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Corrosion Study of Metals in Marine Atmosphere

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

Key Words: Marine atmosphere, Aluminium, Zinc, Mild-steel, Salinity, Sulphation rate.

INTRODUCTION

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. The main factors which aggravate or catalyze the corrosion process are sea salts and relative humidity. It is known that the corrosion process can occur at relative humidities as low as 35 %[1].

Many of the complexities and difficulties inherent to atmospheric corrosion research stern from the great diversity of meteorological and pollutant conditions that characterize the outdoor environment[2]. In polluted atmospheres, chlorides and SO_2 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 varies cities[5-10] are available along with that in USA, UK and other European countries[11].

The present study was carried out in the marine atmosphere under outdoor exposure at Dumas (Dist. Surat) 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

Samples of Al, Zn and mild-steel plates were tested. Size of all the plates was kept 12.5 cm × 7.5 cm × 0.16 cm. Mainly two types of time duration monthly and yearly is considered for the determination of corrosion rate. Before exposure, the samples were cleaned from rust by grinding and buffing to produce a homogeneous and reproducible surface. The frame was placed in parallel position in fully exposed condition 10 feet above the ground level making an angle of 45º towards the horizontal plane. Another set of mild-steel samples were fully exposed vertically.

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 samples were corrected accordingly. Corrosion products on Al plates were removed by using a solution of concentrated HNO_3 containing CrO_3 (chromic acid 50 g/L) at room temperature for about 10 min[12]. Zinc plates were cleaned by solution made by dissolving 10 % CrO_3 and about 0.2 g of $BaCO_3$ in distilled water at 298 K for about 2 min[13]. Hudson used Clark's solution to remove the rust from mild-steel which is prepared by dissolving 2 % Sb_2O_3 and 5 % $SnCl_2$ in concentrated HCl (100 mL) at room temperature with constant stirring for about 15-20 min[14,15].

The atmospheric salinity content (mg NaCl/dm^2/month) in the air was assessed by adopting the same principle as that of the wet candle method described by Ambler and Bain[16]. The lead peroxide method for monitoring for SO_2 described by Diab[17]. Measurement of sulphation rate was done by candle method.

RESULTS AND DISCUSSION

Meteorological parameters: Monthly variation in temperature was observed and was found March to June are hot months, average maximum and minimum temperature are about 307 and 298 K, respectively. Whereas December to February are cold months. Generally, the rain starts in June continues up to October. Total annual rainfall was measured 1410 and 775 mm in the year of 1998 and 1999, respectively.

Monthly atmospheric salinity rate was found to be in the range of 263 to 491 and 30 to 85 mg NaCl/dm^2/month at exposure sites of 0.25 and 1.5 km from the sea, respectively. 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/dm^2/month at Cochin (marine)[7], 495 mg/dm^2 Cl (average 6 months) at Cuba (coastal station)[18] and average 5.4 mg NaCl/dm^2/month at Mumbai (industrial cum marine)[5].

A sulphation rate measured at marine station was ranging from 7.2 to 13.0 mg SO_3/dm^2/month (Table-1). A sulphation rate of 0.9 mg SO_3/dm^2/month is usually accepted as representative of clean air[19]. Sulphation rate was reported from 3 to 40 mg SO_3/dm^2/month at Mumbai (industrial cum marine)[5], 4 to 10 mg SO_3/dm^2/month at Kolkata[6] and 3.5 mg SO_3/dm^2/month at Cochin (marine)[7].

TABLE-1
ATMOSPHERIC SALINITY (in mg $NaCl/dm^2$) AND SULPHATION (in mg SO_3/dm^2)

Month	Salinity rate		Sulphation rate
	Distance from sea		Distance from sea
	0.25 km	1.5 km	0.25 km
1998			
September	451	73	12.0
October	418	66	10.9
November	263	39	9.2
December	281	40	10.0
1999			
January	272	35	11.3
February	327	46	11.7
March	298	30	12.1
April	424	64	13.0
May	460	70	12.8
June	491	85	11.6
July	388	69	12.0
August	341	33	11.0
September	395	38	13.0
October	400	60	10.2
November	281	31	7.2
December	309	34	8.5

Aluminium: Monthly corrosion rate of Al was found in the range of 1 to 5 mg/dm^2 (0.45 to 2.2 μm/y); whereas yearly corrosion rate was found in the range of 16 to 30 (0.59 to 1.1 μm/y) mg/dm^2. 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 which the surrounding environment. Chlorides are capable or breaking the passive film formed on the surface. This is very noticeable in the coastal station.

Average seasonal corrosion rate was obtained in the rainy months (3.3 mg/dm^2) is approximately twice compared to the corrosion rate in winter months (1.6 mg/dm^2) and 1.3 times higher compared to summer months (2.4 mg/dm^2), respectively (Table-2). Monthly corrosion rate of aluminium indicates a close correlation with rainfall ($r = 0.57$).

TABLE-2
AVERAGE SEASONAL CORROSION RATE (mg/dm^2)

Season	Corrosion rate (mg/dm^2)		
	Aluminium	Zinc	Mild-steel
Winter	1.6	71	115
Summer	2.4	80	232
Rainy	3.3	106	250

Zinc: Monthly corrosion rate of Zn was found in the range of 45 to 170 mg/dm^2 (7.7 to 29.0 µm/y); whereas yearly corrosion rate was found in the range of 270 to 390 (3.8 to 5.5 µm/y) mg/dm^2 (Fig. 1). 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.

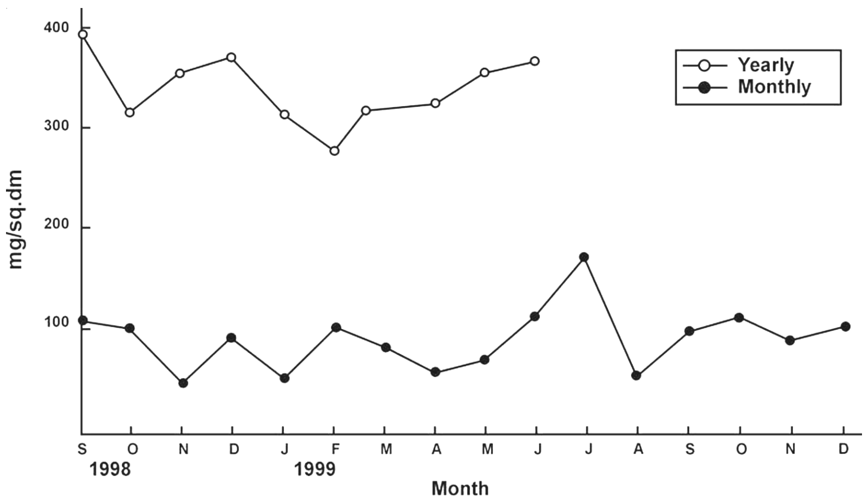

Fig. 1. Monthly and yearly corrosion rate of zinc under outdoor exposure during different months

Average seasonal corrosion rate was obtained in rainy months (106.8 mg/dm^2) is 1.3 to 1.5 times higher compared to the values obtained in summer months (80 mg/dm^2) and winter months (71 mg/dm^2) respectively (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 = 0.70).

Mild-steel (MS): Monthly corrosion rate of MS was found in the range of 80 to 400 mg/dm^2 (13.9 to 69.5 µm/y); whereas yearly corrosion rate was found in the range of 1500 to 2900 (21.4 to 41.4 µm/y) mg/dm^2 (Fig. 2). The corrosion suffered by a mild-steel was mainly of a general type. Table-3 indicates the minimum corrosion take place during November-1998 to January-1999 and November-1999. It was observed that the pollution values are also lower during this period, which indicates corrosion rate was affected by pollution.

Average seasonal corrosion rate was obtained in rainy months (250 mg/dm^2) is higher compared to the values obtained in hot months (232 mg/dm^2) (Table-2). Samples exposed in winter months indicates lower corrosion rate in 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 correlation with rainfall (r = 0.60) as well as with atmospheric salinity (r = 0.68).

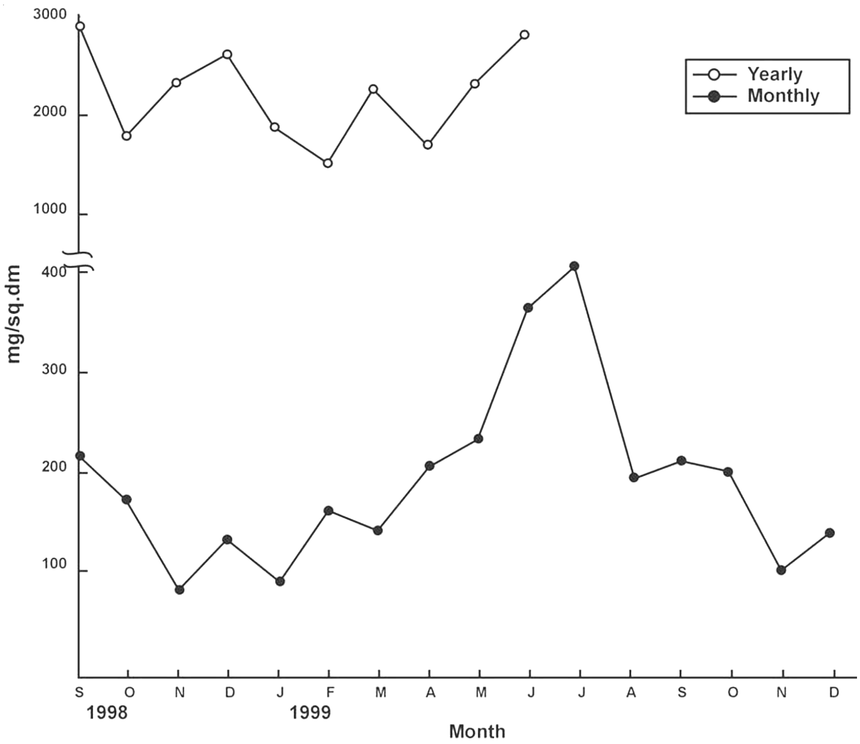

Fig. 2. Monthly and yearly corrosion rate of mild steel under outdoor exposure during different months

Positional effect: The results indicate that the plates exposed vertically suffer less corrosion than those exposed at an angle of 45º. Average value of corrosion rate was 104 mg/dm^2/month in vertical position and 218 mg/dm^2/month at an angle of 45º position (Table-3). The reason undoubtedly being the retention of moisture and atmospheric particles for longer periods on samples exposed at an angle of 45º.

TABLE-3
POSITIONAL EFFECT ON CORROSION RATE OF MILD-STEEL (MS)

Month	Corrosion rate (mg/dm^2)	
	Vertical	At 45º
1998		
September	131	220
October	92	170
1999		
February	77	160
March	73	140
April	101	200
May	103	230
June	168	360

Comparison

Monthly corrosion rate ratio of mild-steel:zinc is not constant and varies from a low of 1 to a high of 3; whereas yearly corrosion rate ratio of mild-steel:zinc varies from a low of 6 to a high of 8. Monthly corrosion rate ratio of mild-steel:aluminium varies from a low of 33 to a high of 112; whereas yearly varies from 76 to 112. Zinc: aluminium corrosion rate ratio (monthly) varies from a low of 16 to a high of 74.

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