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THE INFLUENCE OF BIOSPECIES ON THE CORROSION OF ZINC IN PALK BAY WATERS

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Influence of macrofouling organisms on the corrosion behaviour of zinc has been studied for a year in Palk Bay waters. Algae, bryozoans and polychaete worms were the dominant species on zinc panels throughout the year. The surface coverage was 100% after one year exposure where dense mat of algae was observed. It indicated that toxicity of zinc on algae was least in Palk Bay Waters. The reason is discussed with product analysis by XRD. The weight loss data indicated that zinc had an annual corrosion rate of 6 mdd and biofouling rate of 0.38 Kg.m^{-2} year^{-1}. The relationship between biofouling and corrosion is discussed with biological and chemical characteristics of Palk Bay.

Keywords: Macrofouling, corrosion rate, product analysis, biofouling load.

INTRODUCTION

The excellent resistance of zinc to corrosion under natural conditions is largely responsible for the many and varied applications of the metal. Zinc in seawater has its contribution as a sacrificial anode [1] and in the development of electrochemical antifouling systems [2]. Long term exposures of metals in the ocean indicate that marine organisms are generally protective against corrosion [3]. However experience in the offshore has revealed several problems arising from marine growth. Settlement of the foulants on a metal surface is influenced by factors like release of toxin from the metal (leaching), formation of corrosion deposits and surface roughness [4]. Red field 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 [5]. An excellent account of macro organisms in seawater and their effects on corrosion of metals are given [6].

In this paper, the influence of macrofouling organisms and their impact on the corrosion of zinc in Palk Bay waters at Mandapam is briefly discussed.

EXPERIMENTAL

Commercially available 1 mm thickness sheets of zinc (0.2% Pb, 0.045% Cd, 0.01% Fe) were cut into test panels of size 150 mm x 50 mm. They were then pickled, polished using emery wheels, degreased and weighed to an accuracy of 10^{-4} g. The panels were fixed in conventionally designed wooden racks where metal to metal and metal to wood contacts were prevented using polyethylene insulators. The racks were immersed 0.5 m below the mean low tide level in the Palk Bay of Mandapam (Longitude: 79°8' East, Latitude: 9°17' North). For data collection, samples were exposed or withdrawn in duplicate. Exposure tests were of monthly, quarterly, halfyearly, nine months and yearly. After retrieval, the panels were examined for the presence of fouling organisms.

The open circuit potentials of the zinc exposure wise were periodically monitored with respect to saturated calomel electrode using high impedance digital multimeter. During the study period of an year (July '93 - June '94) the monthly, quarterly and half yearly removals were subsequently followed by exposure of panels to cover the reset of the exposures in the respective cycle. In addition, data on the environmental parameters

such as temperature, salinity, *p*H, wave velocity and dissolved oxygen were also recorded.

Corrosion rates were calculated from weight loss data. Biomass was calculated after scrapping the mass adhered on the metal surface and drying in the air oven for an hour at 333 K. The corrosion products were analyzed with X-ray diffractometer (JEOL JDX 8030).

RESULTS AND DISCUSSION

Table I summarizes the maximum and minimum values of salinity, dissolved oxygen, *p*H and temperature recorded during the study period.

Settlement of algae species of green and red were recorded in the monthly exposure panels. Species of bryozoa were seldom recruited over the zinc specimens (October '93). Settlement of fouling organisms comprising of algae (red, green) bryozoa, polychaete worms, barnacles, molluscs were recorded round the year in the cumulative exposure of zinc panels I, II, III & IV quarterly, half yearly, 9 months and yearly. Bryozoans were recorded during I quarterly and III quarterly panels. Settlement of molluscs were recorded during 9 months, yearly exposure panels. Settlement of barnacles were recorded 1 or 2 per panel in IV quarterly and yearly panels respectively. Settlement of organisms were influenced by the surface temperature of the water, salinity, tidal waves and water currents. Sunlight plays a major role in influencing the settlement of larvae in the shallow waters of Mandapam.

Hypnea, Padeina, Lyngbya majescula (blue green algae) and Enteromorpha intestinalis (green algae) were also recorded in yearly exposure panels, in a biomass of 0.38 $Kg.m^{-2}$.

Fig. 1 portrays the monthly corrosion rate of zinc in Mandapam Palk Bay waters. The corrosion rate is uniform throughout the study period, except 2 months in December 93 and January 94. The higher values in December '93 and January '94 could be attributed due to the action of wave velocity [7].

Fig. 2 shows the cumulative exposures of (quarterly, half yearly, 9 months and yearly) zinc panels in Mandapam Palk Bay waters. The exponential decrease in the corrosion rate values of cumulative exposures are indicative of the protective nature of corrosion products such as zinc oxide, zinc chloride and zinc carbonate formed along with marine growth accumulations. As duration extends the toxic effect of zinc reduces, thereby enhancing the bioadherence more on to the metal surface.

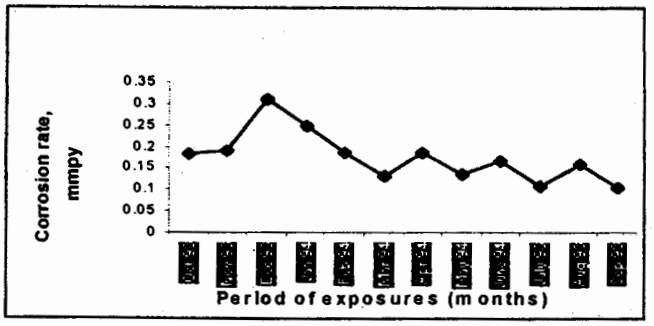

Fig. 1: Monthly corrosion rate of zinc in natural seawater

TABLE I: Seawater characteristics during the study period (July 1993 to June 1994)

Wave velocity (m/sec)	Salinity (x 10^{-3})*	Dissolved oxygen (ml/l)	*p*H	Temp K
Max 1.5	35.6	6.5	8.3	304.6
(Dec '93)	(Sep '93)	(Apr '94)	(Jul '93)	(Sep '93)
Min 0.9	26.5	2.98	8.0	299.8
(May '94)	(Dec '93)	(Jun '94)	(Nov '93)	(Dec '93)

Key to the table: * = Parts per thousand

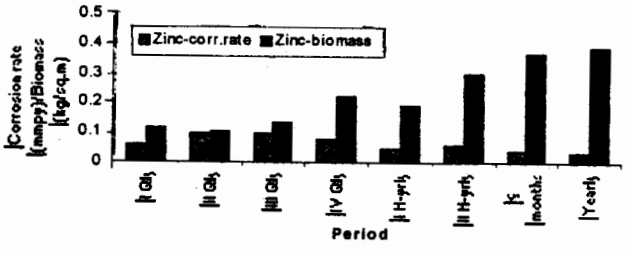

Fig. 2: Corrosion rate and biomass of cumulative exposure of zinc in natural seawater

TABLE II: XRD data on corrosion products of zinc in natural seawater

Periods	Presence of inorganic compounds
Monthly	$ZnCl_2$
3 months	ZnO
6 months	ZnO, $Zn(OH)_2$
12 months	$4ZnO.CO_2.4H_2O$

In seawater, the corrosion rate of sheet zinc is normally between 0.0256 mmpy and 0.051298 mmpy for exposures spanning 2 to 3 years [8] and the usual impurities in rolled or cast zinc have no significant effect on normal corrosion by seawater [9] of Pacific Ocean. Earlier studies in Gulf of Mannar have shown that corrosion rate of zinc is 0.0558 mmpy [10]. It is evident that the rate of zinc in Mandapam Palk Bay water is comparatively lesser than that of Gulf of Mannar site.

The corrosion product was analyzed using XRD and the results are presented in Table II. Initially the corrosion product was zinc oxide, but in later periods of exposure, it was converted into zinc hydroxide and basic zinc carbonate.

Studies on the effects of zinc and *p*H on larval attachment under laboratory conditions [11] have indicated the existence of a complex antagonistic relationship between zinc toxicity and *p*H. The antagonistic effect diminishes as *p*H approaches that of normal seawater, and the inhibitory effects of zinc dissolution are observed. Since the leaching rate of zinc was insufficient, the growth of biospecies remains unaffected.

The fouling tendency over zinc is of importance in cathodic protection system. One particular instance reported from the North sea experience was that some zinc anodes were completely fouled and had been passivated, while some others just a few meters apart, were free of fouling and functioning properly [12]. There appears to be a general agreement among corrosion engineers that the marine growth may interfere on the performance of an anode. The overall results of the study indicate that the fouling free zinc anodes are to be developed.

CONCLUSIONS

- The rate of corrosion of zinc in Palk Bay waters is about 0.0306 mmpy after a year's exposure.
- Fouling depends on the duration of exposure period and the rate is 0.38 $Kg.m^{-2}$ $year^{-1}$.
- The exponential decrease in the corrosion rate values of cumulative exposures is indicative of the protective nature of corrosion products formed, as well as the larger accumulations of marine growth on the metal surface.

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