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BIOFOULING STUDIES RELATING TO CATHODIC PROTECTION OF SOME METALS IN SEAWATER

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ABSTRACT

Biofouling studies relating to cathodic protection of mildsteel, stainless steel and brass in sea water have been conducted in the shallow waters of Mandapam coast, to understand the role of biological factors operating. Rationale for the investigations were the response to cathodic protection of marine fouling, the occurrence and growth rate of calcareous deposits. Cathodic protection to the metals was effected using zinc. Results indicate that the severity of fouling on mildsteel and brass is increased and inhibition of fouling on stainless steel is obtained due to cathodic protection. Barnacles, the chief calcareous shell dwelling group were found to occur with selective abundance on cathodically protected mildsteel and brass panels, with a significant increase in their shell size. These organisms were found to contribute largely to the calcareous deposits on mildsteel and brass, and to a smaller extent on stainless steel. The selective abundance of barnacles on cathodically protected mildsteel and brass is discussed in the light of the chemical, biological and electrochemical bases for their gregariousness.

INTRODUCTION

Fouling of structural materials has long been recognised as a major hazard to the marine industry owing to high economic losses on it. Marine fouling is a natural cumulative phenomenon in which various species of organisms settle and grow over an exposed material, following an initial surface conditioning by micro-organisms. While the ill-effects of fouling on sea-going vessels are obvious, its exact role on the corrosion of metals has been little understood. Long-time exposures of metals in the marine environment [1] indicate the protective nature of fouling. Of late, however, its hindrance in cathodic protection systems [2] has become important and is the subject for concern in this paper.

It is well-known that cathodic protection in seawater results in the creation of an alkaline region at the metal/seawater interface. Deposition of salts from seawater usually occurs. The nature of these calcarious deposits (mainly $CaCO_3$ and $Mg(OH)_2$) and their protective effects have been extensively dealt with in the literature [3-5] Although several factors such as water velocity, depth, temperature and oxygen content have been shown to affect current density requirements for cathodic protection [5] conventional experiments have been conducted in the absence or negligence of biological factors. On a practical basis as in the natural seawater environment where biological factors also operate, conditions may be altered. For instance, it has been observed [4] that the current density required to polarize steel to a particular range reduces rapidly in natural seawater drawn afresh, while it remains constant in artificial seawater. This has been attributed to some factor in natural seawater. The role of marine bacteria in deposition of calcium is apparently evident. A more important factor is the presence of calcareous shell dwelling organisms. No data is available on the occurence of these organisms on cathodically protected structures and their contribution to the calcareous deposits.

Fouling has been reported to have resulted in heavy loading of North sea platforms interfering in the electrochemical measurements and inspection of structures [6] Again, little has been understood on the potential effects of fouling on corrosion. Consequently, data are required on the effect of cathodic protection on marine fouling and vice versa. Unfortunately, there have not been enough studies on these lines. It is believed that a pH value of 8.2 to 8.5 is most suitable for fouling and there is a progressive decline in attachment at pH values greater than 9 or 9.5 [7] Studies on the effect of cathodic polarization of metals on th initial stages of fouling in Cochin backwaters [8] have indicated that cathodic polarization has inhibitory effects on fouling. Their results have been discussed in the light of the pH factor. But tests in the Gulf floor [9] indicate the reverse. It is very much surprising to note that fouling increased with applied current density on mildsteel. No explanation has been offered in the discussion of their results.

In view of the two contrasting results it was decided to get reliable data from the shallow waters of Mandapam coast. Rationale for the present investigation include, the response to cathodic protection of marine fouling, the occurence of calcareous shell dwelling organisms on cathodically protected surfaces and their contribution to the calcareous deposits. It was an attempt for consideration of biological factors.

EXPERIMENTAL

(i) Exposure site and water characteristics : The location of the test site and surface water characteristics during the study period are given in Table I.

Table I : Location of the test site and surface water characteristics

Location of test site			Surface water characteristics		
Latitude N	Longitude E	Period	Temp (°C)	Salinity (ppt)	pH
9 deg 15 min	79 deg 5 min	Jul '84	31	36.12	8.2
		Aug '84	30.5	35.40	8.2
		Sep '84	30	35.28	8.2

(ii) Materials: The materials tested were the commercially available rolled sheets of mildsteel (0.1 % C; 0.46% Mn; 0.074% Si; 0.07% P, 0.028% S), stainless steel (type 316) and brass (32% Zn). The sheets were cut into 150 mm × 100 mm × 1mm size panels, pickled, ground with emery mob and buffed using cloth mob wheel with appropriate soaps. They were finally degreased prior to immersion.

(iii) Cathodic protection studies: The panels were mounted on wooden racks and exposed in the sea, 30 cm below the mean low-tide level. One set of each metal was kept as control while the other was cathodically polarized using zinc panels, galvanicallly coupled. Observations were recorded for m.s. and s.s. on the 10th, 30th and 72nd day of exposure and for brass, only on the 72nd day. Each time duplicate sets were withdrawn and the average of the two was assessed. Open circuit potentials (OCD) of control panels and the cathodicallly protected panels were measured after five days when the system attains a steady state using a multimeter against saturated calomel electrode (SCE) and the values are shown in Table II.

Table II : Open circuit potentials of control panels and the cathodically protected panels

Metal	OCP of control panel (V)	OCP of polarised panels (V)
Mildsteel	−0.65	−0.88
Stainless Steel	−0.30	−0.55
Brass	−0.25	−0.90

RESULTS AND DISCUSSION

(I) General observations on corrosion and fouling

(a) In the absence of cathodic protection, the order of corrosion and fouling for metals were as follows :

Corrosion:Mild steel > Stainless steel > Brass

Fouling:Stainless steel > Mild steel > Brass

(b) In the presence of the cathodic protection, the order of corrosion and fouling for metals were as follows :

Corrosion:Stainless steel > Mild steel > Brass

Fouling:Mild steel > Brass > Stainless steel

(II) The incidence of fouling and response to cathodic protection : The first observation made on the 10th day indicated the predominant growth of Entermorpha on all panels. Barnacles (all balanids), polychaete tube-worms and hydroiods were the other chief fouling organisms. In the latter two observations barnacles were found to contribute nearly 75% of the fouling community.

Table III : The quantum of fouling on panels, expressed as dry (weight in grams)

Metal	Exposure time					
	10 days		30 days		72 days	
	Control panel	Polarized panel	Control panel	Polarized panel	Control panel	Polarized panel
Mildsteel	1.39	1.75	5.02	6.21	15.33	25.06
Stainless Steel	1.30	1.11	6.24	2.89	17.30	9.23
Brass	—	—	—	—	No fouling	22.44

It can be observed from results presented in Table III that cathodic protection resulted in severity of fouling on mildsteel and brass, and in inhibition of fouling on stainless steel. One interesting feature was the greater abundance of barnacles on polarized mildsteel panels than on the control panels (Table IV). There was also significant difference in their average size by the 72nd day. Barnacles that occurred on cathodically protected mildsteel and brass panels had reached size nearly two-fold as those on all control panels. No such difference in size was observed for stainless steel which continued to exhibit antifouling property in case it was polarized.

Table IV : The number of barnacles settled on panels (Average size : 0.25 cm on 30th day and 0.5 cm on 72nd day on all control panels except brass; 0.9 cm on 72nd day on cathodically protected mildsteel and brass panels only)

Metal	Exposure time			
	30 days		72 days	
	Control panel	Polarized panel	Control panel	Polarized panel
Mildsteel	142	222	159	228
Stainless Steel	155	78	156	87
Brass	—	—	None	180

Brass remained completely free of fouling but cathodic protection resulted in intense settlement of organisms. It is obvious that for a toxic film-forming metal like brass cathodic protection would result in retarding the release of toxic ions and its antifouling property is thus lost. Our results for brass are in accordance with that for copper [10] A very large shift in potential for brass (polarized by 650 mV) accompanied by pH increase, seems to have had no inhibitory effects on fouling as indicated by our results. Although brass requires no cathodic protection it has helped us to understand that pH increase may not be a limiting factor. Previous results [7] on the pH factor in larval settlement carried out in bulk solution took into account the large buffering capacity of seawater to offset increasing alkalinity and also the limitations set forth by calcareous deposits. It is therefore a question if the pH values that inhibited larval settlement in laboratory studies could at all be created at the metal/natural seawater interface.

(III) Selective abundance of barnacles—explanation : We attribute the selective abundance of barnacles on cathodically protected mildsteel and brass to the following fact. The chemical basis for gregariouness in cirripedes [11] is said to be due to the influence of calcareous deposits of their own species. Thus barnacles can be attracted in large numbers to surfaces treated with calcium. It seems possible that barnacles are attracted by the calcareous deposits formed during cathodic protection. The utilization of these deposits for their sheel formation probably results in an increase in shell size. On this basis the results of tests from the Gulf floor [9] can also be explained as due to the influence of calcareous deposits since they are a linear function of applied current density. However, the antifouling behaviour of cathodically polarized stainless steel requires proper explanation. It could be due to release of chromium ions through the porous calcareous deposits. The nature of the calcareous deposits on stainless steel could also be different from that on mildsteel or brass. Experiments are being carried out to study this behaviour of stainless steel in detail.

Table V : A comparison of the amount of calcareous deposits formed and calcium content deposited in biomass on cathodic surfaces (wt. in grams)

Metals	Exposure time					
	10 days		30 days		72 days	
	(a)	(b)	(a)	(b)	(a)	(b)
Mildsteel	1.07	0.16	2.45	3.87	2.89	13.22
Stainless Steel	1.13	0.15	1.30	0.49	2.64	1.53
Brass	—	—	—	—	1.84	8.18

a) Calcareous deposits b) Calcium content in biomass

(IV) Calcareous deposits and calcareous shell dwelling organisms : Results presented in Table V indicate that barbacles contribute largely to the calcareous deposits on mildsteel and brass, and to some extent on stainless steel. In fact, for mildsteel and brass, the calcium content present in biomass exceeds the amount of calcareous deposits by many times. Thus the gross amount and thickness of deposits are considerably increased. Whether the growth of these organism affects the quality of the calcareous scale remains to be studied.

The utilization of calcareous deposits by selective groups of organisms and their contribution in turn thus lead to the conclusion that future work should take into account biological factors also. It is thus understood that conventional experiments carried out in the laboratory do not reveal the conditions actually operating in the natural seawater environment. Extensive work has been taken up in Mandapam coast on these lines.

CONCLUSION

i) Cathodic protection results in severity of fouling on mildsteel and brass, and in inhibition of fouling on stainless steel

ii) The calcareous deposits formed during cathodic protection of mildsteel and brass seem to offer excellent growth conditions for calcareous shell forming organisms like the barnacles.

iii) Barbacles contribute largely to the calcareous deposits on mildsteel and brass, and to a smaller extent on stainless steel, considerably increasing the gross amount and thickness of the calcareous scale in all cases.

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