Contractor Report

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INCRA Technology **Market Development**

ICA PROJECT 436

RESISTANCE OF 90/10 COPPER/NICKEL BOAT SHEATHING AND FISH CAGE MESH TO FOULING AND CORROSION

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CONTENTS

EXECUTIVE SUMMARY

Long term exposure tests of 90/10 copper nickel in the form of 1.2 mm strip, expanded metal mesh and 0.15 mm adhesive-backed sheathing have been carried out in a sea water loch (Loch Carron) in Scotland and Emsworth yacht harbour on the south coast of England. The objective was to seek explanations of failure of an expanded mesh fish farm cage at Loch Carron and of anti-fouling sheathing on two yachts in a yacht basin adjoining Emsworth. The effects of iron contents within and below the requirements of UNS C70600 and of whether the iron was in or out of solution on the performance of the materials were investigated.

All the materials/conditions tested showed excellent resistance to macrofouling. Microfouling by diatoms and associated slimes affected all but the samples containing iron out of solution but the deposits were easily detached by a rapid water stream. No microfouling occurred on mesh samples. The plastic coated racks and plastic plates on which samples were supported developed extensive hard fouling at Loch Carron and heavy soft fouling at Emsworth.

The Loch Carron tests afforded some (inconclusive) evidence supporting the view that the earlier fish cage failure had been due to stratification between fresh water near the surface and sea water beneath. The Emsworth tests provided strong evidence that the yacht sheathing failures had resulted from the combination of an iron content below specification and long periods of idleness which permitted the build-up of diatom microfouling with non-protective corrosion products beneath. Material with the correct iron content was shown to resist such conditions. It is concluded that sheathing material to the UNS C70600 specification can be relied on to behave satisfactorily in respect of fouling and of corrosion under any likely conditions of service.

RÉSUMÉ

Des essais avec des temps d'exposition prolongés ont été réalisés sur des échantillons de cuivre-nickel 90/10 dans un bras d'eau de mer (Loch Carron), en Écosse, et dans le port de plaisance d'Emsworth, sur la côte sud de l'Angleterre. Ces échantillons se présentaient sous forme de lame de 1,2 mm d'épaisseur, de grille en métal déployé et de revêtement de 0,15 mm d'épaisseur sur plaquette adhésive. Le but de ces recherches était d'expliquer les détériorations apparues dans le métal d'une cage d'une ferme à poissons de Loch Carron et sur le revêtement anti-incrustation (anti-fouling) de deux bateux situés dans un bassin voisin d'Emsworth. Le comportement et les performances des matériaux ont été étudiés en fonction de leur teneur en fer : teneurs conformes ou inférieures aux spécifications UNS C70600 et si le fer était à l'état dissous ou pas.

Tous les essais effectués suivant différents rapports conditions/matériaux ont montré une excellente résistance a la macro-incrustation (macro-fouling). La micro-incrustation (micro-fouling) par des diatomées et des vases associées ont affecté tous les échantillons a l'exception de ceux contenant du fer non dissous et ceux en forme de grille. Cependant ces dépôts étaient facilement détachable par l'action d'un fort jet d'eau. A Loch Carron, les casiers revêtus de matière plastique et les plateux en plastique sur lesquels étaient fixaient les échantillons ont subi une incrustation dure et étendue; à Emsworth l'incrustation était massive et molle.

Les essais de Loch Carron ont donné quelques résultats (peu concluants) étayant l'hypothèse que la détérioration antérieure d'une cage à poissons était due à une stratification entre l'eau plus douce de la surface et l'eau de mer située en dessous. Les essais menés à Emsworth ont montré d'une manière évidente que les détériorations du revêtement des bateux résultaient d'une teneur en fer inférieure aux spécifications ainsi qu'aux longues périodes d'immobilité des bateaux. Cette combinaison favorisait le développement de la micro-incrustation des diatomées avec des produits non protecteurs de corrosion en dessous. Les matériaux avec une teneur en fer adéquate ont montré qu'ils résistaient à ces conditions. En conclusion, les matériaux de revêtement qui répondent aux spécifications UNS C70600 se comportent d'une manière sûre et satisfaisante contre le fouling et la corrosion dans n'importe quelles conditions probables d'utilisation.

ZUSAMMENFASSUNG

Es wurden Langzeitversuche zur Exposition von 90/10 Kupfer-Nickel Legierungen in der Form von 1,2 mm dicken Streifen, weitmaschigen Metallgittern und 0,15 mm dicken, klebestrefenverstärkten Metallbeschlägen in einem Salzwassersee (Loch Carron) in Schottland und im Yachthafen von Emsworth an der Südküste von England durchgeführt. Das Ziel dieser Versuche war, eine Erklärung für das Versagen eines weitmaschigen Fischkäfigs in einer Fischfarm bei Loch Carron und von algenabweisenden Beschlägen zweier Yachten in einem Hafenbecken in der Nähe von Emsworth zu finden. Der Einfluß von Eisengehalten sowohl im Rahmen als auch unterhalb der Anforderungen der Bestimmung UNS C70600, und von gelöstem Eisen auf die Leistung der Materialien wurde untersucht.

Alle getesteten Materialien und Bedingungen zeigten ausgezeichneten Widerstand gegen makroskopischen Algenbewuchs (macrofouling). Mikroskopischer Bewuchs (microfouling) durch Diatomeen und damit verbundenem Schleim befiel alle Proben bis auf diejenige, die kein gelöstes Eisen enthielt; die Ablagerungen ließen sich jedoch leicht durch einen starken Wasserstrahl entfernen. Auf den Gitterproben war kein mikroskopischer Bewuchs festzustellen. Die plastikbeschichteten Gestelle und Platten, an denen die Proben befestigt waren, entwickelten ausgedehnten starken Befall (hard fouling) in Loch Carron und schweren Befall (soft fouling) in Emsworth.

Die Versuche in Loch Carron lieferten einige (nichte schlüssige) Hinweise, welche die Theorie unterstützen, daß das frühere Versagen des Fischkäfigs auf die Schichtung von Frischwasser an der Oberfläche und Salzwasser darunter zurückzuführen war. Die Versuche in Emsworth ergaben starke Hinweise darauf, daß das Versagen der Yachtbeschläge aus der Kombination eines Eisengehaltes unterhalb der Bestimmungen und langer Zeiträume von Untätigkeit bestand, die den Aufbau von mikroskopischem Diatomeenbewuchs mit darunterliegenden ungeschützten Korrosionsprodukten erlaubten. Es wurde gezeigt, daß Material mit dem korrekten Eisengehalf diesen Bedingungen widerstand. Daraus kann geschlossen werden, daß Beschlagsmaterial, das der UNS C70600 Bestimmung entspricht, sich in Bezug auf Algenbefall und Korrosion unter allen voraussichtlichen Betriebsbedingungen zufriedenstellend verhält.

RESUMEN

Tres tipos de pruebas Cobre Niquel 90/10 de exposición prolongada fueron llevadas a cabo en la ensada marina del Loch Carron (Escocia) y en el puerto deportivo de Emsworth (Sur de Inglaterra) Las pruebas consistieron en tiras de 1.2 mm; mallas de metal ensarchado y en un revestimiento adhesivo de 0.15 mm. El objectivo de las mismas era explicar el mal funcionamiento de la malla ensanchada de un compartimento de pisciifactoría en Loch Carron, y el fallo del revestimiento que protege de acumulaciones marinas al casco de dos barcos a Emsworth. Se investigaron los efectos de la proporción de hierro de acuerdo con las exigencias de la UNS C70600, y de si el hierro estaba dentro o fuera de la disolución.

Todos los materiales/condiciones probados mostraron gran resistencia a la acumulación masiva de residuos marinos. La acumulación progresiva de diatomeas y otros limos ascociados, afecto a todas la muestras excepto a aquellas que contenían el hierro fuera de la disolución, pero dichas incrustaciones se desprendieron fácilmente con una potente corriente de agua. Esta acumulación progresiva no se produjo en las muestras con malla. En las rejillas y placas plastificadas sobre las que se colocaron las muestrag se desarrollo, en Loch Carron, una extensa formación de residuos resistentes y, en Emsworth, una gruesa pero débil capa de residuos.

Las pruebas en Loch Carron proporcionaron alguna evidencia (aunque inconcluyente) apoyando la teoría de que el fallo de el anteriormente citado compartimento para peces, se debió a la estratificación de el agua fría en la superficie y el agua marina por debajo de la misma. Los ensayos en Emsworth proporcionaron la firme evidencia de que los defectos del revestimiento del barco habían sido el resultado de la combinación de una proporción de hierro por debajo de lo especificado, y de largos períodos de inactividad que permitieron la creación de diatomeas con productos que no protegían al casco de la corrosión. El material con la correcta proporción de hierro resistia dictas condiciones. Se comprobó que el material de revestimiento que se ajusta a las condiciones UNS C70600 es fiable, bajo cualquier conditión probabile, en cuanto a la acumulación de residuos marinos y corrosión.

TECHNICAL SUMMARY

90/10 copper nickel sheathing in the form of adhesive-backed panels of material 0.13 to 0.15 mm thick has been used - generally successfully - as a permanent anti-fouling treatment for small boats but severe corrosion was experienced on two of three yachts sheathed between December 1986 and October 1987 and berthed at Chichester Yacht Basin on the south coast of England. An investigation carried out for the shipyard concerned attributed the failure primarily to the iron content of the alloy being only 0.7% instead of the 1.0% minimum required for Alloy 706. Long idle periods for the boats concerned were also considered to be a factor. The importance attached to the iron content was based principally upon comparison with the behaviour of strip material with 1.8% iron in which the iron was out of solution. University of Surrey proposed to ICA research to establish whether material with a more usual iron content of 1.5% would show similar good performance and to check whether the difference between the 1.2 mm strip and 0.15 mm sheathing was due only to iron content or whether differences in manufacturing conditions for the very thin material contributed. It was also proposed to investigate differences between materials with the same iron content in and out of solution and to investigate further the suggested effect of long idle periods on the incidence of corrosion. ICA asked that the project should cover also an investigation of the possible causes of corrosion which had caused dissolution of areas 150-200 mm below the water line in a 90/10 copper nickel expanded mesh fish cage in Loch Carron in Scotland.

Two series of exposure tests of 90/10 copper nickel strip, sheathing and expanded mesh have been carried out at both Loch Carron and Emsworth Yacht Harbour. It had been shown earlier that the low iron sheathing material corroded when exposed at Emsworth in the same way as it did in neighbouring Chichester Yacht Basin. In the first series of tests all materials were tested at both sites for periods up to 16 months with examinations on site and/or in the laboratory at 3-4 month intervals. In the second series only mesh samples were exposed at Loch Carron and only strip and sheathing samples at Emsworth.

Throughout the tests no significant fouling occurred on any of the copper nickel samples at either site although the plastic coated frames and plastic sheets which were used to support the samples developed heavy hard shell fouling (small mussels and barnacles) at Loch Carron and soft fouling (sea squirts, ascidians etc) at Emsworth. Microfouling by diatoms and associated slimes occurred at both sites on strip and sheathing samples but to a much smaller extent on those which contained iron out of solution. Mesh samples remained free of microfouling at both sites - probably because of the local turbulence induced by the topography of the surface.

The mesh samples generally showed no corrosion apart from the formation of thin protective films but during one winter/spring period an area of bright metal, looking as if it had been acid cleaned, was observed extending about 120 mm below the waterline. The samples exposed during the corresponding period in the following year were lost in a storm and it was not possible therefore to check whether this type of attack had occurred again. The similarity between this attack and that on the fish cage which corroded in service gives some support to the view that both were caused by stratification between fresh snow-melt water near the surface and sea water below.

Little corrosion occurred on any of the strip or sheathing materials exposed at Loch Carron but at Emsworth there was a marked difference between the 0.7% iron sheathing material which suffered severe corrosion and the higher iron materials (strip with 1.8% iron in or out of solution and sheathing with 1.5% iron in solution) which formed good protective films. The iron-rich black film which formed on material with iron out of solution appeared to be less stable than the greenish or golden brown film which formed with the iron in solution. On some samples it continued to grow, reaching a thickness at which blisters developed with very shallow (25 μm) pits or more widespread equally shallow corrosion beneath. The corrosion product was principally magnetite.

In the first series of tests the potentials of all samples were measured at each inspection. In the second series the samples were designed so that they could be returned to the laboratory after exposure and anodic and cathodic polarisation tests run on them. Unfortunately no reproducible results were obtained from any of these electrochemical measurements.

The conclusions reached from the extended exposure tests are that the fish cage mesh material showed complete resistance to both hard shell and soft macrofouling and also to microfouling by diatoms. It also showed excellent corrosion resistance except for the case described above which is possibly attributable to water stratification. The tests demonstrate that sheathing material of composition meeting BS CN102 or UNS C70600 will provide a combination of anti-fouling properties and excellent corrosion resistance under any likely conditions of service. It is recommended that the materials should have the iron wholly in solution.

1. INTRODUCTION

90/10 copper nickel was originally developed for sea water piping and heat exchanger tubing - applications for which resistance to erosion corrosion is the primary consideration. Later applications based on the anti fouling properties of the alloy involve service under relatively low flow conditions in which the factors responsible for satisfactory performance are different. Two such applications in which unexpected corrosion failures were experienced were as expanded metal mesh for fish farm cages and as very thin, adhesive-backed panels applied to small boats for long term antifouling protection.

Brief investigations of two fish cage failures in Scotland were carried out for INCRA in 1981-83 with no satisfactory conclusion being reached in one of the cases. Severe corrosion of 90/10 copper nickel sheathing on two of three yachts sheathed between December 1986 and October 1987 and berthed at Chichester Yacht Basin was investigated for the shipyard concerned and was attributed primarily to the iron content of the alloy (0.7%) being below the specified minimum for alloy 706 (1.0%). Since the one yacht on which the sheathing performed satisfactorily, in spite of its low iron content, had been sailed much more than the two on which it was unsatisfactory, some experiments on effect of water flow were carried out. These suggested that the low-iron material could be satisfactory if not submitted to lengthy periods of stagnation. Further details of these earlier investigations are given in Section 2.

The ICA-sponsored research reported in Section 3 was undertaken primarily to investigate further the relationship between composition, metallurgical condition of the alloy and flow conditions in service on the behaviour of sheathing material. Expanded mesh from two batches of material, with the iron in and out of solution, was also tested. Exposure tests were conducted at Emsworth Yacht Harbour, where it had been shown that the corrosion behaviour of 90/10 copper nickel sheathing materials was similar to that in Chichester Yacht Basin, and in Loch Carron, Scotland, at a fish farm where corrosion of experimental fish cages had occurred. Details of the materials tested are given in Section 3.2. and of the test sites in Section 3.3.

Two series of exposure tests were carried out. The test procedure used for the series 1 exposures and the results obtained are reported in Section 4; those for the second series are in Section 5. A general discussion of the results is presented in Section 6 and summarised conclusions in Section 7.

2. EARLIER INVESTIGATIONS

2.1. FISH CAGE FAILURES AT LOCH CARRON

The author, when employed by BNF Metals Technology Centre, investigated two corrosion failures of experimental 90/10 Cu/Ni mesh fish cages at Loch Carron. The first failure was shown to be the result of the cage being sited in the path of a galvanic current passing through the water between aluminium scaffold poles lying on the bed of the loch and mild steel piling at the water's edge, the two being connected by heavy iron anchor chains lying on the bottom. The second failure was not satisfactorily explained. The fish cage concerned showed an area of corrosion between about 150 and 200 mm. below the surface and extending virtually all round the cage. Over most of this area the metal simply had a bright "acid-cleaned" appearance but there were a number of areas up to about 4" long where the mesh had corroded away completely. It was suggested that the attack might have been related to stratification between the salt water forming the bulk of the loch and fresh water from feeder streams at the head of the loch but no detailed investigation was carried out.

2.2. ADHESIVE-BACKED SHEATHING FAILURES

A system for control of fouling on small boats by the application of adhesive-backed 90/10 Cu/Ni panels was developed by F C Mitchell, who marketed the panels under the name Mariner 706. The panels are 20" (508 mm) x 8" (203 mm) x 0.005" (0.13 mm) or 0.006" (0.15 mm) thick with a bituminous mastic backing. The panels are applied to the hull with the aid of a hot air gun, with an overlap of ca 0.5" (13 mm), over an area extending from the keel to little above the water line where the sheathing is finished off with a covering strip of the same material. The rudder and propeller bracket are similarly sheathed. For the lower edge of the keel or other areas where abrasion is to be expected in service panels 0.010" (0.25 mm) thick are used.

Experience with Mariner 706 sheathed boats has generally been good but two of three GRP yachts sheathed by one boatyard and all moored in Chichester Yacht Basin suffered extensive corrosion with complete penetration of the sheathing over areas up to 60 x 25 mm. The most seriously affected boat, "Seamogs", was sheathed in April 1987 and found to be severely corroded when lifted and pressure washed for survey for sale in July 1988. The corrosion was distributed in a random manner over the sheathed surface indicating that it was not attributable to stray currents or electrical leakage from on-board equipment. The 0.010" sheathing applied to the lower edge of the keel had behaved differently, developing a protective black film. In view of the extent of corrosion, the owner had the sheathing removed and replaced by antifouling paint.

The other affected boat, "Roebuck", was sheathed in October 1987 and first examined in July 1988 following the observation of corrosion on Seamogs. Corrosion was present but less severe than on Seamogs. Subsequent examinations at intervals up to May 1989 revealed further development of corrosion, including some on replacement patches applied in July 1988. The copper-nickel sheathing was therefore replaced by antifouling paint.

The third boat, "Dido", was sheathed in December 1986. She was examined in July 1988 and at intervals up to May 1989. No significant corrosion was found at any inspection. The sheathing had developed a protective greenish-brown film, except for a repair patch (following mechanical damage) which was made with 0.010" sheathing and had formed a black film. No problems with the sheathing on Dido were subsequently reported.

The 0.005 sheathing used on the three boats had all been rolled from the same billet but the 0.010" sheathing came from a different manufacturer. Tests of the 0.005" sheathing, applied to plastic laminate backing plates and exposed in Chichester Yacht Basin, reproduced the type of corrosion observed on Seamogs and Roebuck after only nine weeks, the attack being accompanied by formation of a slimy biofilm with many diatoms present. None of the 0.010" sheathing was at that time available for test.

Chemical analysis showed that the 0.005" sheathing (Sheathing F1 in Table 1) contained only 0.7% Fe compared with the minimum of 1.0 specified for 90/10 copper-nickel in British Standard Designation CN 102 and ASTM specification C70600. The 0.010" material (Sheathing F3 in Table 1) contained 1.6% Fe. The formation of a black film on this material suggested that part of the iron present was out of solution. This was confirmed by showing that the material was magnetic. Since it is well established that maximum resistance to erosion corrosion is obtained with the iron fully in solution 90/10 Cu/Ni is usually supplied in that condition. The influence of metallurgical condition on corrosion in slower flowing water, however, was unclear.

The principal difference between the histories of Seamogs, Roebuck and Dido was the extent to which they had been sailed as opposed to lying at their berths. Seamogs had only been sailed on one or two occasions, Roebuck rather more frequently but Dido very frequently indeed. It was considered that the development of corrosion of the sheathing was due to idle conditions not being conducive to formation of a satisfactory protective film such as formed under the flowing water conditions experienced during sailing. This idea was supported by 14-week exposure tests of the 0.005" sheathing, F2, applied to one side of samples of strip (Strip S1 in Table 1) in the Yacht Basin and at a site in the main Chichester Harbour channel where there is strong tidal flow. The strip samples at both sites formed a nearly black film with a few very small shallow pits up to 0.001" (25 μm) deep. The sheathing material exposed in the Yacht Harbour showed patches of loose green corrosion product under slimy microfouling deposits but the samples in the open channel formed adherent brown tarnish films with no corrosion patches. On drying out, the cuprous oxide film on the sheathing samples with corrosion patches curled away from the metal beneath revealing attack similar to that seen on Seamogs and Roebuck.

A further set of samples of F2 sheathing applied to Perspex panels was exposed from November 1988 to January 1989 in Emsworth Yacht Harbour. Chichester Yacht Basin and Emsworth Yacht Harbour both open off Chichester Harbour but, whereas Chichester Basin is closed by lock gates, Emsworth Harbour is open. One sample was exposed opposite one of the entrances to the Harbour where tidal flow is up to 8 m/sec and three others at positions progressively further towards the back of the harbour. The sample opposite the harbour entrance formed an adherent green/buff protective film but those exposed to the relatively low flow conditions further back formed non-protective corrosion products with attack on the metal beneath similar to that seen on Seamogs and Roebuck. This test showed that attack was not peculiar to Chichester Yacht Basin and indicated that differences in behaviour, related to water flow conditions, could be conveniently studied at Emsworth Harbour.

3. ICA-SPONSORED INVESTIGATIONS

3.1. OBJECTIVES

The University of Surrey put a proposal to ICA for research, to be conducted at Emsworth Yacht Harbour, to establish whether the superior performance of the strip material, as compared with the sheathing material, in the test described in Section 2, was simply related to the iron contents of these materials or whether other factors involved in the production of the very thin sheathing material might be significant. This was to be studied using sheathing material of similar thickness but normal iron content. It was also proposed to investigate whether the corrosion resistance of 90/10 Cu/Ni under low-flow conditions was influenced by the metallurgical condition of the alloy (iron in or out of solution) and the effects of iron content and metallurgical condition on its antifouling properties. ICA asked for the research to be extended to include an investigation of the performance of fish cage mesh material in exposure tests at Loch Carron. A test programme was therefore drawn up to cover the behaviour of both types of material in Loch Carron and in Emsworth Yacht Harbour.

3.2. MATERIALS

3.2.1. FISH CAGE MESH

ICA provided two batches of 90/10 Cu/Ni expanded metal mesh.

M1 was taken from the batch of material used to build the fish cages which had suffered corrosion at Loch Carron. It had a mesh size of 14 x 8 mm and had been produced from 18 swg (1.22 mm) strip. It was non-magnetic.

M2 was lighter gauge material of the same mesh size but produced from 22 swg (0.71 mm) strip. This material was magnetic.

3.2.2. ADHESIVE-BACKED SHEATHING

Material from four batches of sheathing were provided by Mr F C Mitchell. Some had black adhesive mastic backing and some white. Mr Mitchell stated that these were essentially of the same formulation. The copper-nickel came from three different manufacturers, designated below as manufacturers A, B and C.

F1 was 0.005" Cu/Ni from manufacturer A, with black adhesive backing and was non-magnetic. As used on Seamogs.

F2 was 0.005" Cu/Ni from manufacturer A, with white adhesive backing - non-magnetic. As used on Roebuck and Dido. F1 and F2 differed only in the adhesive backing.

F3 was 0.010" Cu/Ni from manufacturer B, with black adhesive backing - magnetic. As used on bottom of keel of Seamogs and Roebuck and as a repair patch on Dido.

F4 was 0.15 mm (0.006") Cu/Ni from manufacturer C, with black adhesive - non-magnetic.

3.2.3. 18 SWG (1.22 mm) STRIP

This material was obtained from BNF Metals Technology Centre.

S1 was in the as-rolled condition and was magnetic.

S2 had been heat treated by BNF to take the iron into solution and was non-magnetic.

S3 was S2 material re-heat treated by University of Surrey at 600°C for one hour and water quenched to re-precipitate the iron and was magnetic.

The analyses of all materials for nickel, iron and manganese are given in Table 1.

TABLE 1

ANALYSES OF TEST MATERIALS
Wt %

Material	Ni	Fe	Mn
Mesh M1	10.1	1.73	0.62
Mesh M2	10.0	1.68	0.63
Strip	10.9	1.82	0.95
Sheathing F1	9.8	0.71	0.51
Sheathing F2	9.8	0.71	0.51
Sheathing F3	9.6	1.62	0.74
Sheathing F4	9.7	1.46	0.54
BS CN102	10.0-11.0	1.0-2.0	0.5-1.0
UNS C70600	9.0-11.0	1.0-1.8	1.0 max

3.3. TEST SITES

3.3.1. LOCH CARRON

Loch Carron is a sea loch on the west coast of Scotland opposite the Isle of Skye. The fish farm where the tests were conducted is approximately two miles from the head of the loch and ten miles from the mouth. The River Carron, fed by Loch Dughaill, and a number of smaller streams feed fresh water into the loch, the quantity varying with the time of year. The test samples were attached to racks suspended from wooden walkways round net fish cages containing salmon. Two sites were used, one approximately 100 m further up the loch than the other. They are identified as the "up-loch" and "down-loch" sites.

3.3.2. EMSWORTH YACHT HARBOUR

Emsworth Yacht Harbour is situated on Chichester Harbour on the south coast of England. Chichester is a natural, open harbour. The Yacht Harbour is connected to the main harbour by two short channels with no lock gates or other constraints. Test sample racks were suspended from the pontoons at which boats are moored. Two sites were used - one immediately opposite an entrance to the Yacht Harbour where it was subject to incoming tides flowing at about 4 knots (8 m/sec) and the other towards the back of the harbour where the flow rate was very much lower.

4. FIRST SERIES OF EXPERIMENTS

Each experiment in the First Series entailed exposure of racks at the up-loch and down-loch sites at Loch Carron and at the harbour entrance and quiet area at Emsworth Yacht Harbour.

The racks employed were 200 mm wide x 450 mm deep, fabricated from 20 x 20 x 3 mm steel angle with suspension eyebolts welded to the top edge. The face side of the rack had three 8 mm dia holes spaced along each of the long sides and two on each of the short sides. Two additional holes were provided on the lower two-thirds of the sides of the long members. After fabrication the complete frame was Vinaflex coated to a thickness of approximately 0.3 mm.

A sample of fish cage mesh 200 x 450 mm was attached to the face of the rack by ten 6 mm 90/10 Cu/Ni screws, nuts and washers with plastic washers between the frame and the mesh. One of the top two attachment bolts carried a PVC insulated lead for electrical measurements, the attachment terminal being protected from contact with the water by hot-applied plastic glue.

Type A racks had Bear brand Tufnol laminate panels, 100 x 300 x 10 mm, bolted to the sides with plastic washers between the laminate and the frame. Adhesive-backed 90/10 Cu/Ni samples, 80 x 200 mm, were applied to the outer faces of the panels. A PVC insulated lead was attached near the top of the Cu/Ni sample by a 6 mm 90/10 Cu/Ni screw into a threaded hole in the Tufnol backing panel. Type B racks had 90/10 Cu/Ni strip samples, 45 x 260 mm, bolted to the sides with plastic washers between the samples and the frame. A PVC insulated lead was attached to the top fixing bolt of each. Hot-applied plastic glue was used to protect the attachment terminals of leads to the strip and adhesive-backed samples, as for the mesh. The racks were suspended with the top 50 mm of the mesh above the water line.

Table 2 records the dates of commencement and completion of each exposure and the make-up of the test racks employed.

TABLE 2

FIRST SERIES: RACK EXPOSURES

Rack No	Materials	<-----------Exposure Details---------->		
		Site*	Start	Finish
1	M1/S1/S2	L Down-loch	09.04.90	15.11.90
2	M2/F1/F3	L Down-loch	09.04.90	15.11.90
3	M1/F1/F3	L Up-loch	09.04.90	03.07.91
4	M2/S1/S2	L Up-loch	09.04.90	03.07.91
5	M1/S1/S2	E Entrance	20.04.90	13.05.91
6	M2/F1/F2	E Entrance	20.04.90	13.05.91
7	M1/F1/F2	E Quiet area	20.04.90	16.07.91
8	M2/S1/S2	E Quiet area	20.04.90	25.10.90
9	M1/F2/S2	E Quiet area	07.08.90	25.10.90
10	M1/F1/F4	L Down-loch	15.11.90	03.07.91
11	M2/S1/S2	L Down-loch	15.11.90	03.07.91
12	M1/S1/S2	E Quiet area	25.03.91	13.05.91

*L = Loch Carron; E = Emsworth Yacht Harbour

To examine further the effect of semi-stagnation two "back-to-back" samples were prepared, each consisting of two 100 x 300 mm Tufnol laminate plates bolted together but separated by plastic washers to leave an 11 mm gap between them. One plate had 80 x 200 mm samples of F1 sheathing applied to each side; the other had F4 sheathing. Each sheathing sample had a separate lead for potential measurements. One such test piece was exposed at the Emsworth entrance site from 25.03.91 to 13.05.91. The other was exposed at Loch Carron up-loch site from 15.03.91 until 03.07.91.

Visits were made to the Loch Carron sites 4, 8½, 12½ and 16 months after the first rack exposure date. The Emsworth sites were visited after 3½, 6, 11, 13 and 15 months. On each visit the potential of each of the material samples was measured against a standard silver/silver chloride electrode immersed in the sea water approximately 0.3 m deep and 0.5 m from the rack. The water temperature was measured and measurements of pH and conductivity were carried out at depths ranging from 10 to 400 mm. The racks were then lifted and photographed and the samples examined for extent of fouling and corrosion before replacing them on test or returning them to the laboratory.

On return to the laboratory the nature of any corrosion was investigated in more detail including, in appropriate cases, scanning electron microscope (SEM) examination and energy dispersive X-ray (EDX) analysis.

4.1. POTENTIAL MEASUREMENTS

The potentials of the exposed samples did not show consistent differences between materials or systematic change with time of exposure or water conditions. Table 3 shows the range of potential measurements.

TABLE 3
POTENTIALS AGAINST Ag/AgCl, mV

Material	**Potential range**	
	Loch Carron	**Emsworth**
M1	-207 to -313	-59 to -191
M2	-167 to -251	-49 to -112
F1	-100 to -179	-52 to -104
F2	-	-65 to -196
F3	-135 to -154	-
F4	-171 to -181	-67 to -153
S1	-167 to -256	-60 to -159
S2	-125 to -257	-56 to -159

The only obvious feature of these figures is that potetials for all materials were consistently 50-150 mV higher (less negative) at Emsworth than at Loch Carron.

4.2.. WATER CONDITIONS

The variation of water temperature, pH and conductivity with time of year and depth is recorded in Tables 4A for Loch Carron and 4B for Emsworth.

TABLE 4A
WATER CONDITIONS, LOCH CARRON

Date	**At surface**			**At 0.4 m**		
	Temp. °C	**pH**	**Conduct. mS**	**Temp. °C**	**pH**	**Conduct. mS**
09.04.90	4.5	6.6	33.0	4.5	7.6	33.9
03.07.90		8.2	49.6		8.2	49.3
14.11.90	11	8.0	56.0	11	8.0	57.6
14.03.91	7	-	56.2	7	-	56.9
04.07.91	15	8.2	57.0	15	8.2	57.7

TABLE 4B
WATER CONDITIONS, EMSWORTH

Date	At surface			At 0.4 m		
	Temp. °C	pH	Conduct. mS	Temp. °C	pH	Conduct. mS
26.04.90	11	8.4	23.6	11	8.5	36.6
07.08.90	21	8.0	59.9	-	-	-
25.03.91	12	7.5	51.0	10	7.8	53.4
13.05.91	16	8.2	40.2	15	8.1	43.9

4.3. OBSERVATIONS OF FOULING

4.3.1. Fouling at Loch Carron

After four months exposure, commencing in February/March 1990, racks 1-4 showed hard fouling (small barnacles) on the frame and on the Tufnol but none on any of the Cu/Ni samples or screws. After 8½ months racks 3 and 4, examined on site, showed hard fouling and flat green seaweed on the frames and the Tufnol. There was loosely attached brown filamentous weed on the mesh and a brown slimy deposit on the sheathing and strip samples. Racks 1 and 2 were returned to the laboratory for examination by Dr A H L Chamberlain of University of Surrey School of Biological Sciences and with a scanning electron microscope (SEM). The hard fouling was identified as barnacles and small mussels and the flat green weed as *Ulva lactuca* (sea lettuce). The brown filamentous weed, entangled with rather than attached to the mesh, was identified as *Pilayella littoralis.* Some tufted brown material on the sides of the Tufnol plates was identified as a bryozoan (animal). The superficial deposit on the S1 strip was entirely silty with no biological content whereas the deposit on the S2 strip was almost entirely biological consisting of a mixture of diatoms - principally *Amphora.* A similar deposit was present on the F1 sheathing but the deposit on the F3 sheathing was mostly silty with only a few diatoms. It appeared therefore that the presence of iron out of solution, as in S1 and F3, discouraged the settlement of diatoms. After 12½ months exposure rack 3 still carried considerable amounts of sea lettuce, barnacles and mussels on the frame and plastic with non-adherent brown filamentous weed on the mesh but rack 4 showed rather less hard fouling than at the previous examination. The S2 strip carried some moderately adherent weed but there was no fouling on the S1. The F1 sheathing carried a thin slimy brown deposit and, surprisingly, a heavier slimy deposit was present on the F3 sheathing. When racks 3 and 4 were finally removed after 16 months, their condition showed very little change since the 12½ month examination but a few adherent barnacles had settled on the S2 strip; there were none on the S1.

Racks 10 and 11, first exposed in November 1990, showed only light fouling on the Tufnol plates and practically none on the frame, with only a very thin slimy deposit on the strip and sheathing samples, when examined after four months. When they were removed after 7½ months hard fouling had developed on the frames and Tufnol plates but there was still only a very thin slimy deposit on the Cu/Ni samples.

The "back-to-back" samples exposed in March 1991 and removed in July 1991 showed very little fouling - only some slimy deposit on the F1 sheathing and less on the F4.

4.3.2. Fouling at Emsworth

The fouling that occurred on the frames and plastic panels at Emsworth was of a different character from that at Loch Carron. During most of the first series exposure the only fouling found was a thin, generally slimy deposit of silty material and diatoms with a small amount of thin brown filamentous weed. The examination carried out in early November 1990 showed, by contrast, massive fouling, entirely by soft organisms which were identified by Dr Chamberlain as tunicates (sea squirts) and ascidians with filamentous diatoms and filamentous *Ectocarpus* also present. This fouling occurred during the three month period August to November and had completely disappeared again when the next inspection was made in March of the following year. The heavy soft fouling was wholly restricted to the frame and the Tufnol panels but the light fouling present throughout most of the exposure period covered the sheathing and strip samples also. It was however easily removed by gentle rubbing with the finger and, often, simply by repeated dunking in the water.

4.4. OBSERVATIONS OF CORROSION

4.4.1. Corrosion of mesh samples

The mesh samples generally showed no significant corrosion at either Loch Carron or Emsworth. The M1 samples developed an adherent golden brown film over most of the submerged surface with green corrosion product on the splash area above the waterline. The M2 samples developed a black film after the first three months. This was slightly less adherent than the film on M1 but appeared nevertheless to be fully protective. An exception to the normal observed behaviour of M1 was found for rack 10 exposed at Loch Carron from 15 November 1990 to 3 July 1991. When examined in March 1991 both sides of the M1 mesh showed a bright area - looking as if it had been acid cleaned - extending down about 120 mm from the waterline. The top pair of fixing screws, which came within this area, had a similar bright etched appearance. The lower part of the mesh and the lower screws had formed a golden brown film which tended to be darker towards the bottom. These features were again observed when the rack was removed in July 1991. No similar band of attack was found on the M2 mesh at either examination.

4.4.2. Corrosion of sheathing samples on racks

The sheathing samples at Loch Carron showed no serious corrosion. The two F3 samples exposed on racks 2 and 3 developed adherent black films with no significant corrosion beneath over their 7-month and 15-month exposure periods. The F1 samples exposed on the same racks developed a light brown film which was less adherent but the samples still showed no significant corrosion. The F4 sample exposed from 15 November 1990 to 3 July 1991 behaved similarly.

No F3 sheathing had been available for exposure at Emsworth. The F1 and F2 samples all developed very poorly adherent brown films beneath slimy organic deposits. The films were not protective; they were easily removed by rubbing with the finger, revealing a bright etched metal surface or loose red crystalline cuprous oxide beneath.

4.4.3. Corrosion of strip samples

The S1 samples developed a black film at both sites. At Emsworth this was protective apart from developing some small blisters beneath which shallow corrosion occurred producing cuprous oxide and magnetite as corrosion products. At Loch Carron the film became thicker and less adherent on some samples. On these shallow corrosion took place beneath the film, the corrosion product being principally magnetite.The S2 samples at both sites developed a protective light brown film which did not blister.

4.4.4. Corrosion of back-to-back samples

The back-to-back samples exposed at Loch Carron from 15 March 1991 until 3 July 1991 showed no difference in behaviour between the F1 and F4 sheathing or between the freely exposed (outer) or shielded (inner) samples. At Emsworth however the corresponding samples exposed from 25 March 1991 to 13 May 1991 showed marked differences as illustrated in Figures 1 and 2. The F1 sheathing used to make up the back-to-back sample had developed a considerable tarnish film before use and, in order to see how this would affect the performance of the freely exposed material, the right hand side of the outward facing sample was lightly abraded to remove the tarnish before exposure. After the 7 weeks exposure there was a marked difference between the abraded and non-abraded areas, as shown in Figure 1A. Clearly the initial oxide tarnish assisted the production of a moderately protective film. The abraded area shows patches of corrosion forming crystalline cuprous oxide as the principal corrosion product. Corrosion was considerably more severe on the inward facing sample although the original tarnish film had not been removed from it before exposure. No adherent protective film was formed - as is clear from the way that the general corrosion product layer flaked off from the surface after drying (Figure 1C). By contrast the F4 sheathing developed a protective film on both the inward facing and outward facing samples as shown in Figure 2.

The results of the back-to-back sample tests at Emsworth show very clearly that, whereas material with the correct iron content of 1.5%, with the iron in solution (sheathing F4), forms a fully protective film under both fully exposed and shielded exposure conditions, material containing only 0.7% iron is unreliable under fully exposed conditions and liable to serious corrosion under shielded exposure conditions.

5. SECOND SERIES OF EXPERIMENTS

5.1. TESTS AT LOCH CARRON

Since there had been no observable corrosion on the mesh samples exposed at Emsworth in the first series of experiments, tests on mesh samples in the second series were restricted to Loch Carron. Racks of the same type as for the first series were used but without strip or sheathing samples attached and without provision for measuring potentials. Duplicate racks were exposed - both with M1 mesh. After the initial installation of the racks, subsequent removals and replacements were carried out by fish farm staff without visits by the corrosion investigator.

Racks 13 and 14, installed July 91 and removed September 91, showed some fouling of the frames. On rack 13 there were a few small mussels. On rack 14 there was little fouling on the top third of the frame but numerous small mussels increasing in number and size from one third down to the bottom of the frame. The mesh on both frames had developed a thin dull oxide film with no significant corrosion.

Racks 15 and 16 were installed in September 1991 but lost, at the end of the year, in a storm which broke up the walkways from which they were suspended.

Racks 17 and 18, were installed in February 1992 and removed in June 1992 but were not received back for examination until November 1993. The frames showed very little fouling - comprising some loose fibrous weed, a few small mussels and serpulids. The mesh samples showed only a light golden tarnish.

Racks 19 and 20 were exposed in June 1992. Rack 19 was removed in November 1993, after 17 months exposure but rack 20 had disappeared - presumed lost in a storm. Rack 19 showed a small amount of fouling in the form of small mussels and barnacles. The mesh had suffered some mechanical damage from storm battering but had developed a protective golden brown patina with no significant corrosion.

5.2. TESTS AT EMSWORTH

Since the potential measurements made during the first series of experiments were not very informative, the second series tests at Emsworth were conducted using specimens designed for mounting on compact flowthrough electrochemical cells, of the type described in Appendix 1, to enable anodic and cathodic polarisation scans to be made after exposure. The strip specimens used were 45 x 65 mm and were pre-drilled for subsequent attachment to the electrochemical cell. The sheathing samples were tested on similarly pre-drilled 5 mm Perspex "tiles" 50 x 65 mm. The specimens were attached by 90/10 Cu/Ni bolts to a 500 x 200 x 10 mm Perspex plate capable of accommodating 12 specimens on each side. Duplicate sets of specimens were attached to both sides of the plate, one set being screened by a 5 mm Perspex sheet fixed 7 mm from the specimens. The test assembly was suspended vertically, with its top edge 30 cm below the surface, at the Emsworth Harbour Entrance site. The freely exposed specimens faced the incoming tide. Specimens were exposed for periods up to 33 weeks, the site being visited at monthly intervals from July to October 1991 and from April to September 1992. One set of samples remained exposed but without intermediate examinations from October 1991 to April 1992. At each visit the specimens on both sides of the 10 mm Perspex mounting plate were examined and photographed after removal of the 5 mm Perspex screening sheet from the reverse side. Specimens that had completed their exposure period were removed and returned to the laboratory suspended vertically in a vessel filled with Emsworth sea water. New samples were attached in the vacant spaces and a clean Perspex screening sheet fitted to ensure that the specimens beneath it were not screened from light as well as from rapid water flow.

5.2.1. On-site inspections

5.2.1.1. Fouling

The fouling on the Perspex support plate and screening sheet varied considerably throughout the 33-week exposure period. During the first month a slimy deposit and ascidians appeared on all Perspex surfaces, the slimy deposit being present also on the freely exposed metal samples but not on the shielded samples. Throughout the rest of the test slimy deposits and some loose fibrous material were found on all the freely exposed metal specimens but generally not on those beneath the Perspex shield. Heavier fouling occurred only on the Perspex and varied in extent and character. In late September, after two months exposure, the amount of slimy deposit was less than after one month but numerous small barnacles were present. After a further month however no barnacles and practically no ascidians remained and virtually no fouling had occurred on the new Perspex cover plates fitted at the end of September. In April of the following year there was still not much fouling - only semi-adherent fibrous material with some mud incorporated in it. There were a few barnacles on suspension ropes but the Perspex cover sheets and the back of the rack were practically clean. There was little change during the next two months but between June and July the amount of filamentous slimy deposit decreased and numerous small barnacles appeared on the Perspex. After a further month the barnacles had disappeared but considerable soft fouling - filamentous slimy material, ascidians and small sea squirts - were found, especially on the shielded side of the Perspex. A month later the situation was much the same but a few small barnacles had reappeared. At the final inspection in December only a light deposit of filamentous material had formed on the cover plate fitted in September but the face side of the support plate still carried many ascidians with a few sea squirts and with barnacles near the edges. It was noticeable that the blank spaces from which samples had been removed in September remained generally free from fouling. This was presumably due to corrosion products remaining on the surface of the Perspex. There was less fouling on the shielded side of the support plate but more tendency there for the fouling to spread over the sites where specimens had been removed in September.

5.2.1.2. Corrosion

The F1 sheathing samples had developed patches of loose red cuprous oxide with shallow corrosion beneath on both freely exposed and shielded specimens after only one month. During the second month this developed further and samples exposed at the end of the first month showed similar attack. This pattern continued for F1 samples exposed at various times and for various periods throughout the test. The shielded specimens were generally slightly worse than the freely exposed specimens but the differences were not great. The F4 samples all developed golden or darker brown protective films but with occasional small patches of corrosion producing shallow green mounds of corrosion product. This tended to occur more on the freely exposed samples - probably because these carried more slimy deposits than the shielded samples.

The S1/S3 samples, in which the iron was out of solution, formed dark films on the freely exposed samples and, generally, a lighter green film on the shielded samples. Both films were adherent and protective and the samples carried less slimy deposit than formed on any of the other materials on test. The S2 samples developed golden brown films beneath brown slimy deposits. Those exposed in June and July 1992 showed a broad streak of adherent green corrosion product down one side. This did not appear to represent continuing corrosion or corrosion to any significant depth and is believed to have been the result of initially slightly different surface condition (degree of oxidation) of the affected area.

5.2.2. Electrochemical measurements

On their return to the laboratory the samples were fitted to compact flowthrough electrochemical cells and aerated Emsworth sea water pumped through four cells in parallel, at 10 ml/min for each cell, from a 2 L reservoir. The water was circulated for at least 30 minutes to allow the potentials of the samples to settle before commencing potentiodynamic polarisation experiments. Initially these were conducted using computer controlled equipment to plot Tafel (log current density against potential) polarisation curves over the range 70 mV cathodic to 70 mV anodic with respect to the rest potential, at a scan rate of 0.2 mV/sec. Cathodic and anodic Tafel slopes over the full range and polarisation resistance over the range ±10 mV vs the zero current potential were calculated by the computer programme (EG&G Princeton Applied Research Model 322 SoftCorr Corrosion Software).

The anodic and cathodic Tafel slopes indicate the extent of polarisation of the anodic and cathodic reactions over the potential range investigated. It was anticipated that differences in the slopes for different materials would indicate whether their relative corrosion resistance was affected by the anodic reaction, the cathodic reaction or both. Decrease in the slope indicates a decrease in the degree of polarisation. The polarisation resistance calculation provides a measure of the corrosion rates without any imposed current. Increase in polarisation resistance corresponds to a decrease in corrosion rate.

The form in which results were obtained from the computer-controlled potentiodynamic scan experiments is illustrated in Figures 2 and 3 and in Table 5. These are for F1 sheathing sample No 5 after five weeks exposure. Figure 2 is a plot of the points produced by the potential scan, with the computer-calculated Tafel lines superimposed. Good coincidence between the two indicates that the calculated Tafel values are reliable. Figure 3 is a plot of potential against current density on a linear scale over the range 10 mV each side of the zero-current potential. It shows the data points from the actual scan and the computer generated best fit straight line from which the polarisation resistance and corrosion current density are calculated.

The results from the Tafel and polarisation resistant plots are presented in Table 5. Since the zero-current potential and the corrosion current density values derived from the polarisation resistance calculation are more reliable, these, rather than the values derived from the Tafel calculations, are used in Table 6, which presents the results of computer controlled experiments carried out on sheathing F1 and F4 samples after five weeks and eleven weeks exposure.

TABLE 5.

RESULTS OF TAFEL SCAN ON SAMPLE F1 5
(COMPUTER-DERIVED FROM FIGURES 2 AND 3

From Tafel calculation

Zero-current potential, $E_{I=0}$	-270 mV
Cathodic Tafel slope	76.4 mV per decade
Anodic Tafel slope	87.8 mV per decade
Corrosion current density, I_{Corr}	1.87 μA/cm^2

From polarisation resistance calculation

Zero-current potential, E_{I-0}	-271 mV
Polarisation resistance	9.19 Kohms/cm^2
Corrosion current density, I_{Corr}	1.93 μA/cm^2

(One decade = a 10-fold change in current density.)

TABLE 6
TAFEL SCAN RESULTS
FOR SAMPLES REMOVED FROM EMSWORTH ON 24 SEPTEMBER 1991

Sample	Rest potl	$E_{I=0}$	Cathodic slope	Anodic slope	I_{Corr}
F1 1	-281	-287	77.8	92.3	1.9
F1 2	-253	-271	61.4	82.3	2.6
F1 5	-260	-271	76.4	87.8	1.9
F1 6	-264	-266	45.9	50.5	0.87
F4 3	-209	-219	70.9	83.0	3.0
F4 4	-162	-172	43.6	67.5	4.4
F4 5	-209	-222	75.5	124	1.8
F4 6	-337	-346	104	146	0.85

Samples F1 5, F1 6, F4 5 and F4 6 had been exposed for 11 weeks.
Samples F1 1, F1 2, F4 3 and F4 4 had been exposed for 5 weeks.
Odd numbered specimens were on the freely exposed side of the mounting plate.
Even numbered specimens were on the screened side.

Units:
Rest potential and zero-current potential, $E_{I=0}$, are mV vs Ag/AgCl/sea water.
Tafel slopes are mV per 10-fold change in current density.
Corrosion current density, I_{Corr}, is μA/cm^2

Since the results of the computer-controlled experiments presented in Table 6 showed no reproducible differences between the F1 sheathing samples which were corroded and the F4 samples which were not, subsequent polarisation experiments were carried out using a potentiostat and linear sweep generator. These experiments were more convenient to carry out and had the advantage that the polarisation scans started from the rest potential. In the first experiment using this technique the potential was varied linearly from the zero current potential to 70 mV cathodic, back through the zero current potential to 70 mV anodic and then back to the zero current potential again, with an overall sweep time of 10 min (5 min cathodic, 5 min anodic). For the later experiments a range of ± 100 mV was employed. Current/time traces were recorded and, from these the maximum cathodic and anodic currents were read off to provide a measure of the cathodic and anodic polarisation characteristics of the sheathing or strip sample following its sea water exposure.

The results of polarisation scans after exposure periods of 5-33 weeks are presented in Table 7 for sheathing samples and Table 8 for strip samples. Odd numbered samples were on the freely exposed side of the mounting plate; even numbered specimens were on the screened side.

The 5-week exposure period ran from June to July 1992
The 7-week exposure period ran from April to June 1992
The 10-week exposure period ran from July to September 1992
The 11-week exposure period ran from April to July 1992
The 15-week exposure period ran from June to September 1992
The 26-week exposure period ran from October 1991 to April 1992
The 31-week exposure period ran from September 1991 to April 1992
The 33-week exposure period ran from October 1991 to June 1992

TABLE 7

RESULTS OF POLARISATION SCANS ON SHEATHING SAMPLES

(±100 mV. Sweep time 5 min cathodic + 5 min anodic)

Sample	**Exposure Weeks**	**Initial $E_{I=0}$,mV**	**Maximum Current, µA**	
			Cathodic	**Anodic**
F1, 21	5	-251	34	36
F1, 22	5	-243	28	30
F1, 17	7	-176	41	62
F1, 18	7	-170	40	58
F1. 25	10	-206	50	69
F1. 26	10	-186	33	61.5
F1, 19	11	-195	30	48
F1, 20	11	-183	24	42
F1. 23	15	-201	42	84.5*
F1. 24	15	-214	18	58
F1. 13	26	-180	(8.5)	(14)
F1. 14	26	-184	(8.5)	(13.5)
F1. 11	31	-196	(10)	(15)
F1. 12	31	-179	(9)	(14.5)
F1, 15	33	-186	38	53
F1, 16	33	-190	44	57
F4, 21	5	-285	24	35
F4, 22	5	-214	27	50
F4, 17	7	-213	47	67
F4, 18	7	-239	30	47
F4. 25	10	-203	46	59
F4. 26	10	-236	37	49
F4, 19	11	-246	24	27
F4, 20	11	-237	22.5	37
F4. 23	15	-216	46	59
F4. 24	15	-236	37	49
F4. 13	26	-219	(7)	(14.5)
F4. 14	26	-201	(7)	(14)
F4. 11	31	-155	(6.5)	(14)
F4. 12	31	-137	(5)	(12.5)
F4, 15	33	-206	39	62
F4, 16	33	-233	33	46

Maximum currents shown in parentheses are for ±70 mV sweeps.

* Abnormal anodic polarisation curve.

TABLE 8

RESULTS OF POLARISATION SCANS ON STRIP SAMPLES

(±100 mV. Sweep time 5 min cathodic + 5 min anodic)

Sample	Exposure Weeks	Initial $E_{I=0}$,mV	Maximum Current, µA	
			Cathodic	Anodic
S3, 21	5	-212	12	23
S3, 22	5	-261	19	18
S3, 17	7	-212	43	58
S3, 18	7	-201	37	53
S3. 25	10	-207	53	69
S3. 26	10	-206	37	72
S3, 19	11	-199	40	47
S3, 20	11	-199	45	51
S3. 23	15	-215	24	89.5*
S3. 24	15	-224	32	53
S1. 13	26	-154	(8.5)	(14.5)
S1. 14	26	-139	(13)	(22.5)
S1. 11	31	?	(12)	(19.5)
S1. 12	31	-100	(13)	(22.5)
S1, 15	33	-199	51	62
S1, 16	33	-189	45	61
S2, 21	5	-236	17	25
S2, 22	5	?	22	33
S2, 17	7	-205	50	62
S2, 18	7	-200	51	63
S2. 25	10	-212	35.5	51
S2. 26	10	-189	22	56
S2, 19	11	-205	51	57
S2, 20	11	-180	34	44
S2. 23	15	-224	39	60
S2. 24	15	-220	29	54
S2. 13	26	-218	(3.5)	(9)
S2. 14	26	-164	(3.5)	(9)
S2. 11	31	-180	(10)	(17)
S2. 12	31	-210	(9)	(16)
S2, 15	33	-220	44	57
S2, 16	33	- ?	40	51

Maximum currents shown in parentheses are for ±70 mV sweeps.

* Abnormal anodic polarisation curve.

6. DISCUSSION

6.1. FOULING

The fouling at Loch Carron consisted principally of small barnacles and mussels with broad flat green fronds of sea lettuce. This fouling was very heavy on the plastic coated frames but the metal specimens remained free except for a few barnacles which settled on an S2 sample between March and July 1991 (after 12-16 months exposure). Brown filamentous weed was found entangled in the mesh but not adhering to it or to the frames. Slimes associated with diatoms - principally *Amphora* - formed on the F1 and S2 samples but there was practically none on the F3 and S1 samples. These showed only silty deposits with a few diatoms on the F3 and practically none on the S1. At Emsworth where filamentous diatoms predominated there was little difference in the extent of settlement on F1 and F4 but the S1 samples again showed very much less. It appears therefore that the presence of iron in solution in the alloy at the 1.5% level, as in F4 and S2, does not affect the settlement of diatoms but that inhibition of settlement occurs when the iron is out of solution and the iron-rich black or dark green film forms, as in F3 and S1.

Settlement of filamentous diatoms and associated slimes in the second series exposures at Emsworth was greater on the freely exposed samples than on the screened samples. It appears that, with the test specimens exposed broadside-on to the tidal flow, the shear stresses developed were insufficient for these deposits to be swept away, as they would be on a boat hull in service. Hard fouling at Emsworth consisted only of periodic deposition of small barnacles. No mussels were seen and no adherent sea lettuce. There were two periods when heavy deposition of sea squirts occurred and ascidians settled on the Perspex frames during most of the second series of experiments. None of these types of fouling settled on the metal specimens.

6.2. CORROSION

6.2.1. Mesh samples

Throughout the whole period of the tests none of the mesh samples developed the flaky non-protective type of corrosion product found on the low-iron F1. Generally no significant corrosion occurred - just the formation of a thin adherent golden brown film on the M1 samples and a slightly thicker adherent black or dark green film on M2. There was however a period between November 1990 and March 1991 when the upper submerged part of the M1 samples and the fixing bolts within the same area suffered slight, very uniform, corrosion producing a film-free bright metal surface very reminiscent of the severely corroded band on the experimental fish cage as described in Section 2.1. No similar band of attack occurred on the M2 samples at the same site. Since this attack occurred over the winter/spring period, it is possible that it was due to stratification following snow melt on the surrounding hills, as was suggested as a possible cause of the fish cage corrosion. The lower severity of attack on the test samples could be due to the much lower ratio of mesh-in-salt-water (cathode) to mesh-in-fresh-water (anode) compared with the fish cage. It was hoped that a similar band of attack would be produced on M1 mesh samples in the second series of exposures. Unfortunately the samples exposed in September 1991 were lost in the storm. Those installed in February 1992 showed no attack. These were probably in place early enough to experience the snow melt period but without sufficiently long prior exposure for a cathodically active film to develop on the lower part.

6.2.2. Sheathing samples

The exposures at Emsworth showed consistent differences between the low-iron F1 or F2 specimens and the correct-iron F4 specimens. F4 developed protective golden brown or green brown films with no patches of corrosion apart from a few very small areas on some of the Series 2 samples. The F1 and F2 samples all showed patches of corrosion producing non-adherent cuprous oxide which tended to break away when samples were lifted out of the water and to curl away from the surface as samples returned to the laboratory dried out. The difference in behaviour between F1 and F2 sheathing was demonstrated most clearly by the results from the back-to-back samples reported in Section 4.4.4. and illustrated in Figures 1 and 2. These tests also show a much greater susceptibility to corrosion of F1 samples when they are shielded from tidal flow. The results fully support the suggestion that the corrosion which occurred on Seamogs and Roebuck (Section 2.2.) was the result of the low iron content of the sheathing material (F1 or F2) combined with the idle periods experienced by these vessels - conditions corresponding to those for the shielded F1 samples in the back-to-back test.

The second series of tests at Emsworth showed less difference between the freely exposed and shielded specimens - probably because, as noted in Section 6.1., the specimens were exposed broadside-on to the tidal flow and the water velocity parallel to their surface would therefore have been much lower than for the series one specimens which were exposed with their faces parallel to the tidal flow.

At Loch Carron there was little difference in corrosion resistance between the low-iron F1 and the correct-iron F3. F1 formed a protective golden-brown film while F3, which was magnetic and so presumed to have part of the iron out of solution, formed a protective black film.

The type of film developed on F1 during exposure depended upon the initial surface condition of the material as illustrated in Figure 1A. The part of the specimen which carried an air-formed tarnish film formed a green film during exposure whereas the part which had been abraded to bright metal formed a brown film. It has been noticed in examining F1/F2 sheathing on boats on which it is performed satisfactorily that some panels formed a green protective film while others formed an equally protective brown film. It appears probable that this difference is the result of differences in the initial condition of the panels before they were applied to the hull, as a result of variation in storage conditions (eg time of storage and whether the panel was wrapped, in the middle of a pile or exposed to the atmosphere) producing differences in the extent to which the panels had tarnished. It is suggested that bright panels produced a brown film while tarnished panels produced a green film.

6.2.3. Strip samples

None of the strip samples showed any serious corrosion but, whereas the S2 samples formed thin golden brown films, the S1 samples formed the black films typical of material with iron out of solution. S2 samples at Emsworth and Loch Carron behaved similarly but the S1 samples at Loch Carron developed black films which were thicker than those formed at Emsworth and tended to blister with very shallow pits beneath the blisters. It is suggested therefore that, although as noted in Section 6.1. the material with iron out of solution shows least deposition of diatoms, the tendency of the black iron-rich film to blister means that the material with iron in solution is, over all, preferable.

6.2.4. Relationship between corrosion and microfouling

On all the F1 samples which suffered significant corrosion it occurred beneath slimy deposits of diatoms. It is possible therefore that the influence of high water flow rates in assisting F1 sheathing to form a satisfactory protective film may be because it sweeps away diatoms which do not, consequently, build up to form a slimy deposit. The presence of a slimy deposit would be expected to reduce the degree of exchange between the cuprous chloride formed as the major initial corrosion product on the metal surface and the oxygenated sea water outside. This would result in build up of cuprous chloride to a level at which its solubility product was exceeded. Subsequent, relatively slow hydrolysis of the cuprous chloride produces a cuprous oxide deposit which is separated from the metal surface by the cuprous chloride beneath it and is consequently non-protective and exfoliates on drying. With free flow of water over the metal surface the initially-produced cuprous chloride is hydrolysed as rapidly as it is formed to produce a protective cuprous oxide film on the actual metal surface.

6.3. ELECTROCHEMICAL MEASUREMENTS

The absence of any correlation between the potential measurements made on samples in situ in the Series 1 experiments and the corrosion behaviour of the specimens concerned was not very surprising since the potential measured under such conditions depends upon a variety of factors. The measurements were carried out more in hope than expectation that they would provide useful results. The polarisation measurements carried out on Series 2 samples after exposure were expected to yield information on the extent to which the corrosion or passivation of the samples was dependent upon the reactions occurring on the anodic and cathodic areas. The failure of the experiments to yield any consistent results was unexpected and no explanation for this can be advanced.

7. CONCLUSIONS

7.1. PERFORMANCE OF FISH CAGE MESH

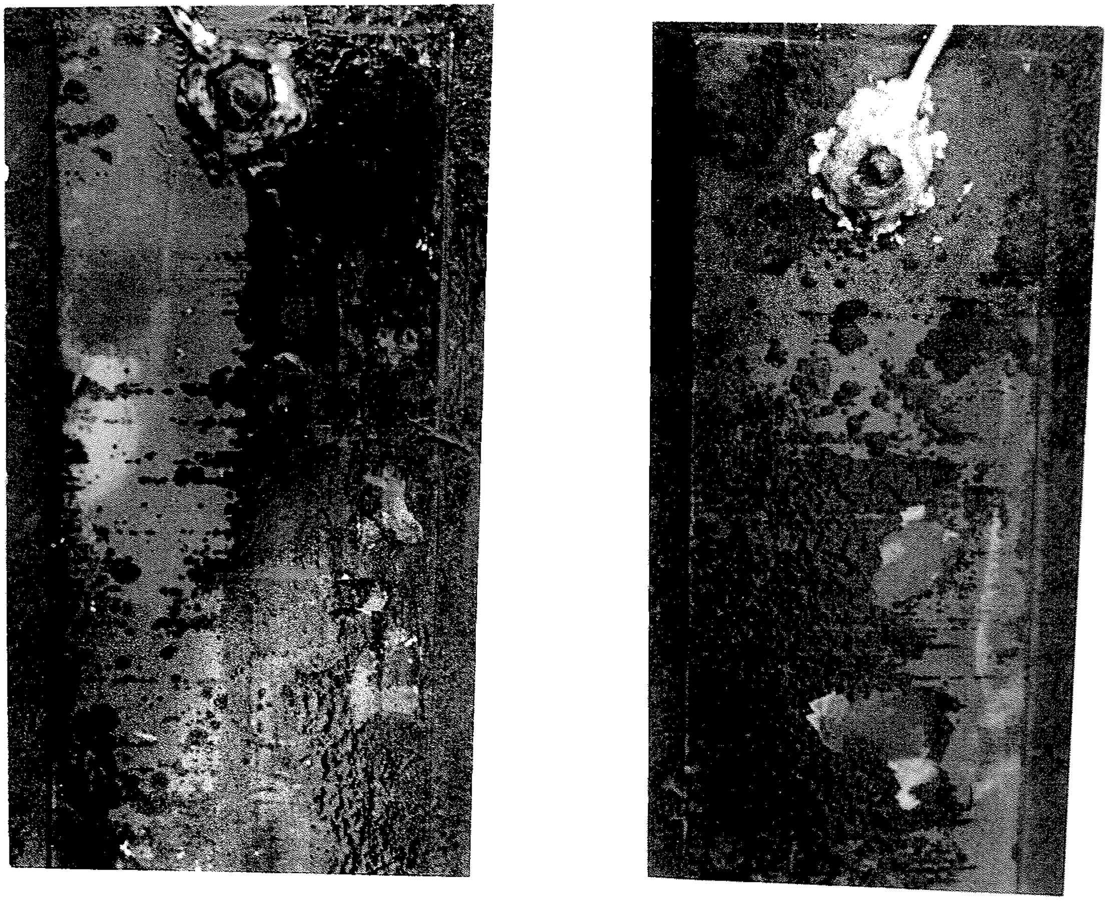
The fish cage mesh showed complete resistance to macrofouling, whether hard shell at Loch Carron or soft (sea squirts, ascidians etc) at Emsworth and also to microfouling by diatoms. The absence of microfouling possibly results from the topography of the mesh inducing local eddies in the water flow which discourage settlement. The development of a bright area on the M1 mesh sample at Loch Carron between November 1990 and July 1991 is of particular interest because of its similarity to the attack that occurred on the top 150 to 200 mm of the fish cage described in Section 2.1. as "the second failure". This result lends some support to the theory that the attack was the result of stratification between snow melt water near the surface and sea water beneath. It is unfortunate that the samples exposed at the corresponding time in the following year were lost in a storm so the result was not confirmed.

7.2. PERFORMANCE OF SHEATHING MATERIAL

The experiments confirmed the impression gained from earlier work that the low iron sheathing material F1/F2 can perform well in respect of resistance to both fouling and corrosion but is liable to severe corrosion under low-flow exposure conditions.

Sheathing material F4 with the correct iron content performed similarly to the strip material of correct iron content which was tested earlier in resisting both fouling and corrosion under conditions which caused severe attack on F1.

It is concluded that sheathing material of composition meeting BS CN102 or UNS C70600 can be relied upon to behave satisfactorily under any likely conditions of service. Neither BS CN102 or UNS C70600 specifies whether the iron should be in or out of solution in the alloy but, as 90/10 copper nickel is generally specified for resistance to erosion corrosion for which it is necessary to have the iron in solution, the material is usually supplied in that condition. Since, however, the 0.010" sheathing, F3, was supplied with the iron out of solution, the relative suitability of the two forms of the material for sheathing needs to be considered. The evidence from service experience of the F3 patches on Dido and the results of exposure tests of F3 sheathing at Loch Carron and of S1 strip at Loch Carron and Emsworth indicates that material with the iron out of solution is as resistant to macrofouling as material with iron in solution and rather less liable to diatom fouling. It has no apparent susceptibility to severe corrosion of the type suffered by the low-iron sheathing F1/F2 but, since the black film on some S1 samples at Loch Carron developed blisters with very shallow attack on the metal beneath, it is recommended that sheathing material should be manufactured under conditions that result in the iron being fully in solution.

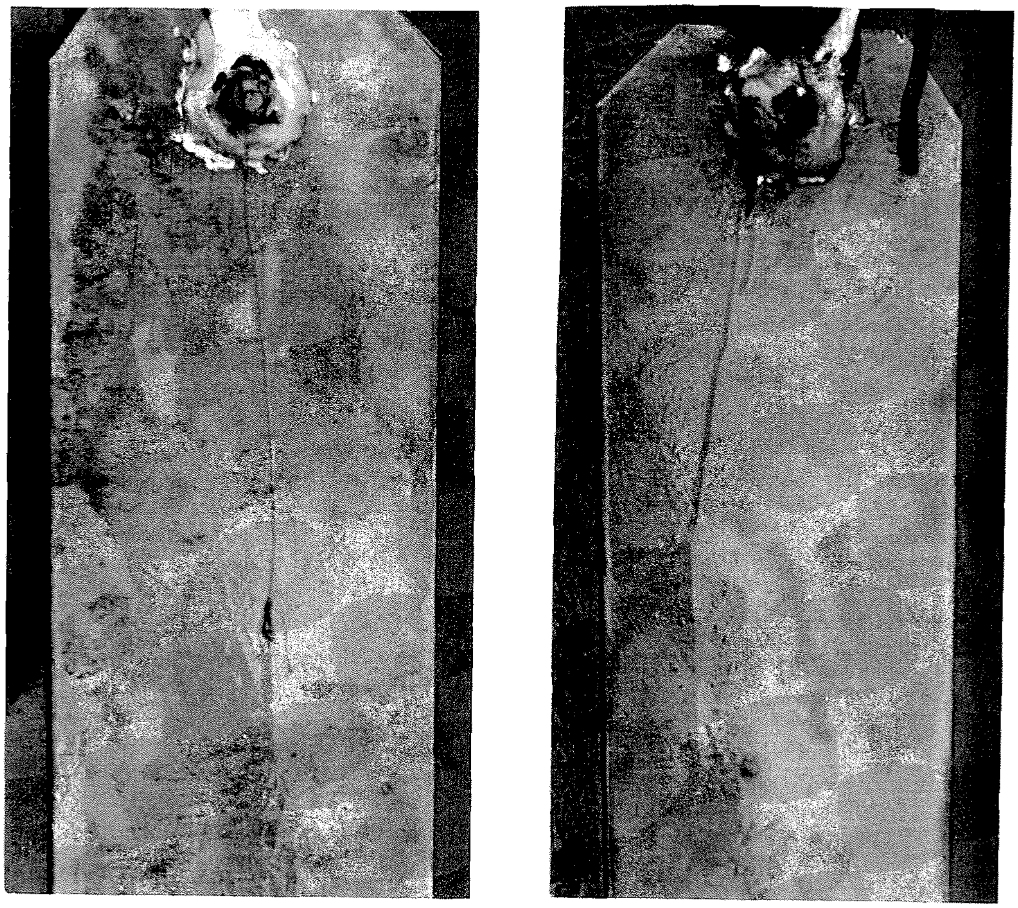


1A. Outward facing

1B. Inward facing

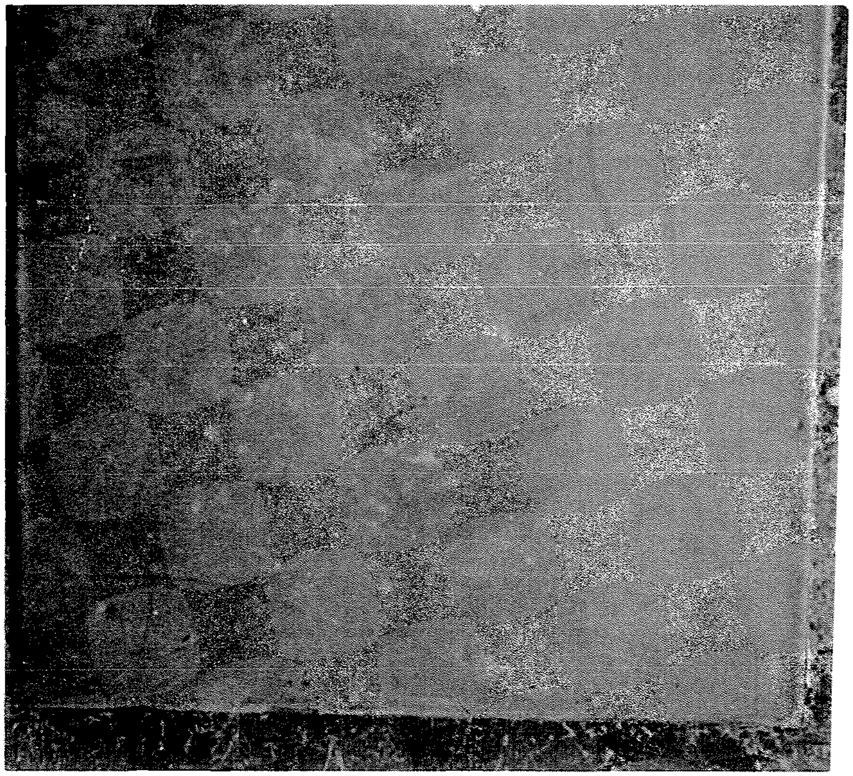
1C. Lower part of inward facing sample after drying

Figure 1. Back-to-back samples of F1 sheathing: Emsworth.



2A. Outward facing

2B. Inward facing



2C. Lower part of inward facing sample after drying

Figure 2. Back-to-back samples of F4 sheathing: Emsworth.

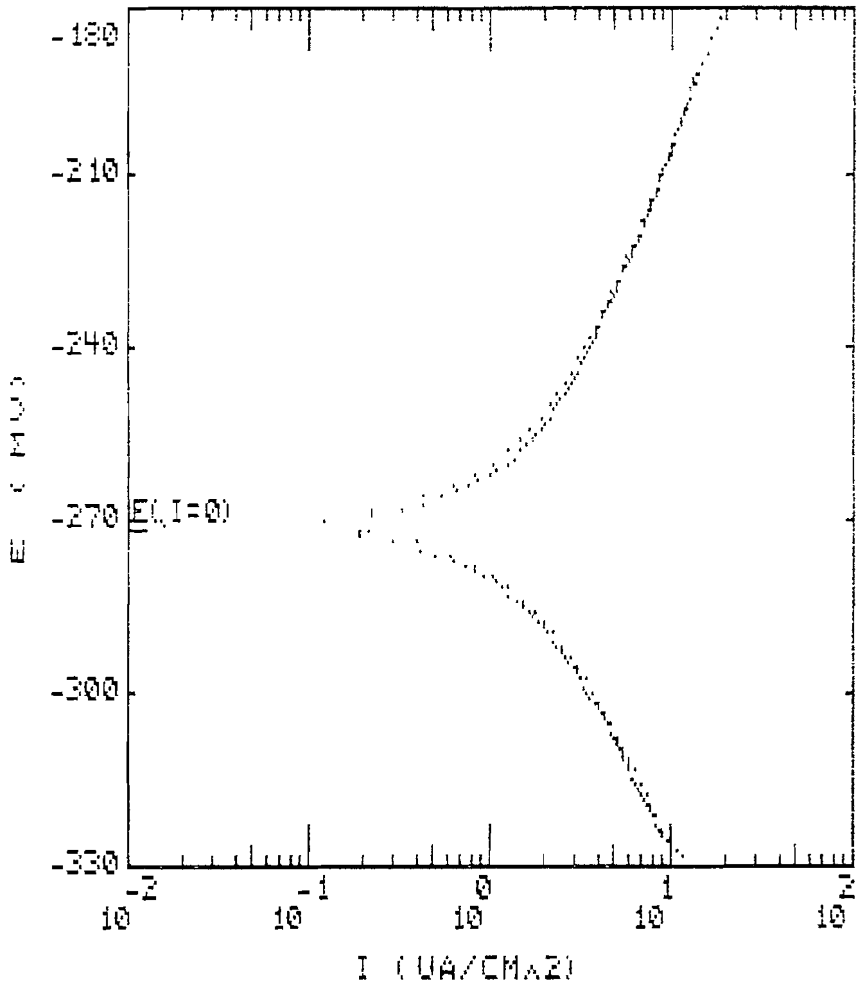


Figure 3. Tafel scan and calculated Tafel points for Sample F1 5.

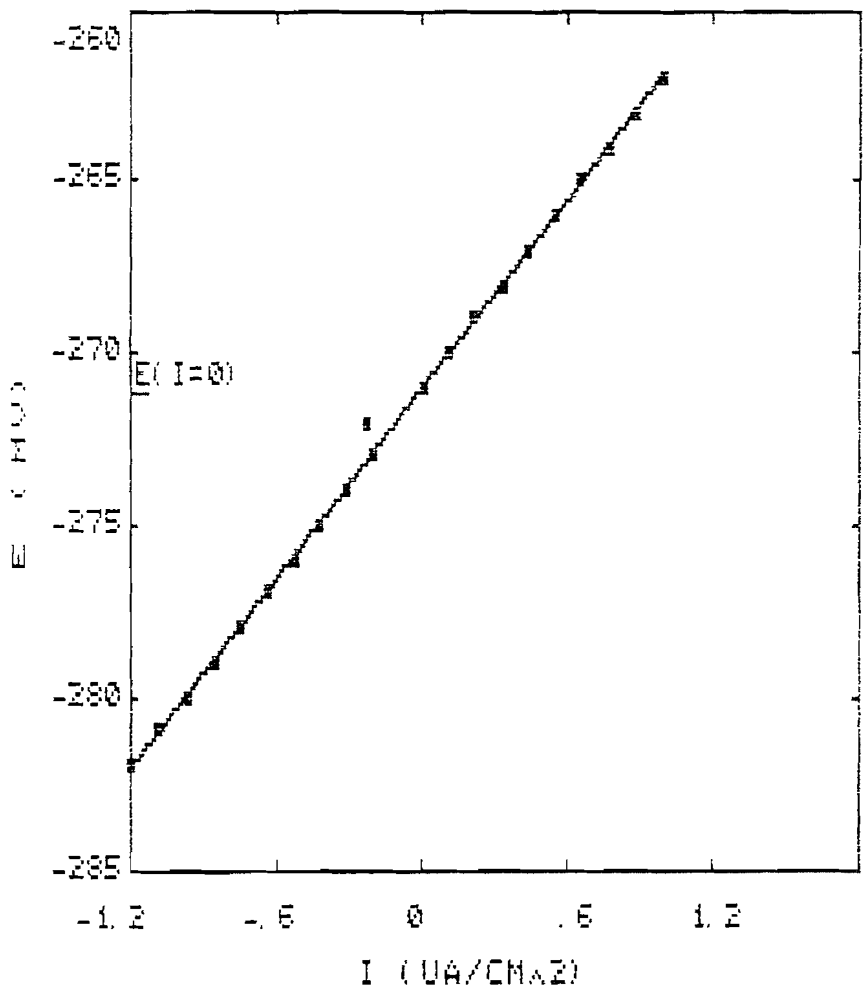


Figure 4. Polarisation resistance plot and calculated best-fit for Sample F1 5.

APPENDIX

Compact flowthrough electrochemical cell

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Technical note

Compact flowthrough electrochemical cell

H. S. CAMPBELL

Details are given of the construction and use of compact, plastic bodied electrochemical cells incorporating working, reference, and counter electrodes, which are cheap and easy to make and have been used in test rigs and in laboratory experiments.

© 1993 The Institute of Materials. Manuscript received 27 January 1993; in final form 19 April 1993. The author is in the Department of Materials Science and Engineering, University of Surrey, Guildford GU2 5XH, UK.

The compact flowthrough polarisation cell shown in Fig. 1 is easily and cheaply manufactured in the laboratory. It employs a working electrode set in a metallographic mount with a silver/silver chloride reference electrode mounted in a glass tube cemented into a conducting bakelite mount which serves as the counter electrode. The resultant composite electrode and the working electrode are held at opposite ends of a cylindrical opaque plastic cell with inlet and outlet tubes to permit upward flow through the cell. The exact dimensions of the components of the cell are not important provided that the tip of the reference electrode is located 1–2 mm from the working electrode. Those given in the following description proved convenient in practice.

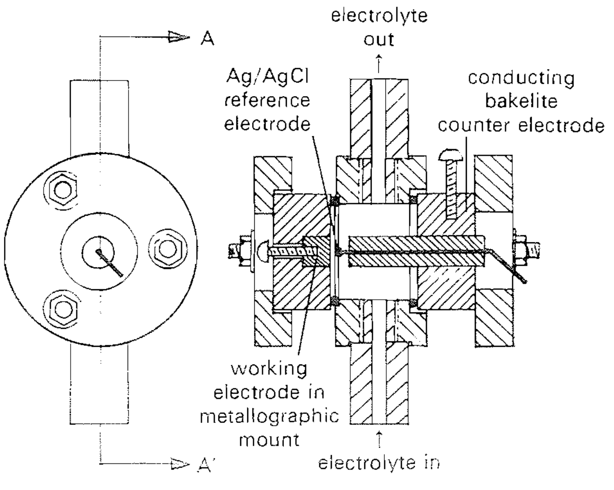
The cell was made from a 25 mm length of polytetrafluoroethylene (PTFE) tube with an o.d. of 50 mm and an i.d. of 25 mm. One end face was counterbored to 31 mm dia. for a depth of 5 mm to locate the counter electrode–reference electrode assembly against a 2·2 mm dia. cross-section O ring. The opposite face was counterbored to 28 mm dia. for a depth of 1·5 mm to locate a similar O ring against which the mount of the working electrode was retained. Inlet and outlet tubes of 15 mm o.d. and 4 mm bore were screwed into the body of the cell immediately opposite one another and seated on 16 mm dia. spot faces. The threads were sealed with PTFE tape.

The working electrode was a 7–8 mm length of 7·9 mm dia. phosphorus deoxidised copper rod mounted centrally in a 30 mm dia. non-conducting metallographic mount, giving an exposed cross-sectional area of 50 mm^2. To ensure a tight mount, diallyl phthalate was used for the part of the mount in contact with the copper. The mount was drilled centrally from the back with a 6 BA clearing size drill and a corresponding blind hole in the copper electrode tapped to receive a 6 BA brass screw which provided the electrical connection to the electrode. The electrode was ground wet on 1000 grit aluminium oxide paper, rinsed with water and methanol, dried in a current of warm air, and stored for 24–72 h in a desiccator before use.

The counter electrode was a 30 mm dia. blank metallographic mount made from conducting bakelite which was drilled and tapped radially for a 6 BA brass screw to provide the electrical connection. It was also drilled longitudinally at its centre to accept a thick walled glass tube which carried the reference electrode.

The reference electrode was prepared by fusion welding lengths of 1 mm dia. silver wire and copper wire end to end, using a butane blowlamp. The silver wire was cut approximately 15 mm from the weld and the end fused to produce a ball of approximately 2 mm dia. The silver/copper wire assembly was inserted into a thick walled glass tube with a bore slightly greater than 1 mm and cyanoacrylic adhesive (Bostik Superglue 4) used to seal it in position with the ball end of the silver wire approximately 1 mm beyond the end of the tube. The glass tube was then fitted into the counter electrode, its position being adjusted so that, when the cell was assembled, the tip of the reference electrode would be 1–2 mm from the working electrode. This was conveniently achieved by placing the cell, working electrode side down, on a flat surface and placing the counter electrode in the opposite side (top), with the O ring in position on the working electrode side but with none on the counter electrode side. The glass tube carrying the reference electrode was slid through the counter electrode until the ball end was resting on the flat surface. Superglue 4 was then introduced into the narrow annular space between the glass tube and the counter electrode to seal it in position. When this had set, additional Superglue was introduced at the opposite end of the annular space. After this had also set, the exposed part of the silver wire was lightly abraded to remove any extraneous Superglue, cleaned by immersion for a few minutes in 25% nitric acid, rinsed, and immersed in a 1% solution of cupric chloride for 3–4 min to form a coating of silver chloride on the silver. The coated electrode was thoroughly rinsed in running water and kept immersed until required for use.

The cells were designed originally for incorporation in copper water pipe test rigs. For this purpose, the working electrode and the composite reference–counter electrode assemblies were held in position by retaining rings made from 10 mm Perspex sheet secured by three equally spaced 2 BA brass studs with nuts and washers. The nuts were screwed up only finger tight, giving effective sealing without danger of compressing the O rings sufficiently to bring the reference electrode into contact with the working electrode. The working electrode was located correctly by using a retaining ring counterbored to 31 mm dia. for a depth of 5 mm, as shown in Fig. 1. The cells were connected into the test rig using 15 mm BS 864 Type A compression fittings of dezincification resistant brass (CZ 132). For experiments in the laboratory the compression fittings were replaced with 4 mm o.d. plastic tubing pushed into the inlet and outlet



1 *Plastic bodied compact flowthrough cell: see text for dimensions and materials of construction*

connectors and the required electrolyte was passed through from a 1 l reservoir at 1 l h^{-1} by a peristaltic pump. Since a silver/silver chloride reference electrode is employed, the electrolyte must contain chloride. The cell has been used successfully with electrolytes ranging from sea water to a supply water containing 15 mg l^{-1} Cl.

The cells have also been used for conducting polarisation experiments on flat samples of 90–10 copper–nickel which had been exposed for various periods in the sea and returned to the laboratory in sea water. The samples were jig drilled with three holes before exposure so that they could be slipped over the 2 BA threaded studs of the test cells in the place of the mounted working electrode and clamping ring and secured by the nuts and washers.

The cells are particularly suitable for use in experiments where tests are to be run over a period with a number of cells operating under a variety of conditions – covering, for example, variations in electrolyte composition or working electrode pretreatment. For such experiments it is convenient to replace the individual retaining rings at the counter electrode–reference electrode ends of the cells by a single, suitably drilled Perspex sheet which can support all the cells. If mounted working electrodes are used and the pressure is low, as in laboratory experiments with pumped electrolyte, the retaining rings can be dispensed with by adopting a modification devised by the Center for Environmental Biotechnology at the University of Tennessee.[1] The cell is counterbored at each end deep enough to accommodate an O ring retained in an annular groove. These O rings retain the working and counter electrodes in position as well as providing seals.

The compact flowthrough cell was designed and used for research projects at the University of Surrey concerned with microbiological influences on corrosion of copper water pipes and with the corrosion and fouling resistance of 90–10 copper–nickel in sea water – both sponsored by the International Copper Association. These two projects will be reported in detail in the relevant journals.

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