CONSIGLIO
NAZIONALE
DELLE RICERCHE

ISTITUTO SPERIMENTALE
TALASSOGRAFICO
"A. CERRUTI" TARANTO

8th INTERNATIONAL CONGRESS ON MARINE CORROSION AND FOULING

ABSTRACT BOOK

with the sponsorship of:

C.O.I.P.M.
COMITE INTERNATIONAL PERMANENT POUR LA RECHERCHE
SUR LA PRESERVATION DES MATERIAUX EN MILIEU MARIN

E.F.C.
WORKING PARTY ON MARINE CORROSION OF THE
EUROPEAN FEDERATION OF CORROSION (Event No. 185)

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September 21-25 1992
TARANTO (ITALY)

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Under the auspices of

ASSOCIAZIONE ITALIANA METALLURGIA
SOCIETA' ITALIANA DI BIOLOGIA MARINA

PAPER SESSION

PROLUSION

MICROFOULING

MARINE CORROSION (General)

FOULING COMMUNITIES

MICROBIALLY INDUCED CORROSION

FOULING CONTROL SYSTEMS

PROTECTIVE COATINGS

CATHODIC PROTECTION

POSTER SESSION

PAPER SESSION

ON SOME APPLICATIONS OF ELECTROCHEMICAL THERMODYNAMICS AND KINETICS TO THE STUDY AND CONTROL OF MARINE CORROSION

M. Pourbaix
CEBELCOR, Bruxelles (Belgium)

The author recalls the joined action of the two twin-organizations CITCE ("Comité International de Thermodynamique et Cinétique Electrochimiques", now "International Society of Electrochemistry I.S.E.") and CEBELCOR ("Centre Belge d'Etude de la Corrosion") both born in Bruxelles in 1949/1950, for promoting the applications of electrochemical Thermodynamics and Kinetics in respectively general electrochemistry and corrosion.

He mentions some results of this action related to marine corrosion and suggests that further research be conduced by international teams working on the three following topics:

- Setting-up of <u>Atlases of Equilibrium Diagrams in the presence of an aqueous solution</u> (potential/pH diagrams) containing derivates of chlorine and of sulphur, from 25 to 300 °C.
- Setting-up of <u>Atlases of Equilibrium Diagrams in the presence of a gaseous phase</u> (potential/temperature diagrams) for oxides, chlorides and sulphides, from 2000 to 6000 °K.
- <u>Electrochemistry of localized corrosion</u> ("occluded corrosion cells o.c.c.").

MARINE MICROFOULING WITH SPECIAL REFERENCE TO SPORE ADHESION IN FUNGI

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A wide range of organisms colonize substrata submerged in the sea. The growth of many can be controlled by the use of specific biocides (e.g. barnacles, *Enteromorpha* growth). However, microbial fouling of marine structures remains a problem, in particular bacteria and diatoms. As biofilms are studied in greater detail, there is a greater appreciation of the diversity of microorganisms involved. One poorly known group are choanoflagellates which can be early colonizers of surfaces exposed in the sea.

Biofilms are not persistent, but are dynamic, as they may be formed, breakdown, "slough-off", and the surface be re-colonized by the same or different fouling organisms. The role of amoeba in the disruption and "sloughing-off" of biofilms is discussed.

The mayor part of the talk will be devoted to fungi and their role in colonizing substrata in the sea. Fungi form an ephemeral biofilm on organic substrata submerged in the sea, prior to colonization of the substratum. Substrata involved included timber structures, senescent leaves (e.g. mangrove, *Posidonia*) sand grains, even manmade materials such as polyurethane.

The sequence of attachment of fungal propagules to surfaces will be followed: repulsion and attraction forces; entrapment; initial attachment mediated by sticky appendages or spore walls; spore germination and secondary attachment by germ tube development and the secretion of mucilage that forms the hyphal sheath around the mycelium. The strength of attachment of spores to surfaces will also be considered. These stages will be illustrated by light microscope micrographs and scanning transmission electron micrographs.

EFFECT OF CULTURE CONSTITUENTS AND ALLOY COMPOSITION ON GROWTH OF SULFATE REDUCING BACTERIA (SRB)

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Although culture of corrosion causing bacteria remains one of the most sensitive and reliable techniques for field and laboratory studies, many recommended media are less than optimal for maximum growth. This is true even for sulfate reducing bacteria (SRB), which are among the easiest to detect the most commonly studied. There is no "standard" medium for culture of SRB, so each researcher must use one of a variety of available media or formulate a new one. The most common approach quoted in the literature today is a "modified Postgate medium". The modification is seldom specified and often authors do not specify which of Postgate's SRB media is modified.

In addition, much of the work on growth of SRB does not take into consideration the effect of the medium constituents on metal. This study was designed to test the effect of important constituents of the medium on bacterial growth on a variety of alloys.

A partial factorial design was used. Four levels each of five culture conditions were tested, together with the amount of the medium constituents salt, iron, sulfate and yeast and the effect of time. Six alloys were tested under all of these conditions in media with and without bacteria collected from actual bacterial consortia present in Ontario Hydro intake heat exchanger cooling water from Lake Ontario. They were: 304L, AL-6XN, Sea-Cure, Titanium, Sanicro 28, and Incoloy 800. All coupons were incubated at 35°C for up to a maximum of 36 weeks.

Data were analyzed using parametric and non-parametric analysis of variance, as appropriate.

The composition of the medium was an important factor in determining the number and size of bacteria on the alloys. Sodium chloride, iron, sulfate, and yeast and time, were all extremely significant in determining attachment by bacteria. Maximum bacterial numbers were achieved with highest salt levels (16.4 mg/L sodium chloride), in spite of the fact that the bacteria were sampled from fresh water.

Although maximum numbers of bacteria were found on samples with the highest iron content, the relationship is clearly not linear. Growth declined with addition of iron until the highest level (0.345 mg/L ferrous chloride).

Increasing sulfate leads to increasing numbers of bacteria relationship. The best growth was achieved with 5.64 mg/L magnesium sulfate.

The relationship between yeast and bacteria numbers is parabolic, with the highest numbers achieved with minimum (0 yeast added) and maximum yeast addition (1.5 mg/L).

The relationship between time and bacteria numbers appears to be exponential. After a lag time, numbers increased rapidly with increasing time of incubation.

There was a significant "edge effect" of attachment by bacteria. Fewer bacteria were found near the edges of the 20 mm sample coupon than in the centers.

There were no statistically significant differences in the number or size of bacteria found on the alloys. That is, bacteria attached to all alloys indiscriminately.

These results indicate that components of the most common SRB media do not contain the optimum concentrations of nutrients for SRB growth. Because of the significant edge effect coupon size may also be limiting and small coupons may lead to unreliable results. In addition, bacteria attached to all alloys tested without preference, indicating that factors other than bacterial abundance are also important in determining corrosion rates of individual alloys. The influence of the medium on corrosion of these alloys forms the second part of this study and will be reported later.

MARINE CORROSION AND TESTING FOR SEAWATER APPLICATIONS

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A brief review will be given of the main factors which make seawater such a corrosive fluid. Some modern developments in marine corrosion control and the peculiarities of marine corrosion testing will be discussed.

CORROSION IN SEAWATER

Corrosion in seawater depends on a large number of variables. A number of these are connected with the alloy as i.e. overall chemical composition, microstructure and surface state. Others are related to the environment, as kind and concentration of redox system(s) which may provoke the corrosion reaction, the presence of compounds which form stable complexes with the dissolved metal ions, etc..

Finally there are a number of physical factors which - depending on the particular system - ma y exert a considerable influence. Examples of these are i.e. potential temperature, stress and flow velocity.

Generally seawater from the open seas can be considered as a dynamic aqueous system, containing dissolved salts, gases and organic compounds, undissolved material and living organisms. The dissolved inorganic material comprises almost all known elements, sometimes in several ionic and molecular forms.

The major constituents as Cl^-, SO_4^{2-}, Br^-, Na^+, K^+, Mg^{2+} and Ca^{2+} account for over 99.85% of the total dissolved salts. The variations in the concentrations of these species with location and depth are generally rather small. Of the minor components in particular dissolved O_2 and CO_2 are important. Dissolved CO_2 is part of the well-known carbonate/bicarbonate equilibrium reactions, which form the main basis for the buffering capacity of seawater and its relatively high pH. The oxygen concentration depends on factors as temperature and salinity. Biochemical processes are also involved, as the concentrations of dissolved carbon dioxide, oxygen and hydrogen ions are closely coupled through the processes of photosynthesis and biochemical oxidation (respiration). The variability of the minor compounds with location and climatological conditions is much larger.

As typical chemically oriented factors which are important in relation to the corrosivity of seawater must be mentioned:

1. oxygen content, 2. dissolved carbon dioxide, 3. high dissolved salt content, 4. calcium and magnesium ions, 5. organic compounds, 6. biological activity, 7.sulphates and hydrogen sulphide, often linked to the presence of organic pollutants and low oxygen content, and 8. heavy metal ions.

More physically oriented factors are: 1. temperature, 2. mass transfer and flow, 3. potential, 4. pressure, and 5. light and illumination.

Generally the corrosion of metals in seawater is strongly affected by the formation of films on the metal surface. These films may be passive films, corrosion product layers, calcareous layers, bacterial films and macrofouling layers or combinations thereof. It is obvious that the effect of the layers is very dependent on both the nature of the layer itself and the underlying metal. So the ability to control and monitor the layer formation is often essential for corrosion control.

CORROSION CONTROL

For an efficient control of corrosion a well-structured materials selection and the adherence to a number of basically simple design rules are very important. Both measures can be adherent to always and everywhere.
However, to modify the environment is not generally applicable, its application mostly being limited to closed systems, like seawater distilling equipment, etc.. Generally the same holds for the addition of inhibiting and/or scale removing substances. However, in a number of cases actions like this are being applied successfully, as for instance the addition of biologically active components.
The application of coatings remains a very important method of corrosion protection. The coatings vary between metallic (in the form of thin layers as well as linings), synthetic resins, rubbers, tar, concrete, paint, ceramics, mortars, etc., or combinations thereof.
Regarding cathodic protection significant improvements can be noted, both in the translations of the theoretical principle of the method into practical rules and codes of practice, as in the development of the actual equipment for control and monitoring.

MARINE CORROSION TESTING

All improvements in materials and protection methods require testing. The ultimate choice of a test method depends strongly on the purpose of the test. So for a first ranking or screening generally accelerated laboratory tests may suffice. However, to be able to say something about the actual service performance in-servie or field tests of sufficiently long duration are essential. Due to the many variables involved such testing aimed at obtaining data on the corrosion performance of alloys in practical situations is a complicated problem. This is the more true for marine applications because of the often overriding influence of layers on the corrosion behaviour. The choice of the test environment is very important in this area. As we have seen there can be a large deviation between the corrosivity of seawater at different locations, in particular at coastal areas, where the water may be brackish and/or polluted to quite different degrees. Apart from using the naturally found seawater for testing, it is also necessary to have knowledge of the peculiarities of seawater. For instance, it is well documented that also the use of recirculated or previously stored seawater may give rise to quite deviating results, depending on the alloy system. So generally synthetic simulations and transported and/or recirculated seawater are only suitable for accelerated laboratory tests intended for ranking and screening purposes.
Finally attention will be given to actual corrosion testing, and in particular regarding some local types of corrosion, i.e. galvanic and crevice corrosion.

CONCLUDING REMARKS

Notwithstanding the many improvements in understanding and technological means to combat and control marine corrosion is still a large problem, of which many aspects require more full understanding. An important area to which this applies is to be found where the formation of layers of whatever nature takes place.

HIGH CYCLE CORROSION-FATIGUE CRACK PROPAGATION BEHAVIOUR OF API 5L -X 65 STEEL IN SALT WATER

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It is widely recognized that corrosion-fatigue is a potentially important failure way both for offshore structures and submarine pipelines. The main factor which determines the fatigue life of welded steel structures is the fatigue crack growth rate since the possible presence of flaws eliminates much of the fatigue crack initiation period. A damage tolerance analysis approach for the evaluation of the safe service life of a structure should rely upon the knowledge of the actual fatigue behaviour of the steel, namely, of the fatigue crack growth rate. This crack growth rate must be determined under test conditions which conservatively simulate the operating ones.

Corrosion-fatigue, in particular for marine structures, is a complex phenomenon controlled by numerous mutually interacting variables: these are related to the loading conditions, the stress states, the structural steel properties and the environmental factors which govern the electrochemical reactions involved in the crack-tip corrosion processes.

An experimental program has been started, aimed at the study of the corrosion-fatigue crack growth behaviour of pipelines in salt water. For the testing program a API 5LX65 steel, microalloyed, fine grained and with very low carbon content (C=0.037%) has been selected. Pipeline sections with 30 in. diameter and 23.8 mm wall thickness, obtained by the UOE process, are circunferentially welded with a combination of semiautomatic GMA and automatic GTA welding processes. Both base and weld materials are being tested; this paper deals with the experimental results so far obtained on the base material. The studied steel has exhibited high ductility and good notch toughness at temperature down to 253 k.

CT specimens ($B=18x10^{-3}m$, $W=72x10^{-3}m$), were fatiguated under constant load amplitude, following ASTM E647-88 Standard, in laboratory air ($RH \leq 50\%$) and in aerated salt water (3.5% NaCl solution, not buffered, with pH=6.5). The following fatigue variables were used both for pre-cracking and crack growing : $P_{max}=12kN$, R=0.2, sinewave loading at f=10Hz (in air) and f=0.5Hz (in salt water). Pre-cracking was conducted in air so as to have a stress intensity factor range, ΔK, between 9 and 10 MPa√m. These variables were selected so as to simulate specific underwater pipeline situations when high cyclic bending stresses can be imposed to long free spans. However, high loads resulting from cumulation of quasi-static and dynamic loads can not be excluded during the laying from a barge or when current flow around the pipe gives rise to turbulence. Both for high load ratios and loading frequencies ($\geq$0.5 Hz), mechanical effects govern the crack growth which practically occurs without environmental influence. Under conditions of medium stresses and low frequencies (0.05Hz), a stress corrosion process can be activated, which largely enhances the crack growth rate.

The air fatigue data of the base steel fitted the Paris equation in the intermediate region of the curve da/dN vs ΔK ($C=2.58\ 10^{-12}$, $m=3.33$). SEM fractographs show that the crack propagation took place by ductile fracture mechanisms: fatigue striations on the favourably oriented grains and tearing fracture are evident and, at high ΔK values (>16-18 MPaVm), secondary cracks are visible.

Through the fatigue tests in aerated salt water at room temperature, under free corrosion conditions (corrosion potential values between -0.670 and -0.680V vs SCE), the ferric ion formation caused a slight decrease both of the pH and the dissolved oxygen content. Crack growth in salt water environment occurred by true corrosion fatigue in ΔK range of 9-15 MPaVm and by stress corrosion fatigue at higher ΔK values.

SEM fractographs, obtained after removal of the corrosion products, show the occurrence of complex fracture mechanisms: tearing fracture, quasi-cleavage, intergranular fracture and secondary cracks in the low ΔK range. At higher ΔK smoothed profiles of tearing fracture and cleavage are evident while secondary cracks are not detected.

DEVELOPMENT OF HIGH STRENGTH LOW ALLOY STEEL FOR MARINE APPLICATIONS.

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The considerable importance of the exploration and exploitation of the sea bed demands a reliable steel construction for marine structures. In most cases commercially available carbon steels have been used as the basic construction material. Due to the very corrosive marine environment - to be divided into the sea bed, the sea water zone, the tidal zone, the splash zone and the atmosphere - it appeared necessary to invest heavily in the application of corrosion protective measures like cathodic protection and coatings. Nevertheless, large sums of money have to be spent both on maintenance and on keeping the protective system operational.

To help solving the problem a programme of investigation was set up to develop low alloy steels combining a better resistance to sea water corrosion with a higher mechanical strength. Although it will not be possible to omit corrosion protection completely, it is expected that such steels will require less protection, possibly resulting in considerable cost savings as well as in a larger life time expectancy.

The first step in the programme was a literature survey to investigate the possible effects of chemical composition and microstructure on the corrosion behaviour of low alloy structural steels in sea water.

The conclusions as to uniform corrosion were as following:

- no effect was observed on long term exposure results of heat treatment and microstructure.
- the effect of alloying elements is dependent on the type of marine environment, i.e. corrosion during immersion may differ from effect in the tidal or splash zone.
- the effect of alloying elements is time dependent, i.e. beneficial effect after a short exposure does not guarantee the same after long exposure times.

As to pitting corrosion Ni appeared to be unfavorable under immersion conditions while Cr had very little effect. This situation was reversed in the tidal zone.

The second step in the programme was the exposure of experimentally prepared and commercially available high strength low alloy (HSLA) steels at a depth of 45 and 90 m in the North Sea. The influence of alloying elements (C: 0.01 and 0.15%; Al and Cr: O and 1.5%; and Mo: 0, 0.5 and 1.5%) on general, pitting and crevice corrosion behaviour was investigated. A statistical analysis of the experimental data yielded the following conclusions:

- the general corrosion rates of the best alloys are a factor 2-4 lower than the reference steel similar to steel Fe 510.

- This lower corrosion rate is accompanied by a lower pitting susceptibility, no influence on crevice corrosion was observe
- Al and Cr are lowering the general corrosion rate.
- Al and Mo show a negative influence on pitting corrosion.
- no significant effects of C on the corrosion behaviour was detected.

The third step in the programme consisted of a further optimization of the alloying elements to improve the corrosion resistance. To avoid the time consuming exposure in practice in the North Sea sixteen experimental alloys were exposed in natural flowing sea water in the laboratory and in the harbour of Den Helder at a depth of 8m for a period of 2 years.

The following conclusions were drawn:

- Al and Cr are beneficial as to general corrosion.
- Cr is beneficial in lowering maximum pit depth.
- Mo has no effect on pitting corrosion.
- although no severe crevice corrosion was observed all alloying elements tend to increase crevice corrosion susceptibility.

These conclusions are in agreement with those found in step two of the programme. The laboratory trials showed that it is possible to make a qualitative ranking between the best and worst alloys as to corrosion performance but no more than that. Moreover the differences found in the laboratory are less pronounced than in practice.

The fourth step in the programme consisted of a technological optimization of the best alloys found as to corrosion performance in the previous development steps. Four alloys with a systematically varied concentration of Al (0.4 and 0.8%) and Cr (1.0 and 1.5%) were investigated on their weldability and cathodic protection current demand. Corrosion behaviour of coal tar epoxy coated alloys under immersion conditions and in the tidal zone were also investigated.

Steel Fe 510 was included as a reference. All materials have been exposed in the North Sea at a depth of 50 m during 1.7 year.

On the basis of these investigations a welding procedure tor the new HSLA steels was set up and a suitable consumable was chosen.

It was again confirmed that the addition of 0.8% Al and 1.0% Cr lower the general corrosion rate and also the pitting corrosion susceptibility.

It was expected that the new HSLA steels under cathodic protection would have a lower current demand as compared to steel Fe 510. However, from cathodic polarization measurements in the laboratory and galvanic coupling with zinc anodes (in immersion at 50 m depth and in the laboratory) no significant difference in current demand could be found.

The coal tar epoxy coated and scribed steel panels showed a decreasing delamination behaviour in the tidal zone compared to the reference steel. The amount of delamination from the scribe depends on the position in the tidal zone. The largest amount of disbonding is found between the high and the low tide levels.

Finally it could be concluded that it is possible to produce a weldable and paintable HSLA-steel with improved general and pitting corrosion resistance.

CORROSION MONITORING IN THE CONDENSERS OF THE PORTO CORSINI POWER PLANT THERMOELECTRIC UNITS 1 AND 3: CHEMICAL TREATEMENT EFFECT

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The management of seawater-cooled steam condensers with copper-alloy tubes includes chemical treatment of the seawater with ferrous salts and Taprogge-ball cleaning systems so as to ensure a suitable corrosion protection and a satisfactory heat exchange.

In order to assess the effectiveness and to optimize this treatment, a corrosion monitoring system was installed in 1989 in two thermoelectric units of the Porto Corsini power plant.

This CISE-designed system is called MACC (Condenser Corrosion Automatic Monitoring) and is based on the corrosion measurement by means of the linear polarization resistance (LPR) technique.

The MACC system consists of a corrosimeter with multiplexer, maintenance software and up to 32 probes installed in the water boxes as tube extensions. This paper deals with the results yelded by the corrosion monitoring of the aluminium brass and 70/30 copper-nickel alloys in the condensers of the 70 MW thermoelectric unit 1, which only works at intervals, and the continuously operating 156 MW thermoelectric unit 3.

The management of the latter includes Taprogge-ball cleaning and the use of ferrous chloride as a corrosion inhibitor. The effectiveness of these treatments was assessed in comparison with the former which receives no treatment at all.

Three years of monitoring showed that in each thermoelectric unit the two alloys under test behaved in a similar manner. Their corrosion rate in the treated unit 3 was eight times lower than in the untreated unit 1. In this assessment allowance is made for normal running and startups periods after the hydro-lance cleaning of the tube bundles, an operation which removes the protective film from the tubes. The reported data showing a significant decrease in out-of-service periods due to tube breakage confirm the effectiveness of the chemical and cleaning treatments.

The discontinuous treatment used when the unit is operating under normal running conditions (1 ppm Fe^{++} for 1 hour/day) is unsuitable during the condenser startups when the continuous one (1 ppm Fe^{++} for 24 hours/day), ensuring a fast and satisfactory film growing, should be used. The latter should also be used whenever abnormal operating conditions destroy the existing film.

Results also confirm the importance of the MACC system for treatment control and the implementation of a correct condenser management.

CORROSION RESISTANCE OF STEEL REBARS IN MORTARA SPECIMENS WITH SANTORIN EARTH

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INTRODUCTION

It has been repeatedly reported that the use of blended cements improve the performance of concrete against the chloride attack and consequently against corrosion. A Greek natural pozzolan, named Santorin Earth, has long been in use for making blended cements showing very good pozzolanic properties. The influence of the addition of Santorin Earth in cement on the resistance of the reinforced concrete against corrosion was studied in a project of long-term exposure in chloride solution.

MATERIALS AND METHODS

Two mixes of Ordinary Portland Cement (OPC) with 15% and 30% Santorin Earth (SE) were tested, using as reference pure OPC. Cylindrical mortar specimens (L= 10 cm, Φ= 4cm) with an axially embedded steel bar were used as test specimens. They were subjected to submerged exposure in 3.5% NaCl solution up to 30 months. Reinforcement potentials were measured during the exposure vs a SCE. The corrosion rate was determined by measuring the gravimetric weight loss (GWL) of the bars, as well as according to the Stern-Geary electrochemical method at defined exposure ages. For the determination of the electrochemical weight loss (EWL) experimental B values for the relation $I_{corr}= B/R_p$ were calculated for all types of specimens as a function of GWL and R_p. Additionally, the total and the soluble chloride contents of the mortar of the exposed specimens were measured by an ion selective electrode. The chlorides linked with the hydration products of the cement were detected in the same samples as chloroaluminate hydrates by XRD analysis.

RESULTS AND DISCUSSION

The potentials of OPC specimens fall very soon to values more negative than those of OPC+SE specimens. All measured potentials are very negative and this should be due to the exposure conditions of this work, which may be considered if limited oxygen availability. The differences of the potential between the types of specimen could predict a more positive performance regarding corrosion for those containing Santorin Earth.

The gravimetric weight losses measured up to 18 months of exposure do not seem to be influenced by the admixture content. After this age the specimens with OPC+SE are possibly more corrosion resistant than the reference OPC ones. This observation is in agreement with that stated above about the development of the potential.

The EWL, calculated as a function of GWL and R_p, indicate more clearly that the mix with 15% SE has a higher resistance behaviour to corrosion than the reference OPC (Fig.1).

All total chloride concentrations measured for the OPC specimens after 18 months of exposure seem to be lower than the corresponding for OPC+SE ones. However, the soluble chloride content of both OPC+SE mixes is almost the same and lower than that of OPC specimens (Fig. 2). The XRD analysis justify the results of the total and soluble - chloride determinations by showing that in OPC+SE specimens more chlorides have been bound in the hydration products than in reference OPC specimens. This proves a more positive performance of cements with Santorin Earth than pure OPC regarding resistance against corrosion.

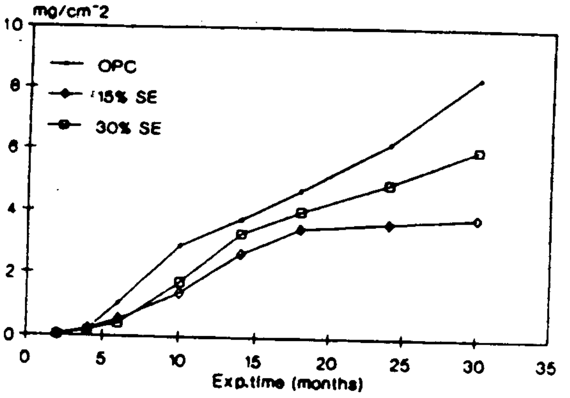

Figure 1 : Electrochemical weight loss vs exposure time.

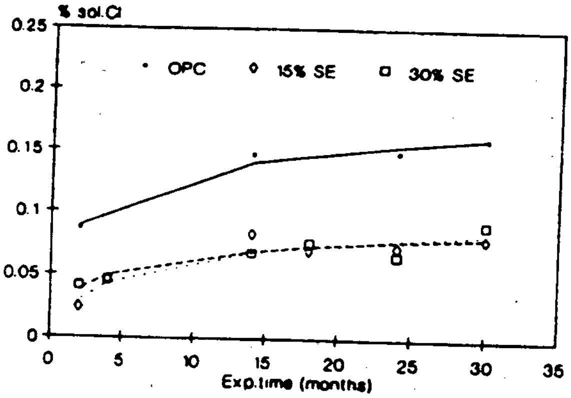

Figure 2 : Soluble chloride content vs exposure time.

CONCLUSIONS

- The OPC+SE specimens appear to be more corrosion resistant than the reference OPC specimens at exposure ages above 18 months.
- This better performance of the OPC+SE specimens is related to their lower soluble chloride content despite their higher total chloride content in comparison to the reference OPC.
- Cements containing Santorin Earth bind more chlorides in their hydration products than pure OPC. This results in a less aggressive environment and consequently in a positive effect on the corrosion resistance of steel rebars.

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ACKNOWLEDGEMENTS

Part of this work was performed in context of the BRITE Project 1552-1-1985, which was financially supported by CEC, to which the authors are indebted.

RESULTS OF LONG TERM GALVANIC COUPLING OF STAINLESS STEEL AVESTA 254 SMO TO CuNi10Fe IN SEAWATER

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ABSTRACT

In support of possible round robin testing within the EFC Working Party on Marine Corrosion super austenitic stainless steel AVESTA 254 SMO was galvanically coupled to CuNi10Fe, the galvanic current and the couple potential being measured. The purpose was to investigate the long-term behaviour of the couple, mainly regarding the cathodic reduction of oxygen on the stainless steel. This might be of interest to detect environmental deviations from normal air saturated seawater as the coupling current is expected to depend on the oxygen concentration. The oxygen concentration is an important parameter, albeit not the only one, for the corrosivity of seawater.

EXPERIMENTAL

a. Seawater exposure.

A cylindrical PVC tank of 65 l was used for the exposure. The seawater was supplied continuously to the tank with a flow of 90-120 liters/hour. In the normal situation the seawater is filtered by a sand filter (swimming pool type) before being supplied to the installation. Two 254 SMO plates (40x20x.3 cm) were used, one as a reference and one for the galvanic coupling. For this purpose this sample was electrically connected with two CuNi10Fe plate samples (30.5x21x.15 cm), which were placed facing the 254 SMO plate on both sides, at distances of 7 cm.

b. Electrochemical measuring equipment.

The free corrosion potential of the reference plate 254 SMO as well as the galvanic couple potential were measured against a saturated calomel electrode (manually, one time a day). During the first period of 30 days the current was measured manually as the ohmic drop across a resistor of 10 ohm. Hereafter a zero current ammeter was used.

c. Monitoring the seawater quality.

The seawater supplied to the tank was measured once a day regarding temperature, salinity and pH.

Also during most part of the exposure the redox potential of the seawater was sampled daily, using a platinum electrode.

RESULTS

The experimental results regarding potential measurements, galvanic currents, salinity, pH, temperature and redox potentials will be given as a function of time.

DISCUSSION

The potential of the reference 254 SMO sample is seen to increase on exposure gradually to very high values in excess of +500 mV SCE, i.e. the usual behaviour of this type of alloy due to biofilm formation.

The potential of the galvanic couple is much lower as compared with the stainless steel free corrosion potential - within a range of about -50 to +50 mV SCE - due to the effect of the less noble CuNi10Fe. The rather sharp increase after about 450 days of exposure is due to a forced decrease of the CuNi10Fe surface which was necessary because of heavy corrosion at the water edge.

The galvanic current tends to be much more irregular than the potentials as mentioned before. The average value was 6 µA/cm² (based on stainless steel surface) during the first 100 days of exposure, to reach a level of about 4-5 µA/cm² at the end of the exposure.

The galvanic current data were also compared with data obtained from polarization measurements, obtained by clamping an electrochemical cell on a plate sample, allowing to polarize only a small fraction of the total sample surface. In this way by locating the cell regularly at different positions, polarization measurements can be performed at locations, which have not been polarized before, avoiding possible artefacts due to previous polarization.

Unfortunately it is rather difficult to try to find any correlation between the results of the galvanic coupling experiment and the seawater conditions. During the period of growth of algae the couple potential and the galvanic current do correlate with each other and also seem to do so with the decrease of pH and redox potential. The free corrosion potential of the stainless steel is somewhat irregular during the same period, however, there is a marked similarity in the electrochemical measurements attaining minimum values at about 310-320 days of exposure.

CONCLUSIONS

On the basis of these experiments it is to be doubted whether a galvanic couple as described can be used to assess the corrosivity of seawater. However, it must be borne in mind that the variations in dissolved oxygen content in this location are rather limited, varying between at the most 1-10% supersaturation and 80% under saturation during the period of enhanced photosynthesis followed by bio-oxidation. So the possibility remains that with more adverse seawater conditions a more decisive indication could be obtained from the measured data of the galvanic couple.

Regarding the source of the galvanic current of the couple stainless steel / CuNi10Fe both components must be taken into consideration. Stainless steel is the noble part of the couple. The cathodic current density passed by the surface depends heavily on the formation of a biofilm.

CuNi10Fe is the active part of the couple, the oxidation being made possible by oxygen reduction on the stainless steel surface as well as on the copper alloy surface itself. The oxidation characteristics of the CuNi10Fe are also strongly influenced by the formation of a layer of corrosion products during prolonged exposure.

So in the end, the question is whether - and if so - to what extent the film formation at both metal surfaces constituting the galvanic couple is related to the seawater corrosivity.

EFFECT OF SURFACE TREATMENTS ON CATHODIC POLARIZATION BEHAVIOUR OF STAINLESS STEEL IN SEAWATER

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PURPOSE

So far no systematic study has been undertaken to determine the effect of chemical pickling and passivation on cathodic polarization behaviour of stainless steel in seawater. However, there is a need to understand this effect to ensure optimum corrosion resistance of stainless steel applications in seawater. In this research the influence of some surface treatments on cathodic polarization behaviour of stainless steel (25Cr7Ni-4Mo) in seawater at 25°C has been studied.

METHODS

The surface treatments comprised pickling, passivation and pickling-plus-passivation. Prior to chemical surface treatment all specimens were wet ground. The pickling solution contained 20% nitric acid and 4% hydrofluoric acid. The passivation solution contained 20% nitric acid. In addition the ground condition was used as a reference.
The surface treated specimens were freely pre-exposed in seawater at 25°C during three weeks. Hereafter the specimens were polarized cathodically at -50 mV (SCE) for more than three months. These exposures simulated cathodic polarization of the surface which sustains the cathodic reaction at the onset of localized corrosion. At the end of the constant potential exposures cathodic polarization curves were determined.
In order to verify the effect of surface treatments on cathodic polarization behaviour galvanic coupling exposures were carried out. With this aim the constant potential exposures of the pickled specimen and the passivated specimen were interrupted after approx. six weeks. These specimens were galvanically coupled to crevice corrosion propagating specimens (25Cr6Ni2Mo). After galvanic coupling exposures of one month the couplings were disconnected, and the constant potential exposures of the pickled specimen and the passivated specimen were restored. After ending the constant potential exposures the biofilms formed on the surface treated specimens have been characterized microscopically.
In order to get more insight into the effect of surface treatment on cathodic properties additional experiments have been performed. Firstly the passive current as a function of time of surface treated specimens has been determined at different potentials in deaerated seawater at 25°C. Secondly cathodic polarization curves have been determined from surface treated specimens freely exposed in seawater at 25°C.

RESULTS

From the pre-exposures at free corrosion potential it appears that passivation and pickling-plus-passivation ennoble the free corrosion potential more rapidly and to higher values than pickling and grinding.

From the constant potential exposures it follows that passivation and pickling-plus-passivation develop more rapidly high cathodic currents and reach higher currents than pickling and grinding.

During the galvanic coupling exposures the anodic current, i.e. the crevice corrosion propagation rate, is higher for the coupling to the passivated specimen than for the coupling to the pickled specimen. For both couplings the anodic currents approximate to the levels of the cathodic currents which were reached during the preceding constant potential exposures. After restoring the constant potential exposures the pickled specimen and the passivated specimen return to the former cathodic current levels.

From the cathodic polarization curves, determined after ending the constant potential exposures, it appears that the curves of the passivated specimen and the pickled-plus-passivated specimen are almost identical. Moreover these curves show higher current levels than the curves of the pickled specimen and the ground specimen.

The biofilms formed during the constant potential exposures probably mainly consist of fine slime with organic debris. Extensive bacterial growth is not observed. The biofilms of the pickled specimen and the ground specimen are dominated by the presence of diatoms. Contrarily, diatoms are scarcely present in the biofilms of the passivated specimen and the pickled-plus-passivated specimen.

From the anodic currents as a function of time at potentials in the passive region it appears that the currents of the pickled specimen are considerably higher during the first hour of the exposure compared to the passivated specimen. However, within an exposure of one day the currents of the pickled specimen gradually reach the same steady state level as reached by the passivated. specimen. From the cathodic polarization curves determined after free exposures of one day, it appears that the passivated specimen develops higher cathodic currents compared to the pickled specimen.

CONCLUSIONS

1. A comparison of the effect of chemical pickling and passivation, including pickling-plus-passivation, applied on stainless steel has shown that passivated surfaces develop higher cathodic currents in seawater. The higher cathodic currents increase the susceptibility to initiation of localized corrosion, due to ennoblement of the free corrosion potential, and increase the propagation rate of this type of attack.
2. To explain the difference between the effect of pickling and passivation it has been proposed that passivation preconditions the surface to enhance the oxygen reduction rate more rapidly and to a higher level, which may be attributed to a decreased release of heavy metal ions during the initial stage of the exposure in seawater.
3. Indications have been found that passivation suppresses the growth of diatoms, probably implicating facilitation or decreased hindrance of the reduction of oxygen in seawater.

MEDITERRANEAN MACROFOULING

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The Echeneis or Remora mentioned by Aristotle as early as the 4th century B.C. was the first, albeit mistaken, record of fouling in the literature. The Ancient Phoenicians, Carthaginians, Greeks and Romans were said to have problem of fouling and borers. The first studies on fouling in the modern age in the Mediterranean Sea are those carried out by Hentschel (1923) and Herpin (1935).

The 'sixties saw an explosion of interest in fouling and in various place in the Mediterranean studies by research groups were initiated and many of these groups are still active today.

The 'eighties saw a considerable decrease in interest in fouling and most studies were concerned with the processes of the colonizations of substrata immersed for the purpose of constructing artificial reefs.

A list of 410 papers on Mediterranean fouling is considered; among these papers 306 are Italian, 31 French, 24 Yugoslavian, 17 Spanish, 9 Egyptian, 8 Israelian, 5 Greek, 5 from Monaco, 2 from Syria and one, respectively, from Lybia, Turkey and Tunisia. As with many other research marine subjects, knowledge is concentrated in the N-W basin and the Adriatic Sea. With the exception of Alexandria and Tripoli (Lybia) harbours there is absence of data on fouling along the entire African coast.

Different localities and environments (harbours, coastal waters, offshore, intakes, brackish lagoon, artificial reefs) of the Mediterranean Sea in which fouling studies have been carried out are referred. Most of the papers are concerned with harbour fouling.

The contingent of species which can be considered typical of Mediterranean and, in particular, of Italian port macro-fouling is composed of about 40 animals species, mainly sessile, and about 10 vegetal species; the list is compiled on the basis of the data from the literature and working experience of the author.

Fouling sessile organisms which are best suited to polluted waters (in particular due to urban waste) are : *Balanus amphitrite, Hydroides elegans, Ciona intestinalis, Botryllus schlosseri, Bugula stolonifera*, and secondarily *Bugula neritina, Balanus eburneus* and *Tubularia crocea*.

These organisms are highly resistant and therefore their disappearance from polluted areas in an extremely serious indication of a state of environmental decay.

PHYTOBENTHIC COMMUNITIES ON FOULING PANELS AT LOANO (SAVONA, LIGURIAN SEA)

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Very little is known about fouling algae in the Mediterranean and, in general, about algae in the Ligurian Sea.

In this respect, to widen both these fields of knowledge, artificial asbestos panels, immersed at Loano (Savona, northern Italy) near an artificial reef in a *Posidonia oceanica* (L.) Delile meadow, were examined.

In June 1990, four series of panels were immersed; then periodically, every three, six, nine and twelve months, one of these series was retired and replaced with anotherone. So, throughout one year, four quarter, two half-yearly, one nine month and one yearly series were obtained. In addition, two yearly series, placed the year before (1989), were considered.

Every series consisted of six panels immersed at four different depths (5m, 10m, 18-20m, 36m).

Taxonomic identification was performed. A list of species was compiled and, for each species, the phytosociological order, the finding rate and the reproductive phenology were reported.

Species number was considered for every series. Also, calculation of intersimilarity among the series was made, according to the Sørensen index.

The quantitative analysis was carried out by means of multiple regression. It was possible to test only two factors: depth and length of immersion, as for the season there were no suitable replicates.

From a qualitative point of view, 92 species were found on the whole, among them: 47 Rhodophyta, 23 Phaeophyta, 19 Chlorophyta, 2 Bacillariophyta, 1 Cianophyta plus unidentified Bacillariophyta and Cianophyta. More than 60% of the species found are reported in literature as epiphyte on P. *oceanica*.

Concerning the number of species, from the data obtained all the three factors, depth, length of immersion, season, seem to be relevant. About the four tested depths, it was observed that the number of species dropped with the increasing of depth. In fact, the highest numbers of species were generally found at 5m, while, sometimes, on 36m panels no species was collected.

An opposite trend was observed for the length of immersion: at the increasing of the number of months, the number of species rose. In general the highest numbers of species were obviously found on yearly panels, the highest one (50) on February 1989-February 1990 panels.

As regards season, it was possible to observe, but not statistically confirm, a general trend towards a more evident attachment during spring months (from April to June). In spring 94% of all the species found is reported, and the series including spring months in their immersion period had a high number of species. While, summer-autumn period seems to be the least fit for attachment. The quarter panels immersed in August and retired in November, were poorly colonized, reaching the lowest number of species (12).

Intersimilarity among series immersed at different depth (but for the same number of months) reached middle values, with the highest one equal to 69% (yearly panels) and the lowest one equal to 36% (quarter panels). Also intersimilarity values among panels immersed for a different number of months (but at the same depth) were middle, with the highest value of 52%. The same was observed for the panels the immersion of which began in different months, with the highest value of 64%.

It cames out that the influence of depth is obviously very strong in determining the typology of a community but can be mitigated by the length of immersion. Similarly, this last factor influences the species composition, as it is well-known that the algae, except pioneer species, need a mature substratum to settle.

SHORT-TERM VARIATIONS IN BIOFOULING (GULF OF TRIESTE, NORTH ADRIATIC SEA)

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Most works on the ecology of communities of attached algae have involved the investigation of populations which develop on artificial surfaces exposed in water for a known period of time.

No studies have been carried out on fouling communities which develop on artificial substrata fixed to the sea bottom (North Adriatic Sea).

The aim of this work is to investigate variations in biofouling communities on short time scales. For this purpose a PVC panel with 10 slides was fixed to the bottom and kept submerged for about 30 days in a station in the Gulf of Trieste.

Six samplings were carried out at 30 day intervals from May to October 1990. At each sampling 10 new clean slides were submerged.

Qualitative and quantitative analyses were made on the fouling populations. Temperature, dissolved O_2 and salinity were also measured using a CTD multiparameter probe.

Bacillariophyta, Cyanophyta and Micro-Macrophyta are the most representative and frequent taxa. Dinoflagellates and Ciliates, benthonic and planktonic forms, were also recorded.

In the period investigated all the taxa show quantitative variations and in particular several fall to the minimum during the 3rd cruise (July-August).

The temperature recorded in August (21.34°C) shows an increase of ca. 4°C in comparison with July (16.87°C). On this date the minimum dissolved oxygen value (4.95 mg/l) was recorded and pH and salinity values reach their maximum (respectively pH= 8.42; S (PSU)= 38.4).

According to this data Bacillariophyta are the taxon which is most sensitive to this physical variations while the Micro and Macrophyta seem to be less affected.

EFFECT OF CULTURE CONSTITUENTS AND ALLOY COMPOSITION ON GROWTH OF SULFATE REDUCING BACTERIA (SRB)

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Although culture of corrosion causing bacteria remains one of the most sensitive and reliable techniques for field and laboratory studies, many recommended media are less than optimal for maximum growth. This is true even for sulfate reducing bacteria (SRB), which are among the easiest to detect the most commonly studied. There is no "standard" medium for culture of SRB, so each researcher must use one of a variety of available media or formulate a new one. The most common approach quoted in the literature today is a "modified Postgate medium". The modification is seldom specified and often authors do not specify which of Postgate's SRB media is modified.

In addition, much of the work on growth of SRB does not take into consideration the effect of the medium constituents on metal. This study was designed to test the effect of important constituents of the medium on bacterial growth on a variety of alloys.

A partial factorial design was used. Four levels each of five culture conditions were tested, together with the amount of the medium constituents salt, iron, sulfate and yeast and the effect of time. Six alloys were tested under all of these conditions in media with and without bacteria collected from actual bacterial consortia present in Ontario Hydro intake heat exchanger cooling water from Lake Ontario. They were: 304L, AL-6XN, Sea-Cure, Titanium, Sanicro 28, and Incoloy 800. All coupons were incubated at 35°C for up to a maximum of 36 weeks.

Data were analyzed using parametric and non-parametric analysis of variance, as appropriate.

The composition of the medium was an important factor in determining the number and size of bacteria on the alloys. Sodium chloride, iron, sulfate, and yeast and time, were all extremely significant in determining attachment by bacteria. Maximum bacterial numbers were achieved with highest salt levels (16.4 mg/L sodium chloride), in spite of the fact that the bacteria were sampled from fresh water.

Although maximum numbers of bacteria were found on samples with the highest iron content, the relationship is clearly not linear. Growth declined with addition of iron until the highest level (0.345 mg/L ferrous chloride).

Increasing sulfate leads to increasing numbers of bacteria relationship. The best growth was achieved with 5.64 mg/L magnesium sulfate.

The relationship between yeast and bacteria numbers is parabolic, with the highest numbers achieved with minimum (0 yeast added) and maximum yeast addition (1.5 mg/L).

The relationship between time and bacteria numbers appears to be exponential. After a lag time, numbers increased rapidly with increasing time of incubation.

There was a significant "edge effect" of attachment by bacteria. Fewer bacteria were found near the edges of the 20 mm sample coupon than in the centers.

There were no statistically significant differences in the number or size of bacteria found on the alloys. That is, bacteria attached to all alloys indiscriminately.

These results indicate that components of the most common SRB media do not contain the optimum concentrations of nutrients for SRB growth. Because of the significant edge effect coupon size may also be limiting and small coupons may lead to unreliable results. In addition, bacteria attached to all alloys tested without preference, indicating that factors other than bacterial abundance are also important in determining corrosion rates of individual alloys. The influence of the medium on corrosion of these alloys forms the second part of this study and will be reported later.

SOME PRELIMINARY OBSERVATIONS ON THE ROLE OF BLUE-GREEN ALGAE AS MARINE FOULING ORGANISMS

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Blue-green algae are described as components of marine fouling communities on a wide range of immersed structures throughout the world, including ships, buoys and offshore platforms. They are well known pioneering organisms on newly immersed structures, are quite resistant to toxic antifouling coatings and are particularly important as fouling organisms in tropical/subtropical waters and in heavily polluted environments.

Drawing information from a recently prepared database, a panel immersion programme and some experimental studies using laboratory cultures, the present paper presents an overview of the role of blue-green algae as fouling organisms. Particular attention is given to preparing a check-list/catalogue of fouling blue-green algae and describing the contribution they make to fouling communities on various fixed and floating structures on the south coast of England, including aspects of their vertical zonation, succession, seasonal distribution and resistance to toxic coatings. Some attention will also be given to investigating their mechanisms of attachment.

THE MARINE FOULING OF COPPER-BASED ANTIFOULANTS, WITH PARTICULAR RESPECT TO THE GREEN ALGA *Pseudoclonium submarinum* WILLE

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Results are presented of a panel immersion programme using copper-based antifoulants. The panels were immersed for approximately 18 months from test rafts situated in Langstone Harbour, south coast of England and observations made on the marine algal fouling communities present. Fouling of the panels was initially observed at copper release rates of 22 µg/cm²/day.

The main fouling algae recorded during the field trial comprised species of the genera *Amphora*, *Ulothrix*, *Enteromorpha*, *Pseudoclonium*, *Ectocarpus*, *Hecatonema*, *Streblonema* and *Polysiphonia*.

Particularly interesting was the occurrence of the previously unrecorded fouling alga *Pseudoclonium submarinum* which dominated the surface of the panels after 18 months. Using a bioassay technique based on vegetative growth, this species was revealed to have a broad tolerance to environmental conditions and appeared to be particularly resistant to copper.

These results are discussed in relation to previous studies on copper-based antifouling systems.

MACROFOULING IN THE CHANNELS OF VENICE LAGOON

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Although some data about fouling in the Venice Lagoon were available, it has been necessary to study in two annual cycles, the macrofouling of the three port-channels for the construction of moving bulkheads in order to check the flow of sea water into the Lagoon.

Standard asbestos panels (20x30x0,4 cm) were submerged for 3,6,9,12 months in suitable structures near the bottom (10-12 m deep) in the inner side of the channels of the Lido, Malamocco and Chioggia, from April 1988 to April 1989 and from December 1989 to December 1990. During the second year also substrata of 45 days were submerged in the Lido. 90 species of macrobenthos were identified: of these 17 belong to the Molluscs (above all *Mytilus galloprovincialis* and *Ostrea edulis*), 15 to the Crustaceans, with a prevalence of Amphipods, while Barnacles proved to be surprisingly few in number. There are 14 species of Polychaetes among which Serpulids are the dominant species (*Hydroides dianthus, Serpula vermicularis* and *Pomatoceros triqueter*), 9 species of Ascidians and 8 of Algae: among these *Ulva rigida* C. Agardh and *Gracilaria verrucosa* (Hudson) Papenfuss are the most frequent.

The specific wealth is relatively similar at the three stations and the highest values were reached in the first cycle in Chioggia and in the second one at the Lido.

After one year (in December , second cycle) in Chioggia, macrofouling is characterized by organisms mainly with calcareous shell, such as Mussels, Serpulids and Oysters with a reasonable presence also of *Bugula*, encrusting Bryozoans and Sponges. In the port-channel of the Lido, the community is mainly made up of a thick settlement of Hydroids (above all in the first cycle and on the back of substrata), Oysters, Mussels, Ascidians and encrusting Bryozoans of the genus of *Schizoporella.*

In Malamocco fouling is very similar to that found at the Lido even if there is a lower number of species; Serpulids of genera *Pomatoceros* and *Hydroides* and Bivalves (Mussels and Oysters) are dominant, to which can be added Sponges, Hydroids (*Tubularia crocea*), non-encrusting Bryozoans of the *Bugula* genus, and colonial Ascidians.

On three-month and six-month substrata, the settlement is highly influenced by the season: on the six-month substrata removed in June, colonization both in qualitative and quantitative terms is lower than that to be found on panels removed in September or also in December, after only three months' exposure. At all stations, the most substantial settlement takes place in summer, the least substantial in winter.

The highest values of biomass (wet weight) after one year were found in Malamocco (45 g/dm^2 average value between the two sides in 1990) followed by Chioggia (37 g/dm^2 in 1990), while for shorter periods of immersion the highest weight values can also be reached in the other port-channels.

Bivalves *Mytilus* and *Ostrea*, which can reach a maximum shell diameter of 7 and 6 cm in the space of one year, should be considered as a priority in any possible antifouling system.

In conclusion, we can say that the differences found in the fouling at the three stations are fewer than those found in the different seasons at the same station.

The fouling in the three openings has an high rate of biomass accumulation.

MACROFOULING OF TWO BRACKISH ENVIRONMENTS OF APULIA (LESINA AND VARANO LAKES)

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Fouling settlement of two Apulian (southern Italy) lagoons have been studied by means of asbestos panels during one year. The two lagoons have about the same surface, are very near and are northward to the Adriatic Sea.
The main fouling species recorded on monthly panels are the barnacles *Balanus eburneus*, the tubeworm *Hydroides dianthus* and the polyzoa *Conopeum seureti* in both the lagoons.
The Lesina Lagoon has a fouling biomass of more than 12 kg/m² after three months during spring-summer period. In the same period at the Varano Lagoon the biomass recorded is less than 2 kg/m². The number of macrofouling species is about 20 in the Lesina Lagoon, the waters of which are eutrophic due to the Lesina village sewage discharge. The Varano Lagoon fouling settlement is typically seasonal and 30 species are represented. Among them only some are in common with the Lesina Lagoon where settlement is more continuous along the year.
Also growth in the two lagoons is different: *B. eburneus* in a monthly panel in the Lesina Lagoon is larger than 10mm, that is about the double of the growth recorded in the Varano Lagoon.
The settlement of *B. improvisus* only on the panels of this latter lagoon seems to be occasional and is discussed together with the use of two different sampling methods of fouling communities.

FOULING COMMUNITY ORGANIZATION AT GUANABARA BAY, BRAZIL: A DIRECTIONAL PROCESS OR A VARIABLE TEMPORAL PROGRESSION?

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Owing to the facility of manipulation and development on artificial substrata, subtidal benthic communities have been the focus of many ecological studies evaluating theories of succession. Moreover, in marine hard substrata, the rate of species turnover is very high and changes in the community structure occur very quickly. Those species are, therefore, very useful for investigations on temporal succession.

Some authors suggest that in fouling communities earlier settlers often fill free spaces and inhibit rather than facilitate subsequent invasions. However, others believe the development is unpredictable and ultimately dependent on the life history of each species.

From the knowledge of temporal patterns of community colonization at different seasons, the present study intended to detect the occurrence of ordered and directional succession or even a variable temporal progression which depends on the start of the colonization period of this community.

In the present paper, the main purpose is to find out whether the substrata immersion period has an effect on the successional process of fouling communities in Guanabara Bay (Rio de Janeiro, Brazil).

Since October 1990 a series of five plywood panels (20x20 cm) was sunk at the beginning of each season of the year for a twelve month period (49 weeks). The percent cover of each sessile species was monthly estimated by a non-destructive point sampling technique. Surface water temperature and salinity of the study site was monitored weekly.

Pronounced differences have been established when the 4 studied series were compared as to their descriptive, mathematical (MORISITA's similarity index and the cluster analysis - UPGMA) and statistical aspects (EVENNESS and SHANNON diversity).

A survey of the wealth of species has shown higher values in the winter/91 series (total # = 30 spp), followed respectively by those of spring/90 (total # = 25 spp), autumn/91 (total # = 20 spp) and summer/91 (total # = 18 spp). Colonization curves have demonstrated that the summer series presented the lowest average values, contrasting with the winter series, whose values, from the 4th week on, were the highest.

Differences as to the main components have been noticed, either along the series or between them. In the spring/90, the hydrozoan *Obelia dichotoma* stood out up to the 4th week and the bryozoans *Bugula neritina* and *Schizoporella unicornis* from the 5th week on. Along the summer/91 series, a predominance of only one species (*O. dichotoma*) was noticed, replaced from the 6th month on by ascideans and bryozoans, whereas in the autumn/91, *O. dichotoma* appeared as the community's main component up to the 4th month of development, when several organisms like the hydrozoan *Ectopleura warreni*, Serpulidae, Balanidae, *Bugula turrita*, *B. neritina*, *Watersipora cucullata*, *S. unicornis* and the ascidean *Styela plicata* began to prevail.

Contrasting with previous series, in the winter/91, predominance of the Chlorophyta *Enteromorpha compressa* was verified in the two earlier months, being then replaced mainly by the bryozoan *B. neritina*.

Due to the low species variety, together with the almost absolute predominance of only 3 species (*O. dichotoma*, *B. neritina* and *S. unicornis*) in the summer series, the diversity values has turned out as lower than those of the other series showing the biggest variations.

As an outcome, in the summer, the lowest rate of average community uniformity was recorded (J'= 0.6), followed by the autumn (J' = 0.7), spring (J' = 0.8) and winter (J'= 0.9) ones.

Expressing the great variability of the 4 analysed series, the similarity percent stayed well under 50%. The low similarity values obtained reflect variability in the specific composition and in the local fouling community organization in immersed substrata at different times of the year.

DISTRIBUTION OF Teredinidae ALONG THE SOUTHEAST COAST OF BRAZIL

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The distribution of Teredinidae wood-boring molluscs along the southeast littoral of Brazil was studied. The experiment comprised the coast of the states of São Paulo, Rio de Janeiro and Espirito Santo, through nearly 1000 Km. From South to North, the study sites are located in the following cities: São Sebastião, Ubatuba, Angra dos Reis, Itacuruça, Rio de Janeiro, Arraial do Cabo, Macaé, Guarapari and Vitória. The hypothesis tested was: there is an infestation gradient of Teredinidae along the southeast coast of Brazil, mainly related to biotic factors and to the availability of wood. Abiotic parameters (temperature, salinity, dissolved oxygen and nutrients) were also monitored for comparing the occurrence of the different species to the characteristics of each study site.

For obtaining the biological samples, pine wood (*Araucaria angustifolia)* panels were used. Panels consisted of 10 pine wood sheets, 100 x 100 x 8 mm, set between two pieces of ceramic plates and two pieces of wood. The assembly was held together by two brass bolts (SILVA, 1985). Such a panel allows the removal of the wood-boring molluscs without causing any damage to the organisms. Individuals were withdrawn for counting and identification. The pieces of wood were used for characterizing the fouling community. Ten replicates remained immersed in each station for 3 months (August to October, 1991).

Abiotic parameters, in each station, showed little variation. However, significant differences (mainly related to temperature and salinity) were noticed when comparing the stations among them. Minimum and maximum temperature values recorded were, respectively, 20°C and 25°C. Salinity values ranged from 23 to 38 10^{-3}.

The mean density values were, in general, decreasing from South to North. The values recorded in the southern stations (São Sebastião, Ubatuba and Angra dos Reis) were among the highest found in literature. Such a great infestation (48 to 149 individuals per panel) is inversely related to the observed biomass of fouling organisms. Intense fouling avoids wood-boring larvae settlement and the usually great number of filtering organisms reduces the availability of these larvae in the plankton (SILVA, 1985). In Rio de Janeiro, no wood-borings were found in the panels, due to a high fouling biomass, mainly composed of ascidians, bryozoans, barnacles and other filtering organisms. Nevertheless, a low mean density value was recorded in Vitória (0.1 individual per panel) despite the reduced fouling biomass observed. In this case, the low infestation is related to the occurrence in great amounts (473 to 1643 individuals per panel) of the space competitor wood-boring crustacean *Limnoria tripunctata.* Another factor enhancing Teredinidae infestation levels is the availability of wood. Southern stations are more protected and receive a constant wood supply from the surrounding vegetation (rainforest). On the other hand, northern stations are not provided with arborescent vegetation.

The species largely dominating the panels from the southern stations was *Bankia gouldi*, its mean frequency varying from 58.47% to 92.21%. These data confirm the observations of CLENCH & TURNER (1946), establishing that this is the most common species of the genus *Bankia* and also the most destructive one found in the Atlantic coast. The high percentage number of individuals of *Bankia gouldi* found in Angra dos Reis is not according to previous studies performed in the same area (SILVA, 1985; LAVRAW, 1986; BARRETO, 1988; JUNQUEIRA *et al.*, 1989; JUNQUEIRA *et al.*, 1991). A large dominance of the species *Lyrodus floridanus* were observed by these authors in other stations also located in Ilha Grande Bay. *Lyrodus floridanus* was the second dominant species in Angra dos Reis (mean value = 26.69%).

Northern stations showed no common dominating species, each being dominated by a different one (*Bankia carinata* in Arraial do Cabo, *Bankia gouldi* in Macaé and *Lyrodus floridanus* in Guarapari).

A greater incidence of the species *Bankia fimbriatula* was always related to the study sites where salinity values were lower (Itacuruça e Guarapari). Such values may be attributed to the discharge of many rivers or to domestic effluents. Many authors consider *Bankia fimbriatula* an eurihaline species, tolerating large salinity variations.

Specific composition and dominance of the species were mainly due to abiotic factors such as salinity whereas infestation level was associated not only to salinity but also to other factors such as the quantity and quality of fouling and the wood supply in each area.

THE INTERRELATION OF CATHODIC PROTECTION AND MARINE FOULING

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Cathodic Protection (CP) utilizes the electrochemical nature of corrosion process. CP to a structure is effected through an impressed current or a sacrificial anode system. Both systems generate alkalinity at the cathodic surface leading to precipitation of calcareous scales.Whereas the beneficial effects of CP are widely recognised, the interactions between this protection system and marine fouling are poorly understood. This paper addresses both the effects of CP on fouling and the possible effects of fouling on corrosion of CP steel.

The effect of CP on fouling was studied with mild steel, stainless steel and aluminium substrata, at applied current densities of 0, 1.6, 2.8 and 4.2 X 104mA/cm². This study was specially meant to investigate barnacle settlements. Further to this, the relative abundance of different fouling species corroding and cathodically protected substrata was computed from several replicates covering different seasons. The influence of cathodic polarisation on the shell growth of *Crassostrea madrasensis* was examined in the laboratory. Shell size on control and CP substratum was measured at various stages over a period of 37 days. The possible effects of fouling on the corrosion of CP steel was assessed through a conventional potential-decay study. Following CP at around -1.0 and -0.8 vs SCE in a laboratory aquarium for a month, sets of steel panels were exposed to the natural seawater environment. CP was terminated on transfer to sea. One series was allowed to foul while the other was protected from any growth inside plankton filter cages similar to those described by Relini *et al.*, (1976). OCP was monitored for 20 days.

In the first instance, CP was found to accelerate the rate of barnacle settlements considerably. The acceleration was a direct function of applied current. Studies covering different seasons revealed that the calcareous shell dwellers, *Pomatoceros caeruleus* and *Crassostrea madrasensis*, and a calcareous alga, *Jania rubens* were substantially prolific on CP steel. Laboratory study with *C. madrasensis* confirmed that CP enhanced shell growth in the oyster. It is suggested that the beneficial effects of CP to fouling could result from both surface modification, in the form of roughening, and interfacial alkalinity favouring calcareous shell formation. The study also shows that fouling could be a potential problem to structures that either suffer termination of CP or are underprotected. Implications of the present findings to the performance of fixed offshore structures are considered. Attention is drawn to the LaQue theory of CP which implicates the danger of localised corrosion during underprotection. It is suggested that fouling can very effectively exacerbate such effects.

MICROBIALLY INDUCED CORROSION

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INTRODUCTION

This Plenary lecture will review the recent developments in Microbially Induced Corrosion.

It is widely acknowledged in the literature that metals immersed in a biologically active liquid media, such as seawater, undergo a sequence of biological and inorganic changes that result in an important modification of the metal/solution interface. It is this modified environment that has to be studied in an inter- and multidisciplinary way in order to begin to understand the complexities of microbial corrosion.

The sequence of events leading to microbial corrosion can be rationalised into the following:

- the first stage of the sequence of biological changes is the development of a thin film (approximately 20 to 80 Å) on the metal surface. This film is formed by inorganic ions and high molecular weight organic compounds that alter the electrostatic charge and wettability of the metal surface. In a second stage, bacterial colonization, facilitated by the conditioning film, leads to the development of a biofilm, consisting mainly of water, bacterial cells and their extracellular polymeric substances (EPS). Subsequent stages in the sequence lead to the settlement, development and growth of other organisms, at first microscopic and finally macroscopic.
- Considering just a bacterial biofilm, there has been a tenancy, until recently, to assume that the film is essentially uniform, both physically and chemically. It has long been recognised that, when compared with the surrounding EPS, the small mass of bacteria in the biofilm, as well as the high degree of hydration of the latter suggests that the interfacial system between the metal surface and the seawater environment will be governed by the different transport processes taking place through the EPS of the biofilm. However, recent studies have suggested that the system is considerably less homogeneous. Not only are biofilms "patchy" being thinner or absent in some areas and thicker in others but there is also a heterogeneity on a smaller scale associated with the development of bacterial colonies or consortia and differences in the nature of the EPS away from consortia and immediately surrounding them.
- The mere presence of a ill-defined region between the metal and the electrolyte radically changes the conventional electrochemical concept of an electrical interface as used in inorganic corrosion studies. That the layer is heterogeneous and in a state of flux further complicates the scenario. On one hand the interface now becomes the junction of the biofilm and the metal (the biofilm being vast compared to metal - metal ion reactions), on the other hand important concentrations gradients, changes in the type of ions, pH values, oxygen levels, and redox conditions are occurring throughout the biofilm thickness and will modify the behaviour of the metal surface and their corrosion products.

- Having considered the biofilm and its possible (though largely unpredictable) influences, the sequence of inorganic changes (corrosion and passivation) that is occurring simultaneously with biofilm formation, immediately after metal immersion in seawater but in the opposite direction has also to be taken into account.

- While these reactions are more easily defined they are no less unpredictable in the fouled environment. The complex ionic interactions that can and do take place are not only inorganic or even organic metal ion reactions, they are also biochemical metal ion reactions in that the bacteria are often able, and indeed require, to incorporate the anodically released metal ions into metabolic pathways (as well as other ions).

- We have learnt a considerable amount about these interactions over the past few years and the understanding is gathering pace as difference disciplines and different techniques are brought into the research teams. A good simple example of the result of this is the recent realisation by many research metallurgist and mechanical engineers that they cannot rely solely on data from artificial seawater tests (even when saturated with hydrogen sulphide) to predict fatigue crack growth rates in offshore structural steels but must, in addition, study environments closer to reality.

- However, while the research is clarifying aspects of microbial corrosion, dissemination of the results, particularly in ways useful to design and mechanical engineers, falls well behind. It is of little use (except to the bank balances of consultants) to have considerably advanced in the understanding of microbial corrosion if the simplest failures due to it are still occurring with increasing rather than decreasing frequency.

CONCLUSIONS

Seawater is a highly specialised environment, both for corrosion and for biological activity. The interactions between a corroding metal surface and a developing biofilm in such a medium are complex and cannot be described solely by one methodology. An interdisciplinary and integrated approach is required.

Biofouling and biofilm formation is the result of an accumulation process which is not necessarily uniform in time or space. Thus, a new "biologically conditioned" metal/solution interface is produced, and there is reciprocal conditioning between the passive layers and the biofilms. Thus, while passivity is a process directed from the metal surface to the solution, due to the progressive accumulation of corrosion products on the metal surface, biofouling is produced from the bulk towards the metal/solution interface.

The Electrochemical concepts and parameters used to assess inorganic corrosion (in the absence of biofilms), will have to be adapted to the characteristics of the biofouled metal surface. Thus, a bioelectrochemical approach is required to understand the complex passive layers/biofilm interaction at the metal/solution interface.

Greater emphasis should be placed on disseminating guidelines and "engineer awareness" of potential problem areas.

HOW TO SOLVE CORROSION PROBLEMS ON STAINLESS STEELS IMMERSED IN NATURAL SEA WATER

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Biological activity is responsible for the particular aggressivity of natural sea water; this leads to localized corrosion of stainless steels. The most common way to solve the problem consists in increasing the amount of alloying elements like chromium, molybdenum and nitrogen; an improved ratio between these elements is presented. Another way to solve the problem has consisted in adding poison alloying elements to a 316L stainless steel: among three of them, stain appears to be very efficient in improving the corrosion resistance of the steel in sea water, probably due to a decrease by 90% of the viable bacteria population.

KEY-WORDS: Pitting Corrosion, Crevice Corrosion, Alloying elements, Biofilm, Electrochemical tests

INTRODUCTION

In general, stainless steels (SS) immersed in chloride containing solutions are susceptible to pitting and crevice corrosion. Natural sea-water appears to be much more aggressive than synthetic solutions so that SS of the 300 AISI series are rapidly corroded. Such a behaviour is generally attributed to bacteria which cause the depolarisation of the cathodic reduction of oxygen.

Our research deals with two proposals to fight the sea water corrosivity: the first one consists in improving the pitting and crevice resistance of stainless steels adding sufficient amount of conventional alloying elements (Cr, Mo, N), the second one consists in reducing the role of bacteria by adding poison alloying elements into the steel.

MATERIALS AND METHODS

Considering that austenitic UNS 08 904 and duplex UNS 31 803 grades are not fully resistant to sea water, we prepared several laboratory heats using these material as a basis, and adding various amounts of Cr, Mo and N.

The effect of chromium, molybdenum and nitrogen addition were investigated using laboratory electrochemical tests in 30 g/l NaCl containing solution. The resistance to pit initiation was determined by measuring the so-called "pitting potential" corresponding to the current density break-through taken from the polarization curve. The resistance to pit propagation or crevice corrosion was studied in NaCl solutions acidified in order to simulate the actual conditions inside a crevice; the dissolution current in active conditions and the repassivation potential were used for the material ranking.

Small laboratory heats derived from a 316L grade were prepared by adding poison alloying elements like As (1%), Sn (3%) or Cu (4%).

The effect of these elements on the pitting initiation was investigated by means of the same electrochemical tests as previously described.

The influence of As, Sn and Cu on the processes related to the biofilm was studied using on the one hand electrochemical measurements of the cathodic reaction of oxygen reduction and on the other hand biochemical (total organic Carbon and Nitrogen) and biological methods (bacteria type characterization).

RESULTS AND DISCUSSION

Results obtained with high alloyed SS showed that Cr and Mo are always beneficial, but Mo appears to be more active to fight pitting initiation and Cr is more beneficial to fight repassivation. Nitrogen additions are beneficial only for pitting resistance. Results obtained in neutral chloride solution fit well the well-known formula PREN = Cr + 3.3Mo + 16N (Pitting Resistance Equivalent), but results of experiments carried out in acidified and concentrated chloride solutions lead to propose new coefficients for Cr and Mo; on the other hand, these coefficients are not the same when considering pit initiation or pit repassivation.

Among the three poison alloying elements investigated, Sn appears to be the most efficient; the results clearly demonstrate that after a one month immersion period in natural sea water, Sn addition to the 316L grade decrease by 10% the total bacteria population and that 90% of viable bacteria are killed. One must stress that during the same period, the polarization resistance of the Sn containing alloy is 10 times higher than for others grades and that the oxygen cathodic reduction is less polarized. Together, electrochemical, biochemical and biological investigations demonstrate that Sn addition improves the corrosion resistance of SS in sea water due to a specific effect on the biofilm.

CONCLUSIONS

High alloyed austenitic or duplex SS containing 20-25 Cr, 3-6 Mo and nitrogen are very resistant to localized corrosion in chloride containing media. Nevertheless, the Cr-Mo-N balance must be adapted on the electrochemical situation. In particular, in conditions simulating the medium inside a crevice chromium and molybdenum are very beneficial; the former is more efficient regarding to repassivation and the later is more efficient regarding to initiation. Nitrogen seems to be beneficial to retard pit initiation but does not appear to be efficient for repassivation.

Adding Sn to a 316L grade improves markedly its resistance in natural sea water, due to the effect on the biofilm.

Further investigations are necessary to optimize the amount of Sn taking into account metallurgical problems, but a combination of higher Cr-Mo content and lower Sn addition could be of interest for future industrial developments.

THE ROLE OF SURFACE CHEMISTRY IN SRB-INFLUENCED CORROSION OF STEEL

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AIMS

The purpose of this research was to determine the influence of the composition of steel, in particular the effect of Cr and Mo, on formation of biofilms by Sulphate Reducing Bacteria (SRB) on mild steel (MS) and stainless steel (SS) surfaces in a marine environment. The anaerobic SRB are one of the most important groups of organism causing corrosion of iron and ferrous alloys. Several studies have demonstrated that the adhesion of SRB cells to steel surfaces and the subsequent formation of biofilms plays a critical role in corrosion process. Although a number of mechanisms by which SRB can enhance corrosion has been proposed there is lack of fundamental research focusing on determining basic mechanisms involved in cell/surface interactions. This communication reports a series of experiments performed by using techniques of light and electron microscopy and atomic absorption spectrometry to elucidate the nature of such interactions, thereby helping to design the appropriate corrosion control measures.

The work served as pilot study leading to a major research project on the role of exopolymer/metal ion interactions in marine biocorrosion of steel.

MATERIALS AND METHODS

Biofilms of two different strains of marine SRB were grown in batch cultures at 37°C on the surfaces of mild steel and stainless steel (304, 316) coupons for a period of 3 weeks. Coupons were polished to obtain uniform surface finish. Both bacterial strains used in this study were associated with cases of severe marine corrosion of mild steel. Epifluorescent light microscopy, scanning electron microscopy techniques and dry weight measurements were applied to monitor bacterial attachment to steel over a period of up to 5 hours and subsequent growth of biofilms. SRB exopolymers (EPS) were recovered from the cultures grown in the presence of Cr, Mo and two different concentrations of Fe. The binding capacity of exopolymers of Fe, Cr and Mo was estimated by atomic absorption spectrometry. The effect of Cr and Mo on bacterial growth was assessed by hemocytometer counts and by dry weight measurements of bacterial biomass.

RESULTS

The epifluorescent microscopy revealed that the initial attachment of both bacterial strains to mild steel was significantly increased comparing with the adhesion of cells to stainless steel surfaces. The initial colonisation of stainless steel 304 was greater than that of 316. Scanning electron microscopy (SEM) and dry weight measurements showed the growth of biofilms on mild steel to be significantly greater than on stainless steel. No significant difference has been found in the formation of biofilms between the two types of stainless steel. SEM observation also revealed the abundance of EPS in biofilms on MS surfaces. In contrast, biofilms on SS contained very low levels of EPS. The growth of SRB estimated by cell counts and biomass measurements in the media containing Mo and Cr was reduced comparing with control media. The increased concentration of Fe ions resulted in the increase of bacterial growth rate. The dry weight of exopolymers recovered from SRB cultures varied depending on cultural conditions. The secretion of EPS was greatest in media with high concentration of Fe and lowest in media containing Cr. The Atomic Absorption analysis of the EPS metal binding capacities demonstrated that the EPS had highest affinity for Fe ions and lowest for Cr ions.

DISCUSSION

The results of this investigation demonstrate the importance of the surface chemistry in the process of SRB enhanced corrosion of steel. Bacterial attachment and the rate of biofilm growth are influenced by the type of steel used. This suggests the presence of a mechanism regulating the response of SRB cells to steel. The only difference in the experimental conditions is the chemical composition of steel surfaces. Stainless steel contains Mo and Cr whereas MS does not have these inclusions. The presence of Cr and Mo ions in culture media have a negative effect on SRB metabolism. Apart from slowing the growth rate these ions also inhibit EPS synthesis. This finding is in agreement with works reporting the effect of the metal-ion content of the surrounding environment on the properties of bacterial EPS. One of the functions of bacterial EPS is to enhance the ability of cells to attach to surfaces and this can occur via complexing of metal ions at the metal/liquid interface. The interactions between bacterial EPS and metal ions are well documented. Furthermore, evidence exists that exopolymers exhibit great selectivity in complexing metal ions. Studies on EPS production of some bacterial species showed the expression of EPS to be variable and controlled by genome rearrangement. Cells would regulate the secretion of EPS in response to the presence of the surface. However, the nature of the signal coming from the surface which regulates metabolic activities of bacterial cells remains to be determined. Results of this investigation together with earlier findings suggest that one of the possible mechanisms of signalling between SRB and steel surfaces could be due to an interaction between bacterial exomolecules such as lipopolysaccharides (LPS) or EPS with ferrous and/or ferric ions present at the metal/liquid interface. The requirement of bacteria for metal ions is often of paramount importance for cell growth. The availability of the type of these ions could have a great influence on the preferential colonisation of a surface. The chemistry of the surface could affect bacterial population positively or adversely. In the first case by facilitating the attachment of the cells to the surface via complexing of the metal ions by bacterial surface molecules. In the second case by preventing surface colonisation due to the toxic effect of some of the metal ion species. This study showed that high concentration of Fe ions stimulated the growth of SRB and production of EPS. The evidence exists that LPS of SRB species has a specific iron-binding site. The availability of Fe ions at the MS/liquid interface is greater than that at SS/liquid interface. The passive layer of Cr oxides formed on SS surfaces prevents dissolution of iron making it inaccessible to the cells. Taking these facts into account it can be concluded that the nature of the SRB/steel signalling is most probably due to binding of Fe ions by polysaccharide components of SRB exomolecules.

MICROBIAL INDUCED CORROSION IN CONDENSER TUBES STRUCTURAL MATERIALS EXPOSED TO SEAWATER

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Power plant cooling water systems are frequently affected by biofouling and MIC. MIC occurs in the majority of the materials used for tube construction such as titanium, cupronickel and aluminum brass.

The corrosion behaviour of these metals is usually monitored *in situ* through corrosion potential measurements. A shift of the open circuit potential (OCP) value in the anodic direction has been found when certain metals are exposed to marine environments. This effect, as well as the cathodic current density increase during polarization, have been reported for stainless steel, cupronickels, nickel, cobalt superalloys and titanium (Dexter, 1991; Mollica *et al.*, 1991). However, these effects were not found when the environmental conditions were changed (Little *et al.*, 1990).

The aim of this paper is to study the corrosion potential evolution for aluminum brass and 70/30 cupronickel in seawater contaminated with *V. alginolyticus.*

The experimental methods used in this study were similar to those recently described (Videla *et al.*, 1992). *V. alginolyticus* inoculum was prepared by suspending agar slants in 2 ml of artificial seawater. The inoculum was poured into two Erlenmeyer flasks containing 200 ml of artificial seawater and after inoculation, the flasks were kept for three hours in a rotary shaker. Then, one of the culture media was bubbled with air. A sharp decrease of the oxygen concentration was observed in the cultures without air bubbling.

Metal specimens were 70/30 cupronickel and aluminum brass disks of 7 mm diameter. Each Erlenmeyer flask was provided with several metal specimens for microbial attachment and biofilm observations. Some coupons had electrical contacts for corrosion potential vs time measurements and polarization experiments. Potentials were referred to the saturated calomel electrode (SCE). Metal coupons were immersed for different periods of time in either sterile or contaminated media. Afterwards, polarization curves were made with these coupons using sterile artificial seawater. Bacterial adherence to the metal surface was verified by SEM.

The corrosion potential of aluminum brass immersed in the culture medium with air bubbling showed a shift in the noble direction with respect to sterile control (Fig. 1). The potential shift was in the cathodic direction for those specimens immersed in the culture medium without air bubbling (Fig. 1). Similar effects were observed for 70/30 cupronickel.

These results may suggest that the dissimilar oxygen concentrations in the media could be the only cause of the particular OCP behavior. If this is the case, the difference between the OCP values of the two similar solutions but with different oxygen concentrations, may be lower or equal than the difference between OCP value of an air-saturated sterile solution (OCP_{Ass}) and a deaerated sterile solution

(OCP_{DS}). However, the difference between the OCP values of the specimens immersed culture media with and without air bubblings were higher than the (OCP_{Ass} - OCP_{DS}) difference.

Besides, potentiodynamic cathodic polarization curves showed high negative current densities for the metal coupons that had been previously immersed in the culture media when compared with those previously immersed in sterile medium.

Consequently, there must be other factors than the bulk oxygen concentration which may influence the electrochemical behaviour of the metal specimens. It has been stated that oxygen and pH levels at the biofilm/metal interface are different from those measured in the solution (Little *et al.*, 1990). Besides, microorganisms are capable of changing pH, oxygen concentrations, chloride activity or the nature of metabolic compounds thus inducing or inhibiting corrosion at the metal/solution interface (Dexter, 1991; Videla *et al.*, 1992). Different types of corrosion products have been found in the presence or in the absence of a biofilm on copper alloys (Bremer and Geesey, 1991). It has been suggested that some chemical contained in the slime could also act as a catalyst for oxygen reduction (Mollica *et al.*, 1991). An additional effect may be linked to the peculiar metabolic characteristics of *V. alginolyticus* as a facultative anaerobic microorganism. In poorly oxygenated media the inner layer of the biofilm could be anaerobic even for thin biofilms. Consequently, dissimilar metabolic products could be found at the interface under aerobic or anaerobic conditions.

It can be concluded that physicochemical and biological factors influence the complex electrochemical behaviour of 70/30 cupronickel and aluminum brass in *V. alginolyticus* contaminated seawater. A detailed analysis of each factor is still needed to understand the whole corrosion process.

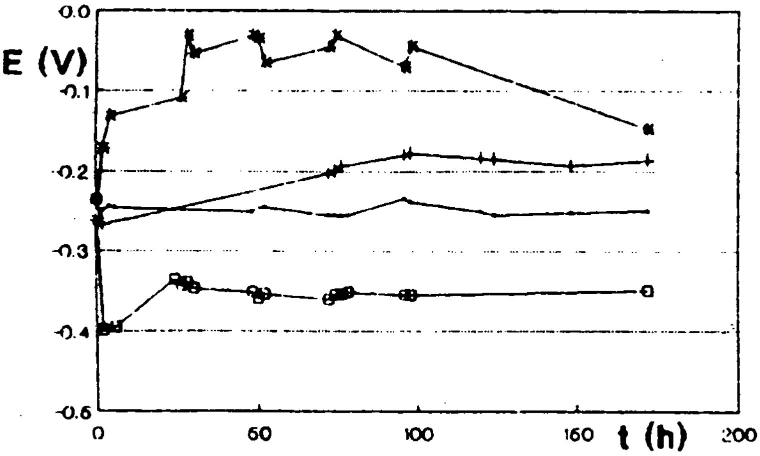

FIG. 1: OCP of aluminum brass immersed in sterile artificial seawater with ( ) and without ( ) air bubbling; artificial seawater inoculated with *V. alginolyticus* with ( ) and without ( ) air bubbling. OCP of aluminum brass in sterile deaerated seawater -0.350 V.

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THE INFLUENCE OF MICROFOULING ON THE CORROSION OF CARBON STEEL IN SEAWATER

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INTRODUCTION

When structures or components are placed in the aerobic, lighted region of the sea, they rapidly become colonised by micro-organisms. The latter can be expected to influence the corrosion processes of metallic materials - especially actively-corroding alloys like carbon steel. This paper describes detailed studies of the influence of microbial organisms, which are usually involved in the early settlement events, on the corrosion of carbon-manganese steel (0.19C%C, 1.25 %Mn, 0.29%Si, 0.01%S).

EXPERIMENTAL METHODS AND RESULTS SUMMARY

Cultures of marine micro-organisms were established from samples collected from the University Marine Biological Station at Millport in the Firth of Clyde and placed in enriched seawater in the laboratory. The cultures were maintained at 15°C with 13 hours per day fluorescent illumination. Two such samples yielded distinctive algal populations. Sample I produced mixed filaments of brown, blue-green and green algae whereas sample II consisted mainly of diatoms with some filamentous brown algae.

Specimens of the C-Mn steel were placed in vessels containing these two microbial communities and, after various periods of time, separate specimens were subjected to anodic and cathodic polarisation. No short-term (i.e. < 1 day) effects were observed in the polarisation characteristics of the steel in the two media but, over longer periods there was evidence of changes in the cathodic-polarization behaviour. Thus, in culture medium II, less-severe cathodic polarisation was seen after 26 and 27 days exposure than after 1-5 days. Similar, though less-pronounced, effects were observed in culture medium I. In contrast, in the control, algal-free, enriched seawater, the steel exhibited opposite trends, that is a steeper cathodic-polarisation curve after 36 days than after 1 day of exposure. The corresponding anodic-polarisation scans, for all the above-described specimens, yielded no detectable differences between the results obtained at the different exposure times quoted above.

Some assistance, in accounting for the different extent of cathodic depolarisation observed in the two cultures, was obtained by some additional experiments carried out on specific diatom species which had been isolated from the cultured sample II. Two isolates, *Achnanthes* and *Amphora* were used for a visual and microscopic study of:

(a) their attachment modes on the carbon steel;

(b) any observable influence of the attachment mechanisms on the corrosion processes of the carbon steel.

It was apparent that the corrosion product forming in the presence of the diatoms was sufficiently abundant to overgrow the diatom layers by the time two weeks had elapsed after admitting the diatom suspensions to the vessel containing the steel specimens. However, the rust layer was loose and porous enough to admit light to sustain the underlying diatoms.

Achnanthes was seen to attach itself to the metallic surface by means of strands produced by mucilage being secreted usually at one corner of the cell and this led to the diatom lying free from the surface. In contrast, *Amphora* cells secured themselves by producing a mucilage pad which had been secreted from all over the surface of the attaching cell and the rapid cell division of the diatom resulted in much of the metal surface becoming covered by the cells. These distinctions were mirrored in variations in the morphology of the corrosion product. In the vessels containing *Achnanthes,* there was evidence of abundant corrosion product with such poor adherence to the steel specimen that the rust was distributed on the base of the vessel all around the metal specimen. In contrast, in the presence of *Amphora* there was a more-dense, adherent layer of corrosion product remaining on the metal surface.

CONCLUSIONS

The correlation of the electrochemical measurements and the attachment studies made in this work has demonstrated that the role of these microbial organisms can be to enhance the lack of adherence of corrosion product forming on carbon steel and, thereby to stimulate the cathodic reaction by facilitating the supply of dissolved oxygen to the metal surface. However, differences in the detailed modes of attachment of distinct microbiological species can be expected to result in variable effects upon the corrosion process of actively-corroding steel in circumstances involving the settlement of different organisms.

ESEM/EDS, SEM/EDS AND EIS STUDIES OF COATED 4140 STEEL EXPOSED TO MARINE, MIXED MICROBIAL COMMUNITIES INCLUDING SRB

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ABSTRACT

Energy dispersive X-ray spectrometer (EDS) analyses detected breaching of epoxy, nylon and polyurethane coatings applied to 4140 steel when coupons were exposed to mixed communities of marine microbes. SEM and ESEM studies have shown that all coated surfaces were heavily colonized with a diverse assemblage of bacteria. These mixed communities consisted of anaerobic bacteria (sulfate reducers) and facultative anaerobic bacteria (non-sulfate reducers). Epoxy, but not nylon coatings were degraded by a non-marine mixed, microbial community including SRB. Some epoxy coatings showed visible signs of coating deterioration (i.e., pinpoint holes, blistering and peeling) after a one month exposure to the mixed communities. ESEM/EDS offered a non-destructive method for observing the relationship of biofilms to corrosive attack of the coatings. EIS was used to assess the properties of the coated steel after exposure to the mixed microbes.

KEY-WORDS: Biocorrosion, MIC, Anaerobic corrosion, Marine corrosion, Sulfate-reducing bacteria, SRB, ESEM/EDS, SEM/EDS, EIS, Coated steel.

INTRODUCTION

Epoxy, nylon and polyurethane coatings are used by the navy and others to protect underlying metals against corrosion. Corrosion is often extremely rapid at small discontinuities in coatings. Breaks or blisters in coatings may allow access of corrosion-inducing microbes, such as sulfate-reducing bacteria (SRB), to the metal beneath. SRB are a diverse group of anaerobic bacteria that can be isolated from many anaerobic environments, but their principal habitat is the marine environment where the concentration of sulfate in seawater is high and fairly constant. Coating deterioration in the presence of an adherent biofilm is of interest to our laboratories. In this report, we describe an investigation of microbial attack on protective coatings using mixed, microbial communities.

MATERIALS AND METHODS

Corrosion coupons (3" x 3" and 3/4" x 3/4") were steel alloy with the following chemical composition (wt%): 0.38-0.43% C, 0.75-1.00% Mn, 0.035% P (max), 0.04% S, 0.15-.030% Si, 0.80-1.10% Cr and 0.15-0.25% Mo. The density was 7.84 g/cm^3.

The surface preparations, primers and coatings were applied following MIL specs. The isolation, maintenance and characterization of the mixed communities containing SRB has been described previously (Jones *et al.*, 1991). At the end of the exposure period of the coated coupons to the mixed communities: (1) a hydrogenase test was performed as described in the Caproco Hydrogenase Test Kit Instruction Manual (Caproco Limited, Edmonton, Alberta, Canada); (2) SEM/EDS analyses involved fixing coupons overnight in 2.5% glutaraldehyde in filtered (0.2 micron pore size) 0.1M cacodylate buffered seawater, pH 7.2. The coupons were taken through a dehydration series with acetone and critical point dried with CO_2. They were sputter coated with carbon and examined using an Amray Model 1000A SEM. EDS analyses were performed using an EDS 9100 Energy Dispersive X-ray spectrometer. At least 6 areas of each coupon were analyzed by EDS and at least 8 spectra were obtained for each area. Coupons were coated with gold/palladium for scanning electron micrographs; (3) surface topography and chemistry were documented using an Electroscan Model E-30 environmental scanning electron microscope and a Tracor Northern Model 5502 energy dispersive X-ray spectrometer (ESEM/EDS). Coupons were removed from the culture medium, carried through a series of salt water/distilled water washes and examined directly from distilled water; (4) electrochemical impedance spectroscopy (EIS) was performed using a Solartron potentiostat Model 1286 and a Solartron Frequency Analyzer Model 1250. The EIS data were collected at the applied corrosion potential after 2 h exposure to 0.5N NaCl. The tested area was 20 cm². A Pt wire pseudo-reference electrode coupled capacitively to a SCE reference electrode was used to reduce the phase shift at high frequencies. The frequency range of the applied signal was 65 KHz to 10mHz. The impedance data were analyzed using the ANALEIS-COATFIT software which was developed at the University of Southern California (USC).

RESULTS AND DISCUSSION

SEM and ESEM showed heavy microbial colonization of the coated coupon surfaces after exposure to the mixed, microbial communities. A variety of cell morphologies (including short rods, long rods, vibrio, spirillum and cocci) were seen in the biofilms. In the control samples, breaching of the coatings was not detected by SEM/EDS. Biodegradation of some coatings (5-10 micron holes/ holidays) with bacteria in and around the holidays was detected using SEM and ESEM. ESEM was used to characterize the topography of wet biofilms on the coated steel surfaces. Bacteria were attached to the coated surface between layers of corrosion product, as well as, in and around breaches in the coatings. The microbes were distributed throughout the biofilm matrix of microbial exopolymers and corrosion products. The chemical composition of the biofilm/corrosion layers was characterized using EDS analyses.

The impedance spectra for the samples within a given coating system were very similar. Some systems (i.e., zinc plate + epoxy + polyurethane; ion vapor deposited aluminum + epoxy topcoat; 5-step iron phosphate + nylon topcoat) showed mainly capacitive behavior which is indicative of very little degradation and some systems showed two time constants for coatings with pronounced degradation. Although EIS is a very sensitive tool for the detection of coating damage, especially in its initial stages, it does not identify the factors which have caused this damage. The applicability and advantages of ESEM/EDS in studies of MIC have been discussed by Little *et al.* (1991) and have been used in this study to show microbial degradation of epoxy and epoxy + polyurethane coatings. It is not yet clear whether the coating deterioration observed resulted from a specific enzymatic degradation or from corrosive, microbial metabolites. The microbial attack on coatings has important implications because such coatings must remain intact for effective corrosion protection.

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THE STANDARD METHOD FOR MEASURING CORROSION RESISTANCE AND FOULING RESISTANCE OF CONDENSER TUBES

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a) Purpose of the study

Condenser tubes made of copper alloys such as aluminum brass has been widely used under the very careful maintenance for coastal steam power stations in Japan. This kind of tube is not so corrosion-resistant that most of them are covered with an iron hydroxide film formed by a ferrous ion injection into a flowing seawater during the operation of power plants. This film is working as a protective film for general corrosion and manganese corrosion under chlorination.

However, from the viewpoint of heat transfer, such a film is one kind of fouling and it exerts a bad influence on heat transfer. In addition to such an artificial film, condenser tubes are fouled with organisms living in a seal, corrosion products and so on. Such a surface film thus formed inside of each condenser tube reduces heat transfer very much. So, it has been very important to evaluate the fouling resistance together with the corrosion resistance of condenser tubes and to choose the optimum conditions for the appropriate maintenance of condenser system.

In order to determine the standard methods for evaluating both of them, two task groups were organized in the Committee on Marine Biofouling Control, Electrochemical Society of Japan, for measuring fouling resistance in 1988 and corrosion resistance in 1990, respectively. Two joint researches were carried out under the Committee using condenser tubes picked out from condensers at some power stations in Japan. After an intensive experiments and discussion, two standard methods for measuring fouling resistance and corrosion resistance were proposed, respectively.

b) Proposed Methods by two task groups

Measurement of Fouling Resistance

Principal features of the measuring method for fouling resistance are: (1) the fouling should be classified into two groups due to removable/non-removable films by conventional cleaning procedures, and (2) fouling resistance due to removable/non-removable film should be measured separately. To be concrete:

1) thermal resistance of a testing tube and a reference one is measured using a fouling resistance measuring apparatus heated by steam or electricity under same conditions as working condensers. Then, the total fouling resistance is calculated .

2) A testing tube is cleaned by conventional cleaning procedures such as a nylon brush cleaning. Then, a washing solution is settled and a sedimentation volume is measured and expressed as a wet volume of removable deposits. Then, the precipitate is dried, weighed and expressed as a dry weight of removable deposits.

3) After a conventional cleaning, a thermal resistance of testing tubes is measured again and a fouling resistance due to non-removable deposits is determined. Then, the total weight of deposits is determined as sum of weight of removable deposits and weight of non-removable deposits. The latter is a weight loss by an acid cleaning of inner surface of a testing tube.

Measurement of Corrosion Resistance

An apparatus is composed of an electrochemical cell and a potentiostat equipped with a strong circulating pump for an artificial seawater and a good thermostat. A polarization resistance of a protective film inside of a testing tube is measured carefully at -10 to -100 mV cathodic polarization from a rest potential at the conditions of 2m/sec of an artificial seawater flow at 30°C.

Handling procedures of testing tubes, that is, picking out condenser tubes from condensers, transferring them, preserving them in good conditions and cutting them into testing pieces were also determined.

c) Conclusion

The following criterion for the polarization resistance of condenser tube has been accepted by some researchers, that is:

<10,000 (Ω cm^2) - A sufficient protective film is not formed yet.

10,000 ~ 20,000(Ω cm^2) - A film formed is not so effective for preventing corrosion.

>20,000(Ω cm^2) - A film formed is fully effective for preventing corrosion.

Same value [20,000(Ω cm^2)] is also recommended by the task group as the criterion of the polarization resistance of condenser tubes for preventing corrosion by a careful inspection of homogeneity, hardness and macroscopic properties of a protective film. On the other hand, the thinner film is more desirable for better heat transfer. Generally speaking, condenser tubes are fouled gradually and their fouling resistance increases with time. And finally it is fouled more than the design value when the condenser should be cleaned.

So, it is considered to be very important for us to select more pertinent cleaning means of condenser tubes and to determine their cleaning conditions in order to satisfy that the criterion [higher than 20,000(Ω cm^2) of a polarization resistance] even after the regular cleaning procedure.

INDICATORS OF MICROBIOLOGICALLY INFLUENCED CORROSION IN COPPER ALLOYS

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PURPOSE

A study was undertaken to demonstrate microbiologically influenced corrosion of copper alloys by sulfatereducing bacteria (SRB) and to identify mineralogical or isotopic fingerprints to relate the observed corrosion to specific activities of the SRB.

MATERIALS AND METHODS

SRB were isolated from corrosion failures, cultured, described and exposed to a series of copper alloys (Jones, *et al.*, 1991). After 3 months exposure, surface topography and chemistry were examined with an environmental scanning electron microscope coupled with an energy-dispersive x-ray spectrometer (ESEM/ EDS) that can accommodate wet, non-conducting biofilms without extensive sample manipulation, dehydration or metal coating (Little *et al.*, 1991). Minerals within the corrosion products were identified by x-ray crystallography (McNeil *et al.*, 1991). Sulfur isotope fractionation within the sulfide corrosion products was analyzed with a dual collecting stable isotope ratio mass spectrometer (Little, *et al.*, 1992). Conventionally, the amplitude of each isotope was reported as a ratio compared to a standard as parts per thousand as follows:

$$\delta\,{}^{34}\mathrm{S}\ \text{‰} = \frac{{}^{34}\mathrm{S}/{}^{32}\mathrm{S}\ \text{sample} - {}^{34}\mathrm{S}/{}^{32}\mathrm{S}\ \text{standard}}{{}^{34}\mathrm{S}/{}^{32}\mathrm{S}\ \text{standard}} \times 1000\,.$$

Negative δ values indicate a concentration of ^{32}S and positive values indicate an accumulation of the heavier isotope. The standard for the sulfur isotope is meteorite troilite (FeS). Copper foils were weighed before and after exposure to establish weight loss as a result of microbial activities.

SUMMARY OF RESULTS

After three months, all foils were covered with a thick gelatinous layer of non-tenacious, black sulfide corrosion products. Bacteria were distributed throughout the black layers associated with the sulfide corrosion products (Fig. 1). Weight loss and isotope fractionation data are included in Table 1. ^{32}S accumulated in all corrosion products resulting from the activities of SRB, and the residual sulfur in the growth medium was enriched in ^{34}S. Weight loss increased roughly with isotope fractionation or microbiologically produced sulfide derivation. Table 2 lists major corrosion products identified by x-ray crystallography. All corrosion caused by SRB produced chalcocite. Strongly adherent corrosion products contained major amounts of djurelite.

STATEMENT OF CONCLUSIONS

Sulfur isotope fractionation was demonstrated in corrosion products resulting from SRB activities on copper surfaces. ^{32}S may be an indicator of microbiologically influenced corrosion. Mineralogical forms of copper sulfide were found in corrosion products on copper surfaces colonized with SRB that would not be predicted by thermodynamic arguments.

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TABLE 1

SULFUR ISOTOPE AND CORROSION DATA AFTER 3 MONTHS EXPOSURE

Sample	Sulfur Concentration in Solid ppm	δ ^{34}S in Solid ‰	Sulfur Concentration in Medium ppm	δ ^{34}S in Medium ‰	Weight Loss mg/mm^2 × 10^{-3} for Similarly Treated Foils
Control	747	10.2	372	0.3	15.9
	900	12.3	514	0.4	30.2
	613	16.5	580	0.2	29.9
SRB Culture I	26627	-0.4	7	*	226.3
	36618	-1.3	20	3.7	131.7
	36695	-0.8	16	8.7	178.6
SRB Culture II	4321	0.6	20	23.8	99.4
	3371	1.5	18	25.8	227.2
	19490	-0.7	11	*	169.5

*Insufficient sulfur

Figure 1. ESEM micrograph of bacteria within sulfide-rich corrosion layers on copper foil.

TABLE 2
MINERALS IN CORROSION PRODUCTS

Bacterial Cultures

	I	II	III	IV	V	VI	VII
99Cu	Low Chalcocite Digenite **	Low Chalcocite Digenite	Low Chalcocite Djurleite*	Low Chalcocite Digenite* Spionkopite*		Low Chalcocite Digenite	Low Chalcocite Djurleite*
90Cu 10Ni	Low Chalcocite Djurleite	Low Chalcocite High Chalcocite Covellite* Digenite*	Low Chalcocite Spionkopite* **	Low Chalcocite High Chalcocite Djurleite*	Low Chalcocite High Chalcocite Djurleite	Low Chalcocite $Cu_{1.8}S$*	Low Chalcocite High Chalcocite Djurleite Digenite*
70Cu 30Ni						Low Chalcocite High Chalcocite Djurleite Anilite*	Low Chalcocite Djurleite

* very low concentration
** pattern has many poorly defined peaks

THE EFFECT OF MARINE FOULING ON HYDROGEN PERMEATION THROUGH BS4360 50D STEEL

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INTRODUCTION

Marine fouling can occur in any system where seawater is present. Even when only very small quantities of seawater are available bacterial biofilms will develop. It is therefore, of great importance to any industry where cooling water and heat exchange facilities are required and especially in the Oil and Gas industry where oil/water/gas mixtures and high-strength steels in seabed mud, for example jack-up platforms, provide both a suitable environment and nutrient supply for biofilm development. Biologically enhanced corrosion has been well documented (Edyvean, 1987 and Hill et *al*, 1986). However, the effect of marine fouling on the permeation of hydrogen through steel has largely been overlooked (Ford & Mitchell, 1990).

Hydrogen atoms produced electrochemically may enter a metallic lattice and permeate through the metal. Such permeation is known to have an extremely detrimental effect upon the mechanical properties of metal as interatomic bonds become damaged causing loss of ductility and tensile strength (Hirth & Johnson, 1976), a phenomenon referred to as hydrogen embrittlement. Hydrogen embrittlement is known to enhance crack propagation and thus, the likelihood of catastrophic failure is increased. Any external supply of monatomic hydrogen is likely to have an effect.

Biogenic hydrogen sulphide is produced by Sulphate Reducing bacteria (SRB) when conditions within a biofilm become favourable for their anaerobic growth. Sulphide ions not only enhance corrosion by stimulating anodic dissolution but also poison the recombination of hydrogen atoms to the gaseous molecule. Thus, more hydrogen is made available for entry into the steel.

To date research involving the hydrogen damage of metals has been performed largely using non-biotic hydrogen sulphide test solutions, for example NACE solution (NACE standard TM10177/90, section 5). The susceptibility of materials to hydrogen entry and failure is then assessed under these 'worst' case conditions. This study looks at the effect of biogenic hydrogen sulphide both with and without the presence of a biofilm on the permeation of hydrogen through BS4360 50D steel.

MATERIALS AND METHODS

In order to measure the permeation of hydrogen generated from a biological culture through the steel specimens two electrochemical techniques were used. Both methods have been developed from a technique first pioneered by Davanathan and Stachurski (1962), which enables the instantaneous rate of hydrogen permeation through a metal to be measured.

A hydrogen permeation cell has been constructed that enables the effect of biogenic hydrogen sulphide in solution to be studied. The metal specimens are made from

BS4360 50D steel ground to a thickness of 0.5mm. Thinner specimens were avoided to ensure that the structural properties of the steel were retained. Prior to insertion specimens were polished and degreased. From a reservoir 0.1M sodium hydroxide was pumped through the measuring chamber at a rate of 30 ml/min. An anodic potential of +200mV was applied to the working electrode and the cell was allowed to stabilise. At this point the charging chamber was filled with the test solution and a cathodic potential of -1000mV was applied to the working electrode. The resultant ionisation current was recorded with time. The hydrogen cell was charged with biogenic hydrogen sulphide solutions taken from both putrid algal culture and SRB batch culture.

In order to measure the effect of a developing biofilm on hydrogen permeation electrolytic hydrogen probes (supplied by British Gas Engineering Research Station) were mounted on a number of BS4360 50D steel off-shore fouling exposure plates. Prior to immersion the plate surfaces were prepared as follows: shot blasted, shot blasted with cathodic protection, coal-tar epoxy (International Paints) coated, coal-tar epoxy coated with cathodic protection and coal-tar epoxy coated with antifouling paint (Ameron). As the biofilm develops the current generated by any hydrogen permeating through the steel is measured by the attached probes. Hydrogen probes were also used in the laboratory to study the effect of a developing anaerobic biofilm in a batch culture on hydrogen permeation with time.

RESULTS

Biogenic hydrogen sulphide produced in both putrid and SRB batch culture increases the rate of hydrogen permeating through BS4360 steel. The rate of hydrogen permeation through the steel is enhanced by cathodic protection. In the field study no significant amounts of hydrogen have been recorded permeating through the plates without cathodic protection. Of the two cathodically protected plates hydrogen was only found to permeate through the one which had not been coated with coal-tar epoxy. Protective coatings appear to provide an effective barrier to hydrogen entry.

CONCLUSIONS

Only relatively low levels of hydrogen are required to cause hydrogen embrittlement. It would seem likely therefore, that the levels of hydrogen sulphide produced within a biofilm would have a considerable effect, especially as cathodic protection is applied to off-shore structures to protect against corrosion.

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THE INFLUENCE OF CATHODIC PROTECTION ON AEROBIC BACTERIAL SETTLEMENT ON STAINLESS AND STRUCTURAL STEEL

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INTRODUCTION

Metal surfaces immersed in seawater are subject to rapid colonisation, with the initial adsorption of organic matter and microbial attachment, preceding the development of a macrofouling community. The microbial biofilm modifies the electrochemical conditions at the metal surface and thus influences metal dissolution reactions.

The use of applied cathodic potentials as a means of corrosion protection is widespread in engineering. Previous work has shown general microfouling activity to be rapid on both cathodically protected and unprotected steel, and studies of bacterial attachment to copper showed increased numbers with cathodic polarisation. However, other workers have found the number of bacteria on tin oxide and titanium cathodes to decrease with cathodic potential. Furthermore, biofouling has been retarded in seawater using pulsed cathodic polarisation of steel, and work in the early 1950's investigated the use of cathodic currents as an antifouling measure for marine vessels.

The objective of this investigation was to determine the effect of applied cathodic potentials on initial bacterial settlement.

MATERIALS AND METHODS

Mixed populations of aerobic bacteria were isolated from the walls of marine aquarium tanks, and cultured on saline nutrient agar (Oxoid Ltd., Basingstoke, U.K). Cells were harvested from 24h plate cultures and suspended in 5ml of sterile artificial seawater (Seawater Corrosion Test Mixture, BDH, Poole, U.K.). The cell concentration was adjusted to 107 cells ml 1 by dilution (using haemocytometer counts) and this stock was used to produce the desired level of 10-4 cells ml-l in the medium to which samples were exposed, which was a 9:1 mixture of sterile artificial seawater and nutrient broth (Oxoid Ltd.).

Stainless steel (BS1449 Grade 304) samples (80 x 25 x 0.75 mm) with a mirror finish and BS4360 50D structural steel samples (80 x 25 x 6 mm), finished to P1200 metallographic grinding paper, were degreased with surfactant, rinsed in alcohol and air-dried, prior to exposure to a bacterial suspension of known concentration (mixed population isolated from marine aquarium). Exposure was for 3,6,12 and 18 hours at 12±0.5°C, and 3, 5, 6, 7 and 9 hours at 20±1°C, with cathodic polarisation of -500,-700 and -900mV SCE for the stainless steel and -800, -1000 and -1200mV for the 50D steel samples, and with unpolarised controls.

Enumeration of attached bacteria was by direct cell count by epifluorescent microscopy. After exposure, the samples were removed, stained with 0.01% acridine orange for 5 min, rinsed in sterile artificial seawater to remove loose cells, and examined under ultra-violet light with an epifluorescence microscope (Olympus BH2, with reflected light fluorescence attachment), at x400 magnification. Cells were counted in 12 randomly chosen 0.0264mm^2 fields of view per sample.

RESULTS

A general pattern of decreasing numbers of attached cells with increasing cathodic potential was observed. The initial application of cathodic protection resulted in the most dramatic decrease in cell numbers. Further though, less pronounced decreases were observed as the cathodic potential shift was increased. This trend is evident for each exposure period, material and temperature.

Cathodic polarisation was found to have a more profound effect on bacterial settlement on 50D steel than for stainless steel. The current density drawn by 50D steel is much greater than by stainless steel for equivalent levels of polarisation.

DISCUSSION

It is widely accepted that in aquatic ecosystems bacteria are pioneer colonisers. Bacterial settlement may be divided into two phases: reversible and irreversible sorption-attraction and firm adhesion respectively. The reversible phase will be affected by electrostatic interactions. A number of workers have demonstrated the negatively charged nature of the bacterial cell under normal conditions, and hence repulsion of cells by the cathodic surface may be expected. However, this may be an oversimplification. The surface conditioning processes preceding bacterial attachment may themselves be altered by polarisation, and the large pH increase at the cathodically polarised surface may influence interfacial pH and hence cell surface charge.

Even accepting simple electrostatic repulsion as being inhibitory, it is widely believed that bacterial cells may attach to negatively charged surfaces by using divalent cations such as Ca^{2+} and Mg^{2+} as a "bridge". Increasing cathodic polarisation results in increased surface pH and leads to the precipitation of calcium and magnesium ions, thereby decreasing the concentration available for "bridging". The generation of H_20_2 at protected surfaces may also inhibit bacterial attachment. Furthermore, the cathodic consumption of oxygen at the polarised surface may be inhibitory for aerobic bacteria.

The greater inhibitory effect observed on 50D steel than on stainless steel may be readily explained by the considerably higher current densities drawn by the 50D steel.

ACKNOWLEDGEMENTS

The authors would like to thank SERC for the funding of this project.

COPPER-NICKEL ALLOYS-RESISTANCE TO BIOFOULING AND RELATED APPLICATIONS

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Marine organisms attach themselves to some metals and alloys more readily than others. Steels, titanium and aluminium will readily foul. Alternatively, copper based alloys have very good resistance to biofouling. In the case of copper nickel alloys, this property is used to advantage to minimise biofouling on intake screens , sea water pipework, water boxes, and mesh cages in fish farming. For this reason too, copper nickel .can be used for the hulls of ships and the sheathing of legs on offshore structures.

The behaviour towards biofouling of copper nickel was assessed by 5 and 14 year exposure trials carried out at the LaQue Centre of Corrosion Technology, USA, which examined both 90-10 and 70-30 copper nickel alloys. More recently, IMI Yorkshire Alloys Ltd carried out trials at Langstone Harbour in the UK for exposures up to 378 weeks. The latter work is as yet unpublished although permission has been given to include the results in this paper. The trials examined the biofouling response of 90-10 copper nickel in the cathodically protected and freely corroding conditions.

During the 14 year trials, copper nickels were exposed to quiet, flowing and tidal conditions. Both 90-10 and 70-30 copper nickel samples showed minimal fouling after removal from all the three types of exposures.

The 5 year trial examined the progress of biofouling under sheltered conditions more closely by immersing plates from a floating dock. After 18 months very little fouling apart from slimes were found on either alloy. Later, some biofouling did occur although it was noticed that at intervals this became detached. Throughout the 5 years, the nickel content had little effect on biofouling response as the two alloys showed almost identical behaviour to each other and also to copper itself.

At Langstone Harbour, cathodically protected copper nickel and steel partly sheathed with copper nickel were compared to cathodically protected steel and freely corroding copper nickel. A hole was drilled in the copper-nickel sheathing to expose a small area of steel.

One test rack was attached to a floating raft so that it would be immersed to the same depth of water whatever the tide, and the second was attached to a sand bank and immersed for at least 8 hours a day. The raft trial lasted 137 weeks and the sand bank trial ceased after 378 weeks.

For the raft trial, it was found that slimes were formed on the steel before any of the copper-nickel surfaces but by the end of the first fouling season, biofouling was evident on all cathodically protected panels. The fouling could however be dislodged more easily on the cathodically protected copper- nickel panel than the steel. The freely corroding panel developed a green corrosion product film during the first weeks. There was minor attachment during successive fouling seasons but these were lost during the following winter periods.

There was no preferential corrosion of the steel on the composite panel adjacent to where the copper-nickel was welded to the steel and only superficial corrosion had occurred on the steel below the drilled hole.

On the half tide site, the pattern of fouling was different and took longer to develop. However, it was again noticed that the fouling on the cathodically protected copper nickel panels could be easily removed by a light rubbing with a finger.

This work confirmed that optimum resistance to biofouling relies on the copper-nickel being in the freely corroding state. With cathodic protection, this resistance is lost. Also, as in the US trials, there were signs of biofouling removal on the freely corroding copper nickel in addition to the regular reduction during the winter season.

The need for copper and copper nickel to be freely corroding to exhibit biofouling resistance has led some researchers to believe that it is the copper ion entering the sea water that is toxic to marine organisms. The 5 year studies led Efird to argue that this was incorrect as 90-10 and 70-30 copper-nickels corroded far more slowly than copper but still exhibited similar biofouling resistance over long term exposures. He considered that it was the surface film itself which was inhospitable to biofouling. To explain periodic biofouling and removal he concluded that the film was duplex in nature.

The trials had allowed some biofouling on freely corroding specimens as they were carried out in relatively sheltered conditions where slime layers were allowed to thicken to a point where this was possible. With the wave action on offshore platforms or with the normal flow velocities in cooling systems, the slime layer would not reach a thickness on copper nickel to permit attachment.

In practice, potential for large scale applications utilising the biofouling behaviour of copper nickels are ships hulls and in the sheathing of offshore structures. In the case of hulls, the first 70-30 copper nickel hull was installed in 1968. Twenty years later, the "Asperida" was located again. The hull was found to be in excellent condition and remained free of fouling and corrosion. Also " the Copper Mariner", a shrimp trawler and the first 90-10 copper nickel hull, was launched in 1971 and when located 16 years later had never needed to be scraped because of biofouling or experienced corrosion. Another form of copper nickel hull has been to use copper nickel clad steel. One instance of this was for 4 fire boats in Italy.

Although, the copper nickel hull concept as yet has only been used for small vessels, sheathing trials have been carried out attached to hulls on a roll on roll off vessel and a tanker for up to 2 year exposures. Although intended to confirm that copper nickel could withstand higher hull velocities than had until then been experienced, the biofouling resistance was also found to be excellent. The advantages of having a hull with inherent resistance to corrosion and biofouling is apparent; low frictional drag, optimum fuel efficiency, no repainting every few years and benefits against environmental hazard An in depth costing study for a sheathed TAO tanker estimated fuel savings of 27% over the vessels lifetime. The next stage in development awaits the full sheathing of a hull on a large vessel.

ELECTROCHEMICAL MONITORING OF THE BIOFILM GROWTH AND CORROSIVITY IN SEAWATER: EFFECT OF INTERMITTENT CHLORINATION

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It is widely recognized that, in seawater, the growth of the biofilm causes an oxygen reduction depolarization on a series of active-passive alloys (like SS, Titanium, Ni-Cr, etc.). This phenomenon causes, in turn, a higher risk of corrosion on the above mentioned alloys and a higher galvanic current on less nobles materials coupled with them. For monitoring purposes the above statements can be reversed: if the biofilm growth causes an increase in corrosion and, therefore, changes in some electrochemical parameters (potential, corrosion current, polarization resistance, galvanic current, etc.), these variations can be utilized to signalize the first phase of the biofilm growth and its corrosivity. In particular, we proposed a very simple monitoring device, based on the measure of the galvanic current between SS and a suitable sacrificial anode for the biofilm monitoring on SS surfaces. In a previous work we showed that the measure of the galvanic current between a SS pipe and an iron anode is able to indicate the efficiency of continuous chlorine additions to prevent the biofilm growth on SS tubes in heat exchangers.
In particular, it was shown that:
- the first phase of biofilm growth is clearly signalized by an increase of the galvanic current close to one order of magnitude;
- this device is able to reveal biofilm layer not detectable by other on-line monitoring device like that based on friction factor measurement;
- this device is able to indicate, in real time, if the local concentration of residual chlorine is sufficient to prevent the biofilm growth.

The present work was carried out to study if the proposed monitoring device is also able to follow the effect of an intermittent chlorination on a pre-existent biofilm.
The following conclusion were reached:
- once the SS pipe is exposed to flowing seawater the increase of the galvanic current between SS and iron anode, from the initial value I_0 to I_{max}, is well described by the law:

$$I = \frac{I_0\, 10^{-(t-t_0)/\tau}}{1 - I_0/I_{max}\left(1 - 10^{-(t-t_0)/\tau}\right)}$$

similar, in shape, to the logistic equation often utilized to describe the biofilm growth. In our test t_0, "incubation time", and τ were respectively close to 3-4 days and 1-1.5 days;
- when an intermittent chlorination is applied to destroy the biofilm, the decrease in

time of the galvanic current follows the law:

$$I - I_0 = (I_{max} - I_0)\ 10^{-t/\tau_d}$$

where τ_d is inversely proportional to the residual chlorine concentration only for residual chlorine concentrations over 0.3 ppm;

- after chlorination, the regrowth of the galvanic current do not show an "incubation time" if the intermittent chlorination has been stopped before the galvanic current was lowered under a value close to $I - I_0 \leq 0.2\ (I_{max} - I_0)$.

FOULING ON A1-BRASS TUBES IN SEAWATER AND ITS ELECTROCHEMICAL MONITORING.

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The fouling formation within A1-brass tubes of a thermal power plant condenser was investigated with an experimental facility located at Vado Ligure ENEL power plant. Some test lines, made of pieces of condenser tubes fed with flowing seawater, were set up to operate with controlled biocide amounts.

The test system included capabilities for measuring heat transfer resistance, pressure drop, corrosion potential, polarization resistance, current density at constant potential and current density distribution under cathodic protection.

The test lines also included:

- stress corrosion test sections, with corrosion potential measurements in proximity of artificial crack initiation;
- biofouling growth monitoring test cells, based on current density measurements at constant potential;
- cells for anodic and cathodic potentiodynamic polarization curves;
- optical test sections to observe the internal surface of the samples by an endoscope.

Particular care was taken to avoid unwanted phenomena induced by stray currents and by the formation of anodic products, the latter being thus completely avoided.

During the whole experimental programme, from February to April 1992, the pressure drop and the heat transfer resistance of the A1-brass test tubes did not significantly vary with time. *In situ* optical observations by endoscope showed fouling growth inside PVC tubes and glass parts of the lines, while no significant fouling on the A1-brass surface was observed.

As regards electrochemical measurements, some tests were also carried out on 254 SMO (UNS S31254) austenitic stainless steel.

The following electrochemical results were obtained.

In the case of the samples free from electrochemical interferences, the corrosion potentials, after an initially light shift to a more noble value, were almost constant within a range of 30 mV.

On the other hand, the samples, weekly tested for polarization resistance and other electrochemical measurements, showed corrosion potential increasing in time to a value more than 150 mV higher with respect to the initial potential.

For the A1-brass samples, the current density at -300 mV(SCE) had values below 1 μA/cm², during the whole experiment.

In the case of 254 SMO, the current density measured was of cathodic type and increased in time from not significant values to more than 20 μA/cm².

The polarization resistance value and the cathodic protection penetration depth, after an initial decrease, greatly increased and then decreased again.

The trend of cathodic current in time, at low potential, as deduced from polarization curves, was reversed with respect to that of polarization resistance. In an other experiment, the chlorination effect was evaluated up to 50 ppm of chlorine added to seawater on unfouled samples. When increasing the chlorine content, it was observed that:

- the corrosion potential increased;
- the cathodic current measured on the A1-brass tubes markedly increased;
- the cathodic current, measured at -250 mV/SCE on 254 SMO tubes, had only a weak increase up to values which turned out to be less than those observed in non chlorinated water;
- the cathodic protection current increased;
- the depth of cathodic protection penetration decreased.

In all the cases no stress corrosion phenomena were observed.

In conclusion, in this facility, in which a very little fouling growth was observed on A1-brass, with no increase heat transfer resistance and pressure drop, potentiostatic current measurements performed on 254 SMO electrodes were very sensitive to fouling formation and practically unaffected by chlorination.

MICROBIAL INTERFERENCES ON CORROSION REACTIONS: THE BIOCORROSIVITY OF MARINE ENVIRONMENTS

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The microorganisms influence corrosion by changing the electrochemical conditions at the metal/solution interface. These changes may have different effects, ranging from the induction of localized corrosion to a change in the rate of general corrosion, and corrosion inhibition.

Any biological influences which either encourage (or restrict) one of the components (anodic or cathodic) of the corrosion reaction, or permanently separate (localize) anodic and cathodic sites, will increase corrosion.

Thus, stimulation of the anodic reaction (e.g. by acidic metabolites), or the cathodic reaction (e.g. by microbial production of a cathodic reactant like H_2S), together with disruption of passivating films and increase of electrolytic conductivity will increase corrosion.

The participation of microorganisms in the process introduces several unique features, the main ones related to the modification of the metal-solution interface structures, through biofilm accumulation.

An entire dynamical system is formed at the biofouled interface, and it will be governed by different transport processes taking place through the biofilm. This is a consequence of the biofilm structure, characterized by a high degree of hydratation, where water percentage covers nearly 90% of biofilm composition .

In this way, microbial colonization of metals drastically modifies the classic concept of electrical interface, commonly used in electrochemical studies. Important changes in the type and concentration of ions, pH and redox conditions, are induced by the biofilm, altering the passive behaviour of the metal substratum and its corrosion rate.

Experimental results showed that the biological interference on corrosion is reduced on active (easily corroding) metal surfaces like aluminium, because biofilms are formed on an unstable and continuously growing layer of inorganic products, and therefore the detachment of the corrosion product deposits is accompanied by the biofilm. Conversely, stainless steel or titanium, because of the lack of corrosion products, allow a rapid and easy colonization by microorganisms on their surfaces and in this case the biofilm presence strongly modifies the corrosion behaviour of the alloys or of the materials coupled to them.

In particular, it was observed an oxygen reduction depolarization during the growth of the biofilm on stainless steel surfaces exposed to natural seawater.

It was demonstrated that this phenomenon can explain the higher probability of localized corrosion onset, the faster propagation of localized corrosion and the higher galvanic currents between stainless steels and less noble materials coupled to them, observed in natural seawater compared with the sterile one.

An analogous phenomenon was observed on other alloys like titanium, Ni-Cr and

Ni-Cu alloys, ...
Microbiological and biochemical methods, coupled with SEM and EDAX analyses, were applied to correlate the structure and nature of the biofilms to their electrochemical effects. The oxygen depolarization, induced by the microbiological colonization of surfaces, appeared critically linked to the presence of bacterial densities higher than of 10^7-10^8 bacteria/cm^2 and to the amounts of the Exopolymeric Substances in biofilms.

The hypothesis of a catalyst toward oxygen reduction, produced by the bacteria settled on surfaces and trapped into their exopolymeric substances seems, at the moment, the most suitable one to explain the corrosive effects exerted by the biofilms on stainless steels (and similar alloys) in seawater.

FOULING CONTROL SYSTEMS FOR WATER TREATMENT

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Water treatment is a widely used practice for reducing the negative consequences of fouling in all industrial systems where sea-water is circulating.

In many instances sea-water is used for cooling purposes and chemicals are added in order to prevent the attachment and growth of fouling organisms. The most widespread method for water treatment is chlorination, but a number of alternatives have been proposed to solve particular aspects of the problem.

Classically a difference is made between microfouling (slime), that is an important factor in reducing the surface characteristics of small size tubes (e.g. thermal exchange properties of condenser tubes) and macrofouling, that is growing intensively in all parts of culverts and pipes of circuits, regardless of their dimensions.

The injection point of chlorine is very important to position, since the relative importance of microfouling and macrofouling problems in a circuit involves consideration of contact time and chlorine demand of the water.

In order to review the current status of water treatment methods, the following items will be examined:

1. Problems involved with chlorine use.
2. Chlorine minimization procedure.
3. The role of biological understanding of life-cycles of fouling organisms for water treatment.
4. Selected alternatives to chlorination .
5. Chlorine dioxide as a promising antifouling agent.

Chlorination is applied by electrolyte generation or by addition of sodium hypochlorite. Following the evolution of both national and international legislation and public concern about the possible detrimental effects of water treatment on the environment, pressure has been put on industry about the minimization of chlorine use. This is coupled with the industry goal of reducing costs and increasing effectiveness of chlorination. Moreover, the formation of halogenated compounds, in waters with high organic content is a possible by-product of chlorination, having a higher persistence in the ecosystem and a residual potential eco-toxicity.

The initial debate between continuous and shock chlorination has been resolved by the general use of continuous low-level chlorination, and recently a technical solution has been found with the improvement of the so-called targeted-chlorination.

In some instances dechlorination has proved necessary and a number of technical alternatives have been proposed, in spite of the high costs involved for the treatment of large volumes of water. In any case, the problems of monitoring on-line the effectiveness of the treatment and to forecast the amount of chemical product needed in a particular situation, have lead to the development of chemical and biological devices to help managers in optimizing chlorination.

In particular, a thorough knowledge of the fouling characteristics of a given site, and especially of the timing of larval settlement and of rate of growth of the attached organisms are of vital importance in preparing an effective schedule of treatment for any particular plant.

Many alternatives to water chlorination have been proposed, from which we can quote copper/chlorine combination, that has been proved effective for macrofouling control in closed systems. The doses can be reduced at least five times in comparison to separate agents. Ozonization has also been proposed as a water treatment.

A different alternative to sea water treatment is the treatment of surfaces, such as antifouling coatings that control macroinvertebrate attachment and accumulation by slowly releasing the toxicant (usually organotin compounds) from the coating material at the water-coating interface. Other organometallic and metallic ions are used as active agent.

Acrylia coatings and epoxy coatings are available, together with self-polishing paints. Non-toxic coatings, due to their low surface energy, prevent attachment of biogrowth. Examples of non toxic materials are hydrophilic co-polymers and silycon elastomers.

A more traditional alternative to water chlorination has recently come to the attention of plant managers.

Chlorine dioxide is particularly interesting in view of the small concentrations of chlorine involved, of the difficulty of forming halo-derivatives, and of the short life of this compound in water. some tests have been conducted both in pilot plants and at whole scale and the results are promising although more information is needed on the environmental fate, toxicity and overall costs of employment.

FOULING CONTROL SYSTEMS USING CHEMICALS, INSIDE INDUSTRIAL PIPINGS: A LABORATORY SIMULATION

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The effect of different toxic chemicals on the growth of marine fouling in an experimental plant situated in the Marine Biology Laboratory of Trieste, a joint project in collaboration between Caffaro S.p.A.-Gruppo SNIA B.P.D.-Brescia and the Department of Biology of the University of Trieste (convention 1.3.1991) is discussed. Solutions of sea water and sodium hypochlorite or chlorine dioxide at different concentrations were made to flow separately through the vats of the plant, in order to simulate industrial cooling circuits pipings.

The aim of the present study is therefore to investigate the optimal use of toxic by useful and necessary metering and then relate this to an analysis of the fouling population dynamics (primary slime) characterized both as presence of species and as relative abundance. The main object of this work is to set up a quick and good method for the fouling study.

The experimental plant consists of four vats fed with a controlled flow of sea water, and a system of pumps which ensures the metering of the toxic under examination. The testing treatments, in each vat, are the following:

- no treatment (so-called "white")
- seawater + active chlorine from NaCl0 at concentr. 0.2 ppm
- seawater + $Cl0_2$ at concentr. 0.1 ppm
- seawater + $Cl0_2$ at concentr. 0.2 ppm

The concentrations mean the residual concentration kept in the treated water. Each vat is designed to accept glass slides used for primary slime surveying. The glass slides, assembled onto a collector board, are collected during seven samplings (5, 10, 15, 20, 60, 90, 120 days of immersion) for a total of four months (3 August-3 December 1991).

After collection, the glass slides are prepared for microscopical analysis, in order to obtain qualitative and quantitative data, for a sampling surface of 25 mm^2. This surface value was chosen having taken into account the dimension of the minimal area, understood as minimal representative surface of a population. After several samplings and applications of control methods, it was ascertained that the minimal area is always included in the range of 25 mm^2. The collected data are:

- floristic list of present species (presence-absence, number of species);
- number of individuals present per species (abundance-dominance).

These data were grouped in four species-by-sites matrices and elaborated by multivariate analysis methods in order to highlight eventual correlations between the treatment types studied. As far as chemical physical parameters are concerned, during the whole period of sampling the sea water temperature was constantly recorded by means of a sensor placed on the control panel of the plant. Other chemical-physical parameters (pH, ClO_2 demand, suspended materials, NO_3, PO_4) are collected at the end of the experimental period (5 December 1991).

From the obtained results it is possible to assume that:

- the water treatment seems to be efficient in limiting fouling growth in the first stage of settlement. Sodium 0.2 ppm active chlorine (NaClO) is less selective for adhesive species than chlorine dioxide, which is specific for this species.
- Seasonal variations in sea water temperature seem to influence both the variety and abundance of every species considerably, but it is possible to show that they are more selective for plankton: from August to December sea water temperature gradually decreases eliminating all planktonic species. Only few adhesive species survive but in a limited number.
- The elaborations obtained from general data lead us to think that the similarity between white and active chlorine treatment is due especially to adhesive species presence. On the contrary these are rare or absent in chlorine dioxide treatments. Besides, the sharp separation between the two groups evidently shows the high selectivity of chlorine dioxide for microphytobenthos in comparison with white and 0.2 ppm active chlorine (NaClO).

This first experimental period illustrates how efficient chlorine dioxide is in limiting marine fouling growth in the first stage of colonization. Besides in these four months, the fall in temperature highlights this effect since it causes the gradual elimination of a large number of species. At present we are working towards optimizing the research in order to confirm previous data and find the proper concentration of chlorine dioxide needed to reduce the use of toxic to the minimum whilst giving the maximum effect.

FIELD AND LABORATORY EFFICACY OF CHLORINE DIOXIDE AS ANTIFOULING IN COOLING SYSTEMS OF POWER PLANTS

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Evidence of dangerous haloderivates formation using hypochlorite as biocide has claimed for the need of studies on other antifouling components to be used in cooling plants. Chlorine dioxide has a much lower reactivity with organic molecules and seems not to form mutagenic chlorocompounds as hypochlorite does. Furthermore, ClO_2 production is highly cost-effective and it quickly disappears as gaseous Cl_2 after use. Nevertheless, studies on its efficacy on marine fouling control are still scant. A first evaluation of ClO_2 toxicity on panel fouler communities of the cooling system of a power plant in Cerano Nord (Brindisi, SE Italy) has been attempted by the CNR (National Research Council) and ENEL (National Agency for Electrical Power Supply). Laboratory tests were designed to evaluate ClO_2 toxicity in both static (sea urchin test) and running seawater systems (hydroid colony growth test). Results with static bioassays demonstrated that ClO_2 significantly affects ($p \leq 0.05$) embryo development of the sea urchin *Sphaerechinus granularis* from 2.2 ppm (nominal concentration), while egg fertilization is largely inhibited by short exposure of sperms already at 0.074 ppm ClO_2. Continuous flow system aquaria with amperometric titration of ClO_2 allowed to perform growth bioassays of *Laomedea flexuosa* hydroid colonies at very low concentrations (0.05 ppm, 0.1 ppm, 0.2 ppm ClO_2). A 96-hour exposure at 0.05 ppm caused a deep inhibition ($p < 0.001$) of colony growth. Higher concentrations more rapidly (24-48 hours) caused growth arrest and shrinkage of colonies. Evidence of ClO_2 toxicity on marine larvae and spores also comes out from the monthly observation of fouling development on suspended panels in the ClO_2-treated effluent of the Cerano plant.

A REVIEW: MACROFOULING TO INDUSTRIAL COOLING SYSTEMS - FOULING ORGANISMS AND CONTROL METHODS

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Worldwide there is a wide range of invertebrates that cause macrofouling in cooling systems of industrial facilities (i.e. power plants, steel mills, refineries). The diversity of organisms that can be found in seawater and brackish water cooling systems encompasses several invertebrate groups: molluscs (i.e. blue mussels, oysters), barnacles, hydrozoans, bryozoans, sponges, tunicates. To the contrary, freshwater macrofouling of industrial systems is restricted to only a few species with two particular mollusks, zebra mussels and Asiatic clams, being the primary fouling organisms. The zebra mussel, *Dreissiena*, is a mollusk indigenous to Eastern and Western Europe. In 1986, the zebra mussel was introduced into the Great Lakes of the United States and has been spreading rapidly. The Asiatic clam, *Corbicula*, was introduced into the United States in the 1930's and has since spread throughout most of the North American continent. In the 1980's, the Asiatic clam was also found in France, Germany and the Netherlands.

The consequences of macrofouling of industrial cooling systems include high maintenance costs and excessive downtime to cleanout macrofouling growth, the impairment and damage of all types of system components and equipment, reduced cooling efficiency, and the functional vulnerability of safety-related cooling systems.

Historically, fouling control technology has been restricted to chlorination, metallic based biocides or thermal treatments. As a result of the more restrictive regulatory limitations and environmental concerns, the administration of these traditional methods to achieve appropriate fouling control within industrial cooling systems has become limited. A summary of these historical methods will be presented.

More recently, new technology with a nonoxidizing biocide has proven to be quite effective for fouling control of both seawater and freshwater cooling systems in the United States, the Caribbean, and Europe. This patented biocide is a water miscible formulation containing two cationic surfactants: alkyldimethylbenzylammonium chloride (Quat) and dodecylguanidine hydrochloride (DGH). This review will summarize results from laboratory studies showing the comparative efficacy of this biocide to different freshwater and marine macrofouling organisms at optimal dosages (0.6 to 2.0 mg/L) and exposure periods (3 to 24 hours) at various temperature conditions (5 to 30°C).

The objective of this new treatment technology for macrofouling control is to eradicate the juvenile fouling organisms which have settled within a cooling system and to prevent the accumulation of macrofouling growth that would hinder the operations of an industrial facility. This can be accomplished by intermittent applications of brief duration during the fouling season. Optimization of a treatment program is site specific and depends upon the growth rates, spawning season, and the extent of setting by the larval stages of the various fouling organisms. A surveillance program should be implemented to determine the minimum number of treatments required per year for a specific cooling system. Case histories employing innovative treatment methods with this biocide for the control of different macrofouling organisms within industrial systems will be summarized. This review will include the eradication of fouling organisms in intake bays, seasonal applications for macrofouling prevention in service and safety-related cooling systems, and the implementation of multiple feed points for system wide treatments.

Procedures will also be reviewed on how these treatments are administered to meet environmental regulations. Both surfactants (Quat and DGH) are short-lived because they are readily adsorbed by naturally occurring substrates such as silts, clays, suspended solids, humic acids and the microfouled surfaces of cooling systems. Bioassay studies have shown that once these surfactants are adsorbed, they no longer exhibit toxicity to aquatic organisms. Treatment programs are designed to maximize the passive neutralization of these surfactants within the cooling system. Other procedures include segmenting treatments so that only a portion of the cooling water is being treated at any one time. This segmented treatment approach allows for the dilution and passive neutralization of the treated water as it mixes with the remaining untreated cooling water. If required, these treatments can also be detoxified by feeding clays to the discharge water.

ASSESSMENTS OF ANTIFOULING CAPABILITY USING A POROUS MEMBRANE TEST

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INTRODUCTION

A porous membrane test has been used as a preliminary screen for antifouling activity of potential additives to surface coatings. Standard amounts of candidate substances are enclosed behind membranes of closely defined porosity which, together with 'blank' and 'active control' membranes, are immersed just below the sea water surface at a suitable location and inspected regularly. In this study the protocol, reproducibility and reliability of the test have been investigated.

MATERIALS AND METHODS

Diuron (3-(3,4-dichlorophenyl)-1-dimethylurea **1**, 97%, Lancaster Synthesis), Simazine (2-chloro-4,6-bis(ethylamino)-s-triazine **2**, 98.8%, Ciba Geigy Agrochemicals), dicyclohexylamine **3** (99%, Sigma Chemicals), bis(tributyltin)oxide **4** and nonylamine **5** (Aldrich Chemical Co Ltd) were used as received. Substituted phenylureas 3-(3,4 dichlorophenyl)-1-ethyl-1-methylurea **6**, 3-(3,4-dichlorophenyl)-1,1 - diethylurea **7**, 1 - piperidine - N - (3,4 - dichlorophenyl) carboxamide **8**, 1-methyl - 4 - piperazine - N - (3,4 - dichlorophenyl) carboxamide **9** and 1,4-piperazine-N,N-di(3,4dichlorophenyl) carboxamide **10** were prepared from secondary amines and 3,4-dichlorophenylisocyanate (Aldrich Chemical Co Ltd) in dry dioxane. For exposure trials, samples (0.300 ± 0.003g) were placed between filter papers in a circular dish, which was covered with membrane paper (Gelman Sciences Ltd, "Versapor 800" 0.8 μm) and located in a test frame. Generally, duplicate membranes were located in corresponding positions in upper and lower halves of the frame. Each frame was placed in the sea (Langstone Harbour, Hants, UK) such that membranes were 0.25 -1 m below the surface and accessible to sunlight. Fouling was assessed at intervals of two to three weeks. On each occasion, fouling (predominantly *Enteromorpha* near the surface and *Ectocarpus* towards the bottom of the frame) was removed from around the membranes, the proportion of each membrane on which organisms had settled was assessed visually (R) on a scale of R = O (in steps of 1/4) to 1 (in steps of 1) to 4. Surfaces covered by the initial layer of slime were deemed to be fouled, and early fouling generally involved only plant species. Porous membranes for laboratory experiments were set up in individual rigs and submerged in distilled water (800 cm^3, 20°C), which were replaced each time analysis was carried out. Concentrations of test substances in water were determined at appropriate intervals by HPLC (UV detection, 10 cm ODS column, methanol (60 vol %) / water). Aqueous solubilities were determined by analysis of saturated solutions, prepared by equilibrating and filtering at 25.0°C.

RESULTS

In a preliminary trial (6 weeks, July/August) compounds including **4**, **6** and **9** were compared with Diuron **1**. Due to warm weather, fouling was extremely rapid and only limited comparisons could be made. However, compounds **4** and **9** showed rather better antifouling than Diuron. The main trial (12 weeks, June - September) included 12 replicate membranes containing Diuron **1**, and two each containing respectively bis(tributyltin) oxide **5** and compounds **3**, **4** and **7**. Four non-toxic controls were fouled by ca. 60% after 4 weeks and almost completely after 6 weeks. For the samples of Diuron, the mean extent of fouling increased from 5% after 4 weeks to 30% after 12 weeks. Individual values showed slight variability, e.g. after 4 weeks there were seven assessments of 0, three of 1/4 and one of 3/4; after 10 weeks there were two of 1/2, eight of 1 and two of 2.

The standard deviation was ca. 0.5 throughout, which corresponds with the precision of individual assessments. In comparing compounds 1, 3, 4, 5 and 7, antifouling performance (P %) may be expressed as 100 (R_c - R)/R_c where R and R_c are the mean assessments respectively for the candidate and the non-toxic control. Results are not significant before the controls are appreciably fouled (4 weeks). On this basis, all compounds were in the range 70-95% after 4 weeks. Therefore Diuron **1** and bis(tributyltin)oxide **5** performed similarly (P after 12 weeks: **1** 71%, **2** 63%; mean P for 4-12 weeks **1** 78%, **2** 74%). These results correspond with the known activity of **5** and the expected activity of **1** against *Enteromorpha* by inhibition of photosynthesis. The substituted phenylurea **7** performed rather less well (P after 12 weeks 38%, mean P for 4-12 weeks 54%). Dicyclohexylamine **3** and nonylamine **4** showed no activity after 10 weeks, but up to 8 weeks, **3** was almost as active (P > 63%) as Diuron. The release of compounds **1**, **2**, **8**, and **9** from membrane enclosures into distilled water at 20°C was measured over six weeks. Released rates were constant over the period for all compounds (in mg/day: **1** 0.85, **2** 0.12, **8** 0.40, **9** 0.65) and showed a qualitative correlation with aqueous solubility (in mg dm^{-3}: **1** 42.4, **2** 5.3, **8** 22.4, **9** not available).

CONCLUSIONS

The membrane test is a short-term screening procedure in which prevention of settling of marine organisms requires the continuous transport of the toxic substance at a sufficient rate. A saturated solution is maintained behind the membrane, so that the substance diffuses at a constant rate until its supply is exhausted. Thus the rating of its antifouling performance will depend on its toxicity principally to marine plants, its aqueous solubility and its diffusion coefficient in water. The amount of each candidate substance used (300 mg) is sufficient for the sparingly soluble substances but not for more soluble compounds e.g. nonylamine. Larger amounts could be used without prejudicing comparisons. The use of membranes with smaller pores may provide a method for determining the minimum rates of release required for antifouling activity. Assessments of activity by this method are clearly influenced by aqueous solubility, which determines the concentration gradient across the membrane. For example, Diuron and bis(tributyltin)oxide gave very similar performances in the test, but the former is more soluble by a factor of ca. 4 (by mass). The membrane test using duplicate membranes is simple, robust and adequate for screening, but the frequency of inspection, relative to the rate of fouling, must be sufficient to achieve discrimination between partially fouled membranes on several successive occasions. The test should be continued until all the membranes have become completely fouled. The usual practice of using duplicate membranes of each material is adequate for screening, but larger samples are advantageous in making more precise comparisons of activity.

APPLICATION OF UV IRRADIATION SYSTEM FOR A POWER STATION INTAKES

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INTRODUCTION

Macro-biofouling problems at power station intakes caused by barnacles, mussels and oysters have been reported. Chlorination has been usually used against this problem so far. However, it has become more difficult to control macro-biofouling by chlorination alone, because the level of total residual chlorine in the effluents is limited by regulations which are becoming more strict. Efforts to find better ways to control macro-biofouling are being made.

We have focused on UV irradiation as a better method. Because UV irradiation has almost no effect on water quality. The influence of UV irradiation on barnacle larvae in the flowing sea water was examined, and found to be effective (Hori *et al.*, 1990).

UV irradiation equipment has been used for sterilization in various fields. However, the equipment for controlling macro-biofouling of powerstation cooling water systems was not previously available.

We have developed a prototype equipment for sea water treatment at power station intake and conducted the field test.

MATERIALS AND METHODS

The field test was performed at The Electric Power Development Co., Ltd. Isogo Plant, Isogo-ku, Yokohama-shi, Kanagawa 235, Japan. There are four intakes (1A, 1B, 2A, 2B) and we set up the equipment between the bar-screen and the rotary-screen in the 2A intake.

The UV equipment consisted of lamp units, brackets holding the lamp units, electric box, electric connection box, and wire.

The bracket was made of steel channel with anticorrosion paint and fixed to the wall of the intake using anchor bolts. A total of 42 lamp units were fixed to the bracket by bolts horizontally and parallel to the sea water flow. Each unit was set at 80mm interval and installed at 75mm away from the wall.

The lamp unit consists of a low pressure mercury lamp AY-10 (lamp watts: 160W; arc length: 1473mm), outer quarts tube, seal and electric connection. Each lamp unit was sealed individually to minimize leakage. The electric wire was connected to the connection box through fitting, using an outer cable. The connection box was fixed to the wall above the water.

Two sets of UV lamps were placed in May, 1991, and operation was checked regularly.

RESULTS AND DISCUSSION

Insulation resistance break down occurred in several lamp units. We continued running the test by disconnecting the lamps which broke down.

However, several lamps had similar problems.

We tried to determine the cause of the problem, but it was difficult, since the equipment was located under water. Then using the same equipment, we tried gas leak tests and water pressure resistance tests in the laboratory. We found, that leakage occurred when the outer quartz tube centering was not good. We thought that incorrect centering would occur because the wall of the intake was not always flat.

When about one third of the lamp units broke down, we decided to set up a modified model in the 1A intake during the annual maintenance period.

MODIFIED MODEL TEST

We discussed modification and reached the following conclusions:

1. The support point of the lamp unit to the bracket must be changed so that the seal is free from any force.
2. The number of seal points must be minimized.
3. A multiseal structure is essential to handle construction errors.
4. As much construction as possible must be done at the factory to increase reliability.

The modified model was set up at the 1A intake in October, 1991.

We have checked the operation since the beginning and have found no failures so far. Insulation resistance break down of the lamp units has not occurred.

CONCLUSIONS

UV irradiation equipment for power station intakes was developed and was tested in the field. Though the initial model suffered leakage, we got good results from a modified model. For practical application, we have to do more research concerning its materials, cost, and structure. Then we can expect various application including direct irradiation of the wall.

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ANTIFOULING SYSTEMS AND ENVIRONMENT

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INTRODUCTION

The fight against biofouling appears to date back to over 2000 years when wooden boats were protected with pitches and tars. The first antifouling paints, based on mercury and arsenic, started to develop in the late 19th Century and were still commonly used in the 1950's.

At that time, they were replaced with more sophisticated systems containing vinyl resins as matrix and copper oxide as active component: the copperpaints. In the 70's, the addition of tributyltin (TBT) considerably increased the durability of antifouling paints while improving certain properties such as reduced roughness, greater variety of available colors, etc.....

ENVIRONMENTAL IMPACTS

The huge success encountered by organotin-based paints (TBT, TPT) was precisely the cause of the extensive damages suffered by the marine ecosystems, and particularly by mollusc populations. The most acute outbreaks were first observed in oyster farming areas.

Studies conducted in the Bay of Arcachon, along the French Atlantic coast, showed that the failure of farmed oysters to reproduce, along with significant shell calcification anomalies, could be imputed to chronic TBT contamination of the environment. As a consequence, production dropped considerably, down to 9000 tons in 1981 when production fell to its lowest level. The loss of income for oyster farmers was evaluated at approximately US $ 147 millions during the 1979-1983 period (Alzieu, 1991).

These economic damages suffered by the commercial utilization of biological resources were further compounded by the effects of the unexploited populations. Thus, GIBBS and BRYAN (1987) identified sexual disorders in gasteropods exposed to low doses of TBT. These disorders, known as imposex, cause the growth of male genital organs in the females. In the final stages of imposex development, the fertility of the species as well as its reproduction capabilities are affected: the decline in certain gasteropod populations can be traced to their proximity to sources of TBT input.

Laboratory and *in situ* research conducted since the early 1980's, has led to the definition of a graduation scale for TBT effects on marine molluscs:

< 1 ng/l	emergence of the imposex phenomenon in *Nucella lapillus*,
> 2 ng/l	development of calcification anomalies (chambering) in the shells of *Crassostrea gigas* oysters,
>20 ng/l	effects on embryogenesis and larval development of oysters,
>40 ng/l	effects on the growth of oysters juveniles.

These toxicity thresholds correspond to concentrations commonly recorded in coastal waters, primarily in the vicinity of port areas where TBT concentrations can reach several hundred ng/l.

CURRENT SITUATION AND PROSPECTS

Due to the problems of exploitation of marine resources generated by chronic TBT contamination of coastal waters, the French government adopted, in January 1982, regulations controlling the use of organotin-based paints. Since then, many countries have taken similar measures: ban on their use for certain categories of boats, lowering of leaching rates, criteria of water quality, etc...

The experience gained in the Bay of Arcachon reveals that the ban of TBT paints for boats under 25 meters, resulted in a reduction of environmental contamination and a return to normal operations in the oyster farming areas.

As a consequence of the restrictions prescribed by regulations, the sales of traditional paint initially increased; although less durable, these paints are less environmentally harmful. However the necessity for efficient means of protection has led to a search for a new system presumed to be both efficient and environmentally safe. Among the various solutions under proposal, some of which are still at the research stage, the following deserve mentioning:

- use of tin copolymers allowing for an improved control of leaching rates,
- use of toxicants with acceptable residual effects on non-target organisms,
- paints having a physical action (anti-adhesion) and produced from substances presenting a low surface energy (silicone, polytetrafluoroethylene....),
- systems preventing the deposition of surface bacterial biofilms, which is a prerequisite to the growth of macrofouling.

CONCLUSIONS

The use of antifouling substances presenting a high toxicity for aquatic organisms, has been shown to be responsible for undesirable effects observed on a large scale, both in culture areas and on wild mollusc populations. Evidence has proved that organotin-based antifouling systems had to be replaced, due to their unacceptable level of toxicity for coastal ecosystems. A number of ongoing research works seem to suggest that it is not unrealistic to expect, within the coming years, the appearance on the market of environmentally safe antifouling paints.

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THE DISCOLOURATION OF COPPER ANTIFOULING PAINTS IN SULPHIDE RICH SEAWATERS

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INTRODUCTION

A problem of copper containing anti-fouling paints is that under certain environmental conditions they discolour and turn black. The phenomenon was first reported in the first vinyl copper paints used by the American navy. The blackening occurred when the paints were exposed to high sulphide containing waters such as found in polluted estuaries and harbours and in anaerobic mudbanks. The sulphide present in these areas having been generated by the action of sulphate-reducing bacteria (SRB). The discolouration has been found to be due to copper sulphide and to permeate through the paint with time and sulphide level from the exposed surface towards the substratum.

While there have been a few reports of this blackening activity the mechanism of blackening has not been extensively studied nor have the effects of the blackening on anti-fouling performance and long term recovery.

MATERIALS AND METHODS

The objective of the study was to assess the behaviour of copper containing antifouling paints in sulphide containing seawater, their subsequent anti-fouling properties and their recovery in performance.

Blackening by sulphide was carried out by immersing four different types of copper containing paints in seawater containing active natural cultures of SRB (using decomposing seaweed as the nutrient source). Exposure to these sulphide cultures was for various time periods up to 24 hours and the levels of sulphide they were exposed to ranges from 25 to 600 ppm (measured as Hydrogen sulphide in acidic titration).

Colour change was determined using the chroma scale as measures on a reflectant spectrophotometer designed and developed at the University of Leeds. This spectrophotometer gives a measure of colour that is close to that observed by the human eye.

RESULTS

Discolouration was detected in seawater containing less than 100ppm sulphide and the discolouration occurred very rapidly under all conditions (less than 10 minutes).

Microscopical studies showed that the discolouration occurs on the surface of the paints and penetrated into the paint matrix. The discolouration was due to the formation of copper sulphide minerals.

Following initial discolouration the blackening faded with time on immersion in seawater (during raft trials). However, discolouration was still detectable following a

years exposure to unpolluted seawater.
The paints that had been immersed in the sulphide environments showed some, though not a severe, reduction in antifouling ability.

DISCUSSION

That copper containing anti-fouling paints can blacken very rapidly on exposure to relatively low levels of sulphide generated naturally explains the reports of blackening in service. Only a few minutes exposure to anaerobic muds of polluted conditions are required for the reaction to occur and such conditions could easily be envisaged in a polluted harbour.
The nature of the blackening, being a surface reaction producing a layer of copper sulphide on and within the paint, would initially lead one to the conclusion that such blackening would provide a barrier to the leaching of copper from the paints and thus severely reduce their antifouling ability. However, this was not found to be the case and the copper sulphide layer, though not easily solubilised (as shown by the persistence of discolouration after one year's immersion) must be sufficiently porous to allow the passage of copper ions to the surface.

CONCLUSIONS

The phenomenon of the blackening of sulphide containing paints may become more important due to three factors:
1. the extreme reduction in the use of organotin compounds on environmental grounds means that more copper based paints will have to be used, at least in the short to medium term.
2. Increased pollution in harbours and estuaries will increase the frequency and levels of high sulphide environments.
3. The use of antifouling paints on static structures, such as offshore oil production platforms is increasing and these environments are likely to have more anaerobic conditions and higher sulphide levels.
The study shows that, although aesthetically detrimental and affecting the performance and life of the paint in some way, sulphide discolouration may not be as damaging as first perceived as the paints do still show a high degree of anti-fouling control.

APPLICATION OF FAST CURING POLYURETHANE COATINGS TO FILL AND PROTECT WELDED JOINTS OF SUBMERGED SEA LINES

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The wide use of sea-lines for crude oil or gas transportation (thousands of kilometers as a whole) led to develop high grade technologies which range from the choice of materials to assembling, joining, welding, coating, cathodically protecting a structure which has to overcome strict specifications as far as durability, reliability and maintenance free service life are concerned. Usually a sea line is made of a series of steel pipes, variable in diameter, length and metal thickness, following API SL X 52 grade standards.

The adopted policy in AGIP for corrosion protection of a sea line is based on the use of advanced both materials and technologies, careless of costs, in view of reliability: the enormous costs of both marine and underwater equipments for maintenance operations on a sea-line, and upmostly the unbearable damage for the environment a spilling might cause led AGIP to the choice of total quality and reliability; to this aim the external coating is a 2 mm thick high built coal-tar polyurethane, on which a thick (10 to 20 cm) reinforced concrete layer is added for sake of weight, since the line has to be anchored to the bottom. The crucial problem arises at the joints, where a 80 cm long area is left discovered for welding. The traditional solution to this weak point as far as corrosion is concerned was the use of stripes followed by mastic moulding. The possible breaking or damage of this coating, followed by corrosion in the welded zone is likely to cause oil spilling and unbearable pollution. Inspection, repair and maintenance are by far more expansive than the use of an alternative, more sophisticated material than mastic. Moreover, both during moulding operations and in service, many tons of polluting materials might be disposed of in the sea if a degradable material like bitumen is used.

AGIP decided therefore after a long term research to adopt the use of cold injected, fast curing, heavily filled two-component polyurethane resin, in order to warrant: a) a reliable sealing of the welded joint, even in case of welding failure; b) an extended service life of the structure; c) the maximum protection of the environment during the whole operations period .

The design procedures were aimed to screening all the possible alternative solutions, as far as protection, durability and "environmental friendship" were concerned. The possible competitors were:

1) light weight polyurethanes - the main defect is the weight itself, followed by excessive water permeability.

2) Epoxy resins - very difficult bonding with non-clean metal; long curing times; need of high curing temperatures.

3) Bitumen or mastic - possible failures in moulding (no way to inspect, since the metal mold has to be left mounted), pollution (possible connections with EEC 75/442 direction).

4) Concrete - many problems both with application and durability.

The research led to the choice of a heavy weight polyurethane (trade mark ISVERBLOCK 3000) loaded and filled with barite and other filling agents. The effects of fillers on curing reactions are remarkable: the polymer achieves a complete chemical inertness. This material was investigated by means of mechanical tests, (loading, shearing, impact, elongation etc.), physical tests (electrical resistivity, water permeation, effect of temperature, pressure, radiation etc. on performances), chemical tests (degradation of composition as a consequence of aging, reactivity with oxygen and water, reactivity with oil and gas, etc.) and corrosion tests, including adhesion to metal, cathodic disbonding, bacterial corrosion.

A pipe sample, on which a hole was drilled, was coated with a 5 cm thick layer of ISVERBLOCK 3000, then filled with crude oil and kept at high pressure at 90°C for six months without any problem.

An impact test was carried out at CAPSIS (UMIST, UK) with a load of 2700 Kg at the speed of 7 knots: no noticeable failure or decrease of protecting properties was found.

As a side result, the material was tested as far as radiation permeability is concerned, obtaining an acceptable opacity, and absolutely no perceivable chemical degrade after impact with 100 MRAD.

As a conclusion, the results led to acknowledge the performances of a material which, suitably engineered, is able to withstand many environmentally dangerous instances, including the possibility to ensure reliable service life without maintenance to a long lasting sea line (a nine years service evidenced no alteration) and allowing a realistic hope to introduce an alternative chance to dispose of toxic or noxious wastes (crude oil being an existing example of safe application) by embedding them in containers made of conveniently and easily moulded polyurethane (A patent on this subject is owned by authors).

BIOCIDE RELEASE FROM ANTIFOULING COATINGS

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In Australia, as in many other countries, concern regarding the environmental effects of organotins on marine life have led to restrictions being placed on the use of antifouling paints containing tributyltin (TBT). In most Australian States, the form of the legislation has been to ban the use of any paints containing TBT on vessels less than 25 m in length, and to restrict their use on larger vessels to those paints with low TBT release rates. Evidence suggests that these controls have been effective in reducing environmental TBT concentrations and associated defects in marine shellfish populations. However, there remains concern in some areas on the impact of continuing input of TBT from naval and merchant vessels. The TBT debate has also stimulated discussion on the environmental impact of other antifouling biocides.

A key to determining the potential impact of antifouling coatings is knowledge of the rate of release of biocide from the paint film. This would allow not only estimation of biocide input rates to inshore systems from shipping data, but would also assist in the formulation of coatings with minimum effective biocide contents. Methods used for measuring release rates have varied, as have the figures derived by these methods. The method adopted in Australia for determining TBT release from antifouling coatings for the purposes of legislation is the draft ASTM method used by the U.S. EPA in its 1986 "data call-in notice". In this method, a polycarbonate cylinder painted with a band of antifouling paint is rotated in a container of artificial seawater and aliquots of seawater taken at set intervals for analysis. We have examined this method in a study of biocide release from a range of antifouling paints including organotin copolymer paints, both with and without cuprous oxide as a secondary biocide, and paints containing only copper. The analytical techniques used were GC-FPD for TBT and ASV for copper. Results have been compared to release rates derived from field performance studies of the same antifouling paints and *in situ* measurements on ship hulls.

In the laboratory, copper and TBT were found to differ in their manner of release. For example, copper release rates were found to decrease over several hours after immersion in the test container. This was apparently due to inhibition of copper release as copper concentrations in the test container approached equilibrium with copper in the surface of the paint. As paints aged, the equilibrium copper concentration decreased. No such concentration dependent effect was observed for TBT, but an initial pulse of TBT was consistently measured after water changes. To overcome these irregularities, revised sampling protocols have been developed for both biocides which enable better characterization of release rate. The revised protocols have been applied to a study of TBT release from antifouling elastomeric materials.

Our studies have highlighted the difficulties in obtaining realistic biocide release rates in the laboratory. Methods such as the US EPA method provide a valid basis for comparing biocide release from different antifouling products, but do not necessarily reflect actual release from an in-service vessel. Caution is therefore necessary if release rate figures are to be used to estimate biocide input in models to predict environmental impact in real ecological systems.

THE ROLE OF SURFACE FREE ENERGY IN DEVELOPMENT OF NON-TOXIC ANTIFOULANTS

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A heavy growth of marine fouling organisms attached to the shiphulls adversely affects the operation of ships, reduce their speed and increase energy requirements and fuel consumption. Both fleet readiness and energy conservation depend on long term protection against marine growth. At present toxic antifouling (AF) coatings are in use, but the recent concern about the environment makes it necessary to develop non-toxic AF system. Instead of killing the attaching larval forms of the fouling organisms, theoretically their attachment can be discouraged by repellents, narcotizers, or by creating surfaces that do not lend themselves for easy colonization. Since all major fouling organisms attach by bioadhesive secretion, one approach would be to block the curing mechanism of the liquid secretion thereby preventing its adhesion.

Although a number of fouling organisms, such as barnacles and mussels use similar type of bioadhesives based on quinone crosslinking of proteinaceous adhesive, this mechanism, even if it could successfully be blocked, may not be ubiquitous enough to provide a target for universal protection. A more general approach may be based on surface energies that govern adhesion.

Our measurements on the liquid barnacle adhesive indicated that solids (coatings) with surface energies lower than 12 dynes/cm are needed to prevent their attachment. Adsorbed monolayers of perfluorinated surfactants have the lowest known surface energies. We simulated these monolayers by mixing such compounds into coating matrix and by synthesizing polymers with long perfluorinated sidechains.

When perfluorinated surfactants are mixed into a still liquid polymer, the surfactant molecules form a monolayer on the surface where they become immobilized by the hardening polymer. Most of the additives lowered the critical surface tension of the epoxy coating matrix dramatically and with only 10 % addition of perfluorooctanoic acid the critical surface tension of the epoxy was reduced from 45 to 16.3 dynes/cm, which is lower than that of Teflon (18-20 dynes/cm).

We synthesized a series of polymers with perfluorinated sidechains. The surface energies of these polymers were around 10 dynes/cm, much lower than that of the polytetrafluoroethylene type of perfluorinated polymers with no sidechains. In general, acrylates were softer and had slightly lower surface energies than methacrylates. Copolymers of acrylates/methacrylates showed better consistency and as low surface energies as the homopolymers. The surface tensions of the siloxanes were as low as those of the methacrylate and acrylate polymers. The low surface energies indicate that these polymers must have surfaces composed primarily of CF3 groups, implying high degree of orientation. Specular reflectance infrared spectra with unpolarized light and with light polarized at 0°(parallel to the sample surface) and 90°(normal to the sample surface) suggest that these polymers are at least partially oriented.

Some of these polymers had good resistance against attachment of fouling organisms upon exposure to marine environment. After two month exposure, the uncoated surfaces of the panel were heavily fouled, but the areas coated with these polymers were not only free of barnacles, but free of algae and slime-film as well. These results indicate that low surface free energy have a major role in combating marine growth without toxics.

ELECTROCHEMICAL EVALUATION OF COAL TAR EPOXY COATED STEEL IN SEAWATER

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INTRODUCTION

Coal tar epoxy paint films are used on marine structures and ship hulls, in thicknesses usually in the range 250-300 µm. The principle of corrosion control by the application of a non-inhibiting barrier coating is to preclude contact of the electrolyte with the metal. In practice, however, many coatings are porous, or have voids or other defects in their structure. The coating will deteriorate with time through natural ageing and the length of time over which corrosion protection is afforded by the coating can be estimated by electrochemical measurements made in the laboratory. However, these measurements are often difficult because of the non-conductive nature of the coatings. Direct current methods may involve relatively large polarisations which may damage the substrate barrier coating, thus giving a false indication of the effective lifetime of the painted metal system. Electrochemical impedance analysis has become a valuable technique for the evaluation of many electrochemical systems, even when the resistive properties of the surface are high. The small voltage perturbations used cause only minimal disruption to the electrochemical test system. This work involves the use of potentiodynamic and impedance measurements for the study of coal tar epoxy painted mild steel coupons in static, natural seawater.

MATERIALS AND METHODS

Coupons were fabricated from mild steel 'A' quality ship plate. Prior to painting, the exposed surfaces were sand-blasted to remove any mill scale, dirt and surface corrosion products and degreased using xylene. Coal tar epoxy paint was applied to the surface in multiple coats to give coating thicknesses of 27, 95, 145, 190 and 200 µm. In the electrochemical measurements, a normal three electrode flat cell arrangement was used with a silver/silver chloride reference electrode. The specimens were exposed to the seawater over the whole of their surface area, but removed at two week intervals and mounted in a flat cell, with 1 cm^2 area exposed, for the electrochemical measurements. The 27 µm coated specimen was left permanently fixed in a flat cell in static seawater at ambient temperature, such that a specific 1 cm^2 area was always in contact with the seawater and was used in every test. Plots were obtained of potential versus current density using an EG&G PARC potentiostat model 273 interfaced with an IBM PS2 model 30 microcomputer. Impedance measurements were made on the coupons over an immersion period of 6 months using an EG&G PARC two phase lock-in amplifier model 5208 and PARC Softcorr 378 software. The lock-in amplifier used single sine wave excitation over the frequency range 100 kHz to 5 Hz and multi-sine wave excitation over the frequency range 5 Hz to 100 µHz; the latter method substantially reduced the impedance measurement time at low frequencies. Evaluation of equivalent circuit parameters was achieved using the EQUIVCRT software program. Measurements were made on all painted samples and on unpainted steel samples for comparison. After 18 weeks, the 27 μm coated specimen was removed from its cell and artificial failure induced by piercing a blister. It was then returned to the same cell such that the same area was exposed for further electrochemical measurements. The natural seawater used was obtained from the Plymouth Marine Laboratory and had an average conductivity of 4.65 S m^{-1}. The seawater was replenished at regular intervals throughout the trial.

RESULTS

An unpainted steel coupon in static, air saturated seawater was found to take, on average, two to three hours after immersion to settle to the free corrosion potential E_{Corr}. The SIMPLER™ corrosion modelling software was used to model the polarisation curve for the unpainted sample. It was shown to be made up of an oxidation reaction of iron to produce iron (II) salts and the reduction of dissolved oxygen to produce hydroxyl ions. The polarisation resistance, R_p, of the experimental curve over a potential range of +20 mV relative to E_{Corr} was determined by Tafel analysis and was found to be 2065 Ω cm^2 , whilst the model value was calculated to be 1860 Ω cm^2 which was in good agreement with the experimental value. Polarisation scans were also carried out on painted mild steel coupons under the same conditions. All of the painted coupons showed unstable open-circuit voltage characteristics during the early part of the immersion period, whatever size of area was being investigated, thereafter the potentials stabilised somewhat, but there was considerable variation in the results obtained for the different coupons. An analysis of the d.c. polarisation scan of a 200 μm painted coupon is given. The modelled curve is obtained by introducing a 100 fold reduction in the oxygen diffusion limiting current density and assuming that the polarisation resistance term was 10^6 Ω cm^2.
Area considerations were found to be important when examining the d.c. electrochemical behaviour. This is because the coating reduces the effective area of the metal/electrolyte interface. In applications using large areas the difficulties are considerably diminished and may be eliminated completely. The electrochemical impedance response and the resulting equivalent circuit fit for a freely corroding mild steel coupon are presented and the polarisation resistance is obtained by extrapolation of the impedance scan to the real axis. The results of the impedance measurements were used to follow changes in the corrosion parameters, R_p and C, over the time of the trial. Visually, blistering on the samples of thicknesses 95 and 145 μm was evident after 24 weeks and on the 27 μm coated sample after 18 weeks, but at no time during the whole of the test on the 190 and 200 μm samples. No paint failure occurred naturally. The 27 μm sample was removed from the seawater after 18 weeks and a blister failure artificially induced. The impedance spectrum of the resulting surface showed a drastic change from previous spectra. The polarisation resistance value decreased by two orders of magnitude from the intact paint film and the interfacial capacitance increased dramatically. For the intact paint films, the capacitance seemed uniformly constant. During early immersion the epoxy paint

coating is in good condition and the film acts as a dielectric. In this case the sample exhibits capacitive behaviour. After longer immersion, the Nyquist plot showed the interaction of two semicircular arcs. The high frequency arc provides information relevant to the condition of the paint film and the low frequency arc represents substrate corrosion activity. It was noticed that there were variations in the impedance response from different areas of the sample. Thus it would seem necessary to carry out impedance testing over a number of areas of a given painted surface in order to be sure of gaining a true picture of the surface condition. It was also observed that the shape of the Nyquist impedance responses rarely depicted a true semicircle, but tended more often to be a depressed semicircle (with or without Warburg diffusion tails). The angle and dispersion of these semicircle centres from the origin has been suggested to indicate the mechanism of the corrosion reaction.

CONCLUSIONS

The electrochemical impedance technique was shown to provide a wider range of information on the corrosion characteristics of the painted metal surface than was available by d.c. methods alone. The importance of analysing a representative area of the sample was highlighted. Studies on the unpainted steel coupons showed good correlations between corrosion parameters obtained by d.c. polarisation and impedance measurements. However, polarisation methods can provide only limited information for coated samples and the impedance measurement was a more useful guide to the coating performance. Changes in the impedance response of the sample were dramatic when failure of the coating occurred. The changes in the impedance response prior to failure were less dramatic but nonetheless detectable.

THE SEARCH FOR ALTERNATIVE ANTIFOULING METHODS: HOW TO LEARN FROM NATURE? A PILOT STUDY

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Antifouling coatings based on organotin compounds have been used for many years to keep ship hulls free from fouling. Because they possess a severe threat to the marine environment they are subjected to growing restrictions. Although a total ban on the use of organotin is not expected on the short term, there is a growing need for alternatives.

One interesting possibility comes from nature: the surfaces of numerous sessile marine organisms remain remarkably free of fouling, due to antifouling adaptations. A whole range of possible defense mechanisms may be used singly or combined: mechanical, physical or chemical. The most widely used mechanism is probably the production of compounds with antifouling properties.

The hypothesis underlying the present study is that it is possible to develop an environmentally safe antifouling system by using natural antifouling compounds. Such a development takes many years and comprises at least the following steps:

- collection and extraction of organisms;
- screening of the extracts on antifouling properties by bioassay guided fractionation, together with ecotoxicological testing;
- identification of the most promising antifouling compounds;
- synthesis of the compounds;
- development of a suitable coating.

The purpose of the pilot study was to test the idea of using antifouling compounds from sponges in antifouling paints. Sponges were chosen as source organisms because a high percentage of these organisms produce biological active products and are free of surface growth.

Fifty one sponge species were collected in the Caribbean and extracted in methanol and dichloromethane. The extract solvents were evaporated *in vacuo* and the crude extracts were tested for their antifouling activity. The extracts were mixed with a clear, nontoxic vinyl resin and applied to small glass panels. Depending on the available amount of extract, 1, 2, 3 or 4 glass slides per extract were used. The panels were randomized, attached to wooden frames and vertically exposed on a raft in the harbour of Den Helder (The Netherlands). The variability in extract colour and solubility in the paint solvent (xylene) resulted in many different types of paint films. Because surface characteristics, such as colour and roughness, are of prime importance for the settlement of fouling organisms, nine different controls were implied, e.g. paint in which different substances (sand, sediment, chalk) were mixed. After 17 days of immersion the fouling by the barnacle *Balanus improvisus* was estimated and found to be low on most of the extract containing panels (13%) compared to the control panels (27%).

From these results it can be concluded that sponge extracts are able to inhibit at least the first stage of fouling by barnacles.

A NEW "MUSSEL TEST" FOR ANTIFOULING SUBSTANCES

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Generally, larvae of some macrofouling organisms are used for the screening of antifouling substances. Some Japanese groups however, adopt the so-called "mussel test", in which the adult mussel's *Mytilus edulis* characteristic of producing byssus threads to attach itself to surfaces is used as an index. In practice, the test is conducted by fixing the mussel along the edge of the sample zone and is evaluated through direct observation of the location and the number of byssus threads produced by the mussel to attach itself.

In nature, the mussel moves around until it finds a suitable substratum surface to attach itself. We designed a new "mussel test" to screen antifouling substances by using this behaviour. Three preliminary experiments were consecutively performed to collect basic information for designing the method: 1) to select a suitable mussel size, 2) to find a suitable surface that will prevent the mussel from attaching to the bottom of experimental containers, and 3) to trace the behavioural pattern of the mussel in the triangular chamber with lapse of time. Finally, the present assay method was tested with bacteria film coated surfaces and with silicone coated surfaces.

MATERIALS AND METHODS

First, mussels collected were grouped into four according to their shell sizes, ranging from 0.5cm to 3.0cm, and each individual was placed in separate containers. Their byssus productivity was measured by counting the number of threads produced, and their activity was estimated by counting the number of thread bundles. Counting of byssus threads was carried out at 1, 3, 5, 24, 48, 72 and 96 hours after the start of experiment. Then, several cylindrical chambers were prepared by 1 - 4% agar. Mussels with shell size of 0.5cm were separately placed in these chambers, which were subsequently immersed in seawater. Byssus threads produced were counted after 24 hours from start of experiment. In a third experiment, mussels were individually placed in triangular chambers built by vertically fixing three slide glasses in each beaker layered with 3% agar. Mussel activity was traced by checking their location at 3, 6, 12 and 24 hours after the start of experiment.

Finally, this assay method was tested with bacteria film and silicone coated surfaces. Attachment behaviour (frequency of movements and number of threads produced) of mussels when exposed to the sample was observed under two conditions: 1) when all three sides of the chamber are coated with the sample and 2) when only two sides are coated with the sample. Untreated slide glasses were used for comparison.

RESULTS AND DISCUSSION

Among the 4 size groups investigated, individuals belonging to the smallest size groups (0.5cm and 1.0cm) were most active in movement and produced byssus threads during the first 24 hour observation period, the smallest individuals were then considered suitable for "mussel test". Mussels were found to discriminate softer agar surfaces and less byssus thread formation was observed on 1 to 3% agar. On the other hand, 4 of 5 mussels attached by byssus threads on the surface of 4% agar. In proceeding experiments, 3% agar was incorporated in the method. Most mussels tested were observed to climb the walls of the chambers and attach to the wall by threads within the first three hours. Four out of 5 mussels showed no further movement until the end of the 24 hour experimental period, thereby indicating that 24 hour experimental period was sufficient.

No significant difference was observed in byssus thread production and frequency of movement between mussels in slide glass chambers and those in bacteria film coated chambers. Mussels also did not show discrimination to either surface when exposed to both simultaneously. On the other hand, all mussels tested did not attach to the silicone coated walls of the chamber. Thus, the present method can be applicable to screen antifouling substances.

NON-TOXIC FOULING CONTROL SYSTEM FOR APPLICATIONS OFFSHORE AND IN SEA WATER INLET PIPES

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INTRODUCTION

Industries which rely on equipment that operate in marine environments are continuously faced with the problem of fouling growth affecting the performance and safety of such equipment. Offshore structures become fouled by marine growths, the most severe fouling occurring between sea-level and a depth of approximately 30 metres. This increases the wave loading and reduces the stability of the platform.

Fouling of sea water intake structures is also a major problem, particularly in power plant cooling water systems. This reduces the effective diameter of the pipe, reducing cooling capacity.

Previously toxic antifoulant marine coatings were effective for controlling the growth of marine organisms. However, recent regulations and further proposed environmental restrictions concerning discharge of leachable toxic materials limits, and in many countries prohibits, the future use of these coatings. This paper considers the use of non-toxic silicone elastomer fouling control coating systems as alternatives.

MATERIALS AND METHODS

All fouling life forms adhere to surfaces by producing extra cellular polymers, special bio-adhesive, or organs of adhesion. Consequently, much attention has been given to coatings which reduce the effectiveness of the bonding mechanism, without the release of toxins. Fluoropolymers and silicone elastomers are distinguished from other polymeric systems by the interesting properties associated with their surface activity and related surface properties, resulting in low energy surfaces.

The silicone elastomers are based on a backbone of repeating (Si-O) units. As well as their interesting inherent surface properties, they also offer good chemical, thermal, UV and biological stability. A number of coating formulations, based on the silicone elastomers have been applied on to test panels, at finish coat thicknesses of 150 microns, which have been exposed on raft trials in excess of 10 years.

RESULTS

Modified silicone elastomers have exhibited fouling control performance over a period in excess of 10 years in raft trials. Their fouling control performance was further highlighted in a comprehensive study to evaluate all available non-toxic surface coatings for application in power station inlets performed by the EPRI. It was observed that silicone based coatings gave the best degree of "easy clean" behaviour and were effective in reducing macrofouling on intake surfaces and in preventing growth on piping.

Following successful raft trials the coatings have been used for a number of coating applications in offshore, coastal power stations and in aquaculture. They have proved to exhibit fouling resistance in each of these environments.

CONCLUSIONS

Environmental legislation is restricting the use of biocides to limit fouling in many environments, especially concerning stationary structures.

Silicone elastomer coating schemes have proved to be effective fouling control alternatives in the offshore and cooling water inlet areas. They are environmentally friendly, releasing no biocides and, provided the surface is not mechanically damaged, a prolonged period of fouling control can be expected.

CORROSION BEHAVIOUR OF COATED MILD STEEL IN ARTIFICIAL SEA-WATER

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ABSTRACT

Corrosion behaviour of coated mild steel in artificial sea-water (air saturated 0.5 M aqueous solution of NaCl) was studied using the Electrochemical Impedance Spectroscopy (EIS) technique. The results obtained indicated that film composition (various amount of during agent) dramatically affects the corrosion of the metallic substrate. Extended lifetime was observed for samples with a content of the curing agent equal to 8.5% by weight. An increase in lifetime was also observed by increasing the film thickness and the curing temperature. These results were interpreted in terms of a model in which the dielectric properties (capacitance and resistance) of the coating strongly depend on coating composition and are affected by both the water and salt uptake into the film.

Key-words: Steel, Coating, Epoxy

INTRODUCTION

The major purpose of the work described herein is to provide an understanding of the effect of level of curing agent on coating performance and failure to further support the view of the inhomogeneous nature of the epoxy-polyamide paint films [1]. The dielectric properties of the coating (resistance and capacitance) will be, thus, related to the level of curing agent in the paint, to the film thickness, and to the curing temperature. Finally, an attempt will be made to relate failure to both the level of curing agent and to the water and salt taken up by the coating when immersed to an air saturated 0.5 M aqueous solution of NaCl.

MATERIALS AND METHODS

The metallic substrate for corrosion testing was a low-carbon stainless steel polished with emery paper, degreased in acetone and stored in a desiccator for 48 hr before painting.

The coating used in this study was a commercial epoxy (Epon 1001 from Shell kindly supplied by Boero, Genoa, Italy) containing FeOH as pigment in the form of fibres 0.2-0.6 µm long. The curing agent was polyamide added to the epoxy in order to obtain paints at different level of the curing agent.

The compositions investigated in this paper were: 2, 4, 6, 8.5,12, 16 and 20% in weight of curing agent. The paints were cured at 25 and 50 °C for 1 hr and then allowed to dry in a vacuum oven at room temperature for one week.

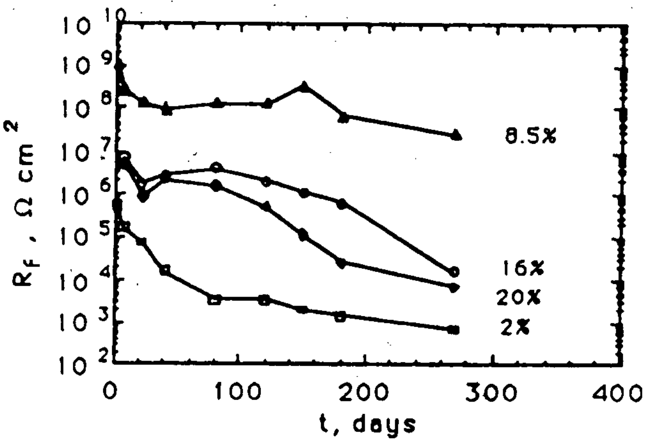

Fig.1. Time dependence of film resistance, R_f, for epoxy-coated mild steel with different level of curing agent when exposed to air saturated 0.5 M NaCl at 25°C.

RESULTS

Figure 1 shows the effect of immersion time on the film resistance, R_f, for paints with different level of curing agent. The R_f is related to the protective properties paint film on thus to the corrosion behaviour of substrate. Results obtained in this paper indicate that the film resistance R_f ,increases with cure temperature and with film thickness. An extended lifetime was observed for films with 8.5% by weight of curing agent. The experimental results show that the film capacitance C_f is related to paint's lifetime. Variation of C_f with time were attributed to water and salt uptake in the film. The diffusion coefficients, D, of water and Cl^- are, thus, the most important parameter to predict metal's corrosion behaviour in aerated 0.5 M NaCl solution.

CONCLUSIONS

Results reported in this paper show that the electrical resistance of epoxy based organic coatings is the dominant factor affecting the degradation of the mild steel metallic substrate in air saturated 0.5 M NaCl. Paint composition dramatically affects their performance and failure. Coatings with low and high level of curing agent are more prone to deterioration due to the low electrical resistance exhibited by these films.

ACKNOWLEDGEMENTS

The financial support of CNR (progetto finalizzato Chimica Fine e Secondaria) is gratefully acknowledged.

A STUDY OF AN ACCELERATED TEST METHOD FOR MARINE ANTIFOULING COATING SYSTEMS

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In the present time the dynamic test method is commonly applied as an important performance test for antifouling coating systems in some countries. In order to evaluate their performance effectively and reduce the period for researching work we made a test apparatus and designed a test procedure for evaluating the performance of ship antifouling coating systems.

The basic principle of the method is to combine the test specimens rotating continuously with a speed similar to ship service in the natural sea water pool with the immersion in a raft during the heavy growing season of marine foulings. The basic system consists of a rotor assembly. The surface velocity of panel is about twenty one knots. A magnetic cycle counter is assembled on the top of shaft in order to show the instantaneous velocity and record the accumulative circles. A 30-day static exposure after 200 hours rotation with 21 knots velocity are recommended as a standard cycle. Two types of test panels can be conducted at the same time. One is a panel with steel substrate which is used for testing fouling resistance. Another is plastics base which is used for measuring toxic leaching rate.

Six comparison tests have been conducted for ship antifouling coating systems both at home and abroad in Xiamen Marine Test Station of LSMRI from 1980 to 1988. It has also compared with the change of toxic leaching rate both dynamic and static methods. From the above comparison tests, results have been obtained as follows:

1. Antifouling coating systems with a service life of two or three years are usually failed after three or four cycles although it has one cycles variation because of the variation of AF film thickness and the early or late of the test start time.
2. As the effect of panel rotation, the reduction of thickness of self-polishing copolymer antifouling coating by erosion is evident. SPC film in plastics panel have been eroded partly after some cycles because of their much higher erosion rate.
3. The result evaluation has closely relationship with the fouling growing period. In order to evaluate the antifouling coating which have a service life of two to three years it is better to arrange the time of immersion of the fourth cycle in August (Xiamen harbour) when it is still the heavy growing season of marine foulings.

The results show that the test procedure has been proved to have a good compatibility with that of ship trial and raft test. It offers a rapid and effective test method for researching and appraising of ship AF coatings. This test method can be used for screening the method for AF coatings. Comparing the AF coatings which come from lab screening test with a control AF coating of known performance in heavy fouling season can reduce the time in raft and ship test. China Standard GB 7789- 87 «Dynamic test method for performance of marine antifouling coatings» which is based on above method has been approved in 1987.

MARINE CATHODIC PROTECTION - HISTORICAL PERSPECTIVE AND FUTURE CHALLENGES

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The various methodologies by which corrosion and marine corrosion can be reduced or eliminated are presented and discussed. Particular attention is focused upon cathodic protection, and a discussion of the historical development of this technology leading to the present state of knowledge is presented. It is concluded that many aspects of the fundamental theory of cathodic protection and what constitutes an appropriate potential criterion for protection are now well established. However, questions such as what transpires when a metal or alloy is progressively polarized from its corrosion potential to the reversible anode potential remain unresolved. These, along with the present practice of marine cathodic protection and the materials which are utilized, are discussed.

A unique feature of marine cathodic protection is the formation of calcareous deposits. Thus, the increase in pH at cathodic sites in association with production of hydroxide ions results in precipitation of certain inorganic species, $CaCO_3$ and $Mg(OH)_2$ in particular. Despite the importance of these surface films to the effectiveness, efficiency and economic viability of marine cathodic protection, studies of their composition/structure-property interrelationships are relatively few. That research which has been performed has focused upon calcareous deposit resistance and adhesion as important attributes. Correspondingly, microscopic examinations have revealed that deposits have a bilayer structure with each of the two forms exhibiting a distinct composition, structure and properties. These and related findings are discussed within the context of optimized cathodic protection for marine structures. It is concluded that future programs should focus upon the feasibility of obtaining improved properties for both calcareous deposit layers, and it is projected that the cost-to-benefit ratio associated with such research should be low.

IMPRESSED CURRENT CATHODIC PROTECTION SYSTEMS FOR THE RETROFITTING OF OFFSHORE PLATFORMS

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Cathodic protection, alone or in combination with organic coatings, represents the first corrosion control method for steel structures immersed in sea water.
Presently, cathodic protection by sacrificial anodes, mainly aluminum alloys, is preferred for new structures - for instance sealines and offshore steel platforms - where sacrificial anode systems reached an excellent reliability as far as anode behaviour and design are concerned; furthermore, they are completely maintenance free.
Impressed current systems have been extensively used for protection of coastal structure - piers, wharf, sheet pilings, etc. - and for corrosion protection of ship hulls. However, one of the most significant application of impressed current systems is on offshore platforms, already in service, after depletion or failure of the original cathodic protection system. This is a situation becoming more and more common in the future: in fact, more than 7000 fixed offshore platforms are in operation today in the world, many of which have reached, or are going to, their design life. Old platforms shall be dismantled, or, alternatively, their service life can be extended beyond the expected one, or they can be re-used for purposes different than oil and gas production: this is the case for instance of reservoirs used for gas storage. In this context, retrofitting of cathodic protection often represents a priority.
Titanium activated with mixed metal oxides, originally developed as anode material for industrial electrochemical processes, has been used for marine cathodic protection since more than 20 years ago.
First applications have been done using rod anodes, fixed by properly insulated supporting systems to the structure to be protected, typically piles or legs; rod anodes have been widely used, and still they are, for cathodic protection of steam condenser water boxes. Main concern was for over-protection of steel surfaces close to the anode, with consequent risks of hydrogen embrittlement and corrosion fatigue damages.
In the eighties, tubular titanium activated anodes have been developed, with center electrical connection and cable to anode connection obtained by plastic deformation of the titanium tube onto the cable (LIDAR system), allowing assembly of several anodes on the same power cable. Based on tubular anodes, different types of anode structures have been developed and applied, in particular for retrofitting purposes on offshore platforms.
One of the most fruitful design concept for impressed current system is the remote anode concept: anodes are placed on sea floor, far from the structure to be protected (distance ranges from a few meters up to 300 m depending on the size of the

cathode).

Several applications have been accomplished, mainly for shallow water platforms; anode have been buried in sea mud, thus reducing risks of mechanical damages (by anchors or drag nets), or supported on sleds. In the last case the anode is in contact with flowing sea water and a higher design anode current density is allowed, compared with buried anodes. Same design has been used for cathodic protection of offshore well casings.

A different design concept consists in the installation of strings of anodes directly on the structure, typically a steel jacket. Strings have been clamped to the jacket, following irregular paths, with anodes placed in appropriate positions from viewpoint of uniform protection requirements; preferentially, the strings of anodes are tensioned between sea bottom and the deck of the platform. In this case the anode structure consists in a tensioned (steel) rope, supporting the anodes, and the power cables, spiralled around. An important advantage of this concept is reduction of underwater work required for installation.

In the paper, the above mentioned cathodic protection systems are documented by some case histories of both deep water and shallow water offshore platforms. Design and operating data are reported on a series of controls carried out on deep water platforms to which the retrofitting by tensioned string system is applied.

Results of shallow water platforms, for gas production, by remote anode systems are also illustrated.

These experiences confirmed the economical competitiveness of the impressed current method for marine retrofitting jobs. Operating results after several years of service demonstrate the effectiveness of the concepts above illustrated also from viewpoint of protection conditions and uniformity of potential distribution.

ANALYSIS OF FACTORS AFFECTING THE PERFORMANCE AND CHARACTERISTICS OF SHIP IMPRESSED CURRENT CATHODIC PROTECTION

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Although impressed current cathodic protection (ICCP) can offer an effective mean for controlling corrosion in an aqueous environment, the protection of ships requires careful design consideration based upon an appreciation of the characteristics of different hull materials and the wide range of operational conditions. A greater theoretical understanding of the factors affecting the distribution of cathodic potentials is also required. An ICCP system can comprise one or more zones each with its own power supply, reference electrode (RE) and anodes. Protection profiles derive from the system configuration, that is, the number of zones and anodes and the location of these and REs relative to the hull itself, propellers and each other. The ideal is for the impressed potential to be achieved uniformly over a hull under all operational conditions. In practice, this is not achieved because of the galvanic effects of bronze propellers upon a ferrous hull, damage to paint coatings and exposure to varying seawater movement as a result of under way conditions or tidal/current flow when moored. A hull is a large, complex cathode, with at least three components - painted steel, exposed bare steel and bronze, which have different polarisation requirements.

Physical scale modelling provides an experimental laboratory technique for developing the understanding of ICCP, evaluating the performance of different marine systems and designing improved configurations, using real structures in real electrolytes. The paper analyses and synthesises results from a range of ship model studies.

The studies employed the Dimension and Conductivity Scaling (DACS) modelling technique. One-sixtieth scale, painted metal models were floated on, or immersed in seawater diluted such that its electrical conductivity was one-sixtieth that of standard seawater. Two types of model were examined. One was a detailed model of a 113.4m WaterLine warship, complete with rudders, stabilisers, bilge keels, A-brackets, propellers and shafts. Stylised models of the underwater area of a 108m WaterLine generic ship were also employed; these comprised a rectangular steel plate to which was attached either a bronze mass or accurately modelled propellers. Models were painted with a coal tar epoxy coating to a thickness of 225 µm (i.e. not scaled). Scale anodes and miniature silver/silver chloride REs were attached, with onboard transformer-rectifiers modelled by potentiostats. Potential profiles were measured by arrays of miniature silver/silver chloride electrodes. Under way conditions were simulated by pumping electrolyte past the models. Three different types of ICCP system were examined: Midship and "All-aft" single-zone configurations, and a combined Two-zone fit. Potential profiles and current outputs were measured under static and flow conditions, with intact and damaged paint coatings.

Results from the stylised models were closely similar to those from detailed hulls, which have been validated against data from warship surveys. The water permeability of the paint coatings, and the participation of the underlying steel surface in the cathodic processes, is demonstrated. Presented profiles and current outputs show that the three ICCP systems performed very differently. Each had its own responses to flow and changes in coating condition. Damage and simulated under way conditions increased current output, with flow having a greater effect when bare steel was exposed. Protection and the factor by which current increased depended upon the ICCP configuration. Current output, in itself, did not determine the effectiveness of protection. The two single-zone systems performed very differently. With an intact paint coating, the "All-aft" system used the lesser current but provided the better protection and under flow conditions the output increased by a greater factor than that with the Midship configuration, resulting in the higher current of the two. The Midship system, however, provided the better protection in response to damage. The characteristics of the two systems changed when coupled together and the Two-zone system was much more reactive to flow without coating damage, the stern zone dominated completely; with paint loss, however, the forward zone produced the greater output. Total current demand was less than the sum of the two component configurations. Overall, there was under-protection associated with areas of coating damage, except in the vicinity of the propellers. It is evident that potential profiles and current outputs are determined by the location of anodes and REs, respectively, relative to the propellers and exposed steel. The non-ferrous propellers dominate the cathodic processes, particularly under flow conditions. Results are discussed in relation to the different polarisation characteristics of the three components of the hull and the location of REs.

It is concluded that:

1. A hull is a complex cathode which experiences a variety of surface and electrolyte conditions.
2. The three components of the cathodic surface possess different polarisation characteristics and respond differently to changes in electrolyte velocity.
3. The performance of ship ICCP is determined by system configuration in relation to all of the hull components, and by operational conditions.
4. Different ICCP configurations have different characteristics and responses to under way conditions and coating damage.
5. Physical scale modelling provides a rational scientific approach to not only the evaluation and design of systems but also to the development of the understanding of ICCP.

APPLICATION OF PHYSICAL SCALE MODELLING TO THE DESIGN AND SURVEY OF MARINE IMPRESSED CURRENT CATHODIC PROTECTION SYSTEMS

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The design of marine impressed current cathodic protection (ICCP) systems is made difficult by the aggressive flowing nature of the aqueous environment, the variety of shapes, complexities and sizes of the structures requiring protection, and the range of changing operational conditions. Retro-fitting is extremely expensive even if the performance of new-fits has already been evaluated. Sea trials and surveys are expensive; it is often very difficult to measure the performance of operating systems and it is rare that operational conditions can be controlled or defined. Physical scale modelling provides a validated, experimental laboratory technique which can address:

a) the evaluation and systematic design of marine ICCP systems
b) the examination of system responses to a range of operational conditions
c) the design of remote-surveys and the analysis of data collected offshore
d) the development of the understanding of the processes involved in the distribution of cathodic potentials over structures.

The method was first pioneered by RNEC in 1984, as Dimension And Conductivity Scaling (DACS), with an initial aim of improving installed ship systems. It has since been shown to be a versatile technique applicable to the solution of a whole range of problems associated with marine structures generally.

The studies described in the paper employed a range of metal scale models which were floated on, or immersed in, seawater diluted such that its electrical conductivity was reduced by the same factor as that employed for the models. In this way the theoretical requirements for a true model are satisfied. Scale anodes and miniature reference electrodes (RE) were attached to the models, with the impressed current provided by potentiostats. Potential profiles were measured by arrays of miniature silver/silver chloride monitoring electrodes. Under-way conditions were simulated by pumping the electrolyte past models. Painted and unpainted models have been employed to:

a) investigate different types of ICCP configurations, relationships between components, and zonal control concepts;
b) examine the effects of seawater flow and coating damage upon protection profiles and system current output;
c) study the nature of the electric field in the surrounding electrolyte.

Specific aspects were addressed by the use of detailed models, while principles and factors were examined by models stylised to represent the general characteristics of different structures. Results are presented for one-sixtieth scale models of ships, offshore oil rigs, seabed pipelines and enclosed seawater systems. It is evident that the approach to the design of ICCP systems for such different types of structure has to be very different. The results illustrate the interrelationships between the components of systems and the responses of different configurations to seawater flow and damage to paint coatings. It is shown that different systems respond very differently both in the protection profiles and in current output. Current output is not a good indicator of system effectiveness. The studies examine single-zone systems, the interactions between zones in multi-zone systems, and the central role of the RE(s) in avoiding under- and over-protection.

It is illustrated how modelling can also be applied to the examination of the nature of the current flow in the electrolyte between different components of a system, in relation to both the direction and magnitude of the electric field. In addition to an examination of the characteristics of a simple bi-metallic model, results are presented from a study of remote-surveys of surface potential profiles and field gradients along a model seabed pipeline.

Results are discussed in relation to the development of a greater theoretical understanding of the mechanisms of ICCP and of the characteristics of large complex cathodes, which often comprise more than one material and are very different from those examined in classical electrochemical studies. The relationships between the size and location of anodic and cathodic surfaces are quite different and represent a distinct area of fundamental study. A number of practical design guidelines are presented in the context of the aim of developing Design Codes.

It is concluded that:

1. Physical scale modelling provides a unique, experimental technique which employs real structures in real electrolytes to produce hard data.
2. Different structures require different approaches to design.
3. System configuration is critical, with anode location determining the shape of protection profiles and RE location the level at which these are established.
4. Different ICCP configurations have very different characteristics and, at present, their performances can not be predicted without modelling.
5. Physical scale modelling provides a basis for a rational, scientific approach to developing the understanding of ICCP in the marine environment and the design of systems.

MISAD - A SYSTEMATIC APPROACH TO THE DESIGN OF MARINE IMPRESSED CURRENT CATHODIC PROTECTION SYSTEMS

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The provision of Cathodic Protection (CP) in the marine environment is made difficult by the variety of shapes, sizes and complexities of structures and by the wide variety of changing operational conditions. CP systems are expensive and require careful specification and design if maximum through-life protection is to be provided. At present, there is no codified method for analysing the requirement and synthesising a solution. In many ways this is analogous to the situation for administrative computing some ten years ago. The most successful approach to addressing this shortcoming was SSADM - Structured Systems Analysis And Design Methodology. The key points behind this methodology are encapsulated in its title - the exact requirement is analysed and specified before the required system is designed, with design taking place in an organised manner. Although the exact mechanics are not applicable to CP, the underlying systems analysis approach has been adopted in a modified form. For a variety of reasons, Impressed Current Cathodic Protection (ICCP) is the strongest contender for the protection of marine structures and this form is addressed below. The paper proposes a Methodology for ICCP System Analysis And Design - MISAD.

The overall process is presented as six major stages: Analysis, Options Short-listing, Options Evaluation, System Specification, Component Specification, and System Verification. Each is discussed in relation to marine structures generally. Specific illustrations are given for offshore oil jackets and ships, with results of Physical Scale Modelling studies of the design and performance of different ICCP system configurations. Presentation of the overall scheme is by block diagram flow charts which show iterative backward paths as well as the uninterrupted forward flow.

<u>Analysis</u> falls into three processes. First, the Operational Regime must identify the variables which will determine the characteristics and performance requirements of an installed system. Many of these relate to the structure itself, and others to environmental factors including geographical location, characteristics of the local seawater(s), magnitude of water movement past the structure, and seasonal variations. Secondly, the Limitation Regime provided by the Operator must specify to the Designer what may not be done to achieve the practical system. Prohibitions may include areas through which penetrations are not permissible and sites where attachments are prohibited. Thirdly, the Draft Verification Regime begins the definition of the acceptance criteria. For example, a ship specification should prescribe that protection (within a given potential range) shall be achieved over a hull with a defined paint damage protocol, for both moored and under way conditions.

The <u>Options Short-listing</u> stage must consider possible solutions and generate a list of candidate options which describe the systems in generic terms. Elements such as the number and location of ICCP zones, and the number of anodes in each, in relation to the structure's type, shape, size, geometrical symmetries and operating characteristics are important factors in this stage. The objective is to produce a short list of options which can be thoroughly tested at the next stage to ensure that the optimum solution is achieved.

Options Evaluation is the most vigorous phase of the whole design process and must be associated with stringent evaluation of the performance of system options in relation to protection over the whole structure, and the draft Verification regime. Of the various design approaches, Physical Scale Modelling uniquely provides a validated, experimental technique that produces hard data from real structures. Real-time iteration is provided between the design and evaluation of the range of detailed candidate configurations. The detailed location and number of ICCP zones, their Reference Electrodes and anodes must be evaluated. Attention is drawn to the types of structural components that have specific protection requirements different from that of the structure as a whole necessitating the provision of dedicated zones. Performance characteristics of different zonal configurations are illustrated, together with the rôle of Reference Electrodes and anodes in determining protection profiles. As the final output is the selection of the optimum system configuration, it is at this stage that preliminary costings are made.

System Specification is the step between system selection and its detailed final specification, allowing the Designer to describe in detail the configuration of the system. The output document will contain such details as number of zones, their impressed potentials and current requirements, the number of anodes in each zone, the positioning of controlling Reference Electrodes and the siting of any fixed monitoring electrodes.

Component Specification: it is at this stage that a hardware specification in terms of commercially available components is produced and any development requirements identified. Procurement costs will be clarified and operating procedures devised.

System Verification is the final proof of the efficacy of the whole design process undertaken. It is inevitably long-term as the performance of a system cannot be absolutely assessed until after it has been fitted and operated within the requirements of the acceptable criteria. Nevertheless, feedback is particularly important in refining the criteria on which design decisions are based, and for aiding the evolution of the methodology proposed in this paper.

In conclusion, a rational, structured approach has been developed for the design of marine ICCP systems, which breaks down the overall process into steps which can be subjected to formal quality assurance and Operator concurrence. The process will encourage close collaboration between Designer and Operator, with the product of each stage being deliverable documents to be agreed by each. This will ensure that areas requiring further work are formally identified.

It is contended that the MISAD approach will also focus attention not only upon areas of cathodic protection that require further study but also upon the development of information banks and design guidelines, with the ultimate aim of producing comprehensive Design Codes.

PROBLEMS ENCOUNTERED IN THE DOCK AREA BY ISAB REFINERY

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In the latter years the refinery experienced some problems in the area nearest to the sea (dock and linked pipelines). They are respectively:
- corrosion of the pipelines discharging ballast water;
- piles corrosion in the offshore structures;
- piles splash zone coating damage.

Recently, these problems have been object of an accurate study by the refinery's inspection people.

This article briefly reviews some characteristics associated to corrosive phenomenons (microbially induced corrosion, differential aeration etc.) and corrosion control (functioning of the cathodic protection system). Then the article presents a discussion about the problems mentioned above.

The study takes account of the following aspects for every item:

a) chemical characterization of ballast water, operating sequence to discharge ballast water and failure analysis in terms of observation of the corroded surfaces and failures, analysis of the corrosion deposits etc.;
b) maintenance history about piles and cathodic protection system;
c) sequence, to coat the piles splash zone, the resin-catalyst ratio of the coating adopted.

The results obtained can be summarized as follows:
- The cause of the corrosive phenomenons was individuated in the discharging sequence.
- It was impossible to discern about microbially induced corrosion or differential aeration as main phenomenon.
- The piles were corroded because of both bad general maintenance and bad performance of the cathodic protection system.

The proposals suggested at the end of the study are described below:
- clean with fresh water or sea water at the end of every ballast water discharging;
- adopt a different maintenance of the piles and more strict surveillance of the cathodic protection system performance;
- test coating with different resin-catalyst ratios.

The results of these proposals will be tested with the service of the following years.

PRACTICAL EXPERIENCE WITH CATHODIC PROTECTION

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A good control and prevention of uniform, galvanic and localised metallic corrosion can be obtained using cathodic protection with impressed current. In fact, if the anodes location is suitable, the current density distribution over the cathodic regions is quite uniform so that it is possible to reduce the corrosion extent to very small values by selecting a proper polarisation potential.

The main problem for its correct application to the protection of waterbox, tubesheet and tube inlet-outlets of a steam surface condenser cooled with sea water is the presence of materials having a different electrochemical behaviour. In this situation the potential should be kept in a restricted range to adequately protect the structure while avoiding the dangerous effects of overprotection (hydrogen embrittlement of titanium, cathodic disbonding of paintings, increase of heat transfer resistance as consequence of carbonate film build-up.). We recall, for istance, that in the steam condenser of Unit 4 at Monfalcone power station the materials in contact with sea water are: carbon steel (waterbox), aluminium brass and titanium (tubes) and aluminium bronze (tubesheet).

Thus, ENEL/DSR/CRTN has been carrying out a research activity with the aim of studying the behaviour under cathodic protection conditions of different materials and developing a fully automated impressed-current cathodic protection system.

This paper describes the single steps of this activity:

- experimental determination of the current density required to protect the different materials under real operating conditions;
- development and validation of computer codes for assessing the current density distribution;
- feasibility study of a computerized control system;
- prototype application;
- installations at Torvaldaliga Sud and Monfalcone power plants;
- final technical specifications.

The criteria applied for the global sizing of the system and the choice of protection level are discussed while the operating experience is illustrated by some practical examples.

In conclusion, the research activity has made it possible to develop and validate theoretical and experimental tools and gain the necessary experience for a correct application of impressed current cathodic protection on the tubesheet and waterbox of a condenser.

In particular, the most significant points of our experience with the design and field application of the computerized system, called PROTEX, can be summed up as follows:

- the PEVACO and BEMCOR computer codes, together with the electrochemical data representing the real operating conditions of the materials, allow the positioning and sizing of the anodes tom be defined and checked accurately;

- the particular potential measurement system used satisfies the requisites of reliability and precision indispensable for industrial equipments;
- the regulation and control system can provide adequate protection even in the event of anomalies;
- the operator interface and the storage system for operating data and anomalous events permit a full control of the system in any situation.

POSTER SESSION

BIOFILM INTERFERENCE ON STAINLESS STEEL CORROSION BEHAVIOUR IN ANTARCTIC SEAWATER

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INTRODUCTION

This work aims to establish if biofilms, grown on stainless steel surfaces in Antarctic conditions, are able to interfere on the corrosion behaviour of these alloys as it happens in temperate seas.

Therefore short (about two months) and long term (one year) exposure tests were carried out in Antarctica at the Italian Base in Terra Nova Bay on stainless steels AISI 304, 316 and 20Cr-18Ni-6Mo.

The analytical characterization of biofilms and the electrochemical data herein collected were compared with the data obtained in the Mediterranean Sea (Genoa).

EXPERIMENTAL WORK IN ANTARCTICA

The main results of the research in Antarctica can be summarized as follows:

- **A cathodic depolarization of oxygen reduction on stainless steel surfaces, due to the biofilm growth, occurs in Antarctica as in temperate seas and needs 20 - 25 days to be completely developed.**

  However, the cathodic depolarization involves less extended potential ranges than in other climatic situations, so that the settlement of corrosion potentials, observed on stainless steels in passive state, is close to +100 mV SCE instead of around +300, +400 mV SCE as it usually happens in the European seas.
- **A lower crevice corrosion onset probability characterizes the behaviour of stainless steels in Antarctica.**

  The corrosion data, coming from the long time tests, show that stainless steels have a lower probability to nucleate crevice corrosion attack than in temperate seas, even though corrosion propagation rates, when the corrosive attack starts, remains substantially unchanged.
- **The Antarctic biofilms do not reveal peculiar differences with the winter Mediterranean ones as regards to EXO/INTRA carbohydrate contents.**

  The biochemical analyses have evidenced that the distribution of the carbohydrate contents between the intracellular materials (INTRA) and the Exopolimeric Substances (EXO) falls in the range of the data observed in the Mediterranean biofilms.

  This observation suggests that any natural seawater, provided cooled at 2°C, could cause on stainless steels the electrochemical consequences observed in Antarctica.

Therefore, it was tried to remake in Genoa the Antarctic experiments by using "local" natural seawater cooled at 2°C.

EXPERIMENTAL WORK IN GENOA

The results obtained in Genoa confirmed that the cooling of natural seawater at 2°C causes a sharp drop of the maximum corrosion potential values (E_{max}) from about +400 mV SCE to around +100÷120 mV as in Antarctica.

On the other hand, the dependence of the E_{max} potentials from the natural seawater temperature compared with that obtained in sterile artificial seawater confirms that the biological interferences are active from 2 till at least 35 °C.

Finally, the EXO and INTRA carbohydrate data, collected on freely at 2°C exposed samples, were compared with three clusters of data previously obtained in Genoa working at ambient temperature.

The EXO, INTRA values, obtained at low temperature agree more with the data collected on samples polarized at -200 mV SCE or exposed in seawater artificially enriched Ca ions than with the data coming from samples freely exposed in untreated seawater.

Therefore this suggest that low temperatures could stimulate the EPS gelification just like Ca ions addition or substratum cathodic polarization do.

Other works are in progress both in Antarctica and in Genoa to better clarify the electrochemical effects of the biofilm at low seawater temperatures; in particular the research of the reasons narrowing the potential ranges involved in the oxygen depolarization at 2°C.

THE THYOCARBAMATE AS A CORROSION INHIBITOR FOR Cu Ni10 Fe ALLOY IN SEA WATER*

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The commercial Cu Ni10 Fe alloy has been successfully used in saline and sea water environment; the corrosion resistance is attributed to protective and adherent surface film (¹).
In some instances, as a result of local turbulences, sea water pollution, low temperature etc., protective film can be damaged and corrosion at isolated spots may occur(²).
So, attempts have been made to improve the protective properties of naturally formed surface layer using corrosion inhibitors, especially those that form sparingly soluble complexes with metal(³).
As part of a programme of evaluation of various organic compounds as corrosion inhibitors to Cu Ni10 Fe alloy, the present study determines the effectiveness of sodium diethyldithio-carbamate (NaDDTC) which contains two active centers able to form coordinate bonds with metal cations. The electrodes were prepared as mentioned elsewhere(⁴) and immersed in various concentrations of stirred solution of NaDDTC in tap water.
The protective properties of the film formed after 24 hrs immersion were investigated in sea water by means of PAR M273 potentiostat interfaced with IBM M386 computer. Four electrochemical techniques were applied: linear polarization, cyclic voltammetry, potential step and time variation of potentiostatic anodic current density. The corrosion potentials of protected and unprotected electrodes were monitored in the cell against a saturated calomel electrode with high impedance voltmeter.
The E_{corr} - **time** variation was strongly stirring dependent, indicating the role of oxygen in cooperative action with inhibitor.
The apparent polarization resistance R_p was measured as function of potential sweep rate. Extrapolating the apparent $\mathbf{1/R_p}$ to zero sweep rate, the true $\mathbf{1/R_p}$ was obtained. Using Stern-Geary equation, the effect of pre-exposure to aerated and deaerated sea water on the subsequent corrosion rate was determined.
The potentiostatic anodic current density was recorded for 5 hrs until constant value has been obtained. The magnitude of this current depends on previously used concentration of NaDDTC; the more inhibitor concentration increases, the more i_a diminishes with time.
By imposing -0.5 V amplitude of cathodic potential, the current decay with time was recorded in various times. Peak current depends on the manner of treatment of electrode surface.
Current density vs potential profiles recorded at 0.2 Vs^{-1} between -1.5 V and 1 V for freshly protected and unprotected electrodes as well as for electrodes after 24 hrs OCP monitoring differ significantly.

The results obtained confirm our conclusion(4) that NaDDTC has a good inhibitive properties for Cu Ni10 Fe alloy in sea water. Satisfactory protection properties may be attributed to the adsorption of the molecule on the metal surface and possible formation of chemical bonds with metal cations as well. Although during polarization the thyocarbamate molecule may be split, its remained part at the alloy surface retains protective properties.

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SPECIATION OF ORGANOTIN COMPOUNDS IN ENVIRONMENTAL SAMPLES BY GC-MS-SELECTED ION MONITORING

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Organotin compounds have found applications in many fields, such as stabilizers for PVC, fungicides in agriculture and biocides, because their properties can be tailored by the variation of the type and number of substituents to meet widely different requirements. In particular, tributylic derivatives are used as antifouling agent both in the industrial cooling waters treatment and in marine paints. Organotin compounds with short alkyl chain or phenyl substituents exhibit high toxicity towards both aquatic organisms and mammals.

In the last years many papers have been published on such compounds trace levels determination in matrices of environmental interest. Traces analysis is complicated because organotin compounds are polar and therefore little volatile. For a speciation study it is necessary, after the extraction of compounds, the use of a high-resolution separation technique, such a gas-chromatography coupled to a derivatization method for volatile compounds formation. Among derivatization procedures, volatile hydrides (stannanes) formation or Grignard alkylation are the most used. Unfortunately stannanes are labile compounds; therefore losses are found, mostly if for environmental matrices (mussels and marine sediments) a purification step of extract is necessary. On the contrary, Grignard alkylation leads to tetra-substituents organotin compounds, which can be easily purified and concentrated.

In this work, organotin compounds extraction from homogenized sediments and mussels has been made with toluene, in the presence of tropolone. The mixture was sonicated for 30 min and then centrifugated at 3000 rpm. The extracted organotin compounds are penthylated by a Grignard reagent, separated from lipids by cleanup on florisil and allumina column and analyzed by high-resolution gas-chromatography coupled to mass spectrometry.

Extraction procedures, gas-chromatographic retention and detection limits are shown and compared with those of GC-FPD technique. Detection limits in mass spectrometry vary considerably according to the use of EI or PCI technique and range in some nanogram injected of Bu_3SnPen. To such a purpose we have discussed problems concerning tri-, di-, and monobutyltin identification with two techniques and molecular fragmentation peculiarities for the optimization of GC-MS-SIM technique.

We also show some examples of such method in environmental samples (mussels and sediments) taken from the Taranto Gulf (Ionian sea). Finally we have shown the main problems concerning organotin compounds pollution in the area examined.

CHARACTERIZATION BY ELECTROCHEMICAL TESTING METHODS OF ORGANIC COATINGS FOR THE PROTECTION OF MARGINALLY PREPARED STEEL SURFACES

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ABSTRACT

The present study, carried out in the frame of a common research programme between the Institute of Chemistry of Engineering Faculty of Genoa's University and AGIP SpA CORM Dept about alternative surface preparation methods, will be a preliminary contribution to the development of the potential use of a series of direct to rust coatings to protect steel structures exposed to aggressive environment.

KEY-WORDS: Corrosion, Surface preparation, Coatings, Alternative systems.

INTRODUCTION

The possibility of obtaining good protection performance by a surface coating is linked to a proper surface preparation.

The removal of all mill scale, rust contaminants from the metallic substratum problem in preparing the steel surface.

Many preparation methods are available but, owing to the type and amount of corrosion products present, mechanical methods, such as tool cleaning and sandblasting, are the most used.

However derusting surfaces by sandblasting can be expensive and is not applicable in many situations.

The durability of steel structures situated in hostile and high aggressive conditions can be achieved by the research and focusing of alternative surface preparation and protection methods.

MATERIALS AND METHODS

The reliability of a series of products of current technology (rust converting products and surface tolerant coatings), applied to marginally prepared steel substrata, has been investigated by electrochemical testing methods (based on Electrochemical Impedance Spectroscopy measurements) after exposition to 3% NaCl aqueous solutions. Their mechanical properties (surface adhesion, hardness, flexibility, etc.) have been tested before and after exposition to the above mentioned environment. A series of similar panels has been exposed to artificial weathering by DRY CORROSION CABINET.

RESULTS AND DISCUSSION

The electrochemical impedance results (total resistance and capacitance values) have been obtained during long term exposition and their values have been compared for a preliminary selection of the protecting features of the different tested products.

A correlation between electrochemical results and the dry corrosion ones has been carried out.

CONCLUSIONS

-Rust converting coatings have some inherent limitation linked to the necessity of an additional protection by a supplementary coating system.

-The performance of the class of "surface tolerant" products seems to provide a more complete approach to the goals of the undertaken research.

EXPERIMENTAL STUDIES ON BACTERIAL CORROSION OF Fe AND Fe-Ni SAMPLES

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ABSTRACT

This study involves two research teams respectively concerned in corrosion and in biotechnological process engineering. Experiments have been led on bacterial corrosion by comparing corrosion effects for Fe and Fe-Ni samples immersed in parallel in bacterial solutions and in the corresponding growth media. The results presented here, related to *Thiobacillus ferrooxidans*, show a rapid corrosion of the samples in the bacterial solution, especially during the first days. This could be observed on photographies by scanning electronic microscopy, and on weight losses measurements.

KEY-WORDS: Bacterial corrosion, *Thiobacillus ferrooxidans*

INTRODUCTION

The negative effects of bacterial corrosion are now well established, in geothermics or in offshore plants for instance (Guezennec,1992) (Moreau *et al.*,1972) (Gomot *et al.*,1990). A few studies have been led in order to appreciate these effects, and to understand their mechanisms. Two research teams of the "Ecole Centrale Paris" (France), respectively devoted to corrosion studies and to biotechnological process engineering, have undertaken together experimental works in this area. Some results will be presented here, related to *Thiobacillus ferrooxidans,* whose corrosive effects were previously investigated by Liu *et al.*, (1988).

MATERIALS AND METHODS

The experiments have been led in order to compare the corrosion effects induced by the growth medium respectively without (solution A) and with (solution B) bacteria. The objective was to point out the specific effects due to the bacteria. Identical metallic samples were introduced simultaneously in beakers fed with the two solutions. Several experiments were led in parallel, so that it was possible to extract samples after 2, 5, 8 and 11 days from separate beakers. During the samples immersion, the following parameters were periodically measured: pH, dissolved oxygen, optical density and electrical potential. When extracting the samples, the weight losses were measured, and surface and transversal cutting observations were made by scanning electronic microscopy (S.E.M.). That procedure was used independently for 2 different types of metallic samples: Fe and Fe-Ni alloy.

RESULTS

Some results are presented here:

- the figure 1 gives the curves of the specific weight losses for Fe and Fe-Ni samples immersed respectively in the solutions A and B;
- the photographies 1 and 2 handle respectively with transversal cuttings of Fe samples 4 and 7. The Fe4 sample was immersed during 11 days in the solution A, and the Fe7 sample 5 days in the solution B. The corresponding specific weight losses were respectively of 0.288 and 0.353 (fig. 1).

DISCUSSION

1. Fe samples

The S.E.M. observation of the transversal cuttings pointed out clearly that the corrosion effect of the bacteria was perceptible since two days. This could be predicted when following the conclusions of Liu *et al.*, (1988), on the Fe consumption by *Thiobacillus ferrooxidans*. That corrosion effect is confirmed by the weight losses measurements (fig.1): the weight losses measured on the different samples immersed in the solution B are significative since 2 days, and only after 11 days in the solution A. However, the photographies 1 and 2, corresponding to Fe4 and Fe7 samples, show that the corrosion mechanisms seem to be different in spite of equivalent weight losses.

2. Fe-Ni samples

The Fe-Ni alloy used here is of austenitic structure. This induces intergranular corrosion, which could be observed on the transversal cutting, for solution A as for solution B.

The passivation action of the nickel leads to little weight losses with solution A, but seems to be rather ineffective in the presence of bacteria, the weight losses being then important since 2 days (fig.1).

When the intergranular corrosion becomes important, some austenitic grains are unbinded, leading to a faster increasing of the weight losses, which can be observed on the fig. 1 for Fe-Ni samples in solution A between 8 and 11 days.

In the presence of bacteria, the starting of the weight losses is rather rapid; the extent of the corrosion effects induces an important modification of the samples surfaces, with the formation of deep crevasses; part of the corrosion deposit is so trapped; this can explain the underevaluation of the weight losses which can be observed on fig. 1 since 8 days in this case.

CONCLUSIONS

These experiments with *Thiobacillus ferrooxidans* show that the specific corrosion effects of the bacteria appear very early (since 2 days), for the Fe as for the Fe-Ni samples. The protective effect of the nickel in the Fe-Ni alloy seems to be considerably decreased when working with bacteria. Further studies will be led in our research teams in order to ensure those results. In parallel, new experiments are going on with *Desulfovibrio desulfuricans* which is an anaerobic bacteria commonly present in the seas.

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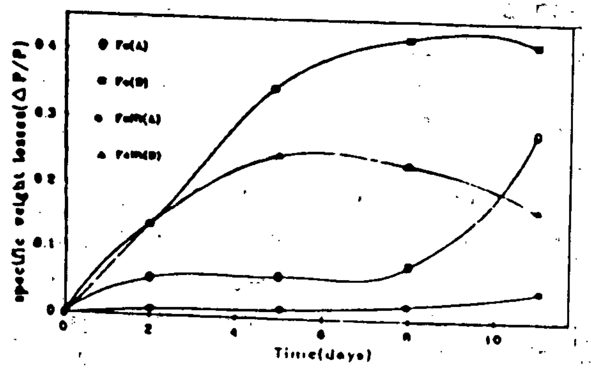
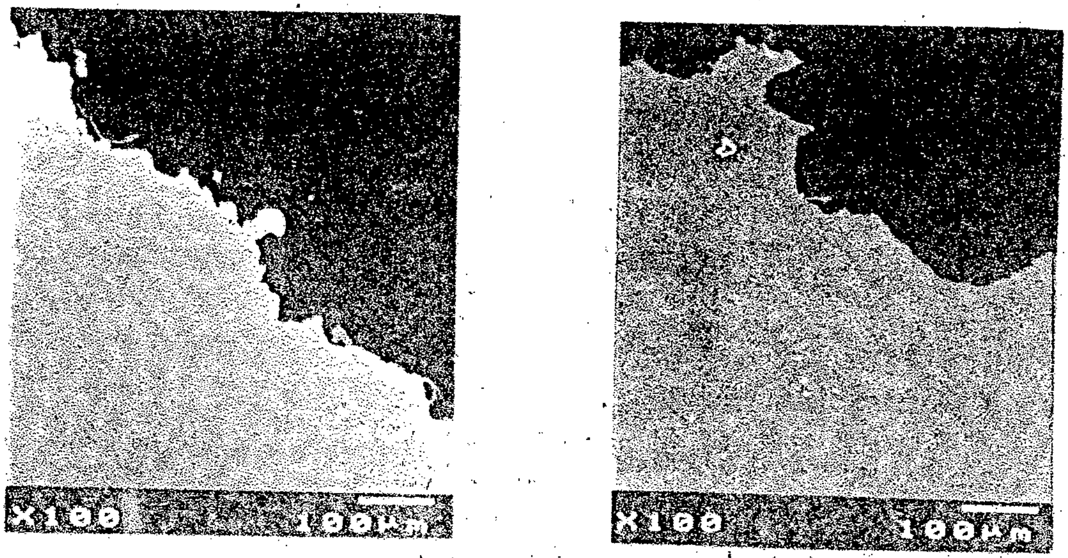


fig. 1: specific weight losses of Fe and De-Ni samples versus time



Photgraphies of Fe samples S.E.M. transversal cuttings
1: after 11 days immersion in solution A
2: after 5 days immersion in solulion B

THE EROSION VELOCITY OF ANTIFOULING COATINGS WITHOUT ENVIRONMENTAL TOXICITY

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The best available binders for realizing antifouling marine coatings are methyl methacrylate and tributylstannyl methacrylate copolymers of an approximate weight of 100,000, but their use is no more compatible with regard to the environment. This is why these chemicals are prohibited by an increasing number of national regulations. The perfecting of compounds which have the same efficiency without any toxicity is therefore been necessary. With the aim in view, we have considered to use organosilyl group as a substitute for organotin groups which permits the conservation of the self polishing nature, the antifouling efficiency being brought by the addition of extenders.

The binders studied herein are copolymers of methyl methacrylate and R_1, R_2, R_3 silyl methacrylate with R_1 and R_2 - CH_3 or C_6H_5 and R_3 - tBu, CH_3 or C_6H_5. The molar mass are between 50,000 and 150,000. They have been formulated and the erosion velocity of this paint under the effect of hydrodynamic parietal shear have been experimentally evaluated at flowing velocities of about those of operational vessels (21 knots).

Several tests on varnish made with copolymer and TiO_2 (60/40) show the following results:

(1) Φ_2tBu always leads to an erosion velocity too weak, whatever are the monomer ratios and the molar mass.

(2) MeΦ_2 (35/65) leads to a good erosion velocity from molar mass of 62,000. Under this value, this velocity is too high.

(3) Me$_2\Phi$ (35/65) 56,000-25000 instantaneously eroded.

(4) Me$_2$tBu (35/65) is eroded too slowly, is its weigh. The incorporation of hydrophilic products gives a coating too fragile. The introduction of 5% of methacrylic acid gives a terpolymer which velocity is fitting for a molar mass to the order of 100,000.

The self polishing nature of the binder being therefore reached, its antifouling action, assured before by the organotin derivate, is obtained by the incorporation of biocidal products at a very weak nuisance for the environment (zinc and copper) introduced in the organic form, conserving the C.V.P. of standards formulations: the erosion velocities are comparable to them (about 1 μm per day).

MICROBIAL CORROSION OF STEEL BY ANOXYGENIC, PHOTOTROPHIC SULPHIDE-OXIDISING BACTERIA

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The corrosion behaviour of mild steel was studied in a putrid model (Efird and Lee, 1979; Edyvean *et al.*, 1986; Eashwar *et al.*, 1990) where macrofouling organisms are allowed to stagnate and decompose in seawater. Evaluation of marine alloys in the putrid system has now become an acceptable and quite useful method for investigating microbial corrosion.

A variety of seaweeds, *Ulva lactuca*, *Caulerpa racemosa*, *Padina pavonica*, *Sargassum* sp., *Gracilaria corticata* and *Hypnea* sp., a Porifera species and an oyster, *Crassostrea cucullata*, were used as organic matter. The sulphur chemistry in the putrefaction sequence was studied following standard methods of seawater analysis. Corrosion was measured by weight loss, free corrosion potentials and potentiodynamic polarization.

Results of the present study with Tuticorin seawater were far different from previous observations. Most interestingly, the putrid seawater became spectacularly coloured after about a week's time the experiments were begun. The colouration was initially pink/purple and later green, after about 20 days. Next, corrosion was substantially low during initial stages but increased dramatically just as the seawater became coloured. Third, a thiosulphate- instead of a sulphate-peak was discernible during aerobic and microaerophilic stages; also a rapid depletion of sulphide occurred under anaerobic conditions.

The causative to colouration as well as to corrosion enhancement was found to be the growth of phototrophic sulphur bacteria (PSB). The PSB were identified based on cell size and morphology, motility, absorption spectra and pigment characterization. Some of the PSB characterised were *Chromatium warmingii*, *Chromatium vinosum*, *Chromatium purpuratum*, *Pelodictyon luteolum*, *Chloroherpeton* sp., and *Chloroplana vacuolata* consortium.

The fact that these organisms are phototrophic prompted corresponding studies in the dark. Neither colouration nor an increase in corrosion occurred when putrid seawater cells were maintained in total darkness.

Studies of sulphur speciation in putrid seawater as well as in pure cultures revealed that the PSB accelerated corrosion under photic conditions through anaerobic oxidation of sulphide to elemental sulphur.

This is the first report of the possible involvement of PSB in corrosion reactions. The exact reason for the prolific growth of PSB in Tuticorin seawater is as yet not fully known. Nevertheless, some preliminary studies suggest that the abundant presence of heavy metals, especially those which catalyse sulphide oxidation reactions, in tissues of macrofouling organisms might have caused the blooming of PSB. Since these bacteria regularly occur in coexistence with sulphate-reducing bacteria, it is suggested that they may promote anaerobic corrosion wherever sunlight is not unlimited.

EXPERIMENTS RELATING TO "EDGE EFFECTS" IN BIOFOULING SETTLEMENTS

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Recently there have been attempts to synthesise patterns in biofouling settlements. Such an approach is important from the point of view of an understanding of biofouling ecology and more precise quantitative assessments as well. This paper addresses: (a) choice of coupon positions by fouling organisms and (b) the question as to why most fouling species, especially barnacles, preferentially settle at coupon edges.

The research was conducted at the Marine Electrochemistry Centre,1.2 km off the shore line in Tuticorin harbour, which is on the south-east coast of India. Most experiments were carried out using aluminium as the substratum. Initial tests with coupons of varying sizes and centre-to-edge ratios conclusively brought out the preference to edges by most solitary forms, e.g. *Balanus* spp., anemones, simple ascidians and molluscs. Density difference between centre and edge - the coefficient of range - was lower on small coupons and considerably high on larger ones. Some organisms, notably colonial ascidians, bryozoans and serpulid worms, on the other hand, preferred to establish more on coupon centres. Further experiments with several substrata (asbestos, mild steel, stainless steel, titanium and cathodically protected steel) confirmed that these effects were not influenced by the nature of substratum but by larval choice.

The second series of experiments was aimed at modelling barnacle settlements with reference to " edge effects ". Patterns of recruitment were analysed taking accounts of 3 variables, namely season (round the year), depth (1, 3 and 5 m) and locality (open and sheltered waters). The preference for edges was found unvarying under all conditions. This was followed by another series of studies where coupons were either polished, or roughened to different degrees. Edge effect was more pronounced on polished surfaces and less significant or virtually absent on roughened ones. When the effects of different surface treatments within a panel were examined, barnacles were found to preferentially colonize roughened centres and/or avoid polished edges.

A crucial examination of "artificial edges" on coupon centres was finally attempted. Results reveal that larval behavioural aspects could be as important as hydrodynamics and primary film in determining the choice of coupon positions by barnacles and possibly other edge preferring macrofoulants.

STEEL CORROSION THROUGH CRACKS IN REINFORCED CONCRETE FOR MARINE STRUCTURES

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ABSTRACT

Cracks in reinforced concrete structures exposed to the action of sea-water can remove steel protection even with good quality concrete. In these conditions commonly used, inhibitor admixtures addition can result in enhanced corrosion, instead of preventing corrosive phenomena.

KEY-WORDS: Corrosion inhibitor admixtures, Cracked concrete, Marine environment.

INTRODUCTION

There is little information concerning the corrosion of rebars in concrete placed in marine environments when it is cracked or when local defects of the cover protecting the reinforcement occur. In these conditions the low electrical resistivity of sea-water can enhance the corrosive phenomena by galvanic contact, since extended areas of the rebars act as cathodes, whilst the smaller areas localized at the apex of the crack act as anodes.

This can result in intensive corrosion of the latter areas, even though the amount of available oxygen is relatively low.

MATERIALS AND METHODS

Reinforced concrete specimens were artificially cracked to obtain different widths of the cracks and then immersed in sea-water. Some specimens were produced by concrete treated with corrosion inhibitor admixtures based on inorganic or organic chemical products. The influence of crack width and inhibitor admixture type on the electrochemical potential of the steel embedded in concrete was studied.

Furthermore, to understand the mechanism of corrosion attack corresponding to the apex of the cracks, measurements of short circuit current between anodic and cathodic areas were carried out.

RESULTS

Cracks in concrete cause a sharp fall in the electrochemical potential of the reinforcement.

This fall appears more or less delayed, with respect to the untreated concrete, depending on the inhibitor admixture type and the crack width, which also affect the minimum potential value.

However, the addition of inhibitor admixtures, beyond changing the morphology of the corrosion products, always enhances the corrosion aspects at the apex of the crack, particularly when an organic product is added.

Short circuit values also appear coherent with the corrosion extent and depth, obtained with different inhibitor admixtures and crack widths, visually observed after specimens splitting.

DISCUSSION

The results of electrochemical measurements and the visual observations would indicate that the localized attack could be assumed to be due to the reduction of hydrogen from the generation of local acidity. This hypothesis is supported by the measured short circuit currents, whose values would be coherent with corrosion rates of a magnitude order lower than those found in the present work.

CONCLUSIONS

In cracked reinforced concrete immersed in sea-water, localized corrosion in the cracked area occurs independent of the addition of corrosion inhibitor admixtures to concrete.

The high corrosion rates found, in spite of the relatively low amount of available oxygen, suggest that another cathodic reaction, different to the oxygen reduction and probably due to hydrogen reduction, takes place.

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MACROFOULING, BORERS AND FUNGI ON WOOD SAMPLES SUBMERGED AT VARIOUS DEPTHS IN LIGURIAN SEA (GENOA, NW ITALY)

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This research aims at acquiring further information on the systematic ecologic composition of fouling, marine borers and microorganisms within an area of the Ligurian Sea (Gulf of Genoa) and namely on the mooring platform for oil-tankers at Genova-Multedo Oil Terminal, which is placed at 1,5 miles off the coast on a 50 m deep sea bottom.

Two series of *Pinus sylvestris* sapwood blocks were submerged from September 1989 till June 1992 and from September 1990 till June 1992 at -2 m, -25 m and -48m.

PART I - MACROFOULING

Out of 41 species detected Algae, Protozoa, Sponges, Cnidarians (Hydroids), Bryozoans, Molluscs (Bivalves), Annelids (Serpulids), Arthropods (Barnacles, Amphipods, Pantopods), Ascidians, the following were found at all depths and throughout the year: *Clytia hemisphaerica* Linneo, *Aetea truncata* Landsborough, *Callopora dumerilii typica* Audouin, *Spirobranchus polytrema* Philippi.

As to vertical distribution, settlement of test blocks at -2 m was generally lower, whereas at -25 m and, to a greater extent, at -48 m, more species are present and each with a greater amount of individuals.

The longer the immersion period, the greater the number of species detected, with maximum levels at 6 and 9 months. After such period, a gradual reduction in the number of species was observed, which however, have a great number of individuals.

Significant differences were observed between the two observation cycles, at one year interval. In the second cycle, there is practically no surface settlement. At medium depth and close to the bottom, no significant differences were noted, though in the second cycle a reduction in Bryozoans and Hydroids and an increase in Serpulids, mainly due to a massive appearance of *Filograna* sp. which becomes the dominant species, was observed.

PART II - BORERS AND FUNGI

Xylophagous organisms were investigated by macroscopic and X-ray analysis; timber degradation, caused by microorganisms, was assessed under electronic microscope. The borers detected belong to some species of Teredinidae (*Bankia carinata* Gray, *Teredo navalis* Linneo, *Nototeredo norvagica* Spengler, *Lyrodus pedicellatus* (Quatrefages), Limnoridae (*Limnoria tripunctata* Menzies) and Cheluridae (*Chelura terebrans* Philippi).

Detected fungi belong to Ascomycetes and Fungi Imperfecti (*Cirrenalia* *macrocephala* (Kohlmeyer) Meyers *et* Moore, *Corollospora maritima* Werdermann, *Halospheria maritima,* (Linder) Kohln, *Hunucola alopallonella* Meyers, *Lulworthia floridana* Meyers, *Zalerion maritimum* (Linder) Anastasion.

Timber degradation due to borers and microorganisms was more significant in the second than in the first test year. Moreover, a clear difference in the species of borers was also observed between the test blocks of the first and second cycle, i.e. *Banka carinata* accounts for 87% of total settlement in the first cycle, whereas *Lyrodus pedicellatus* is the largest species settling second cycle test blocks.

Teredinidae settlement is lower in test blocks at -2 m, whereas Limnoridae and Cheluridae settlement was only observed on blocks at -48 m.

As to fungi, a more remarkable aggression was observed on blocks at -2 m, with no differences in the species detected between the two cycles.

Under electronic microscope, degradation of the cell wall, typical of soft rot, was observed.

EXPERIMENTATION AND PILOT-PLANT DEVELOPMENT OF AN ULTRASONIC SYSTEM FOR THE NON POLLUTING ANTIFOULING TREATMENT OF STEELWORKS COOLING WATERS

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OBJECTIVE

The objective of the research is to develop to pilot-scale level an ultrasonic system for eliminating or reducing colonies of organisms present in the waters used for indirect cooling in steelworks, because these organisms cause fouling.

MATERIALS AND METHODS

Larvae of fouling-forming organisms (lamellibranch veligers, serpulid trocophores and balanid nauplii) at known concentrations have been subjected to the action of ultrasonic waves of varying frequency (25 - 40 KHz) and power (44, 90 and 130 W) for diverse exposure times (1, 3, 5, 15, 30 and 60 sec).

The most effective operating conditions in the static laboratory tests were applied at pilot-plant scale to check the results. The pilot-scale plant consisted of two fiberglass channels, one being fitted with eight transducers connected to the relative generators, and the other being used as control.

The larvae carried in the stream of water within the channel were subjected to ultrasonic waves at a frequency of 25 KHz and a power of 130 W for twelve seconds. Six cement-fiber panels on which fouling-forming organisms could create colonies were positioned at regular intervals in both channels. Comparison of the weight of the panels in the two channels provided an indication of the efficiency of ultrasonic treatment.

RESULTS

It emerges from the laboratory tests that the percentage mortality of the larvae varies with the power applied and the treatment time. No significant differences were noted at the different frequencies tried (25 and 40 KHz). Mortality rates of 80 to 95 were obtained with exposure times amounting to >5 seconds and power of 130 W.

The results achieved in the field indicate an average reduction of fouling amounting to between 26 and 30 %, with high points in the 40 to 44 % range.

DISCUSSION AND CONCLUSIONS

The field investigations and the data processing performed indicate that ultrasonics also act on the larval stages of the fouling-forming organisms under dynamic conditions, and that they overcome the barriers of natural interference represented by the natural planktonic biomass.

The difference between the results obtained in the laboratory and those involving dynamic conditions is attributable to the enormous load of plankton present in the seawater.

The fact that the laboratory results were better may be ascribed to superimposition phenomena and hence the amplification of the ultrasonic waves in the container.

The exclusive use of ultrasonics as an antifouling tool will not guarantee protection in large industrial systems that depend on seawaters.

CRUDE EXTRACTS OF SETTLEMENT FACTORS FROM THE BARNACLE *Balanus amphitrite*

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The free-living larvae of many sedentary marine animals respond to the presence of adults of their own species by settling in close proximity to them. This phenomenon, strongly demonstrated by barnacles, is termed gregariousness. Chemical bases for the gregarious response of the barnacle *Balanus balanoides*, consist of a polymorphic system of closely related proteins derived from sub-units of molecular weight 5-6,000 and 18,000 daltons (Larman *et al.*, 1982). On the other hand, Rittschoff (1985) reported that barnacle pheromone, a 3-5,000 dalton peptide, enhances the settlement rate and metamorphosis of *Balanus amphitrite* larvae. From these reports, multiple settlement factors are thought to exist for barnacle cyprids. For this report, the effect of two settlement factors extracted from conspecific adults on *B. amphitrite* cyprid larvae were studied.

METHODS

Larval culture. Adult *Balanus amphitrite* settled on plates were air-dried and soaked in seawater. Following this treatment, nauplii were released and were subsequently fed with the diatom *Chaetoceros gracilis* (30 x 10^4 cells/ml) in 1l becker, at 25°C. These beakers were rotated slowly throughout the culture period. Larval density was lower than two individuals/ml. More than 60% of the original nauplii reached the cyprid stage in 6 days. Newly-transformed cyprids were collected and used the following day (Day 1 cyprids) for bioassay.

Extraction and fractionation of settlement factors. Adult *B. amphitrite* were collected, air-dried and soaked in methanol for one week, allowing lipophilic and water-soluble substances to be obtained. The residual whole barnacles were crushed, additional water-soluble substances extracted with distilled water. The two water-soluble extracts were mixed, and boiled for 10 min. Previous studies (unpublished) have shown settlement activity to be stable following such treatments. The water-soluble substances were further subjected to gel filtration (Biogel P-10, molecular weight 1,500-20,000) with distilled water, resulting in three fractions (F-1-F-3) being obtained. The molecular weight of the substances contained in F-1 were higher than those of F-2. F-3 were the substances absorbed on the gel.

Settlement bioassay. The lipophilic substances, water-soluble substances, and fractions F-1-F-3 were each bioassayed for settlement activity of *B. amphitrite* larvae, using a 15 l glass-tank containing 10 l of filtered seawater. A 3 l capacity plankton net (opening: 96 µm) was set up in the tank. Water circulation was maintained by a pump directing seawater to each corner of the cage. Two hundred laboratory-reared, *B. amphitrite* cyprid larvae were placed into the cage, along with 12 ceramic plates to serve as substrata for settlement. Six plates were pre-treated by coating 1 ml of extract on each and allowing to air-dry. The remaining plates were not treated. Each 1 ml sample was equivalent to 10 g (wet weight) of adult barnacles. After 24 hours the plates were removed, and the number of cyprids permanently settled on each plate counted. For each bioassay, all treatments were replicated three times.

SUMMARY RESULTS

Balanus amphitrite cyprids settled in greater numbers on the plates treated with the water-soluble substances than on the untreated plates. The total number of permanently settled larvae was about 80 on the 12 plates (approximately 40 % of the total number of test larvae), the six treated plates accounting for about 70 of these. A control experiment using 12 untreated plates resulted in less than 10 of the 200 test larvae becoming permanently settled. Clearly, the water-soluble substances resulted in both high settlement activity and high substrata selectivity.

Among the fractions (F-1-F-3) from Biogel P-10, F-1 showed the highest settlement activity (45%) and substrata selectivity similar to the watersoluble substances. Although F-2 indicated high settlement activity, with more than 40% of larvae settling on the 12 plates, substrata selectivity tended to favour the untreated plates. F-3 showed a similar response to that of F-2, but with lower settlement activity.

CONCLUSIONS

Settlement factors for *Balanus amphitrite* cyprids were found only in the water-soluble substances extracted from the conspecific adults. The crude extract showed high settlement activity and also high substrata selectivity. Lipophilic substances did not induce settlement activity.

The results observed following gel filtration of the water-soluble substances, suggested the existence of two different settlement factors, with differing characteristics. The first was included in substances of molecular weight more than 20,000, the factor resulting in both high settlement activity and high substrata selectivity. The cyprid larvae apparently reacted only to the absorbed layers on the plates. The second settlement factor, which was included in rather low molecular weight substances (1,500-20,000), induced high settlement activity but no significant substrata selectivity. In this case, the cyprid larvae appeared to have responded to the settlement factor in solution, rather than on the plates.

ATMOSPHERIC CORROSION OF METALS ON BOARD OF HIGHSEA CARGO VESSELS

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Results of many years research of environmental and corrosive hazard on board of ocean-going ships have been presented in this report. The reason to undertake the research was the offshore openair conditions on board of ocean ships appeared to bring about the corrosion attack performance and intensity quite different than those met at most sea shore places. However, the effect of both mentioned corrosive actions is usually defined as sea corrosion.

Testings were performed on boards of dozen or so cargo vessels during their maritime commercial courses on various routes over the globe through different climatic zones within the period of different seasons of the year. This report includes only results of measurements that were carried out by the author in outdoor atmosphere conditions on board of the ships. The results obtained for indoor atmospheres of the ships (e.g. for those in engine rooms or others) will be published in separate report.

The testings comprised measurements of the air relative humidity, temperature and chloride content as well as corrosion development estimation for eight different metals and alloys. The corrosion rate was determined as a loss of weight (g/m^2) of metal samples after the assumed time lapse. The samples were mainly installed on the upper-deck of the ship (the highest exposure point). On several ships the comparative testings were also made on similar metal samples, being exposed at the same time on lower located fore deck. The dependence of corrosion rate on exposure time was examined as well as on sea area type, state of the sea, weather conditions, etc. Comparison was done, as well, of mean corrosion rate values for metals tested in environments of ships in relation to those obtained for the same metals exposed by the author in other environmental conditions, such as saline coal mines, tropical, industrial or other atmospheres. The results obtained have indicated the following:

- the mean chloride content in the air, measured on the upper deck (12 ÷ 20 m above sea level), equals to about 80 mg m^{-1} d^{-1};
- the mean air temperature and the mean relative humidity are, respectively, 21°C and 80 % for routes of vessels from Gdynia to tropic regions;
- the mean corrosion rate for metals exposed during the ocean routes appeared to be threefold higher than that for the same metals exposed during East Baltic Sea route within the same period of time (exemplified by copper corrosion after 30 days exposure during ocean routes, which amounted to about 12 g/m^2);
- the copper corrosion rate on the Baltic Sea during the storm season (February - March) seems to amount approx. two times higher than that ascertained during the calm sea season (May - June) for the same route within the same period of time. Similar dependence was stated for the Atlantic Ocean routes;

- corrosivity of high-sea atmosphere acting on tested metals was stated to be the most severe compared to all other natural environments. For example, the corrosion effect on metals tested close to the sea shore on Hainan Island (P.R. of China) was about ten times lower than that on board of the ships.

METAL CORROSION BY SULFATE REDUCING BACTERIA

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Although many microorganisms can play a role in the corrosion process, one of the most important is reserved to Sulfate Reducing Bacteria (SRB).

In the last few years a reasonable understanding of biochemical mechanisms and enzymatic equipment of this group of bacteria has been acquired (1).

We have been studying the action mode of some chemicals (biocides) on enzymes activities and on whole cells viability of the Sulfate Reducer *Desulfovibrio desulfuricans* (ATCC 27774).

Compounds selected and tested include metronidazole [1-(2-hydroxyethil)-2-methyl-5-nitroimidazole] (a radical generator), organosulfur compounds (chelating agents), aldehydes (reactive towards amino groups of membrane proteins).

Inhibition of hydrogenase, aldenylylsulfate (APS) reductase and aldehyde oxidase were performed on pure enzyme and on whole cells, using a wide concentrations range of the referred compounds.

The bacteriostatic or biocide effect of the compound selected were also observed on cells grown in a batch culture(2,3).

In order to extend these studies to a situation close to a everyday life one, the influence of the activity of SRB on mild steel was also studied. So to reproduce an everyday life situation, the metal place, utilized in these studies, were obtained from the Lisbon shipyards, LISNAVE - Estaleiros Navais de Lisboa S. A. and were of the kind used in repairing the hulls of large ships.

The steels samples obtained were cut into suitable size coupons, and lined with PTFE, so as to be able to define an accurate surface area. This naked surface was then exposed to the action of a culture of *D. desulfuricans*, and surface state analysis were carried out a different contact times. These analysis included Electrochemical Impedance and Scanning Microscopy techniques. Simultaneously, for control by the effect of the culture medium on the surfaces, other coupons were exposed to this medium without cells and underwent the same kind of analysis. The results obtained through impedance analysis, indicated that during the testing period the predominant corrosion process was controlled by charge transfer. Furthermore, observations showed that the activity of SRB has a destructive effect on the exposed surface. Scanning Electron Microscopy revealed irregularities on the surfaces studied and the deposition of solid matter in some of the crevices observed.

Another aspect of this study included the assessment of the influence of biocides in corrosion control. Metronidazole, at different concentrations was introduced in batch reactors containing mild steel coupons and cells at the exponential stage of growth. As expected, at biocide concentrations above 40 mg/dm^3 (2), the cells were irreversibly inhibited and the corrosion observed was similar to that found in experiments without cells. This fact led to the belief that metronidazole could become a very efficient compound in biocorrosion control.

Despite the results obtained so far, further studies in this field are now being pursued enabling to determine, with some accuracy, corrosion rates and the mechanisms involved in the process.

INIC, JNICT, Nato Science Po-Lisfood and LISNAVE - Estaleiros Navais de Lisboa S. A. are acknowledge for financial support.

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THE GAS THERMAL AND MICROPLASMA COATINGS TO CORROSION PROTECTION OF SHIP STRUCTURES

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The most critical and complicated structures and products are considered whose reliable and long time corrosion protection and also high decorative properties are not provided by the familiar means.

The principles of corrosion protection by electroarc, gas flame, plasma and microplasma coating application in a controlled medium, in the atmosphere and electrolyte accounting the variety and features of the corrosion processes in nature are discussed.

The investigation results arguing the possibility of the corrosion and corrosion-erosion damage prevention and also an enhancement of a decorative properties of the ship structures are discussed.

The examples of structure corrosion prevention and an application of the coatings of high decorative properties are given.

The possibility of efficiency control and assurance of the service life of the coating of 5-20 years is shown.

METALLIC CHELATE DERIVATIVES: TOXICITY TESTS AND EFFICIENCY IN ANTIFOULING PAINTS

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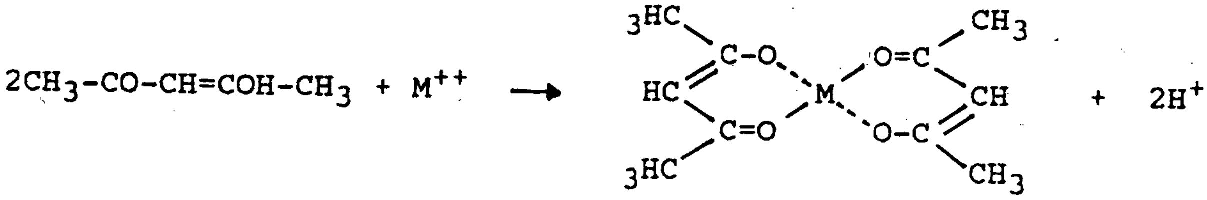
Chelation is a chemical process involving the formation of a heterocyclic ring compound which contains at least one metal cation in the ring. Metal chelate compounds are a group of complex substances known as Werner coordination compounds. One of the most striking properties of chelate ring compounds is their unusual stability. In this respect they resemble the aromatic ring of organic chemistry. In ß-diketones the equilibrium of keto and enolic form is regulated to enolic form

$$\text{-CO-CH}_2\text{-CO-} \rightleftarrows \text{-COH=CH-CO-}$$

Acetylacetone (acac) contains about 76% of the enol form which can lose a hydrogen ion and coordinate with a metal cation to give a 6-membered ring of unusual stability.



These closed ring or chelate derivatives are typical non-electrolytes, almost insoluble in water the $(acac)_2$ Cu and the $(acac)_2$ Zn; more soluble are: $(acac)_n$ of Cr, V, VO, Fe, Sr, Ba.

The acetylacetonates are entirely or partially soluble in benzene, chloroform or in other organic solvents.

Some of these metallic complexes were used in toxicity tests with larvae and individuals of the most common organisms of macrofouling (barnacles and mussels) and with unicellular plankton algae of *Monochrysis lutheri* and *Tetraselmis suecica* species.

The trial tests were done in laboratory with natural sea water, filtered by Millipore at 0.22 micron rearing the organisms according to Rittschof (1984; 1989) and Furman (1989) methods. The quantity of the various metallic acetylacetonates tested were 0.02 g in 100 ml of sea water. After 24 hours with $(acac)_2$ of copper and that of zinc, there was a 100% mortality rate of the barnacles, mussels, serpula and algae; there was an inferior percentage of mortality with $(acac)_2$ of vanadium, vanadyl, cromium and iron; any mortality was observed for $(acac)_n$ of strontium and cadmium. Trial toxicity tests based on derivative of lead, mercury, arsenic and antimony were not considered because no antifouling based on these metal compound are found nowadays.

The mayor attention was thus aimed towards copper and zinc acetylacetonates: also the action on mussels and barnacles larvae on the part of vanadium $(acac)_3$ is noteworthy, but the compound is too soluble in sea water, for which its eventual use

as toxic in antifouling paint would have a brief and moderate effect in time.
The $(acac)_2$ Cu and $(acac)_2$ Zn, like the rest of the other acetylacetonates tested can be prepared in various ways; the most simple and rapid method - demonstrated that the enol form of acac acts as fairly strong acid - is from metal ion solution and the acetylacetone.
The $(acac)_2$ Cu appears under the form of ting sky-blue easily pulverizable needles; the $(acac)_2$Zn appears under the form of white and friable needles.
To test and confront the effectiveness of $(acac)_2$ Cu and that of $(acac)_2$ Zn and eventually the difference of their behaviour in an antifouling paint, they separately were embedded in a mixture of soluble matrix resins based on rosin and coal tar using a porcelain ball mill.
The paints obtained were applied on panels of inert material and immersed in sea water - Genoa harbour -.
After seven months of immersion during the most favourable season of fouling settlement, the results can be outlined as follows:

Exposure (months)	Control	$(acac)_2$ Zn	$(acac)_2$ Cu
1	slime, algae bryozoa	slime	slime
3	algae, barnacle serpula, bryozoa 100% cover	slime, algae	slime
5	as above	algae, bryozoa serpula, barnacle 40% ≈ cover	algae some barnacle 15% ≈ cover
7	as above	as above 70% ≈ cover (binder nearly dissolved)	as above 20-30% ≈ cover (binder nearly dissolved)

The results obtained are interesting and suggest further tests with fixed mixtures of acetylacetonates and cuprous oxide, which is the conventional and more used toxic in antifouling paints. Cu_2O never gave rise to great objections and moreover no information on alternative toxic to organotin compounds is available. The $(acac)_2$Zn and $(acac)_2$ Cu, almost insolubles in sea water, could help Cu_2O efficiency.

ENNOBLEMENT OF STAINLESS ALLOYS BY BIOFILMS: EXPOSURE RESULTS AND DISCUSSION OF MECHANISM

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It is well known that the corrosion potentials of alloys are ennobled by marine biofilms. Whereas that this phenomenon is influenced by microorganisms, is legendary, there is no agreement yet reached on the mechanism of ennoblement. Recently there have also been speculations regarding the effects of light on corrosion potentials.

This study was carried out in Tuticorin harbour waters with 304 stainless steel and Gr.2 Ti as the test materials. Natural seawater exposures were made during two seasons - February to March, 1991 and June to July, 1991. Corrosion potentials of the alloys were measured with reference to a saturated calomel electrode. Two experimental conditions were set: "dark" exposure inside PVC pipes and "natural" exposures in wooden rafts. Microbiological slime was analysed right from the first hour of immersion till completion of the experiment. Additionally laboratory tests were made on titanium using filter-sterilized natural seawater and natural but acidified and/or deareated seawater.

Microfouling was rapid on coupons immersed under natural conditions but substantially low in the dark. Heterotrophic as well as thiosulphate oxidising bacteria were detected at the earliest stages of immersion. The thiobacilli, cultured at pH 4, dominated the fouling in both cases. Also diatoms were represented in good number on coupons of natural exposure but were almost absent in dark exposures. With coupons immersed under conditions of total darkness, microfouling caused polarization of corrosion potentials to nobler values (an ennoblement) during early stages and towards active values thereafter. Under natural conditions, on the contrary, ennoblement occurred consistently in presence of sunlight and the values fell considerably at night. This effect was particularly emphatic during the first 10-12 days but became much reduced on prolonged exposure. These results are contradictory to the observations of Dexter and Zhang (1990; 1991) where ennoblement occurred only in dark.

Laboratory test results revealed that: (i) pH decrease causes only minor positive shifts in potentials and (ii) acidity can not account for ennoblement in absence of oxygen. These data and the potential excursions observed in natural seawater exposure severely limit Dexter's implication of interfacial cause for ennoblement.

Further, this paper analyses the ennoblement concept on the basis of microbial ecology of marine biofilms and examines the merits and demerits of proposed theories. A crucial question: "which class of microorganisms in the biofilm is responsible for ennoblement?" is carefully analysed. By summarizing a range of literature results which apparently utilized different exposure and light conditions, a possible involvement of all 3 classes of microorganisms - aerobic and anaerobic bacteria and diatoms - is highlighted. Since these microorganisms have apparently different modes of metabolism, it is argued that enzyme activity could hold the key to ennoblement phenomenon. Based on the fact that enzymes are pH specific, it is hypothesised that ennoblement invariably occurs as a result of all biofilms at neutral pH, and that the "loss" is influenced by acidic or alkaline shifts. Accordingly, ennoblement occurs during day with a biofilm dominated by acidophilic bacteria such as that noted in Tuticorin waters, where the acidic pH is restored by photosynthetic diatoms. The opposite trend in potential excursions should be expected for other biofilms such as in Dexter's exposures where acidophils are probably low and photosynthesis leads to alkalisation.

SETTLEMENT AND SUCCESSION OF MACROFOULING COMMUNITY AT MAR DEL PLATA HARBOR. ARGENTINA. (1991-92).

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Studies related to the development of the fouling community were undertaken in the Mar del Plata harbour in the following periods: 1966-69, 1970, 1974 and 1976-77; but they were interrupted and there exists a gap of about 14 years. Some years ago some changes in the fouling community were observed.

The present communication deals with the settlement and succession of the microfouling community, from May 1991 to April 1992. The aim of this work is to establish the taxa attachment cycles and to examine the seasonal developmental sequence of the community structure in order to make a comparison with previous papers.

The fouling community was followed by ceramic tile plates (128 cm^2) suspended vertically at different depths (between 0.5 and 1.5 m).

Short-term panels were used to follow settlement cycles and long-term panels to determine the community development.

Censuses of macrofouling species were carried out at each panel, every month.

Data corresponding to the abundance percentage of the species/panels/months, was analyzed throughout the clustering method using the Bray-Curtis Similarity Index (NTSYS program).

On short term panels the most important macrosessile species seem to be presently: *Enteromorpha intestinalis* (green filamentous algae), *Obelia longissima* (foliose hydroid), *Polydora ligni* (sandy tubeworm), *Hydroides elegans* (calcareus tubeworm), *Balanus amphitrite* (barnacle), *Ciona intestinalis* (solitary tunicate). Their relative abundance was differentially distributed along the year.

The dendogram from cluster analysis showed two large groups:

Group 1: which corresponds to the end of autumn, winter and spring, gathers three subgroups:

1- late autumn: where the major species settled were represented by *Polydora* (96%), *Enteromorpha* (70%), and *Ciona* (67%),

2 - winter: dominated by *Enteromorpha* (99%), and

3 - spring: characterized by an assemblage of *Enteromorpha* and *Polydora* (98%).

Group 2: corresponds to summer and early autumn. In this group, two subgroups were distinguished:

1 - summer: the arrival of recruits was mainly represented by *Polydora* (95%) and *Ciona* (91%),

2 - early autumn: the arrival of recruits was represented by *Polydora* (97%), *Hydroides* (83%), and *Obelia* (81%).

From autumn to spring (group 1), the assemblage of settlers was dominated by

Polydora and *Enteromorpha*. Between summer and early autumn (group 2) *Polydora* was dominant, and *Hydroides* and *Obelia* accompanied it, with little abundance differences, *Enteromorpha* decreased and *Bugula* began to settle.

Comparing with previous settlement cycles studied, some changes in the settlement period of species have been observed.

In this period *Enteromorpha* attached deeper than during other periods.

Balanus amphitrite showed a longer period of recruitment compared to that of 1977.

Ciona intestinalis showed a similar settlement pattern as during the 1966-69 period.

In opposition to the 1966/69 and 70 periods, in the present study only *Hydroides elegans* appeared between the serpulid species. *H. elegans* showed a higher settlement than during the latter period. *Bugula stolonifera* and Mytilidae underwent a great decrease in their settlement cycle.

Cluster analysis in long-term panels was carried out by years seasons.

Here, only species which in the average occupy more than 25% of the space are included.

During late autumn and winter, *Ciona* recruited and developed in a tightly grown-together mat; *Polydora* settled on it, and species formerly attached like *Enteromorpha*, could not develop and their abundance decreased.

In spring, *Ciona* began to slough off and the majority of the accompanying species are taken away with it. Free spaces were left, where *Ciona* remaining individuals could grow to its maximum size, being only possible for *Bowerbankia* and *Ceramium* to enter.

At the beginning of summer *Ciona* sloughed off and *Polydora* abundance increased. During the course of this period, new recruitments of *Ciona*, *B. amphitrite* and *Polydora* have been produced. But in the late summer, *Hydroides* was invading successfully and became the dominant species, producing a high mortality of the species settled during this season.

A lower recruitment of *Polydora* and *B. amphitrite* than in the short-term panels was observed. This suggested that *Hydroides* filtered out *Polydora*, *Ciona* and *B. amphitrite* larvae.

From the results obtained, it may be concluded that the community was dominated by *Ciona* (during autumn- winter) and *Hydroides* (in summer).

MACROFOULING IN ANTARTIC WATERS

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Studies on fouling make it possible both to examine the dynamics of the colonization of the immersed surfaces in terms of biotic and abiotic factors and to test solutions designed to prevent fouling settlement on immersed artificial structures. Equally, the analysis of the quantitative and qualitative composition of the fouling associations makes it possible to obtain substantial information on the quality of the environment in which these are formed.

These considerations have given rise to the idea of studying the communities of the hard artificial substratum immersed on the bottoms facing the Italian Scientific Station "Terra Nova Bay" in the Ross Sea (Antarctica). The aim is to make comparisons with the communities of the hard natural substratum in order to see if it is possible to use the former - which would definitely be more convenient to monitor on a routine basis - and to check possible modifications induced in the latter by man's increasing use of the area. Moreover, such a survey would be a way of supplying indications of possible fouling on structures and instruments immersed in Terra Nova Bay and to follow possible variations in the colonization of substrata by various organisms over a period of some years.

In order to study fouling, in particular macrofouling in the Antarctic waters of Terra Nova Bay, during a campaign in 1986-87 two stations were immersed at a depth of 15 m. In the following campaign (1987-88) the panels of the first two stations were replaced (St. 1-87, St. 2-87) and a further four stations were added, (A-88 and B-88 at a depth of 25 m, W-88 and X-88 at 115 m).

6 substrata immersed for one year between 1987 and 1988 at a depth of 15 m, 13 substrata immersed for one year between 1988 and 1989 (8 at -25 m depth, 5 at -115 m depth), 6 substrata immersed for two years between 87 and 89 at -15 m depth, 3 annual panels (89-90) immersed at - 15 m depth, two panels positioned for three years from 1987 - 1990 at the same depth (15 m), 4 substrata immersed at -15 m for four years from 1987 to 1991 were examined on the whole.

Settlement on panels was studied both qualitatively and quantitatively (covering index, density and dimensions and when possible, biomass).

All the one-year substrata immersed in the 87-88, 88-89 and 89-90 periods showed a very poor settlement. Only algal film covers all the surface of some sides. Good settlement was recorded on a substratum immersed for three years at the depth of -25 m in Terra Nova Bay. It was formed of 287 Spirorbids, 4 colonies of Hydroids, 9 encrusting Bryozoans and some Folliculinids which had settled on the lower side of an horizontal panel. Some Hydroids and one specimen of *Adamussium colbecki* (Smith) (3 mm of diameter) together with a substantial algal film were present on the upper side.

The lack of Spirorbids on wood substrata is noticeable.The settlement on four-year panels is much higher: Bryozoans, mainly *Beania livingstonei,* reach 80% of surface cover. Algal film is found on the whole surface of both sides; Folliculinids, Hydroids, Serpulids and Spirorbids are very common.

BIOASSAYS WITH MARINE ORGANISMS TO DETERMINE THE EFFICACY OF ANTIFOULING PAINTS

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The wide use of the antifouling paints (e.g. on the hulls of pleasure crafts) could be a source of marine coastal pollution. Consequently, the needing of low-environmental-impact paints induced industries, operating in this field, to set up experimental formulations that, if possible, associate antifouling properties to environmental compatibility.
The aim of this work is the evaluation of the *in vitro* activity of the sea-water-dissolved chemical compounds arising from the slow leaching of antifouling coatings, versus different marine organisms.
Eight different antifouling paints were assayed by leaching 82 cm^2 coated surfaces (4 test panels) in 1.5 litres of sea water. Test leaching waters have been prepared according to a method based on a 24 hours-submersion of painted panels in fast-stirred and aerated natural sea water.
Three different marine organisms were used in the bioassays: 1) the eterotrophic bacteria *Alteromonas haloplanktis;* 2) the unicellular flagellate alga *Tetraselmis suecica* Prasinophyceae class; 3) *Artemia salina* Crustacean class (adult stage).
Time-kill experiments were performed by adding test-organism pure-cultures to the leaching waters; at different times (0, 2, 5, 7 days in bacteria; 0, 24, 48, 72 hours in algae; 0, 24, 48 hours in crustaceans) viable counts were performed by (1) plating water aliquots on Zobell agar and evaluating colonies after 5 days of incubation at 20° C; (2) microscope evaluation in Burker cell of *Tetraselmis* algae; (3) mortality evaluation of *Artemia* crustaceans.
Leaching waters activity was compared to control tests in natural sea water and to the activity of 20 ppm of potassium dichromate (20 and 200 ppm in bacteria tests), dissolved in natural sea water, that was assumed to be the reference toxic compound.
Results indicated that *Tetraselmis suecica* was more susceptible to 100% of leaching waters than to 20 ppm of potassium dichromate; *Artemia salina* showed a higher sensibility to 12% of the leaching waters than to the reference toxic compound, whereas A*teromonas haloplanktis* showed 25% of leaching waters more active than 20 ppm of potassium dichromate and 12% more active than 200 ppm.
The global evaluation, based on the results of the 3 bioassays for each tested paint, showed that 2 paints were more active than 20 ppm of dichromate, 3 paints showed an activity similar to the reference toxic, whereas 3 paints had low toxic effects.
These results, obtained by laboratory assays, will be compared to 1-year field-tests that are actually running in 5 different stations of the ligurian coast. Laboratory bioassay and field test results will allow to evaluate the ratio efficacy/environmental impact of antifouling paints in standard conditions.

BIOLOGICAL CONTROL OF MARINE BIOFOULING

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Marine biofouling is a mat made of bacteria, sea-weeds, and sessile invertebrates, which develops on man-made objects submerged in the sea. The mat makes the surface of ships' hulls uneven and rough. Due to the rough surfaces friction during movement increases, and speed is reduced. On stationary installations, biofouling corrosion, increases the mass of the installation and distorts its configuration. To combat biofouling, prior to submergence the object's surface is painted with "antifouling paints", which contain toxichemicals. The toxins initially prevent, later slow down the development of the mat, but eventually fade away. The vessel has to be drydocked, scraped and repainted. Stationary objects are scraped periodically by scuba-divers. These solutions are costly and never foolproof. Striving to improve effectiveness the chemical industry produces chemicals of ever-increasing toxicity. The invention of Tributyltin has crossed the threshold between environmentally-safe and environmentally detrimental toxichemical. This chemical poisons the marine biota and damages mariculture.

We explore an alternative solution, biological control by limpets, applied to surfaces that should be protected. Limpets *Patella coerulea* can easily be detached from the shore and transplanted onto metal panels simulating a ship docked in the port of Ashdod, Israel (SAFRIEL & EREZ, 1987). The transplanted limpets eat the unicellular algae and sporelings of the larger algae. While foraging for them, the limpets crush and dislodge recruits of the fouling invertebrates. We found that the limpets accelerated the detachment and mortality of young recruiting barnacles *Balanus amphitrite*, presumably by repeated running over by the foot, thus undermining the barnacles' hold. Only when barnacles are >ca 1.5 mm in rostro-carinal diameter, they become safe from both physical detaching forces, and limpets.

We found that during winter, when fouling recruitment was slow, 15 limpets reduced the ca 90% biofouling cover of 20 x 20 cm experimental panels down to 1-3%, and barnacles' density from 2.6-3.8 to 0.7-0.8 individuals/cm^2. With the commencement of the spring surge of fouling recruitment, the limpets' controlling effect steadily deteriorated, but they continued to check the development of the high-mass bryozoan cover by the end of the 8 months-long experiment. The decline in limpets' controlling effect was due to a feed-back loop: heavy settlement of barnacles brought about an initial reduction in control that increased barnacles' sizes and density. This induced accelerated mortality among limpets, bringing about a further increase in barnacles' density.

To achieve effective control, it is necessary to measure "Return time", tr, the time it takes a foraging limpet to return to previously foraged location on the surface, and "Critical time" tc, the time it takes a fouling individual to get established on the surface such that limpets cannot remove it. The preferred density and size distribution of limpets is the one that achieves tr≥tc for the whole surface. The critical time for *Balanus amphitrite* ranges between 3-6 days. The recruitment rate with which the limpets have to deal with can be as high as 0.44 *Hydroides elegans*/cm^2/day and 0.06 *Balanus amphitrite*/cm^2/day.

Return time of *Patella coerulea* depends on its movement pattern. As of transplantation, limpets gradually increase their home range and mould territories. Their rate of movement increases with the density of recruiting algae, on which they forage. But the presence of other limpets also elicits movement, presumably for marking the surface with mucus, as a non-aggressive territorial defense measure. Even when algal density is low, a limpet moves more when there are many than when there are few other limpets on the surface to be protected. To find the optimal control we develop a mathematical simulation model which is driven by these and other data on the life history of the fouling organisms, and the behavioural ecology of the limpets, obtained in field and laboratory experiments.

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CORROSION BEHAVIOUR OF CuNiFeMn ALLOY IN SULPHIDE POLLUTED AND UNPOLLUTED SEA WATER.

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Corrosion problems can occur in new plants when, after testing or down-time, are left full of stagnant sea water for long periods before service use.

In this case corrosion can be particularly aggressive owing to sulphide pollution.

The behaviour of 66Cu-30Ni-2Fe-2Mn commercial alloy in quiescent, hermetically closed, sulphide polluted and unpolluted sea water was examined.

Before the hydrogen sulphide addition, the dissolved oxygen (D.O.) was 6.5 ppm, but this value decreased after sulphide injection and became zero for high sulphide content (≥10 ppm). For hydrogen sulphide values lower than 10 ppm sulphide ions and D.O. can be simultaneously present.

Free corrosion experiments were carried out by exposing the specimens for different periods (120,240,360 h) in sulphide polluted (0,1,4,8 ppm) sea water, at temperature of 25° C.

The pH value of corrosive solution, even at the highest H_2S concentration, never decreased below 8.

From free corrosion experiments the average corrosion rate was measured and the morphology of corrosive attack was observed.

The corrosion products adherent to the corroded surfaces were characterized with chemical, X-Ray diffractometry, FT-IR spectroscopy and surface analysis (XPS) methods, by attempting to correlate the composition of the corrosion layer of the alloys with their corrosion resistance.

Electrochemical tests were carried out on specimens which had been kept in the corrosive solution for different periods (2,120 h).

Corrosion current density and polarization resistance were measured with polarization potentiodynamic curves obtained with 250 mV/h scanning speed.

Free corrosion potential measurements were moreover carried out. From these data it appears that, by increasing sulphide solution concentration, potential values decrease.

Weight loss and polarization potentiodynamic tests show the greatest corrodibility of Cu-Ni alloy with an initial sulphide concentration of 4 ppm. In this case sulphides and D.O. are simultaneously present and have a synergic effect by acting as corrosion accelerators.

This may be due to stimulation of the anodic process since the cathodic process is depleted owing to the low amount of D.O.. In fact the corrosion product layer formed at the metal surface is a porous, non-protective film that contains mainly copper compounds.

Chemical and instrumental analyses show that copper sulphides are present in corrosion layer while surface examinations do not reveal nickel compounds, only chemically detected.

Therefore, the corrosion resistance of this alloy can be correlated to the different composition of passivating films, influenced by experimental conditions.

ANTIFOULING SYSTEM FOR SHIP HULL BY ELECTRO-CONDUCTIVE COATING

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Mitsubishi Heavy Industries (MHI) and Ship and Ocean Foundation (S&OF) have developed a new antifouling technique using electrolysis technology, that prevents marine growth from fouling the surface of ship's hull.

KEY-WORDS: Antifouling System, Electro-Conductive Coating

INTRODUCTION

Today, ships are usually coated with self-polishing antifouling paints that contain substances harmful to the marine ecosystem. This system of painting relies on dissolving toxic substances into the sea, which results in the ship's surface being protected from marine growth.

MHI's new technique does not contain any toxic substance harmful to sea organisms, allowing for a healthier marine ecosystem.

BASIC PRINCIPLE OF THE TECHNOLOGY

The water contact surface of the hull shell plating is coated with an electro-conductive paint film through an insulated coat film, a small current is passed through this paint film to form the anode, while the electrode surface layer of the electro-conductive film is coated with hypochlorous ions by the aforesaid electrolyzed reactions. In this way, adhesion of marine growth such as microorganisms, algae, and seashells may be prevented.

RESULTS

(1) A two-layer structure was designed, with the electro-conductive material in the lower layer and the electrolysis-resistant material in the upper layer, to develop an electro-conductive film possessing both high electro-conductivity and excellent electrolysis resistance.

(2) By the results of the immersion test using raft outside Nagasaki Port and full scale test using small ships, it was confirmed antifouling performance of this system.

(3) It was confirmed that fouling may be prevented by supplying electric currents at regular intervals, instead of supplying continuously. Therefore, the coat film itself is used alternately as anode and cathode so that no counter electrode was necessary. This current supply method was applied to the small ships, and favourable results were obtained.

CONCLUSIONS

By means of the fundamental tests conducted so far, feasibility in small ships was verified.

This technology is in the process of research and development for practical use, and MHI and S&OF are now accelerating the pace of development in order to contribute to the protection of the ocean and global environment as early as possible in the context of recent mounting interest in ecology and nature and supporting prevention of ocean pollution.

The Scientific and Organizing Committees wish to acknowledge the invaluable contribution offered to the organization of the Congress by:

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