

**MARINE MICROBIAL FILMS AND THE CORROSION OF STEEL**

M. EASHWAR, P. CHANDRASEKARAN and G. SUBRAMANIAN

Corrosion Testing Station, CECRI Unit, Mandapam Camp-623 519, INDIA

[Received:1987 February; Accepted:1987 December]

Succession of aerobic and anaerobic bacterial films on mild steel has been studied for 100 days in two contrasting seawater sites at Mandapam. The relation between primary film microfouling and initiation of anaerobic corrosion has been attempted. The ecological aspects in anaerobic corrosion beneath marine fouling are discussed in the light of the results of present work and already available data on marine corrosion.

**Key words:** Mild steel, sea water, sulphate reducing bacteria, corrosion

**INTRODUCTION**

Microbial corrosion has received such a wide recognition that there are, at present, at least three theories to explain the phenomenon. The classical theory or the cathodic depolarization theory of bacterial corrosion was postulated as early as 1934 [1]. It states that bacteria, particularly the sulphate-reducers, utilize hydrogen atom from the metal surface for their metabolic activity thereby depolarizing the cathode. Since then, a number of research papers have appeared either in support of the theory [2, 3] or questioning its validity [4,5]. In 1973, the Fe/FeS galvanic cell theory was put forth [6]. Accordingly, FeS formed as an end product of bacterial activity acts cathodic to the iron surface thereby allowing the metal to go into solution. Of late, the situation has further been complicated by the emergence of the corrosive metabolite theory [7] where evidence has been presented that sulphate-reducing bacteria (SRB) produce extracellularly, under anaerobic conditions, a highly corrosive product in addition to hydrogen sulphide. This has provided enough explanation on the conflicting observations on corrosion noted in the field and laboratory.

Contributions to literature on bacterial corrosion, in general, have primarily come from underground or nonmarine instances. Records on participation of marine bacteria in corrosion processes have been relatively few despite the fact that most marine bacteria lead an attached mode of living which makes them metabolically more active [8]. In fact, bacteria are the first organisms to colonize an immersed material by one or more mechanisms [9-11]. Therefore, the intimate contact of marine bacteria with metal surface is of consequence in corrosion phenomena.

The rate and density of bacterial fouling on metals depend on the placement of the latter in the galvanic series [12]. Zinc, aluminium and steel are thus placed in perfect order, the tendency for film formation being maximum for zinc. Cathodic polarization of mild steel, therefore accelerates microfouling, since the rate of slime formation is influenced by electronegativity of the metal [13].

Whereas the mechanisms and ecological events in marine microbial fouling have been well known [14, 15], the association of this event with metal corrosion is poorly understood. Bacterial

colonies of the genera *Lepothrix* and *Bacillus* have been observed to produce volcano-like structures on aluminium and accelerate the electrochemical process of metal corrosion [16]. An investigation on the role of putrifying bacteria revealed that corrosion of steel was due to differential aeration and decreases in pH where bacteria concentrated [17]. The protective effects of bacteria which concentrate  $\text{CaCO}_3$  over the metal surface have been discussed elsewhere [18]. A review on the types of attack upon non-ferrous metals induced by marine bacteria has also appeared [19] in addition to a few other general articles [20,21]. Investigations in the deep ocean, where macrofouling is absent, have brought out the role of microbes on carbon steel and aluminium alloys [22]. However, the most significant contribution has come from tests in sea and brackish waters of Heligoland and Cuxhaven [23]. In the said investigation, a very detailed account of aerobic marine bacterial corrosion is provided. It has been suggested that these bacteria influence corrosion during certain periods through their capability to dissolve protective and covering layers over the metal surface. Bacteria, it has been pointed out, could under some circumstances level the potential differences existing within an exposed steel surface.

In another investigation where continuous flow of natural sea water and natural but millipore filtered seawater were employed, aerobic marine bacteria were found to induce no significant change in the performance of mild steel [24]. It comes as a surprise in the light of the fact that most marine heterotrophs produce organic acids during their growth [25]. Laboratory tests using cultures of marine bacteria have revealed their corrosive action through measurement of weight loss and electrical charge at metal/solution interface [26]. With regard to passive metals like stainless steel, considerable influence on corrosion has been observed with more severe localized attacks due to the modification of oxygen reduction kinetics by the bacterial slime [27, 28].

In a series of investigations on microfouling, aerobic bacteria alone have been studied. It is obvious that SRB can grow in the micro-environments beneath the primary microbial film or the voluminous corrosion products on iron [29]. Although accelerated tests have been performed in the laboratory in presence of SRB with a view to understand its effect on marine corrosion [7, 30], studies on the relation between primary film-fouling and initiation

of anaerobic corrosion have been very few [31, 32].

**SCOPE OF STUDY**

It was of interest to examine the succession of aerobic and anaerobic bacteria on mild steel in seawater. The reason was that in a comprehensive study on the behaviour of metals and alloys in Mandapam coast (Fig. 1), astonishingly high corrosion rates (100 to 134 mdd) were recorded for mild steel, during certain months in the Palk Bay.

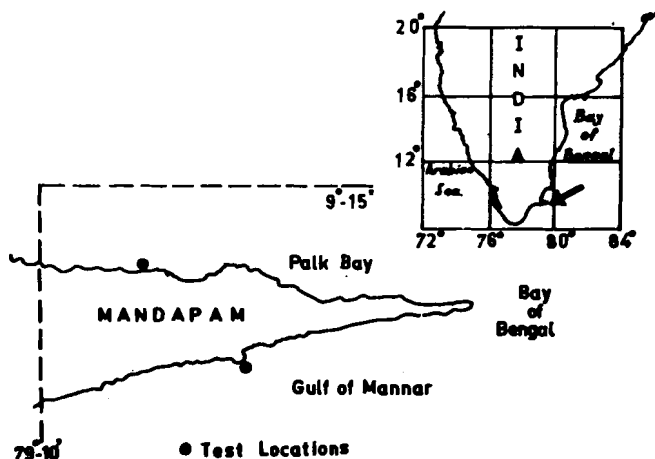


Fig.1: Coastal map of Mandapam indicating the test sites

The existence of the NE and SW monsoons causes striking variations in seawater characteristics between Gulf of Mannar and Palk Bay. Table I presents the average seawater characteristics during the study period, July to Sept '86, When SW monsoon prevailed. A sampling station at Gulf of Mannar was chosen to make a comparison of the results at Palk Bay.

TABLE-I: Seawater characteristics at the test locations during the study period (July-sept. '86)

Parameters	Gulf of Mannar	Palk Bay
Salinity, x 10 <sup>-3</sup>	34.4 - 35.3	34.8 - 37.8
Temperature, K	305	306
Dissolved oxygen, mg/l	5.0 - 5.5	3.6 - 3.8
Calcium, x 10 <sup>-6</sup>	415	455
Magnesium, x 10 <sup>-6</sup>	1020	1220
Sulphate, x 10 <sup>-6</sup>	274	312
Wave velocity, m/sec.	2 -2.2	Zero

Rationale for the present investigation was to examine the nature of microbial fouling at Gulf of Mannar and Palk Bay, and to find if a relation between this event and anaerobic corrosion existed.

**MATERIALS AND METHODS**

Commercially available, 1mm thick mild steel sheet (C 0.1%; Mn 0.46%; Si 0.074%; P 0.07%; S 0.028%) was cut into pieces of size 50mm x 75mm for microfouling studies. Test panels of the same material but 150mm x 100mm in size were used for corrosion evaluation. All panels were derusted, polished, degreased and where necessary weighed to an accuracy of 10<sup>-4</sup>g. Prior to exposure, samples for microfouling were washed with rectified spirit to avoid contamination from air-borne micro-organisms.

Test panels for microfouling studies were transported aseptically to the laboratory. Triplicate samples were used each time and dilutions from swabbed 1cm<sup>2</sup> area were inoculated. For enumeration of total viable heterotrophs, Zobelle's 2216-e marine agar was used. For SRB, a double-strength broth medium of Baars [33] was used and enumeration done by the MPN method [34]. Acid production by heterotrophic bacteria was tested by addition of phenol red, methyl red and methyl orange (0.05g/l) to Zobelle's medium. All samples were incubated at room temperature (303°K)

Corrosion rates were calculated from weight loss and surface area data. Iron and sulphur in the corrosion products were analysed by photocolourimetry and gravimetry respectively.

**RESULTS AND DISCUSSION**

Of the two locations, film formation was quicker at Gulf of Mannar (GM) where there was intense wave action. Fig. 2 shows the density of bacteria during various stages of exposure

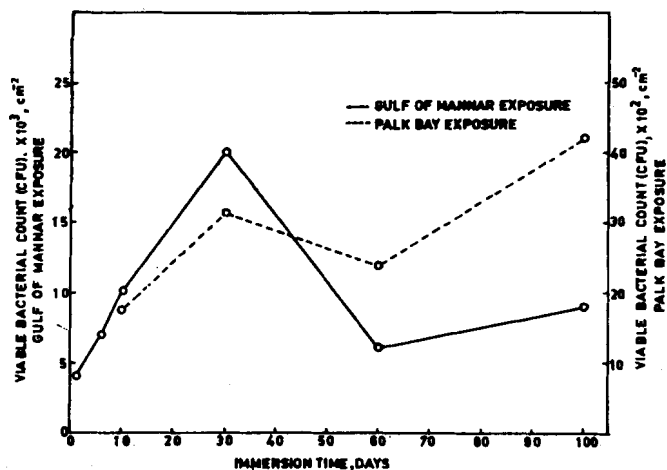


Fig.2: Viable total aerobic bacterial populations on mild steel during various stages of immersion.

Enumeration of bacteria at Palk Bay was restricted to a total of four times only, because of the problems in transporting the samples from far-off. Variations in the total isolates of bacteria attached at the two environments was also evident (Fig. 3).

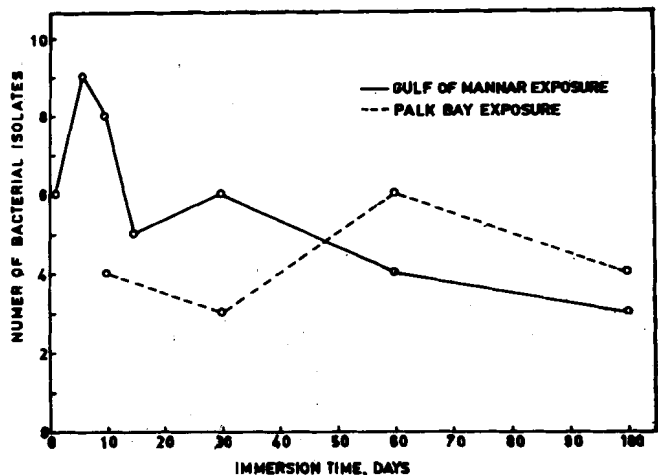


Fig. 3: Bacterial isolates on mild steel during various stages of immersion

The most interesting feature in the ecological succession of microbes was the development of an inner tier of anaerobic bacteria identified as the sulphate-reducing bacteria. The onset of SRB activity was evident at Palk Bay (PB) even by 24 hours (from the black products beneath red rust) and enumeration after 72 hours of initial immersion revealed their density to be of the order of  $10^4$ . This was presumably due to the favourable conditions such as low concentration of dissolved oxygen, high availability of sulphates and 'stagnation' of water. Even at GM, SRB activity was recorded as

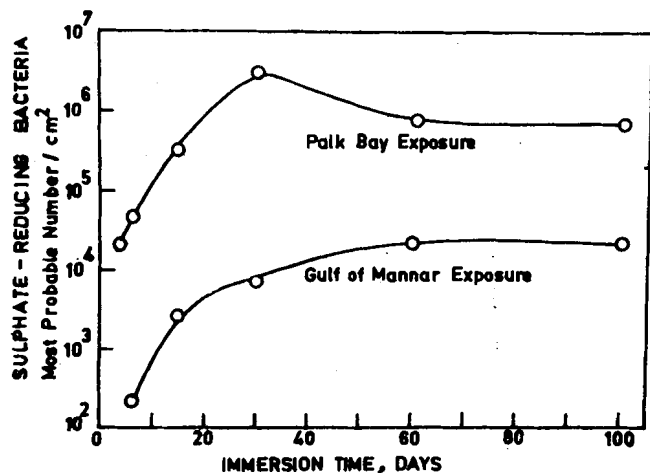


Fig. 4: Most probable number of sulphate-reducing bacteria during various stages of mild steel exposure

early as the 6th day after initial immersion in spite of the well aerated conditions. The density was however only about  $10^2$ . The density levels of SRB during various stages of immersion time can be read from Fig. 4. At GM, there was fluctuation in density due to periodic slough-off of corrosion products, while at PB there was not much variation with respect to time. Biofouling by macroorganism was poor at both environments and only less than 40% coverage could be achieved by the 100th day of exposure

Tests for acid production indicated that a majority of heterotrophs produce acids between pH 6.8 and 4.2. However, a relation, as reported elsewhere [25], between time of immersion and the ratio of acid producers to total heterotrophs, was not evident.

Results on the rate of corrosion of mild steel at GM and PB are given in Table II.

TABLE-II: Corrosion rates of mild steel at the test stations

Time after immersion (Days)	mdd	
	Gulf of Mannar	Palk Bay
30	62.7	101.2
60	53.3	90.5
100	46.1	78.0

It can be observed that corrosion at PB was 101 mdd after 30 days, considerably higher than the rate of GM which was the more dynamic and well aerated environment. By the 100th day, the rates fell to 78 mdd at the respective locations

Analysis of corrosion products (Table III) show high values of sulphur and iron on specimens immersed at PB. Evidently, the presence of tremendous populations of SRB has accounted for sulphur, while, on account of 'stagnation', accumulations of iron products have been held in tact on the corroded metal. The presence of iron products would have not only favoured SRB activity but set up Fe/FeS galvanic cell also.

It is clear from the results that sulphate reducing bacteria are responsible for the more severe attack at PB, and are potentially aggressive enough to offset electrochemical predictions. Thus, the present results are contradictory to the well established data on the effects of dissolved oxygen concentration in sea water on the corrosion of mild steel [35]. The discrepancy could be explained on the basis of ecological factors. The ecology of SRB has been well discussed elsewhere [36] pointing out that these bacteria have poor activity in cool, deep waters. Thus, the deep sea which has offered the workers [35] a suitable representative environment for low oxygen concentration, has poor bacterial activity as compared to shallow warm waters

Sulphate-reducers, therefore, appear to be the most important microbial genera affecting corrosion in seawater even though a majority of aerobic forms are capable of acid production. Limitations

Table-III: Amount of iron and sulphide in the corrosion products

Time after immersion (Days)	Iron, g m <sup>-2</sup>		Sulphide, g m <sup>-2</sup>	
	Gulf of Mannar	Palk Bay	Gulf of Mannar	Palk Bay
30	7.60	17.31	4.02	9.63
60	9.64	26.41	5.07	15.96
100	12.29	30.77	11.07	19.23

for aerobic clime formers is set forth by the settlement of macro-organisms, and grazing by motile organisms such as small crabs and gastropods. Moreover, the large buffering capacity of seawater offsets extreme acidity or alkalinity [37]. On the other hand, SRB proliferate in the micro-environments beneath slime formers and are independent of such factors.

In the following text, the present results are discussed in the light of already available data on marine corrosion. Anaerobic corrosion beneath marine growths is a complex phenomenon and is affected by the type of macro-organisms growing or decaying. It has been found [38] that actively growing *Enteromorpha*, by virtue of photosynthesis, can offset favourable conditions for SRB thereby reducing corrosion. However, photosynthetically produced oxygen in natural seawater and artificially bubbled oxygen in NaCl solution induce the same rate of attack on steel [39]. Similarly, natural and millipore-filtered seawater have been shown to be alike in their aggressiveness towards steels [24] which means that in the absence of macrofouling the acidic conditions created by SRB are efficiently buffered by seawater. As discussed elsewhere [38], one is made to believe that accelerated coverage by macro-organisms would favour SRB activity and increase the rate of corrosion. However, long term tests [40] indicate that SRB induce corrosion at a reduced rate of about 25 mdd only. Moreover, heavy growths of barnacles, which would most readily create ideal conditions for SRB, have been found to inhibit corrosion considerably [41, 42]. Also, enormous corrosion rates in presence of luxurious growths of algae have been recorded at Mandapam [42]. These facts seem to implicate that the non-biological constituents of seawater, particularly dissolved oxygen, predominate in corrosion reactions. Severe attack by SRB, in the present study, appears to be due to alarming changes in the 'bulk' seawater, namely low dissolved oxygen, high availability of sulphates, stagnation, and retention of sulphur products on the metal surface. SRB-induced corrosion in seawater, therefore, appears to be influenced when conditions in the bulk, rather than at interfaces, are more encouraging. The paper further dismisses the notion that macrofouling is a prerequisite for anaerobic corrosion.

#### CONCLUSIONS

1. Primary microbial film develops quicker where there is appreciable wave action.
2. Onset of activity of sulphate-reducing bacteria, however, is earlier in calm seawater.

3. SRB influence corrosion of mild steel considerably even in absence of macro-fouling organisms.
4. Where conditions are favourable for SRB, corrosion of mild steel does not depend on oxygen concentration in seawater.
5. SRB-induced corrosion in seawater is more severe when conditions in the bulk, rather than at interfaces, are encouraging.

#### REFERENCES

1. C A H von Wolzogen Kuhr and L W van der Vlugt, *Water*, **18** (1934) 147
2. W P Iverson, *Science*, **151** (1966) 956
3. J A Hardy, *Br Corr J*, **18** (1983) 190
4. J A Costello, *Int'l Biodetn Bull*, **6** (1969) 101
5. W P Iverson, *Proc 3rd Int'l Cong Mar Corr and Foul*, Gaithersburg, USA (1973) p 61
6. R A King, J D A Miller and J S Smith, *Br Corr J*, **8-1** (1973) 41
7. W P Iverson, *Underground Corrosion*, ASTM STP - 741, E. Escalante-Ed. (1981) p 33
8. S W Hendrick, *Appl Microbiol*, **28** (1974) 572
9. C E Zobelle, *J Bacterial*, **28** (1943) 36
10. K C Marshall, *Proc 3rd Int'l Cong Mar Corr and Foul*, Gaithersburg, USA (1973) p 625
11. R Mitchell, *Biofoul Corr Symp*, Seattle, USA (1977) p 625
12. G E Sechler and K Gunderson, *Proc 3rd Int'l Cong Mar Corr and Foul*, Gaithersburg, USA (1973) p 610
13. M Eashwar and S V K Iyer, *B Electrochem*, **2** (1986) 341
14. W A Corpe, *Proc 4th Int'l Cong Mar Corr and Foul*, France (1976) p 105
15. K Pederson, *Appl Environ Microbiol*, **44** (1982) 1196
16. V D Kalineko, *Mikrobiol*, **28** (1959) 750
17. I B Ulanovskii and N S Nikitana, *Mikrobiol*, **25** (1956) 66
18. L A Rozenburg, *Mikrobiol*, **32** (1963) 689
19. T H Rogers, *J Inst Metals*, **25** (1948) 19
20. J D A Miller and A K Tiller in *Microbial Aspects of Metallurgy*, J. D. A Miller-Ed., Elsevier, NY (1970) p 61

21. G Kobrin, *Mater Perform*, 15 -7 (1976) 38
22. E Fischer, Naval Applied Science Lab, Report No.NASL-TM-2 (1965) p 18
23. I Ehlert and M Pantke, *Werkst u Korr*, 23 (1972) 196
24. C A Smith, K G Compton and F H Coley, *Corr Sci*, 13 (1973) 677
25. S M Gerchakov, et al., *Proc 4th Int'l Cong Mar Corr and Foul*, France (1976) p 203
26. B L Little and P A Wagner, *Prog Int'l Conf on Biodeter in Indian Ocean*, NIO, Goa (1986)
27. V Scotto, R Di Cintio and G Marcenaro, *Corr Sci*, 25 (1985) 185
28. S C Dexter, K E Lucas, and G Y Gao, *Biologically Induced Corrosion*, NACE Ref. Book-8 (1986) S. C Dexter-Ed., p 144
29. J W Costerton and G G Gesey, *ibid*, p 223
30. H Togano and H Sasaki, *Proc 6th Int'l Cong Metall Corr Sydney, Australia (1975)*
31. P F Sanders and Maxwell, in *Microbial Corrosion*, (1983) Metals Soc., London, p 74
32. P F Sanders and W A Hamilton, *Biologically Induced Corrosion*, NACE Ref. Book-8 (1986) S. C Dexter-Ed., p 47
33. G H Booth, *Microbiological Corrosion*, M & B Monographs, London (1971) p 19
34. *Techniques of Water-Resources: Investigations of the U. S Geological Survey*, U. S. Govt. Printing Office, Washington (1977) Chapter 44-Edited by P. E. Greeson, et. al.
35. F M Jenkins, et al., *Proc 3rd Int'l Cong Mar Corr and Foul*, Gaithersburg, USA (1973) p 562
36. R A King, *Mater Perform*, 19 -1 (1980) 39
37. K G Compton, *Corrosion*, 26 (1970) 448
38. R C G Edyvean and L A Terry, *Int'l Biodeter Bull*, 19-1 (1983) 1
39. A Hache, L Barriety and J Debyser, *Corr et Anti Corr*, 7 (1959) 56
40. M Schmacher, *Seawater Corrosion Handbook.*, Noyes Date Collection, USA (1979) p 366
41. L Riumu et al, *Proc VI Int'l Cong Mar Corr and Foul*, Greece (1984) p 443
42. M Eashwar, et al *Proc 10th Int'l Cong Metal Corr*, Madras (1987) Session 15, Marine Corrosion, in Press.