

Corrosion of Biofouled Ferrous Metals in Tropical Waters

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The study is aimed on the selection of various structural materials like mild steel, galvanised iron, stainless steel 304 and stainless steel 410 for ocean engineering applications. Results of one year exposure of these metals to the free attack of marine corrosion and fouling at the Cochin Harbour (9°58'N, 76°16'E) are presented. The corrosion rates of metals after one year exposure were 103, 129.3, 6.3, 43.68 microns year⁻¹ for CS, GI, SS 304 and 410 respectively. The carbon steel and galvanised iron were free from pitting and perforations occurred on stainless steel. The fouling load varied considerably with the metals. A maximum load of 20.7 kg m⁻² were observed on stainless steel panels during this period but on continuous exposure the fouling load decreased. Statistical equations were derived with which the fouling load on harbour structures could be predicted.

Key words : Marine corrosion, biofouling, structural materials.

The scientific exploration and exploitation of the ocean have gained considerable importance in recent times. With shortage of structural materials, energy conservation measures, high man power costs and environmental considerations an efficient and cost effective material selection for marine structures has become an important subject. The corrosion and microfouling are simultaneous process when any metallic objects are put in ocean. The corrosion and the fouling are interrelated and depends on the interaction of metals, biota and other environmental factors.

A detailed account concerning the fouling of metallic surface and the toxicity of metals in relation to fouling is given in the monograph of Woods Hole Oceanographic Institution (1952). A unified theory of the effect of fouling on the corrosion of easily corrodible

metal, passive metal and toxic film forming metal was recently put forward by Efird, (1976). De Palma (1969, 1972 & 1984) made significant contribution to the understanding of fouling in the world oceans and developed a growth curve monogram. Comprehensive long term studies on corrosion of wrought and cast structural ferrous metals in natural tropical environment in Panama Canal zone were the subject of investigations by the U.S. Navy which has reported that the corrosion rate of the metals stabilized to a steady state between 1 and 8 exposure (Forgeson *et al.* 1960).

A beginning on the corrosion behaviour of some structural metals in tropical waters at Bombay and Cochin Harbours was made by De *et al.* (1968). The works were further extended by them to the Vishakapatnam Harbour (De *et al.* 1977). The dependence of fouling

on corrosion was not taken into account in these studies. The accumulation of fouling on marine structure is a serious problem to the designers and manufactures as it increases the hydrodynamic load. A study on the interrelation of marine corrosion and fouling in a tropical environment was recently reported (Ravindran & Pillai, 1984). In the context of increased activities in ocean engineering works in the country a comprehensive investigation on the corrosion behaviour of ferrous metals was taken up.

Materials and Methods

Cochin Harbour (9°58'N, 76°16'E) having wide variations of hydrographic features is an ideal site for the evaluation of metals and alloys. The South-West monsoon during the period, May to July and precipitation from North-East monsoon during August to October exert a profound influence on the environment. The salinity, dissolved oxygen, surface water temperature and pH during the period under study showed wide variation (Pillai & Ravindran, 1983).

Four common metals and alloys namely low carbon steel (CS), stainless steel (SS) 304, stainless steel 410 and

Table 1. Hydrographic data at the Cochin Harbour

Month	Surface water temp. °C	Dissolved oxygen ml l ⁻¹	Salinity %	pH	H ₂ S ml l ⁻¹
Dec.	30.3	5.6	18.7	8.2	0.0
Jan.	30.1	2.5	28.5	8.1	0.0
Feb.	31.1	4.4	26.5	8.1	0.0
Mar.	31.6	4.1	24.6	8.2	0.0
Apr.	32.0	4.2	25.8	7.6	0.0
May	30.0	4.1	18.7	7.3	0.0
June	28.8	6.0	10.3	7.4	0.0
July	29.5	6.3	1.0	7.6	0.0
Aug.	29.5	6.2	0.6	7.5	0.0
Sept.	30.5	6.1	1.7	7.5	0.0
Oct.	30.5	6.0	4.4	7.7	0.0
Nov.	30.9	7.0	8.5	7.9	0.0

galvanised iron (GI) were exposed at the Cochin Harbour together with painted carbon steel panels (Fig. 1). The metals and alloys used in the studies were obtained in the form of rolled sheets which were cut into a size of 10 x 7.5 cm along the rolled direction using guillotine with utmost care. The cut edges were

Table 2. Chemical composition of the metals and alloys used

Sl. No.	Metals and alloys	Thickness mm	Elements present	Percentage
1	Carbon steel	0.71	Carbon	0.18
			Manganese	0.41
			Silicon	0.14
			Iron	Remainder
2	Galvanised carbon steel	0.71	Coated with Zinc	
3	Stainless steel 304	0.71	Nickel	0.24
			Chromium	13.00
			Manganese	1.29
			Iron	Remainder
4	Stainless steel 410	0.71	Nickel	0.24
			Chromium	13.00
			Manganese	1.29
			Iron	Remainder



Fig. 1. Cochin Harbour showing the test station

finished by machining. The panels were identified by drilling 0.8 mm holes in a regular manner in specified places (Champion, 1951).

Carbon steel was cleaned initially with coarse abrasive cloth No. 50 so as to remove a layer of metal to eliminate variations in conditions of the original metallic surface. Final surface finish was given with No. 120 abrasive paper. For preparing stainless steel, grade 120 emery on leather buffs was used. A paste of pure magnesia was used in the preparation of galvanised steel specimen. All panels were finally degreased by scrubbing with water and acetone, air drying and then weighing to an accuracy of 0.1 mg.

The metal plates were mounted on mild steel racks of Carnegie Illinois Steel Corporation design (LaQue, 1948). The galvanic action between specimens and rack was prevented by the use of plastic insulator. The test panels were kept submerged at one metre level from the low water level in the Cochin Harbour.

Long term exposure tests for thirtynine panels of each of the 4 metals at the Test Station were carried out. Three panels each were removed at monthly intervals for evaluation and a quantitative assessment of the biogrowth was made. The corrosion product was removed as per ASTM methods (1974). Three extra panels of each metal were also included to compensate for loss of panels. The corrosion rate determined and the data analysed statistically.

Analysis of variance technique was employed for testing the significance of difference between metals and days of immersion on corrosion rate of metals.

Results and Discussion

The rate of corrosion of carbon steel, galvanised carbon steel, stainless steel 304 and stainless steel 410 and the corresponding wet weight of fouling organisms on the panels as a function of the period of exposure are given in Figs. 2, 3, 4 and 5 respectively. The representative growth curves of barnacles settled on the fouled stainless steel 304 panels (over 150 cm²) are presented in Figs. 6 & 7. Data concerning hydrographic parameters are given in Table 1 and the data of chemical composition of the metal alloys used in the tests are given in Table 2.

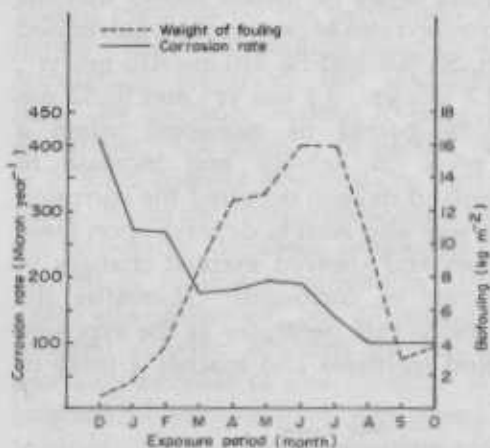


Fig. 2. Performance of carbon steel

As the Cochin Harbour shows wide fluctuations in hydrographic features, species diversity and numerical abundance with respect to microfouling communities is a common phenomena. All the exposed specimens of metals showed very large accumulation of barnacles, oysters and hydroids. Figs. 2, 3, 4 & 5 show the influence of hydrographical features on the corrosion behaviour of metals and alloys and also the fouling behaviour. The effect of the

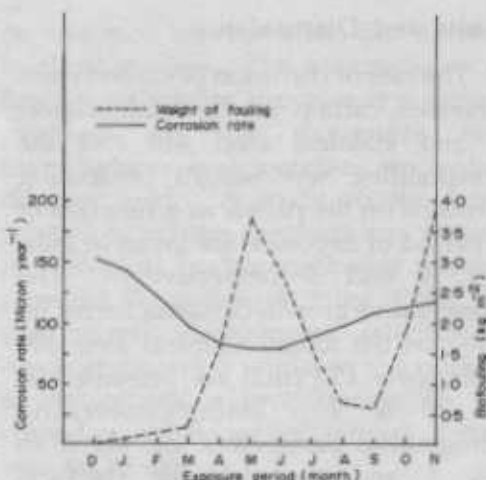


Fig. 3. Performance of galvanised carbon steel

period of exposure on the corrosion of ferrous series of metals shows that the corrosion rates of carbon steel, galvanised iron, SS 304 and SS 410 are $410 \mu\text{m yr}^{-1}$, $154.2 \mu\text{m yr}^{-1}$, $3.1 \mu\text{m yr}^{-1}$ and $92.52 \mu\text{m yr}^{-1}$, a period of monsoon, when a decrease in salinity and increase in dissolved oxygen occurred the corrosion rate was also seen to depend upon these factors and showed marked changes in the rate of corrosion. Thereafter the corrosion rate decreases as the exposure period increases and reaches a more or

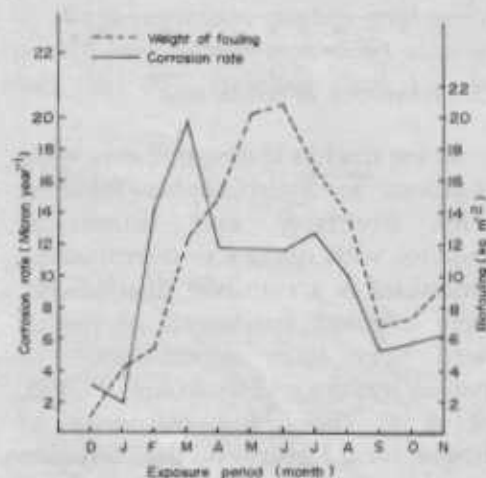


Fig. 4. Performance of stainless steel 304

less constant value after a period of 270 days. During the entire period of exposure no pitting corrosion was observed on any of the carbon steel.

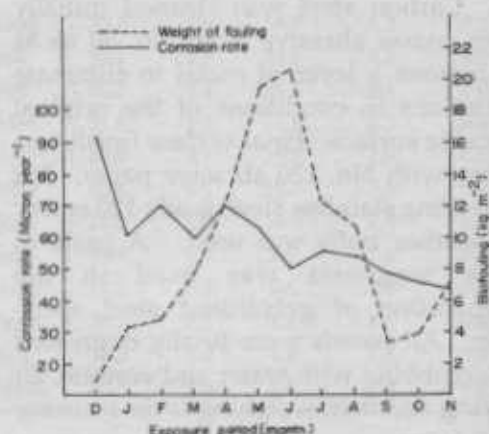


Fig. 5. Performance of stainless steel 410

The corrosion of galvanised carbon steel was more or less uniform without showing any increased rate of corrosion in the initial period. The scrutiny of Fig. 3 shows that corrosion rate of galvanised carbon steel approached that of carbon steel in a period of about a year. The effect of galvanising was also perceptible

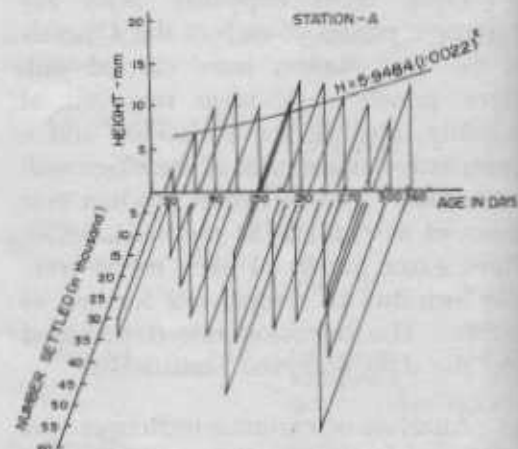


Fig. 6. *Balanus* sp. settlement, age and growth in height on stainless steel (304)

for a period of 150 days. The observed corrosion rates were higher than the value reported by LaQue (1948). The increased demand of zinc for cathodic protection of exposed iron accounts for the increased corrosion rate of galvanised iron.

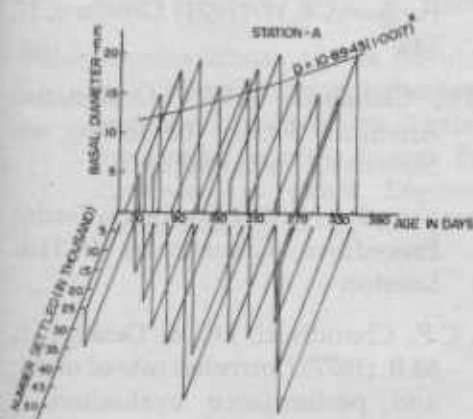


Fig. 7. *Balanus* sp. settlement, age and growth in basal diameter on stainless steel (304)

The maintenance of passivity which is responsible for the protection of stainless steel in seawater is often impaired owing to many factors. The corrosion of stainless steel was characterised by deep pits progressing into perforations. The corrosion rate and pitting of type 410 martensite stainless steel may be seen from Figs. 4 & 5. The pitting resistance of type 410 was low, as severe pitting and perforations occurred within a month of immersion. Crevice attack and perforations occurred beneath the barnacle's base in fouled panels. Several localised corrosion and perforations of stainless steel were also noticed by several workers (Forgeson *et al.*, 1960; Alexander *et al.*, 1971). In this study much significance cannot be attached to the corrosion rate of stainless steel based

on weight loss as the metal loss is due to severe localised pitting and perforation. These studies show that SS 304 and SS 410 are unsuitable for marine environment without proper protection.

The hydrographic features exert a direct influence on the fouling pattern of ferrous alloys (Figs. 2, 3, 4 & 5). A maximum fouling load of 20.7 kg m⁻² was recorded both for SS 304 and SS 410 and 16 kg m⁻² for carbon steel. On prolonged exposure the fouling diminished as a result of changes in the environmental conditions, especially the salinity. The toxicity of zinc might have influenced the reduced settlement of fouling complex on the galvanised iron panels. The heavy fouling complex also apparently protected the underlying metal by partially sealing it from the electrolyte. On scrutiny of Figs. 2, 3, 4 & 5 three distinct observations can be made. When the hydrographic conditions are favourable, increased settlement and growth of fouling organisms occurred. This was followed by a period of reduced activity, retarded growth and mortality because of low salinity. With increase of salinity fresh settlement of foulers take place resulting in superimposed growth even over dead animal bases.

The corrosion rates of the four metals were compared by employing

Table 3. Analysis of variance of corrosion rate

Source	SS	df	ms	F
Total	28170.72	43	6934.20	
Between metals	203498.25	3	67832.75	34.83**
Between days	36253.69	10	3625.37	1.86
Error	58418.78	30	1947.29	

Least significant difference = 38.4

F-test in analysis of variance. Significant variations in corrosion rates were observed between metals (Table 3). The average corrosion rates in microns year⁻¹ are also given (Table 4). The averages were found to be significantly different. The lowest was observed in the corrosion rate of SS 304. Comparison among pairs was carried out by employing the critical difference (LSD). LSD worked out to 38.4. Therefore, from the average it is easy to see that all the metals are different from one another in terms of corrosion rates.

Table 4. Mean corrosion rate of different metals in microns yr⁻¹

Carbon steel	Galvanised carbon steel	SS 304	SS 410
194.78	106.43	9.71	61.02

The increased hydrodynamic drag as a result of fouling on structural materials is a matter of concern. Fouling by barnacles is of great concern in tropical waters and it contributes to the major share of weight of the fouled structures. The rate of growth of barnacles (*Balanus* sp.) in terms of basal diameter and height on stainless steel 304 fits in the following statistical equation.

$$H = 5.9484 (1.0022)^x$$

$$D = 10.8943 (1.0017)^x$$

where H is the height of barnacles in mm, D the basal diameter in mm and x the age in days. With the help of the statistical equation and the number of animals settled as shown in Figs. 6 & 7 an approximation of the weight of the biomass could be found out for any period.

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