

Corrosion and Biofouling Resistance Evaluation of 90-10 Copper-Nickel

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Abstract

Copper-nickel alloys for marine use were developed for naval applications in the early part of the 20th century with a view to improving the corrosion resistance of condenser tubes and seawater piping. They still enjoy widespread use today not only for many navies but also in commercial shipping, floating production, storage and offloading vessels (FPSOs), and in multistage flash desalination. The two popular alloys contain 90% or 70% copper and differ in strength and maximum sea water velocity levels they can handle but it is the 90-10 copper-nickel (CuNi10Fe1Mn) which is the more economic and extensively used. An additional benefit of this alloy is its high resistance to biofouling: in recent years this has led to sheathing developments particularly for structures and boat hulls.

This paper provides a review of the corrosion and biofouling resistance of 90-10 copper-nickel based on laboratory test data and documented experience of the alloy in marine environments. Particular attention is given to exposure trials over 8 years in Langstone Harbour, UK, which have recently been completed by Portsmouth University on behalf of the Nickel Institute. These examined four sheathing products; plate and foil as well as two composite products with rubber backing. The latter involved copper-nickel granules and slit sheet.

The trial results are consistent with the behaviour of the alloy in the overall review. There is an inherent high resistance to marine biofouling when freely exposed. Prolonged exposure to quiet conditions can result in some growth of marine organisms but this is loosely attached and can readily be removed by wiping or a light scraping. The good corrosion resistance of 90-10 copper-nickel in sea water is also confirmed and associated with the formation of a thin, complex, protective and predominantly cuprous oxide surface film, which forms and matures naturally on exposure to seawater. Sound initial oxide film formation is also known to help protect against susceptibility to sulphide pitting in subsequent exposure to polluted water. Corrosion resistance is maintained at higher flow rates than for steel and most copper alloys due to the resilience of this surface film. However, above a certain breakaway velocity, dependent on component geometry with respect to hydrodynamics of flow, the film can become damaged leading to impingement attack. In piping systems this is well understood and controlled by design. For flatter surfaces such as on marine structures and boat hulls upper flow limits are higher and still to be defined. Copper-nickel is found to have a good resistance to crevice corrosion and is not susceptible to chloride or sulphide or ammonia stress corrosion cracking in sea water.

Keywords : Copper-nickel, CuNi10Fe1Mn, Long-term exposures, Biofouling, Sheathing

Introduction

Marine grades of copper-nickel were developed over 50 years ago and still enjoy substantial application in desalination, offshore oil/gas and power industries. They were initially introduced for naval condenser systems and seawater piping service, and continue to be used by many of the world's navies and merchant shipping. The two main grades contain 10% and 30% nickel respectively, but it is the 10% alloy which is the more economical and more widely used.

Although the 90-10 copper-nickel is primarily used for its corrosion resistance in seawater, it also has an inherent high resistance to macrofouling. This property can be used to advantage in reducing or eliminating the need for biocide dosing in piping systems or condensers, avoiding antifouling coatings on boat hulls and minimising cleaning regimes on offshore platform legs or other marine structures.

The behaviour and performance of 90-10 copper-nickel in marine environments is well documented and is reviewed in this paper. The findings are compared with information recently obtained from 8 year exposure trials carried out on behalf of the Nickel Institute by Portsmouth University examining four products which can be used for sheathing marine structures[1]. These were hot rolled sheet, adhesively backed foil as well as two composite products with rubber backing. The latter involved copper-nickel granules and slit sheet.

90-10 Copper-Nickel

The 90-10 copper-nickel alloy contains small but important additions of iron in levels carefully chosen to provide the best combination of resistance to flowing seawater and localised corrosion. Composition ranges vary for different standards but a typical range and more common international standard designations are given in Tables 1 and 2.

Table 1
Typical 90-10 Copper-nickel Chemical Composition Ranges
Mass %

Ni	Fe	Mn	Cu	Zn Max	C Max	Pb Max	S Max	Other Max.*
9-11	1.0-2.0	0.5-1.0	Rem	0.5	0.05	0.02	0.05	0.2

*Total other impurities

Table 2
Designations for 90-10 Copper-Nickel Alloy

UNS No.	ISO	CEN
C70600	CuNi10Fe1Mn	CW352H

Maximum composition levels are tightened for some specific impurities because of their effects on hot ductility, and consequently on hot workability, and weldability. These same elements can also arise from external contamination during forming and welding and so good workshop practices are important.

The 90-10 alloy is readily welded by most common methods [2]. Consumables of the 70-30 alloy are normally used as they offer superior deposition characteristics to those based on 90-10 compositions. 65% nickel-copper alloy consumables are used to weld copper-nickel to steel as they can tolerate more iron dilution from the steel than the 70-30 copper-nickel alloy consumables.

Corrosion Resistance

General

The corrosion resistance of copper-nickel relies on the formation of a protective surface film which forms quickly on exposure to sea water and continues to mature over a period of years. Initial exposure to clean seawater and good surface film formation is important to the long-term performance of copper-nickel. The surface film is complex [3,4,5], multi-layered and can be brown, greenish brown or brownish black. It is predominantly comprised of cuprous oxide although it can contain nickel, iron oxide, cuprous hydroxychloride and cupric oxide. The initial film forms quite quickly over the first few days [6] but takes about 2 to 3 months to mature in temperate waters. At low temperatures the process is slower but the film will form even in Arctic and Antarctic waters. In higher temperatures water of around 27°C common to inlets for Middle East desalination plants, the film can be expected to form in a few hours.

Once a good surface film forms, the corrosion rate will continue to decrease over a period of years which makes it difficult to predict the life of copper-nickel alloys based on short term exposure. Specific corrosion rate measurements at the LaQue Center for Corrosion Technology taken over fourteen years [7] in tidal, flowing (0.6m/s) and quiet seawater show the corrosion rate decreases over a period of 5-6 years, stabilising out at about 1.3µm/yr, Figure 1.

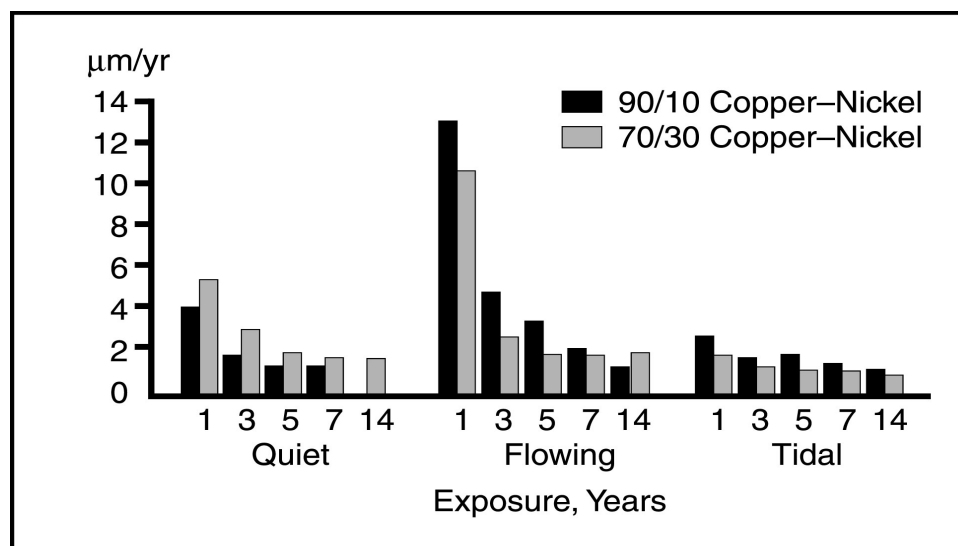


Figure 1 *The change in corrosion rate with time for 90-10 and 70-30 copper-nickel in quiet, flowing(0.6m/s) and tidal seawater [7].*

Generally, corrosion rates are anticipated to be between 0.02-0.001 mm/yr depending on seawater conditions and exposure time. However, sulphides [8] and ammonia in polluted water can lead to higher corrosion rates.

As seawater flow rate increases, corrosion rates remain low due to the tenacity of the protective surface film. However, when the velocity exceeds a critical value for a given geometry, the shear stress acting on the film can lead to its breakdown resulting in high corrosion rates. General experience has shown that 90-10 copper-nickel alloys can successfully be used in condensers and heat exchangers with velocities up to 2.5m/s. For pipeline systems, higher seawater velocities can be used in larger diameter pipes. BS MA18 [9] gives a maximum design velocity of 3.5m/s in pipes of 100mm and larger for 90-10 copper-nickel. Such guidelines are considered conservative but nevertheless have worked well because they take into account normal velocity raisers within piping systems which can cause areas of high local flow rates. However, extreme turbulence caused by conditions such as tight radius bends, partial blockages and areas downstream of partially throttled valves need to be avoided.

Higher velocities can be acceptable in specific situations. Experience has shown copper-nickel can readily withstand intermittent velocities to much higher levels than experienced under the continuous flow conditions in condensers and seawater pipework. Fire-mains often undergo flow of around 10-15m/s, during actual fires and test practices. Also, the hydrodynamics around ship hulls are different to piping systems. An upper service velocity for hulls is still to be established. Experience to date for the 90-10 alloy has shown minimal corrosion after 14 months at 24 knots(12m/s) [8] whereas the highest recorded velocity is 38 knots(19m/s) for a patrol boat which showed no measurable thickness loss after 200 hours at maximum operating speed.

Localised Corrosion Resistance

Copper-nickel alloys have good resistance to chloride pitting and crevice corrosion. Crevice corrosion rarely occurs and is a metal ion concentration cell type where, unlike stainless steels, any corrosion occurs outside the crevice. Copper ions released by surface reactions concentrate within the shielded area of the crevice making that area more noble than the adjacent exposed region. The resulting corrosion occurs next to the crevice and tends to be shallow in nature. Copper-nickel alloys are not susceptible to chloride or sulphide stress corrosion cracking or hydrogen embrittlement, and unlike brasses have not been found to suffer cracking due to ammonia in seawater service.

De-alloying is not a common occurrence in 90-10 copper-nickel. Denickelification has been identified to occur under heat transfer at near ambient temperature seawater if ammonia is present[10]. Dosing the cooling water with ferrous ions is an advantage although prevention normally requires avoidance of slow flow or stagnant areas. Minimum flow rates of more than 1m/s are usually preferred to avoid sediment build up.

Sulphides are present in polluted seawater and can also occur under stagnant conditions due to decomposition of organic matter. Their effect on copper-nickels is to interfere with the formation of the surface film producing a black film containing cuprous oxide and sulphide. The film is not as protective as those formed in clean water, and higher corrosion rates and pitting can be experienced. Exposure to sulphides should be restricted wherever possible and particularly during the first few months of contact with seawater while the oxide film is maturing. However, once formed, the sulphide film will gradually be replaced by an oxide film during subsequent exposure to aerated conditions, although high corrosion rates can be expected in the interim. Also, if an established cuprous oxide film is already present, then periodic exposure to polluted water can be tolerated without damage to the film.

Galvanically, copper-nickel alloys are more noble than zinc, aluminium, and steel. They are less noble than passivated stainless steels, high nickel alloys and titanium. The 70-30 alloy is slightly more noble than the 90-10 alloy. As with all bimetallic couples, due consideration needs to be given to favourable relative surface areas.

Seawater Treatments.

Copper-nickel tubing is resistant to chlorination at normal dosing levels used to control biofouling. Excessive chlorination, however, can be detrimental.

Ferrous sulphate treatment has been found to suppress corrosion rates of copper-nickel in both polluted and unpolluted conditions. It is not absolutely essential to the successful performance of copper-nickel and most ships in service have operated successfully without any dosing. However, ferrous sulphate can be viewed as a remedy when corrosion has occurred or as a precaution if corrosive conditions are likely.[4,8]

Iron anodes can also be used to release ferrous ions. This method however, is better for maintaining the protective layer than for initial oxide film formation and will also reduce the biofouling resistance.

Chlorination treatment and ferrous sulphate treatment should not be carried out simultaneously as ferric ions are formed which provide no beneficial effect.

Biofouling Resistance

General

To achieve the optimum resistance, the alloy should be freely exposed to seawater and not be cathodically protected or connected galvanically to less noble materials. General experience has indicated that in open seas, microfouling (slime layers) do not build up sufficiently to support macrofouling. When exposed to quiet conditions for long periods, some macrofouling will occur eventually but is loosely attached and will slough away at intervals or can be easily removed by finger pressure or a light scraping action [5,11,12,13].

The full reason for the biofouling resistance is not totally clear and requires more detailed work. The most likely explanation is that the biofouling resistance is a combination of copper ion release and the nature of the surface film. This may be linked with the unoxidised copper ions normally present within the protective film.

New Zealand Ferry Trials

An evaluation programme on the performance of adhesively backed 90-10 copper-nickel foil sheathing, gave practical insight into biofouling properties of 90-10 copper-nickel. The evaluation commenced in August 1993 [12] with two commercial passenger ferries, the MV *Koru* and the MV *Osprey*; both of which were in-service around Auckland Harbour, New Zealand. MV *Koru* was a slow ferry (10 knots), constructed of fibreglass reinforced polymer, which was retro-fitted with copper-nickel sheathing in 1993. The other vessel, a fast catamaran ferry (22 knots) with a FRP hull, was sheathed during construction in 1994. The older monohull vessel, MV *Koru*, was kept in reserve most of the time, whereas the

catamaran, MV *Osprey*, had been in service for about 40,000 nautical miles since construction by the time the work was reported in 1999.

The corrosion resistance of the copper-nickel appeared good. Slime (microfouling) formed on the copper-nickel but macrofouling was restricted. If colonisation did eventually occur, it was readily removed, such that a light water blast would quickly remove any growth. The turnaround time for cleaning the MV *Koru* on the slip by this method was about 1.5 hours whereas removal of fouling from the equivalent painted vessels in the fleet could take up to one day.

Flow velocity and sunlight appeared to influence biofouling behaviour. More algae formed on the copper-nickel foil just below the water line on both vessels and was more prevalent on the side of the MV *Koru* hull facing the sun during out of service time. Typically, the stern and waterline tended to show earlier signs of fouling than other hull areas. Areas between the hulls of the MV *Osprey* which experienced higher velocities remained almost entirely free.

Langstone Harbour Sheathing Product Trials

A 7 and 8 year raft exposure trial study in Langstone Harbour, UK, evaluating the corrosion and biofouling behaviour of the adhesive backed foil and three other copper-nickel sheathing products has also recently been completed [1].

Sheathing offshore platforms in copper-nickel[15] can be applied either for splash zone corrosion protection and/or to reduce biofouling and therefore wave drag, or minimise cleaning regimes on legs and risers. For straight splash zone corrosion protection, the copper-nickel is usually in sheet/plate form and welded into position e.g. Phase 1, Morecambe Field, UK. For biofouling protection, insulation from the structure is required. One commercially available product that has been successfully used for splash zone and biofouling protection of structural legs, cross bracings and riser pipes involves discrete rod like granules of copper-nickel, 1mm diameter and 1mm long bonded into the surface layer of 3mm thick rubber sheet [13,14]. The processing ensures that the granules are distributed and exposed over the surface such that about 30% of the surface is copper-nickel and each granule is close enough to its neighbour to allow surface protection. The product can be hot bonded onto elastomeric corrosion coatings or cold bonded directly onto steel. Application dates back to 1984 with over 25,000 square metres supplied for several platforms world-wide.

A second product was being developed for splash zone sheathing at the time the trials were initiated. It involved an expanded mesh design based on slits in the sheet and was conceived to allow ease of bonding to the rubber compared to full sheets. The product never became a full commercial product but was included in the programme to represent a third variation on surface coverage.

Copper-nickel has been used as solid sheet or roll clad onto steel for boat hulls [8]. It has also been applied as an adhesive backed foil. A system of sheathing of a ship's hull mentioned earlier with 90-10 copper-nickel involved the application of adhesive-backed panels (approximately 210mm x 500mm) to prepared hulls, allowing about 15mm overlap. The copper-nickel foil thickness is about 0.15mm and panels are easily cut and manipulated even over the most difficult of contours. The bonding system acts as an insulator, and as a barrier to seawater thus further protecting the hull from the corrosive action of seawater. The system

has been applied to new hulls and as a retrofit [12]. The foil adhesive backed panels used for the trials were manufactured in New Zealand and applied to the backing plates in the UK.

The testing of the granules/rubber product commenced in September 1994, and the foil, expanded mesh/rubber and a 3 mm hot rolled copper-nickel sheet sample in the period between July and November 1995. The samples were inspected at regular intervals over the exposure period, particularly prior to and after the spring and autumn fouling seasons. No cleaning regime was employed to the panels although small, localised areas were occasionally wiped manually to assess adherence of fouling. Photographic records of the appearances of these alloys as a function of time were obtained, the nature and development of the associated fouling community monitored and laboratory testing of removed samples carried out at exposure periods of 1, 3-5 and 6-8 years. The final samples were removed in November 2002. Table 3 summarises sample details.

Table 3.
Product and panel details

	Embedded Granules	Expanded mesh	3mm Hot Rolled Sheet	Adhesive backed foil
Description	90-10 Cu-Ni rods (1 mm dia, 1mm length) embedded by hot bonding into a 3mm thick polychloropropene rubber sheet	90-10 Cu-Ni expanded mesh, bonded to an elastomeric rubber base (EPDM)	As-manufactured and retaining surface oxide film	90-10 Cu-Ni foil sheets, with adhesive backing, hot pressed onto suitably prepared steel, aluminium and GRP surfaces.
Sample Details	18.4 x 24.0 cm. Mounted on GRP backing 6 samples	~9 x 19.0 cm curved samples 0.1 cm thick mesh, with slits 0.3 x 1 cm 6 samples	19.8 x 19.2 x 0.3 cm 1 sample	Alloy and backing plate: 61.0 x 31.0 cm 3 panels each with Al, steel and GRP backing plates.

Langstone Harbour Trial Results

Embedded Granules:

After an 8 year exposure trial period, the embedded granule product panels appeared to have successfully withstood the aggressive exposure conditions. A limited amount of macrofouling was present on the alloyed surface of the panel predominantly located on the polychloroprene, the GRP backing and at the edges with very little above the alloy itself. When wet, fouling deposits could be manually removed to expose the alloy surface.



Figures 2, 3, 4. *Embedded granule panels after 1, 5 and 8 years exposure*

A certain amount of corrosion and roughening of the copper-nickel rods exposed to the sea had occurred; some pits were seen at the ends directly exposed to the sea. However, little reduction in the measured rod diameters was observed; values of *ca.* 1.1 mm were found, similar to the specifications for new material. After 8 years, the rods were still embedded in the rubber matrix, although they could be removed by flexing the supporting matrix.

Expanded Mesh:

After a 7 year exposure trial period, the panels were largely undamaged by the exposure conditions. A very small amount of macrofouling was present on the alloyed surface of the panel. The fouling, where present, was predominantly located on the EPDM rubber, at the interfaces between the alloy and the rubber, and at the edges of the panels. Very little macrofouling was found on the alloy mesh. When wet, any fouling deposits could be manually removed from the alloy containing side of the panel to expose the alloy surface, Figure 5.

The rear surfaces of the panels were heavily fouled and the detritus could not be removed. Some corrosion and roughening of the surfaces of the copper-nickel exposed to the sea was observed.



Figures 5 and 6. *Expanded mesh panels after 2.5 and 7 year exposures*

Hot Rolled Sheet:

After a 7 year exposure trial period, the hot-rolled copper-nickel panel showed the best overall fouling resistance. It was only in the latter years that any deterioration in the condition of the surface was observed.



Figures 7 and 8. *Hot rolled sheet after 13 month and 7 year exposures*

A limited amount of macrofouling was present on the alloyed surface of the panel. Even after drying, macrofouling organisms and films could be easily removed from the surface. When wet, any fouling deposits could be manually removed to expose the alloy surface. Light generalised corrosion of the copper-nickel surface had occurred.

Adhesive Backed Foil:

After extended exposure periods, the GRP and steel based-panels had performed extremely well and remained largely free of macrofouling. After approximately 3.5 years exposure, the aluminium samples had corroded with concomitant detachment of the copper-nickel and were removed. In the case of the steel and GRP based samples, the alloy surfaces did not show any signs of detachment from the underlying substrates.

Considerable thinning and removal of the copper-nickel on the knife-edge of the panels was observed. This was attributed in part to erosion-corrosion of the alloy. Fouling plants and organisms were predominantly found at these edges and in overlap regions of the panels. Barnacles and fibrous material were also present after extended exposure times. Where present, macrofouling and detritus were loosely attached and could be wiped away with varying amounts of force. The copper-nickel on the flat surfaces of foil had thinned by a decreasing rate which is consistent with Figure 1 and was measured as averaging 5.5 mm per annum over a 7 year exposure period.



Figures 9,10 and 11. *Adhesive Backed Foil panels as immersed and after 18 month and 7 year exposure*

Conclusions

The review has shown 90-10 copper-nickel to have a unique combination of good resistance to both corrosion and biofouling in marine environments. Attention to maximum velocity

guidelines and good fabrication and commissioning procedures help ensure such behaviour is achieved. Recent Langstone Harbour, UK, trial results on sheathing products confirm this expectation and show that all products showed restricted colonization of fouling species and remained largely free of macrofouling. Where present it could be wiped away fairly readily. Some surface corrosion was observed and was measured on the foil product. This had thinned at a decreasing rate during the 7 years averaging at 5.5 μm per annum which was consistent with earlier US data showing corrosion rates decreasing over that time and stabilising at less than 2 μm per annum.

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