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Long-term Exposure Trials Evaluating the Biofouling and Corrosion Resistance of Copper-nickel Alloy Sheathing Materials.

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Abstract

The modern equivalent of copper sheathing, so successful on Nelson's ships, is the use of a 90-10 copper-nickel alloy applied as an adhesive backed foil to ships and as granules embedded in polychloroprene rubber used on legs and risers of offshore structures. The 10% nickel alloy is reported to have better corrosion resistance than copper whilst maintaining similar biofouling resistance. While independent long term evaluation studies for copper-nickel itself are widely available, little data exists for these types of composite products.

A 7 and 8 year raft exposure trial study in Langstone Harbour, UK, evaluating the corrosion and biofouling behaviour of the foil and granule composite products respectively has now been completed. Removals of panels for destructive assessment after 1, 4 or 5 and 7 or 8 years were made. In addition, a third product under development at the start of the study, involving expanded mesh with a neoprene backing, and also a single sample of hot rolled plate were included in this study. The adhesion of the foil product was measured by peel resistance tests on 3 occasions over the exposure time.

The results 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. The foil product had thinned 5.5 μm per annum when averaged over a 7 year period. Some reduction in bond strength was observed for the foil, being less pronounced on steel than GRP.

INTRODUCTION

Copper-nickel alloys have long been employed for the protection of submerged marine structures and vessels from fouling by marine organisms. Although significant data exists for the corrosion resistance and antifouling behaviour of wrought copper-nickels, namely those based on 90-10 and 70-30 copper-nickel ratios [1-4], the long-term behaviour of more recently developed composites of the 90-10 alloy is not well documented. The results detailed in this paper allow an assessment of the viability of composite assemblies as sheathing for the prevention, or reduction, in the fouling of marine vessels and structures.

The findings are based on an 8 year exposure trial study in Langstone Harbour, UK, by Portsmouth University on behalf of the Nickel Institute, into the behaviour of 90-10 copper-nickel sheathing materials in a marine environment [5]. The materials under observation were an adhesive backed foil, granules embedded in neoprene, expanded mesh with a neoprene backing and a sample of 3 mm hot-rolled copper-nickel. The main aims of this study were to establish the overall stability of these products, their corrosion resistance and the extent to which the samples were able to resist fouling in a marine environment. In the case of the adhesive backed foil, information on the resistivity of the combination of the primary coating and adhesive backing as an indication of its efficiency as an insulator, as well as an evaluation of the adhesion of the panels to the substrate, as a function of time of immersion in the sea were also required.

TEST DETAILS

The exposure trials were carried out on a raft located in Langstone Harbour. This harbour is the centre of three linked harbours on Hampshire's southeast coast, with Portsmouth Harbour to the west and Chichester Harbour to the east. The harbour is important for its environmental designations, and commercial shipping; fishing and recreational boating have been supported there for many years. Langstone Harbour experiences two tides each day with temperatures ranging from ~8 - 16 ^{o}C for the winter and summer months respectively. There are two fouling seasons in spring and autumn each year. Flow rates in the harbour can reach 1m/s.

Descriptions of the materials exposed are given in Table 1.

Sample	Description	Sample Details
Embedded granules	90-10 Cu-Ni rods (1 mm dia, 1mm length) embedded by hot bonding into a 3mm thick polychloropropene rubber sheet	184 x 240 mm Mounted on GRP backing 6 samples
Expanded mesh	90-10 Cu-Ni expanded mesh, bonded to an elastomeric rubber base (EPDM)	~90 x 190 mm curved samples 1mm thick mesh, with slits 3 x 10 mm 6 samples
Hot Rolled Sheet	As manufactured 90-10 Cu-Ni sheet retaining surface oxide film	198 x 192 x 3 mm 1 sample
Adhesive backed foil	90-10 Cu-Ni foil sheets, with adhesive backing, hot pressed onto and around suitably prepared steel, aluminium and GRP surfaces.	Alloy and backing plate: 610 x 310 mm Foil :510 x 310 x 0.28mm 3 panels each with Al, steel and GRP backing plates.

Table 1 Product and Sample Description

The testing of the embedded granule product commenced in September 1994, and adhesive backed foil, expanded mesh and the 3 mm hot rolled sheet samples 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. Photographic records of the appearances of these alloys as a function of time were obtained and the nature and development of the associated fouling community monitored. The samples were not cleaned although occasionally the ease with which the fouling could be removed by hand was investigated in local areas. Samples and laboratory testing of removed samples were carried out at exposure periods of 1, 3-5 and 6-8 years. The final samples were removed in November 2002. Table 2 details sample exposures.

Year	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**
Embedded granules		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Date of immersion	09-94	09-95							
Dates of removal		09-95				10-99			11-02
Expanded mesh			**1**	**2**	**3**	**4**	**5**	**6**	**7**
Date of Immersion		11-95							
Dates of removal			12-96			10-99			11-02
3 mm hot-rolled sheet			**1**	**2**	**3**	**4**	**5**	**6**	**7**
Date of immersion		11-95							
Date of removal									11-02
Adhesive backed foil			**1**	**2**	**3**	**4**	**5**	**6**	**7**
Date of immersion		07-95							
Dates of removal			12- 96 *Steel, GRP and Al*		11-98 *Al panels*	10-99 *Steel, GRP panels*		06-01[a] *Steel panels*	11-02 *GRP panels*

Table 2. Sample exposure history.

The 6 embedded granules panels were attached securely to a single steel frame using nylon screws, Figure 1. The frame itself was slotted into position on the raft and secured by ropes to prevent loss in heavy weather conditions. When in place, all of the samples were below the water level. Six expanded mesh samples were received and mounted on one frame initially as shown in Figure 6 with the single hot rolled sheet sample positioned towards the bottom of the same frame. These were repositioned on other frames as the number of frames decreased due to removal of samples for laboratory evaluation.

In total, 9 samples of copper-nickel adhesive backed foil sheathing mounted on steel (x 3 panels), fibreglass (x 3 panels) and aluminium (x 3 panels) were supplied. Nine specially designed frames were constructed with additional features to ensure electrical insulation of the copper-nickel from the frame itself. Nylon washers were machined to provide the necessary insulation for the stainless steel screws fixing the metal panel in place. To allow as great a surface area as possible to be exposed to the environment and also to help support the weight of the panels a nylon rack was also bolted to the frame. The construction of this was such that the panels fitted into these without being wedged in place thereby allowing free flowing seawater in this region, see Figure 12. The frames themselves were slotted into position on the raft and, when in place, ideally about a third of the alloy clad surfaces of the panels were above the water level.

All unremoved frames were transferred to a second raft when it became available in June 1999. In June 2001 the coated steel frames were sufficiently corroded to be replaced with new ones. During the exposure study, only one frame was lost, and that occurred over the winter of 2000-2001 and held a single steel backed adhesive backed foil sheathed panel. The second remaining steel backed panel was removed at that stage to prevent further loss.

RESULTS

Biofouling

Embedded Granule Panels.

After exposure, no marked fouling was observed until the spring/summer of 1995. This was not unexpected as the panels were initially put out in September 1994 after the main fouling season and there would have been little growth during the cold winter months. Figure 1 shows the appearance of the panels after a period of 12 months in the sea. The first change observed was the appearance of a brown sludgy layer on top of the copper-nickel surface obscuring the rods. There was some fouling on the panels themselves but a more dense deposit was beginning to build up on the rear side of the GRP, the screws and the frame itself. Inspection of the panels showed that the fouling was not present above the copper-nickel rods but only on the polychloroprene.

Figures 2 and 3 show the appearance of the panels after an immersion periods of 4 and 5 years. The brown layer could be removed manually. Although there were small barnacles and some red/green seaweed found attached to the copper-nickel loaded surface after 5 years, the heavier fouling was again located on the rear surfaces of the panels with a variety of organisms including seaweeds, barnacles and sea squirts.

The samples were removed from the sea on 22 October 2002, after an exposure period of 8 years. The general appearance of the panels is shown in Figure 4. The main copper-nickel containing surfaces were covered with a brown slime layer but some macrofouling was also present in certain areas in the form of seaweeds and tiny barnacles. The slime layer could be removed by light wiping although the macrofouling required more pressure.

Expanded Mesh Panels

The appearances of the expanded mesh samples after an exposure period of 2.5 years is shown in Figures 7 and 8. The panels lying closest to the splash zone were less fouled than those lying lower in the water. The main fouling present was on the frames and ties supporting the samples and on the rear surfaces of the panels. As shown in Figure 8, the brown/grey slime deposit on the panels could easily be wiped away to reveal the underlying copper-nickel mesh.

Figure 9 shows the appearances of the samples after removal from the exposure raft in October 2002 after 7 years. As noted previously, the main fouling was located on the frames themselves, and at the edges and rear surfaces of the panels. The panels were also covered with a brown slime layer, which was thicker on the lower section; much of this layer could be removed manually. After drying in the laboratory, the alloy-containing side of the panels could be seen to be coated with a green-grey deposit. These surfaces were largely free from macrofouling but did contain a few barnacles on the rubber and at the copper-nickel rubber interfaces. The attachment of the fouling material was seen to be predominantly in the regions of the EPDM rubber substrate.

3mm Hot Rolled Sheet

The appearance of the hot-rolled copper-nickel after a 13-month exposure period is shown in Figure 10. The panel remained very bright with no fouling on its surface. Throughout the exposure trials the panel remained relatively free of fouling. Figure 11 shows the appearance of the rolled sample after removal from the exposure raft in October 2002 after 7 years. The main fouling was located on the frame, with some on the ties securing the plate to the frame. A loose deposit present on the surface of the alloy could be manually dislodged.

Adhesive Backed Foil Panels

After 18 months, Figure 13, exposure, two regions were distinguishable on each panel; a green coloured area of copper-nickel above the water line and a lower region covered by brown slime. The latter deposit was easily removed on wiping. Little macrofouling was present on the panels.

By 3 year 8 months, the overall appearance of the panels had not changed significantly from that observed at earlier exposure times. The lower sections of the panels were covered with an easily removable brown slushy layer. A small amount of macrofouling was observed but it was predominantly located in regions where the mastic used in the bonding process had been exposed or at edges where thinning of the copper-nickel had occurred.

The final steel panel was removed from the sea in mid-2001. Generally, this panel was not dramatically different from those observed during earlier inspections. The nylon rack supporting the panel and the frame itself had been heavily fouled with sea squirts and other marine plants and organisms. The slime layer was seen at a much lower level than previously observed due to the re-positioning of this sample on the new raft in Langstone Harbour. In general, the macrofouling on this panel was minimal with a few organisms on the copper-nickel surface. It was predominantly located in (i) regions where the mastic used for bonding was exposed *e.g.* at individual sheet interfaces and (ii) at the side edges where thinning of the copper-nickel had occurred. The thick slime layer present, as noted previously for other panels, was easily wiped away to reveal the underlying yellow-coloured copper-nickel surface. Even barnacles, where present, were relatively easily wiped away from this surface. The panel was streaked with rust marks from the frame, and there was also a small area of rust on the right-hand side of the panel where thinning of the alloy followed by removal of the primary coating had occurred. There was no evidence of any disbondment of the alloy from the steel/primary coat base.

After the 7 year exposure period, the GRP based panels exhibited a similar fouling pattern to that observed for steel-based, Figure 14. The copper-nickel surfaces were again covered with the brown slime, which was easily removed in areas to display a clean metal surface. However, on one side of one panel there was more macrofouling on the lower section with barnacles and a moderate amount of fibrous material present. Thinning of the alloy was again noted at the panel edges and small organisms and plants could be seen settling in these locations. There was no evidence of any disbondment of the copper-nickel from the GRP base.

Description of the Fouling Community

Marine algae played the most important role in the colonisation of all the types of test panels. They were revealed to be the most dominant fouling group with animals playing only a secondary role in the fouling community.

After 7 and 8 years exposure for the expanded mesh and adhesive backed foil panels, and the embedded granule panels, respectively, the fouling on all the panels followed almost identical patterns. Full details are given in [5].The algal community present on the plates comprised a mixed community of diatoms, blue-green algae and representatives from the green, brown and red macroscopic algal groups. Microscopic diatomaceous algae, which also played an important early colonisation role, largely comprised species of the procumbent genus *Amphora*, along with scattered colonies of species of the genera *Licmophora* and *Navicula*. Together with some filamentous (*e.g. Lyngbya spp.*) and coccoid (*e.g. Aphanocapsa spp.*) blue-green algae, they formed a distinct slime community amongst a mixed community of macroscopic green, brown and red macroalgae.

There was 100% cover by fouling organisms on the panels but the community structure continued to be restricted. Essentially, except for scattered patches the surface of the panels was covered by a thick dark green encrustation, usually less than 100 μm in height.

A number of animal foulers were also identified on the panels. These included:
<u>Tubularia laryx</u>. This colonial animal formed small white tufts scattered on the panel surface. It reached up to 15% cover on most panels, although exceptionally it reached 70% cover on some surfaces.
<u>Bryozoans.</u> These formed occasional colonies on the panel surface.
<u>Mussels</u>. Two mussels were observed on one panel (2% cover)
<u>Barnacles</u>. Scattered barnacles were observed on some panels, not exceeding 5% cover.
Also found were scattered seasquirts, both colonial (Botrylus) and solitary (Ciona), along with occasional tubeworms.
<u>Jassa sulcata</u>. These mobile amphipods formed homes amongst the fouling and were not uncommon on the panel surface.

All the preceeding erect fouling growths were generally limited in size and somewhat isolated in nature. Most of the surface was covered by the encrusting growths and clearly the nature of the surface was still exerting an effect on the community structure.

Corrosion Resistance

Embedded Granule Panels
The general appearance of an "as received" embedded granule sample, mounted onto a GRP backing plate for the exposure testing experiments, is shown in Figure 5. The distribution of the rods showed a random arrangement with some lying parallel to the rubber whilst others were embedded at right angles to the surface.

By 5 years exposure, although some localised corrosion products were detected on the rods there was no significant alloy degradation and the rods were still firmly embedded in the polychloroprene.

After 8 years, a 2 cm^2 section of the exposed panel was cut away from the GRP backing plate and several of the rods removed from the polychloropropene. The latter was fairly easily effected by simply bending the polymer allowing the rods to spring out. To investigate corrosion and thinning, the rods were initially examined microscopically. This showed the surface of the rods had roughened and some localised corrosion occurred. The measured cross-section of a typical rod, at its widest point and without removal of any corrosion products, was 1.07 ± 0.03 mm. Prior to the exposure period, a similarly shaped rod had a measured cross-sectional diameter of 1.08 mm indicating that, in this direction, little thinning of the rods had occurred during the 8 years. However, it is very difficult to accurately assess the degree of thinning because although the rods were quoted as having a nominal thickness and diameter of 1.0 mm, in practice many different shapes and sizes of the alloy rods were present, immobilised at different orientations in the background polymeric matrix. Conversely, the end of the rod, which would have been exposed to the seawater, did show signs of corrosion. At high magnification, SEM images clearly showed that shallow pitting of the alloy surface had occurred. EDX analysis showed the presence of the main alloying elements, copper, nickel and iron with a small amount of manganese; chlorine was also observed.

Expanded Mesh Panels
On sectioning the material and inspection with an optical microscope after 13 months exposure, it was found that the whole surface of the copper-nickel, as well as the surrounding rubber, was covered with a greenish-brown layer, very similar in nature to the type of deposit seen on the embedded granules. However, on the expanded mesh, long tracks of a copper coloured residue could be seen running along in the direction of the copper-nickel substrate (in the case of embedded granules, such deposits were rounded corresponding to the spherical copper rods).

After 7 years, a section of the copper-nickel was cut away from the EPDM substrate. The surface, when examined microscopically, showed that in the apex in the mesh some roughening and localised corrosion of the surface had occurred.

Hot Rolled Sheet
After 7 years, a section of the panel was sawn off and the surface examined. High magnifications showed the presence of surface roughening which had the appearance of a slight etching.

Adhesive Backed Foil Panels

By 18 months, scratching and pitting could be seen along the water line. The depths of these scratches and pits were 10±3 and 50±18 μm respectively. Although quantitative testing of the bond strength of the copper-nickel to the underlying surface had not been carried out at that time, there was no evidence of any deterioration in the adhesion of the metal to the panel. However, at the edges of the panels, considerable thinning of the copper-nickel was observed. This can be partly attributed to erosion corrosion as a result of the hydrodynamic conditions that would be experienced in these locations. Despite this reduction in alloy thickness, the underlying metal surfaces, even that of the aluminium panel, remained protected by the black primary coat layer.

However, at the end of 1998 after a 3 year 5 months exposure period, the aluminium backed adhesive backed foil panels had to be removed from the raft due to extensive failure. This was directly related to the thinning of the copper-nickel at the panel knife edges and the subsequent deterioration of the primary coat resulting in an exposure of the aluminium to salt water. As would be expected, this resulted in a rapid corrosion reaction and the subsequent lifting away of the copper-nickel panels from the aluminium substrate. Deterioration of primary coat was also observed on the aluminium surface above the cladding.

Examination of the steel backed panel after 6 years showed a roughened surface with small pits with diameters ranging from 5-20 μm .

To evaluate the overall thinning of the a copper-nickel during the 7 year exposure period, samples were removed from (a) an unexposed sample and (b) from the centre of a panel in a region free from overlapping surfaces. These were then mounted in a resin, polished and the thicknesses evaluated by observation in an optical microscope. This demonstrated that thinning of the exposed sample had occurred. The thickness measured at the thinnest cross-sections ranged from 260 – 300 μm for the unexposed sample. After exposure the thickness was measured at 220 – 260 μm and indicates a thinning rate of 5.5 μm per annum over the 7 year exposure period.

Adhesive Backed Foil Panel Resistance Measurements

The electrical resistance between the steel and the upper surface of the copper-nickel after 6 years was > 1 MΩ indicating that the primary coat was still acting as an insulator and had not deteriorated in the region measured. The resistance of the primary coat underneath stripped regions of panels was also above 1 MΩ indicative of the coherence of the insulating layer.

Adhesion

The bond strength of the mastic used on the adhesive backed foil panels was measured using the Floating Roller Peel Test according to BS EN 1464 (1995) and the results reported according to BS EN 1464 (1995) and BS 5350 Part E1 (1976). This procedure is widely used to assess the performance of adhesives and in particular for measuring bond strengths of flat composite structures. The method is applicable to any type of adhesive over a wide range of temperatures and can also be used for pieces that have been subjected to environmental testing.

For this experiment, a composite test piece, in the form of a sandwich in which two thin facing sheets are bonded by the test adhesive to a core material, is fixed by a secondary adhesive to a traction jig. The test piece is strained to rupture by a tensile force and the reported result is the observed force at rupture. The Floating Roller Peel Test is designed for a flexible-bonded to rigid test specimen assembly. This is used to determine the peel resistance of two adherends where at least one is flexible. For a constant angle of 90 ^{o}, a roller-peeling device is used. The adherends are pulled apart at a steady rate starting at the open end of the bond in such a way that separation occurs progressively along the lengths of the bonded adherends. The force is applied approximately normal to the plane of the bond through the separated part of the flexible adherent.

Control samples, which consisted of copper-nickel bonded onto GRP, together with exposed samples on GRP and steel were machined into 25 x 150 mm sections and tested as described above.

The average peel resistance measured for the steel control sample was 119.0 ± 4.0 N which fell to 101.3 ± 7.5 N after a 3 year exposure period. After a total of 6 years a peel resistance of 87.7 ± 8.2 N was measured. These results show that the bond strength between the panels and the substrate has gradually lessened over the exposure period. It should be noted however that no signs of any detachment of the panels was seen after 6 years. Only wear at edges where higher seawater flow rates would have been experienced was seen.

The GRP control sample had a higher initial peel resistance of 160 ± 7.1 N with a value of 165 ± 3.3 N measured after 3 years. After the full exposure period of 7 years, the value had fallen to 72.8 ± 14.6 N.

These results show that immersion of structures for extended periods in seawater does reduce the adhesion between the copper-nickel and the substrate with similar values measured after 6-7 years for the different substrates.

DISCUSSION

Sheathing offshore platforms in copper-nickel 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 welded into position. For biofouling protection, it is supplied as a composite product of half cylinder sheets, perforated sheet, granules or wire bonded onto an insulating backing, e.g.neoprene [7].

The product involving embedded copper-nickel granules is commercially available and has been successfully used for splash zone and biofouling protection of structural legs, cross bracings and riser pipes. It involves discrete granules of copper-nickel, 1mm diameter and 1mm long bonded into the surface layer of 3 mm thick neoprene sheet. 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 complete surface protection. The product can be hot bonded onto elastomeric corrosion coatings or cold bonded directly onto steel[8]. The track record dates back to 1984 with over 25,000 square metres supplied for several platforms world-wide.

The exposure trials show that after an 8 year exposure trial period, the panels have successfully withstood the aggressive exposure conditions. A limited amount of macrofouling was present on the alloyed surface of the panel by the end of the trials which could be removed manually when wet. The fouling present was predominantly located on the polychloroprene, the GRP backing and at the panel edges with very little above the alloy itself. Corrosion and roughening of the copper-nickel surfaces exposed to the sea had occurred; shallow pits were seen at the ends of rods directly exposed to the sea. However, little reduction in the measured rod diameters was observed; values of *ca.*1.1mm 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 easily removed by flexing the supporting matrix. Although the adhesive hold of the granules of copper-nickel in the product was shown to decrease with time when exposed to sea water, the rubber is known in service experience to expand and compensate for this. Unless the product is significantly flexed or picked at, the granules are said by the manufacturer to remain intact.

The expanded mesh product at the time the trials were initiated was being developed for splash zone sheathing. The design, based on slits in the sheet, was conceived to allow ease of bonding to the neoprene compared to full sheets. The product never became a full commercial product but was included in the programme to represent a third variation of copper-nickel surface area coverage, namely 60%.

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. Alternatively, the rear surfaces of the panels which did not expose copper-nickel were heavily fouled and the detritus could not be removed. Some surface roughening of the copper-nickel surfaces was observed at higher magnifications.

Copper-nickel has been used as solid sheet or roll clad onto steel for boat hulls and as splash zone sheathing on platform legs [7] e.g. the Morecambe Field. After the 7 year exposure trial period, the hot-rolled copper-nickel sheet 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. Only a very limited amount of macrofouling was present on the alloyed surface of the panel and even then when wet and after drying, macrofouling organisms and films could be easily removed from the surface. A generalised roughening had occurred on the plate surface by the end of the trials when observed at high magnification.

Copper-nickel has also been applied to boats as an adhesive backed foil. A system of sheathing of a ship's hull with 90-10 copper-nickel foil was developed in the UK and involved the application of adhesive-backed panels (approximately 210mm x 500mm) to prepared hulls, allowing about 15mm overlap. The copper-nickel foil thickness is normally about 0.15mm although in these trials the thickness averaged 0.28mm 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 which further protects the hull from the corrosive action of seawater. The system has been applied to new hulls and as a retrofit [4]. The foil panels for the trials were manufactured by a New Zealand company and applied to the backing plates in the UK by the inventor.

After extended exposure periods, the GRP and steel-based panels sheathed with the foil had performed extremely well and remained largely free of macrofouling. By approximately 3.5 years exposure, the aluminium samples had corroded with concomitant detachment of the copper-nickel. In the case of the steel and GRP based samples, however, the alloy surfaces did not show any signs of detachment from the underlying substrates. The primary coating proved to be an efficient surface protector but after 7 years it showed evidence of degradation where it was the only coating on the panel. Blisters were seen beneath the exposed primary coating on the top surfaces of the steel samples.

The panels were all covered with bound brown slimes that could be removed manually. Fouling plants and organisms were predominantly found at 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 reduced over time which is consistent with published data on long term corrosion rates [1,6]and thinned by 5.5μm per annum when averaged over a 7 year exposure period. (References [1,6] for flowing sea water (0.6m/s) in North Carolina found initial corrosion rates in the order of 13μm per annum falling to 1.3 μm per annum after extended periods of about 5 years). Considerable thinning and removal of the copper-nickel on the edge of the panels was observed. This was attributed in part to erosion-corrosion of the alloy. It may also be due to the forming process around the knife edge leading to thinner foil section in this area. Although this needs to be examined further to provide an accurate explanation, knife edge geometries would not be sheathed in practice on a boat hull.

No disbondment was experienced on the steel or GRP panels. Quantitative measurements of the bonding of the alloy to the underlying substrate according to the Floating Roller Peel Test BS EN 1464 (1995) showed that the bond strength between the alloy and steel, and GRP, reduced with exposure time from 119.0 to 87.7 N and 160.0 to 72.8 N respectively.

CONCLUSIONS

The results of the 7 and 8 year trials confirmed the stability and suitability of all the 90-10 copper-nickel products for long term protection of offshore structures and boat hulls.

The trials also confirmed documented experience that microfouling will eventually colonise on 90-10 copper-nickel surfaces but macrofouling is restricted. Most of the macrofouling identified had colonised on the rubber substrates or adhesive exposed at overlaps. Where microfouling and macrofouling had colonised on the copper-nickel, it could normally easily be removed with a wipe when exposed and wet but with slightly more effort when taken from the raft and dried out.

Surface area coverage of copper-nickel had some effect on biofouling but this did not seem to be a linear relationship. The embedded granule product, having the least copper-nickel surface area cover, might have been predicted to show higher fouling levels than the other products. In reality it showed very good resistance for the majority of the exposure. The hot rolled sheet provided the best biofouling resistance which might be taken to be associated with the 100% copper-nickel surface area but it also had a thicker oxide surface film and the composition of this could also have played a part.

Corrosion rates of the copper-nickel on flat surfaces, where measured, decreased to low levels with time in agreement with published data. Thinning of sheathing around knife edges was experienced and might be due to erosion corrosion in those areas or due to thinning during fabrication and this needs to be examined further before a final explanation is given. Such knife edge geometries on the sheathed areas of a ship hull would not be experienced in practice.

The adhesive backed foil product showed no disbondment from the steel and GRP based panels during the trials. Destructive testing showed some adhesion decrease over the exposure time.

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Embedded Granule Panels

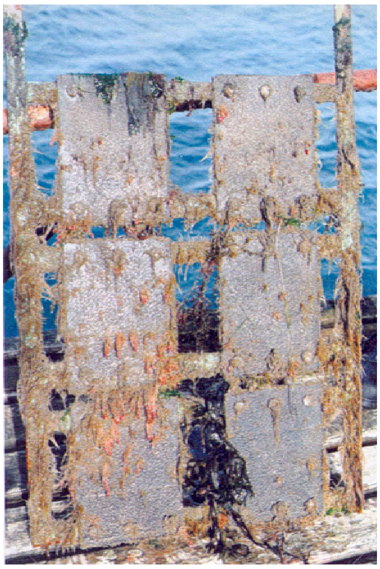

Fig 1. 12 month exposure

Fig 2 4 year exposure showing areas of brown slime removed after manual wipe

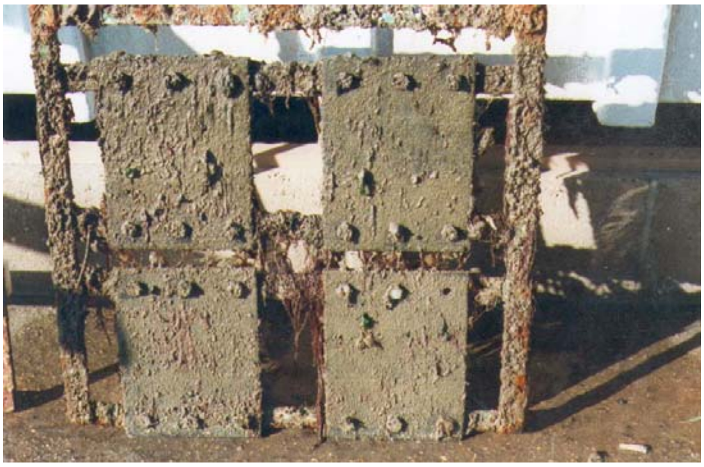

Fig 3 5 years exposure

Fig 4. 8 years exposure

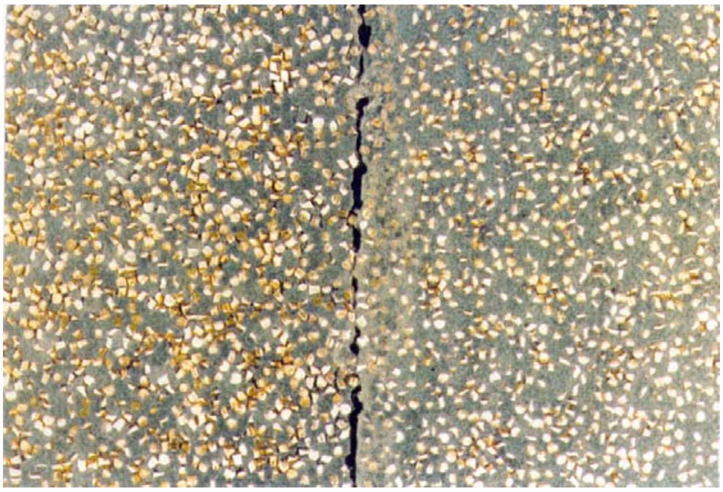

Fig 5.Before exposure, showing Copper-nickel rods

Expanded Mesh Panels

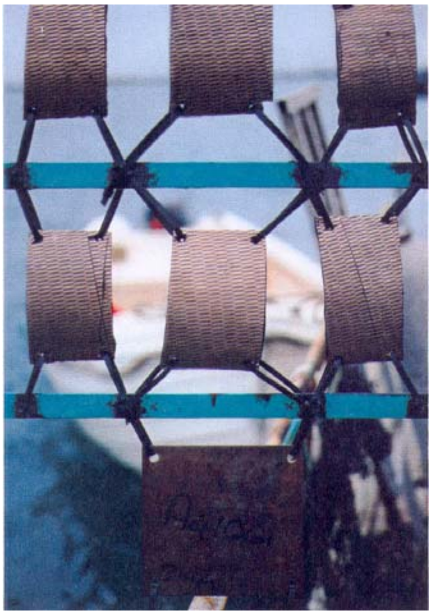

Fig. 6. Prior to exposure

Fig 7. 2.5 years exposure, top row

Fig 8.   2.5 years bottom row
Showing manual wipe

Fig 9. 7 year exposure

Hot Rolled Sheet

Fig 10 13 month exposure

Fig 11 7 year exposure

Panels sheathed with Adhesive Backed Foil

Fig 12 Sheathed panel prior to exposure

Fig 13   18 month exposure

Fig 14   7   year exposure