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Observations of the Inter-relation of Marine Corrosion
and Fouling in a Tropical Environment

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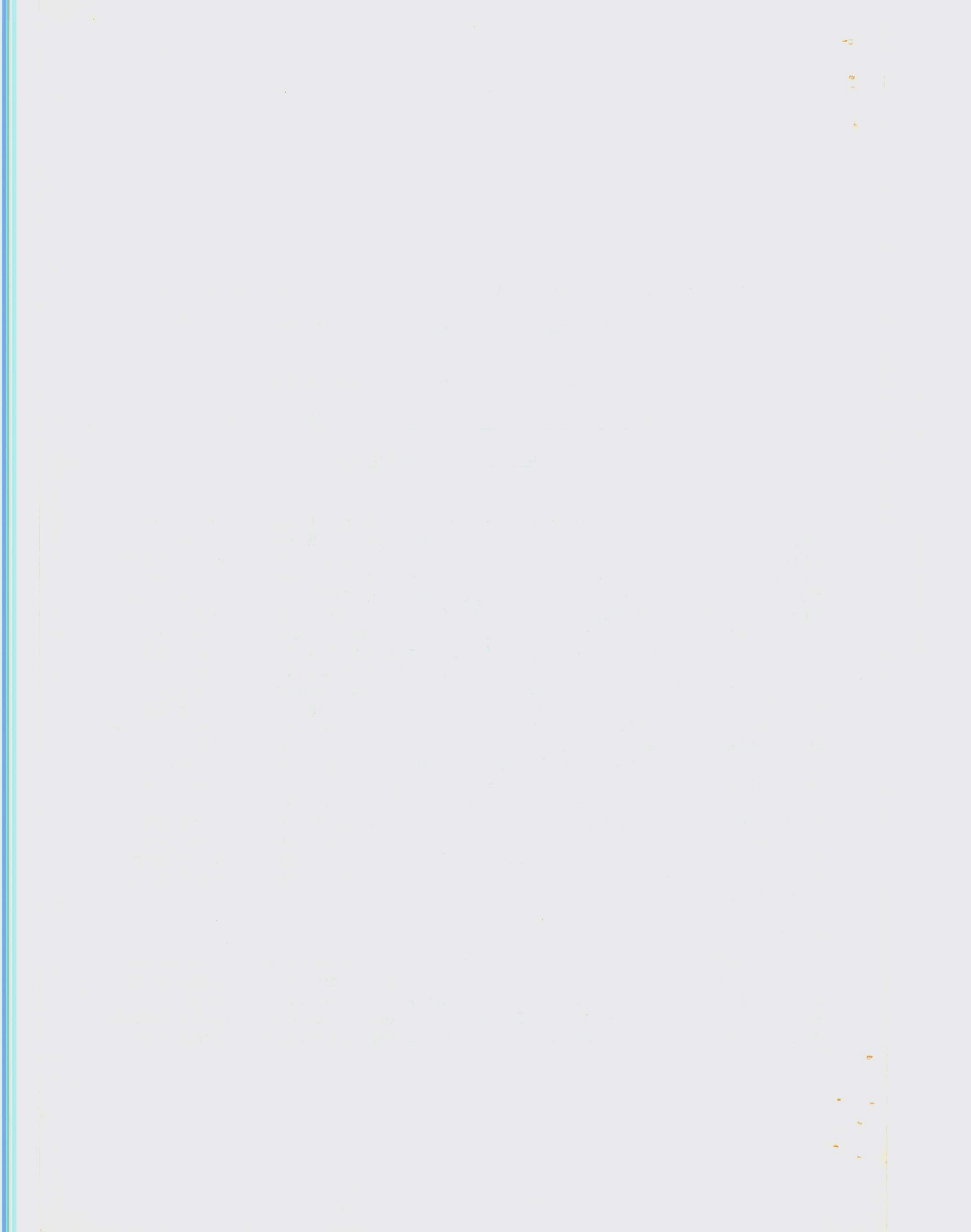
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Results of one year exposure of carbon steel, stainless steel type 304, aluminium 2S and aluminium M57S to the free attack of marine corrosion and fouling in Cochin Harbour (9°58'N, 76°16'E) are presented. The corrosion rates of metals in the fouled state after a year of exposure were 103, 6.3, 5.6 and 6.4 micron year⁻¹ for CS, SS 304, Al 2S and Al M57S respectively. Carbon steel and aluminium alloys were free of any pitting and crevice attack but severe pitting, tunnelling and perforations occurred on SS 304. The fouling load (wet weight per unit area) varied considerably with metals. A maximum load of 21.9 kg m⁻² was observed on Al M57S in six months but on prolonged exposure the fouling diminished as a result of decrease in salinity of the environment. Based on fouling load on metals investigated, Cochin Port appears to fall under fouled port. Growth curves developed for barnacles, may help in the prediction of fouling in Cochin Harbour. The theoretical growth curves fitted for barnacles on different metals would aid in an understanding of the inter-relation of fouling and corrosion and in the prediction of the quantum of fouling. These results are of considerable importance to the ocean engineering community especially in the tropics.

Introduction

Man's endeavours to exploit the oceans have gained considerable momentum in recent years. Offshore drilling, ocean mining, desalination, offshore metallurgy, alternate food and energy resources are some of the areas of ocean engineering which registered rapid progress. The increased activities coincided



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with the demand for a host of materials, equipment and facilities which can withstand the hostile and demanding marine environment. Several factors merit consideration before a material is recommended for ocean service: the structural strength, predicted life expectancy, knowledge of uncertainty and a thorough fundamental understanding of the marine corrosion and marine fouling behaviour. According to Gerchakov & Sallman cited by Schumacher (1) the last mentioned two factors are inter-related which in turn depend upon the interaction of metal, biota and the natural aquatic environment.

Theoretically, microfouling and corrosion are simultaneous processes occurring immediately upon introducing a metallic object in ocean, but in scientific pursuit these aspects have been dealt with by different groups of investigators, generally in isolation.

The net work of interaction and feedback system bringing in biota into metal/seawater interface allows a realistic prediction of performance of materials in seawater. The natural phenomena of biofouling follows a sequence of events like modification of surface by adsorbing biopolymers, the attachment and proliferation of pioneer cells followed by cellular or animal growth and finally mineralisation (2).

The fouling consisting of corrosion product films, precipitated salts, suspended solids deposition and biological growth (3) alters corrosion processes, increases the frictional resistance of ships, destabilises submerged oceanic structures, increases the weight of buoys and navigational equipment, clogs seawater conduits, generates noise which interferes with the sonar operations and increases wave action loadings on structures (4). Tighe-Ford estimated that fouling prevention and anti-fouling maintenance cost the maritime industry in USA over 500 million dollars in 1971 (5).

Redfield has reviewed the results of researchers upto 1948 concerning the fouling of the metallic surfaces and the influence of corrosion on the toxicity of metals in a monograph prepared by the Woods Hole Oceanographic Institution (4). An excellent account of macroorganisms in seawater and their effects on corrosion of metals are given by Clapp (6). Extensive investigations carried out at the LaQue Center for Corrosion Technology at North Carolina USA and the works of Efirid (7) have brought to focus a unified picture of corrosion and fouling of metals in seawater.

Considerable research efforts to study the simultaneous phenomena of marine corrosion and fouling have been made recently in response to the urgent requirements of high performance materials for Ocean Thermal Energy Conversion Systems and

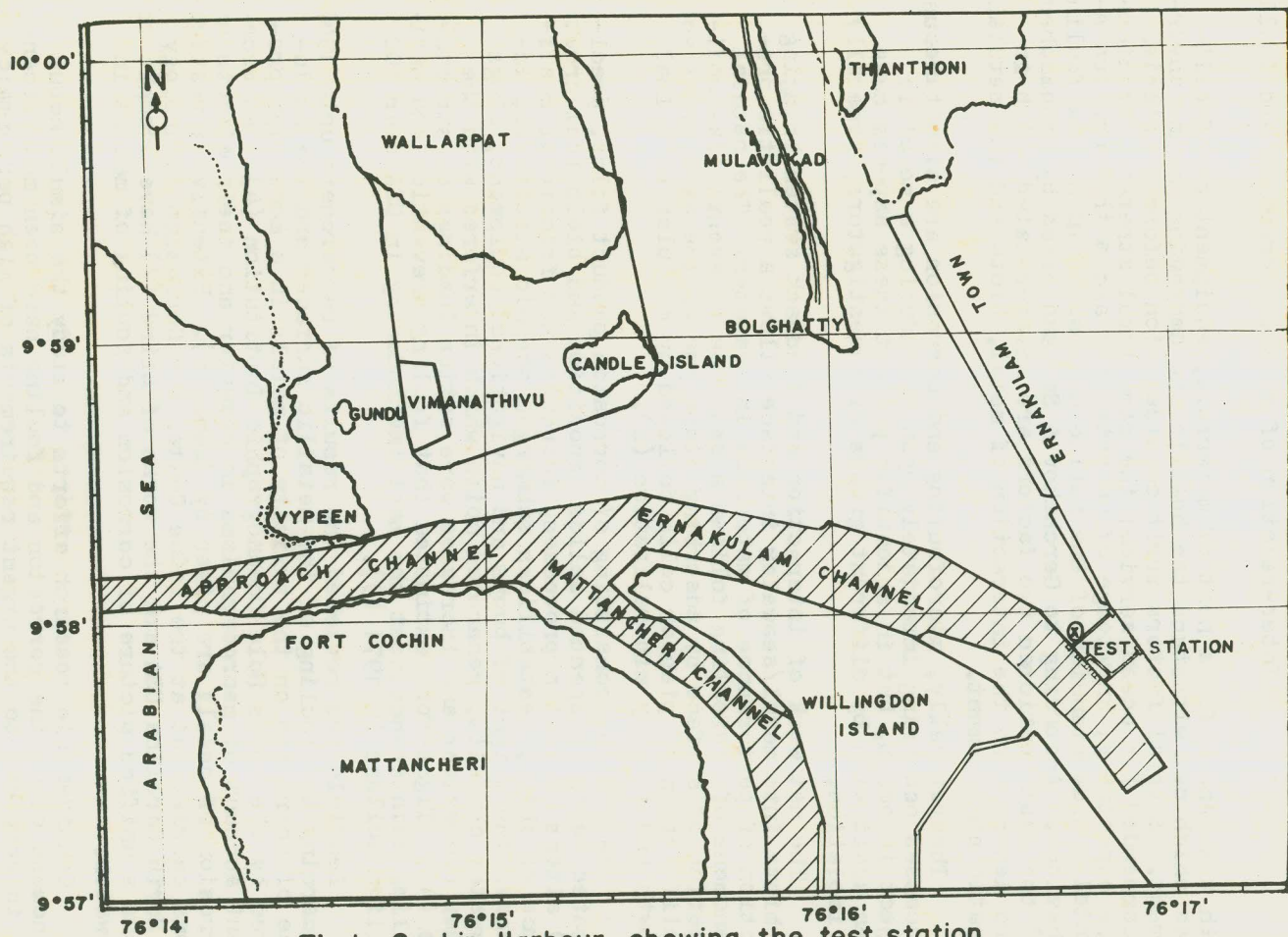


Fig. I. Cochin Harbour showing the test station

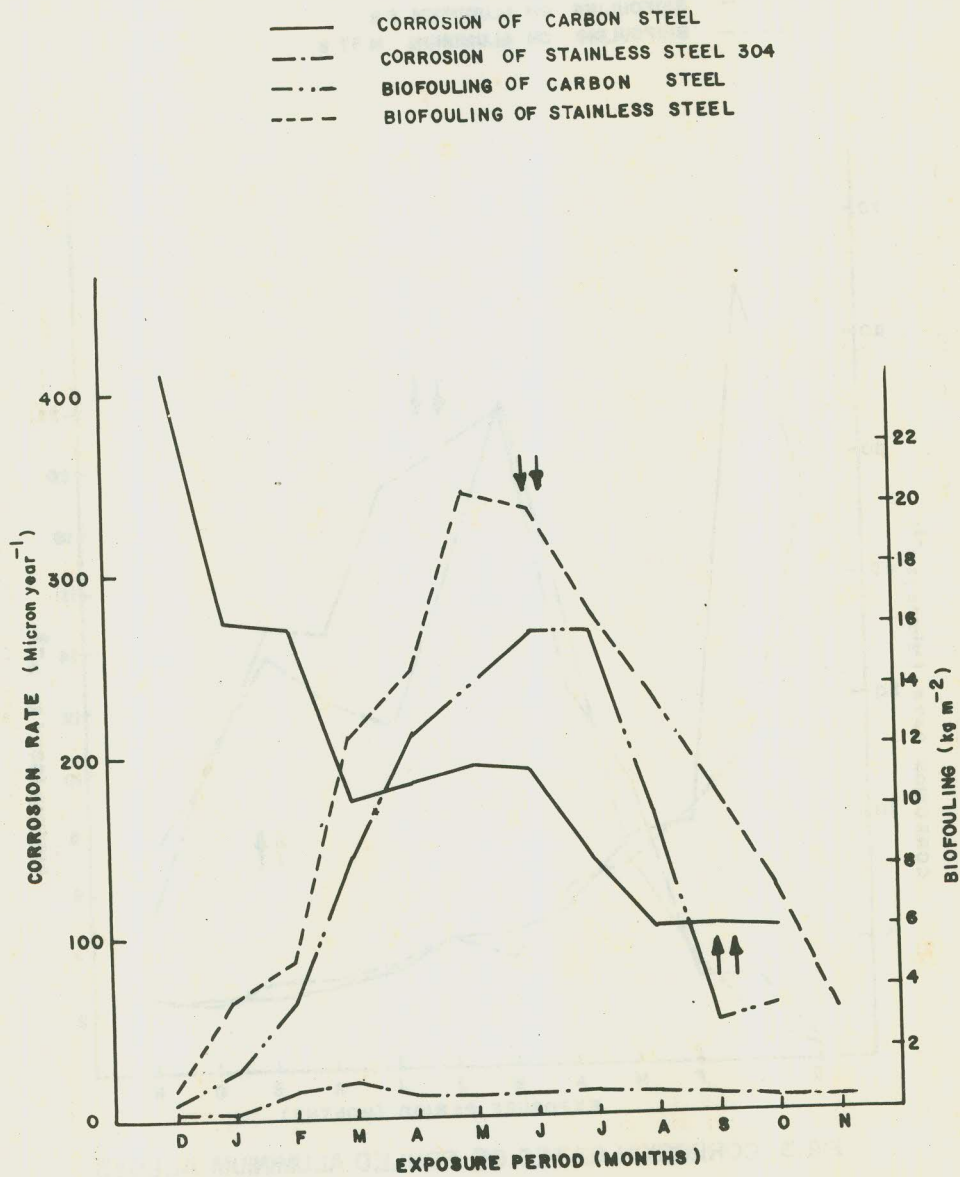


FIG.2. CORROSION RATES OF FOULED FERROUS ALLOYS

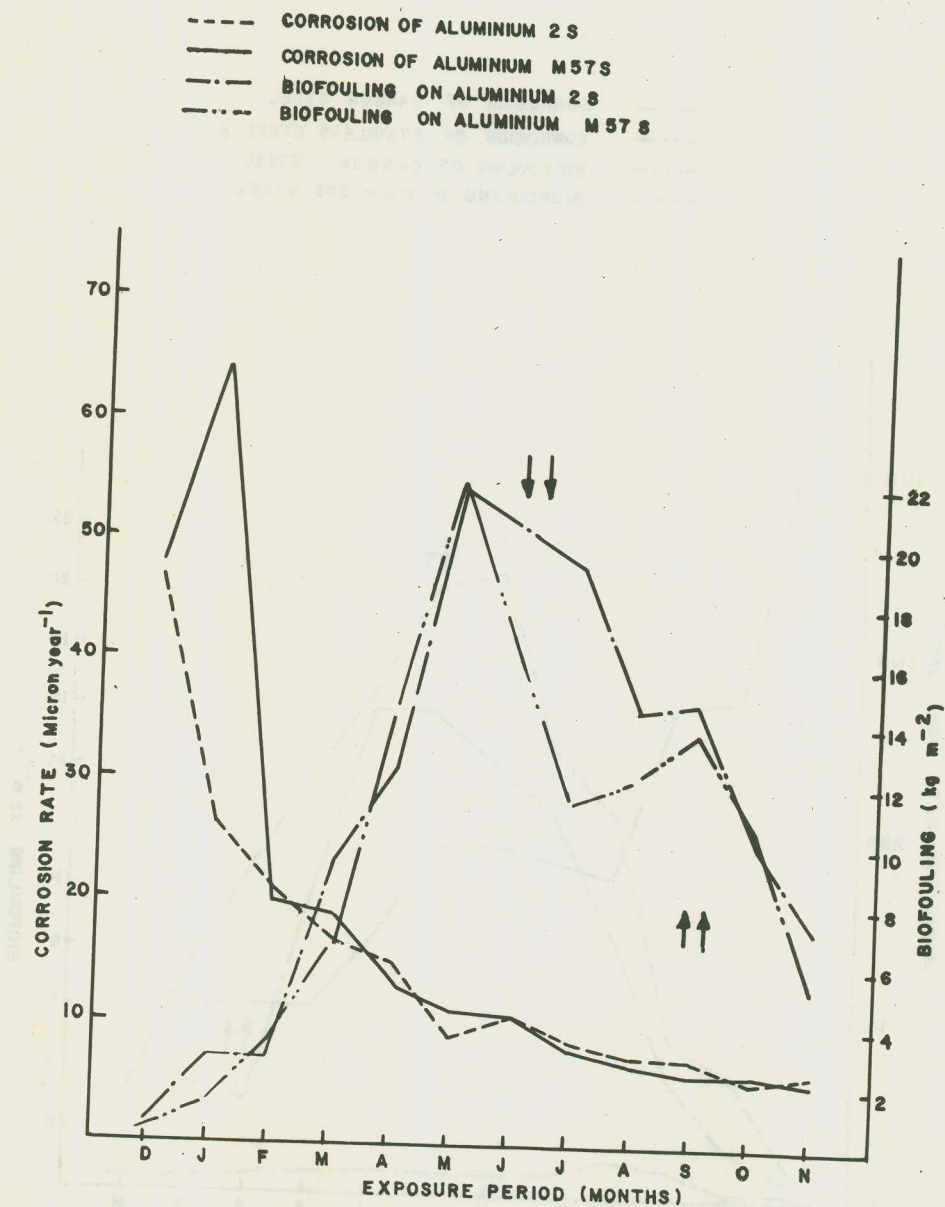


FIG.3. CORROSION RATES OF FOULED ALUMINIUM ALLOYS

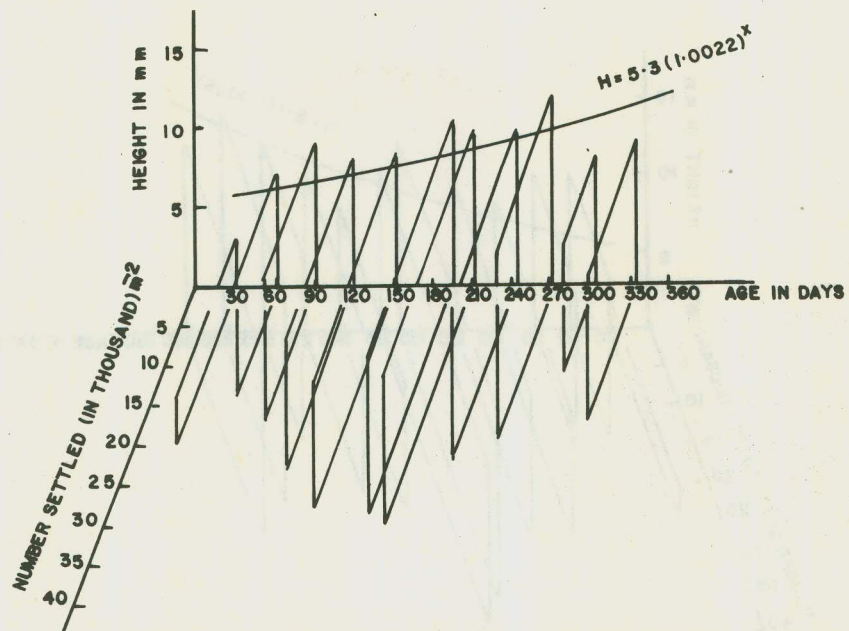


FIG. 4. GROWTH OF BARNACLES ON FREELY CORRODING CARBON STEEL

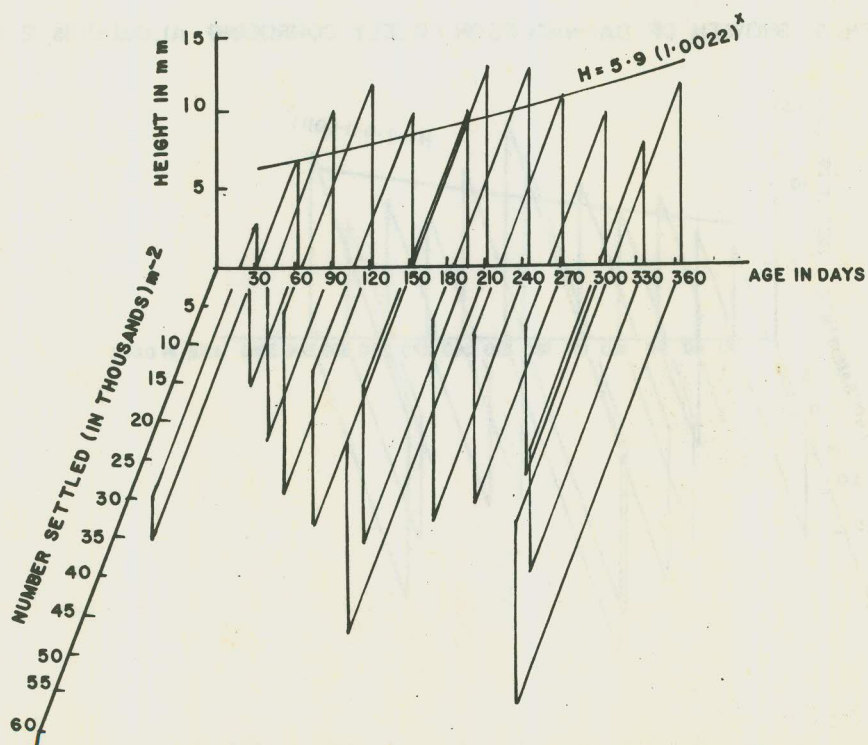


FIG. 5. GROWTH OF BARNACLES ON FREELY CORRODING STAINLESS STEEL 304

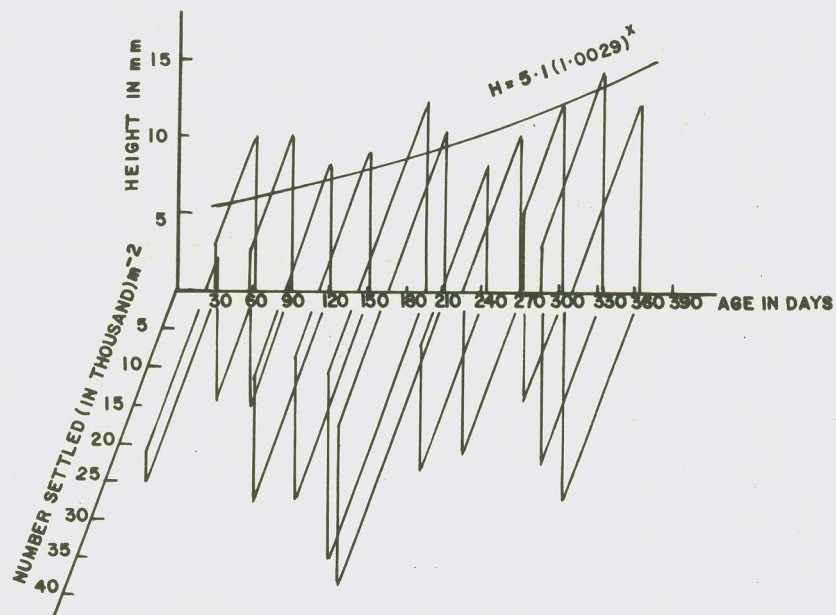


FIG.6. GROWTH OF BARNACLES ON FREELY CORRODING ALUMINIUM 2 S

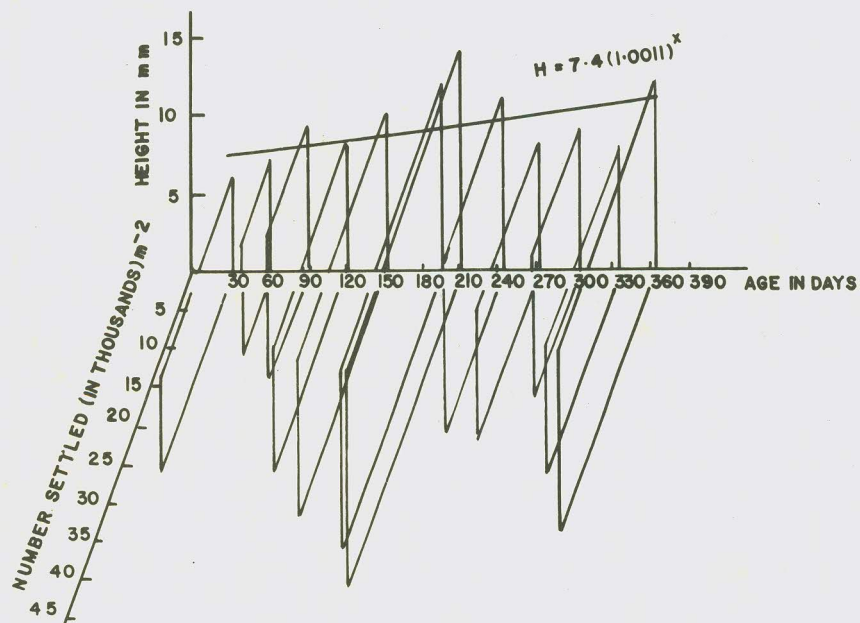


FIG.7. GROWTH OF BARNACLES ON FREELY CORRODING ALUMINIUM M 57 S

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subsystems. Fouling in thickness less than 100 micrometre can render an OTEC system inoperative by impairing the heat transfer efficiency (8).

Notable works (9,10) on the distribution of macrofoulers at near shore and offshore site in the Straits of Florida and Bahamas enabled DePalma at the US Navy to develop the growth curve nomogram from which "fearless fouling forecast" could be made within various marine environments. Based on extensive investigations DePalma (11) predicted the effects of macrofouling which may occur on a generalised ocean structure. The problems of macrofouling of hull, heat exchangers and cold water pipes of different designs of OTEC machines and an estimate of maximum organismal growth, weight displacement as a result of fouling were the subject of detailed investigations recently (12).

De et al. (13) who did pioneering works in India, contributed to our understanding of corrosion behaviour of some structural metals at Bombay and Cochin Harbours, but the fouling dynamics in relation to corrosion was not studied by them.

As far as we are aware of no detailed studies on fouling on structural metals, inter-relation of corrosion and fouling and forecast of fouling on submerged metals in seawater in a manner required by the ocean engineers and planners have been carried out in the tropics. This paper presents a part of the results obtained under a comprehensive investigation on the behaviour of structural materials in Cochin Harbour (9°58'N, 76°16'E).

Test programme

The metals and alloys for use in this work were cut to 10x7.5 cm from rolled sheets of carbon steel, stainless steel type 304, aluminium 2S and aluminium M57S. The metal plates were cleaned and weighed as recommended by Ailor (14) and Champion (15) and were mounted on mild steel racks of Carnegie Illinois Steel Corporation design (16) whereby the galvanic action between different specimen or between the specimen and the rack was prevented. The racks containing the metal plates were kept submerged at one metre level from the low water level in the vicinity of Oil Tanker Berth at Cochin Harbour (Fig.1). The plates were thus exposed to the natural assemblage of marine fouling on freely corroding metals. The retrieval of the panels in triplicate were made at monthly intervals and a quantitative assessment of the biogrowth was made. The plates were cleaned off the corrosion products (16), the corrosion rates determined and the relevant data analysed statistically. A detailed account of the test programme is given by Pillai & Ravindran (17).

Results and Discussion

The rates of corrosion and the wet weights of the fouling complex on carbon steel, SS 304, Al 2S and Al M57S as a function

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of the exposure period are presented in Fig. 2 and 3. Graph representing the age in days on the X-axis, the height in mm on the Y-axis and the number settled per square metre area on the Z-axis of one of the major foulers are given in Fig. 4 to 7.

Corrosion behaviour in relation to fouling

The application of carbon steel as a marine hardware depends much on its corrosion and fouling characteristics which in turn depend upon the environmental factors. At Cochin Harbour, carbon steel corrodes at a rate of 410 micron year⁻¹ initially but the rate decreases as the period of exposure increases and attains a value of about 103 micron year⁻¹ after 270 days. This near steady state of corrosion is controlled by several factors principally the salinity, dissolved oxygen and water temperature as well as the mass and the nature of the biota on the metallic surface.

Cochin Harbour presents certain unique hydrographic features as there is progressive dilution of seawater owing to South-west monsoon during the period May to July and precipitation from north-east monsoon during August to October. The discharge of fresh water by numerous rivers also lowers the salinity of Cochin backwaters especially during monsoon. An excellent account of the general hydrography of Cochin Harbour is given by Nair (18) and the monthly variations of salinity, dissolved oxygen, surface water temperature and pH pertaining to the period of study by Pillai & Ravindran (17).

The influence of biofouling and calcareous deposits formed on the metallic surface is evident from the slopping trend of the corrosion rate curve as they would restrict the availability of oxygen to the metal surface. Pitting was absent throughout. The biofouling on carbon steel being less adherent, gets sloughed off periodically along with the corrosion film exposing fresh surface of the metal for attack. Based on several tests, Larrabee & Mathay (19) concluded that the corrosion of iron in deaerated unpolluted seawater is 100 to 125 micron year⁻¹ for the first year of exposure. Values ranging from 165 to 175 micron year⁻¹ were obtained by De et al. for carbon steel at Cochin (13), and Vishakhapatnam (20). Comparable corrosion rate of carbon steel in tropical and temperate waters is in conformity with the reasoning that in tropical waters the fouling is massive and restricts access of oxygen whereas temperate waters contained more of dissolved oxygen, but less of fouling organisms. These factors are self compensating (1).

Type 304 stainless steel showed pitting, tunneling and perforations within a period of 2 months. The crevice attack and perforations occurred beneath barnacle base. The maintenance of passivity which is responsible for the protection of stainless steel is impaired due to the formation of differential

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aeration cells (oxygen shields) beneath the settled foulers. The corrosion rate, as determined by the weight loss, was very low: the initial rate is 3.1 micron year⁻¹ in one month and attained values of 5.2, 5.7 and 6.3 micron year⁻¹ during the 10th, 11th and 12th month of exposure. As the attack was highly localised in nature the average corrosion rate values do not reflect a realistic picture of the deterioration of the metal.

The general corrosion behaviour of aluminium 2S and M57S were comparable as there are very little variations in their corrosion rates after 180 days. Though aluminium alloys are susceptible to crevice and pitting attack in seawater (13,21, 23) aluminium 2S and M57S were free of any localised attack. An adherent heavy mat of fouling on entire surface of the metal in a period less than 2 months and subsequent superimposed growth provided considerable shielding to the metal from the environment. In the absence of pitting, corrosion rates based on weight loss determination are meaningful though such computation may give a misleading picture in case corrosion is localised. The observed corrosion rates were extremely low and were in the range of 6.1 to 5.6 micron year⁻¹ for Al 2S and 7.6 to 6.4 micron year⁻¹ for Al M57S during 300 to 360 days of exposure.

Fouling behaviour of freely corroding metals.

The quantum of fouling expressed as wet weight in kg m⁻² on carbon steel, SS 304, Al 2S and Al M57S as a function of period of exposure is shown in Fig.2 and 3. The upward and the downward arrows in the figures correspond to a period of commencement of fresh settlement of larval forms and the general sloughing off of settled biota with the non-adherent corrosion products respectively. The fouling complex mainly consisted of barnacles, hydroids and modiolus with few (less than 10%) bryozoans, tube worms and oysters but the major share of the weight was due to barnacles.

The graph representing quantum of fouling shows three distinct periods characterised by: (a) a period of increased settlement and progressive luxuriant growth of foulers with the complete coverage of the surface, (b) a period of reduced activity, retarded growth, mortality (70 to 80%) and absence of fresh settlement and (c) a period during which the calcareous structures of the animals remained intact with metals like stainless steel and aluminium alloys, but excessive sloughing off on carbon steel. Fresh settlement of the larval forms also took place during this period.

Maximum fouling loads observed in the present study during the period from December 1980 to May 1981 are 16, 20.7, 21.6 and 21.9 kg m⁻² on carbon steel, SS 304, Al 2S and M57S respectively. The heavy biogrowth on non-toxic corroding metals in terms of mass and unit of exposure period would indicate that Cochin Port

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may fall under 'fouled port'. Continued exposure had shown a decline in fouling load per unit area which might be attributed to sloughing off especially from carbon steel, mortality, diminished growth rate etc consequent to environmental changes. Periodical sloughing off from solid corrosion products from carbon steel occurred much before attaining the maximum fouling load.

On non-toxic metals like, Al 2S and Al M57S the fouling load in Cochin Harbour was found to be related to salinity changes and does not appear to depend upon small changes of temperature from 28.8 to 32.0°C at the harbour area. Previous studies (4) have shown that when the water temperature is from 21 to 38°C, biogrowth is prevalent with maximum accumulation from 27 to 32°C. The major role of salinity on settlement of foulers on glass (24) and sand blasted black acrylic sheets (25) was also reported by other workers. While in temperate waters the effects of temperature overshadow that of salinity (4).

The assemblage of foulers, seasonal pattern of species recruitment, larval transport etc are complex functions of several parameters of the environment (26) and the biogrowth appears to depend on physical (4), chemical (4) and electrochemical (27) characteristics of the metal and the nature of the corrosion film (7).

At Cochin Harbour where the salinity influences fouling, the maximum fouling load attained as given in Figs 2 and 3 can be taken for engineering computations. This is suggested on the premise of DePalma (11) that once a surface is totally covered, there is a minimal increase of added weight with time and therefore the fouling rates are similar even though some are based on 10 to 11 months and others are on a 12 years prediction.

The average density of the biofouling when it was predominantly composed of barnacles was 1500 kg m^{-3} while that constituted by oysters showed a density of 1470 kg m^{-3} . Heavy inter-lace of fouling with superimposed growth on Al M57S caused a maximum fouling load of 21.9 kg m^{-2} . Interesting is a comparison of this value with that of DePalma (11) that a structure totally covered by hard shelled organisms will increase in weight by approximately 17 kg m^{-2} . The painstaking works done by DePalma (9,10,11) were of immense value in predicting the expected mass of fouling organisms and their percentage weight to the hull of the OTEC-1, APL (10-20 MWe) and Spar Configuration (10 MWE and 40 MWe) (12).

While studying the economic implications of fishing fleet management it is reported that Al M57S sheathed fishing boat hull gathered 10 to 15 kg m^{-2} of fouling in a period of 7 to 8 months (28). Observations of heavy biogrowth of varying intensities on fishing trawlers operating in offshore waters and high seas do provide a reflection of the efficacy of antifouling paints available in the country.

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Statistical approach to fouling prediction

For a clearer comprehension of complex inter-related and competing phenomena involving unit factors such as time and space, number of occurring individuals and their growth "an analytical graph" was developed by Tatu Kawahara (29). Following a similar trend, in an attempt to predict the quantum of biogrowth on metals, the three inter-related parameters, namely, the period of exposure, the height and number of barnacles were plotted on a graph. As barnacle fouling is of concern in view of fouling load per unit of exposure time, the regression curves were fitted for the growth in terms of height and basal diameter of barnacles settled on carbon steel, SS 304, Al 2S and Al M57S. These are shown graphically in figures 4 to 7 and the corresponding equations are presented in Table 1. These equations describing two important basic dimensions of barnacle (the shape of

Table 1. Regression equations of barnacle fouling dynamics on freely corroding metals

Metal	Growth rate (mm)	
	Height	Basal diameter
Carbon steel	$5.3 (1.0022)^x$	$8.4 (1.0021)^x$
SS 304	$5.9 (1.0022)^x$	$10.9 (1.0017)^x$
Al 2S	$5.1 (1.0029)^x$	$8.8 (1.0023)^x$
Al M57S	$7.4 (1.0011)^x$	$10.0 (1.0013)^x$

which can be approximated to that of a cone) computed with the density of biomass would lead to reliable prediction of the bio-fouling load that can be expected on submerged metals. This data may also eventually be applicable to evaluate the environmental conditions of near shore ecosystem.

It is emphasised that for the rational design of hardware for ocean engineering projects a fore-knowledge of the materials behaviour in the environment would aid in proper planning and decision making.

Conclusions

Intense pitting, tunneling and perforations of SS 304 under heavy deposits of fouling limit the use of this alloy in ocean engineering. Carbon steel, Al 2S and Al M57S were free from pitting. Fouling in general was very heavy on all metallic surfaces and a maximum fouling load of 21.9 kg m^{-2} was observed on non-toxic metal. Based on the fouling load Cochin Port appears to fall under fouled port. With the help of growth curves meaningful prediction of fouling on different freely corroding metals could be made.

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Les observations sur l'entre-relation de la corrosion marine
et des salissures dans un milieu tropical

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Les résultats d'une année d'exposition de l'acier carbone, l'acier inoxydable du type 304, l'aluminium 2S et l'aluminium M57S à l'attaque libre de la corrosion marine et des salissures au port Cochin (9°58'N, 76°16'E) ont été présentés. Les taux de la corrosion des métaux dans un état de salissure après un an d'exposition étaient 103, 6.3, 5.6 et 6.4 micron/année pour CS, SS 304, Al 2S et AlM57S respectivement. L'acier carbone et l'aluminium alliage étaient libre de toutes fosses et des attaques crevasses mais des fosses sévères, tunnel et perforations ont eu lieu sur SS 304. Les poids des salissures (poids mouillés par unité aire) étaient variés considérablement avec les métaux. Un poids maximum de 21.9 kg m⁻² était observé sur AlM57S en six mois mais à l'exposition prolongée, la salissure a été diminuée comme résultat de décroissement dans la salinité de l'environnement. Basé sur les poids des salissures sur les métaux examinés, le port Cochin semble être sous les 'ports des salissures'. La croissance courbe développée pour les barnacles pourrait aider dans la préatiction des salissures au port Cochin. La croissance courbe théorique convenable pour les barnacles sur les métaux différents pourrait aider dans une compréhension des entre-relations des salissures et de la corrosion et dans la prédiction du quantum des salissures. Ces résultats sont d'une importance considérable pour la communauté des génies océaniques surtout dans les tropiques.