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Copper alloys versus stainless steels for seawater cooling systems - the pros and cons

A GUIDE TO THE USE OF
NICKEL-CONTAINING ALLOYS

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by Roger Francis, November 2020

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1. INTRODUCTION

Many industrial processes require cooling and in numerous cases seawater is the only source of a large volume of coolant. There is a long experience with seawater cooling systems, both onshore and offshore. Because of the varying requirements of these plants there is no single material solution for all systems. Two common options are copper alloys and high alloy stainless steels, and both of these have advantages and disadvantages. This paper discusses the properties and corrosion resistance of both alloy classes and points out where one alloy option might be preferred. Provided the recognized limits of use of these alloys are observed in design, both options can give a long and successful life. Some case histories are presented to demonstrate both successes and premature failures.

2. ALLOYS

In seawater cooling systems utilising copper alloys, it is common for the pipes, fittings and flanges to be 90/10 copper-nickel (UNS C70600), while the valves and pumps are cast nickel aluminium bronze (NAB, C95800). The nominal compositions of these alloys are shown in *Table 1*. Very large diameter (≥ 1 m) piping may be fibre reinforced plastic (FRP), but the valves are commonly cast iron or steel with neoprene lining and NAB internals. While 90/10 copper-nickel is often used for heat exchanger tubing, there are two 30% nickel alloys that can be used when the fluid is more corrosive. Their compositions are shown in *Table 1* and their specific use will be discussed in section 4.

The compositions of some common austenitic and duplex stainless steels are also shown in *Table 1*. The pitting resistance equivalent number, or PREN, is an empirical formula that relates the composition to the resistance to pitting and crevice corrosion in near neutral chloride solutions, including seawater. The higher the PREN, the greater is the resistance to corrosion. This is discussed in more detail below. For every austenitic alloy there is a duplex stainless steel with a similar corrosion resistance, but usually containing less nickel and molybdenum. Duplex alloys are often more cost-effective than the austenitic ones of comparable corrosion resistance, provided that they are available.

Also included in *Table 1* are the compositions of two high nickel alloys. The use of these will be discussed in section 3.

The minimum mechanical properties of the copper alloys and stainless steels are shown in *Table 2*. Note that 90/10 copper-nickel pipe can be supplied hardened with increased strength. This does not affect its corrosion resistance. It can be seen that the stainless steels are stronger than the copper alloys, and the duplex stainless steels are stronger than the austenitic alloys. This means that the stronger alloys have higher design stresses. However, it is difficult to utilise this in most seawater cooling systems, as pressures are generally low (≤ 10 bar) and temperatures rarely exceed 70°C. Hence, thin-walled pipe is the norm, often schedule 10S.

Table 1 Nominal composition of the alloys in the text.

Alloy type	UNS No.	GENERIC NAME	NOMINAL COMPOSITION (wt.%)								PREN*
			Fe	Cu	Ni	Cr	Mo	W	N	Other	
Copper-base	C70600	90/10	1.7	Bal	10	-	-	-	-	1 Mn	N/A
	C71500	70/30	0.8	Bal	30	-	-	-	-	0.7 Mn	N/A
	C71640	66/30/2/2	2	Bal	30	-	-	-	-	2 Mn	N/A
	C63300	Alloy E	3	Bal	5	-	-	-	-	10 Al	N/A
	C63200	NAB	4	Bal	4.5	-	-	-	-	9 Al	N/A
	C95800	NAB	4	Bal	4.5	-	-	-	-	9 Al	N/A
Austenitic stainless steel	S31603	316L	Bal	-	10	17	2	-	-	1.5 Mn	24
	N08904	904L	Bal	1.5	25	20	4	-	-	1 Mn	34
	S31254	6%Mo	Bal	0.7	18	20	6	-	0.2	0.7 Mn	43
	N08367	6%Mo	Bal	-	25	20	6	-	0.2	1 Mn	43
	N08926	6%Mo	Bal	1	25	20	6	-	0.2	1 Mn	43
Duplex stainless steel	S32205	2205	Bal	-	5	22	3.2	-	0.17	1 Mn	35
	S32550	Alloy 255	Bal	2	6	25	2.5	-	0.2	1 Mn	37+
	S32760	Z100	Bal	0.7	7	25	3.6	0.7	0.25	0.6 Mn	>41
	S32750	2507	Bal	-	7	25	3.7	-	0.27	0.5 Mn	>41
Nickel-base	N06625	625	3	-	Bal	21	9	-	-	3.5 Nb	51
	N06022	C-22	3	-	Bal	22	13	3	-	-	70

Bal = Balance N/A = Not Applicable * PREN = $\%Cr + 3.3(\%Mo + 0.5\%W) + 16\%N$ +- This alloy may be ordered to PREN>40

Table 2 Minimum mechanical properties of the common copper alloys and stainless steels. (ASTM B543 for Cu-Ni alloys; B763 for NAB and A240 for stainless steels)

ALLOY TYPE	UNS No.	GENERIC NAME	0.2% PROOF STRESS (MPa)	TENSILE STRENGTH (MPa)	ELONGATION (%)
Copper-base	C70600 (A)	90/10	140	320	40
	C70600 (H)	90/10	300	450	10
	C71500	70/30	170	400	40
	C71640	66/30/2/2	175	450	35
	C95800	NAB	270	660	15
Austenitic stainless steel	S31603	316L	170	485	40
	N08904	904L	220	490	35
	S31254	6%Mo	310	655	35
	N08367	6%Mo	310	655	30
	N08926	6%Mo	295	650	35
Duplex stainless steel	S32205	2205	450	655	25
	S32550	Alloy 255	550	760	15
	S32760	Z100	550	750	25
	S32750	2507	550	795*	15

(A) – annealed (H) – hardened; * Only for thin sections, otherwise as S32760

When selecting alloys for seawater cooling systems, it is necessary to consider not only the corrosion resistance, but also price and availability. These latter two factors may tilt the material selection one way rather than another. Finally, there are considerations of fabrication, and these are discussed in section 3.

2.1 Heat exchangers

When copper-nickel tubes are used for heat exchangers they are usually rolled into the tubesheets, which can be made from a number of wrought copper alloys. Nickel aluminium bronze is common and both C63200 and C63300 have been used successfully. Less common is 90/10 copper-nickel, either solid, or clad onto steel (for larger heat exchangers). Naval brass (C46400) has been used for tubesheets, but it does dezincify in seawater, so tubesheets must be thick (typically 35mm or more). The dezincification can be slowed by fitting sacrificial mild steel ($C < 0.15\%$) anodes in the water box. These need to be correctly sized to avoid creating undue turbulence and to allow a reasonable service interval between replacements.

Water boxes for copper alloy systems may be carbon steel coated with neoprene or lined with 90/10 copper-nickel sheet. Smaller units may have solid NAB water boxes. None of these combinations of tubesheet and waterbox alloys gives any cause for concern about galvanic corrosion (see section 4.7)

When 6%Mo austenitic or superduplex stainless steel tubes are used in a heat exchanger, it is common to use superduplex stainless steel for the tubesheets. The austenitic alloys can be rolled into the tube plate but it requires more care than with copper alloys to obtain a satisfactory seal. When both tubes and tubesheet are superduplex, it is common to seal weld the tubes to the tube sheet. This is not difficult with automatic multi-head GTAW welding machines.

The water boxes with high alloy stainless steel tubes may be solid 6%Mo austenitic or superduplex (Z100 or 2507) stainless steel (see *Table 1*). For larger units carbon steel water boxes can be clad with 2mm thick 6%Mo alloy. It is much more difficult to clad thin superduplex sheet onto curved water box surfaces and austenitic alloys are

preferred. Some desalination plants in the Middle East have used 2205 duplex for the water boxes and have fitted sacrificial mild steel ($C < 0.15\%$) anodes to prevent crevice corrosion of the 2205 duplex. This has been very successful when the anodes are correctly designed and installed.

Sometimes it is desired to use titanium tubes in a heat exchanger and this presents no galvanic problems with high alloy stainless steels in the water box, tubesheet or piping. Where space is at a premium titanium plate heat exchangers are sometimes installed, and high alloy stainless steel piping is galvanically compatible with this. Copper-nickel piping can also be made compatible with titanium heat exchangers, as described in section 4.7.

3. FABRICATION

The copper-nickel alloys are often used in seawater and welding is preferred for high strength joints. The iron content of 90/10 copper-nickel exceeds the solubility limit at room temperature and so iron may come out of solution if a matching composition filler is used and the weld cools too slowly¹. This can reduce the corrosion resistance of the weld metal, particularly the erosion-corrosion resistance¹. For this reason, it is common to weld 90/10 copper-nickel with 70/30 (C71500) copper-nickel filler. The higher nickel content greatly increases the iron solubility limit and there is no risk of iron precipitation on cooling. Note that slow cooling of thick section welds may cause iron to precipitate out of solution in the HAZ. This can be avoided by suitable joint design and the selection of appropriate welding parameters when qualifying the welding procedure.

When welding nickel aluminium bronze (NAB) it is common to use a matching filler. However, the weld bead cools very quickly and not all the beta phase present at high temperature may transform to alpha and kappa phases^{1,2}. Beta phase is highly anodic to alpha phase and will corrode rapidly in seawater. Hence, a post weld heat treatment (PWHT) is desirable to ensure that all the beta phase transforms. The most common heat treatment is that specified by the Royal Navy (UK) for all welds to NAB. This involves heating at 675°C for six hours followed by air cooling. Where post-weld heat treatment is not possible, then the use of Cu/8Al/3Fe filler is an alternative. Although

no post weld heat treatment will be required, the joint will not be as strong as one made with matching filler, and may not be as strong as the parent metal. The use of a single-phase filler does not result in any preferential weld corrosion in seawater as the potentials of both aluminium bronzes are similar. *Figure 1* shows a seam welded NAB pipe that had not been post-weld heat treated. After exposure to seawater, the beta phase corroded rapidly with the result that the seam weld “unzipped”.

The 6%Mo austenitic alloys are usually welded with a high nickel alloy filler metal, such as alloy 625 (N06625). This is because a weld with matching filler has a very dendritic structure in the as-welded condition and the dendrites are depleted in chromium and molybdenum, reducing corrosion resistance. The alloy 625 weld metal also has a dendritic microstructure, but the higher alloy content means that it still retains enough corrosion resistance in seawater. The exception to this is where the weld is to be inside a crevice. The crevice corrosion resistance of as-welded alloy 625 is less than that of parent 6%Mo metal³, and it is necessary to use a more highly alloyed welding consumable, such as alloy C-22 (N06022) or similar.

The best properties in duplex stainless steels are achieved when the phase balance is roughly 50/50 austenite/ferrite. As the weld cools very quickly, it would be very ferritic if a matching composition filler were to be used, so the

Figure 1 Corrosion of the beta phase in an NAB seam welded pipe that had not been post weld heat treated.



filler metal usually contains 2 to 3% more nickel to ensure a suitable phase balance. It is imperative to prevent the formation of third phases, such as sigma and chi, during welding, so it is important that the joint is correctly designed and the heat input and interpass temperatures are carefully controlled. Third phases, such as sigma, are intermetallics that deplete the local matrix in chromium and molybdenum, and reduce both toughness and corrosion resistance. *Figure 2* shows a corroded superduplex weld that had significant third phases present.

The performance of stainless steel welds can be improved by pickling, but this is difficult inside a small diameter piping system⁴. Where pipework is being spooled for mechanical assembly on site, the spools can be pickled by commercial establishments with large pickling tanks. The author has done this in the UK for a number of projects.

An alternative is to use a soft start up, and one was described by Francis and Byrne⁵.

- Start in cold seawater for two days (minimum)
- Run in cold chlorinated seawater for 5 days (minimum)
- Turn on heat exchangers and operate normally.

Francis and Byrne give an example where this enabled superduplex piping after some gas coolers to be operated at high seawater temperatures (~55°C) without pitting of welds or crevice corrosion of flanged joints⁵. This can be of benefit

Figure 2 Corrosion and leakage of a superduplex weld due to precipitation of sigma phase in the HAZ.



whether the welds have been pickled or not and can also increase the resistance to crevice corrosion for parent metal.

Where fabrication on-site is required, rather than bolting prefabricated spools together, the availability of suitably qualified local welders may influence the choice of alloy system. In some parts of the world local welders may be familiar with superduplex stainless steel, for example, but may have no experience with welding 6%Mo alloys.

4. CORROSION

It is well established that for a stainless steel to resist pitting and crevice corrosion in seawater it must have a PREN > 40 (e.g. ref 4). This has been written into standards, such as NORSOK, the Norwegian oil and gas standard, as well as some major company technical specifications⁶. As such it can be seen from *Table 1* that only the 6%Mo austenitic and superduplex stainless steels satisfy this criterion. The higher alloy Ni-Cr-Mo alloys also have a PREN > 40, but these alloys are much more expensive. The discussion below deals with the corrosion resistance of these two classes of high alloy stainless steel, as well as 90/10 copper-nickel and NAB.

4.1 Pitting

Neither 90/10 copper-nickel nor NAB is susceptible to pitting in natural seawater, but NAB can suffer from selective attack of the kappa III phase¹. This only happens when a protective

film has not formed on the NAB, and it is rarely seen in commercial service.

The 6%Mo austenitic alloys are not susceptible to pitting in seawater up to at least 40°C, and neither are welds, when made with a suitable nickel alloy filler metal. Superduplex stainless steel welds will not pit in seawater up to about 40°C, although this temperature may be increased by pickling or a soft start up, as described in section 3.

4.2 Crevice corrosion

Both 90/10 copper-nickel and NAB can suffer crevice corrosion in seawater, but it is very shallow, and there are no known instances of it causing a failure in service¹. The attack does not vary much with temperature and copper alloys have been used at high seawater temperatures.

All stainless steels are susceptible to crevice corrosion in seawater and the resistance to attack increases with alloy content. *Figure 3* shows the depth of crevice attack from three different laboratories at three natural seawater temperatures⁷⁻⁹.

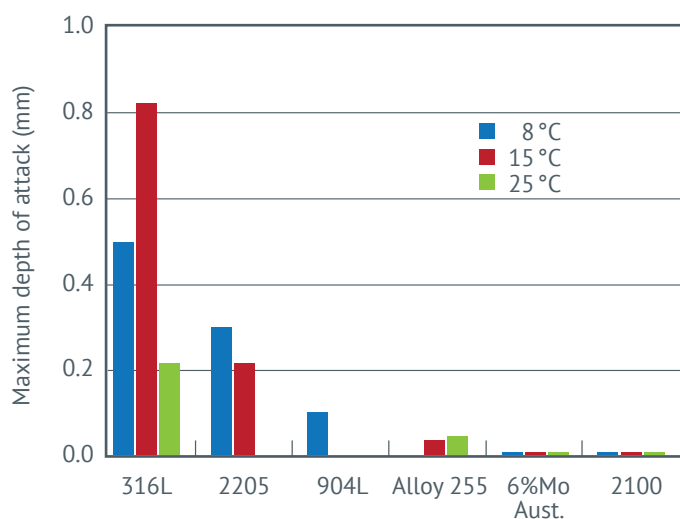
Only the 6%Mo and superduplex alloys were free of attack. The severity of attack varies with the tightness and depth of the crevice and a typical ASME B.16 style flanged joint is regarded as a moderate crevice, while a screwed joint is a severe crevice. Typical limits of use in seawater with a flanged joint are 35°C for 6%Mo alloys and 40°C for superduplex alloys⁴. The limits of use with screwed joints are not known, but will be much lower.

As crevice corrosion of copper alloys occurs outside the crevice, rather than inside, as for a stainless steel¹, the tightness of the crevice is not very significant.

4.3 Erosion corrosion

Erosion corrosion occurs when the water flow is so turbulent that it disrupts the protective film, causing metal dissolution and the film reforms, which is then further broken down. It is well known that copper alloys can suffer erosion corrosion in seawater and the velocities shown in *Table 3* have been recommended for heat exchanger tubes and piping¹. The maximum velocities in pipe are greater than for heat exchanger tube, because of increased turbulence in smaller diameter tubing. Note that the speed of rotation of the

Figure 3 Depth of crevice corrosion of some stainless steels in natural seawater at three temperatures⁷⁻⁹. (Alloy 255 had a PREN = 37)



perimeter of a pump impeller is not the maximum velocity in a pump, because the water there is also moving. The actual velocity in a pump can be calculated from the impeller dimensions and the maximum flow¹⁰. The velocities in *Table 3* are meant as guidelines and must be used in conjunction with good design practice.

Table 3 Recommended maximum velocities for copper alloy piping in seawater ¹		
Alloy	Maximum velocity (m/s)	
	Heat exchanger	Pipe (>nps 3)
90/10 Copper-Nickel	2.0 – 3.0	3.0– 3.5
70/30 Copper-Nickel	2.5 – 3.5	3.0 – 4.0
66/30/2/2 Cu/Ni/Fe/Mn	2.5 – 4.0	3.5 – 4.5
NAB	-	3.5 – 4.5

When silt is present in cooling water it can cause increased erosion corrosion of copper alloys, particularly heat exchanger tubes. The 66/30/2/2 Cu-Ni-Fe-Mn alloy (C71640) has been found to give increased resistance to erosion corrosion in the presence of silt¹. It is also very good under more aggressive conditions, such as in the brine heater in multi-stage flash desalination plants (~110°C)¹.

The successful use of copper alloys and the avoidance of erosion corrosion depend on the quality of the design. Utilisation of the velocities in *Table 3* alone is not sufficient. It is important to avoid designs that increase local turbulence. Hence 5-D bends are preferred to 3-D bends, and 3-D bends are preferred to elbows. Traditional 90° elbows produce a lot of turbulence just downstream of the bend, which can lead to erosion corrosion. Smoothing out the flow with a radiused bend minimises this effect.

Similarly, in heat exchangers, it is important not only to use a suitable velocity for the tubes, but also to use a water box design that distributes water evenly to all the tubes without raising turbulence. Shone and Grimm¹¹ warn against just increasing water box dimensions proportionately when designing a large heat exchanger. To avoid turbulence, water boxes need to be deep, particularly if sacrificial anodes must be accommodated. Also, the water inlet should not be immediately opposite the tubesheet, because this tends to force most of the water down the central core of tubes. An angled inlet, or one at right angles to the tubesheet,

is preferred, with internal baffles if necessary, to ensure uniform water flow to all tubes¹².

The protective chromium-rich film on stainless steels is very resistant to erosion corrosion and Kain et al observed the following depths of attack after 30 days at 30 m/s and 30°C¹³.

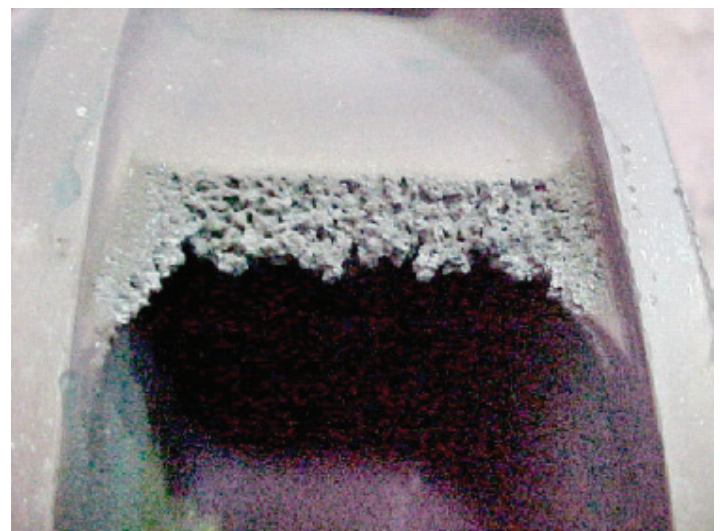
Alloy	Depth (mm)
316L	0.06
6%Mo	0.00
Z100	0.00

It might be assumed that stainless steel seawater pipework could be operated at much reduced diameter and higher velocity than copper alloys to reduce costs. This is possible to a certain extent, but in practice the maximum velocity is ~10 m/s because of increased noise at higher velocities and the much increased cost of pumps.

4.4 Cavitation

Cavitation is a corrosion phenomenon that can result in the loss of large amounts of metal over a relatively small area. It occurs when there is a sudden drop in pressure, usually at a high flow velocity. This creates a series of vapour cavities that may be up to 1 mm in diameter¹⁴. These cavities or “bubbles” migrate along the pressure gradient, until the external pressure is sufficient to cause their collapse. The

Figure 4 Typical appearance of cavitation damage.



energy release when they collapse can be sufficient to mechanically remove metal from the adjoining surface. This is termed cavitation damage and often presents a jagged honeycomb appearance, as shown in *Figure 4*.

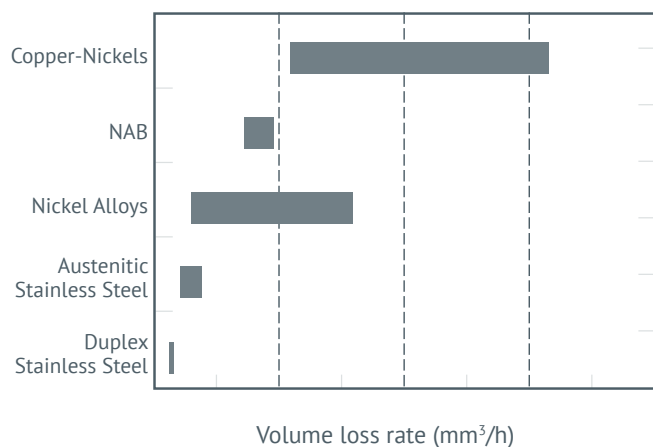
Cavitation can occur in pumps, particularly when they are being operated under conditions well removed from the design optimum. Cavitation damage occurs towards the eye of the impeller, while any damage at the outer edge of the impeller is usually erosion corrosion. Cavitation is also seen after partly throttled valves or orifice plates, where the pressure drop is large and the flow is often high. Hence, cavitation in a seawater cooling system would be seen in both cast NAB and cast superduplex stainless steel.

Angell reports tests on a wide range of engineering materials in a seawater cavitation tunnel at a velocity of 40 m/s and a cavitation number of 0.08¹⁴. These conditions are very severe, much worse than might normally be seen in a poorly operated seawater pump. The results in *Figure 5* show that there was very little attack on duplex stainless steel and only a little more on NAB. This demonstrates the good resistance to cavitation of both these alloys.

4.5 Stress corrosion cracking

Stress corrosion cracking (SCC) occurs with many alloys and requires the combination of a stress with an environment that will cause SCC. While copper alloys and stainless steels can suffer SCC in some environments, these do not occur

Figure 5 Cavitation data obtained in seawater with a cavitation tunnel at 40 m/s and a cavitation number of 0.08¹³.



in seawater cooling systems. Copper alloys can suffer SCC in ammonia, but very high concentrations are required, compared with the few mg/L described in the next section¹. Superduplex stainless steel can suffer from SCC in chloride solutions, but it requires high chloride concentrations (around saturation) and high temperatures (>100°C) to initiate SCC⁴.

4.6 Chemical additions and pollutants

There are a number of chemicals that may be added to seawater systems, or may be present as pollutants. The first of these is chlorine, which is added to control fouling and thus increase heat transfer. Copper alloys will resist macrofouling, but can harbour slime films¹. Stainless steels do not resist fouling in seawater and some form of anti-fouling system will be required. This is usually the addition of chlorine or hypochlorite.

Francis carried out tests with the common copper alloy heat exchanger alloys and showed that the main effect was on erosion corrosion (impingement attack)¹⁵. As the chlorine concentration increased the depth of attack increased, but at different rates for different alloys. The following safe continuous dosing levels were recommended¹.

Alloy	Chlorine (mg/l)
90/10 Cu-Ni	0.5
70/30 Cu-Ni	1.0
66/30/2/2 Cu/Ni/Fe/Mn	2.0
NAB	0.5

A dose of 0.5 mg/L is more than adequate to control fouling in a seawater system¹⁶. If the chlorine is dosed intermittently, say for ½ to 1 hour per day, then higher levels of chlorine are safe¹⁵.

Chlorine increases the risk of crevice corrosion of stainless steels. Norwegian experience suggests an upper temperature limit of 20°C for superduplex and 6%Mo alloys with tight crevices (such as screwed couplings) with 1.5 mg/L chlorine¹⁷. Some companies have had better experiences with these alloys and permit use up to 30°C or higher for less severe crevices (e.g., flanged joints). The NORSOK limit is considered overly conservative by some, and a combination of service experience and laboratory

data suggests the maximum temperature is a function of chlorine concentration, as shown by Francis and Byrne⁵. They recommended the following chlorine limits for moderate crevices for superduplex stainless steel in seawater at different temperatures from a combination of laboratory data and service experience⁵.

Temperature (°c)	Chlorine (mg/l)
10	200
20	5
30	1
40	0.7

This shows the tolerance of superduplex stainless steels to chlorine in cooler waters. Concentrated chlorine/hypochlorite should not be injected directly into the suction intake of pumps as it is likely to exceed the maximum safe dosing level. Instead the chlorine should be injected a few meters from the suction to allow it to dilute before entering the pump.

It is well known that the presence of even small amounts of sulphide (≥ 0.01 mg/L) in an aerated seawater line can cause severe corrosion of copper alloys¹. The sulphide may have a number of origins, but it is often caused by sulphate reducing bacteria in bottom mud or in deaerated water.

Figure 6 Severe corrosion of an NAB pump impeller due to sulphide pollution.



The attack is velocity related and is deepest in regions of higher velocities¹. *Figure 6* shows severe corrosion of an NAB pump impeller due to sulphides.

If the sulphide contamination is intermittent or low, then one option is to use 10% tin bronze (C92400) for the pump impellers, as this alloy is very resistant to sulphides¹. For heat exchanger tubing 70/30 copper nickel is more resistant to sulphides than 90/10 copper-nickel¹. An alternative is to monitor the redox potential and to inject low levels of chlorine/hypochlorite when the redox potential drops, indicating the presence of sulphide. This has been very successful in a Belgian power station¹⁸.

Ferrous sulphate dosing can be used to build up a protective film on copper alloy heat exchanger tubes that can protect against intermittent exposure to sulphides¹. Dosing is usually 1 mg/L Fe²⁺ for one hour per day into the water box or close to it. Details of ferrous sulphate dosing are explained in the Appendix.

High alloy stainless steels are not affected by sulphide pollution in seawater and they have been used to replace NAB pumps and valves where sulphide pollution was severe.

Ammonia can also occasionally be a pollutant in seawater. There are a number of possible origins for the ammonia, but when it is present from 1 to 10 mg/L it can cause severe pitting/crevice corrosion in heat exchangers, particularly under deposits or at low flow regions¹. It only occurs in combination with heat transfer. Alloy 90/10 copper-nickel is most susceptible to this form of attack, but it can be prevented by ferrous sulphate dosing until protective films have formed¹, as described in the Appendix. Francis describes a case history in the Middle East where ferrous sulphate dosing cured the problem in a multi-stage flash desalination plant¹. Ammonia does not affect the corrosion of high alloy stainless steels in seawater.

4.7 Galvanic corrosion

When metals are immersed in a conducting liquid they adopt an electrochemical potential, usually measured with respect to one of the standard reference electrodes. When two metals with different potentials are connected together a current will flow between them, called the galvanic current. Corrosion will increase on the anode (more electronegative)

metal, and the greater the current, the greater is the galvanic corrosion. This is controlled in practice by the area ratio of the anode and cathode and the cathodic efficiency of the cathode. For a detailed explanation and discussion of galvanic corrosion refer to reference 19.

Francis reviewed the published data on galvanic corrosion in seawater and concluded that alloys could be put into groups, with alloys in the same group suffering no significant galvanic corrosion when coupled together¹⁹. The groups are shown in *Table 4*, and there is plenty of evidence that all the alloys in group 1 can be safely coupled together, e.g. superduplex stainless steel piping and titanium heat exchangers. Similarly the copper alloys have slightly different potentials, but there is a large body of experience showing that different copper alloys can be connected together without any significant galvanic corrosion.

Table 4 Alloy groupings for seawater at ambient temperature

Category	Type	Alloy
1	Noble; passive	Ni-Cr-Mo alloys (Mo>7%) 6%Mo Austenitic stainless steel superduplex stainless steel titanium and its alloys
2	Passive; not resistant to crevice corrosion in seawater	Alloy 400/ K-500 904L 22%Cr duplex Alloy 825 Alloy 20 316L
3	Moderate corrosion resistance	Copper alloys Austenitic cast iron
4	Poor corrosion resistance	Carbon steel Cast iron
		Aluminium alloys

Carbon steel and the cast irons and the aluminium alloys are in separate sub-sections of group 4, because there is plenty of evidence to show that aluminium alloys will suffer galvanic corrosion when coupled to carbon steel or cast iron¹⁹.

Problems can arise when copper alloys (group 3) and alloys from group 1 are connected together. The copper alloy is the anode and the corrosion can be severe if the cathode to anode area ratio is large. The author saw severe corrosion

of 90/10 copper-nickel piping coupled to a titanium plate heat exchanger on a large tanker. The solution was to fit titanium piping with a good quality internal coating either side of the heat exchanger to electrically separate the anode and cathode. Ideally the isolation pipes should be ~6 pipe diameters long to significantly reduce the galvanic current, but there was only space for pipes 5 diameters long. However, this prevented further failures of the copper-nickel piping.

Because NAB valves are lower cost and more readily available than superduplex valves, a number of projects have fitted NAB valves into superduplex seawater piping. This has caused accelerated corrosion of the NAB valves until they will no longer seal when closed¹⁹. *Figure 7* shows a badly corroded NAB valve after two years in a superduplex seawater piping system. Francis discussed the factors that affect the galvanic corrosion of NAB coupled to superduplex stainless steel and described several service failures²⁰. The only solution was to replace the NAB with superduplex valves. There have been similar failures of NAB sprinkler heads in superduplex stainless steel firewater systems, and again replacement with superduplex sprinklers was the only solution²⁰.

There is one material that can cause galvanic corrosion of group 1 alloys and that is graphite¹⁹. Graphite is sometimes

Figure 7 Badly corroded NAB valve from a superduplex stainless steel seawater line.



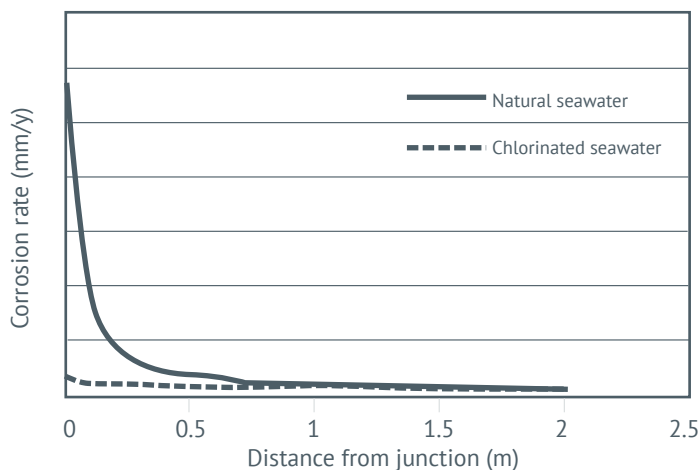
used in gaskets for low pressure seawater systems and it has caused galvanic corrosion and leakage in service. Francis and Byrne reviewed the published corrosion data and recommended suitable gasket materials to avoid this problem²¹. They also recommended suitable materials for spiral wound gaskets, used in higher pressure systems, to avoid galvanic corrosion²¹. The gasket materials recommended for low pressure seawater systems are synthetic fibre gaskets and neoprene. For spiral wound gaskets the metallic winding should be galvanically compatible with the piping material, as shown in *Table 4*.

It is sometimes asked if chlorination can affect galvanic corrosion in seawater. With NAB/superduplex stainless steel couples, the rate of galvanic corrosion is reduced, but it still occurs¹⁹. The NAB valve in *Figure 7* was exposed in a chlorinated seawater system. Chlorination can significantly reduce the galvanic corrosion between 90/10 copper-nickel and high alloy stainless steel. However, the galvanic corrosion rate without chlorine is very high and if the chlorination should fail there could a catastrophic leak before it was fixed. *Figure 8* shows the corrosion rate of a 90/10 copper-nickel pipe coupled to a high alloy stainless steel in natural and chlorinated seawater.

5. SERVICE EXPERIENCE

There are thousands of seawater cooling and firewater systems in both copper alloys and high alloy stainless steel,

Figure 8 Corrosion of 90/10 copper-nickel pipe coupled to a high alloy stainless steel in seawater¹⁹.



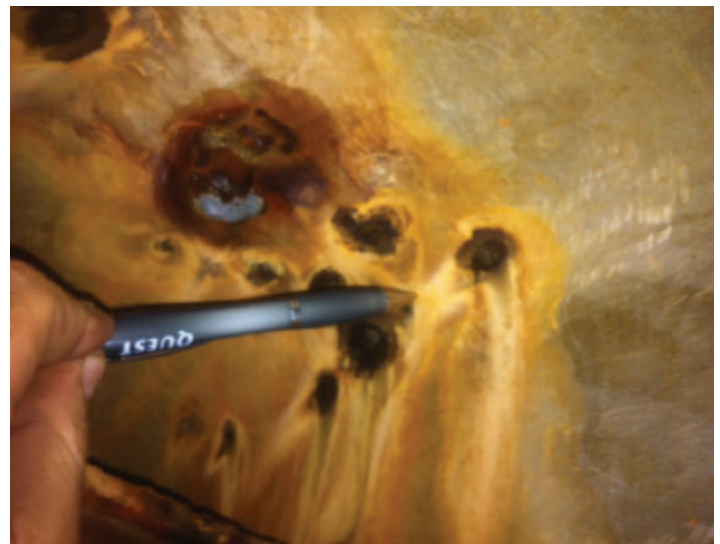
both onshore and offshore, which have given excellent service. Some examples are shown on the next two pages. It is important to follow the design rules as discussed above to avoid problems.

The few problems with copper alloys have mostly been due to excessive seawater flow velocities or pollution by sulphides or ammonia. The counter measures described above are usually satisfactory.

There have been a few corrosion problems with 6%Mo austenitic stainless steel, and the most common are crevice corrosion and excessive seawater temperatures²². With superduplex piping systems the major problems have been excessive chlorination and poorly made welds⁵.

More recently there have a number of problems with the supply of poor quality material. This has largely been due to inadequate heat treatment of castings, pipe, flanges and fittings⁴. *Figure 9* shows severe corrosion of a superduplex seawater pump due to poor heat treatment. It is imperative that a project technical specification with appropriate testing is prepared, in addition to the applicable ASTM material specification when procuring high alloy stainless steels²³. It is also necessary to have adequate QA/QC to police the specification and ensure full adherence⁴.

Figure 9 Deep pitting of a superduplex stainless steel pump due to poor heat treatment.



Examples of the use of copper-nickel and superduplex alloys in seawater

90/10 Copper-nickel piping on a tanker.



Photo courtesy of Wieland-Eurcaro

Two sections of a superduplex stainless steel manifold for the seawater cooling system of a large alumina plant.



Photo courtesy of Rolled Alloys

A large superduplex stainless steel seawater pump



Photo courtesy of Rolled Alloys

90/10 Copper-nickel deluge skid



Photo courtesy of Blaze Manufacturing Solutions

A superduplex stainless steel heat exchanger with a seal welded tubesheet.



Photo courtesy of Rolled Alloys

High alloy stainless steels have often been preferred for offshore cooling systems because of the opportunities for reduced weight by using smaller diameter piping and higher flow rates. However, in firewater systems these velocities are not a problem for copper alloys. A firewater system may operate at 5 to 10 m/s but it is only tested for about 1 hour per week. At a velocity of 9 m/s Francis observed a depth of attack of 0.2 mm after 60 days with 90/10 copper-nickel¹⁵. For a firewater system this equates to over 25 years' service to achieve the same depth of attack. In practice it would probably be far longer, because the copper-nickel would be reforming protective films during the non-operating time. In fact copper alloys and stainless steels are not mutually exclusive. The author knows of at least two offshore platforms in tropical waters where the seawater cooling pipework was superduplex stainless steel and the firewater system was copper-nickel/NAB, because of the latter's greater resistance to crevice corrosion at elevated temperatures. Temperatures up to 70°C have been measured on firewater pipes in tropical regions when the water is not flowing.

It is important that NAB have PWHT to remove all beta-phase, as described in the Fabrication section. There have only been a few failures due to lack of PWHT of NAB, but they can be costly.

As described above, the maximum operating temperature for superduplex stainless steel can be increased by a soft start up, and Francis and Byrne describe a case from the North Sea where the final operating temperature was ~55°C and there was no crevice corrosion or pitting of welds⁵. Pickling of welds or using welding gases containing nitrogen can also increase the resistance of superduplex welds to corrosion⁴.

When selecting materials for seawater piping and heat exchangers it is important to assess the requirements for the particular plant with regard to location, water quality, cost and availability of materials, and availability of suitably qualified local fabricators. There will be instances where copper-nickel/NAB is more suitable and others where stainless steels are more cost effective. As described above, not all of the systems need to be in the same alloy.

CONCLUSIONS

1. There are both advantages and disadvantages to the use of copper alloys or high alloy stainless steels for seawater cooling systems.
2. When selecting materials for a specific plant it is important to consider a range of factors to determine the most cost effective option.
3. For a single plant not all the systems need be in the same alloy and examples have been quoted where this has been effective.

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Appendix

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 correctly¹. 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.

Role of ferrous sulphate

When ferrous sulphate is added to water it forms a fine colloid with a negative charge or zeta potential². With time (tens of seconds) the colloidal particles agglomerate, forming larger particles with a lower charge³. The ferrous sulphate works by the colloidal particles being attracted to a metal surface by an extension of the metal's natural electric field². This is stronger in flowing water compared with static water². 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 treated⁴. 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 easily³. Hence, it is recommended

that chlorine dosing to control fouling be turned off while ferrous sulphate dosing is performed⁵.

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^{3,5}.

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.

Dosing practice

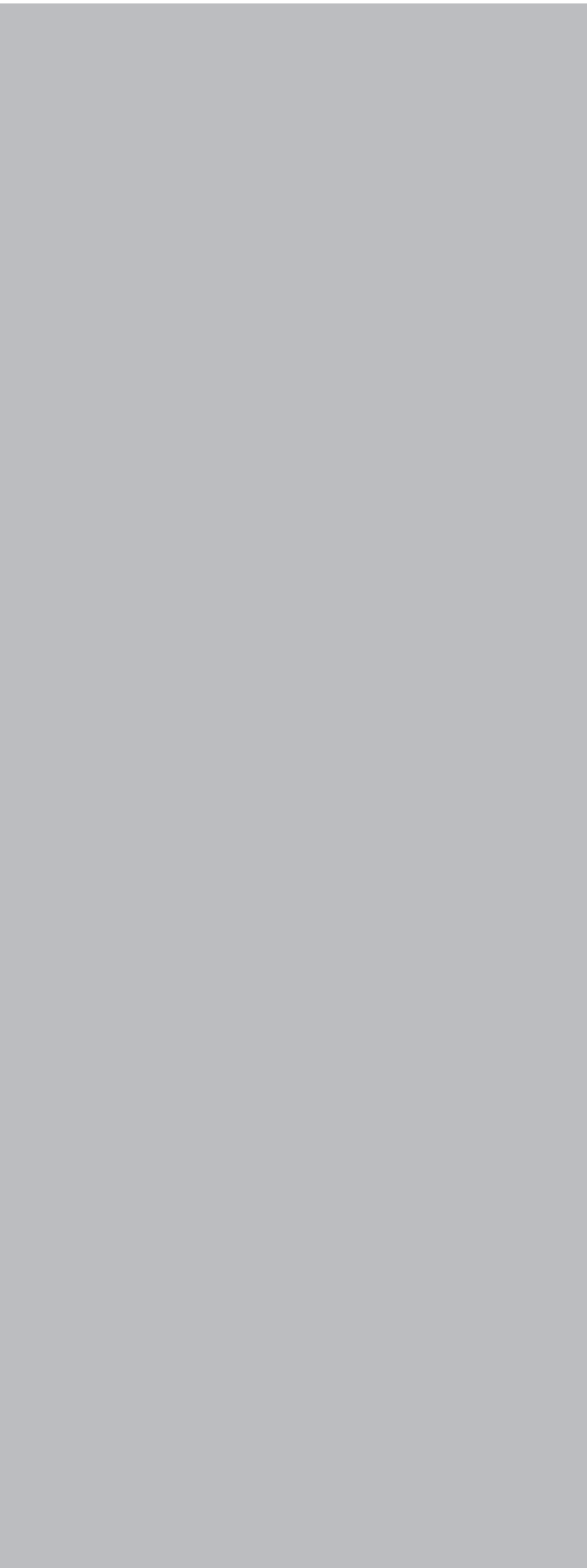
Because ferrous sulphate decomposes in aerated solution, it should only be prepared immediately prior to use. It should be prepared in condensate or boiler feed water, as it decomposes quickly in fresh water or seawater. It is usually prepared as ~10% w/v solution of commercial ferrous sulphate and this should be stirred vigorously until the ferrous sulphate dissolves. This solution has a pH ~3, so care should be exercised when preparing 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/chlorine dioxide dosing should be turned off during dosing time plus 15 minutes before and after dosing.

It has been found that coastal plants using aluminum brass heat exchanger tubes 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 60 days until a protective film has formed. Thereafter the ferrous sulphate dosing can be stopped.

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