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MARINE FOULING AND CORROSION STUDIES IN THE COASTAL WATERS OF MANDAPAM, INDIA

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Results of a comprehensive study on marine fouling conducted in the coastal waters of Mandapam,India, are presented. Based on data from different tests, the effects of fouling organisms on the phenomena of corrosion and cathodic protection are discussed.

Key words: Biofouling, marine organisms, corrosion, cathodic protection

INTRODUCTION

Biological intrusion into the performance and behaviour of metals is greatest in the ocean, where micro- and macro-organisms, individually or together, affect corrosion processes. Based on biofouling characteristics, metals and alloys have been classified as (a) highly corrodible alloys which readily foul but fouling sloughs off at intervals with the corrosion products (e.g. mild steel, carbon steel) (b) passive metals and alloys which also get readily fouled but organisms remain tightly adhered to the metal surface (e.g. stainless steel, aluminium) and (c) toxic film-forming metals and alloys that are antifouling (e.g. copper, zinc) [1].

The exact role of marine organisms on corrosion of metals remains rather unclear. In fact, two schools-of-thought exist since promotion as well as inhibition of corrosion resulting from marine biological activities have been documented [2, 3]. Long time exposures of metals in the ocean indicate that marine organisms are generally protective against corrosion [4]. Of late, however, experience in the North Sea has shown fouling to be a menace giving rise to several potential hazards against the performance of offshore platforms [5].

Research investigations on biofouling and marine corrosion in Indian waters have been relatively few. Studies in Bombay harbour [6] and Cochin backwaters [7] have provided reasonable background to the problem. In order to understand the interrelation of marine fouling and corrosion more closely, a series of studies was conducted in the shallow, coastal waters of Mandapam, southeast coast of India.

MATERIALS AND METHODS

Mandapam is a tropical marine environment where the southwest and northeast monsoons influence the weather and the nature of fouling [8]. All studies reported in this communication were conducted in the Gulf of Mannar.

Commercially available sheets of mild steel (C=0.1%; Mn=0.46%; Si=0.074%; S=0.028%; P=0.07%; Fe=rest), stainless steel (type 316, Cr=18%; Ni=11%; Mo=2.5%; C=0.1%; Fe=rest) and aluminium (3004 alloy, Mn=1.05%; Mg=1.12%; Al=rest) were the materials chosen for the present investigation. The thickness of the materials were as follows: mild steel - 1mm for quarterly exposures and 2mm for exposures over 6 months; stainless steel and aluminium - 1.7mm each. The metal sheets were cut into test panels of size 150 × 100mm. They were acid-cleaned, polished and degreased as recommended[9], and fixed in conventionally designed wooden racks where metal-to-metal and metal-to-wood contacts were prevented using polyethylene insulators. The racks were immersed 1m below the mean low tide level. For data collection, samples were exposed or withdrawn in triplicate.

The tests were of three types: (1) natural immersion for corrosion evaluation (ii) corrosion tests in presence and absence of fouling and (iii) natural immersion for cathodic protection studies.

For tests in presence and absence of fouling, an apparatus of dimension 250 × 250 × 250mm was employed and specimens of size 100 × 75mm were held inside. For prevention of fouling, plankton filter approximating a pore size of 100 microns was used. A complete description of the apparatus has appeared elsewhere [10]. Cathodic protection was effected using zinc or magnesium anodes.

Corrosion rates were calculated from weight loss and surface area data. Fouling load was estimated after removal of marine growth from the panels and oven-drying the mass. Pit depths on stainless steel and aluminium were measured using a vertical-moving microscope in conjunction with a vernier scale unit. Where necessary, sulphate-reducing bacteria were detected or enumerated in a marine version of Baar's medium [11].

RESULTS AND DISCUSSION

Fouling - Corrosion

Seasonal variations in hydrological parameters and biofouling have appeared elsewhere [8]. Amongst the different fouling organisms, algae and barnacles were the two major groups which contributed to fouling and corrosion. Two distinct periods, viz. Feb - Apr. and

Nov - Jan were the seasons of prolific attachment of barnacles and algae respectively.

The relation between the rates of corrosion, organsim coverage and biofouling load can be seen from Fig. 1 for quarterly exposures. The general trend was an inverse relation between corrosion and fouling with the exception of the winter months. Hard growths of barnacles and serpulids seem to have provided considerable protection against corrosion. Thus, the lowest rates of quarterly corrosion values were associated with the heaviest settlement rates (approximately $3 \times 10^4.m^{-2}$) of *Balanus reticulatus* and *Balanus amphitrite*. The beneficial effects of barnacles agree with earlier results in the coastal waters of China [12]. Luxurious growths of algae caused a peak in corrosion during the winter months. The mechanism of corrosion acceleration by algae appears to be a combination of photosynthetically produced oxygen and bacterially produced H_2S which can yield highly corrosive elemental sulphur. There was another peak in corrosion, due entirely to the severe wave action, during the poorest fouling span of May - July. In fact, the quarterly rate of corrosion was higher than the monthly rates which amply speaks for the highly aggressive action of seawater.

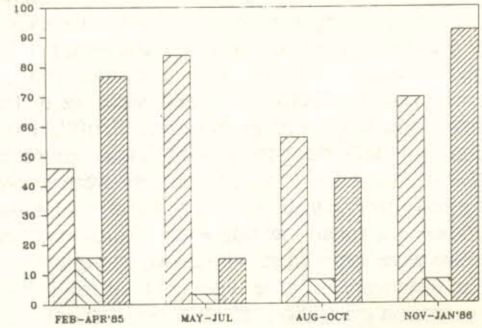

Fig. 1: Corrosion and biofouling relationship for mild steel during different quarterly periods
▨ *Corrosion* ▧ *Fouling load* ▨ *Fouling coverage*

Values of corrosion for cumulative exposure periods are presented in Fig. 2. Quite interesting is the effect of initial exposure condition on the annual rates of metal-loss. Specimens exposed during Feb.1985 reached an annual corrosion rate of 32 mdd whereas those exposed during May 1985, the most aggressive season, ended up in 41 mdd. The beneficial effects of barnacles are evident again. These corrosion values are considerably higher than those reported for other coasts [13].

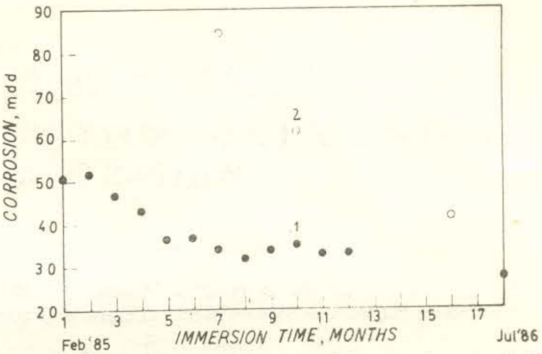

Fig. 2: Effect of initial exposure conditions on the cumulative corrosion behaviour of mild steel
● *February 1985 exposure*
○ *May 1985 exposure*

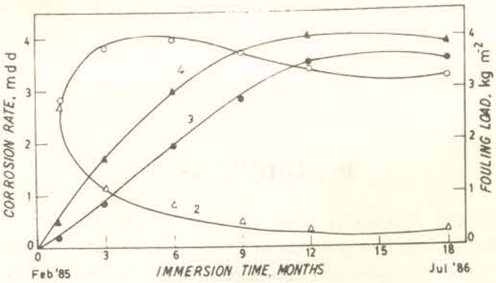

Fig. 3: Corrosion and biofouling of stainless steel and aluminium
○ *Corrosion - Stainless steel* △ *Corrosion - aluminium*
● *Biofouling - Stainless steel* ▲ *Biofouling - aluminium*

Whereas mild steel was subject to periodic slough-off of fouling, stainless steel and aluminium continued to build up appreciable load. Biofouling followed a similar pattern on the two alloys, although the intensity and coverage of marine growth was quicker and more on aluminium (Fig. 3). The potential effects due to biofouling were quite different for the two alloys. Stainless steel was severely attacked by way of pits and crevices while aluminium was not. The contrasting behaviour of the two metals can be observed from the corrosion rates during various stages of exposure (Fig. 3), data on pit density (Table I) and pit depth (Fig. 4). Values of average pit depth and percent area attacked increased with duration of exposure, but those of deepest pits were independent of immersion time after 6 months. Values of pit depth are in agreement with data from Kure beach [13]. Calculation of general corrosion rates (from weight loss) provided poor reflection on the actual performance of the alloy. Here, pitting was very specific because all pits had occurred beneath barnacles, irrespective of the organism's size and age. The mechanism of barnacle-induced crevice corrosion is discussed elsewhere [14]. Aluminium, on the other hand, was less susceptible to pitting, and, where pits occurred, did not provide obvious reasons to suspect barnacles as to their origin.

TABLE I: Data on pit density and percentage of pit surface to flat surface for stainless steel and aluminium in seawater

Months of exposure	Pit density ($No.dm^{-2}$)		Percentage of pit surface to flat surface	
	Stainless steel	Aluminium	Stainless steel	Aluminium
1	1	Nil	1.25	Nil
3	4.4	1	1.80	0.028
6	16.4	27.5	5.66	2.25
9	27.8	5.67	11.06	0.86
12	29.7	8.33	10.80	0.53

TABLE II: Corrosion rates of mild steel in presence and absence of macrofouling

Parameter Seasons	Salinity ($\times 10^{-3}$)	Dissolved oxygen ($mg.l^{-1}$)	Corrosion, mdd		Organism type
			Presence of macroorganisms	Absence of macroorganisms	
1986 November-December	28.5	5.5	78.2	70.7	Heavy algae
1987 January-February	31.2	5.4	52.7	69.3	Heavy barnacles

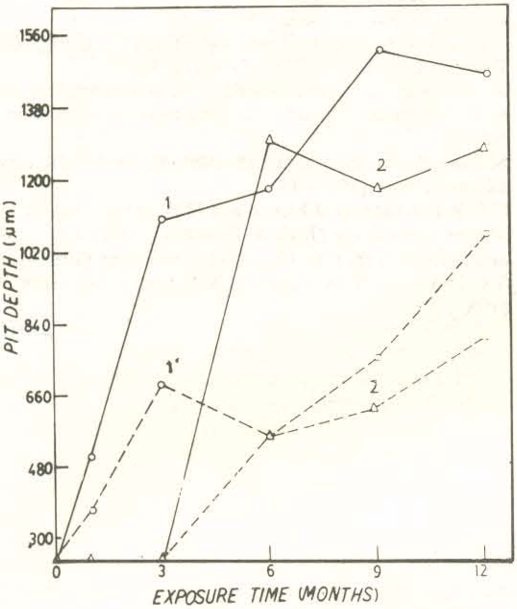

Fig. 4: Average and maximum pit depth on stainless steel and aluminium
o *Stainless steel* △ *Aluminium*
- - - *Average pit depth* —— *Maximum pit depth*

In order to confirm the potential effects of barnacles and algae, tests using the apparatus for prevention of fouling were conducted during the respective periods of their abundance. Results presented in Table II show that, in their relative behaviour, the inhibitive effects of barnacles overshadow the acceleration due to algae.

Fouling - Cathodic protection

Earlier studies in Mandapam [15] have indicated that cathodic protection (CP) accelerates biofouling. This was attributed to modification of substrate condition and interfacial alkalinity. Results presented in Fig. 5 indicate that the largest influence of CP on biofouling settlement was during extreme turbulence of seawater (May - July) when the wave velocity exceeded a value of 3 $m.sec^{-1}$ Whereas there was poor settlement on freely corroding steel, intense fouling gathered on protected substratum presumably as a result of surface roughening by calcareous deposition which aided in firm anchorage of organisms.

In order to understand the possible potential effects of marine growth on CP systems, a rapid, potential-decay study was carried out. Steel specimens, 100 × 75mm, were initially subjected to cathodic protection in seawater under laboratory conditions. After about a month's protection at about - 1V vs SCE, CP was terminated. The coupons were immediately transferred to natural seawater for tests in presence and absence of fouling (using the apparatus already mentioned in text).

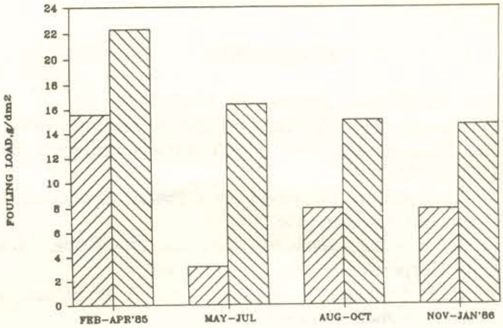

Fig. 5: Response to cathodic protection of biofouling on mild steel
▨ *Control* ▧ *Cathodically protected*

As seen in Table III, biofouling resulted in acceleration of the decay in potential. This, apparently, was due to the acidic conditions created beneath the fouling mat by the sulphate-reducing bacteria. These results are interesting and important from the point of view of the performance of offshore structures. On some North Sea platforms protected by CP systems, removal of marine growth has been reported to result in removal of base metal [16]. A recent experimental clarification of the LaQue theory of CP has implied that local anodes on protected steel can function independently if there were considerable roughening of the metal prior to installation and functioning of CP [17]. Present results indicate that such potential differences can be effectively exacerbated by fouling organisms.

TABLE III: Potential-decay, corrosion and sulphate-reducing bacteria in presence and absence of biofouling

Variable	Potential (mV vs SCE)	Weight loss* (mdd)	MPN, SRB (No. cm^{-2})
Presence of organisms	−770	17.1	3×10^4
Absence of organisms	−860	9.5	3.6×10^2

* Assuming no corrosion loss in the laboratory

CONCLUSIONS

Marine organisms, particularly barnacles, considerably inhibited the corrosion of steel. Algae, on the other hand, appeared to accelerate corrosion during seasons of prolific growth. Stainless steel was heavily attacked by barnacles, which resulted in severe pitting and crevice corrosion. Aluminum, which showed the tendency to foul maximum, received considerable protection from marine growth with few instances of localized attack. By manner of accelerated coverage and creation of anaerobiosis beneath their attachment, marine growth was found to affect the performance of cathodically protected steel significantly.

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