁾ did not include NAB, but the author has seen erosion corrosion of NAB pump impellers due to excessive chlorination and it is suggested that the safe levels of chlorine recommended for use with 90/10 copper-nickel also be used with NAB. The recommended safe levels are shown in Table 4. Note that these are mean levels, as fluctuations will always occur in service, and excursions to 1.0 mg/L with a mean level of 0.5 mg/L would not be uncommon in practice. Copper-nickel alloys are perfectly capable of tolerating these variations. It is pointless dosing with very high concentrations of chlorine/hypochlorite, because fouling can be controlled with a concentration of around 0.5 mg/L in the inlet water box or 0.1 to 0.2 mg/L at the discharge ⁽¹²⁾. With intermittent dosing it is acceptable to dose at lesser chlorine concentrations or longer intervals than are shown in Table 4, but there is no data to support higher doses at longer intervals.

Table 4 - Recommended Safe Chlorine Dosing for some Copper Alloys

Alloy	Maximum Safe Chlorine Dose (mg/L)	
	Continuous	Intermittent
Aluminium Brass	*	1.0 for 1h/12h
90/10 Copper-nickel	0.5	1.0 for 1h/12h
70/30 Copper-nickel	1.0	2.0 for 2h/12h
66/30/2/2 Cu-Ni-Fe-Mn	2.0	2.0 for 2h/12h
Nickel Aluminium Bronze	0.5+	1.0 for 1h/12h

* May be 0.5 mg/L with ferrous sulphate dosing, but not at the same time (see Section 12.0 and text)

7.0 Coupling to Other Alloys

When dissimilar metals are coupled together in a corrosive, conducting medium, such as seawater, it is possible for the more electronegative, or less noble alloy, to corrode more. This is known as galvanic or bimetallic corrosion, and there are some simple rules to avoid this in seawater ⁽¹³⁾.

It is well established that in most cases the coupling of different copper alloys together does not cause any significant galvanic corrosion. Rolled naval brass tube plates will slowly dezincify in seawater, but coupling such plates to copper-nickel tubes will not significantly increase the rate of attack.

The commonly used engineering alloys can be arranged in a series of groups according to potential and corrosion resistance, as shown in Table 5 ⁽¹³⁾. It can be seen that copper alloys and austenitic cast irons may be connected to each other without any problem. If copper alloys are connected to alloys from Groups 1 or 2 in seawater, then they may suffer galvanic corrosion, but the severity of the attack will depend on the area ratio. Provided the wetted area of the Group 1 or 2 alloy is significantly less than that of the copper alloy (<1:10), the galvanic corrosion will not be significant.

Table 5 – Alloy Groupings for Galvanic Corrosion in Seawater at Ambient Temperature

Category	Type	Alloy
Group 1	Noble; passive	Ni-Cr-Mo Alloys (Mo>7%) 6% Mo Austenitic Stainless Steel Superduplex Stainless Steel Titanium and its Alloys
Group 2	Passive; not truly corrosion resistant	Alloys 400/K500 904L 22% Cr Duplex Alloy 825 Alloy 20 316L
Group 3	Moderate corrosion resistance	Copper Alloys Austenitic Cast Iron
Group 4	Poor corrosion resistance	Carbon Steel Cast Iron
		Aluminium Alloys *

* Carbon steel/cast iron and aluminium alloys are separated by a line because aluminium alloys will suffer galvanic corrosion if coupled to cast iron or carbon steel in seawater.

If a copper alloy is connected to an alloy from Group 4, then it will increase the Group 4 alloy's corrosion rate, the degree depending on the area ratio. The smaller the area of the copper alloy compared with the Group 4 alloy, the less will be the galvanic corrosion.

If the area ratio cannot easily be adjusted to minimise galvanic corrosion, then changing one of the alloys to something compatible may be required. Coatings can help, but it is the cathode that must be coated. The cathode is the alloy from the lowest group number in the couple, e.g. stainless steel in a stainless steel/copper-nickel couple (Group 1/Group 3). The coating must have a reasonable life so it does not have to be replaced too often and it must be correctly applied to get good adhesion with minimum defects. Coating the anode alone works while the coating is intact, but should it break down locally it creates very small anodes, which results in high rates of attack at the exposed anode metal. The problems of galvanic corrosion and other methods of avoiding galvanic corrosion in special cases are discussed in reference ⁽¹³⁾.

In some cases the addition of chlorine to the seawater may reduce, or even prevent, galvanic attack. Figure 9 shows the metal loss at the junction of a 6% Mo austenitic stainless steel pipe with a 90/10 copper-nickel pipe for natural and chlorinated seawater. In chlorinated seawater there is no significant galvanic corrosion of the 90/10 copper-nickel, while in natural seawater there is a rapid loss of metal at the dissimilar metal junction. Experiences on North Sea oil platforms have shown this to be true ⁽¹³⁾. The problem is if the chlorination system fails. Rapid corrosion of the copper-nickel will not start immediately, but would be expected to start within a day or two, so a prolonged shutdown of the chlorination system could

8.0 Start-up

lead to a leak at the junction in a matter of weeks. Hence, it is advisable to design the system assuming that galvanic corrosion is possible. For piping, coating the stainless steel (or other high alloy material) for about six pipe diameters from the junction, including the flange faces, will minimise the attack⁽¹³⁾. Isolating flanges can also be used, but it is important to check that there is no continuity before first filling the system with seawater. It is common for metal pipes, valves and pumps to be electrically connected via the electrical earthing system or via supports and hangers⁽¹³⁾. This prevents the isolating flange from working and another preventative method must be adopted.

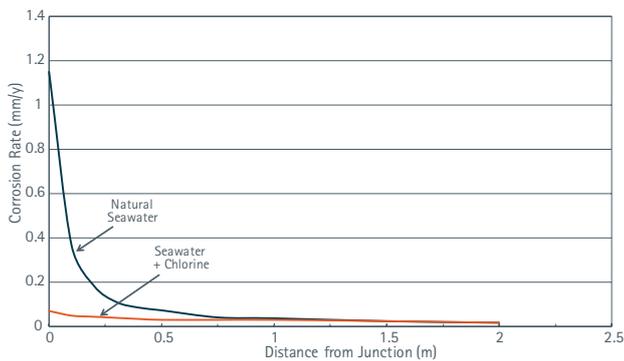


Figure 9 - Effect of chlorine on the corrosion of a 90/10 copper-nickel pipe coupled to one of 6% Mo austenitic stainless steel

The low corrosion rate of copper alloys in seawater is provided by the protective corrosion product film that forms on the surface during exposure to seawater. This is different to the film that forms in air, so it cannot be formed on the alloy prior to installation. If the film forms in clean seawater it can give excellent resistance to incidents that might cause accelerated corrosion of bare metal, such as excessive chlorination, or a temporary ingress of pollutants. The bare metal may be new material inserted to replace badly corroded material or included as a plant modification, or it could be existing material that has had the protective film removed by acid cleaning, to remove scale or other unwanted products. Hence, it is most important to get the material into service in clean seawater as soon as possible.

It is common to pressure test seawater systems before they enter service. The preferred method is to fill the system with clean, fresh water, but sometimes this is not possible and dock water is used. In this case the system must be drained immediately after pressure testing and then washed thoroughly with fresh water to remove anything that might lead to corrosion before entering service. Any retained polluted water, or water containing SRB that can become active, can result in accelerated corrosion before the system enters service.

Once the unit has first entered service it might be necessary to use ferrous sulphate dosing, to encourage protective film formation (Section 5.0 and Section 12.0). First start-up should not be attempted when there are significant pollutants in the water as non-protective films will form. However, where this is unavoidable, either the redox probe with low level chlorine dosing technique, or ferrous sulphate dosing, may be used to minimise the damage to the films (see Section 5.0 and Section 12.0). Films formed in polluted seawater will slowly revert to their protective composition over a period, when exposed to clean seawater. The time for this to happen can vary from a couple of weeks to a couple of months, depending on the severity of the pollution incident.

In addition to the start-up of a new system, there can be a risk of corrosion when a system must be shut down for extended periods. Corrosion can occur if the system is left full of stagnant seawater for some time and SRB become active (Section 5.1). Accelerated corrosion can then occur when the system is restarted. While the films that form in natural seawater can give some resistance, there are additional precautions that are advised depending on the water quality and the shutdown time. Reference⁽²⁾ (Table 23) gives advice on the best procedures to avoid corrosion for long and short shutdowns in both clean and polluted seawater.

9.0 Quality

When purchasing all corrosion resistant alloys it is usual to use common engineering standards, such as ASTM. However, most of these are fairly basic and other tests or requirements often need to be added to ensure that good quality material is supplied. This is also true for copper alloys for seawater service ⁽¹⁴⁾.

It is important to use reputable suppliers with a good track record of supplying copper alloys for seawater applications. Low cost suppliers may not meet all the requirements and the cost to correct a problem after supply and installation is often more costly than using a reputable supplier initially. It is also important to put proper QA/QC procedures in place to ensure all the requirements are met.

Below some useful extra requirements, not included in all standards for the copper alloys mentioned above, are discussed.

9.1 90/10 Copper-nickel

The iron content of this alloy is vital to ensure good resistance to erosion corrosion and some standards permit iron contents of 1.0 to 2.0 wt%. It is important to specify a minimum iron content of 1.5% for optimum resistance. This should present no problem to reputable suppliers.

At this iron concentration it is not in solution at room temperature and the alloy must be annealed at high temperature and rapidly cooled to hold the iron in solution, where it imparts optimum corrosion resistance. Iron does not come out of solution to any significant extent during welding of good quality 90/10 copper-nickel because the thermal cycle is too fast ⁽⁶⁾.

A particularly fast cool is also important in applications such as mine sweepers, where a low magnetic signature is required for 90/10 copper-nickel (e.g. relative magnetic permeability < 1.08).

9.2 Nickel Aluminium Bronze

Nickel aluminium bronze is mostly used as castings, either to BS EN 1982 or to ASTM B148, although the alloy may also be used as wrought plate or bar. In either case it is recommended that the alloy be specified with the nickel content around 0.5 wt% greater than the iron content, as this has been shown to give the best microstructure and corrosion resistance ⁽⁹⁾.

In addition, it is necessary to give a final heat treatment after all hot working/welding has been completed for optimum seawater performance. This is mandatory in some UK MOD navy standards, and it is beneficial for other marine applications too. The recommended heat treatment for castings is $675 \pm 15^\circ\text{C}$ for 4 to 6 hours followed by air cooling, while for wrought product it is $740 \pm 20^\circ\text{C}$ for 1 to 2 hours followed by air cooling. The heat treatment has been shown to optimise the mechanical properties and it also removes any residual beta phase, which will corrode rapidly in seawater ^(3, 15). Figure 10 shows a seam welded NAB pipe that had

not had a final heat treatment, and corrosion of the residual beta phase caused the pipe to corrode along the seam weld after a few months in seawater.



Figure 10 - Corrosion of nickel aluminium bronze pipe along seam weld due to residual beta-phase

It is important that castings are inspected by both DPI (dye penetrant inspection) and X-ray radiography to check for defects and porosity, in addition to a visual inspection.

9.3 Heat Exchanger Tubing

All copper alloy heat exchanger tubing needs a range of tests in addition to those of dimension and straightness. A typical specification for aluminium brass is discussed in reference ⁽¹¹⁾ and this includes some extra tests that are not in the usual standards. The most important of these is a test for residual carbon films from the manufacturing process, as these are known to cause rapid corrosion of copper alloy heat exchanger tubes in seawater service ^(3, 14). The most commonly specified method is based on the LECO test, where a small sample is heated in oxygen at progressively higher temperatures and the carbon is measured as CO_2 . The carbon given off at the highest temperature ($\sim 900^\circ\text{C}$) is from any residual carbon film. It is common to specify that this carbon be $\leq 0.2 \text{ mg/dm}^2$, and this should be done regularly, say every 300 tubes. Manufacturers using modern production methods should have no trouble satisfying this requirement.

The additional minimum iron content for 90/10 copper-nickel should also be included.

10.0 Conclusion

Copper alloys have been used successfully for over 50 years in seawater systems, mostly with great success and high reliability. Like all materials, copper alloys have their limitations and the main ones, for seawater service, have been highlighted in this document. Taking these points into account during design will ensure a high reliability system or component with a long life and requiring minimum maintenance.

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12.0 Appendix

12.1 Ferrous Sulphate Dosing

Ferrous sulphate dosing has been widely used to aid in the formation of protective films on aluminium brass, in particular, but also occasionally with copper-nickel alloys. In order for ferrous sulphate dosing to work properly it must be carried out correctly^(A1). There are many instances where ferrous sulphate dosing has not worked because it was not done in the correct manner. To help understand why this is important, the role of ferrous sulphate should be understood.

12.1.1 Role of Ferrous Sulphate

When ferrous sulphate is added to water it forms a fine colloid with a negative charge or zeta potential^(A2). With time (tens of seconds) the colloidal particles agglomerate, forming larger particles with a lower charge^(A3). The ferrous sulphate works by the colloidal particles being attracted to a metal surface by an extension of the metal's natural electric field^(A2). This is stronger in flowing water compared with static water^(A2). This explains why ferrous sulphate dosing has little beneficial effect under stagnant conditions, while it has proved to be very efficacious under flowing conditions around 2 m/s, typical of that in heat exchangers.

Because the colloid loses its charge as it grows, there is less tendency for it to be attracted to metal surfaces as it progresses through the system. This is why it is recommended that ferrous sulphate be dosed close to, or into, the inlet water box of the heat exchanger being treated^(A4). However, where two are in series, experience has shown that injection near the inlet of the first heat exchanger produces a satisfactory film on the tubes in both heat exchangers, as described below.

It has also been shown that chlorine accelerates the growth of the colloid and thus reduces its effectiveness, as it is not attracted to metal surfaces as easily^(A3). Hence, it is recommended that chlorine dosing to control fouling be turned off while ferrous sulphate dosing is being carried out^(A5).

Because the colloid starts growing as soon as the solution is made up, it is also recommended that the solution be made up fresh each time, immediately before dosing into the seawater flow^(A3, A5).

Because the solution and the seawater are aerated, the ferrous sulphate oxidises rapidly to an oxy-hydroxide of iron, FeOOH. This is the orange-brown deposit that is found on the tubes, and it works by allowing the natural protective film to form while being shielded from the most aggressive effects of the seawater flow.

12.1.2 Dosing Practice

The ferrous sulphate solution should only be made up immediately prior to use, because ferrous sulphate decomposes in aerated solution and this practice also reduces colloid growth (see above). It should be made up in condensate or boiler feed water, not tap

water or seawater, as it decomposes more quickly in these. It is usual to make it up as ~10% w/v solution of commercial ferrous sulphate and this should be stirred vigorously until the ferrous sulphate dissolves. This solution has a pH ~3, so care should be exercised when making up the solution.

The solution is dosed into the inlet water box, or as close to it as possible; certainly no more than a few metres upstream. It should be dosed to give a concentration of Fe²⁺ of 1 mg/L for one hour. Because chlorine accelerates the colloid growth, all chlorine/hypochlorite dosing should be turned off for the dosing time plus 15 minutes before and after dosing, as discussed above.

With aluminium brass it has been found that coastal plants often require ferrous sulphate dosing once a day for the life of the plant. With copper-nickel alloys it is often sufficient to dose daily for sixty days until a protective film has formed. Thereafter the ferrous sulphate dosing can be stopped, or significantly reduced.

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