

An Assessment of the Biofouling Resistance and Copper Release Rate of 90-10 Copper-Nickel Alloy

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ABSTRACT

90-10 copper-nickel is one of the few engineering alloys available which offer both high resistance to seawater corrosion and biofouling. The alloy is not immune to microfouling but colonization of macrofouling is much restricted. The mechanism is not fully understood and is thought to be at least partially linked to copper ion release from the complex protective surface film. There may also be an effect of the nature of the surface film itself.

There are no suitable standards available to assess copper release from solid alloys but ASTM* D6442¹, Standard Test Method for Copper Release Rates of Antifouling Coating Systems in Seawater was developed for coatings. Although coatings are designed to release copper in a totally different way to the behavior of solid metal, 90-10 copper-nickel has been evaluated using the method to assess whether it could be used or modified to provide data which has a relevance to service conditions and experience.

This paper reviews existing knowledge about corrosion rate and biofouling resistance of 90-10 copper-nickel and then reports and evaluates test work carried out to ASTM D6442. It is apparent from the results that protective surface film build up on the metal in live sea water is compromised by the test technique and reproducibility is poor. The work does however provide indicators about how a more relevant method could be developed.

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Key words: C70600, copper-nickel, copper leaching, ASTM D6442, corrosion, biofouling, surface film, cuprous oxide.

INTRODUCTION

90-10 copper-nickel (C70600) has been widely used in marine engineering for sea water piping, condensers and heat exchangers on offshore platforms, desalination, and naval and commercial shipping. It has an established reputation for sea water corrosion resistance and it is also known to be one of the few alloys available which has a high inherent resistance to macrofouling. The latter has led to its use in sea water intakes, aquaculture, boat hulls and offshore sheathing applications.

There are some interesting benefits when the alloy is used to avoid fouling compared to antifouling coatings. The main one being that it does not need recoating periodically and foregoes the time and effort of removal, preparation, reapplication, and disposal. The alloy is also fully recyclable.

At present, antifouling coatings are under scrutiny. Many such coatings include cuprous oxide which is designed to be released into sea water to help control the fouling. Issues include copper release rates, concentrations relative to regulatory standards, effects on "non-target" organisms, fate and accumulation in sediments.

Release of copper is a complex process influenced by diffusion from the solid surface, dissociation of the copper oxide and leaching into seawater, binding to abundant ligands like Dissolved Organic Matter and concomitant reduction in bioavailability of free copper ions, dispersion by natural current regimes, and flocculation and burial in sediments.

The environmental effects are complicated therefore by bioavailability and dispersion into the aquatic environment, much of which is still being assessed and understood. While the ultimate aim can be to minimize the release rate as much as possible while still controlling biofouling for as long as possible before re-application, leaching rate measurement is perceived as a straight forward method of ranking coating products. To compare solid copper alloy with antifouling paints by this simple method could be misleading. However, there is a growing perception that this at least needs to be examined and understood for today's environmentally aware offshore industry base. The following paper aims to review the available understanding about the mechanism by which solid copper-nickel achieves biofouling resistance and how this relates to corrosion resistance and leaching. It then assesses ASTM D6442, Standard Test Method for Copper Release Rates of Antifouling Coating Systems in Substitute Ocean Water, as a potential means of evaluation.

Current Understanding of Biofouling Properties of 90-10 Copper-Nickel

Maximum resistance to biofouling relies on 90-10 copper-nickel being freely exposed and not galvanically or cathodically protected by less noble alloys. It is thought that this allows the availability of free copper ions in the surface film to inhibit the growth of macrofouling (grasses and hard shell growths) although some microfouling (slimes) will colonize².

In open seas, copper-nickel normally remains free of macrofouling but under quiet conditions, some colonization may occur. However, this has been found to only be loosely attached and periodically sloughs away. It can also readily be removed by a light brushing or water blast or, when used as a hull, by extended sailing in open waters at 3-8 knots³.

It was in the 1970's that observations at the LaQue Center for Corrosion Technology in North Carolina suggested the surface film itself was largely responsible for the biofouling resistance and that when freely corroding and under quiet conditions, the initial cuprous oxide film would gradually convert to cupric hydroxychloride⁴. The converted film was considered to be less adherent and protective than the

cuprous oxide type and would allow fouling to become established. Being less adherent, after a time it would slough away leaving the underlying protective cuprous oxide film exposed again. The observations did not identify any unfouled areas directly adjacent to copper-nickel boundaries which would indicate a copper ion release mechanism. However, since that time, other products have been developed for protecting offshore structures which are composites of copper-nickel wire or granules embedded into an insulating substrate, such as rubber or polyester gel, with discrete areas of copper-nickel exposed on the surface⁵. These products have shown full protection of the surface although they only expose about 30% of the surface area as copper-nickel. Thus, there must be some antifouling effects in close proximity to copper-nickel.

It appeared, therefore, the most likely explanation is that the biofouling resistance is a combination of two effects; ion release and the nature of the surface film itself.

Surface Films on Copper-nickel

For a greater understanding, it is necessary to appreciate that the corrosion resistance of copper-nickel is also related to the formation of the surface film which is complex and protective, and forms slowly and naturally when the alloy is exposed to sea water. This process can be subdivided into primary and secondary reactions⁶. During the primary reaction, a cuprous oxide film is formed. The anodic part of the reaction takes place at the metal/oxide interface and the cathodic part at the water/oxide interface.

Since the cuprous oxide film does not represent a completely dense layer, it is thought⁶ the copper-nickel continuously releases small amounts of copper ions. Because the ions cannot be tolerated by many organisms, this ionic discharge is capable of decelerating the establishment of the primary bacterial film. If the copper-nickel alloy is cathodically protected, however, the copper ions are not released and the biofouling resistance is decreased.

Subsequent secondary corrosion reactions also play an important role in the biofouling resistance of the material. During this part of the corrosion process another oxide layer is generated by a reaction of released ions with compounds in seawater. This top layer consists usually of cuprous hydroxide or cupric hydroxychloride and represents a thick and porous structure. Similar reactions can be developed for Fe and Ni – the other main alloying elements.

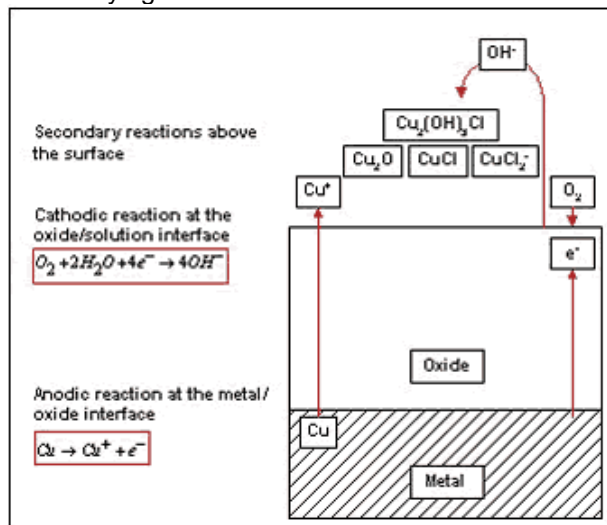


Figure 1: Corrosion reactions during formation of protective oxide layers on copper-nickel⁶

Bacteria of certain genera, which are protected by a polysaccharide cell wall from the copper ions, have been found within the oxide layers⁷ and attributed to the coverage of organisms by products of the secondary corrosion reactions, Figure 2. It is thought this is helpful for the sloughing process, as described later.



Figure 2: Transmission electron microscope micrograph of corrosion products of Cu-Ni exposed in Langstone Harbor after 22 weeks found B – bacteria between layers of corrosion products, S – no bacteria found on the surface (12,000:1)

The outer layer can be regarded as a barrier for the diffusion of copper ions into the seawater, and the copper-nickel surface may become susceptible to biofouling. Therefore, during initial stages of exposure, the biofouling resistance of copper is controlled by the release of copper ions. During the following exposure, a poorly adherent layer is formed on the top of a cuprous oxide layer and the surface may foul. However, the top layer can be easily removed and thus prevents the attachment of macro-organisms. The freshly exposed film remains intact and is resistant to biofouling as shown in Figure 3⁴.

It should also be noted that some studies have found the surface film to be even more complex than indicated above and have found a thin initial layer of copper chloride at the metal surface as part of the primary reaction⁸.

To further complicate this scenario, long term trials and practical experience of copper-nickel splash zone sheathing on pilings and offshore structures has found much reduced levels of fouling (~ 50%) and looser attachment even when cathodic protection is applied and copper ion release is prevented⁹.

Clearly this is a very complex process. Current understanding is based on theories that have yet to be confirmed and more detailed work is required in this area.

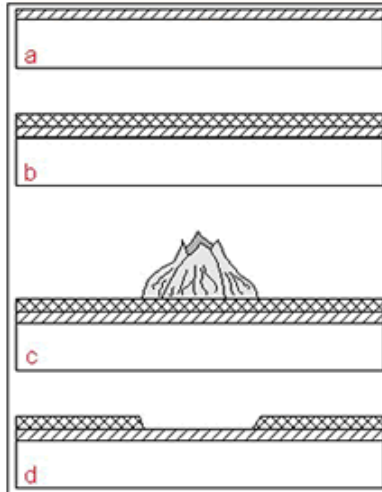


Figure 3: a. Initial formation of protective cuprous oxide film (establishment of fouling is prevented by release of cuprous ions), b: Establishment of non-toxic top layer, c: Settlement of the surface by fouling organisms, d: Removal of fouling organisms leaving the protective Cu_2O film intact.

Leaching rate as part of the corrosion process

There has been very little evaluation of copper leaching levels from direct surface measurements of solid copper-nickel. In spite of the complex nature of the surface films, the data is associated with derivations from corrosion rates, which in themselves are subject to many variables.

Efird found that ETP copper (C11000) samples in 5 year exposures⁴ corroded at 3 times the rate of 90-10 and 70-30 copper-nickel ($8 \mu\text{m}/\text{y}$ compared to $2.5 \mu\text{m}/\text{y}$ which is equivalent to metal leaching rates of $18.6 \mu\text{g}/\text{cm}^2/\text{d}$ compared to $6.2 \mu\text{g}/\text{cm}^2/\text{d}$ respectively). However, all had similar levels of fouling further indicating that the corrosion product surface film was important. In another trial, 70-30 was found to have corroded at $1.3 \mu\text{m}/\text{y}$ after 14 years with only slight fouling¹⁰. This was at variance to the normal copper leaching theory for copper based alloys in natural sea water that requires $\sim 18 \mu\text{m}/\text{y}$ or more to prevent fouling⁴.

Tuthill¹¹ showed that the initial film forms fairly quickly over the first couple of days but takes 2-3 months to fully mature. Figure 4 shows the rate of film formation on 90-10 copper-nickel in seawater at 16°C measured by copper in the effluent of a condenser over a 3-month period after start up. Copper content was found to decrease to one tenth in ten minutes and one hundredth in an hour. After three months, the copper in the effluent was virtually the same level as that of the intake water. Indirectly, this shows that the maturity of the protective film reduced the corrosion rate of the condenser surface.

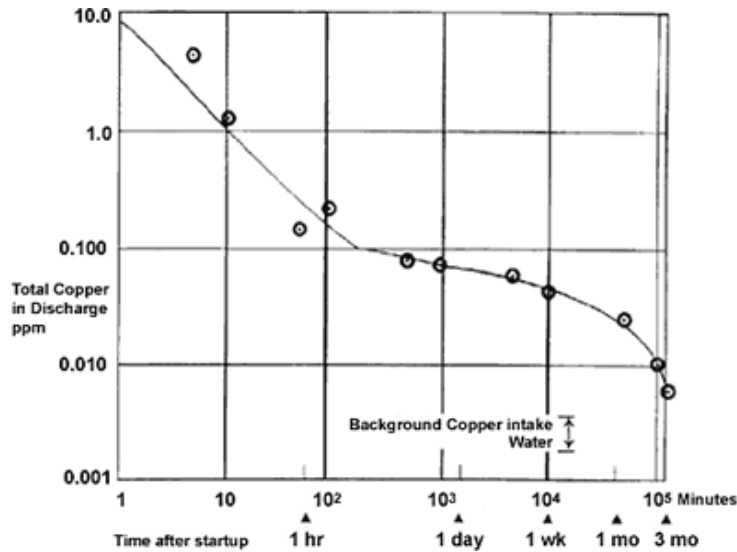


Figure 4: Formation of Corrosion product film on 90-10 copper-nickel in natural sea water.

At higher temperatures, the film would be expected to form and mature faster.

Once a good surface film forms, the corrosion rate has been shown to 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 based alloys based on short-term exposures. Normally, corrosion rates of 0.02-0.002 mm/y are anticipated.

Specific corrosion rate measurements at LaQue Center for Corrosion Technology¹⁰ taken over fourteen years in tidal, flowing (0.6m/s) and quiet seawater show the corrosion rate decreases over a period of 5-6 years, stabilizing out at about 1.3µm/y, as shown in Figure 5.

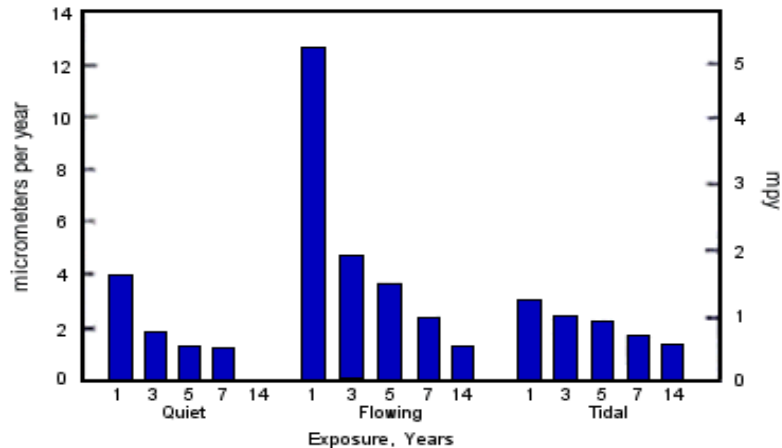


Figure 5: The change in corrosion rate with time for 90-10 copper-nickel in quiet, flowing (0.6m/s) and tidal zone natural sea water.

Interestingly, corrosion rates for 7 year trials in the UK also agreed with the stabilized corrosion rates⁵. The LaQue work equated to a maximum copper release rate of around 32 $\mu\text{g}/\text{cm}^2/\text{d}$ the first year decreasing to 2.5 after 14 years with an average of 10 $\mu\text{g}/\text{cm}^2/\text{d}$ over 14 years.

Figure 6 reproduces the original data as a chronogravimetric curve: the long term corrosion rates are seen to stabilize at 1.2-1.3 $\mu\text{m}/\text{y}$.

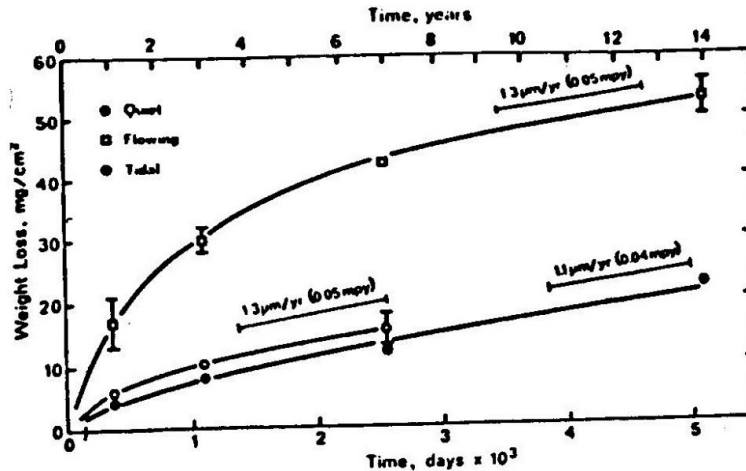


Figure 6: Chronogravimetric Curves for 90-10 Cu-Ni in Quiet, Flowing and Tidal sea water¹⁰.

Trying to assess leaching data from these results raises a variety of issues. Should the corrosion rates used for design or assessments be taken from initial years or be taken from the stabilized rates? Logically, the corrosion rate should represent the number of years that the alloy in any particular application is intended for service. Also, data is often taken from weight loss measurements after the films have been removed by acid cleaning. As the films are a permanent feature of the corrosion and biofouling resistance in service, would removing them make the rates calculated overly high and misleading?

From the above, it can be seen, how complicated it is to provide sensible leaching data from corrosion rates in sea water as the corrosion rate is influenced by time of exposure, flow rate, temperature and final method of measurement. In other offshore corrosion evaluations of a range of alloys, short term ranking tests become a means of assessing this and very often deceptively become perceived as the actual data indicative of rates in the field. Often these might be evaluated in artificial sea water as this is one method of producing a reproducible environment conveniently and cheaply without the many interactions of the natural environment. However, it is apparent for copper-nickel that both the corrosion and biofouling resistance are so closely tuned to the reaction of the surface with the biological and chemical ingredients of natural live sea water that this could be grossly undervaluing the alloy and misleading¹².

In recent times, several studies have been carried out to optimize the surface film on copper-nickels from a corrosion resistance view point in early condenser service¹³. It has been found that exposure to clean natural flowing aerated sea water is still one of the best methods of achieving this.

Langer et al¹⁴ have found from artificial sea water studies using tubing in a test loop that pH and temperature were important in providing optimum films in that media. Films formed quicker at 40°C rather than at 25°C and at pH 8.6 rather than 8.2 at 25°C as shown in Figure 7.

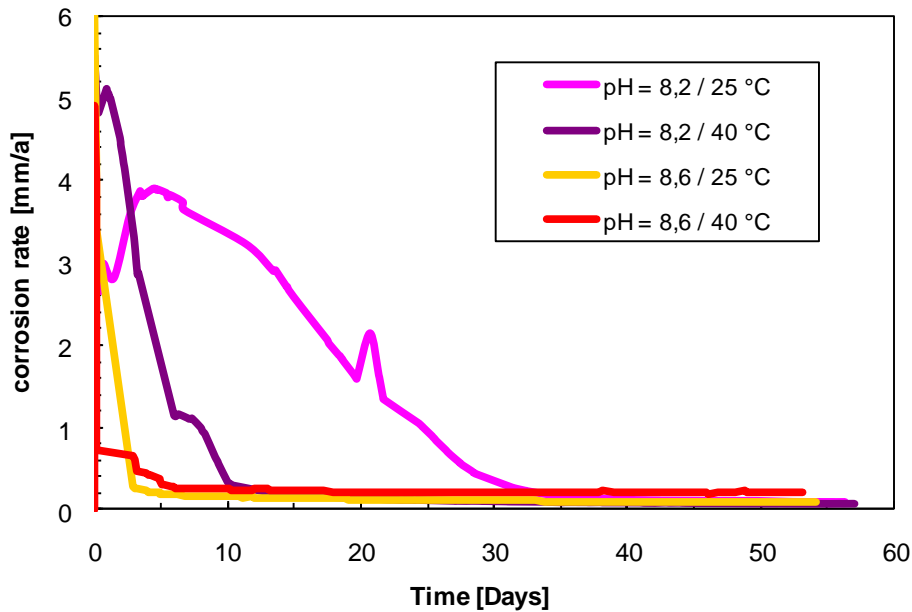


Figure 7: Corrosion rates for tubing in artificial sea water loop tests; films form quicker with higher temperature and pH

Interaction with Biota

For antifouling coatings, cuprous oxide dissociates very slowly in seawater, diffusing copper ions into the thin stagnant boundary layer adjacent to the solid surface. In the presence of dissolved oxygen, the predominant dissolved species of copper will be the cupric ion, Cu^{2+} . Within this superficial boundary layer, the relatively high concentration of free copper ions is sufficient to penetrate the cell membranes of any colonizing bacteria, protozoa, algae, and settling larvae of invertebrates, overwhelming their normally-robust cellular regulatory mechanisms for this essential trace element, so that (a) the ion retards organism's vital processes by inactivating enzymes, and (b) the ion acts more directly by precipitating cytoplasmic proteins as metallic proteinates. Thus, almost all organisms attempting to live at the surface (e.g., the hull of a vessel) or in the micrometer-scale boundary layer adjacent to it, are killed, and only a slime or biofilm of dead cell material is left behind. This slime layer further inhibits the dissociation of copper oxides on the solid surface beneath, reducing apparent metal leaching rates over time. This sequential process is only minimally understood and not quantified. Also, the inability of the laboratory test protocols to incorporate these complex chemical, biological and diffusive processes is the reason that these tests have failed to reproduce in situ leach rates observed in the field (see following section).

Beyond the superficial boundary layer, the cupric ion will be dispersed rapidly by turbulence and currents, and almost all of the free cupric ion will become bound to natural ligands like Dissolved Organic Matter, thus greatly diminishing its bioavailability and potential for toxicity to organisms away from the solid surface. Therefore attached or pelagic organisms can exist in close proximity to the ship – in adjacent waters and on pilings of piers and docks.

The full similarity in the behavior of surface films built up on solid copper-nickel with the processes and interactions involved for antifouling coatings still requires investigation.

Existing Methods of Copper Release Evaluation for Marine Service

Although there have been no standards for evaluation of copper release from solid metals, leaching test techniques have been developed for copper containing antifouling coatings and are still in the process of being refined to be more relevant. Finnie¹⁴ provides a good overview of the types of tests available and their shortcomings in relation to coatings.

Currently, the main test techniques are ISO[#]/ASTM¹ (ASTM D6442-06 and ISO 15181-1,2¹⁶) test method for copper leaching of coatings in synthetic sea water, the Dome Method and the Mass Balance (or Calculation) Method.

The ISO/ASTM method involves a revolving coated cylinder test carried out in synthetic sea water and is described in more depth later. However, a correction factor is required to make the results more predictive of practical situations as the test results are much higher than field observations.

The Dome method gives more realistic results and is favored by the US Navy. It involves using divers operating from a pilot boat. A polycarbonate dome (30.5cm diameter) is filled with ambient natural seawater and attached directly to an immersed antifouling paint film on a hull or panel by light suction in such a way that any biofilm growing on the surface of the paint film remains essentially undisturbed. Water samples are periodically drawn off over a 1-hour period. The dome is removed after sampling and analysis of the water samples allows the instantaneous biocide release rate to be determined. No set sampling schedule is prescribed and the method has been used to take single leaching rate measurements or samplings over periods of up to several years. Testing is site specific however, expensive and not widely commercially available. The results are assumed to be representative of field situations, so the test method is used to calculate the correction factors for other methods.

The third method is the Mass Balance calculation. There is a CEPE Mass balance method based on the service life of the product and an ISO Mass balance method which is still under development at the time of writing. The method is based on the assumption that the total amount of biocide released by a coating cannot exceed the amount of biocide that was originally present in the coating when manufactured. The model assumes that the biocide release rate falls linearly with time over the first 14 days following immersion, and thereafter remains constant for the remainder of the specified lifetime. Correction factors are again required as the data significantly over-estimates the field environmental release rates but to a lesser extent than the ASTM/ISO cylinder method.

Finnie¹⁵ suggested that where ASTM/ISO or CEPE mass balance copper release rate data are used for environmental risk assessment or regulatory purposes, the release rate values should be divided by a correction factor to enable more reliable generic environmental risk assessments to be made. Using a conservative approach based on a realistic worst case and accounting for experimental uncertainty in the data that are currently available, he proposed default correction factors for use with all paint types of 5.4 for the ASTM/ISO method and 2.9 for the CEPE calculation method allowing this to be modified as more practical data becomes available.

A modeling evaluation system called MAMPEC¹⁷ (Marine Antifoulant Model to Predict Environmental Concentrations) uses measured or assumed leaching rates as well as many other factors as model inputs to predict and manage copper concentrations in the far field (away from the ship hull(s)) in typical marinas and other restricted areas.

The relevance and accuracy of these methods to solid alloy is not known; but, as there is a growing interest from end users for data, some initial exploratory release rate measurement testing was required. The mass balance method is based on release of biocide over the life of a coating which is

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difficult to calculate from solid metal. So Instead, it was decided to make leaching rate measurements using the ASTM method, ASTM D6442-06 Standard Test Method for Copper Release Rates of Antifouling Coating Systems in Substitute Ocean Water, as a reasonable starting point.

EXPERIMENTAL PROCEDURE

For full details of the test, the reader is referred to ASTM D 6442-06¹. It is a method covering the laboratory determination of the rate at which copper is released from antifouling coatings using substitute (i.e., artificial) ocean water. Normally the candidate paint would be applied to a cylindrical test specimen and the specimens placed in a tank of substitute ocean water where the copper levels are kept below 100ug/l by circulating the water through a suitable filtration system. At specific intervals, each specimen is placed in 1500ml of substitute ocean water and rotated at 60 rev/min for 1 hr or less. The specimens are then returned to the holding tank until the next leaching interval. The rate of copper release from the paint is determined by measuring the copper concentration of the water in the individual measuring containers. The substitute ocean water conforms to D1141-98(Reapproved 2003) and is maintained at a pH of between 7.8-8.1 and a salinity between 33 and 34 parts per thousand.

The cylinders for coating are normally 6.4cm outside diameter by 17.8 cm long exposing a central band of coating 10cm long and 200cm² and are immersed and freely rotated in beakers. Both ends of the cylinder are sealed. For the purposes of solid metal testing the cylinder was replaced by a tube of 90-10 copper-nickel, C70600, sealed at each end and masked by epoxy coatings at the top and bottom to reveal a central portion of bare metal. The copper-nickel surfaces were scrubbed with a nylon scrubbing pad and any surface oxide removed so that they were bright when the test began. The alloy was supplied by KME; an established German supplier of the alloy. The test work was carried out by Case Consulting Laboratories in New Jersey, USA.

The standard requires the cylinders to be removed from the holding tank on days 1, 3, 7, 10, 14, 21, 24, 28, 31, 35, 38, 42, 45. Each specimen was placed in a 1500ml beaker of substitute sea water and rotated at 60 revs/minute for 20min. Longer trials can be carried out. In the latter part of the CDA work 49, 56, 63, 70, 77, 84 and 91days were also included.



Figure 8: Attaching test cylinders to rotating apparatus.

RESULTS

The experimental work became 3 sets of trials. Each had 3 specimens. The tube diameter used to make the cylinders was 57mm. In the first trial, the exposed test surface was 200cm² of metal. The results of this test series are shown in Figure 9.

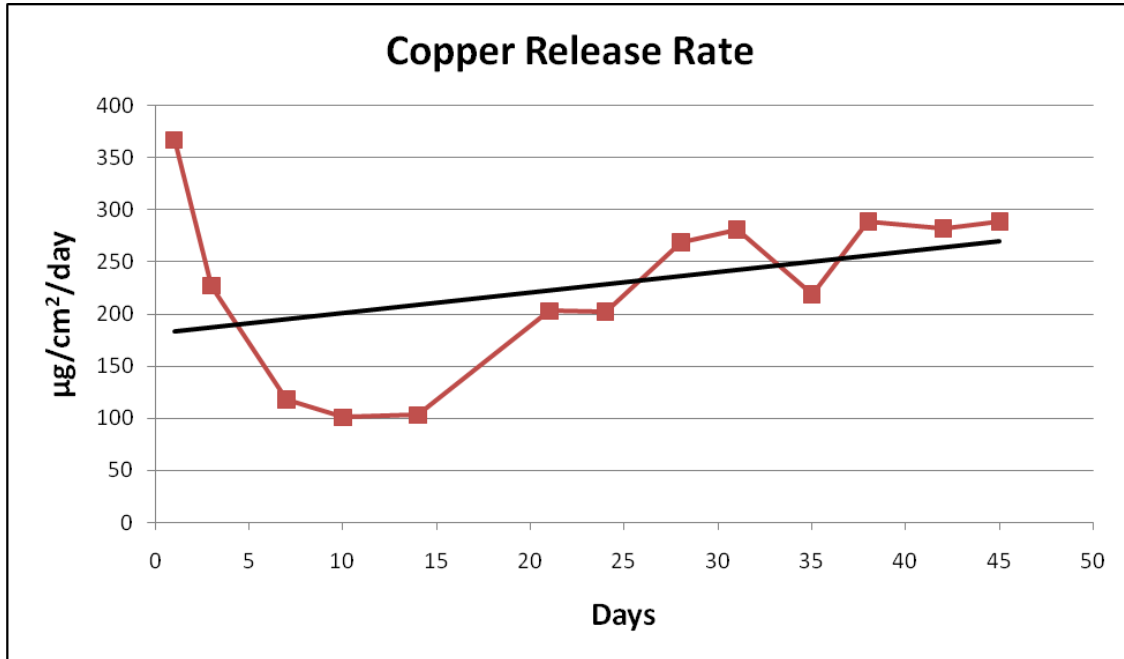


Figure 9: Average copper release rate from first 45 day trial taken as an average of those taken from the 3 samples.

An observation of the surface films formed on the 3 specimens was that they were black in color and flakey which is very unusual for copper-nickel in such an environment. Flakiness usually means the film has dried out at some stage which put the handling of the specimens into some doubt.

The leaching rates were highly variable and showed no sign of stabilization. It was decided therefore to repeat the trial.

According to the test protocol in ASTM D6442, the testing facility has the option to only expose 100 cm² rather than 200 cm² if they feel the amount of released copper will be high. Based on this and the earlier testing which showed a higher than expected release rate, Case chose to only expose 100 cm² in the second set of tests. The tube diameter used for the specimens was again 57 mm.

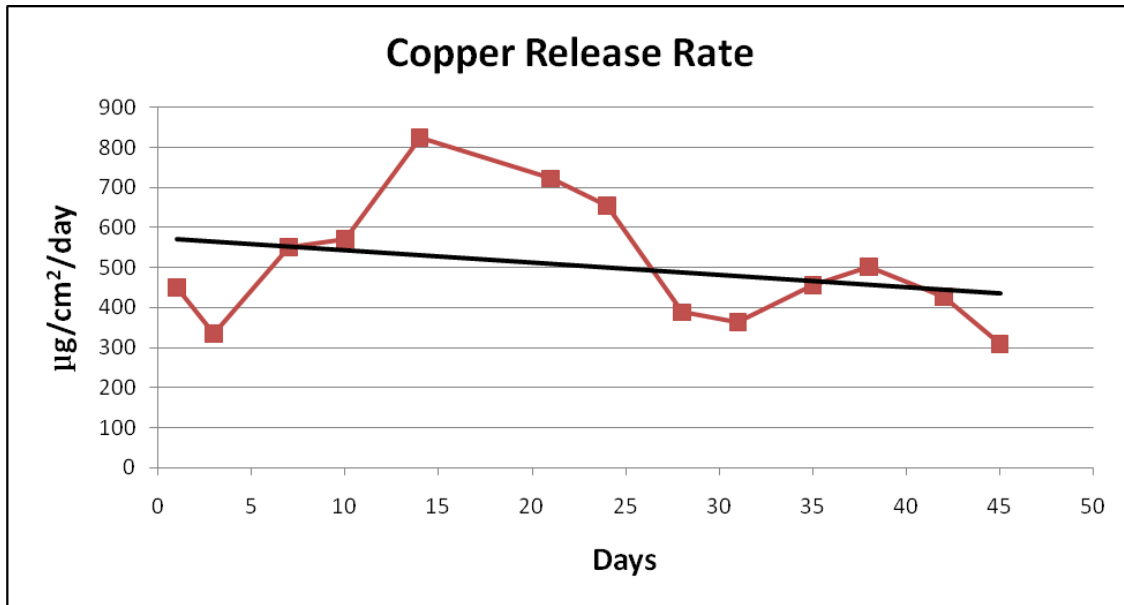


Figure 10: Average Cu release rate of the 3 specimens from the second 45 day trial

The results this time followed a downward trend which was more in line with that expected. However, the leaching rates showed no signs of stabilizing. The specimens were a golden brown color which was closer to the anticipated surface film, see Figure 11.

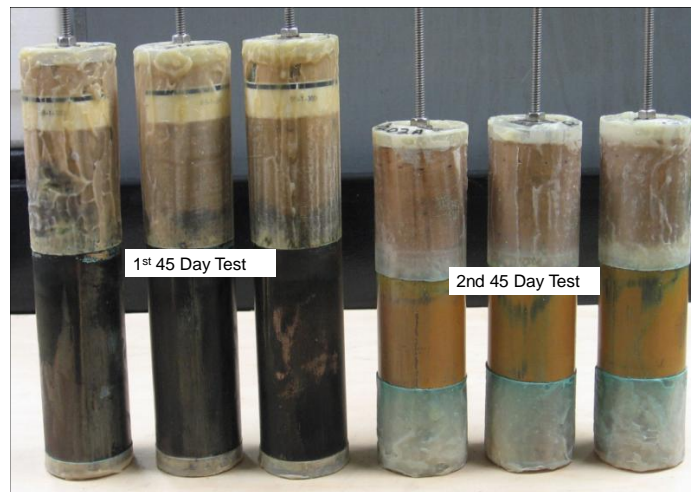


Figure 11: Extracted samples after the first two trials showing differences in the surface film.

Following these results, it was decided to carry out a third trial to 91 days using new material. The copper release rates are shown in Figure 12.

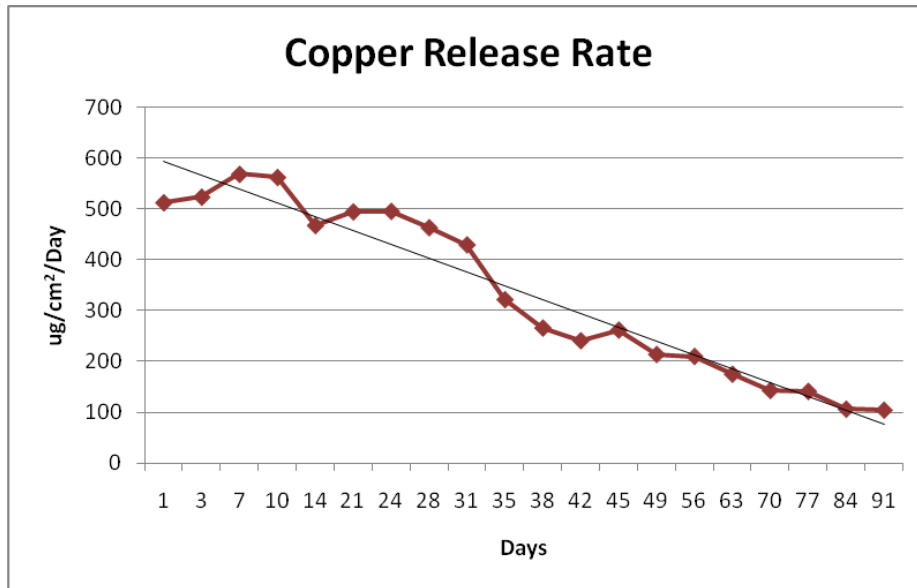


Figure 12: Average Cu Leach rate of 3 specimens for the 91 day trial

This produced data which indicated stabilization was beginning to occur. However, if the results of the three individual specimens are examined as shown in Figure 13, there is still a significant difference between them. Even after 91 days, the release rates were 69, 104 and 140 $\mu\text{g}/\text{cm}^2/\text{day}$ respectively.

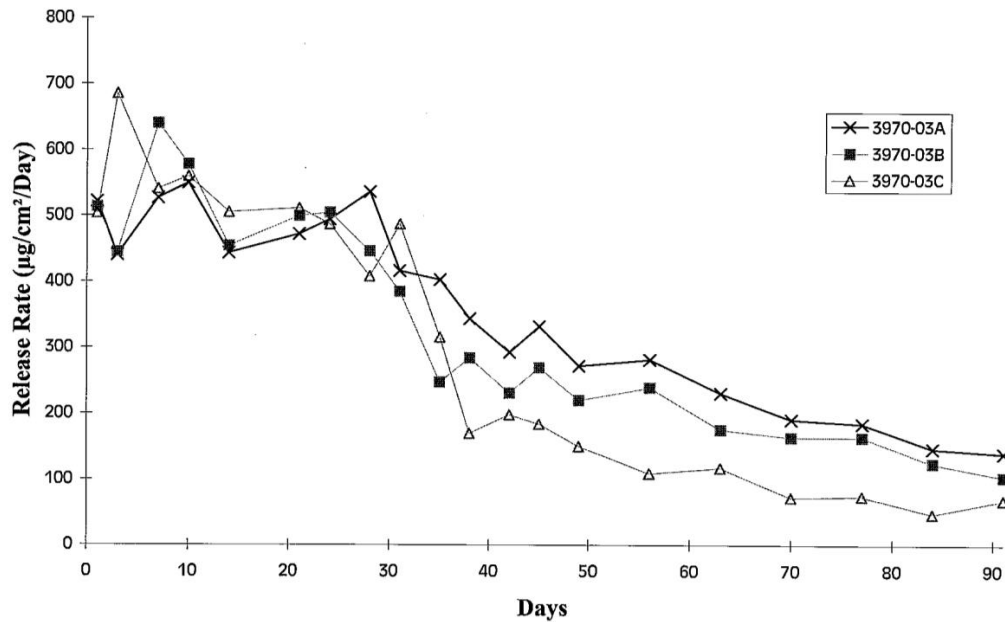


Figure 13: Graphic plot of Cu Leach rates of the three individual test specimens from the third trial.

The final film is shown in Figure 13 and shows a uniform red brown film. The photo was taken several weeks after the test was complete.



Figure 13: Surface film formed by end of 3rd trial taken several weeks after removal from the tank.

DISCUSSION

Although 90-10 copper-nickel was first developed over 50 years ago and its corrosion and biofouling behavior in service is well documented, detailed understanding about the mechanisms involved is largely undeveloped. A survey has indicated that the areas still requiring more data and accurate explanation are:

- Realistic figures for copper leaching rates of copper-nickel in sea water establishing whether corrosion rate evaluations are as accurate as direct leaching measurements.
- Actual biofouling mechanisms.
- Whether given the complexity of the biofouling and corrosion mechanisms, it is realistic to take measurements from artificial sea water.
- The minimum leaching rate at which biofouling resistance is controlled and whether copper leaching is a realistic way of evaluating biofouling resistance if the properties of the surface film itself are part of the mechanism.

Although there are no standardized tests for evaluating copper release from solid copper alloys, it was decided as a first examination to modify ASTM D6442-06 and assess its accuracy and relevance. For coatings, the ASTM D6442-06 test normally produces copper release rates which begin high at about 90-100 $\mu\text{g}/\text{cm}^2/\text{day}$ and by day 21 are down to about 40 $\mu\text{g}/\text{cm}^2/\text{day}$. Clearly however, the solid metal trials have produced release rates much higher than coatings using this test method. The results also show an unacceptably high variability from specimen to specimen with the leaching rates still not stabilizing properly even after 90 days. Normally a pseudo steady state condition requires 24 days where the release rates vary by less than 15%.

For copper alloys under service conditions, it is known that formation of a mature surface film is required before the alloy becomes fully corrosion resistant. This does not seem to be occurring in the synthetic ocean water used in these trials as quickly or as protectively as would occur in live sea water. Biofilms in live sea water are known to decrease the release rates of coatings by the formation of the slime or biofilm, and it is also true of solid copper alloy. However, it is thought that other factors are involved for the solid alloy as well, predominantly linked with the rate of formation of the surface film. If

corrosion rate is an indication of copper release in service exposure, data from the Efirid and Anderson trials indicate values of between 2.5- 32 $\mu\text{g}/\text{cm}^2/\text{d}^{10}$.

Chemical analysis was not carried out on the surface film of the three sets of samples and there is no obvious explanation for the dramatic difference in visual appearance of the two 45 day trials from the base metal compositions or feedback from the laboratory about differences in the way the trials were conducted. A brownish red film would however have normally been anticipated.

Current understanding about film formation is limited but it does seem to be complex and associated with a natural interaction with live sea water providing layers of cuprous oxide, trapped bacteria and cupric hydroxychloride. There is insufficient information from these trials to suggest why the surface films are not forming as well as they do in live sea water. Further trials will be required to provide this information and a better understanding of the mechanisms involved.

However, it is recognized that leaching rates by ASTM D6442-06 do not reflect environmental copper release rates even when used for antifouling coatings and states:

The results of this test method do not reflect environmental copper release rates for antifouling products and are not suitable for direct use in the process of generating risk assessments, environmental loading estimates or for establishing release rate limits for regulatory purposes.

The standard itself also recognizes that the test method significantly over estimates the release rate of copper when compared to release rates under in-service conditions:

The difference between the results from this test method and panel and ship studies can be up to about 30 times higher based on data from several commercial antifouling coatings.

Realistic estimates can therefore only be obtained where the difference between results for this test method and the release rate from an antifouling coating in service are taken into account and a correction factor applied.

It would seem therefore that the same could apply for solid copper alloy products and that other trials are required to realistically discover leaching rates in live sea water and apply a correction factor to the ASTM test. This perhaps could be achieved by the Dome method. It would also seem that much longer exposures than for antifouling coatings are required to achieve a steady state release rate if the ASTM method is to be used. More extended trials would need to be carried out until this had been fully established but are likely to be longer than the 91 days given here when testing in substitute ocean water.

CONCLUSIONS

1. The ASTM D6442-06 laboratory test method does not give realistic corrosion/release rates for solid copper-nickel alloys.
2. Historic corrosion testing has shown a difference between artificial and real seawater during corrosion studies.
3. The most meaningful data on copper-nickel to date is from earlier corrosion testing and shows a very low corrosion rate for 90-10 copper-nickel in seawater. This low corrosion rate also indicates that the rate of copper ion release is low.
4. Further work would be required to establish a realistic correction factor if the ASTM method is to be applied to solid alloys for the prediction of in situ field releases. It would also require additional data from the Dome method.

5. More explanation is required to fully understand the composition and growth of the surface film in relation to corrosion and biofouling properties and their relationship to leaching from the alloy.

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