



# The atmospheric corrosion kinetics of low carbon steel in a tropical marine environment

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## ABSTRACT

The atmospheric corrosion kinetics of low carbon steel exposed for up to 36 months in marine and industrial sites was studied by weight loss measurements. The results show that the mechanism and kinetics of the atmospheric corrosion process presents transition behaviour in marine environments with high chloride ion content and high relative humidity, whereas no transition appears in industrial environment. The average corrosion velocity in marine site reaches a maximum during the period of transition and then fluctuates in a certain range; however, the instantaneous corrosion velocity follows different exponential functions before and after the period of transition.

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## 1. Introduction

The atmospheric corrosion of structures such as towers, bridge and construction materials to mention but a few is a source of concern in modern societies. 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 technologies [1]. It is therefore advantageous to develop more advanced corrosion control technologies and cost reduction strategies in terms of investigating the atmospheric corrosion mechanism of structural materials. The mechanisms of atmospheric corrosion including the enhanced effect of alloy element [2–5], the accelerated effect of corrosive pollutant [6–9], the influence of environmental parameter [10–12] and the protective mechanism of corrosion product [13–17], have been widely studied in different environments and excellent results have been obtained. Nevertheless, it should be more beneficial from the point of view of practice-based applications to focus on the atmospheric corrosion kinetics, which can provide pivotal parameters to forecast the long-term corrosion of structural materials [18,19].

From extensive field tests in different environments the atmospheric corrosion kinetics can be determined by the following empirical equation [20–23]:

$$D = At^n \quad (1)$$

where  $D$  is thickness loss ( $\mu\text{m}$ ),  $t$  is exposure time (month),  $A$  and  $n$  are constants. The validity of the equation and its reliability to predict long-term corrosion has been demonstrated by many authors

[12,24–26]. Normally, the severity of corrosive environment can be best measured by  $A$  values, while the protectiveness of rust layer can be best measured by  $1/n$  values [27]. However, the value of  $n$  as related to the atmospheric corrosion kinetics of structural materials has not received much attention [28]. As a matter of fact, it is instrumental in comprehending the mechanism of atmospheric corrosion kinetics. The present study was undertaken to evaluate the relationship between  $n$  value and mechanism of corrosion kinetics as well as to clarify the fundamental nature of the abnormal kinetic phenomenon for low carbon steel in a tropical marine environment.

## 2. Experimental procedure

### 2.1. Materials preparation

Low carbon steel (Q235) was used as the test material and its composition is listed in Table 1 [29]. The specimens were cut into  $100\text{ mm} \times 45\text{ mm} \times 5\text{ mm}$  coupons and polished down to # 800 grade emery paper, cleaned ultrasonically in acetone and then rinsed with distilled water. All the specimens were weighed and prepared for exposure test.

### 2.2. Atmospheric exposure tests

Atmospheric corrosion tests were undertaken at two different test sites, i.e. atmospheric corrosion station in Wanning city (marine site:  $110^\circ 05'$  eastern longitude and  $18^\circ 58'$  northern latitude; SITE 1) and Shenyang city (industrial site:  $123^\circ 24'$  eastern longitude and  $41^\circ 32'$  northern latitude; SITE 2). The climatic characterization and the main environmental parameters measured are listed in Table 2. According to ISO-4542 specification, the low

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**Table 1**

Chemical compositions of the low carbon steel studied (wt.%).

Steel	C	S	P	Mn	Si	Cu
Q235	0.176	0.023	0.019	0.57	0.233	0.033

**Table 2**

Environmental conditions of natural exposure sites.

Test site	Environment	Average temp. (°C)	Average relative humidity (%)	Cl <sup>-</sup> (mg m <sup>-2</sup> /day)	SO <sub>2</sub> (mg m <sup>-2</sup> /day)
Wanning	Marine	24.7	87	38.7	6
Shenyang	Industrial	9.2	66	2.48	76.51

carbon steel specimens (Q235) were exposed at 30° to the horizontal, with skyward surface facing the sea; Three test specimens were retrieved from the marine site for analyses after 3, 6, 9, 12, 18, 24 and 36 months of exposure. For gravimetric measurements, corrosion products on the specimen surfaces were removed chemically by immersion in a specific solution (500 ml HCl + 500 ml distilled water + 3.5 g hexamethylenetetramine) that was vigorously stirred for ~10 min at 25 °C. After corrosion products had been completely removed, the specimens were rinsed with distilled water, dried with warm air, and then weighed to determine their mass loss.

### 3. Results and discussion

#### 3.1. Atmospheric corrosion kinetics

The thickness loss (thinning) ( $\mu\text{m}$ ) of low carbon steel in different sites can be calculated using the following equation:

$$D = W_t \times 10^4 / \rho A \quad (2)$$

where  $D$  is thickness loss ( $\mu\text{m}$ ),  $W_t$  is the weight loss (g),  $\rho$  is the density ( $7.86 \text{ g cm}^{-3}$ ) of the low carbon steel and  $A$  is the exposed area ( $\text{cm}^2$ ) of the specimen. Fig. 1 shows the rate of thinning of low carbon steel specimens exposed in the different sites. The thinning process increased gradually with prolonged exposure time, and was always more pronounced in SITE 1 indicating a higher

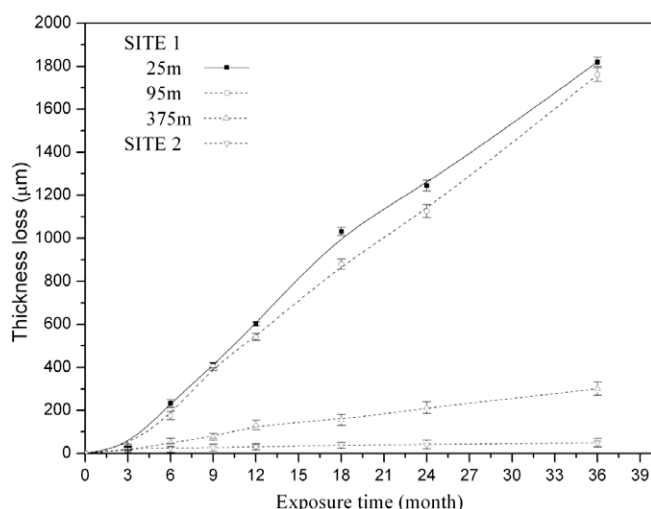
corrosion susceptibility of the test specimens in this environment. Furthermore, the nearer the specimen is to the sea line, the greater the rate of thinning.

According to the field test, the evolution of atmospheric corrosion kinetics followed Eq. (1). The corrosion data obtained from different environments can be fitted using the empirical equation, aiming to forecast the corrosion behaviour of steel during the extended exposure periods. Unfortunately, emphasis has been laid on variations of  $A$  and  $n$  values, while kinetic and mechanistic information have been more or less neglected. Townsend and Zoccola [24] have proposed a method to analyze corrosion data using linear regression analysis to fit a straight line on log–log plot of weight loss vs. exposure time. Although this method can be effectively used to study the evolution of atmospheric corrosion, it is still superficial to provide detailed insight into the kinetics of the process.

Fig. 2 reproduces the results in Fig. 1 by plotting the thickness loss against exposure time in log–log coordinates. It is obvious that the log–log plots in SITE 1 (Fig. 2a–c) consist of two discontinuous line segments; the slope of the second segment being smaller than that of initial segment, corresponding to the results in Ref. [7]. Such discontinuity is not observed in the log–log plot for SITE 2 (Fig. 2d), which comprises a single linear plot. These line segments can be fitted by equation (3) by taking logarithm of Eq. (1):

$$\log D = \log A + n \log t \quad (3)$$

The fitting expressions and correlation coefficient ( $R^2$ ) are shown in Fig. 2. From the fitting results, two different kinds of corrosion process have appeared in three stations in SITE 1. For the first step (I) in SITE 1, all the values of  $n$  are more than 1, meaning acceleration process; however, the values of  $n$  in 25 m and 95 m stations are still more than 1, indicating the acceleration process of second step (II) except at 375 m station. The change in slope of the log–log plot in SITE 1 means that the kinetics of atmospheric corrosion of low carbon steel manifests a transition step during the period of exposure. Furthermore, the time of transition moves forward the further the exposure station away from the sea line. The value of  $n$  really reflects the character of atmospheric corrosion kinetics, that is to say,  $n < 1$  means corrosion deceleration process and  $n > 1$  means an acceleration process;  $n = 1$  means the corrosion rate is constant [9]. Fig. 3 shows the variation of  $n$  obtained from Fig. 2 using linear regression. In SITE 2,  $n$  is less than 1, indicating the corrosion deceleration process during the whole period of exposure and the corrosion products formed on low carbon steel inhibits the corrosion process. In the three exposure stations of SITE 1, the values of  $n$  are all more than 1 before transition, indicative of corrosion acceleration process during the initial stage of exposure and become more pronounced closer to the sea line. In the 25 m and 95 m station, the values of  $n$  are still greater than 1 after transition, indicating persistence corrosion acceleration process, although the slightly lower values of  $n$  in the region implies that the accelerating effect is slightly reduced. In the 375 m station, the value of  $n$  is consistently less than 1, which is indicative of transformation from corrosion acceleration to deceleration. To account for these observations one must first realize that the concentration of chloride ions in marine environments decreases initially as we move away from the sea line and subsequently maintains almost steady values after a certain distance [30]. Accordingly, the concentration of chloride ion in the 25 m and 95 m stations is high and accelerates the corrosion process, resulting in  $n$  values greater than 1 before and after the transition step. At the 375 m station, the concentration of chloride ion becomes much reduced, leading to lower corrosion rates and hence  $n$  values less than 1. In other words, there is a transformation from corrosion acceleration to corrosion deceleration.



**Fig. 1.** Thickness loss of low carbon steel as a function of exposure time in different exposure sites. (■) Samples exposed at 25 m station from the sea line; (○) samples exposed at 95 m station from the sea line; (△) samples exposed at 375 m station from the sea line; (▽) samples exposed at industrial environment.

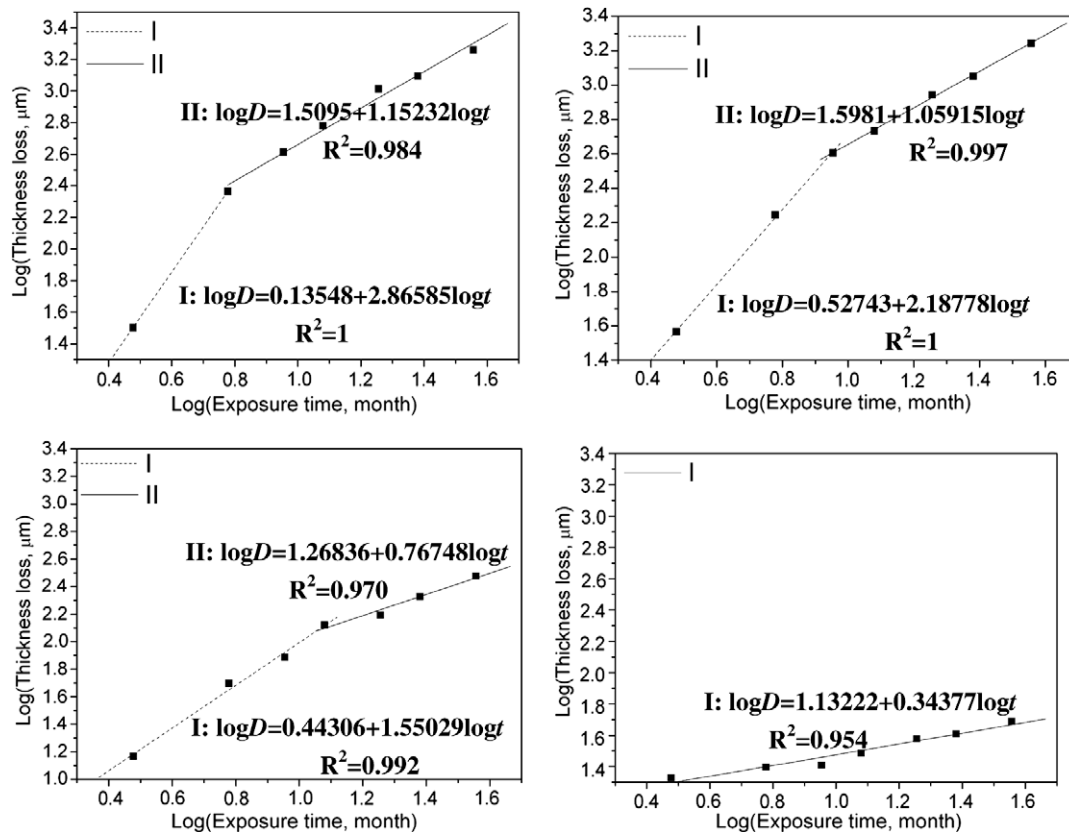


Fig. 2. Bilogarithmic plots of data points from Fig. 1: (a) 25 m station in SITE 1; (b) 95 m station in SITE 1; (c) 375 m station in SITE 1; (d) SITE 2.

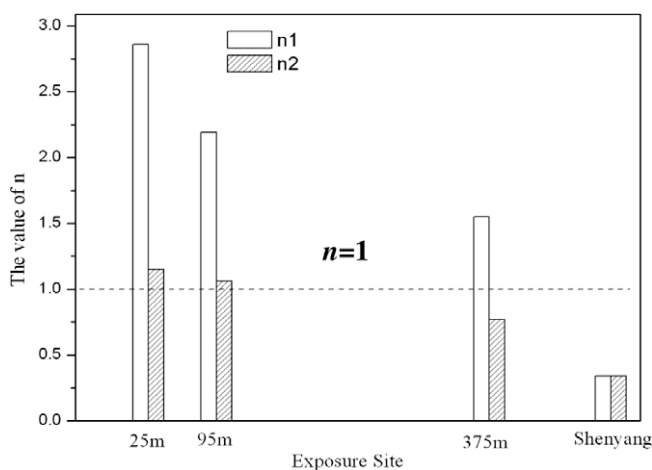


Fig. 3. The variation of  $n$  value in different exposure sites.

### 3.2. Corrosion rate of low carbon steel

The average corrosion velocity ( $V_a$ ,  $\mu\text{m}/\text{year}$ ) was calculated using the following equation [31]:

$$V_a = \frac{D_m - D_{m-1}}{t_m - t_{m-1}} \quad (4)$$

where  $V_a$  is the average corrosion velocity ( $\mu\text{m}/\text{year}$ ),  $D$  is the thickness loss ( $\mu\text{m}$ ),  $t$  is the exposure time (month),  $m$  is the period of sampling (when  $m=1$ , it means the sample is exposed for 3 months, in turn  $m=2, 3, 4, 5, 6, 7$ , means the sample is exposed for 6, 9, 12, 18, 24 and 36 months, respectively). Fig. 4 shows the variation of  $V_a$  with exposure time. The three stations in SITE 1

show similar trends of remarkable fluctuations in the average corrosion velocity during the whole period of exposure; further inspection of the figure reveals that  $V_a$  gradually increases as the sea line is approached. Conversely, for SITE 2,  $V_a$  presents a distinct trend, diminishing steadily with the prolonged exposure time.

In general, the atmospheric corrosion rate decreased with the prolongation of exposure time [32]. However, it has been reported that the corrosion rates in marine environments manifest a so-called "Reverse Phenomenon" in which the average corrosion velocity firstly augments, and then decreases, and again suddenly increases in a certain period [33]; that is to say, the average corrosion velocity reaches minimum in a given period and subsequently

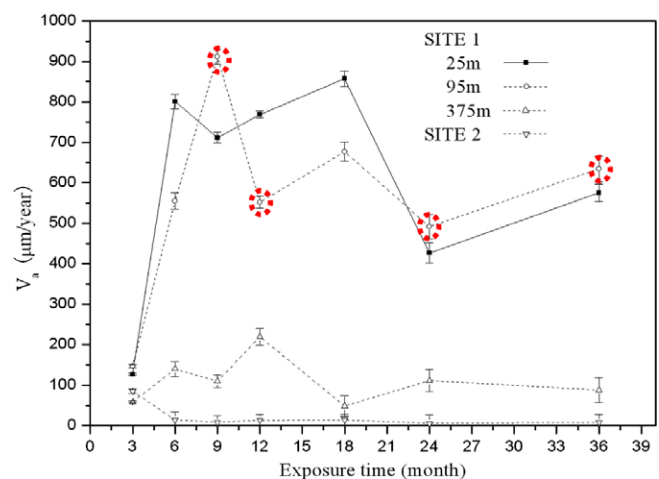


Fig. 4. The variation of average corrosion velocity ( $V_a$ ) of low carbon steel as a function of exposure time in different sites.

represents accretion trend. This decline and accretion trend about the average corrosion velocity can be called “Reverse Phenomenon”. In my opinion, it is not reasonable to define the “Reverse Phenomenon” on corrosion rate. For instance, in the 95 m station the reverse phenomenon is expected to occur for the selected period of retrieving the samples (9, 12, 24 and 36 months) marked red circle as shown in Fig. 4. The sudden increase in  $V_a$  after 24 months, implies the existence of reverse phenomenon. However, this is not the actual reverse phenomenon, just because of the different period of retrieving samples. Likewise, the other two stations in SITE 1 manifest similar character during the whole period of exposure. The truth is obvious that this special behaviour which the average corrosion velocity fluctuates with exposure time only occurred in marine environment because of the effect of chloride ion [9].

The first derivative of the Eq. (1) yields the instantaneous corrosion velocity ( $V_i$ ,  $\mu\text{m}/\text{year}$ ) as follows:

$$V_i = dD/dt = Ant^{n-1} \quad (5)$$

where the values of  $A$  and  $n$  are obtained from the fitting results of Fig. 2. Fig. 5 shows the variation of instantaneous corrosion velocity with exposure time for low carbon steel in three stations of SITE 1. It is obvious that the instantaneous corrosion velocity follows different trends during the whole period of exposure at the three exposure stations, it increases with the prolongation of exposure time before the transition point; but shows different trends after transition. In the 25 m station, the instantaneous corrosion velocity also increased rapidly with exposure time, but drops drastically on the 6th month and thereafter maintained a gradually but steady increase with time. The other stations in SITE 1 manifest similar behaviour, though the magnitude of the maximum and final values differ slightly.

### 3.3. The analysis of “Reverse Phenomenon”

As an important parameter, corrosion rate had been applied to forecast the long-term atmospheric corrosion of metallic materials in various environments [32,34]. There is no doubt that the above corrosion rate referred in Refs. [32,34] represents an average corrosion velocity rather than the instantaneous corrosion velocity. According to ISO 9223 [35] the corrosion rate represents fluctuating trends during the period of exposure, indicating existence of maximum and minimum values for the corrosion rate. The reason is that the mass loss of the rust material generated during exposure

is determined by measuring the difference in weight before and after the exposure time, whereas the corrosive attack rate does not frequently follow a linear dependence with time [36]. This implies that the effect of corroder species on the corrosion rate can be neglected when calculating corrosion rates. As mentioned above, the average corrosion velocity can be used to forecast the long-term corrosion of metal material, but it can not authentically reflect the trend of atmospheric corrosion because of procedural limitations. Fortunately, the instantaneous corrosion velocity obtained from the Eq (5) truly reflects the trend of atmospheric corrosion because it specifically takes into consideration the effect of corroder attack. Comparing the variation of average corrosion velocity with instantaneous corrosion velocity, it is obvious that the average corrosion velocity in SITE 1 primarily increases in short order and reaches vertex at a certain time, then fluctuates in a certain range, as can be seen in Fig. 4. The so-called reverse phenomenon on corrosion rate is ascribed to the period of retrieving samples. Nevertheless, the variation of instantaneous corrosion velocity as a function of exposure time distinctly follows different continuous monotone functions before and after transition time in SITE 1, as shown in Fig. 5. This implies that the trend of instantaneous corrosion velocity changes with prolonged exposure time. Thus, it could be inferred that the reverse phenomenon is not the transition of average corrosion velocity but the transition of exponential function followed by instantaneous corrosion velocity.

## 4. Conclusions

- (1) The atmospheric corrosion kinetics of low carbon steel in marine site represents transition phenomenon, whereas no transition occurs in industrial site. Furthermore, the transition point moves forward with the increase in chloride ion concentration.
- (2) The variation of  $n$  values indicates the degree of corrosion process,  $n > 1$ , means corrosion acceleration process, whereas  $n < 1$ , indicating corrosion deceleration process.
- (3) Both average corrosion velocity and instantaneous corrosion velocity present maxima, among which the former fluctuates in a certain range after transition; the latter follows another function after transition. The “Reverse Phenomenon” should imply the transition of exponential function followed by the instantaneous corrosion velocity.

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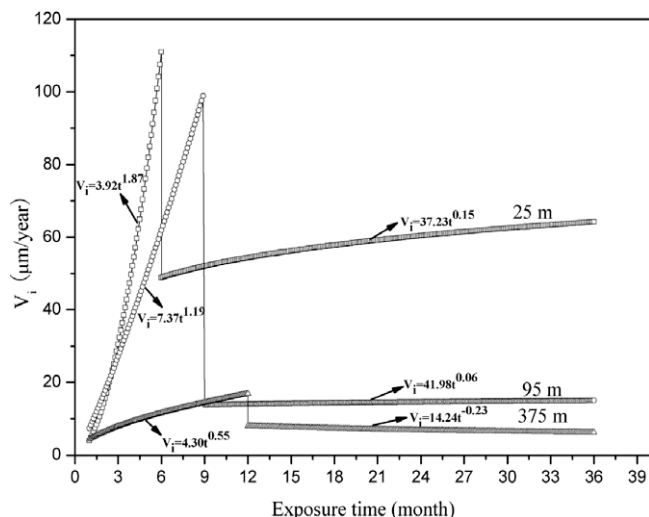


Fig. 5. The variation of instantaneous corrosion velocity ( $V_i$ ) of low carbon steel as a function of exposure time in three stations of SITE 1.

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