Corrosion Behaviour of Copper Alloys used in Marine Aquaculture

The excellent marine corrosion resistance of copper has been known and used to good effect for centuries. Copper alloys used in sea water service have low general corrosion rates but also a high resistance to many localised forms of corrosion which can lead to rapid failure. However, no alloy is totally immune and this overview addresses corrosion behaviour of three copper alloys used in marine aquaculture in order to allow engineers to design equipment and select conditions which can allow optimum performance.

The alloys specifically addressed are:

- 90-10 Copper-Nickel, CA 70600. This alloy contains 10% nickel and small amounts of iron and manganese which are important in providing high corrosion resistance.
- Seawire ™, a Copper-3% Silicon alloy containing manganese and microalloying elements; a proprietary trademarked product from Luvata.
- UR 30 ™, a 64% Copper-Zinc brass alloy with 0.6% tin, 0.3 % nickel and effective microelements; a proprietary trademarked product from Mitsubishi-Shindoh.

The three are very different types of copper alloy but, as a general observation, all have low general corrosion rates up to moderate sea water flow rates and with little tendency to pit. All rely on the formation of a protective surface film to form naturally by exposure to the sea water to provide their basic corrosion resistance.

The three alloys have high resistance to biofouling and this occurs when the alloys are freely exposed and their corrosion rates are unhindered by cathodic protection or are not galvanically protected by contact with less noble alloys. This means that their natural corrosion resistance needs to be fit for the environment as no other means of corrosion protection will be employed.

Types of corrosion.

All metals have the capability of corroding in certain environments and applied conditions. It is useful therefore to have some understanding of the types of aqueous corrosion which can occur in copper alloys in sea water.

General corrosion - This type of corrosion is a uniform thinning that occurs when alloys are exposed to aqueous environments. In many environments this may be negligible but, in aggressive ones, the rate of corrosion may be too high for the thickness of the metal and will lead to short service life. General surface corrosion is normally measured in rate of thickness loss as mm per year (mm/yr) or annum (mm/a). For copper alloys immersed in sea water, the general corrosion rate is usually less than 0.02mm/yr decreasing with time as the protective surface films mature.

Pitting - Pits are discrete sites of corrosion at areas where the protective surface film is damaged or breaks down. They can occur in copper alloys by surface contamination or sulphide pollution.

They can also be caused by sulphides generated in sediment or deposits by anaerobic bacteria. Copper alloys, unlike stainless steels, are not subject to chloride pitting.

Crevice corrosion - Crevices are shielded areas created where conditions are similar to the bulk environment and occur under deposits and tight metal or non metal contact areas such as washers, O-rings and flanged connections. In copper alloys, this leads to metal ion concentrations within the crevice and corrosion outside the crevice. It is generally shallow in nature and not as critical as crevice corrosion caused by chlorides in stainless steels where the corrosion occurs within the crevice and has a different mechanism.

Stress corrosion cracking - Most alloys when stressed and subjected to corrosion in certain specific environments can fail by cracking. For this to happen, three conditions have to be fulfilled:

- a susceptible alloy
- a tensile stress of sufficient magnitude
- a specific corrodent must be present

The elimination of one of these factors will prevent cracking; for example by changing the alloy or removing the stress by a stress relief anneal.

In marine environments, the main causes of stress corrosion cracking in copper alloys are the presence of ammonia or mercury. Brass alloys are the most susceptible to this type of attack and copper-nickel alloys have the best resistance. Mercury, in fact, causes a form of liquid metal attack and is capable of cracking all copper alloys.

Erosion corrosion - The protective surface film which forms on copper alloys is not removed by flow until the shear stress from the flowing water is sufficient to damage it, leading to much higher corrosion rates. This critical shear stress and associated breakdown velocity vary from alloy to alloy and are also determined by the prevailing hydrodynamic conditions. Breakdown velocities in tube and piping are well understood and various standards define maximum velocity limits. In other geometries, the breakdown conditions are less well defined. For example, the maximum flow rate within a 90-10 copper-nickel pipe is typically 3.5m/s but for a copper-nickel boat hull, boat speeds of 12-19m/s (24-38knots) have been successful with out causing erosion. In relative terms, copper, silicon bronze and low zinc brass alloys have the lowest resistance; higher zinc brasses are better, with copper-nickels having the greatest tolerance for higher velocity effects.

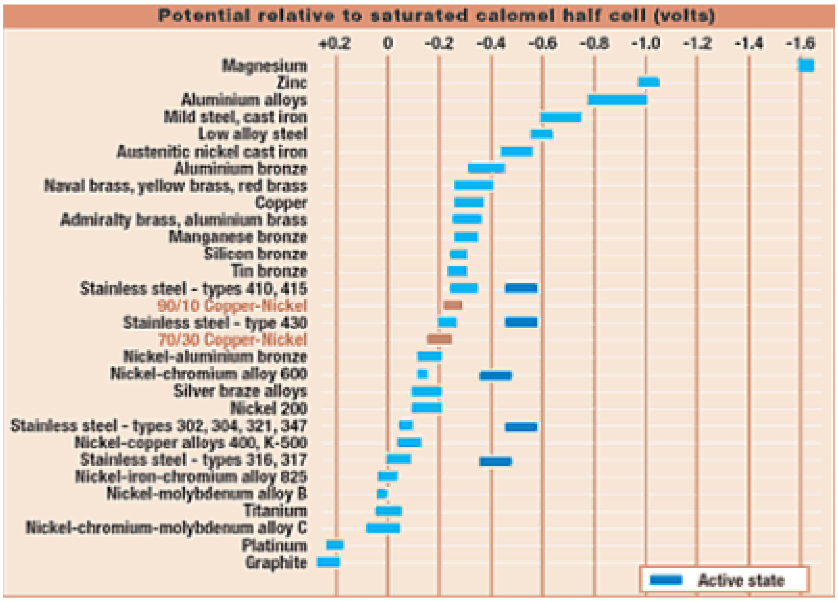
De-alloying - Many copper-zinc alloys are prone to selective corrosion in sea water. This is a form of corrosion in which the alloy is corroded and replaced by a porous deposit of copper. The rate of attack can be high and the copper deposit is porous and brittle. This type of corrosion is called dezincification. Resistance to dezincification in single alpha phase Cu-Zn alloys can be markedly improved by the addition of minor elements such as arsenic and tin.

De-nickelification has only occasionally been observed in copper-nickel alloys but usually under low flow rates and heat transfer conditions in heat exchangers.

Corrosion fatigue - The corrosive effects of seawater can reduce fatigue endurance limit of many alloys. It is not a common problem with copper alloys.

Galvanic corrosion - It is often necessary to use a number of different alloys to construct a sea water system and in order to ensure anticipated lives of the components are achieved, the galvanic compatibility of the materials used must be considered. Galvanic corrosion is the enhanced corrosion which occurs to the least noble metal within a mixed metal system, in electrical contact with the other metals and exposed to an electrolyte. To predict which of the metals in contact is the least noble and whether higher corrosion rates may occur than might otherwise be expected, a Galvanic Series for sea water can be used.

Galvanic Series



Alloys are listed in order of the potential they exhibit in flowing sea water. Certain alloys as indicated may become active and less noble exhibiting a potential near 0.5volts in low velocity or poorly aerated water, and at shielded areas

Alloys nearer the top of the Galvanic Series, as shown in this chart, are less noble than those towards the bottom. It is seen that copper base alloys are in the middle of the Series whereas steel, zinc or aluminium are appreciably less noble and would be expected to corrode preferentially when coupled to them in a system. Passive stainless steels, highly alloyed nickel alloys, titanium and graphite are all more noble than copper alloys and the copper alloys would therefore risk galvanic corrosion. The further apart the metals are in the Series, the greater the risk of corrosion. Graphite containing gaskets, packing and lubricants have all been responsible for serious galvanic corrosion of copper alloys in sea water and should not be used.

The relative surface areas of the galvanically coupled metals exposed to the sea water also have an important influence on the extent of corrosion. The surface area of the more noble alloy normally limits the galvanic current. Therefore, a small area of the more noble alloy in contact with a large area of a less noble alloy can have little effect on the overall corrosion rate of the less noble material. Alternatively, if the relative area of the more noble area is high, then excessively high corrosion rates of the less noble alloy might be experienced.

In general, the copper base alloys have similar nobility and are all galvanically compatible with each other in seawater unless the surface area of the more noble alloy is significantly greater than the less noble alloy.

Problems with galvanic corrosion can usually be avoided by following the rules below:

- use alloys situated close together in the galvanic series
- where this is not possible make the key component of a more noble material
- ensure that the less noble material is present in a much larger area than the more noble material
- paint the more noble material. This can be beneficial as it reduces the exposed area of the more noble material even when the paint film is incomplete. An imperfect coating, if the less noble alloy alone was painted, would lead to intensified attack at breaks in the paint film.
- insulate to prevent metal-to-metal contact and thus break the galvanic current e.g. using non-conducting sleeves, washers and gaskets etc.

Of additional importance to the behaviour of copper alloys is that galvanic coupling to less noble alloys, or the use of cathodic protection, can inhibit their biofouling resistance. This is thought to be due to the resultant restricted copper ion release from the surface film.

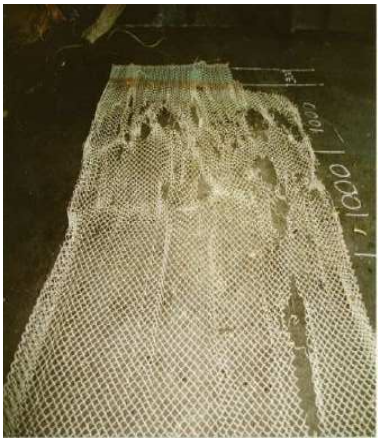
For practical examples related to galvanic corrosion, see Annex 1 of this document.

Additional design and application considerations

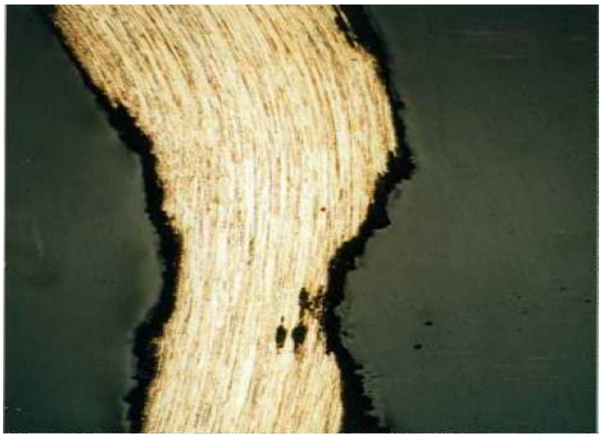
Polluted sea water - Sulfides and ammonia are present in polluted water as industrial effluent, or occur in stagnant conditions as a result of decomposition of organic matter. Sulfides may also occur when the water conditions support the growth of sulfate reducing bacteria. Copper alloys can be subject to pitting or high corrosion rates when the sea water is polluted and extended exposure is therefore not advisable.

Depth of immersion - There is very limited data about the effect of depth of immersion on corrosion rate of these alloys. Data from steel pilings, however, show a corrosion profile with peaks in the splash zone and just below mean low tide. Experience with copper-nickel sheathing used to protect steel pilings or legs of offshore platforms has shown minimal corrosion through the splash to immersed zones. For floating structures, experience of copper-nickel boat hulls and UR 30 mesh has indicated that the more sensitive area seems to be the first 200mm or so below the water line. This may be from the greater effects on the protective surface films of scuffing from debris, impinging spray and wave splash effects in that area

Sea conditions – Wind, waves, subsurface surge, and tidal or oceanic currents can create movements in aquaculture enclosures. In addition to normal conditions, the aquaculture enclosure must occasionally tolerate storm conditions without failure. The form of the copper alloy material used for the enclosure must be selected to avoid premature failure caused by motion under all conditions. Submerged structures will experience significantly less motion than structures floating on the surface. In general, copper alloys fabricated into relatively inflexible forms such as expanded metal and welded mesh can withstand repetitive motion over a prolonged time period better than flexible forms such as chain link or woven mesh. This is because relative motions between wires can cause mechanical abrasion of the wire and can remove the protective film that inhibits corrosion. Abrasion and corrosion combined can significantly shorten the operational lifetime of flexible cages. Although many copper alloys are available in wire form, care must be taken when applying these materials as flexible nets in semi-exposed sea conditions. In research trials some copper alloys exhibited early failure as shown below. However, these materials may be appropriate for use in consistently calm conditions.



Failure of C704 95-5 CuNi wire test net after 4 months.



Metallurgical section of a 3mm diameter C725 wire (nominally 88.2-9.5-2.3 CuNiSn) showing the effect of mechanical abrasion and corrosion after 1 year.

Biofouling behaviour - Marine biofouling is commonplace in open waters, estuaries and rivers. It is commonly found on marine structures including pilings, offshore platforms, boat hulls and even within piping and condensers. The fouling is usually most widespread in warm conditions and in low velocity (<1m/s) sea water. Above l m/s, most fouling organisms have difficulty attaching themselves to surfaces unless already secured. There are various types of fouling organisms, particularly, plants (slime algae) sea mosses, sea anemones, barnacles and molluscs (oysters and mussels). In steel, polymers, and concrete marine construction, biofouling can be detrimental, resulting in unwanted excess drag on structures and marine craft in sea water or causing blockages in pipe systems.

Marine organisms attach themselves to some metals and alloys more readily than they do to others. Steels, titanium and aluminium will foul readily. Copper-based alloys have very high inherent resistance to biofouling. This is particularly so for macrofouling (grasses and shell fish) although microfouling (slimes) will still occur albeit to a reduced extent. When exposed to long periods under quiet conditions, some macrofouling can eventually occur but this has been observed to slough away at intervals and can readily removed by a light wiping action.

The most important requirement for optimum biofouling resistance is that the alloy should be freely exposed or electrically insulated from less noble alloys and cathodic protection. Galvanic coupling to less noble alloys and cathodic protection prevent copper ion release from the surface film and reduce the biofouling resistance.

Corrosion behaviour of specific copper alloys used in aquaculture

90-10 Copper-nickel

The small iron and manganese alloying additions in 90-10 copper-nickel are very important in maximising corrosion resistance to flow and localised corrosion and the alloy composition should be to international standards to ensure this is so.

Protective surface films will form by exposure to clean sea water over the first couple of days but take longer to fully mature depending on the sea water temperature. At 16°C this has been found to be 2-3 months. At higher temperatures, the film forms and matures faster: at 27°C, a common inlet temperature in the Middle East, rapid film formation and good protection can be expected in a few hours. At lower temperatures; the process is slower but the film does form even in Arctic and Antarctic waters.

Once a good surface film forms, the corrosion rate will continue to decrease over a period of years and to exhibit the classical parabolic growth rate of protective layers. For this reason, it has always been difficult to predict the life of copper-nickel alloys based on short-term exposures. Normally, corrosion rates of 0.02-0.002 mm/yr are anticipated.

Of the wrought copper alloys, copper-nickels have the best resistance to flow. In defined conditions of pipework; the maximum flow rate for 90-10 copper-nickel is normally about 3.5m/s but in more open structures, the hydrodynamic conditions are different and the flow rate before erosion occurs can be much higher as already mentioned for ship hulls. (see Erosion Corrosion section)

Copper-nickel alloys also have good inherent resistance to chloride pitting and crevice corrosion. In fact, crevice corrosion seldom occurs and is therefore not well documented. The mechanism is a metal ion concentration cell type and is different to that occurring in stainless steels as any corrosion occurs outside the crevice. Copper ions, which are released by surface reactions within the crevice, are not swept away and concentrate there. The area within the crevice becomes more noble than either the mouth of the crevice or the adjacent exposed region. The resulting corrosion occurs adjacent to the crevice, and tends to be shallow in nature.

Copper-nickel alloys are not susceptible to chloride stress corrosion as nickel containing stainless steels do and unlike some brasses have not been found to suffer cracking due to ammonia in seawater service. The presence of ammonia may however cause higher general corrosion rates.

If exposed to polluted water, especially if this is the first service water to come in contact with the alloy surface, any sulfides present can interfere with surface film formation, producing a black film containing cuprous oxide and sulfide. This is not as protective as films formed in clean water and higher general corrosion rates and pitting can be experienced. The sulfide film can gradually be replaced by an oxide film during subsequent exposure to aerated conditions, although high corrosion rates can be expected in the interim. However, if an established cuprous oxide film is already present, then periodic exposure to polluted water can be tolerated without damage to the film. Exposure to sulfides by copper alloys should be restricted wherever possible and particularly during the first few months of contact with seawater while the protective oxide film is maturing.

There have been situations in tubing where the metal surface becomes exposed to sulfides under deposits or sediment caused by sulfate reducing bacteria. In aquaculture, if surface deposits build up or detritus is trapped; scheduled cleaning would be required. In tubes, such cleaning is often scheduled at 2-6 month intervals and accomplished by water flushing or cleaning with non-metallic brushes.

General observations of copper-nickel have led to the understanding that for open seawater exposures, the slime layers (microfouling) do not build up sufficiently to support macrofouling. When exposed to long periods under quiet conditions, some macrofouling will eventually occur but this has been observed to slough away at intervals. Connection to 70-30 copper-nickel and more noble alloys in the galvanic series will not impede biofouling resistance although due consideration of galvanic surface areas is required to ensure corrosion of the 90-10 copper-nickel is not too high.

Ni-Cu alloy 400 and Nickel Aluminium Bronze fasteners have been found to be acceptable with copper-nickel; silicon bronze has shown mixed results (also see Annex 1). Type 304 stainless steel fasteners have shown active crevice corrosion as the copper-nickel did not adequately galvanically protect them. Higher stainless grades such as alloy 2205 or superduplex (with or without insulation) might be more acceptable but need evaluation.

In order to maintain the corrosion and biofouling properties of copper-nickel, it is important that good handling and fabrication practices are employed. Cleanliness is important so that the surface does not become contaminated sufficiently to inhibit the surface film formation and biofouling properties.

Copper-nickel can be welded. If weld consumables are used, the 70-30 Cu-Ni electrodes and filler metals are normally preferred. No post weld heat treatment is required to maintain corrosion resistance. Copper-nickel can be welded to steel using the appropriate Ni-Cu consumables but as steel is less noble than copper-nickel, the biofouling resistance will be compromised.

A wealth of additional information about the corrosion performance, mechanical properties, fabrication and biofouling properties of copper-nickel can be found at www.coppernickel.org.

UR 30 ™

This alloy is a higher copper brass containing 64% Copper. It has an alpha single phase structure which makes it particularly good for cold forming. Controlled alloying and processing significantly improves its resistance to de-zincification in sea water to which some brass alloys can be susceptible. In over 10 years experience in aquaculture, the chain link mesh product fabricated this alloy has not suffered from dezincification, stress corrosion cracking or erosion corrosion.

UR30 is specifically designed to resist mechanical abrasion and retains this property when formed into wires and fabricated into chain link fence mesh. Nets made from 4mm diameter wire have been shown to provide a service life of around 4 years in semi-protected sea conditions with up to 1.5 meter waves. UR30 is also available in tube and sheet forms for aquaculture applications.

The average reported corrosion rate for UR 30 from 2 and 5 year exposure trials in sea water is <5µm/yr. Maximum depth of corrosion after 2 years was 15µm and after 5 years was 20µm. Experience from actual pens, typically 10m deep, indicates there is a waterline effect of higher corrosion which may extend 200mm deep. The corrosion rate of wire at the bottom of the pens is low: wire diameter decreases by less than 0.1mm/yr.

The thermal effects of welding and brazing for joining can affect the corrosion resistance and mechanical methods are preferred. Typically, twisted wire attachments are used. If the wire is welded, it requires heat treatment to recover the original properties.

As for all copper based alloys, exposure to polluted water should be avoided and this includes sites for assembly of the pens as well as service conditions.

Additional information about the alloy can be found on:
www.mitsubishi-shindoh.com/en/urphys.htm

Seawire ™

The more common silicon bronze alloys contains about 3% silicon and 1% manganese and have very good sea water corrosion resistance and high resistance to stress corrosion by ammonia. They have a long history of use as fasteners in marine environments including screws used in wooden sailing vessels.

The composition of Seawire falls within this alloy group and has an alpha phase metallurgical structure. It generally has the same corrosion resistance as copper but with higher mechanical properties and superior weldability. The silicon provides solid solution strengthening and the alloy is tough, with good shock resistance.

Data for similar alloy compositions indicate that the general corrosion rate is 0.025-0.050mm in quiet waters which decreases to the lower end of the range over long term exposures of 400-600 days. There is generally no pitting and, if it does occur, the pits are small. Also there is good resistance to erosion corrosion up to moderate flow rates.

As with copper-nickels, the corrosion resistance is due to protective surface films which form over a period of time. Polluted waters containing sulphides or ammonia can lead to higher corrosion rates.

Silicon bronze is a popular alloy for marine and pole line hardware resulting in a readily available supply of screws, nuts, bolts, washers, pins, lag bolts, and staples used for fastening. These fasteners can be used with Seawire to avoid galvanic incompatibility.

Good practice guidelines

The guidelines for good practice are very similar for all three alloys;

- Careful handling during transport, assembly and installation to avoid surface contamination and allow uniform protective surface films to form once exposed to sea water
- Exposure to non polluted sea water is important particularly in the first few months of exposure to sea water.
- General corrosion rates in sea water will decrease over a period of years in sea water; it is misleading to take the corrosion rates measured over the first couple of month's exposure to predict their long term exposure corrosion.
- If detritus or silt build up occurs, occasional brushing (non metal) or water jetting to clean up the surface should be employed to remove any deposits which can promote unnecessary crevices or colonisation of sulphate reducing bacteria.
- If coupling to other metals is required, the coupled metals should be <u>more noble</u> and of a relatively small relative surface area so that they do not interfere with the biofouling resistance or cause excessive galvanic corrosion. Alternatively; the metals can be electrically insulated from each other to avoid galvanic effects.
- It is anticipated that all three alloys will be suitable for most flow conditions met in Aquaculture and to date there have not been any problems for any of the alloys. However, if sea flow is particularly high, the copper-nickel would offer the better resistance.
- All three alloys are unlikely to experience ammonia stress corrosion in this type of application. UR 30 is the most susceptible but in practice it has been used for fish pens in Japan for 10 years without any reported incident. However, it should be a consideration if extreme conditions are anticipated.
- Thicker section could be employed for water line service and for 300mm below as corrosion rates can be higher in this area.

Useful documents

- Design Guide-Copper Alloy Mesh in Marine Aquaculture 1984 International Copper Research Association (INCRA) 704/5

- Metal Corrosion in Boats Nigel Warren Adlard Coles Nautical 1998
- Galvanic Corrosion: A Practical Guide for Engineers. R. Francis.2001 NACE Press
- Marine Corrosion Causes and Prevention F. LaQue. John Wiley and Sons 1975
- The Selection of Materials for Seawater cooling Systems: A Practical Guide for Engineers. R.Francis. 2006 NACE Press
- Guidelines for the Use of Copper Alloys in Sea water. A.Tuthill. 1987. CDA/ Nickel Institute Publication
- The Brasses: Properties and Applications. CDA UK Publication 117
- For detailed Cu-Ni information see down loadable papers on www.coppernickel.org
- Properties of UR 30 http://www.mitsubishi-shindoh.com/en/urphys.htm

Annex 1

Practical examples to avoid galvanic corrosion.

1. *UR30 chain link mesh is attached to steel attachment bar in splash zone. The bar is wrapped with insulating tape. Why does this work?*

There are three issues here. The first is the need to prevent the corrosion of the steel in the splash zone and secondly how to avoid any acceleration of its corrosion rate because it is attached to the UR 30 chain link mesh. It can be seen from the galvanic series that brasses are more noble than steel and so it will be the steel that will corrode preferentially given it is sufficiently wetted at the water line to allow corrosion to occur. Of even more importance in aquaculture is the risk that galvanic connection to the less noble steel will inhibit the biofouling resistance of the UR 30.

Wrapping the bar in insulating tape protects the steel from corrosion and also avoids the risk of galvanic corrosion which would reduce the biofouling resistance of the copper alloy. The application of the tape has to be very thorough; any damage to the tape or gaps exposing the steel could concentrate corrosion at those areas if a galvanic circuit can operate and cause unwanted fouling of the copper alloy.

2. *Attaching copper-nickel mesh to a HDPE frame with silicon bronze staples. Is this the best choice of materials? What is recommended?*

Although silicon bronze is readily available for this application, it may not be the best choice. Copper-nickel and silicon bronze are very close in the galvanic series and are normally compatible unless the relative surface areas are extreme. Copper-nickel can be slightly more noble and, if its relative surface area is high as it would be in this case, there could be a risk of accelerated corrosion of the silicon bronze.

Early work on expanded copper-nickel mesh by Huguenin and Ansuini looked at the issue of fasteners and found that, because of a small overlap in electro-potential range between copper-nickel and silicon bronze in sea water, some silicon bronze fasteners could be acceptable and others not. This indicates that, to be sure of avoiding any problems, copper-nickel itself or more noble alloys should be used instead. Type 304 was found to under go crevice corrosion and so become less noble than the copper-nickel and fail. Nickel aluminum bronze and Ni-Cu alloy 400 were found to be acceptable. Although not examined in these trials, more corrosion resistant stainless steels may be suitable too such as 22 or 25%Cr duplex alloys.

3. *Attaching a UR30 mesh to a steel tube with non-conductive ropes 20 meters beneath the surface. Is there a corrosion issue?*

If bare steel was immersed below the surface and in direct contact with the UR 30 mesh, the biofouling resistance of the mesh would be compromised as the UR30 is the more noble alloy. Depending on the relative surface areas, the steel may have an increased corrosion rate. The two alloys therefore need to be galvanically insulated from each other. Non conducting ropes would break any galvanic current and allow both components to achieve their respective functions. The required length of rope or other insulating connection is that required to keep the UR 30 and steel out of direct contact.

It is also useful to consider the scenario which could occur if the bar had been coated and the more noble copper alloy is directly attached to it. Once the copper alloy has established contact with the underlying steel at damaged areas or by wear etc, then galvanic processes can take place. The larger exposed area of the copper alloy would concentrate the galvanic current at the small exposed areas of steel. This can lead to unexpectedly high corrosion rates in those steel areas and, of course, may lead to biofouling on the copper alloy. Hence, whether the steel is coated or not, it is preferable to have insulation between the two alloys.

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