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.

Materials 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. A detailed account of the different fouling organisms and their effects on corrosion appeared in 1948. Since then, a number of workers have contributed to this topic, with reference to shallow water, offshore, deep ocean, shipping, and estuarine environments. Acceleration and long-term inhibition of corrosion by marine organisms have been demonstrated. Data also indicate the protective nature of fouling organisms. This article describes the effect of fouling on the corrosion rate of steel in Mandapam waters.

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

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.

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

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Characteristics</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surface temperature (°C)</td>
<td>31.2</td>
<td>26.1</td>
<td>29.8</td>
</tr>
<tr>
<td>2</td>
<td>Salinity (ppt)</td>
<td>35.0</td>
<td>25.6</td>
<td>30.3</td>
</tr>
<tr>
<td>3</td>
<td>Dissolved oxygen (mL/L)</td>
<td>3.0</td>
<td>1.8</td>
<td>2.2</td>
</tr>
<tr>
<td>4</td>
<td>Calcium (mg/L)</td>
<td>332</td>
<td>329</td>
<td>331</td>
</tr>
<tr>
<td>5</td>
<td>Magnesium (mg/L)</td>
<td>1.175</td>
<td>1.158</td>
<td>1.166</td>
</tr>
<tr>
<td>6</td>
<td>Carbonate (mg/L)</td>
<td>15.5</td>
<td>15.4</td>
<td>15.5</td>
</tr>
<tr>
<td>7</td>
<td>Calcium (mg/L)</td>
<td>157</td>
<td>105</td>
<td>131</td>
</tr>
<tr>
<td>8</td>
<td>Sulphate (mg/L)</td>
<td>8.2</td>
<td>6.1</td>
<td>7.1</td>
</tr>
<tr>
<td>9</td>
<td>pH</td>
<td>4.5</td>
<td>4.1</td>
<td>4.2</td>
</tr>
</tbody>
</table>
Corrosion rate and biomass of cumulative exposure of mild steel in natural seawater.

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 January 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.

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 the corrosion rate. Instances of uneven corrosion of steel beneath shell dwellings have been reported. 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. The corrosion product was analyzed by X-ray diffraction. Initially, the product was iron oxyhydroxide and iron chloride (FeCl₂) 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). 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 Macro-Fouling on Corrosion of Mild Steel

The corrosion rates obtained by gravimetric test 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. In exposure testing, the effects of fouling on the corrosion rate are seen to decrease with time. The figures in Table 2 have been compiled from the mean of two repeats. Corrosion of Mild Steel

Corrosion rates obtained by gravimetric test indicate that higher corrosion rates occur 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. The influence of the steel in natural seawater is also apparent in the deposition of corrosion products on the surface. With exposure to natural seawater, the corrosion rate decreases with time due to the formation of protective film ascribed to biofouling. The corrosion product was analyzed by X-ray diffraction. Initially, the product was iron oxyhydroxide and iron chloride (FeCl₂) 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). 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.
The presence of organisms on the surface of mild steel in seawater may affect the corrosion rate. The depolarization effect from porous corrosion product layers on the steel surfaces is significant. 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. 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.

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 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 and barnacles occurred in cumulative exposure, however. The annual corrosion loss of mild steel in Palk Bay water is 0.152 mmpy with a fouling load of 0.89 kg/m².

Gravimetric tests indicated that the effect of micro-fouling on the corrosion rate 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)**

<table>
<thead>
<tr>
<th>Medium</th>
<th>Sl. No.</th>
<th>Duration (Months)</th>
<th>Ecorr (mV)</th>
<th>icorr (μA·cm⁻²)</th>
<th>b⊥ (mV/dec)</th>
<th>b∥ (mV/dec)</th>
<th>Corrosion Rate (mmpy)</th>
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</thead>
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<tr>
<td>NSW</td>
<td>1</td>
<td>3</td>
<td>-688</td>
<td>130</td>
<td>112</td>
<td>138</td>
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<td></td>
<td>2</td>
<td>6</td>
<td>-792</td>
<td>70</td>
<td>64</td>
<td>62</td>
<td>0.7958</td>
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<tr>
<td>SSW</td>
<td>1</td>
<td>3</td>
<td>-740</td>
<td>35</td>
<td>74</td>
<td>140</td>
<td>0.3979</td>
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<tr>
<td></td>
<td>2</td>
<td>6</td>
<td>-790</td>
<td>40</td>
<td>58</td>
<td>78</td>
<td>0.4547</td>
</tr>
</tbody>
</table>

SEM photographs on mild steel after (a) 6 months and (b) 12 months of exposure in natural seawater (original magnification 200X).
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G. VENKATACHARI has worked in the fields of corrosion inhibitors, corrosion monitoring, and protective coatings for the past 35 years and has published approximately 100 papers.