



# Kinetics of atmospheric corrosion of mild steel, zinc, galvanized iron and aluminium at 10 exposure stations in India

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## Abstract

As a part of updating Corrosion Map of India project, atmospheric corrosion behaviour of commercially available engineering materials such as mild steel, galvanized iron, zinc and aluminium metals was studied in marine, industrial, urban, and rural environments by weight loss method at 10 exposure stations in India over a period of 5 years. The results of these studies demonstrated that galvanized iron, zinc and aluminium metals were several times more durable than mild steel. Compared to galvanized iron and zinc, aluminium provided superior protection in industrial and marine environment except at Mormugao Port Trust (MPT). It also offered much better resistance to corrosion in rural environments. At certain places, galvanized iron proved to be more durable than aluminium. The results obeyed well with the empirical kinetics equation of the form  $C = Kt^n$ , where  $K$  and  $C$  are the corrosion losses in  $\mu\text{m}$  after 1 and ' $t$ ' years of the exposure, respectively, and ' $n$ ' is a constant. Based on ' $n$ ' values, the corrosion mechanisms of these metals are predicted. The corrosion products formed on the metal samples in Chennai marine atmosphere were identified by X-ray diffraction analysis.

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## 1. Introduction

Atmospheric corrosion is a process of practical importance as it degrades the structures, devices and products exposed to atmosphere. It is mainly depending on exposure time ( $t$ ) and some climatic factors, like relative humidity (RH), temperature ( $T$ ), sulfur content, salinity (chloride) and the presence of some other pollutants [1]. Global studies have shown that the overall cost of corrosion amounts to at least 4–5% of the GNP and that 20–25% of this cost could be avoided by using appropriate corrosion control technology [2]. Atmospheric corrosion makes the major contribution to this cost [3]. The aggressiveness of the atmospheric constituents can be assessed by measuring climatic and pollution factors or by determining the corrosion rate of exposed metals [4]. It has been customary to classify environments as rural, urban, industrial, marine, or combinations of these. Rural environment is the least corrosive and normally does not contain chemical pollutants, but does contain organic and inorganic particulates, where as the urban environment is similar to the rural type but with little industrial pollutants. Industrial atmospheres contain considerable amount of sulfur dioxide ( $\text{SO}_2$ ), chloride ( $\text{Cl}^{-1}$ ), and oxides of nitrogen, etc. Chloride containing environment can be considered as the marine atmosphere.

Studies of the atmospheric corrosion behaviour of different metallic materials [5–8] were reported. Corrosivity maps were produced for a number of geographic regions illustrating the macroscopic variations in the atmospheric corrosivity. Such maps enormously facilitate the task of selecting materials, protection systems, maintenance intervals, etc. for the metallic structures exposed to the atmosphere. Corrosion of ferrous and non-ferrous metals were extensively studied both in the field and laboratory exposure [9–20] and various mathematical models have been developed [21–28].

In countries like India, due to wide spread use of mild steel, zinc, aluminium and galvanized iron, it was considered desirable to study the corrosion behaviour of these materials in a wide variety of atmosphere. Because of excellent mechanical properties and relatively low prices, carbon steels are now chosen for the structures for petroleum, nuclear, lignite, marine, and agricultural industries.

Hot-dip coatings are generally based on zinc, aluminium or aluminium–zinc alloys. Zinc coatings and zinc sheets are also used in various industries [29,30]. Models for predicting the corrosion damage of metals in the atmosphere are useful for answering the questions regarding the durability of metallic structures [31], determining the costs of damages associated with the degradation of materials, and acquiring knowledge about the effect of environmental variables on the corrosion kinetics. Hence, the atmospheric corrosivity in a particular area (location) is an important factor to engineers and general users, helping them to select proper materials and suitable protective coatings for highly populated India.

In 1970, atmospheric corrosion data for 26 field exposure stations in India were published [32]. The rate of corrosion was found to vary from region to region and the intensity of attack was as expected to be more in the industrial area and along the seacoast. Recently results from 41 field studies were analyzed and published in the form of updated corrosivity maps of India [33–35]. It is reported that the rate of corrosion is found to be spot specific and not region specific, and for most of the regions, owing to insufficient data it was found difficult to evaluate atmospheric corrosivity.

This paper presents the data obtained in an experimental study of mild steel, zinc (Zn), galvanized iron (GI) and aluminium (Al) corrosion in different atmospheres during a

5-year exposure programme, at about 10 exposure stations located in different parts of India. The results obtained are analyzed and discussed as a function of exposure time, environmental pollution levels and durability of galvanized iron (GI), zinc (Zn) and aluminium (Al) with respect to bare mild steel (MS). Statistical analysis has been carried out from these results and corrosion mechanism has been predicted.

## 2. Experimental

Scope and methodology of conducting the atmospheric corrosion studies were similar for all the 10-exposure stations. The climatic parameters, which influence atmospheric corrosion, are salinity, SO<sub>2</sub>, RH, temperature and other pollutants. Exposure stations were chosen according to the local atmosphere, convenience of installations and facilities for technical assistance. Locations of these exposure stations are shown in Fig. 1. The exposure stations are numbered and the corresponding numbers are used in the subsequent citations. These stations vary considerably with respect to moisture content, temperature and contaminants such as dust content and gaseous impurities. These stations, therefore, have been divided into four types. The stations 1, 2 and 3 (Chennai, Cuddalore and Nagapattinam) are located on the east coast of India (i.e. Bay of Bengal). The number 1 is about 150 m away from the Bay of Bengal coast, and situated near the port of Chennai. The port is handling coal, crude oil, iron ore, and other industrial products, and there-

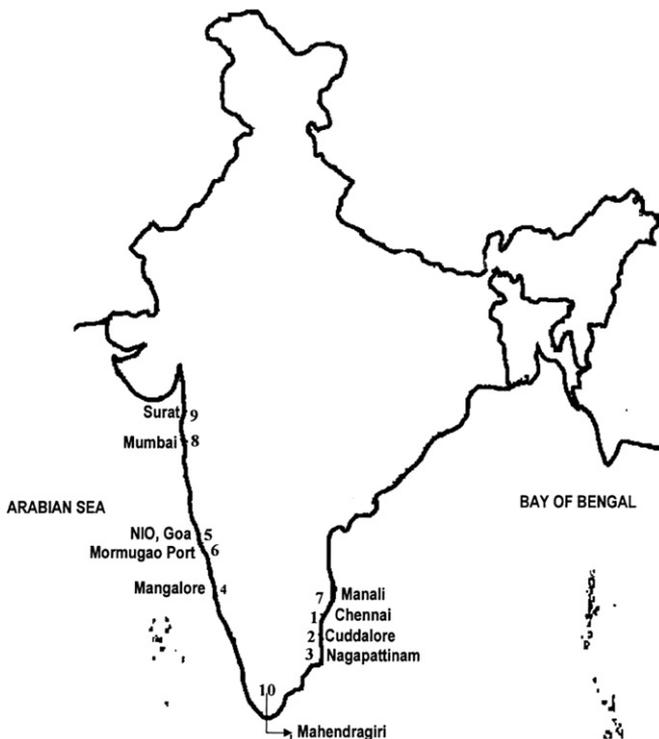


Fig. 1. Location of the atmospheric exposure stations in India.

fore a lot of dust particles were found deposited on the metal surface. The stations 2 and 3 are about 50 m away from the seacoast. The stations 4, 5 and 6 [Mangalore, National Institute of Oceanography (NIO) Goa, Mormugoa Port Trust (MPT)] are another set of exposure stations located in the West seacoast of India (Arabian Sea coast). The station 4 is about 130 m away from the sea, whereas the station 5 is about 50 m away from the sea and at a height of about 30 m above the mean sea level (MSL). The station 6 is opposite to the station 5 and the exposure stands were erected within the port area. A mixture of iron ore; carbon particles and other dust particles were found deposited on the exposed set of metal surfaces, the concentration of which was found to be  $480 \text{ mg m}^{-2} \text{ day}^{-1}$ . These exposure stations are classified as marine. The exposure stations 7 and 8 (Manali and Mumbai) are classified as industrial area having heavy industrial manufacturing activities.  $\text{SO}_2$ ,  $\text{Cl}^{-1}$ ,  $\text{NO}_3^{-1}$  and other specific industrial emissions that were released from the sources located nearby. The station 7 is located on an industrial area and it is also in close proximity to the seacoast and hence it is classified as industrial–marine atmosphere. The station 9 (Surat) is classified as urban station. It is subjected to normal precipitating patterns and typical urban contaminants emitted by the road traffic and it is about 5 km away from the Gulf of Khambhai. The station 10 (Mahendragiri) is located on the hill (100 m from the ground levels) area and it is classified as hill station.

The average climatic parameters such as temperature, RH and rainfall have been collected from meteorological observatory stations, Govt. of India. Pollution due to  $\text{SO}_2$  and air-borne salinity represented by chloride, were evaluated continuously every month for the period of 1 year by the deposition methods (by lead peroxide candle and wet candle methods, respectively) [36,37].  $\text{SO}_2$  of the atmosphere absorbed by the lead per oxide was transformed into  $\text{PbSO}_4$ , which was then analyzed by gravimetric method. The amount of chloride captured by the wet candle was determined by the titration method.

MS, Zn, GI and Al were used for the field exposure studies at each test location. The chemical compositions of the materials exposed are given in Table 1. Specimens of size  $150 \text{ mm} \times 100 \text{ mm}$  were cut from the respective metal sheets. They were polished, with 120 emery wheels, degreased with trichloroethylene; and weighed prior to the exposure. Then the specimens were mounted on the exposure stands at an angle of  $45^\circ$  from the horizontal. In order to identify the exposed specimens, stamped code numbers were used. The exposure stands were located in open atmosphere carefully avoiding shadows of trees; buildings or structures.

Four specimens (MS, Zn, GI and Al) were removed from each station after specific exposure periods of 1, 2, 3, 4 and 5 years. The corrosion products were removed using the respective pickling solutions [38]. The specimens were then dried, reweighed and the weight losses were calculated. The amount of metallic corrosion was determined by weight loss method. Guideline from Indian Standard [36], ASTM [39,38] and the international organizations to standardization (ISO) [40] were used for the exposure and cleaning procedures required before exposure and for cleaning and evaluation after the exposure.

To predict the mathematical model, the data for the 5 years of exposure were used. The variation of weight loss ( $C$ ) due to corrosion expressed as micrometres ( $\mu\text{m}$ ) with time ( $t$ ) can be described by the general empirical equation in the form

$$C = Kt^n \quad (1)$$

Townsend and Zoccola [42] in 1982, used linear regression analysis to fit straight line to a log–log plot of corrosion loss ( $C$ ) vs time ( $t$ ) in logarithmic form

Table 1  
Chemical composition of test materials, wt.%

Metal	C	Mn	Si	P	S	Cr	Mo	Ni	Al	Cu	Sn	Mg	Cd	Pb	Zn	Fe
MS	0.01	0.196	0.007	0.009	0.014	0.043	0.015	0.013	–	–	–	–	–	–	–	Bal.
Zn	–	–	–	–	–	–	–	–	0.001	0.007	0.001	–	0.0045	0.012	Bal.	0.00145
GI <sup>a</sup>	–	–	–	–	–	–	–	–	0.002	–	<0.01	<0.01	–	0.10	Bal.	–
Al	–	0.015	0.32	–	–	<0.005	–	–	Bal.	0.015	–	0.13	–	–	0.003	0.51

<sup>a</sup> GI (in Zn coating).

$$\log C = \log K + n \log t \quad (2)$$

where  $K$  is the intercept (equal to the corrosion loss in first year) and ' $n$ ' is the slope of the log–log plot. The first year corrosion rate is an important parameter not only for determination of corrosivity of the atmosphere but also for long-term corrosion forecasting. Both ' $K$ ' and ' $n$ ' are dependent on the type of metal and climatic parameters. The validity of the equation and its reliability to predict long-term corrosion has been demonstrated by many authors [43,44,41,45–50].

The composition of corrosion products scraped off from the exposure of first year samples was determined by X-ray diffraction analysis (XRD) using JEOL-IDX-800 computer controlled equipment. The XRD patterns were scanned between  $10^\circ$  and  $80^\circ$  two theta.

### 3. Results and discussion

#### 3.1. Environmental and corrosivity characterization of exposure stations

The list of exposure stations with a short characteristic and the mean climatic parameters of the exposure period are indicated in Table 2. The RH was found to be the lowest at station 3. The rainfall was varying from location to location. Of the 10 atmospheric exposure stations, six stations viz. 1–6 have marine characteristics. They were placed into two main groups on the basis of their different  $\text{SO}_2$  pollution levels (Table 3). The first group is referred to as pure marine atmospheres (stations 2–5) without significant  $\text{SO}_2$  pollution levels (i.e. deposition rate of  $<10 \text{ mg m}^{-2} \text{ d}^{-1}$ ) and showed the different chloride pollution levels. The environmental characteristics and corrosivity categories of the stations are given in Tables 3 and 4 classified as per ISO 9223 [51]. In ISO criteria the environments are classified in terms of  $\text{SO}_2$  (class P) and chloride (class S), whereas  $\text{S}_0$ ,  $\text{S}_1$ ,  $\text{S}_2$  and  $\text{S}_3$  correspond to chloride deposition rate of  $<3$ , 3–60, 60–300 and 300–1500  $\text{mg m}^{-2} \text{ d}^{-1}$ , respectively, and  $\text{P}_0$ , and  $\text{P}_1$  correspond to  $\text{SO}_2$  deposition rates of  $<10$  and 10–35  $\text{mg m}^{-2} \text{ d}^{-1}$ , respectively. Using this classification, the pure marine atmospheres were classified into the following subgroups two  $\text{S}_1\text{P}_0$  (stations 2 and 3) atmosphere (atmospheres with a chloride contaminations level of 3–60  $\text{mg m}^{-2} \text{ d}^{-1}$ ), one  $\text{S}_2\text{P}_0$  (station 4) atmosphere (atmospheres with chloride contamination level of 60–300  $\text{mg m}^{-2} \text{ d}^{-1}$ ) and station 5 was apparently unpolluted ( $<3 \text{ mg m}^{-2} \text{ d}^{-1}$  of chloride and  $<10 \text{ mg m}^{-2} \text{ d}^{-1}$  of  $\text{SO}_2$ ) atmosphere and was designated as  $\text{S}_0\text{P}_0$  category even though it is located near the sea. The second group (mixed marine atmospheres) included two atmospheres of stations 1 and 6 showing higher  $\text{SO}_2$  pollution levels. These two were designated as  $\text{S}_3\text{P}_1$  and  $\text{S}_2\text{P}_1$  atmospheres (300–1500 and 60–300  $\text{mg m}^{-2} \text{ d}^{-1}$  chloride and 10–35  $\text{mg m}^{-2} \text{ d}^{-1}$   $\text{SO}_2$ ), respectively. Stations 7 and 8 are situated in the middle of industrial area and they are classified as  $\text{S}_2\text{P}_1$  and  $\text{S}_1\text{P}_0$ , respectively, based on their pollution levels in the atmospheres, respectively. Stations 9 and 10 (Surat and Mahendragiri) are situated in urban and hill areas and based on the pollution levels; they were classified as  $\text{S}_1\text{P}_0$  and  $\text{S}_0\text{P}_0$  categories, respectively.

As defined by ISO 9223 [51] another way to evaluate the corrosivity categories of atmospheres (Table 4) consists of determination of the corrosion rates for the set of metals after 1-year exposure. This standard classifies the corrosivity category of different environments under class C, where in  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$  and  $\text{C}_5$  correspond to the corrosion rates of very low, low, medium, high and very high, respectively. It can be seen from the table that the majority of  $\text{S}_1\text{P}_0$  atmospheres such as stations 2, 3, 8 and 9 showed the relatively

Table 2  
Average climatic parameters for each test exposure station

Exposure station			Average temperature [°C]		Average relative humidity [RH%]		Average rainfall [mm]
No.	Location	Type of atmosphere	Min	Max	Min	Max	Max
1	Chennai	Marine, 150 m away from eastern sea coast (Port Trust area)	20	39	59	98	355
2	Cuddalore	Marine, 50 m away from eastern sea coast	21	35	64	90	702
3	Nagapattinam	Marine, 50 m away from eastern sea coast	22	34	61	80	750
4	Manalore	Marine, 130 m away from western sea coast	19	34	63	92	308
5	NIO	Marine, 50 m away from western sea coast and 30 m above the MSL	16	31	63	89	248
6	Mormugoa Port Trust (MPT)	Marine, within the Port Trust area (western sea coast)	17	33	61	86	248
7	Manali	Industrial area cum Marine, 2 km away from eastern sea coast	19	39	61	86	309
8	Mumbai	Industrial	19	33	56	94	945
9	Surat	Urban, 5 km away from Gulf of Khambhai	15	40	62	89	450
10	Mahendragiri	Rural (Hill area)	19	37	50	98	83

Table 3

Average sulfur di oxide and chloride deposition rate and atmosphere classification categories according to ISO/DIS 9223

Exposure station		SO <sub>2</sub>		Chloride	
No.	Location	Deposition rate (mg m <sup>-2</sup> d <sup>-1</sup> )	Category	Deposition rate (mg m <sup>-2</sup> d <sup>-1</sup> )	Category
1	Chennai	18	P1	304.60	S3
2	Cuddalore	Nil	P0	39.49	S1
3	Nagapattinam	Nil	P0	18.18	S1
4	Mangalore	Traces	P0	69.00	S2
5	NIO	Nil	P0	Nil	S0
6	MPT	22	P1	266.40	S2
7	Manali	25	P1	75.21	S2
8	Mumbai	9	P0	30.00	S1
9	Surat	8	P0	13.80	S1
10	Mahendragiri	Nil	P0	Nil	S0

Table 4

Classification of corrosivity categories (CC) corresponding to the first year corrosion rate (CR,  $\mu\text{m y}^{-1}$ ) of metals according to ISO/DIS 9223

Exposure station		MS		Zn		GI		Al	
No.	Location	CR	CC	CR	CC	CR	CC	CR	CC
1	Chennai	524.00	C5	7.10	C5	11.66	C5	8.6	C5
2	Cuddalore	51.30	C4	2.20	C4	4.20	C4	1.16	C3
3	Nagapattinam	28.90	C3	2.70	C2	3.22	C2	1.16	C3
4	Mangalore	108.40	C5	1.37	C2	2.31	C2	5.10	C5
5	NIO	30.00	C3	1.26	C2	2.26	C2	0.25	C1
6	MPT	453.30	C5	19.41	C5	18.41	C5	11.0	C5
7	Manali	111.50	C5	3.07	C4	4.56	C5	1.41	C3
8	Mumbai	44.00	C3	2.60	C4	3.64	C4	2.50	C4
9	Surat	27.30	C3	2.08	C4	2.54	C4	1.82	C3
10	Mahendragiri	13.57	C2	6.25	C5	3.52	C4	5.32	C5

low chloride levels with corrosivity categories C<sub>4</sub>, C<sub>3</sub>, C<sub>3</sub> and C<sub>3</sub> for MS, C<sub>4</sub>, C<sub>2</sub>, C<sub>4</sub> and C<sub>4</sub> for Zn and GI and C<sub>3</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>3</sub> for Al, respectively. The S<sub>0</sub>P<sub>0</sub> atmospheres at the stations 5 and 10 showed the unpolluted atmospheres with corrosivity categories C<sub>3</sub> and C<sub>2</sub> for MS, C<sub>2</sub> and C<sub>5</sub> for Zn, C<sub>2</sub> and C<sub>4</sub> for GI and C<sub>1</sub> and C<sub>5</sub> for Al, respectively. The station 7 had S<sub>2</sub>P<sub>1</sub> atmosphere which showed the mixed polluted atmosphere with corrosivity category C<sub>5</sub>, C<sub>4</sub>, C<sub>5</sub> and C<sub>3</sub> for mild steel, zinc, GI and aluminium, respectively. The station 4 had S<sub>2</sub>P<sub>0</sub> (high Cl<sup>-1</sup> contamination levels) atmosphere with corrosivity category C<sub>5</sub>, C<sub>2</sub>, C<sub>2</sub> and C<sub>5</sub> for Ms, Zn, GI and Al, respectively. In the case of stations 1 and 6, they were designated as S<sub>3</sub>P<sub>1</sub> and S<sub>2</sub>P<sub>1</sub> atmospheres showing contamination levels with corrosivity category C<sub>5</sub> for all the metals.

### 3.2. Time dependence of corrosion rate

The corrosion rates for MS, Zn, GI and Al for a 5 years period are given in Table 5. It can be seen from the table that the corrosion rates obtained depend on the nature of

Table 5  
Summary of average corrosion rates of metals ( $\mu\text{m y}^{-1}$ ) at 10 exposure stations for every year upto 5 years

Period of exposure (year)	Exposure stations									
	Chennai	Cuddalore	Nagapattinam	Mangalore	NIO	MPT	Manali	Mumbai	Surat	Mahendragiri
<i>MS</i>										
1	524.0	51.30	28.90	108.40	30.00	453.3	111.50	44.00	27.30	13.57
2	448.0	36.40	18.49	78.15	18.40	298.0	68.40	26.72	20.31	9.40
3	399.4	41.27	14.95	64.90	16.36	244.4	54.33	18.71	16.23	6.96
4	360.7	36.95	13.54	55.32	15.45	209.9	54.20	16.70	12.99	5.44
5	342.1	32.42	12.04	47.48	10.35	191.8	48.20	14.93	9.44	5.04
<i>GI</i>										
1	11.66	4.2	0.32	2.31	2.26	18.41	4.56	3.64	2.54	3.52
2	– <sup>a</sup>	2.99	2.01	1.95	1.50	12.94	4.06	3.01	1.94	3.55
3	–	2.15	2.28	1.60	1.45	10.50	2.95	2.00	1.44	2.97
4	–	1.97	2.43	1.47	1.39	8.04	3.11	1.58	0.23	3.02
5	–	1.83	2.48	1.39	1.07	7.60	2.90	1.31	0.21	2.94
<i>Zn</i>										
1	7.10	2.20	2.70	1.37	1.26	19.41	3.07	2.60	2.08	6.25
2	8.57	4.62	1.74	0.99	1.15	18.07	2.30	1.88	1.29	3.52
3	8.44	3.48	1.43	0.79	0.88	14.17	1.82	1.60	1.13	4.10
4	10.20	4.52	1.28	0.81	1.25	13.18	1.66	1.50	0.93	3.43
5	11.52	4.04	1.13	0.74	1.47	12.21	1.79	1.43	0.84	3.22
<i>Al</i>										
1	8.60	1.16	1.16	5.10	0.25	11.00	1.41	2.50	1.82	5.32
2	11.02	1.67	0.41	3.07	0.21	7.60	1.32	1.85	1.22	4.12
3	12.15	1.25	0.77	2.10	0.19	14.05	1.25	1.28	1.02	3.44
4	16.00	1.08	0.66	1.91	0.19	15.83	1.48	1.17	0.83	2.61
5	16.36	–0.92	0.52	–	0.20	–	1.31	–	–	2.81

<sup>a</sup> GI specimen completely corroded after 11/2 years.

material. Higher corrosion rates were obtained for MS and the lower ones for Al. On the other hand, the corrosion rates varied from one station to another. Coastal atmosphere at the stations 1–6 generally showed several times as much corrosion rate as the inland station 10. The stations 7, 8 and 9 were located in industrial, industrial–marine, and urban atmospheres caused moderate, severe, and moderate corrosion rates, respectively, depending on the pollution levels. The results for Al, Zn, and GI showed significantly high rates of corrosion at the stations 1 and 6 compared to the other exposure stations. The highest corrosion rates were also recorded at these stations for MS, which was correlated with the highest category of air-borne chloride and SO<sub>2</sub> and high rate of dust depositing from the harbor. The corrosion rates were decreased (except for Zn at stations 1 and 2, for GI at stations 1 and 3, and for Al at stations 1 and 6) with the time of exposure for all the set of metals at all the exposure stations due to the protective nature of the corrosion products.

Fig. 2 shows a typical surface appearance of MS after 1-year exposure at station 1. Flaky and powdery rust product (brown in colour) has covered the entire surface within a period of 1 year. X-ray diffraction studies were carried out for MS, Zn, and Al at the end of first year at station 1. The corrosion products formed at the marine atmosphere were characterized by XRD. For the oxide identification the PCPDFWIN [52] system was employed. The composition of the corrosion products was determined based on the strongest reflection lines in the XRD patterns.



Fig. 2. Appearance of MS after 1 year exposed at station 1.

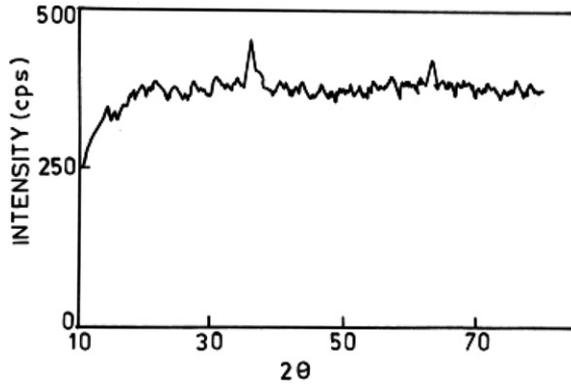


Fig. 3. XRD pattern of MS corrosion products exposed for 1 year at station 1.

Fig. 3 shows the main phase in the oxide layer formed on MS exposed at station 1. According to XRD results, the ' $d$ ' values of 2.51 Å unit is a well defined strong line and is due to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. But at the same value, a line with ' $d$ ' values of 6.2 Å unit obtained corresponds to the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O. There are also other peaks whose ' $d$ ' values of 1.94; and 1.69 Å are due to the formation of Fe<sub>3</sub>S<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, FeS · H<sub>2</sub>O, respectively. Lepidocrocite is also present which is characterized by the peak intensity ' $d$ ' value of 3.26 Å unit. A corrosion product consisting of lepidocrocite was therefore likely to be protective, whereas one high in magnetite and or FeS was likely to be aggressive. Mainly chloride and SO<sub>2</sub> were deposited on the corroding surface resulting in the formation of the above stated corrosion products containing S. At the 1 and 6 sites, with higher pollution levels sulphate nests were formed, giving rise to a localized form of corrosion and higher losses of corrosion products due to the flaking off of the rust particles. The corrosion rate is decreased markedly with time and the corrosion loss obeyed the power function,  $C = Kt^n$ .

Fig. 4 shows the XRD pattern of corrosion product of Zn at station 1. The most commonly found corrosion products on Zn surfaces are mainly 4ZnO · CO<sub>2</sub> · 4 · H<sub>2</sub>O ( $d = 6.41$  Å), basic ZnCl<sub>2</sub> · 4Zn(OH)<sub>2</sub> and ZnCO<sub>3</sub> ( $d = 2.70$  Å) and ZnO ( $d = 2.51$  Å),

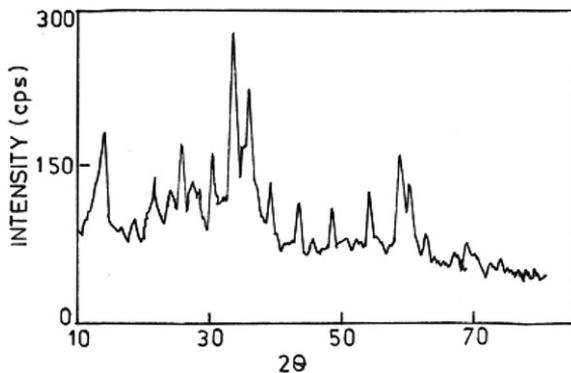


Fig. 4. XRD pattern of Zn corrosion products exposed for 1 year at station 1.

$\text{ZnCO}_3$ ,  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  ( $d = 3.49 \text{ \AA}$ ). Odnevall and Leygraf [53] suggested that the corrosive attack by chloride of the protective hydrozincite layer formed initially involves the transformation of this carbonated into a hydroxy chloride. This compound was detected in the zinc corrosion products formed in marine atmosphere. It obviously has a high solubility and gets easily dissolved in weak acid solutions such as rainfall or dew [54].

At stations 3 and 5, Zn and GI corroded at a very slow rate (about  $1.2\text{--}3 \mu\text{m y}^{-1}$ ), which was 5–10 times slower than that at stations 1 and 6 (mixed atmospheres). Earlier studies [55,56] suggested that the presence of atmospheric pollutants was not necessary for significant corrosion rates to be obtained for Zn. As with other metals, the corrosive attack of Zn at stations 3 and 5, the product is discontinuous in nature, varied only during humid periods. The resistance of Zn to atmospheric corrosion was dependent on the nature of the corrosion products formed. The main component was usually basic  $\text{ZnCO}_3$ . The corrosion rate of Zn, although much lower, correlated well with those of the MS sample. At higher pollution levels, localized corrosion appeared on GI surface exhibiting the corrosion products very similar to the sulphate nests found on the MS surface. Zn coating normally exhibited excellent and predictable performance. Zn provided protection to MS in two ways. First and foremost it served as a very effective barrier coating due to its inherently better corrosion resistance compared to the MS, since the corrosion rate of Zn is 1/10th of MS. The second protective mechanism exhibited by Zn is the result of its galvanic relationship to the MS. In most environments, Zn is corroded preferentially to protect steel at scratches and sheared edges. The corrosion rate of Zn coating mainly depended on the environmental pollution factors. There has been little corrosion progression over a period of 5 years at stations 3–5 and 8–10. The highest corrosion rates for GI were observed at 1 and 6. The results from the station 1 indicated that after one and half years, the GI panels were completely corroded. At stations 2 and 7 severe corrosion of GI panels was observed. The corrosion rate of GI was in the range from  $0.32$  to  $18.41 \mu\text{m y}^{-1}$  for exposure period of first year. This rate was almost similar to that of Zn. Interestingly in the case of zinc,  $C_5$  corrosivity category is very less.

Fig. 5 shows the XRD pattern of the corrosion products formed on Al at station 1. The corrosion products are mainly  $\text{Al}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  ( $d = 3.07 \text{ \AA}$ ),  $\text{Al}_2(\text{SO}_4)_3\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  ( $d = 3.31 \text{ \AA}$ )  $\text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  ( $d = 7.02 \text{ \AA}$ ) and  $\alpha\text{-Al}_2\text{O}(\text{OH})_2$  ( $d = 6.46 \text{ \AA}$ ). The climatological condition prevailed at 1 and 6 stations promoted the attack on Al surfaces, which

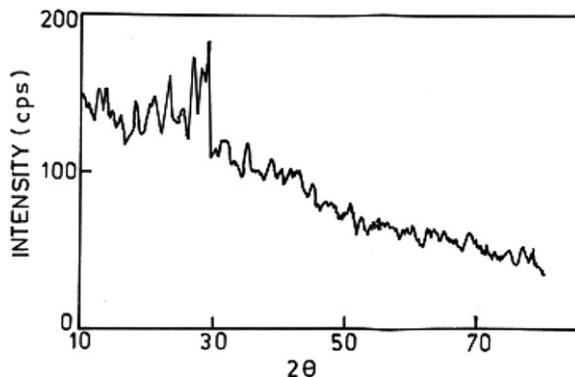


Fig. 5. XRD pattern of Al corrosion products exposed for 1 year at station 1.

is not seen in any other exposure stations. Al corrosion in these types of mixed atmospheres was practically generalized due to the highest level of  $\text{Cl}^{-1}$ ,  $\text{SO}_2$ , despite large amount of moistures and dust particles from the harbors. Macroscopically uniform attack was observed at the low pollution stations whereas at the stations with a higher pollution level localized form of attack and even deeper pitting was visually observed. For Al, only 4 exposure stations have C5 corrosivity category. Out of four stations, three are located in the east and west coast, and another one in the interior part. The interesting feature for Al is that the corrosion rate varied widely from location to location and therefore the performance of Al is more location specific than MS, Zn and GI.

The results indicated that the lower polluted environment (at 5 and 10) had lesser corrosive attack than the other marine and rural environments. At stations 1 and 6, MS suffered corrosion above the limiting level ( $>200 \mu\text{m y}^{-1}$  extremely severe). The corrosion rate of Zn at 6 was above the limiting level ( $>10 \mu\text{m y}^{-1}$  extremely severe) whereas GI at 1 was above the limiting level ( $>20 \mu\text{m y}^{-1}$  extremely severe). The corrosion rate of Al was below the limiting level ( $<20 \mu\text{m y}^{-1}$ ) at all the exposure stations. These metals can be ranked in order of decreasing atmospheric corrosion resistance as

*Mild steel:* Chennai > MPT > Manali > Mangalore > Cuddalore > Mumbai > NIO > Nagapattinam > Surat > Mahendragiri.

*Zinc:* MPT > Chennai > Mahendragiri > Manali > Nagapattinam > Mumbai > Cuddalore > Surat > Mangalore > NIO.

*Galvanized iron:* MPT > Chennai > Manali > Cuddalore > Manali > Mahendragiri > Surat > Mangalore > NIO > Nagapattinam.

*Aluminium:* MPT > Chennai > Mahendragiri > Mangalore > Mumbai > Cuddalore > Surat > Manali > Nagapattinam > NIO.

### 3.3. Kinetic studies

When modeling the data relative to the corrosion rate, we have used the Eq. (1) for all the stations. Very high correlation coefficient ' $r^2$ ' was found in all the cases. The representation of the corrosion data vs time on log–log coordinates will therefore give points

Table 6  
Corrosion kinetic parameters  $K$ ,  $n$ , and correlation coefficient  $r^2$  for MS, GI, Zn and Al

Testing station		MS			GI			Zn			Al		
No.	Location	$K$ ( $\mu\text{m}$ )	$n$	$r^2$	$K$ ( $\mu\text{m}$ )	$n$	$r^2$	$K$ ( $\mu\text{m}$ )	$n$	$r^2$	$K$ ( $\mu\text{m}$ )	$n$	$r^2$
1	Chennai	531.61	0.79	0.99	11.36	–	0.99	7.13	1.28	0.99	8.47	1.46	0.99
2	Cuddalore	58.57	0.65	0.90	5.51	0.30	0.44	2.85	1.36	0.95	2.35	0.47	0.98
3	Nagapattinam	32.43	0.35	0.94	0.49	2.39	0.94	3.02	0.37	0.93	1.42	0.49	0.94
4	Mangalore	115.04	0.50	0.99	2.46	0.66	1.00	1.41	0.58	0.97	5.31	0.26	0.92
5	NIO, Gao	30.58	0.62	0.99	2.27	0.77	0.99	1.25	1.12	0.95	0.26	0.93	0.98
6	MPT	468.01	0.46	0.99	19.37	0.43	0.99	23.22	0.62	0.99	7.99	1.46	0.94
7	Manali	107.74	0.49	0.96	4.52	0.70	0.99	2.99	0.63	0.97	1.41	0.99	0.98
8	Mumbai	44.31	0.29	0.97	3.95	0.42	0.87	2.53	0.63	0.99	2.60	0.44	0.98
9	Surat	29.65	0.46	0.98	2.98	0.42	0.97	2.27	0.37	0.95	1.83	0.46	0.99
10	Mahendragiri	14.52	0.35	0.98	3.75	0.86	0.99	5.90	0.62	0.88	5.61	0.55	0.96

approximately on the straight lines of slope ' $n$ ', and intersections of ordinate ' $K$ ', for  $t = 1$ . Figs. 5–8 show the log–log plots obtained and Table 6 shows the values for ' $n$ ', ' $K$ ' and correlation coefficients ' $r^2$ ' for each one of the metal.

### 3.3.1. Mild steel

The weight loss data were analyzed by power function (Eq. (2)). Figs. 6a–6c show the weight loss data for MS exposed at 10 locations. On log–log coordinates, the points lie close to a straight line for all the stations. Thus, it is reasonable to accept the verification of law of power function to estimate long-term corrosion of MS. The correlation coefficient ' $r^2$ ' for the analysis was 0.94 or greater, indicating an excellent correlation of the data.

For exposure stations 1 and 6 with a very high ( $C_5$  category) degree of atmospheric aggressiveness, the corrosion data obtained during a period of testing of 5 years were not deviated from the straight line. Regarding the exponent ' $n$ ' for the atmosphere in which this study was carried out, it was in the range of 0.3–0.8 (Table 6). In general, this value was greater for the aggressive atmosphere in which more significant amount of  $SO_2$  and salinity was found.

For the exposure stations 3, 4, 6, 7, 8, 9 and 10 the ' $n$ ' value was  $\approx 0.5$ , indicating that corrosion of MS was under the diffusion controlled and the diffusion of corrosive species was the rate determining step (i.e.  $n = 0.5$ , when the corrosion product was protective and inhibit further corrosion by diffusion). The ' $n$ ' values of greater than 0.5 were observed at exposure stations 1, 2 and 5 indicated that the acceleration of the diffusion process as a result of the rust detachment by erosion, flaking, cracking, etc. The value of ' $n$ ' for station 1 was 0.785. This result suggested mixed diffusion and charge transfer control and also a

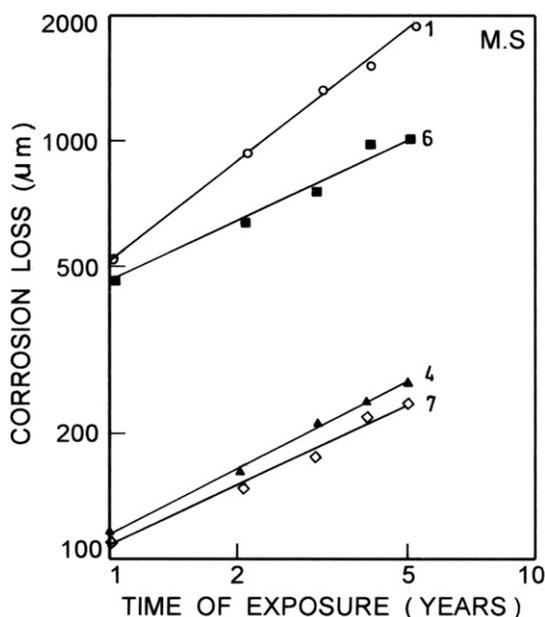


Fig. 6a. Log corrosion loss as a function of log time for MS: 1—Chennai, 4—Mangalore, 6—MPT and 7—Manali.

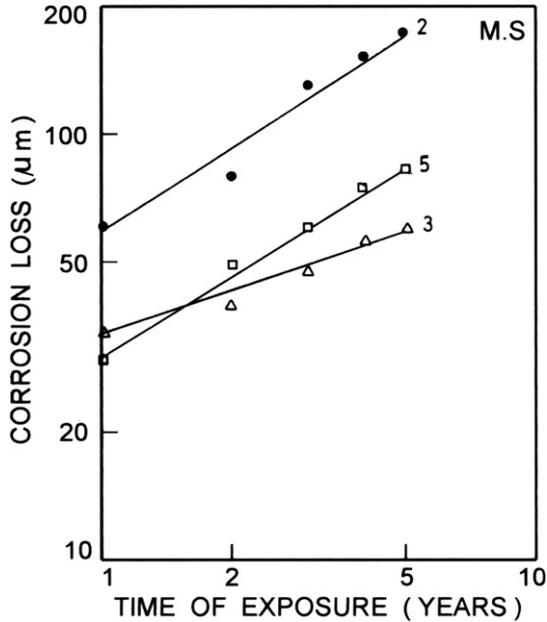


Fig. 6b. Log corrosion loss as a function of log time for MS: 2—Cuddalore, 3—Nagapattinam and 5—NIO.

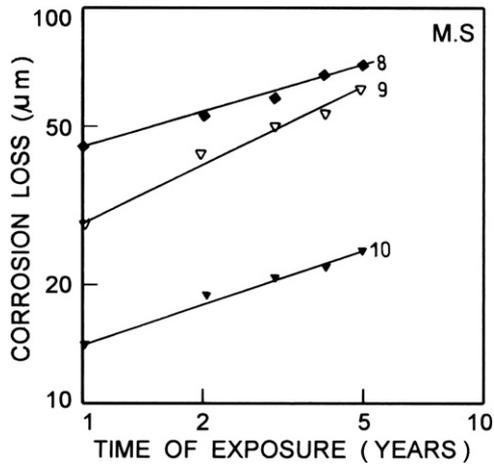


Fig. 6c. Log corrosion loss as a function of log time for MS: 8—Mumbai, 9—Surat and 10—Mahendragiri.

gradual change from the diffusion control due to the presence of the protective corrosion product layers to charge transfer control which was either bare or not covered with layers which lowered diffusion of corrosive species to the metal surface.

The value of ' $K$ ' was equal to the corrosion loss after a first year exposure and indicated the vulnerability to rusting at the beginning of the exposure. The value of ' $K$ ' was fluctuating a little at various exposure stations (from 14.517 to 58.57  $\mu\text{m}$ ). Only the stations 1, 4, 6 and 7 showed a higher value of ' $K$ ', between 107.54 and 531.61  $\mu\text{m}$ .

### 3.3.2. Zinc

In Figs. 7a–7c, the corrosion data of Zn obtained for different periods up to 5 years of exposure are shown. It can be seen that the points are well aligned at all of the test sites and ' $r^2$ ' value is very near to unity. Thus, Eq. (2) was verified, with ' $n$ ' values are between 0.36 and 1.35. The highest value of ' $n$ ' ever reported was 1.2 as reported by Morcillo et al. [26] for Zn at Barcelona in the Spain. However, in the present study, the value of  $n$  was  $>1$  at station 1, 2 and 5 for Zn. These three marine exposure stations had an annual average maximum and minimum temperature of 39, 35 and 31 °C and 20, 21 and 16 °C, respectively, and the RH was greater than 65%. Although the ' $n$ ' values were very high at station 1, 2 and 5 for Zn, their ' $K$ ' values were two of the lowest of the 3 exposure stations except station 1.

### 3.3.3. Galvanized iron

Figs. 8a and 8b show a good correlation between the corrosion data of galvanized iron vs time. Most of the points are found on the straight line. For two exposure stations (1 and 6), very high corrosion loss was observed. The value of ' $n$ ' was close to 0.5 for GI at the

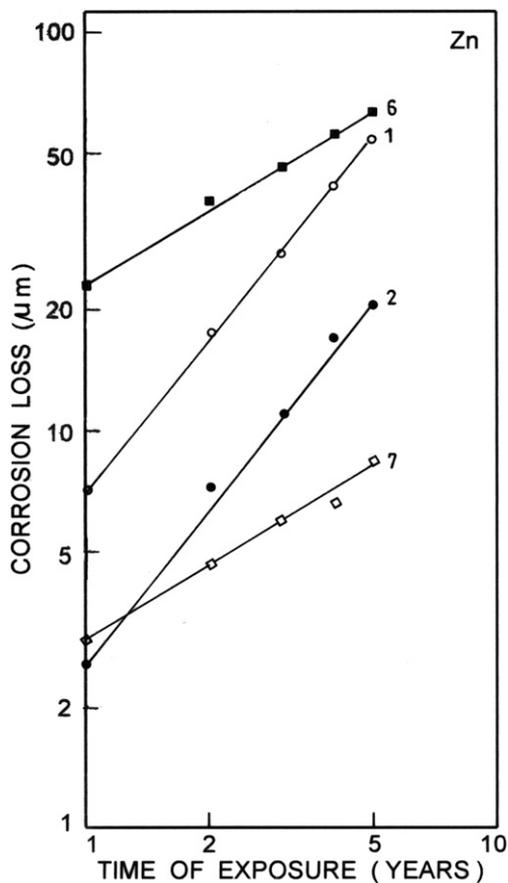


Fig. 7a. Log corrosion loss as a function of log time for Zn: 1—Chennai, 2—Cuddalore, 6—MPT and 7—Manali.

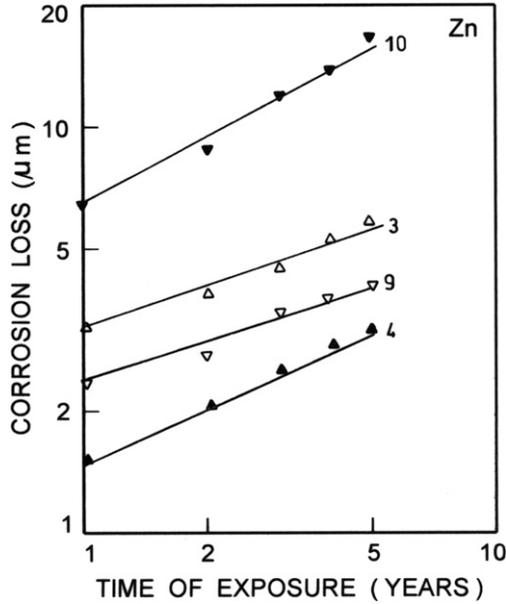


Fig. 7b. Log corrosion loss as a function of log time for Zn: 3—Nagapattinam, 4—Mangalore, 9—Surat and 10—Mahendragiri.

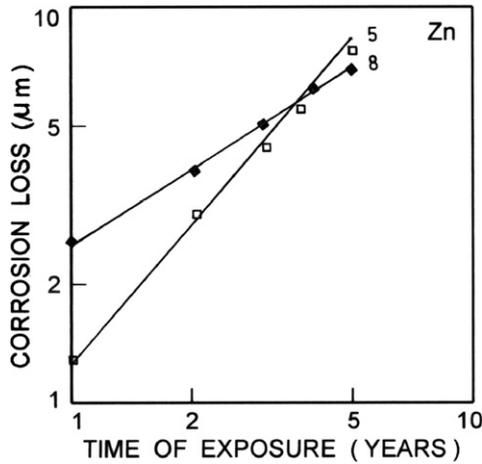


Fig. 7c. Log corrosion loss as a function of log time for Zn: 5—NIO and 8—Mumbai.

stations 4, 6, 8 and 9 indicating a diffusion controlled mechanism and  $n = 0.6-0.9$  at the stations 5, 7 and 10 indicating a gradual change from diffusion control mechanism to charge transfer control mechanism. For the station 3, the value of  $n$  was greater than 1. Based on the corrosion rate data, the of corrosivity of various stations found is given below:  $C_5$  for 1, 6 and 7;  $C_4$  for 2, 8, 9 and 10;  $C_2$  for 3, 4 and 5. It was observed from

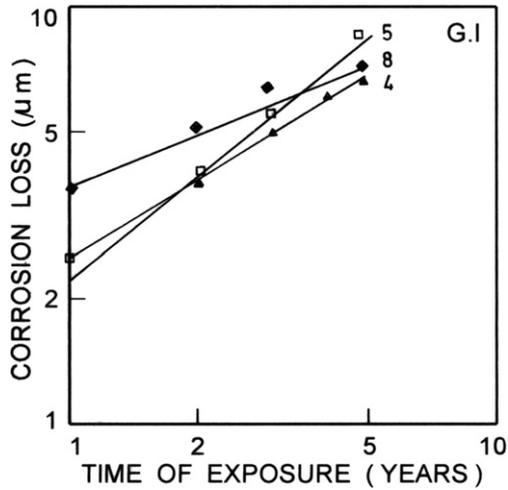


Fig. 8a. Log corrosion loss as a function of log time for GI: 4—Mangalore, 5—NIO and 8—Mumbai.

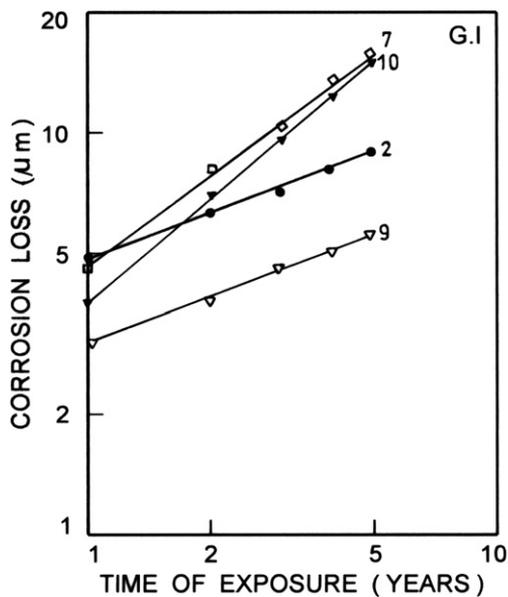


Fig. 8b. Log corrosion loss as a function of log time for GI: 2—Cuddalore, 7—Manali, 9—Surat and 10—Mahendragiri.

the log–log plot (Figs. 8a and 8b) that the corrosion rate of GI exposed at the station 3 (marine environment) consisted of two linear segments of an initial slope ‘ $n$ ’ 0.43 followed by a second segment with a high slope of ‘ $n$ ’ 2.38. This type of anomalous behaviour was observed where no SO<sub>2</sub> was present.

### 3.3.4. Aluminium

The corrosion loss of Al as a function of the exposure time (Figs. 9a and 9b) shows that the data usually fall close to the straight line based on power function; with 'n' exponent values are in the range of 0.26–1.45. Very low corrosion loss was observed for the Al at the station 5 ( $C_1$  corrosivity category). The highest corrosion loss were observed at the stations 1, 4, 6, and 10 ( $C_5$  corrosivity categories) whereas  $C_3$  and  $C_4$  corrosivity categories (medium corrosion loss) were found at stations 2, 3, 7 and 9 and 8, respectively.

The graphically determined values of 'K' and 'n' thus obtained, are given in Table 6 together with the corresponding correlation coefficients ' $r^2$ ' to provide an indication of quality of fit. Additional evidence of the quality of fit is presented in Figs. 10–13 in which predicted values of corrosion loss in terms of  $\mu\text{m}$  are plotted against the corresponding experimental values for MS, Zn, GI and Al for the period of 5 year exposures at all 10 stations. Reasonable agreements between experimental and predicted results are observed as shown in Figs. 10–13.

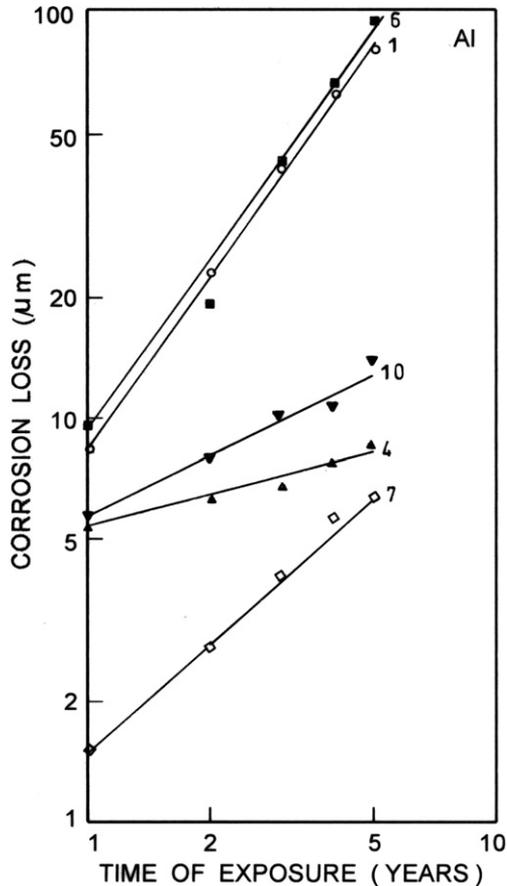


Fig. 9a. Log corrosion loss as a function of log time for Al: 1—Chennai, 4—Mangalore, 6—MPT, 7—Manali and 10—Mahendragiri.

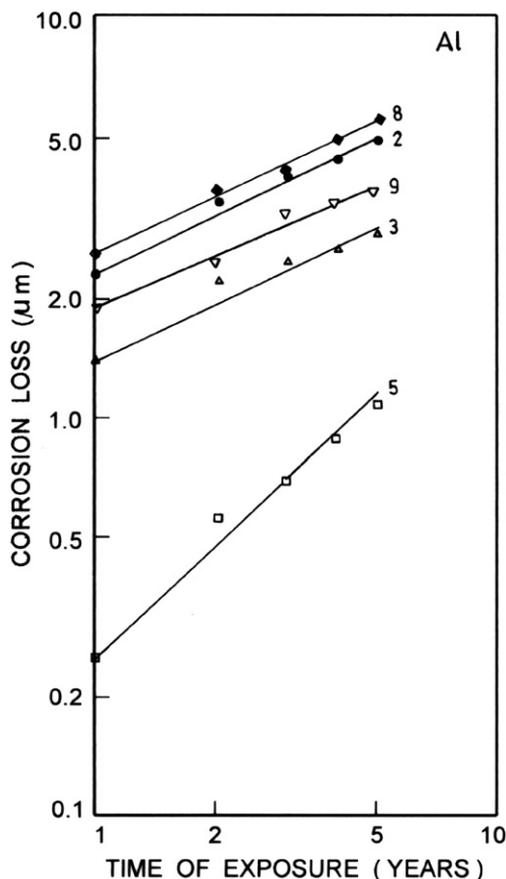


Fig. 9b. Log corrosion loss as a function of log time for Al: 2—Cuddalore, 3—Nagapattinam, 5—NIO, 7—Manali, 8—Mumbai and 9—Surat.

### 3.4. Comparison with previous data

It is of interest to compare the results of the survey with both the previous studies carried out in India, and the corrosion rates found in other parts of the world. The average corrosion rate of 25–50, 50–120 and 120–250  $\mu\text{m y}^{-1}$  were reported for MS in Inland, West and East coast of India, respectively, during the year 1968 [32]; Sundaram et al. [57] studied the corrosion behaviour of MS, Zn and Al in marine environment at the corrosion testing center, Mandapam Camp India and found the rates 56, 8 and 0.55  $\mu\text{m y}^{-1}$  for MS, Zn and Al, respectively. In the present study (the data given in Table 5) the average corrosion rate of MS in Inland appeared to be reproducible indicating that atmospheric corrosivity in these regions is not changed whereas the marine and industrial areas, the rate of corrosion for MS, Zn and Al showed a very high corrosion rate.

In global terms, the corrosion rate of MS in India appeared particularly to be on the higher side. In comparison with Japan (159  $\mu\text{m y}^{-1}$ ), Sweden (206  $\mu\text{m y}^{-1}$ ), South Africa (429  $\mu\text{m y}^{-1}$ ), USA (2088  $\mu\text{m y}^{-1}$ ), France (801  $\mu\text{m y}^{-1}$ ), and Great Britain (429  $\mu\text{m y}^{-1}$ )

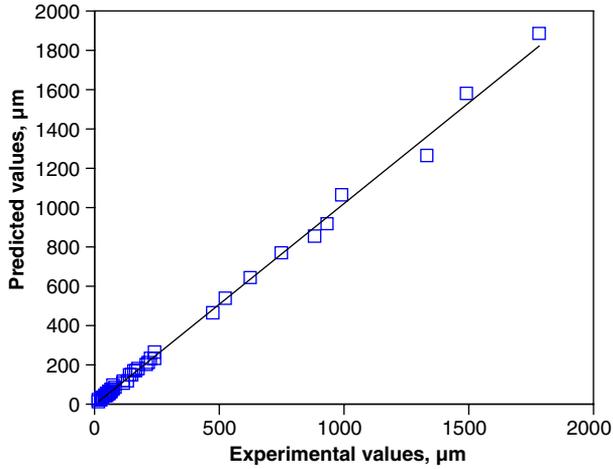


Fig. 10. Experimental values vs predicted values of corrosion loss of MS in 10 exposure stations.

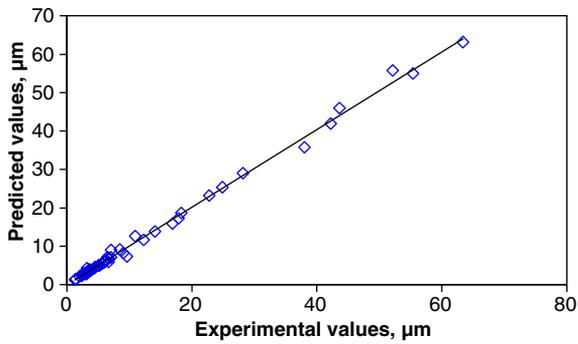


Fig. 11. Experimental values vs predicted values of corrosion loss of Zn in 10 exposure stations.

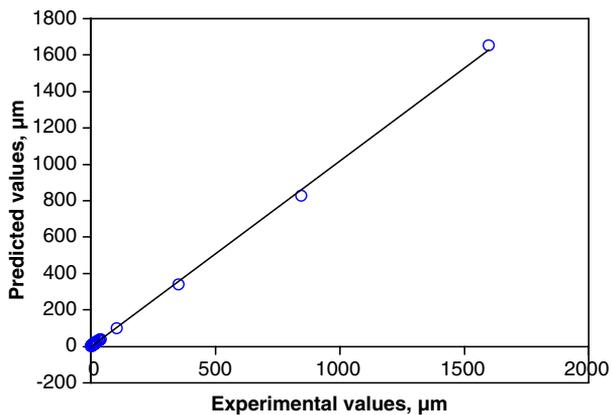


Fig. 12. Experimental values vs predicted values of corrosion loss of GI in 10 exposure stations.

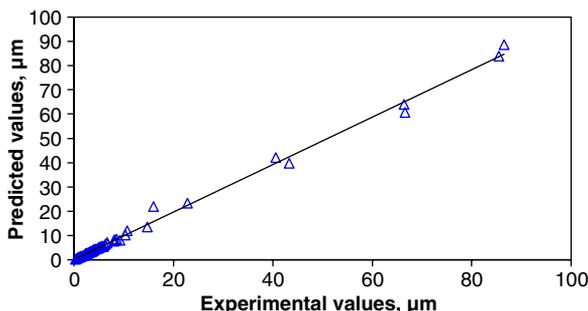


Fig. 13. Experimental values vs predicted values of corrosion loss of Al in 10 exposure stations.

[14], corrosion rate in India occupied second place ( $1600 \mu\text{m y}^{-1}$ ) for the location 50 m away from the sea [33] and fourth place for location 150 m away from sea ( $520 \mu\text{m y}^{-1}$ ). In heavily industrialized and polluted parts of the world much higher corrosion rates have been reported. (e.g. corrosion rate of steel  $110 \mu\text{m y}^{-1}$  in Chicago and  $150 \mu\text{m y}^{-1}$  in London, respectively) [58]. Comparison of the corrosion rate in industrial environments in India, Mettupalayam occupies the top most position ( $300 \mu\text{m y}^{-1}$ ) [33] followed by Manali ( $110 \mu\text{m y}^{-1}$ ). Studies carried out in Australia [59] have shown that the corrosion rates are slightly lower than India. The corrosion rate of GI on comparing with that in New Zealand [18] the rate in India is higher than that of New Zealand.

### 3.5. Durability factor

Durability factor is defined as the ratio between the corrosion rate of MS and corrosion rate of non-ferrous metal exposed at a particular site. The determined durability data have been analyzed and the values are presented in Table 7. It is an important parameter, which will be of immense help to designers in the selection of durable engineering materials for a particular area. Correct selection will lead to enormous savings. The durability data clearly indicated that non-ferrous metals viz. GI, Zn and Al have better durability factors than that of MS. However the factor varies from exposure station to station. The durability

Table 7  
Typical relative durability factor for MS, GI, Zn, and Al

No.	Testing station location	Durability factor			
		MS	GI	Zn	Al
1	Chennai	1	45	74	61
2	Cuddalore	1	12	23	44
3	Nagapattinam	1	90	11	25
4	Mangalore	1	47	79	22
5	NIO, Goa	1	13	24	121
6	MPT	1	25	23	41
7	Manali	1	25	36	79
8	Mumbai	1	12	17	18
9	Surat	1	11	13	15
10	Mahendragiri	1	4	2	3

factor varies from 4.0 to 90, 2 to 79 and 3 to 121 for GI, Zn and Al, respectively. Very high durability factor for Zn was observed at marine ( $S_1P_0$ ) exposure station 4 and lowest durability was observed at 10, which is situated in the  $S_0P_0$  atmosphere. For GI, the highest durability factor was observed at station 3, which is situated in the  $S_1P_0$  atmosphere, and the lowest was at station 10. In the case of Al very high durability factor was observed at ( $S_0P_0$  category) station 5 and lowest was at exposure station 10.

The above durability data were determined from 1-year corrosion data. Generation of long-term data will yield realistic picture on relative durability. Particularly in the case of Al, long-term exposure may some time result in to localized corrosion.

### 3.6. Conclusions

Test specimens exposed to 10 different stations exhibited extremely large difference in the corrosion loss. The corrosivity categories according to ISO/DIS 9223 showed large variations for the different stations.

At all exposure stations, a linear relationship between corrosion losses is with exposure time was observed.

These metals can be ranked in order of decreasing atmospheric corrosion resistance as

*Mild steel:* Chennai > MPT > Manali > Mangalore > Cuddalore > Mumbai > NIO > Nagapattinam > Surat > Mahendragiri.

*Zinc:* MPT > Chennai > Mahendragiri > Manali > Nagapattinam > Mumbai > Cuddalore > Surat > Mangalore > NIO.

*Galvanized iron:* MPT > Chennai > Manali > Cuddalore > Manali > Mahendragiri > Surat > Mangalore > NIO > Nagapattinam.

*Aluminium:* MPT > Chennai > Mahendragiri > Mangalore > Mumbai > Cuddalore > Surat > Manali > Nagapattinam > NIO.

The compositions of corrosion products found in the metals have been identified by XRD method. The durability data clearly indicated that non-ferrous metals viz. GI, Zn and Al have better durability factor than that of bare mild steel. However this factor varies from exposure station to station.

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