le Jon & Design

Corrosion and Biofouling Characteristics of Mild Steel in Mandapam Waters

S. PALRAJ AND G. VENKATACHARI, Central Electrochemical Research Institute, India

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

(a)

Car

10-

dup

ma

int€

mu

Wak

mag

GQU

for

Six

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

Bay on te there I northhrough bruary,

US

n-thick 50 mm %, Mn-.028%, %.Table cs.

nd polop and ouvenfts and olyethtied to an low totally evalually, at panels ence of uit podically elecneter.

mwere racy of

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

SI. No.	Characteristics	Maximum	Minimum	Average
1	Surface temperature (°C)	31.2	26.4	28.8
2	Salinity (ppt)	35.0	25.6	30.3
3	Dissolved oxygen (mL/L)	5.0	2.8	4.2
4	Calcium (mg/L)	332	329	331
5	Magnesium (mg/L)	1,173	. 1,158	1,166
6	Carbonate (mg/L)	20.5	15.4	18.0
7	Bicarbonate (mg/L)	115	105	110
8	Sulfate (mg/L)	2,165	2,153	259
9	pH	8.3	8.1	8.2

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. Sinultaneously, 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.

June 2006 MATERIALS PERFORMANCE 47





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-

48 MATERIALS PERFORMANCE June 2006

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.

The icorr of the steel in natural seawater

after mA depo sion Witt seaw ster char

Dis

and in th Man stud annu tests corre wate Ir

micr sion deter rates steril cated correc ing i time have the c macr steel

Con A

on n of fc and

TA

CI

(1)

Me

NS

SST

FIGURE 4

e of organer the subof oxygen, stances of eath shell 14 The deure corrobiofouling metal and he oxygen nalyzed by

oduct was chloride the prodntly stable $e(Fe_2O_3),$

mild steel vater was icroscopy starts on neral coruniform s of quarlly.

ES

by gravicorrosion r immerhis could hat influeen cov-

travimettorrosion in than in buted to reduring lecreases e of foul-

ion rates gain, the ural sea-

seawater

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	ir	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

June 2006 MATERIALS PERFORMANCE 49

References

K.D. Efrd, MP 15, 4 (1976): pp. 16-25.
 K.G. Compton, Corrosion 26, 10 (1970): pp. 448-449.

3. W.E. Clapp, Corrosion Handbook, 11.11. Uhlig, ed. (New York, NY: John Wiley and Sons, Inc., 1948), pp. 433-36.

 LaQue, EC, Proc. 3rd Intl. Congress on Marine Corrosion and Fouling Gaithersburg, U.S. (1972), pp. 2-7.

5. C.R. Southwell, J.D. Bultman, C.W. Hammer, Bio-Corrosion of Structural Steels in Seawater (1974), Naval Research Laboratory, Washington, Report 7672.

 D. Kirkwood, Conference on Marine Fouling of Offshore Structures (1981), Vol. 11, Society of Underwater Technology, London.

 R.G.J. Edyvean, L.A. Terry, G.B. Pickon, International Biodeterio. Bull. 21, 3 (1985): pp. 105-109.

8. J.S. DiGuegorig, J.P. Fraser, Corrosion in Natural Environments, ASTM-STP-554 (1974), pp. 185-208.

9. B.L. Moss, Proc. 3rd Ind. Cong., Marine Corrosion and Fouling, Gairhersburg, U.S. (1972): pp. 37-49.

10. G.H. Booth, A.W. Cooper, and Foul., France (1976): pp. 445-55.

11. Annual Book of ASTM Standards, Part 10 (West Consliohocken, PA: **AST**M, 1980), pp. 781-786. E.M. Reinhart, Corrosion of Materials in Hydropace Part-I, "Iron, Steels, Cast Irons and Steel Products," U.S. Naval Civil Engineering Lab., Technical Note, N=900 ((Port Hueneme, CA: July 1967).

13. C.P. Larrabeg, MP 1, 12 (1967): p. 95.

14. L. Ruinu, L. Dekai, H. Xuebac, Z. Jiancheng, Proc. 6th Intl. Congress on Marine Corrosion and Foul., Athens, Greece (1984): p. 211.

 K. Ravichandran, A.G. Gopalakrishna Pillai, Proc. 6th Intl. Congress on Marine Corrosion and Foul (Athens, Greece: 1984), p. 370.

16. C.P. De, Proc. of Seminar on Metallurgy in Ocean Technology, Bombay 2.1 (1982).

 M. Eshwar, G. Subramanian, P. Chandrasekaran, S.V.K. Iyer, Proc. 10th Intl. Congress on Metal. Corrosion, Madras 4 (1987): p. 3,271.

S. PALRAJ is a scientist at the Central Electrochemical Research Institute, Corrosion Science and Engineering Division, Karaikudi, 63006, Tamilnadu, India. He received his Ph.D. in 2000 on the corrosion behavior of metals in marine environments. He has worked in the fields of atmospheric and seawater corrosion, conversion and protective coatings, and the preparation of nanoparticles for the past 25 years. He has published approximately 60 papers. 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.

Need reprints of *MP* ads, articles, or covers?

REPRINTS ARE A GREAT INVESTMENT!

Professionally printed reprints and photocopied reprints of all *MP* ads, articles, and covers are available for purchase. Reprints can be customized with your company's logo, additional product information, or the magazine cover—with no limits on creativity!



Denso Protective Coatings

The Single-Source Solution for Pipeline Coatings.

- Protal Liquid Coatings Protal 7000, Protal 7200, Protal 7125, and Protal Repair Cartridges
- Denso Petrolatum Tapes Densyl Tape, Denso LT Tape, Denso ColorTape, and Denso Hotline Tape
- Denso Bitumen & Butyl Tapes
- SeaShield Marine Systems



Denso Petrolatum Tape The original petrolatum tape since 1929 that can be applied to minimally prepared surfaces.



Denso Protal 7200 100% solids epoxy that can be backfilled in one hour @ 80°F. Excellent cathodic disbondment results of 4 mm @ 150°F and can be brush, roller or spray applied.



SeaShield Series 2000 HD Heavy duty pile protection system that can be easily applied with low material and installation cost.



New! Denso Product Training Videos For a free DVD, please call 1-888-821-2300



DENSO NORTH AMERICA INC.

HOUSTON: TORONTO:

18211 Chisholm Trail, Houston, Texas, U.S.A. 77060 Tel: 281-821-3355 Fax: 281-821-0304 90 Ironside Crescent. Unit 12, Toronto, Ontario, Canada M1X1M3 Tel: 416-291-3435 Fax: 416-291-0898

www.densona.com

A Member of Winn & Coales International

50 MATERIALS PERFORMANCE June 2006