The use of controlled copper dissolution as an anti-fouling system

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The use of copper as an anti-fouling surface is discussed and an electrochemical method for improving its performance is proposed. Seawater exposure trials of freely corroding, cathodically protected and electrochemically controlled copper specimens are described. The results show that the anti-fouling performance of copper surfaces may be improved by electrochemical control of its dissolution rates. The ultimate failure of the copper to anti-foul is due to insufficient dissolution rates. This may be due to electrochemical constraints, to the formation of insoluble corrosion products or to the precipitation of cathodic chalks at its surface.

1. Introduction

Copper was the first anti-fouling surface to receive general recognition. Its first authenticated use was as a sheathing material on H.M.S. Alarm (1758) to protect the wooden hull from "worm" [1]. Trials indicated that not only was the copper successful for this application but it has the added advantage of reducing marine fouling. The cleaner hulls are credited for allowing Admiral Rodney (1780) to out-manoeuvre and defeat the Spanish whose ships were slowed by the accumulation of marine growths [2].

The introduction of iron hulled ships invalidated the use of copper sheathing due to galvanic action between the two metals, and the need for anti-fouling surfaces has since been met by paint systems. These have been made from a variety of compositions of which only a few are effective and of these many such as arsenic, cadmium and mercury have been restricted due to environmental considerations [3–6]. The only two substances that are presently recognised as providing safe and effective anti-fouling are copper and tributyl tin.

Although these paint systems provide good results there are serious limitations. These are:

(a) The paint only works providing biocide dissolution rates are sufficient to maintain poisonous concentrations at the paint surface—organism interface.

(b) The working life of a paint is limited by its biocide loss rate and the amount of biocide carried in the paint film.

(c) The biocide dissolution rates are greatest at high water velocities but this is when settlement by marine organisms is least likely to occur.

(d) Anti-fouling paint surfaces may become neutralized and therefore ineffective, by organic compounds and debris in the water.

Numerous studies have been made to produce improved anti-fouling systems [7, 8]. This paper reports on the study of a system which is based on the controlled release of copper by a modified impressed current cathodic protection system. The nature of the chemical changes which occur at the copper surface have been monitored in order to ascertian why such a surface slowly looses its anti-fouling property.

2. Toxicology of copper to marine organisms

The toxicology of copper to marine organisms has been the subject of numerous reviews [4, 9]. Although copper is not considered to be a hazard to man, it is the most toxic metal to marine organisms, with the exception of silver and mercury.

The effectiveness of copper as a poison relies on it being taken up into the organism. In seawater,

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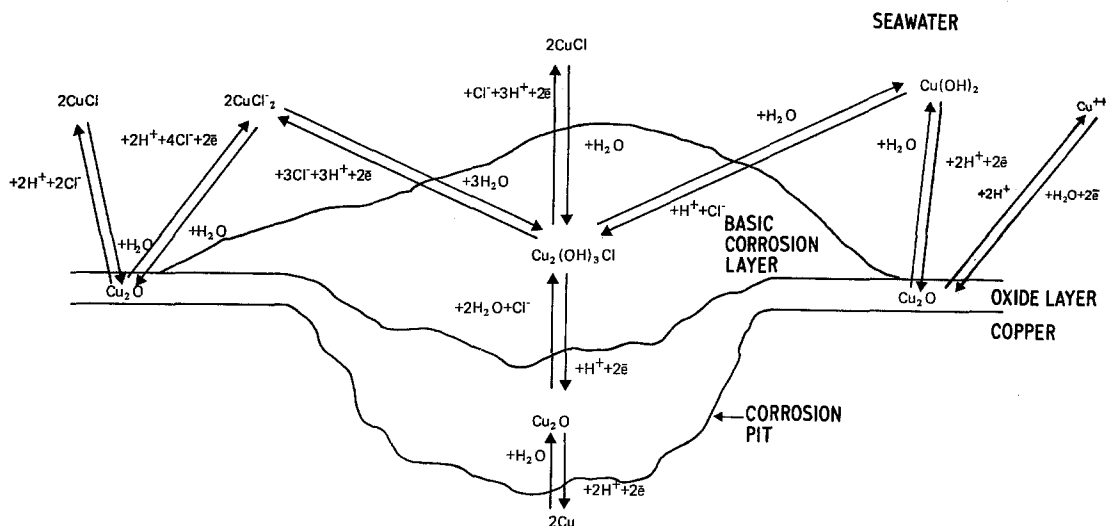
Figure 1 Chemical model for freely corroding copper in seawater.

adsorption will occur through the general body surface and through specific areas as gills and gut wall, the actual up-take being controlled by the diffusion gradient and the speciation of the copper. The cupric ion (Cu^{2+}) is recognised as the most lethal form and it is known to overload enzyme systems and to interfere with the basic molecular structure of the organism.

The toxicity of copper is affected by many factors [4]. These include the condition and age of the organism, behavioural responses of the organism, ambient physical and chemical seawater conditions, and the presence of other biocides. The naturally occuring copper levels lie between $0.3 \mu g l^{-1}$ for the open oceans [10] and $3.0 \mu g l^{-1}$ in coastal waters although values of up to $24 \mu g l^{-1}$ have been found associated with industrial effluents [11]. Copper levels of a few milligrams per litre are sufficient to cause mortality amongst most marine organisms [12, 13].

3. The interaction of copper with seawater.

We have noted that the toxity of copper depends on its being available in the cupric form and at concentrations of a few milligrams per litre. At the copper surface this may be translated into a uniform corrosion rate greater than $10 \mu g cm^{-2} day^{-1}$ [14], but freely corroding copper may react in several different ways.

Fig. 1 illustrates the various reactions that might occur in seawater. It shows that copper dissolution is not always a uniform process and that localized anodic and cathodic areas may be set up. In the cathodic areas copper dissolution rates may be depressed below the level necessary to prevent fouling whilst at anodic areas pitting and wasting of the metal may occur. Anodic areas also encourage the formation of insoluble corrosion products and these may allow settlement by marine organisms.

A more detailed picture of the chemical reactions involved with the seawater corrosion of copper can be obtained from the electrode potential–pH diagram devised by Bianchi and Longhi [15]. These diagrams indicate the reactions most likely to occur at known pH and potential values, and although they are subject to modification by inorganic constituents and other ambient parameters, they are valuable in predicting the direction which a reaction may take. Fig. 2 illustrates the possible corrosion reactions of copper at $25°C$. The most favourable reaction for marine anti-fouling is:

$$2Cu + H_2O \rightleftarrows Cu_2O + 2H^+ + 2e^-; \quad (1)$$

$$Cu_2O + 2H^+ \rightleftarrows Cu^{2+} + H_2O + 2e^-. \quad (2)$$
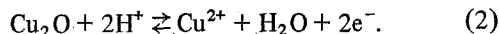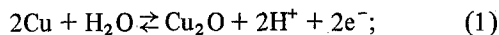
Another important factor, however, is the fate of the copper speciation once it enters solution. The work of Zirino and Yamamoto [16] has indicated that the thermodynamic stability of given species depends upon the local pH; Fig. 3 illustrates this variation. It is particularly significant that the cupric ion concentration varies rapidly in the pH range 7 to 8.6 and would therefore be strongly dependent on local pH changes
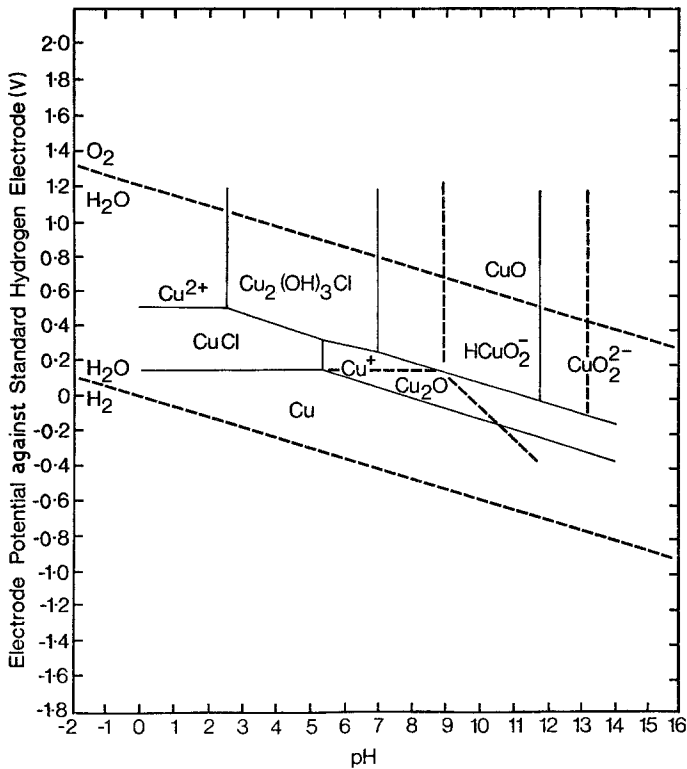
Figure 2 Equilibrium diagram for copper in seawater at 25° C. Solid phase taken into consideration. Cu, Cu_2O, CuCl, CuO, $Cu_2(OH)_3Cl$ (after [15]).

brought about through surface conditioning by marine organisms.

It would appear, therefore, that although freely corroding copper provides an effective anti-fouling surface it may fail due to the gradual formation of insoluble products reducing the cupric ion concen-

tration at the surface. Another practical disadvantage, is the inability to control the corrosion rate as the water velocity is changed. This is particularly significant in the case of ships' hulls, where it has been reported that many fouling organisms are unable to settle above certain water velocities, e.g.
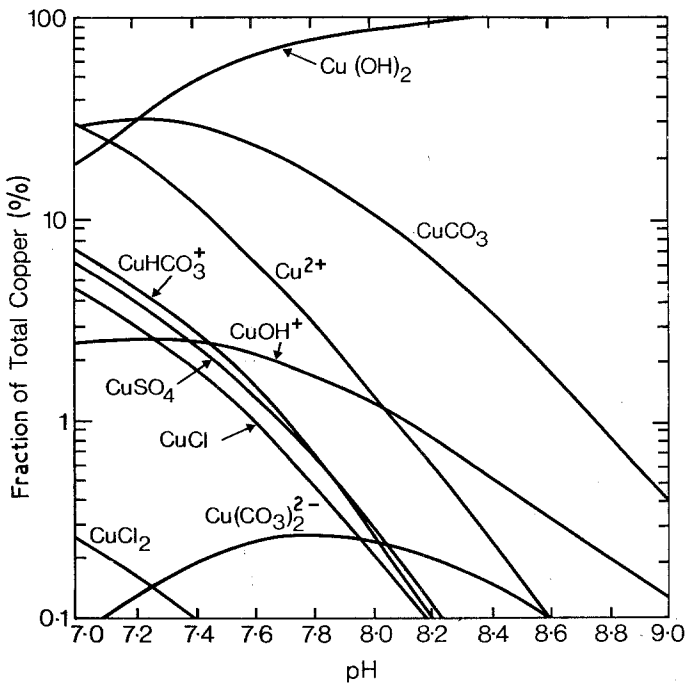

Figure 3 The effect of pH on the speciation Cu^{2+} in seawater at 25° C (after [16]).

Cu

$+H_2O \longleftarrow Cu_2O + 2H^+ + 2e^-$

$2e^- + H_2O + \frac{1}{2}O_2 \longrightarrow 2OH^-$

$2OH^- + Ca \longrightarrow Ca(OH)_2$

$Ca(OH)_2 + 2CO_2 \longrightarrow Ca(HCO_3)_2$

$Ca(OH_2) + Ca(HCO_3)_2 \longrightarrow Ca\,CO_3\ H_2O \downarrow$

Calcium carbonate hydrate

$Ca\,CO_3 \downarrow + H_2O$

Aragonite

Cathodic protection reactions

"Spike" Reactions

Cu

$\div H_2O$

$\longrightarrow Cu_2O + 2H^+ + 2e^-$

$+2H^+$

$Cu_2O \longrightarrow H_2O + 2Cu^{++}$ cupric ion (toxic)

$+2H_2O$

$Cu_2O \longrightarrow Cu_2(OH)_3Cl + H^+ + e^-$ copper hydroxychloride
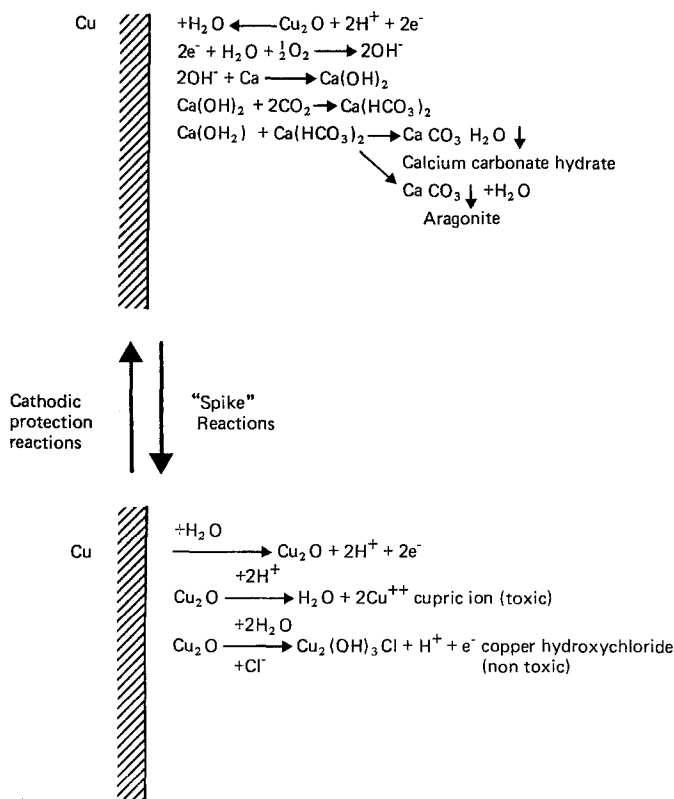
$+Cl^-$ (non toxic)

Figure 4 Surace reactions for the electro-chemically controlled copper specimens ($\downarrow$ indicates precipitation of insoluble products).

$2\ m\,sec^{-1}$ for barnacles [17] and $5\ m\,sec^{-1}$ for *Enteromorpha* [18].

4. The electrochemical control of copper dissolution in seawater

In a patent of Osborn and Prows [19], it was suggested that the dissolution of copper could be controlled by the use of impressed current. This method cathodically protects the copper, hence preventing copper dissolution and then produces the toxic copper ions by reversing the polarity and increasing the current density at periodic intervals.

In theory this method should improve the life performance of a copper surface in four ways, firstly the controlled dissolution will ensure that adequate concentrations of cupric ions are made available, secondly, the formation of insoluble corrosion products may be avoided, thirdly, because the treatment is intermittent, there will be a reduction in the total quantity of copper required for effective anti-fouling and finally copper dissolution may be prevented when there is no likelihood of fouling, i.e. at high water velocities.

The possible changes that may occur at the surface of the copper are illustrated in Fig. 4. The important factor to notice is that, in both the cathodic and anodic modes, the surface may become non-toxic. In the cathodic regime there will be no copper released and a slow build up of hydrated calcium carbonate, whereas in the anodic regime, the cuprous oxide layer will eventually be converted into non-toxic copper hydroxychloride.

The purpose of this present work has therefore been to develop this method, and to seek to optimize the electrical parameters by studying the nature of the surface changes produced and their subsequent effect on the anti-fouling properties.

5. Experimental details
5.1. Exposure tank trials

A preliminary set of experiments were conducted at the Exposure Trials Station (M.O.D.) Eastney. The copper specimens were exposed to running seawater in a fibre glass tank 3.04 m long, 61 cm wide and 30.5 cm deep.

Although the fouling conditions varied during the experiment, the following species became well established; diatomaceous slimes *Entermorpha sp.* and *Ectocarpus sp.* The fouling type and pressure was quantified by the empirical classification devised by Littauer and Jennings [20], and summarized in Table I. This classification is based

TABLE I Empirical classification of marine fouling (after Littauer and Jennings), a stage classification of biotic progression involved in marine fouling

Stage[*]	Predominant organisms
Primary (1, 2 and 3)	Microscopic unicellular slimes such as bacteria, diatoms and protists, etc.
Secondary (4, 5 and 6)	Microscopic organisms such as multicellular sessile organisms; i.e., bryozoans, barnacles, sedentary tube building polychaetes, brown and green algae.
Tertiary (7, 8 and 9)	Evidence of secondary attachment of sessile species and some subsequent over-growth of the previous stage's forms although they may still remain dominant; i.e. tunicates, mussels, sponges, larger algal growths etc.
Quaternary (10 = climax)	The most biologically complex: Depending upon the ecology of the region the community is generally dominated by one or two organisms; i.e. tunicates, mussels, sponges, bryozoans.

[*]The number from 1 to 10 assigned to a fouling condition is intended to indicate the relative stage of a surface in the fouling progression and, to a lesser degree, its intensity.

on a 0 to 10 scale, where 0 represents no fouling and 10 indicates that a seasonal climax exists.

The metal coupons (100 mm by 100 mm by 1 mm), together with platinized titanium counter electrodes and silver—silver chloride reference electrodes were coupled so that the current was supplied from either a potentiostat or a galvanostat (see Fig. 5). When the potentiostat was in use, the copper was cathodically protected with respect to the reference electrode, but in the galvanostat mode the polarity was reversed and the coupon forced to corrode at a predetermined rate. During this so called "spiked" condition, toxic copper ions were released into the seawater. Details of the precise voltages and currents are indicated in Table IIA, together with the details of the full cathodically protected and freely corroding control samples.

Following these preliminary trials, a second set of copper coupons were exposed in the tank at varying copper release rates in order to reduce this rate below the accepted threshold of 10 μg cm^{-2} day^{-1}; details are given in Table IIB.

During both sets of experiments, the surface potentials and the current requirements for cathodic protection and spiking were monitored for analysis.

5.2. Fawley sea trials
This set of trials was conducted in the cooling water intake channel of the Fawley Power Station,
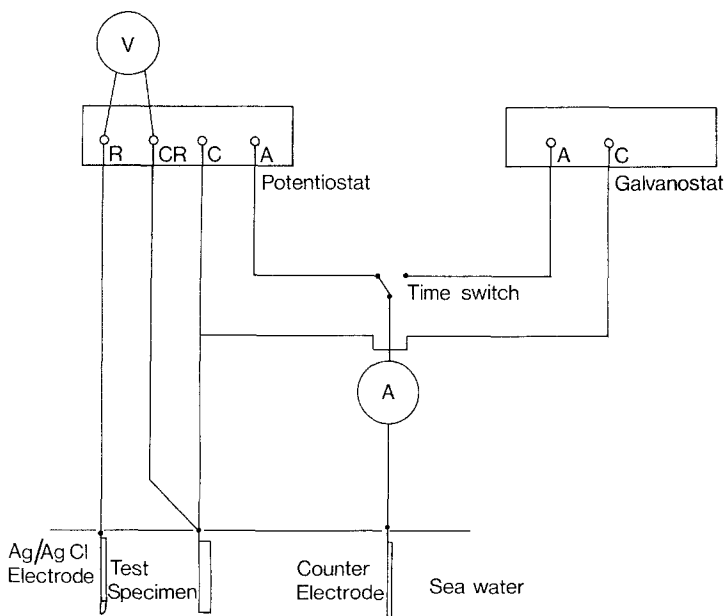

Figure 5 Electrochemical control arrangement.

TABLE II A description of specimens and electrical parameters (Tank tests)

Specimen number	Description	Protection voltage [Ref Ag/Ag Cl] (V)	Spike current density (μA cm^{-2})	Theoretical Cu^{2+} output (μg cm^{-2} day^{-1})
1	Freely corroding			
2	Cathodically	−0.4		0
3	protected	−0.45		0
4	Spiked for	−0.4	10	9.4
5	2 min h^{-1}	−0.4	20	18.8
6		−0.4	25	23.5
7		−0.4	30	28.2
8		−0.4	40	37.6

TABLE IIB Description of specimens and electrical parameters (Tank tests)

Specimen number	Description	Protection voltage [Ref Ag/Ag Cl] (V) (μA cm^{-2})	Spike current density (μA cm^{-2})	Spike frequency	Theoretical Cu^{2+} output (μg cm^{-2} day^{-1})
9	Freely corroding				
10	Cathodically protected	−0.35			0
11	Spiked	−0.35	15	1 min h^{-1}	7.1
12		−0.35	15	2 min h^{-1}	14.1
13		−0.35	15	2 min 2h^{-1}	7.1
14		−0.35	15	2 min 3h^{-1}	4.7
15		−0.35	15	2 min 6h^{-1}	2.4

using the dock facility as a mooring site for an exposure raft. This dock is adjacent to Southampton Water and has a unidirectional water flow with velocities between 0 and 1 m sec^{-1}. There was a high fouling pressure on the dock walls, which was dominated by the barnacles, *Elminius modestus* and *Balanus sp.*

The copper and polyvinyl chloride control coupons (200 mm by 300 mm by 1 mm), together with suitable reference and counter electrodes similar to those used at the Eastney site were suspended on PVC "T" pieces hung beneath the moored raft.

The electrical parameters used in these tests are given in Table III. Owing to a shortage of suitable control equipment a PVC control coupon (Specimen 17) was substituted for the cathodically protected copper samples used at Eastney.

As with the previous experiments, the progression of fouling, surface potentials, and the current requirements for the cathodic and spiked anodic modes were monitored throughout the test.

5.3. Observation of surface changes
5.3.1. Visual examination
During the exposure sequence, detailed observations were made in order to determine the nature and degree of both fouling and corrosion occurring. In the case of the Fawley samples these were arranged so as to allow removal of suitable samples for microscopical analysis.

At the termination of the exposure sequence, the samples were weighed to assess the amount of fouling biomass, and then after treatment with 10% formic acid, the thickness and weight of cathodic protection and/or corrosion products, produced.

5.3.2. Microscopical examination
After the removal of the fouling biomass, the nature of the surface layers was investigated. Small powder samples were taken from the layers and studied using X-ray Debye–Scherrer techniques to determine the compound formation.

The surface was also studied by electron probe microanalysis in order to determine the elements present and in particular the concentration level of the copper in the layer in contact with the seawater.

By combining the results of these two approaches together with the electrochemical information gained during exposure sequence, it was hoped to establish the precise changes that occur when freshly polished copper is placed in seawater.

Specimen number	Description	Protection voltage [Ref. Ag/AgCl] (V)	Spike Current Density (μA cm^{-2})	Spike frequency	Theoretical Cu^{2+} output (μg cm^{-2} day^{-1})
16	Freely corroding				
17	Polyvinyl chloride Control sample				
18	Spiked	-0.35	10	(0 to 83 days) 2 min per 4 hours (after 84 days) 4 min per hour	2.36 18.88

6. Experimental results
6.1. Preliminary exposure tank trials
6.1.1. Fouling
The fouling progressions are summarized in Figs 6 and 7. It is clear from these that the cathodically protected samples (Specimens 2, 3 and 10) fouled early in their life, due to the fact that no copper was being released from the surface.

In the case of the freely corroding samples, the onset of fouling occurred somewhat earlier, around 60 days exposure, compared to some of the electrochemically controlled samples in which approximately 100 days were required. This is quite surprising as the total copper release rate for the freely corroding samples was substantially greater than for any of the spiked samples. Interesting differences were also noted between the spiked samples, those which were subjected to the higher "spike" current densities (Specimens 7 and 8), fouled more rapidly compared to those with lower "spike" densities (Specimens 4 and 5). Rather smaller differences were noted between the samples subjected to different "spike" frequencies. This can be partially explained by the fact that the silver—silver chloride electrodes kept failing during the test which allowed the uncontrolled corrosion of samples until the electrode was replaced. The reference electrode failures were due to their construction being insufficiently rugged to cope with the test tank conditions.
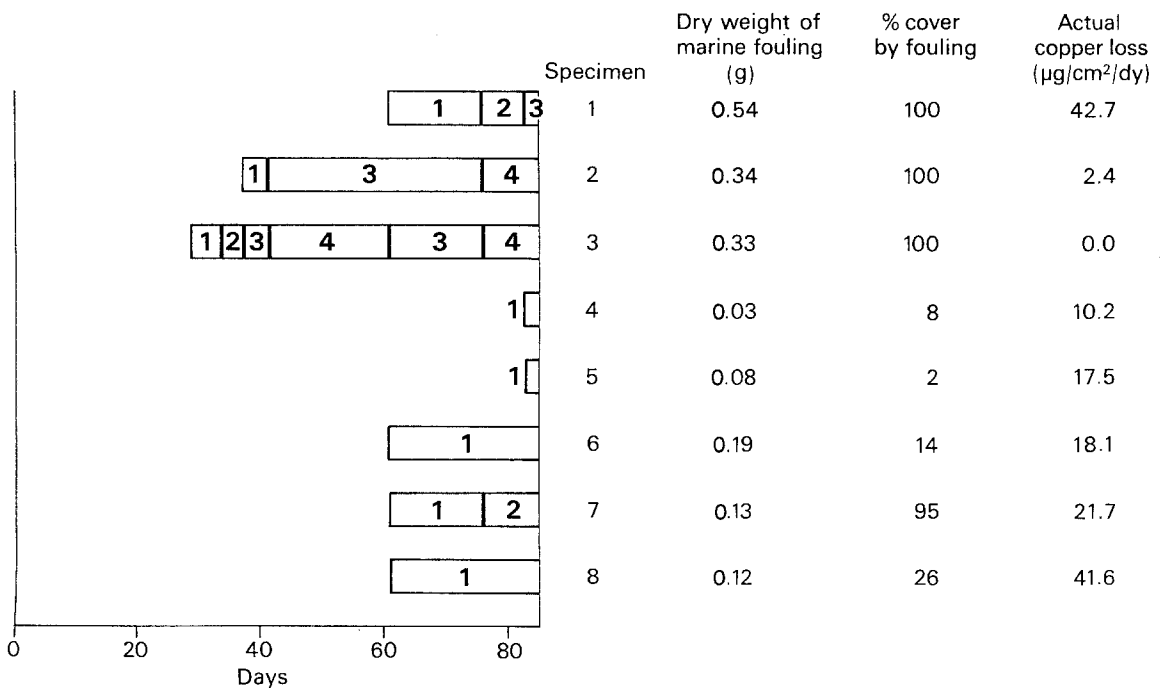

Specimen	Dry weight of marine fouling (g)	% cover by fouling	Actual copper loss (μg/cm²/dy)
1	0.54	100	42.7
2	0.34	100	2.4
3	0.33	100	0.0
4	0.03	8	10.2
5	0.08	2	17.5
6	0.19	14	18.1
7	0.13	95	21.7
8	0.12	26	41.6

Figure 6 The progression of marine fouling on freely corroding (1), cathodically protected (2, 3) and spiked copper plates (4—8) during the exposure period. The dry weight gain and percentage cover by marine organisms at the termination of the experiment are noted. See Table I for fouling types.
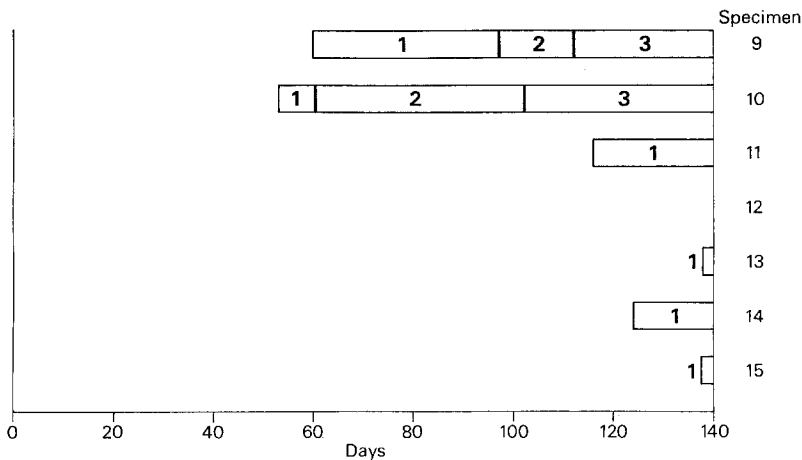
Subsequent electrodes were designed to greater strength and tolerance.

In all those cases, in which settlement occurred, the fouling progression was diatomaceous slimes, short monofilamentous algae and finally bryozoans and associated infauna of *Gammarus*, nematodes, etc. No large fouling organisms, e.g. barnacles, sea squirts, kelps, etc., became established in the test tank and because of this, the second set of tests were transferred to a seawater site where a more representative potential fouling community was present.

6.1.2. Electrochemical measurements

The surface potential of the freely corroding copper specimens started at $-0.23/0.25$ V, but showed at tendency to increase during the exposure sequence to values of $-0.15/0.18$ V at the termination of the test. In the case of the cathodically protected samples, the potentials were maintained constant by the potentiostat settings (see Tables II and III).

The surface potentials of the spiked specimens became more positive during the anodic phase indicating their tendency to corrode (see Fig. 8).

Although the rate of corrosion is theoretically porportional to the current passing through the specimen, in practice the release rate will be complicated by the nature of the seawater, any cathodic chalk layers, the pH of the surface at its localized potential. It is apparent from a study of Figs 8 and 9, that the changes in surface potential depended upon the current density employed in the anodic mode. At low current densities (Specimens 4, 5, 11 and 13) there was only a slight increase in the potential value, whereas at higher current densities (Specimens 6, 7 and 8) the potential definitely increased with exposure time. This increase may be due to the formation of insoluble corrosion products such as
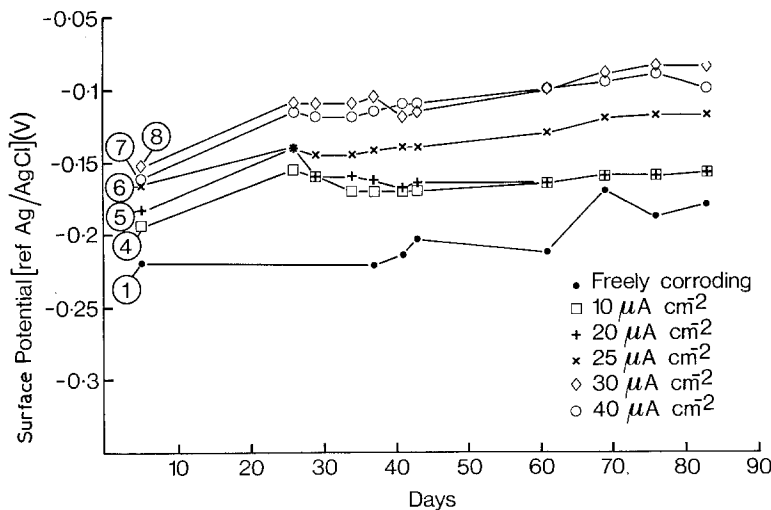

Freely corroding
$\square$ 10 μA cm^{-2}
$+$ 20 μA cm^{-2}
$\times$ 25 μA cm^{-2}
$\diamond$ 30 μA cm^{-2}
$\circ$ 40 μA cm^{-2}

Figure 8 Variation in maximum surface potential due to spike current during exposure period in test tank (specimen numbers defined in Table IIA and B).
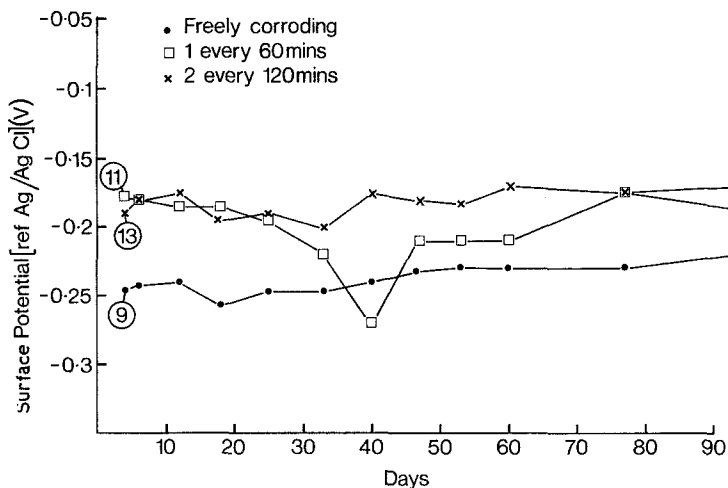
Figure 9 Variation in maximum surface potential due to spike current exposure period in test tank (specimen numbers defined in Table IIA and B).

Cu(OH)$_3$Cl, similar to those observed on the freely corroding samples.

A similar trend (Figs 10 and 11) was also noticed with the variations in the maximum cathodic protection current (this being measured immediately after the return from the anodic mode). In the case of the lower current densities, this value remained essentially constant in the range 90 to 110 μA cm^{-2}; but as the current density was increased the increased the initial current demand was higher at 200 μA cm^{-2} (Specimen 8) and continued to increase with exposure time, values of about 320 μA cm^{-2} being observed for Specimen 8 after 80 days.

It should be noted that these high current demands only persisted during the period required

to re-establish cathodic protection (about 1 minute), after which the current demands stabilized between 2 to 10 μA cm^{-2}, depending on the exact water conditions.

These changes in surface potentials and current demands must reflect the energy required to repolarize the copper surface from the anodic to cathodic states. The values will therefore indicate the nature of the surface states and correlate with changes such as the development of insoluble corrosion products, cathodic and fouling progression.

Because of the complex chemistry of natural seawater, the changes that will occur may take place through a variety of mechanisms, and this is further complicated by the reduction of the
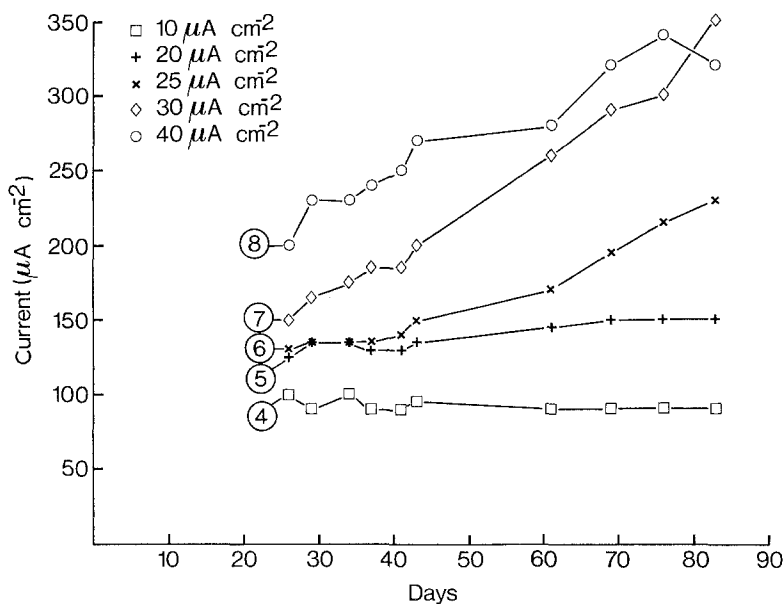

Figure 10 Variation in maximum cathodic current during exposure in test tank (specimen numbers defined in Tables IIA and B).
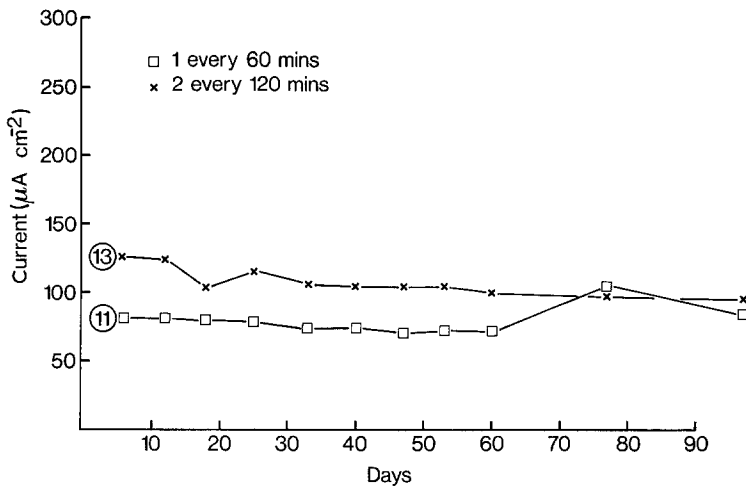
Figure 11 Variation in maximum cathodic protection current during exposure period in test tank (specimen numbers defined in Tables IIA and B).

active surface as the specimen becomes conditioned through exposure.

6.1.3. Surface corrosion products

After the removal of any fouling debris, the surface corrosion products on the different samples were studied using both X-ray powder diffraction and electron-probe microanalysis.

6.1.3.1. Freely corroding specimens. After short immersion periods, the samples became covered with a coherent brown film, which consisted entirely of cuprous oxide. This is consistent with the initial reaction in seawater which is thought to be

$$2Cu + H_2O \rightleftarrows Cu_2O + 2H^+ + 2e^-. \quad (3)$$
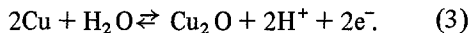
As the time of immersion increased the brown colour slowly changed to the natural blue-green patina developed by copper. Close examination of the surface by optical microscopy revealed that the corrosion layer was not uniform and that pitting had occured.

At the termination of the test, the surface was completely covered by the blue-green patina. Using carefully extracted powder samples, X-ray diffraction analysis indicated that there were distinctive layers in the corrosion product. These consisted of the base copper, cuprous oxide and copper hydroxychloride. Careful extraction of samples indicated that the corrosion pits were filled with cuprous oxide.

Electron-probe microanalysis of these surfaces is characterized by Sample 1 in Table IV. These results confirmed the high concentration of copper, oxygen and chlorine at the surface, coupled with a very thin layer of calcium carbonate.

A chemical model for freely corroding copper was presented earlier in this paper and illustrated in Fig. 1; the present results appear to confirm this model. This indicates that freely corroding copper loses its anti-fouling action when insoluble

TABLE IV Microprobe analysis of the copper surface at the termination of the experiment (biological fouling removed) and thickness of chalk layer after acid stripping[*].

Specimen	Element								Chalk thickness (μm)
	Cu	Ca	Mg	Si	C	O	Cl	S	
1	5	3	0	1	0	4	4	0	16
2	1	5	1	1	4	4	1	1	136
3	0	5	1	2	4	4	1	1	164
4	3	4	1	1	4	4	0	1	50
5	4	3	1	1	4	4	1	1	46
6	4	3	1	0	3	4	1	1	39
7	3	4	1	0	4	4	1	1	40
8	4	4	1	0	4	4	1	1	29

[*]Key: 0 – Absent 1 – Low Trace 2 – Traces, concentrated in patches 3 – Low continuous distribution 4 – Continuous distribution and cover 5 – Very dense continuous cover.
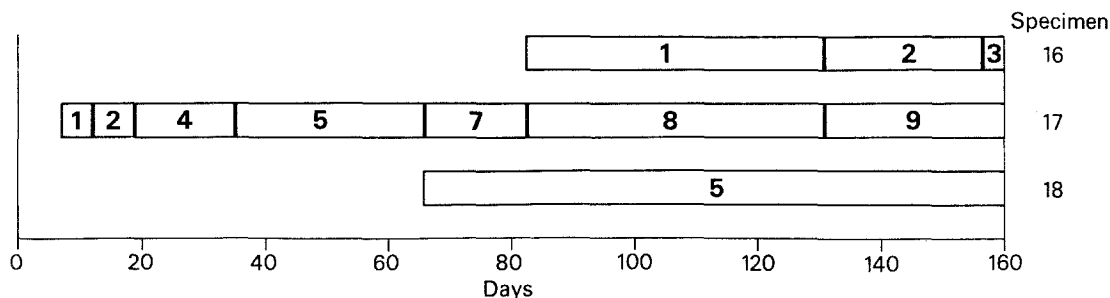
Figure 12 The progression of marine fouling at the Fawley site on freely corroding (16), P.V.C. control (17) and spiked copper plates (18) during the exposure period. See Table I for fouling types.

copper hydroxychloride compounds form on the surface. This severely limits the out-diffusion of cupric ions from the cuprous oxide layer underneath.

6.1.3.2. Cathodically protected specimens. Visual observations indicated the development of a glazed layer after a very short immersion time (about 3 to 4 days), this layer grew during continued immersion into a thick opaque electrolytic chalk which was quite adherent by the termination of the test.

X-ray diffraction revealed that the surface was covered with the dense tabular aragonite form of calcium carbonate. Microprobe analysis confirmed the presence of thick calcium-rich layers on the surface (Table IV, Specimens 2 and 3). The absence of copper at the surface was consistent with the control provided by the electrochemical method.

6.1.3.3. Spiked specimens. The surfaces of these samples appeared to be covered with a mixture of corrosion and other products. X-ray diffraction revealed that both the aragonite and hydrated forms of calcium carbonate were present. The aragonite form occurred at the edges of the sample and allowed Stage 1 and 2 fouling to develop. The chalk thicknesses obtained were intermediate to those found with the freely corroding and fully protected specimens (Table IV). The presence of cuprous oxide on the surface indicated that the specimens were behaving in a similar manner to the freely corroding samples, when they were in their anodic mode. Little or no evidence of chlorine-rich compounds were found, indicating that the secondary conversion of cuprous oxide to copper hydroxychloride was not occurring with these samples.

Microprobe analysis confirmed the X-ray

diffraction results (Table IV, Specimens 4 to 8). In all cases, there was clear evidence of both copper and calcium-rich compounds and little evidence for chlorine containing compounds. It was of interest to note that in those specimens which had been subjected to the higher spike current densities (Specimens 7 and 8) free copper nodules were detected within the chalk layer.

The reasons for these copper nodules is not clear, but it is suggested that copper ions became trapped in the chalk layer, and on current reversal they are deposited as copper nodules, and accumulate in the chalk layer giving specimens a distinctive mottled appearance.

In summary it is thought that the spiked specimens follow a corrosion mode determined by the spike current density. This may be adjusted to allow the long term production of cuprous oxide without the secondary conversion to the insoluble hydroxychloride.

6.2. Fawley sea trials
6.2.1. Fouling
The progression of the fouling is indicated in Fig. 12, and the condition of the samples at the termination of the test is illustrated in Fig. 13. As with the experiments at Eastney, the control sample (in this case PVC) fouled very early in the exposure sequence and rapidly developed tertiary fouling. The fouling pressure at Fawley was obviously far higher than anything noted with the previous sets of experiments.

The nature of the fouling with the freely corroding sample appeared to follow the pattern observed at Eastney, with slimes only developing at the end of 157 days exposure. In the case of the spiked samples, the rapid increase of fouling after 66 days was disappointing. It was suspected that the initial theoretical copper release rate of 2.4 μg cm^{-2} day^{-1} was in fact insufficient (after 84 days

Figure 13 Surface condition of (a) P.V.C. control sample, (b) freely corroding copper plate and (c) spiked copper plate after 110 days exposure at the Fawley site.

of exposure). It was therefore decided to increase the spiked current density to give copper outputs of $18.9 \, \mu g \, cm^{-2} \, day^{-1}$. The results in Fig. 12 seem to suggest that this increase in copper release did influence the fouling progression, and a close examination of the surface indicated that the barnacles were in a severely stressed condition and that some of the lower orders of fouling were beginning to die back.

As the siting of the exposure raft meant that one side of the plate specimens was shaded from direct sunlight it was of interest to note that the barnacle concentration was higher on the shaded side, whilst there was a higher plant concentration on the sunlight side. The establishment of this plant material will give rise to diurnal changes in oxygen concentration due to photosynthesis at the copper surface. If the plant community is discontinuous, this will cause variations in the oxygen potential at the surface and could there-
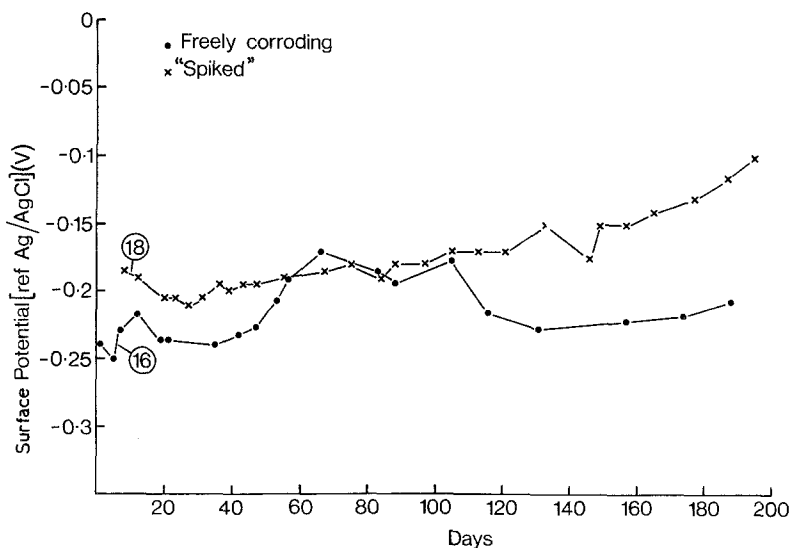
fore interfere with the conditioning of the surface with regard to differential corrosion cells.

6.2.2. Electrochemical measurements

The surface potential of the freely corroding copper specimen appeared to follow similar trends to those obtained at the Eastney site, starting at about − 0.24 V and rising to − 0.18 V as illustrated in Fig. 14 (Specimen 16). In the case of the spiked sample, the earlier trends at Eastney were repeated, with the potential values during spiking rising to − 0.15 V after 140 days and to −0.1 V after 200 days exposure (Fig. 14, Specimen 18). These values are consistent with the behaviour of the

freely corroding sample, but are significantly less than those developed by the high spike current density samples (Fig. 8, Specimens 7 and 8).

The values obtained for the maximum cathodic protection current are illustrated in Fig. 15, and are consistent with the lower spike current density samples of the previous tests (Specimens 4, 11 and 13) which also displayed the relatively uniform pattern once the corrosion regime had been established (within 25 days). The minimum cathodic protection current was again established within 1 minute after reversal from the anodic mode and values of 8 to 12 $\mu A\,cm^{-2}$ were measured throughout the 200 day exposure period.
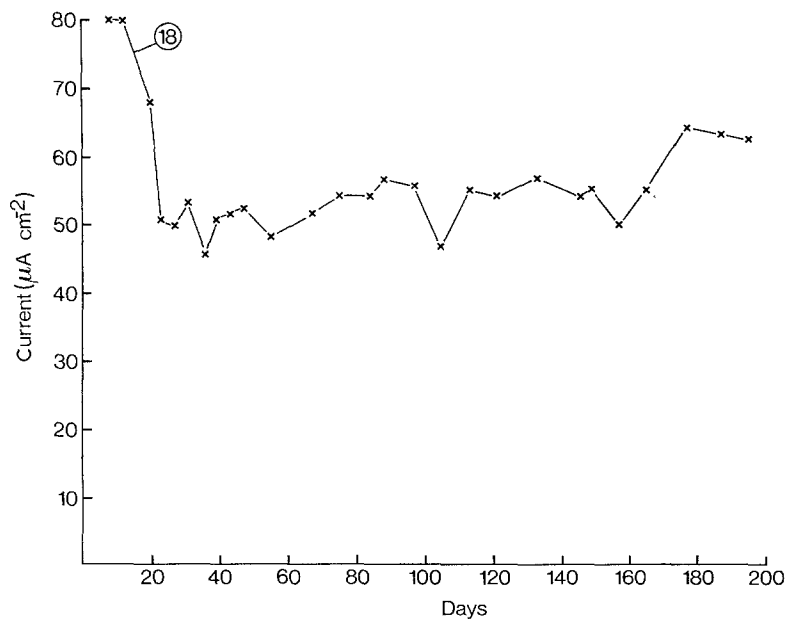

Figure 15 Variation in maximum cathodic protection current during exposure period at the Fawley site (specimen number defined in Table III).

It was noted that there did not appear to be any significant changes in any of the above electrochemical values when the copper release rate was altered after 83 days.

6.2.3. Surface corrosion products

By removing suitable tokens at intervals during the exposure sequence, the progression of surface changes was closely monitored. These studies revealed a slow but definite build up on the spiked samples of a calcium-rich layer which was identified by X-ray diffraction as the aragonite form of calcium carbonate. No evidence was found for the hydrated form which was noted in some of the Eastney samples.

Analysis of the freely corroding samples again indicated a progressive build-up of insoluble copper hydroxychloride with increasing exposure time.

The actual copper loss from the freely corroding sample was found to be approximately $48 \mu g \, cm^{-2} \, day^{-1}$ * compared with an average of about $10 \mu g \, cm^{-2} \, day^{-1}$ for the spiked sample.

7. Discussion

The results obtained from these sets of experiments have provided a much clearer understanding of how the freely corroding copper and the copper controlled by the electrochemical method maintain an anti-fouling surface. They also show the conditions under which the copper looses its anti-fouling properties.

In discussing these results it is useful to compare the behaviour of the freely corroding samples with those that were subjected to the controlled corrosion. It should also be noted that in this paper the anti-fouling properties of the copper surface were considered to have failed the moment sustained biological activity was detected on the surface. This includes slimes, which in pratice would not necessarily be disadvantageous to marine operators.

7.1. Freely corroding samples

The behaviour of these samples both in the test tank and seawater environments has shown that copper is an extremely effective toxin for marine fouling, especially in the early part of the exposure sequence. However, as the exposure time increased, these surfaces began to display fouling of the Types 1, 2 and 3 as indicated in Figs 6 and 7.

The presence of slimes is thought to be due to the slow build-up on the surface of the insoluble non-toxic copper hydroxychloride, which also inhibited the out-diffusion of cupric ions. This build-up was consistent with the steady increase in the surface potential from typical starting values of -0.25 V and -0.1 V after 200 days.

As was suggested by the model illustrated in Fig. 1, the conversion of the cuprous oxide to the hydroxychloride will slow down the copper release rate to below the minimum $(10 \mu g \, cm^{-2} \, day^{-1})$ required to prevent the settlement of slimes.

Once these slimes are firmly attached, the settlement of other organisms such as barnacles can occur, this taking place with increasing ease as the underlying slime and hydroxychloride thickens with time.

This settlement of fouling is somewhat surprising considering that the average copper release rates were 43 to $87 \mu g \, cm^{-2} \, day^{-1}$ which is significantly higher than those encountered in modern copper-based paint systems. This may partly be explained by enhanced corrosion occurring at the edges of the copper specimens and a certain amount of pitting. Although we may conclude that freely corroding copper is initially an effective anti-fouling surface, the copper loss rate is both very high and uncontrolled and the effectiveness against slimes decreases steadily with exposure time due to build-up of insoluble non-toxic salts.

7.2. Spiked specimens

In both sets of experiments, this method of controlling the copper output has proved to be a successful alternative to the modern paint systems. The results have indicated that within a 200 day exposure period, the copper release rate can be reduced from the freely corroding levels of about $50 \mu g \, cm^{-2} \, day^{-1}$ to at least the minimum level for preventing marine fouling about $10 \mu g \, cm^{-2} \, day^{-1}$ and it may be possible further to reduce this as the process becomes more fully understood.

These results have indicated that the effectiveness of this system is controlled by three major factors, namely, spike current density, minimum spike frequency and incidence of cathodic chalking.

7.2.1. Spike current density

The results presented in Figs 8 and 10 clearly indicate that the electrochemical control of the

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*A freely corroding sample which had been exposed for 682 days in the area of Lanstone Harbour at Eastrey developed the typical hydroxychloride patina, the fouling level was 2 and the copper loss amounted to $86.5 \mu g \, cm^{-2} \, day^{-1}$.

system becomes increasingly more difficult with prolonged exposure, when the current density is greater than 20 to $25\,\mu A\,cm^{-2}$. At these higher current densities it is suspected that irreversible chemical reactions occur in the surface layers, such as the formation of the copper hydroxychlorides and the build-up of copper nodules. The occurence of such reactions will then lead to a highly heterogeneous dissolution of the toxin, and the settlement of fouling species at points of low copper output.

The slow change in the maximum cathodic protection current (Fig. 10) is a clear indication of the increasing difficulty being encountered in returning the sample from its anodic mode. This maximum value must represent the energy required to return the sample from a particular regime in the effective pH-potential diagram, and we may conclude that when this value is low, the surface is in a suitable state for maintaining the antifouling condition.

These studies suggest that the optimum spike current density lies within the range 10 to 20 $\mu A\cdot cm^{-2}$.

7.2.2. Minimum spike frequency

The incidence of relatively severe fouling (Types 4 and 5) on the Fawley site on the anodically samples, indicated that the copper release rate was below the minimum required for anti-fouling, and that the spike frequency was also too low. A similar effect was noticed in the earlier experiments (Fig. 7, Specimens 11 and 13) where although the copper release rate was the same at 7.1 μg $cm^{-2}\,day^{-1}$ for both the specimens, the longer spiking period was more effective in controlling the fouling. The problem appears to be associated with the exact concentration of copper ions seen by the settling fouling species. If there is a high concentration for a short period of time, they may be deterred from settlement, whereas a lower release rate, even though it is extended over a longer time period may not be sufficient to prevent settlement. If however, the spike frequency is too low, settlement may occur in the cathodic periods and the subsequent high dose rate will not be sufficient to produce the desired anti-fouling effect.

A close examination of the barnacles that had settled in the Fawley sample (Fig. 12, Specimen 18) revealed that they showed signs of stress after the copper output was increased at day 83. It is however more difficult to poison an adult barnacle than the settling cypris stage.

Fom the limited number of results obtained it is difficult to estimate the optimum spike frequency, but it is suggested that values of 2 mins per 2 hours at a spike current density of 15 μA cm^{-2} will provide a theoretical release rate of 7.1 $\mu g\;Cu^{2+}\;cm^{-2}\;day^{-1}$ and will be available in a manner which provides adequate anti-fouling protection.

7.2.3. Cathodic chalking

The results obtained from the second set of specimens at the Eastney site indicated that the development of this chalk layer was a major factor in allowing settlement to occur. At high current densities and long cathodic protection times, the build-up of the aragonite form of calcium carbonate seriously reduced the out diffusion of copper ions to the seawater surface. As the chalk layer thickened the build-up of the copper ions during the anodic mode meant that some were precipitated as copper nodules when the specimen was returned to the cathodic mode.

In the case of the fully cathodically protected samples, these chalk layers grew to approximately 140 to 170 μm after 83 days exposure and displayed significant fouling settlement. In Fig. 4, the possible electrochemical reactions were illustrated and it was noted that cathodic chalking will occur and that it will become increasingly difficult to reverse the reaction as the chalk layer thickens due to the insolubility of the calcium salts.

7.3. Summary

These experiments have shown that the electrochemical "spiking" of pure copper does offer several advantages compared with either freely corroding or copper-based paint systems, and these may be summarized as follows

(a) The copper release rate may be controlled at between 7 $\mu g\;cm^{-2}\;day^{-1}$ and 10 $\mu g\;cm^{-2}$ day^{-1} to prevent fouling settlement, without the excessive corrosion rates encountered for freely corroding copper.

(b) The surface may be stabilized, the formation of insoluble non-toxic copper salts and the formation of pits reduced to a minimum.

(c) Because the copper release rate may be controlled, the working life of the surface may be extended. In theory a 100 μm thick copper coating could last for over 20 years.

(d) For situations, such as ship hulls which may spend periods of time at high water velocities and hence have no fouling settlement problems, the electrochemical system could reduce the copper release rate to a minimum.

8. Development of the system

Although it appears unlikely that the average copper release rate provided by this system can be reduced much below the $10 \ \mu g \ cm^{-2} \ day^{-1}$ required for anti-fouling, it should be possible to extend the practical working life of the system by modifying the surface corrosion reactions.

In the present experiments, when current densities of $15 \ \mu A \ cm^{-2}$ were employed, the limitation for preventing settlement was the slow development of a chalk layer. If the copper were alloyed with a second element, such as magnesium or zinc, this situation might be improved by altering the solubility product of the complex carbonate formed. Another possible approach would be to use a copper alloy which contained a second toxin, such as zinc, beryllium or cadmium, so as to increase the toxin potential in the near surface region. In both these cases it is essential to note that these alloys must be single-phase because if the surface were a duplex structure, preferential corrosion would occur and impede the release of the toxin.

A further series of experimens is now being undertaken to study these developments and early results are highly encouraging.

9. Conclusions

These may be summarized as follows:

(a) The electrochemical spiking of pure copper does provide a controlled and effective method of anti-fouling.

(b) The ultimate failure of freely corroding copper as an anti-foulant surface occurs when insoluble hydroxychlorides are formed on the surface.

(c) Electrochemically controlled samples may eventually fail as anti-foulants when the surface becomes covered by layers of cathodic chalk.

(d) The anti-fouling life of the electrochemically controlled samples may be extended by controlling the spike current density and the spike frequency.

(e) The condition of the controlled surface may be directly monitored by the surface potential and maximum cathodic protection current demands. Changes in these values can give early warning of chalk or fouling developments.

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