Corrosion Study of Metals in Marine Environment

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Abstract: Atmospheric corrosion rate of Al, Zn and mild steel (MS) as well as salinity and sulphation rate have been determined under outdoor exposure at Tithal (Dist. Valsad) situated in South Gujarat, India. MS samples exposed vertically suffer less corrosion than those exposed at an angle of 45°. Monthly corrosion rate was in the decreasing order of Al < Zn < MS; whereas yearly rate also follow the same trend.

Keywords: Marine Environment, Al, Zn and MS metals, Salinity and Sulphation rate.

Introduction

The corrosiveness of a marine environment depends on the topography of the shore, wave action at the surf line, prevailing winds and relative humidity. While the corrosiveness decreases rapidly with increasing distance from the shore, severe storms can carry salt spray inland as much as 15 km. A marine atmosphere is laden with fine particles of sea salt carried by the wind to settle on exposed surface. At marine sites, the main corrodant in the air is sodium chloride which may be dispersed either as liquid aerosol or dry particles. It is known that the corrosion process can occur at relative humidities¹ as low as 35%.

Many of the complexities and difficulties inherent to atmospheric corrosion research stem from the great diversity of meteorological and pollutant condition that characterize the outdoor environment². In polluted atmospheres, chlorides and SO₂ are the common pollutants influencing metallic corrosion. Though chlorides come from natural airborne salinity, they are considered to be a significant pollutant as a consequence of their strong action on metals during atmospheric exposure. Relationships between chloride concentration in corrosion products, atmospheric salinity and corrosion rates have been reported^{3,4}. In India, data regarding the relative corrosivity of atmospheres at various cities⁵⁻¹⁰ are available along with that in USA, UK and other European countries¹¹.

The present study was carried out in the marine atmosphere under outdoor exposure at Tithal (Dist. Valsad) situated in South Gujarat. This area is three metres above the mean sea level and about 0.25 km away from the Arabian Sea.

Experimental

Metallic plates of Al, Zn and MS were taken for testing. Size of all the plates was kept 12.5 x 7.5 x 0.18 cm. Two types of time duration monthly and yearly were considered for the determination of corrosion rate. Before exposure, the plates were cleaned from rust by grinding and buffing to produce a homogeneous and reproducible surface. The frame was placed in parallel in fully exposed condition 10 feet above the ground level making an angle of 45° towards the horizontal plane. Another set of MS plates were exposed vertically in fully outdoor condition.

After exposure period, test plates were wrapped in plastic bags and brought to the laboratory for cleaning. Every exposure was carried out in duplicate and mean of the two values are taken. Control sample plates were used to determine the loss of metal in the cleaning solution and the final figures of the loss in weight of exposed plates were corrected accordingly. Corrosion products on Al plates were removed by using a solution of concentrated HNO₃ containing CrO₃ (chromic acid 50 g/L) at room temperature for about 10 minutes¹². Zinc plates were cleaned by solution made by dissolving 10% CrO₃ and about 0.2 g of BaCO₃ in distilled water at 298 K for about 2 minutes¹³. Hudson used Clark's solution to remove the rust from mild steel which is prepared by dissolving 2% Sb₂O₃ and 5% SnCl₂ in concentrated HCl (100 mL) at room temperature with constant stirring for about 15-20 minutes^{14,15}.

The atmospheric salinity content (mg NaCl/sq.dm/month) in the air was assessed by adopting the same principle as that of the wet candle method described by Ambler and Bain¹⁶. The lead peroxide method is used for monitoring of SO₂ contain in air described by Diab¹⁷.

Results and Discussion

Meteorological parameters

Monthly variation in temperature was observed and it was found that March to June are hot months, average maximum and minimum temperature are about 308 K and 290 K respectively; whereas December to February are cold months. Temperature and relative humidity data are shown in Figure 1. Generally, the rain starts in June continues up to October. Total annual rainfall was measured 1817 mm and 2114 mm in the year of 2006 and 2007 respectively.

Figure 1. Minimum and maximum temperature and relative humidity at marine environment.

Monthly atmospheric salinity rate was found to be in the range of 160 to 502 and 26 to 84 mg NaCl/sq.dm/month at exposure sites of 0.25 and 1.5 km from the sea respectively (Figure 2). Monthly salinity values are shown in Table 1. The data indicates that amount of salinity in the atmosphere decreases dramatically as distance increases from the seashore. An increase in salt content increases the rate of corrosion. Atmospheric salinity rate of different sites are reported as follows: 2 to 8 mg NaCl/sq.dm/month at Cochin (marine)⁷, 495 mg/dm² Cl (average 6 months) at Cuba (coastal station)¹⁸ and average 5.4 mg NaCl/sq.dm/month at Mumbai (industrial cum marine)⁵. A sulphation rate (Figure 3) measured at marine station was ranging from 9.6 to 19.8 mg SO₃/sq.dm/month (Table 1). A sulphation rate of 0.03 mg SO₃/sq.dm/month is usually accepted as representative of clean air¹⁹. Sulphation rate was reported from 3 to 40 mg SO₃/sq.dm/month at Bombay (industrial cum marine)⁵, 4 to 10 mg SO₃/sq.dm/month at Kolkatta⁶ and 3.5 mg SO₃/sq.dm/month at Cochin (marine)⁷.

Figure 2. Atmospheric salinity rate of different distance from sea at marine environment.

Figure 3. Sulphation rate at marine environment.

Aluminium

Monthly corrosion rate of Al was found in the range of 2 to 21.8 mg/sq.dm; whereas yearly corrosion rate was found in the range of 15.9 to 47.8 mg/sq.dm (Figure 4). Minimum corrosion was observed in the monthly exposures from January to April and maximum corrosion was observed in June, July and August. The maximum corrosion was observed due to rain and salinity values also high. In outdoor exposure Al is attributed with the formation of more protective oxide film on the metal surface which might have offered protection to the metal from reacting with the surrounding environment. Chlorides are capable of breaking the passive film formed on the surface. This is very noticeable in the coastal station.

Figure 4. Monthly and yearly corrosion rate (CR) of aluminium under outdoor exposure during different months at marine environment.

Figure 5. Monthly and yearly corrosion rate of zinc under outdoor exposure during different months at marine environment.

Table 1. Atmospheric salinity (in mg NaCl/sq.dm) and sulphation rate (in mg SO₃/sq.dm).

Month	Salinity rate		Sulphation rate
	Distance from sea		Distance from sea
	0.25 km	1.5 km	0.25 km
2005			
November	278	26	9.6
December	414	39	11.1
2006			
January	160	33	16.8
February	213	41	14.7
March	230	37	15.6
April	434	69	19.5
May	502	78	12.3
June	479	84	16.2
July	396	67	13.1
August	331	31	14.2
September	408	39	17.2
October	463	63	14.8
November	294	29	12.2
December	317	35	11.6

Average seasonal corrosion rate of Al was obtained in the rainy months (55.3 mg/sq.dm) is approximately 5 times higher compared to the corrosion rate in winter months (12.2 mg/sq.dm) and 3 times higher compared to summer months (17.4 mg/sq.dm) respectively (Table 2). Monthly corrosion rate of aluminium indicates a close correlation with number of rainy days ($r = 0.68$).

Table 2. Average seasonal corrosion rate (in mg/sq.dm).

Season	Corrosion rate, mg/sq.dm		
	Aluminium	Zinc	Mild steel
Winter	12.2	354	573
Summer	17.4	167	1611
Rainy	55.3	299	2462

Zinc

Monthly corrosion rate of Zn was found in the range of 24 to 134 mg/sq.dm; whereas yearly corrosion rate was found in the range of 244 to 541 mg/sq.dm (Figure 5). Zinc probably corrodes fairly rapidly during the early stages of exposure, but the corrosion slow down quickly with the formation of the protection films. There is a general type of attack on Zn plates.

Average seasonal corrosion rate of Zn was obtained in rainy months (354 mg/sq.dm) is 2 times higher compared to the values obtained in summer months (167 mg/sq.dm) (Table 2). Higher corrosion rate of Zn in rainy months may be due to the effect of rain. Monthly corrosion rate of Zn indicates a close correlation with rainfall ($r = 0.67$) and number of rainy days ($r = 0.56$). The monthly corrosion rate of zinc has a close positive correlation with minimum relative humidity ($r = 0.72$).

Mild steel (MS)

Monthly corrosion rate of MS was found in the range of 119 to 1132 mg/sq.dm; whereas yearly corrosion rate was found in the range of 2743 to 4286 mg/sq.dm (Figure 6). The corrosion suffered by mild steel was mainly of a general type. Figure 5 indicates the minimum corrosion take place during November-2005 to January-2006 and January-2007. It was observed that the pollution values are also lower during this period, which indicates corrosion rate was affected by pollution.

Figure 6. Monthly and yearly corrosion rate of mild steel under outdoor exposure during different months at marine environment.

Average seasonal corrosion rate of MS was obtained in rainy months (2462 mg/ sq.dm) is higher compared to the values obtained in hot months (1611 mg/sq.dm) (Table 2). Samples exposed in winter months indicate lower corrosion rate compared to rainy months. This suggests that protective film is formed on metal surface which can resist attack during subsequent exposure. Higher corrosion rate in rainy months may be due to the effect of rain. Monthly corrosion rate of MS indicates a close positive correlation with rainfall ($r = 0.94$) and number of rainy days ($r = 0.86$). Monthly corrosion rate of MS indicates a weak correlation with sulphation rate ($r = 0.38$). Monthly corrosion rate of mild steel indicates a close positive correlation with minimum humidity ($r = 0.85$) and positive correlation with atmospheric salinity ($r = 0.68$).

Positional effect

The results indicate that the plates exposed vertically suffer less corrosion than those exposed at an angle of 45° . Mild steel plates exposed from January-2006 to December-2006, shows average value of 641 mg/sq.dm/month at vertical position and 556 mg/sq.dm/month at an angle of 45° position (Table 3). The reason was undoubtedly being the retention of moisture and atmospheric particles for longer periods on a panel exposed at an angle of 45° .

Table 3. Positional effect on corrosion rate of mild steel (MS).

Month	Corrosion rate mg/sq.dm	
	Vertical	At 45°
2006		
January	226	185
February	360	275
March	262	217
April	428	397
May	892	494
June	1335	889
July	1611	2131
August	1207	842
September	672	617
October	469	378
November	96	115
December	138	140

Conclusions

Monthly corrosion rate ratio of MS : Zn is not constant and varies from a low of 2 to a high of 26; whereas yearly corrosion rate ratio of MS : Zn varies from a low of 8 to a high of 16. Monthly corrosion rate ratio of MS : Al varies from a low of 32 to a high of 155; whereas yearly corrosion rate ratio varies from 57 to 264. Monthly corrosion rate ratio of Zn : Al varies from a low of 6 to a high of 30, whereas yearly varies from a low of 8 to a high of 27.

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