WHITE PAPER

BALMORAL CuNiCLAD™ MARINE ANTIFOULING SYSTEM

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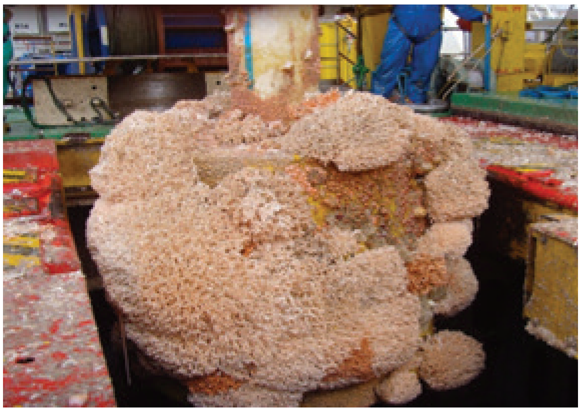
1 INTRODUCTION

Marine biofouling is an issue which must be seriously considered when installing any structure or launching any vehicle into an aquatic environment. Biofouling may be divided into microfouling - biofilm formation and bacterial adhesion - and macrofouling - attachment of larger organisms, of which, the main culprits are barnacles, mussels, polychaete worms, bryozoans, and seaweed.

1.1 **Microfouling** The initial process in biofouling is the formation of a 'conditioning film' on the substrate surface. This film formation commences immediately upon immersion. The composition of the conditioning film varies with the composition of the water and the substrate but typically develops through the absorption of organic molecules such as humic substances, polysaccharides and proteins, and ions onto the substrate surface. Subsequent colonisation of the conditioning film by bacteria, fungi and microalgae to form the initial biofilm occurs within minutes, and is rapidly followed by the attachment of macroalgae and protozoa. Microbial cell adhesion follows the attachment of these microorganisms. These microbes produce proteins, glycoproteins and lipids, polysaccharides and other so-called 'extracellular polymeric substances' (EPS) to produce a matrix which binds together the microbes and other microfouling species. The EPS provides a substrate and nutrients for diatoms and algae which in turn facilitate the settlement of other fouling species.

1.2 **Macrofouling** The presence of the EPS microbial film promotes the settlement and survival of drifting invertebrate planktonic larvae and early life forms of macro-organisms such as polychaetes, hydroids, molluscs and barnacles. The 'hard fouling' filter feeders form dense colonies with high growth rates and in appropriate environmental conditions, cause a particularly severe fouling problem.



Recovered Distributed Buoyancy Module Fouled with Lophelia perusa

The biological nature and degree of marine fouling is strongly influenced by environmental factors such as temperature, salinity, light levels and nutrient levels, as well as geographical location. In most marine service environments, 'hard fouling' in significant thicknesses only extends down to 30-50msw, with 'soft fouling' in progressively reducing thicknesses thereafter, down to typically around 100msw. There are however a significant number of locations worldwide where 'hard fouling', specifically by deepwater corals, is known to flourish down to extreme depths. The primary species, Lophelia pertusa has a main depth distribution band of 200–1000msw, particularly 200-400msw, although the species has been identified as deep as 3000msw. As Lophelia corallites grow 5-10mm pa, major accumulations can accumulate on marine installations during project lifetimes.

Accumulation of fouling organisms leads to increases in submerged weight but, far more importantly, such fouling significantly affects the hydrodynamic performance of subsea structures and equipment.

A range of coating systems and technologies has been developed to prevent marine biofouling to susceptible structures and equipment.

2 TYPES OF MARINE ANTIFOULING COATINGS

Marine antifouling systems are of three generic types:

2.1 Biocide release systems, based on dissolution or hydrolysis of the binder. These systems release the biologically-active ingredient at a slow rate, the rate depending upon the identity of the binder system and the local environmental conditions. These are relatively new systems, with somewhat restricted track record however the performance is often outstanding, providing long term resistance to all types of fouling organisms. Some of these treatments are now specified for up to (& even beyond) 20 years untended service.

2.2 External coatings with 'low surface energy' characteristics which prevent strong fouling adherence. When newly applied, the surface is so 'slick' that any initial adherence of fouling species is readily removed by the hydrodynamic drag resulting from vessel movement. However, there is no track record to support the use of such systems in permanent (eg, 20+ years') service & indeed it would appear likely that general wear & tear of the thin (150mic DFT) fouling resistant coating from continual fouling detachment will gradually degrade the surface coating. It is therefore standard practice is for vessels A/F-treated with these materials to be dry-docked and the 'old' coating removed & replaced at 2 (max 4-5) year intervals. Importantly, for effective operation the coating needs significant water movement across the surface (>2.5m/s) to sweep away initial deposits. Where this surface water velocity is not routinely achieved (eg, as would be the case with tethered systems such as risers), periodic cleaning by water jetting or brushing using a ROV is essential. It should be noted that this cleaning operation is likely in itself to damage the very soft and fragile coating and thereby reduce subsequent antifouling performance and coating longevity.

2.3 Inherently toxic surfaces, which inhibit the deposition or growth of the EPS pre-film essential for the deposition of all macro-fouling species. The standard systems of this type are based on copper metal or alloys which are inherently toxic to marine fouling organisms and are subject to ultra-slow dissolution into seawater- these properties deliver outstanding long term marine antifouling service

The primary antifouling systems using this technology are solid 90:10 CuNi alloy sheeting bonded to Neoprene-coated steelwork and systems using CuNi granules embedded in Neoprene sheet cold-bonded or vulcanised onto a neoprene coated substrate. Both solid CuNi sheeting and Cuproprene have massive track record, in many cases going back 25 years, for splashzone antifouling protection of platform jacket steelwork. Neither is suitable for use on complex shapes such as buoyancy modules nor on moulded polymer products such as VIV mitigation strakes.

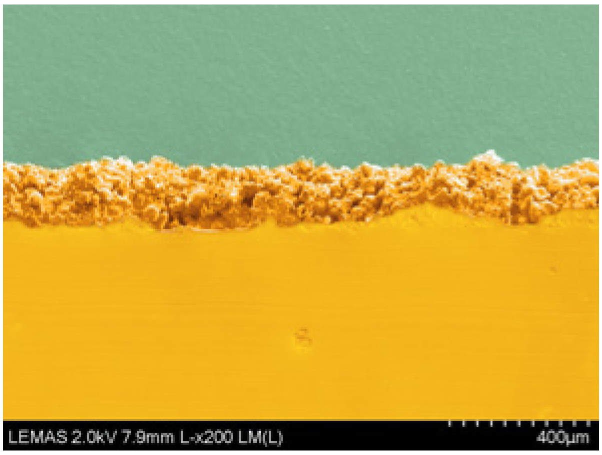
3 BALMORAL CuNiCLAD™ MARINE ANTIFOULING SYSTEM

Whilst copper-nickel alloy systems are unique in their combination of outstanding antifouling performance and extended service track record, neither of the current standard systems are suitable for use on complex shapes, due to their flat sheet form.

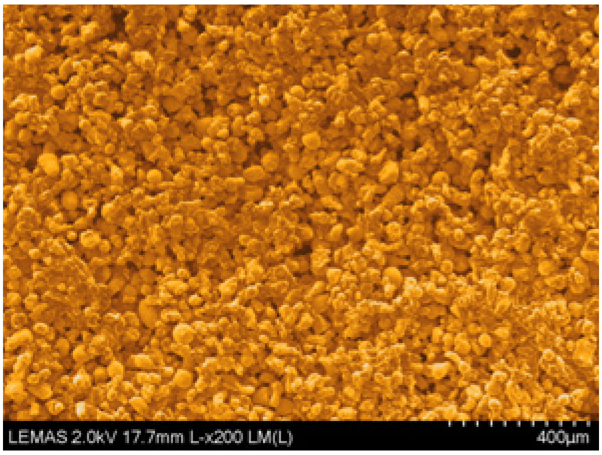
Like existing CuNi-based systems, Balmoral CuNiClad is based upon the use of marine grade 90:10 copper-nickel alloy, with the major advantage of being a spray-applied system. It is therefore ideally suited to application to complex shapes. The entire surface is coated with discrete CuNi granules so that there are no gaps in the protection onto which fouling can accumulate. As each granule is supported on, and in, a polyurethane matrix, despite the nobility of copper metal there is no possibility of galvanic corrosion of underlying steelwork and, additionally, no electrical continuity across the coated surface which, if applied to a CP-protected substrate, could otherwise interfere with the anti-fouling properties of the copper alloy.

Balmoral CuNiClad is cold-applied in a two-stage process, with the stages taking place sequentially. The application process is insensitive to local environmental conditions, with application temperatures across the 5-50°C range and relative humidities up to 90% being acceptable. A specially developed single pack/moisture-cured polyurethane binder is typically sprayed onto the clean substrate surface (roller and brush application are also possible) to a nominal 350 micron wet film thickness and the CuniClad copper nickel granules are then immediately applied in a low pressure spraying process to give a dense and tightly-bonded CuNi granule layer 150-200 mic thick in a final dry film thickness for the coating of nominal 350 microns.

Excess CuNi granules are applied to ensure the entire area of the PU primer is completely filled with granules; excess granules are recovered for later re-use. The entire coating process has minimal safety and environmental implications, with standard personal protective equipment such as respirators and hoods providing complete operator protection. The coating system is fully cured and ready for service 24 hours after application.



SEM cross section of CuNiClad coating



SEM surface view of CuNiClad coating

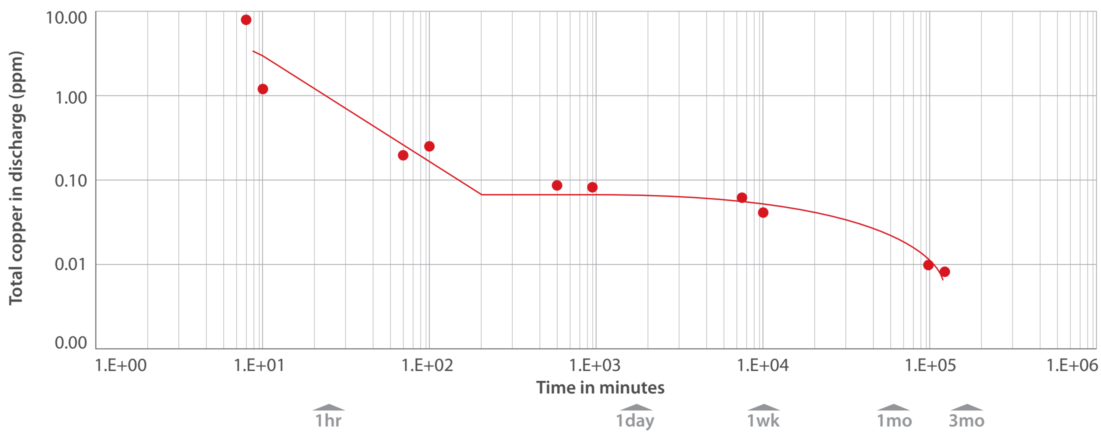
When first applied, the Balmoral CuNiClad antifouling system demonstrates the matt brown colour of the CuNi granules, however the coating will progressively turn green within weeks of immersion. The green colour may darken to near-black depending upon localised marine conditions.

4 SERVICE LIFE OF BALMORAL CuNiCLAD

The erosion/corrosion rate of 90:10 copper nickel alloy in seawater has been extensively studied since the introduction of the alloy over 50 years ago.

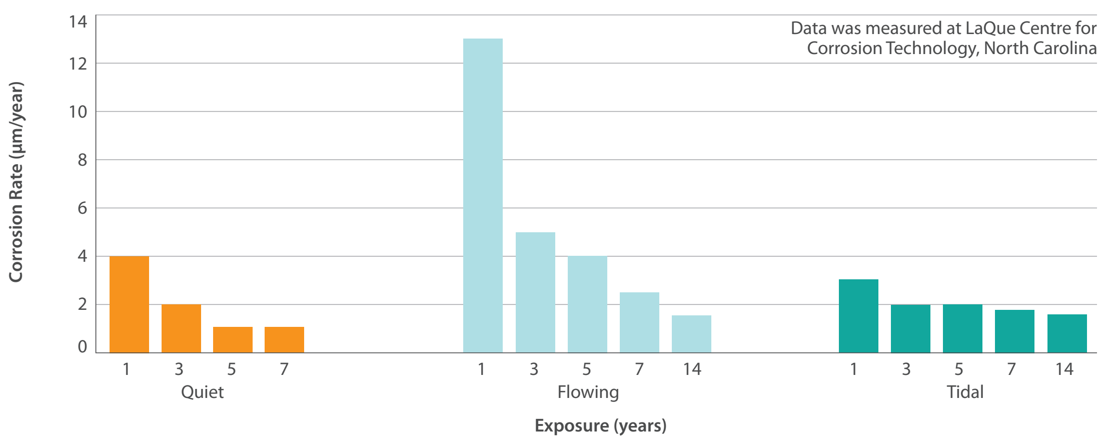
The erosion/corrosion resistance results from the formation of a thin protective film primarily of cuprous oxide but also containing nickel metal, iron oxide, cuprous hydroxychloride and cupric oxide. Film formation commences within days of immersion but may take 2-3 months to fully mature. This film formation has been monitored through its massive inhibiting effect on copper release rate. The copper content of the seawater effluent from a condenser with 90:10 CuNi piping was monitored for three months after startup. The initial release rate was observed to decline by 90% within 10 minutes and 99% within one hour. After three months, the concentration in the water flow was essentially identical to the background level of copper in the incoming seawater.

Seawater corrosion of copper from 90:10 CuNi piping



Once a good protective layer has formed, the erosion/corrosion rate will continue to decrease over a period of several years and to exhibit the classical parabolic protection growth rate of protective layers. For this reason, it is impossible to predict the service life of copper-nickel alloy systems based on short term testing. For 'worst case' calculations, corrosion rates of 2-20 microns per year are assumed, however in the definitive 14 year study at LaQue Corrosion Services, the corrosion rate of 90:10 CuNi alloy stabilised after six years at 1.3 microns per year.

Corrosion rate over time for 90-10 Copper-Nickel (in quiet, flowing (0.6m/s) and tidal sea water)

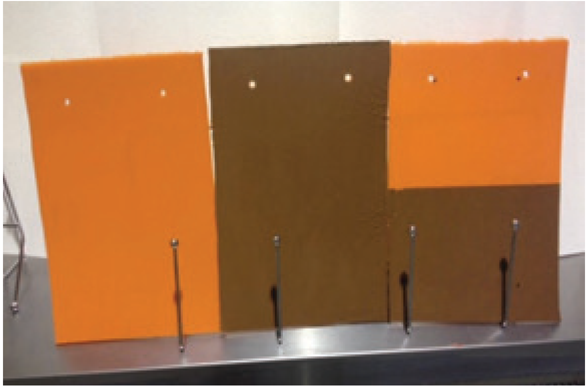


The erosion/corrosion rate of the copper-nickel alloy remains low with increasing seawater velocity, due to the resilience of the protective film, with velocities of 3m/sec having minimal effect(6). For copper-nickel alloys used on vessel hulls, velocities up to 12m/sec have been shown to give minimal erosion(7). The copper-nickel thickness in Balmoral CuNiClad is nominal 175 microns. Even allowing for the reduced volume fill of copper-nickel in CuNiClad vs. solid alloy, the service life of the Balmoral CuNiClad system in typical seawater velocities of <3m/sec is anticipated to easily exceed 30 years.

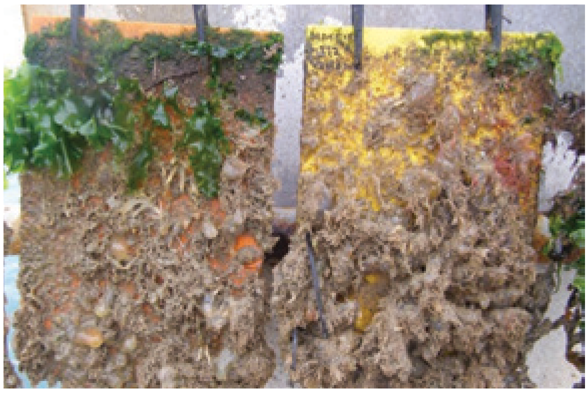
5 PERFORMANCE IN FIELD TRIALS

The antifouling performance of Balmoral CuNiClad has been monitored in marine field trials.

5.1 By the Institute of Marine Science, University of Portsmouth, on a trials raft in Langstone harbour, UK. The CuNiClad was applied onto orange and yellow LLDPE sheets. (See Appendix 1 for full report)



Orange sheet samples before immersion



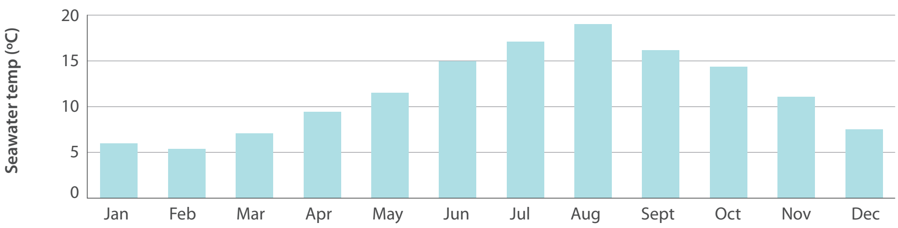
Untreated orange and yellow sheets after one year

Half-treated sheets after one year

Fully-treated sheets after one year

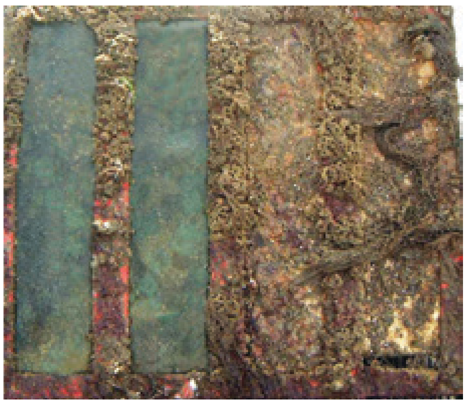
Environmental conditions at the test site were as follows:

Mean daily water temp (°C) Langstone Harbour 5 year period 2009-2013



Mean flood 0.7ms-1
mean ebb 1.6ms-1;
maximum spring ebb 1.8ms-1
max spring flood 0.9ms-1

5.2 At Weymouth harbour under the supervision of the Port Authority. After two years of immersion, the antifouling performance of PU sheets was as below (CuNiClad on left).



Half-treated sheets after one year

6 COATING ADHESION

The standard substrates used in marine polymer products are rotationally moulded polyethylene (buoyancy module shells) and cast polyether polyurethane (pipe/cable protection products and buoyancy module coatings).

Adhesion testing has been performed on sheet samples of each substrate.

Substrate	Test	Standard	Result	Comment
Polyethylene	X-Cut	ISO 16276-2:2007	Level 0 (no coating removal)	Pass
Polyethylene	Dolly pluck adhesion	In-house	Av. 4.4MPa (Range 3.2-5.8MPa)	Adhesive failure- binder to substrate
Polyurethane	X-Cut	ISO 16276-2:2007	Level 0 (no coating removal)	Pass
Polyurethane	Dolly pluck adhesion	In-house	Av. 2.7MPa (Range 1.8-3.1MPa)	Adhesive failure- binder to substrate

All of the dolly pluck adhesion test failures for both the polyethylene and polyurethane substrates were adhesive between the binder and the substrate. In order to determine the bond strength between CuNi granules and binder, the CuNiClad system was applied directly onto blasted steel and the dolly pluck adhesion tests repeated.

Substrate	Test	Standard	Result	Comment
Blasted carbon steel	Dolly pluck adhesion	In-house	Av. 11.8MPa (8 tests) (Range 10.0-14.0MPa)	Part adhesive, part cohesive failures

APPENDIX 1

Report of work undertaken for efficacy of the fouling resilience of Balmoral CuNiClad™ marine antifouling system (2013-2016)

By Dr Ian Hendy, University of Portsmouth, Institute of Marine Sciences - Published March 2017

1 Summary of work

1.1 Fouling resilience trials

The objective of the fouling resilience trial was to test the novel Balmoral CuNiClad coating for its anti-fouling properties in comparison to untreated control panels. Experimental design consisted of six panels in total with two replicates of various coating conditions (Figure 1):

1 Two panels both with one side coated with 100% surface area of the Balmoral CuNiClad
2 Two untreated panels
3 Two panels both with one side coated with 50% surface area of the Balmoral CuNiClad

The panels were suspended from marine grade steel frames mounted on the University of Portsmouth Inshore exposure testing platform in Langstone harbour (Figure 2). Panels were attached to the frames using copper wire. The frames remained fully immersed in the marine tidal waters for the 36 month project duration, and were inspected monthly using digital images to monitor efficacy of treatments. Images from every second month are displayed in this brochure (images from interim months are available). To date, the UoP have conducted 36 inspection visits to the inshore platform.

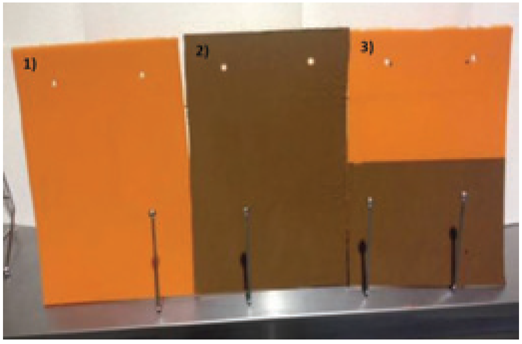


Figure 1 | Examples of the various treatments used to test the efficacy of the Balmoral CuNiClad coating:
1 One-sided 100% treated Balmoral CuNiClad coated panels
2 Untreated control panels
3 One-sided 50% treated Balmoral CuNiClad coated panels

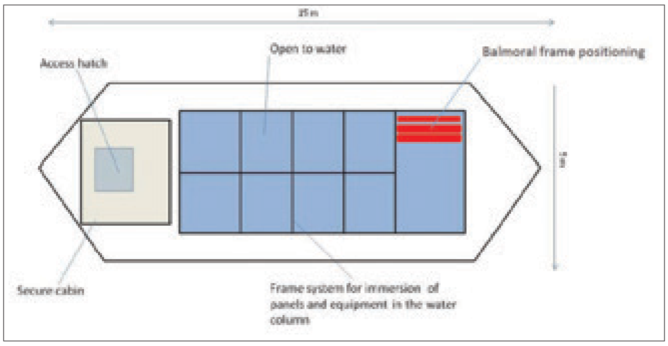


Figure 2 | The position of the Balmoral frames on the UoP inshore testing platform

1.2 Statistical analyses

To fully validate the efficacy of the novel Balmoral CuNiClad coating, a series of statistical tests were employed to explore the non-coated and coated panels – to determine the degree of significant differences after 24 months immersion in Langstone Harbour.

Parametric tests within the statistical package MiniTab 13, were used to test for significant differences of comparisons with the percent surface area of marine fouling organisms on coated and non-coated panels. The univariate and non-parametric multivariate techniques of the multi-dimensional scaling plot (MDS) contained in PRIMER 6.1 (PrimerE Ltd: Plymouth Routines in Multivariate Ecological Research) were used to compare differences of the percentage surface area of biofouling communities on non-coated panels with panels coated with the Balmoral CuNiClad. Similarities of percentage surface area of biofouling communities between the treatments were examined using PERMANOVA, based on square-root transformed data in Bray-Curtis similarity matrices, followed by post-hoc pair-wise tests to highlight similarities. Significance is accepted when $p = < 0.05$.

2 Biofouling analyses

In total six panels were used, giving twelve sides to test. The treatments used and number of replicates tested varied, see table below.

Treatments

non-coated	50% coated	100% coated
8	2	2

In total three treatments were tested:
No coating = without Balmoral CuNiClad
50% and 100% coating = surface area of Balmoral CuNiClad
The number of each treatment (replicate) tested varied

After twenty-four months (Dec 2015) exposure to the non-coated panel sides were almost completely covered with biofouling communities (algae, sessile filter feeders e.g. tunicates and encrusting sponges). However, both the 50% and 100% Balmoral CuNiClad coated panel sides had no sign of macro biofouling communities (Figure 3a), except only for the non-coated areas. Although, a thin black biofilm was found on the Balmoral CuNiClad surface. Although, a thin black biofilm was found on the Balmoral CuNiClad surface. Even after thirty-six months (December 2016) exposure in the marine environment, no biofouling communities were found growing on the fully coated CuNiClad panel sides (Figure 3b).

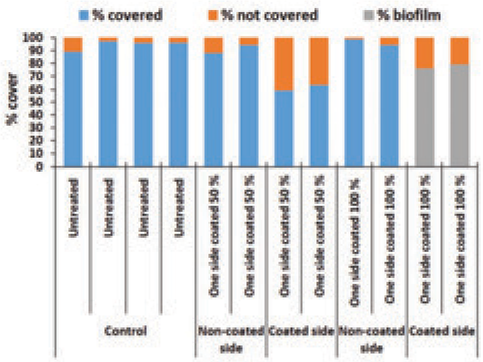


Figure 3a

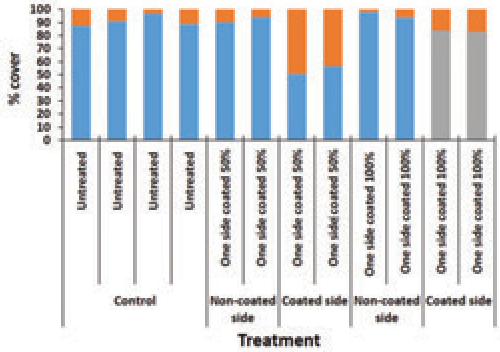


Figure 3b

Figure 3 | The percent surface area of biofouling
The percent surface area of biofouling communities on non-coated 'control' panel sides and panel sides coated with Balmoral CuNiClad.
3a - the efficacy of CuNiClad after 24 months exposure (2015) , and 3b - the efficacy of CuNiClad after 36 months exposure (2016) to marine fouling organisms.
Panel sides coated with the Balmoral CuNiClad showed very little or no sign of macro biofoulers after 36 months of marine exposure.

Differences of the percentage surface area between the three treatments were significant (PERMANOVA main test, % surface area vs. treatment: F2, 9 = 185.8, p = < 0.001). Multidimensional scaling (MDS) illustrated that each treatment (No coating, 50% coating and 100% coating) applied to the sides of the panels were very similar within treatments, but mutually exclusive between treatments (Figure 4). However, the non-coated and 50% coated panels had a greater similarity of the percent surface area of biofouling communities (60%) when compared with the 100% coated CuNiClad panels.

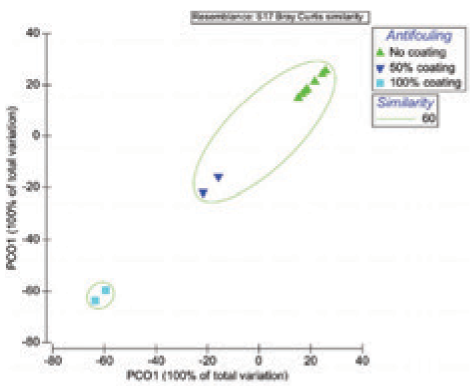


Figure 4 | MDS
Plot illustrating that the percentage surface area of biofouling communities recorded from each treatment were significantly different between treatments, but very similar within treatments. Panels coated with 100% CuNiClad shared the least similarity to the non-coated and 50% CuNiClad panels – as no biofouling communities were found on the 100% coated panels.

Similar results were also found with the mean biofouling communities between treatments, especially when disregarding the biofilms found on the Balmoral CuNiClad coating (Figure 5a and b) after 24 and 36 months. After 24 months, panel sides with 50% of the Balmoral CuNiClad coating reveal that >60% had been fouled by macro organisms. However, less surface area of biofouling communities were recorded after 36 months (Figure 5b). This was not the case, on each panel all areas exposed to the Balmoral CuNiClad were not fouled by macro organisms. The reason for the 50% Balmoral CuNiClad coated sides recorded at >60% fouled was due to over-hanging of macro fouling organisms from the non-coated side on to the coated side. The Balmoral CuNiClad coating had significantly fewer biofouling communities compared with non-coated surfaces after 24 and 36 months exposure in the marine environment (1-way ANOVA, $F_{2,9} = 415$, $p < 0.001$).

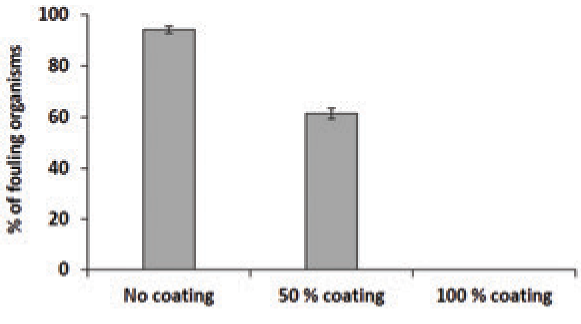


Figure 5a

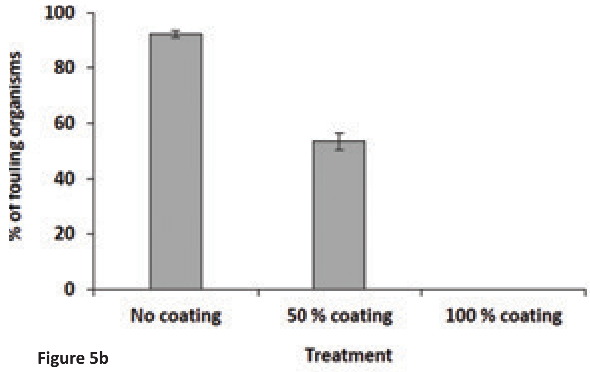


Figure 5b

Figure 5 | Percent surface area of macro foulers

5a - after 24 months, and 5b - after 36 months. Panel sides without the Balmoral CuNiClad coating had the greatest percent surface area of macro fouling organisms, with 50% and 100% coated panels sides having significantly reduced or zero macro-fouling communities (mean ± SE).

3 Conclusions

In this study, we used the Balmoral CuNiClad, as it is applied via a spray system. It is hypothesised that the spray-applied system has greater efficacy on complex shapes. This was reflected in the present study. The results from this on-going, and to date three-year trial were very conclusive, the balmoral cunicladtm has a significant and continued affect towards the inhibition and prevention of recruitment and settlement of marine macro bio-foulers.

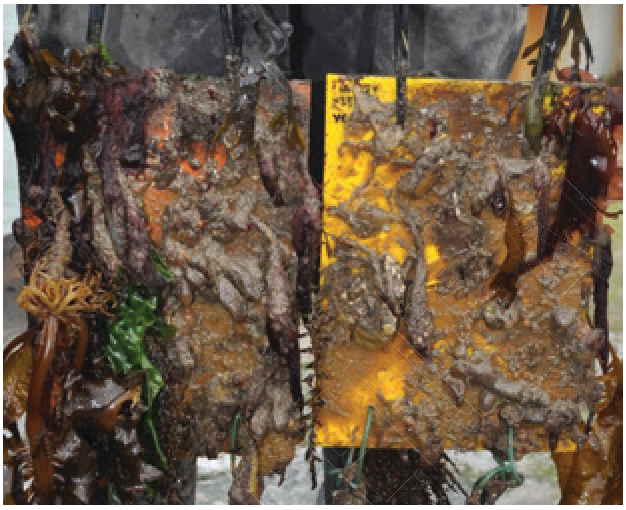
After three years exposure no biofouling organisms were found or recorded on the panel sides in areas exposed with either 50 % or 100 % of the Balmoral CuNiClad coating. However, it was noted that a thin brown/black ‘biofilm’ had developed on the Balmoral CuNiClad surface. This may not had been a biofilm, as the Balmoral CuNiClad coating is known to change from brown-to-green, and also black when immersed (depending on local conditions). In comparison, the non-coated panel sides in all cases were almost completely covered in fouling organisms.

The Balmoral CuNiClad coating when exposed to marine biofouling communities in the marine environment has a significant affect at preventing settlement and colonisation of marine biofouling organisms.

Dr Ian Hendy
University of Portsmouth, Institute of Marine Sciences

University of Portsmouth

March 2016 panels



1a

1b - Untreated panels

2a

2b - 50% coated with Balmoral CuNiClad

3a

3b - 100% coated with Balmoral CuNiClad

May 2016 panels

1a

1b - Untreated panels

2a

2b - 50% coated with Balmoral CuNiClad

3a

3b - 100% coated with Balmoral CuNiClad

July 2016 panels


1a


1b - Untreated panels


2a


2b - 50% coated with Balmoral CuNiClad


3a


3b - 100% coated with Balmoral CuNiClad

September 2016 panels

1a

1b - Untreated panels

2a

2b - 50% coated with Balmoral CuNiClad

3a

3b - 100% coated with Balmoral CuNiClad

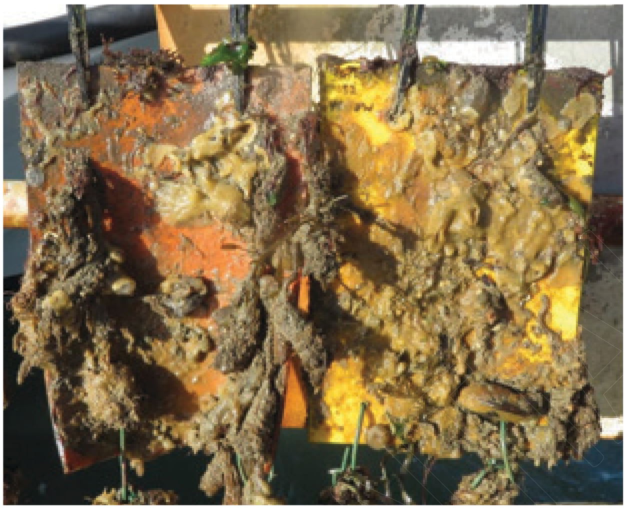
November 2016 panels

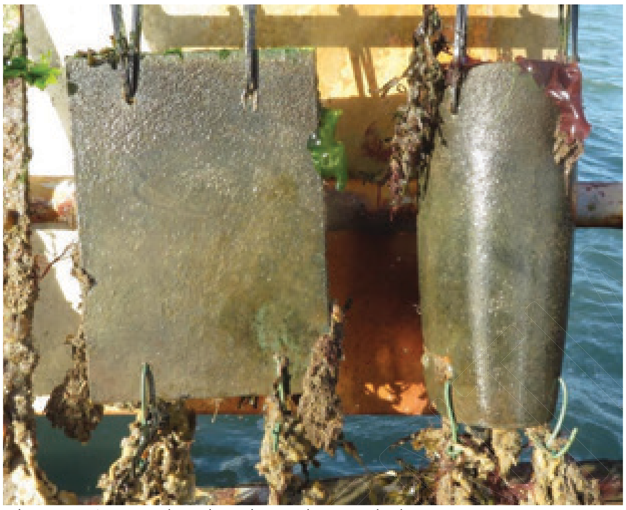

1a


1b - Untreated panels


2a


2b - 50% coated with Balmoral CuNiClad


3a


3b - 100% coated with Balmoral CuNiClad

December 2016 panels

1a

1b - Untreated panels

2a

2b - 50% coated with Balmoral CuNiClad

3a

3b - 100% coated with Balmoral CuNiClad

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