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Corrosion and Biofouling Characteristics of Mild Steel in Mandapam Waters

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The corrosion and biofouling characteristics of mild steel were investigated in the waters of the Mandapam coast of India over a year's time. Field exposure and laboratory studies were conducted. Corrosion rates were measured by gravimetric and Tafel polarization. Algae and barnacles were the dominant fouling species. Corrosion products were analyzed by x-ray diffraction and surface analysis by scanning electron microscopy. The effect of micro- and macrofouling on the corrosion rate was investigated. The annual corrosion rate of mild steel was 0.152 mmpy with a fouling load of 0.89 kg/m².

> aterials submerged in the ocean undergo physical, chemical, and biological surface changes. Marine fouling organisms adhere to structures in the

ocean, and this can affect corrosion.¹⁻² A

detailed account of the different fouling organisms and their effects on corrosion appeared in 1948.³ Since then, a number of workers have contributed to this topic, with reference to shallow water,⁴⁻⁵ offshore,⁶⁻⁷ deep ocean,⁸⁻⁹ shipping,¹⁰ and estuarine environments.¹¹ Acceleration and long-term inhibition of corrosion by marine organisms have been demonstrated.⁴ Data also indicate the protective nature of fouling organisms.⁵ This article describes the effect of fouling on the corrosion rate of steel in Mandapam waters. S

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Experimental Procedures EXPOSURE SITE

The exposure site was in Palk Bay on the Mandapam Coast. The climate there is influenced by the southwest and northeast monsoons during April through August and November through February, respectively.

METHODS AND MATERIALS

Commercially available 2-mm-thick sheets of mild steel specimens, 150 mm by 50 mm (composition C-0.1%, Mn-0.46%, Si-0.074%, P-0.07%, S-0.028%, Fe balance), were used in this study. Table 1 shows the seawater characteristics.

FIELD EXPOSURE

The specimens were cleaned and polished and had holes drilled on the top and bottom. They were secured to conventional wooden racks, using brass bolts and nuts, isolated from the steel with polyethylene washers. The racks were tied to stationary piles ~0.5 m below mean low tide so that the test specimens were totally immersed. The exposure tests were evaluated monthly, quarterly, semi-annually, at nine months, and annually. The panels were also examined for the presence of fouling organisms. The open circuit potential (OCP) of steel was periodically monitored vs a saturated calomel electrode (SCE) using a digital multimeter.

LABORATORY STUDIES

Mild steel coupons 5 cm by 2 cm were polished and weighed to an accuracy of fouling rrosion number to this varer,⁴⁻⁵ g,¹⁰ and eration sion by lemonotective sarticle on the dapam

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TABLE 1 SEAWATER CHARACTERISTICS OF PALK BAY AT MANDAPAM COAST (OCTOBER 1996 TO SEPTEMBER 1997)

Surface temperature (°C) Salinity (ppt) Dissolved oxygen (mL/L)	31.2 35.0	26.4 25.6	28.8
Salinity (ppt) Dissolved oxygen (mL/L)	35.0	25.6	20.2
Dissolved oxygen (mL/L)		= 219	
District Cargell (IIID/D)	5.0	2.8	4.2
Calcium (mg/L)	332	329	331
Magnesium (mg/L)	1,173	. 1,158	1,166
Carbonate (mg/L)	20.5	15.4	18.0
Bicarbonate (mg/L)	115	105	110
Sulfate (mg/L)	2,165	2,153	259
pH	8.3	8.1	8.2
	Calcium (mg/L) Magnesium (mg/L) Carbonate (mg/L) Bicarbonate (mg/L) Sulfate (mg/L) pH	Calcium (mg/L) 332 Magnesium (mg/L) 1,173 Carbonate (mg/L) 20.5 Bicarbonate (mg/L) 115 Sulfate (mg/L) 2,165 pH 8.3	Calcium (mg/L) 332 329 Magnesium (mg/L) 1,173 . Carbonate (mg/L) 20.5 15.4 Bicarbonate (mg/L) 115 105 Sulfate (mg/L) 2,165 2,153 pH 8.3 8.1

FIGURE 1



(a) (b) Corrosion of mild steel in natural seawater (a) after 6 months of exposure and (b) after 12 months of exposure.

10⁻⁴ g. For marine fouling experiments, duplicate coupons of mild steel were immersed in natural seawater for regular intervals of seven days and 30 days. Simultaneously, another set of specimens was immersed in sterilized seawater. For macro-fouling experiments, duplicate coupons were exposed in natural seawater for regular intervals of three months and six months. Another set was simultaneously immersed in sterilized seawater. The natural seawater that was used for micro-fouling experiments at the laboratory was renewed with fresh seawater once every 48 h.

Direct current (DC) polarization was done in a three-electrode cell consisting of working electrode, platinum auxiliary electrode, and SCE using the Solartron 1280B Electrochemistry System^{*}.

Results and Discussion FIELD EXPOSURE

Fouling Production and Community Development Pattern

The general fouling organisms along the Mandapam coast are algae, bryozoans, barnacles, and oysters. During the exposure period, fouling was mainly from algae

°Γrade name.

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and barnacles. Algae were seldom found on monthly exposure panels, but a dense mat of fouling organisms made up of algae and barnacles occurred with cumulative exposure of mild steel surfaces.

Figure 1 shows the typical appearance of the mild steel panels after (a) six months of exposure and (b) after 12 months of exposure.

Corrosion Behavior of Mild Steel

Figure 2 shows monthly corrosion rates, which ranged from 0.16 to 0.43 mmpy during the study period. The high rates between December 1996 and Janu-

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ary 1997 are attributed to the turbulent wave actions prevailing at the site. There was another corrosion rate peak during the poorest fouling span, between May 1997 and July 1997, because of moderate dissolved oxygen levels and high salinity of the water. Sloughing off of corrosion products along with fouling attachments is a common feature.¹²⁻¹³

Cumulative Exposure

Figure 3 shows the cumulative exposure corrosion rate. The steady decline in the corrosion rate implies the protective nature of corrosion products and biomass during exposure. The adherence of organisms creates dense coverage over the substrate and reduces the diffusion of oxygen, thus reducing corrosion rate. Instances of uneven corrosion of steel beneath shell dwellings have been reported.¹⁴ The decrease in the cumulative exposure corrosion rate is attributed to the biofouling acting as a barrier between the metal and the seawater, thereby reducing the oxygen diffusion to the metal surface.¹⁵

The corrosion product was analyzed by x-ray diffraction. Initially, the product was iron oxyhydroxide and iron chloride (FeCl₃) but in the latter periods, the product was found to be predominantly stable oxides of iron such as ferric oxide (Fe₂O₃), Fe₃O₄, and carbonates.

The surface appearance of mild steel after exposure to natural seawater was analyzed by scanning electron microscopy (SEM) (Figure 4.) Corrosion starts on grain boundaries and leads to general corrosion. The metal experiences uniform corrosion in the exposure periods of quarterly, semi-annually, and annually.

LABORATORY STUDIES Effect of Micro-Fouling on Corrosion of Mild Steel

The corrosion rates obtained by gravimetric tests indicate that the corrosion rate is higher in natural seawater immersion than in sterilized seawater. This could be caused by microbial action that influences differential aeration between covered and uncovered areas.

Effect of Macro-Fouling on Corrosion of Mild Steel

Corrosion rates obtained by gravimetric tests indicate that higher corrosion rates occurred in natural seawater than in sterilized seawater. This is attributed to the photosynthetic activity of algae during daylight. The corrosion rate decreases with time because of the coverage of fouling organisms.

Table 2 summarizes the corrosion rates obtained by polarization tests. Again, the corrosion rates are higher in natural seawater than in sterilized seawater.

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FIGURE 4

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after three months of exposure was 130 mA·cm⁻². This may be because of depolarization effects from porous corrosion product layers on the steel surfaces. With time, the corrosion rate in natural seawater was cut in half, but the rate in sterilized seawater exposure did not change significantly.

Discussion

When comparing the corrosion rate and biological activity of different waters in the world, including Indian waters, Mandapam is first in corrosivity (0.244 mmpy) and third in biofouling.¹⁶ Earlier studies in Mandapam have indicated an annual corrosion loss of 0.148 mmpy in tests in the nearby Gulf of Mannar and a corrosion loss of 0.204 mmpy in Palk Bay waters in 1986.17

In the laboratory studies, the effect of micro- and macro-fouling on the corrosion behavior of mild steel in seawater was determined by comparing the corrosion rates obtained in natural seawater and sterilized seawater. Gravimetric tests indicated that the effect of micro-fouling on corrosion is negligible, while macro-fouling increases corrosion by two to four times. However, DC polarization studies have revealed that micro-fouling enhances the corrosion rate with time, whereas with macro-fouling, the corrosion rate of mild steel decreases with time.

Conclusions

Algae species were seldom encountered on monthly exposure panels. A dense mat of fouling organisms composed of algae



(h)

SEM photographs on mild steel after (a) 6 months and (b) 12 months of exposure in natural seawater (original magnification 200X)

loss of mild steel in Palk Bay water is 0.152 mmpy with a fouling load of 0.89 kg/m^{-2} .

Gravimetric tests indicated that the efand barnacles occurred in cumulative fect of micro-fouling on the corrosion rate

exposure, however. The annual corrosion is not significant. Macro-fouling enhances the corrosion rate by two to four times in natural seawater. Polarization studies revealed that the effect of micro-fouling on the corrosion rate of mild steel is significant and the rate increases with time.

CORROSION RATE VALUES FOR MILD STEEL BY POLARIZATION METHOD (MACRO-FOULING)

Medium	SI.	Duration	Er	i₀₀r	b	b	Corrosion
	No.	(Months)	mV	(µA∙cm⁻²)	(mV/dec)	(mV/dec)	Rate (mmpy)
NSW	1 2	3 6	-688 -792	130 70	112 64	138 62	1.4780 0.7958
SSW	1	3	-740	35	74	140	0.3979
	2	6	-790	40	58	78	0.4547

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