Atmospheric and Marine Corrosion: Influential Environmental Factors and Models

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Abstract. The corrosion of metals exposed to the atmosphere and marine environments is expensive to our societies in terms of structure safety and durability. In this paper, the effects of environmental factors on atmospheric and marine corrosion are reviewed as well as the accelerating models. It is revealed that relative humidity, temperature, sulfur dioxide, and chloride are the major influential factors to atmospheric corrosion. Generally, the increase of these factors would cause the increase of corrosion rate and the accelerating effects are nonlinear in most cases. Interactive effects exist between different factors and the mechanisms are complicated. In marine environment, salinity, temperature, dissolved dioxide, pH, oxidation reduction potential and water velocity can influence the corrosion process simultaneously in even more sophisticated mechanisms. Meanwhile, as the marine environmental factors that mentioned above are strongly dependent on each other, it is difficult to analyse the marine environmental factors and the corrosion rate.

1. Introduction

Corrosion has been reported to account for more failures in terms of cost and tonnage than any other type of material degradation process. The components and structures corrosion are inseparable from the environmental factors. At present, the more extensive research is corrosion in the atmosphere and the marine. Under each environment, there are some models about the environmental sensitive factors on corrosion rate, and each environmental factor has different influence on the corrosion rate. So, it is difficult to analyze the influence of a single factor due to the existence of complex interactions between them. In addition, there is also a correlation between different environmental factors. Therefore, environmental factors have a long and complex impact on the corrosion process. Many works have been done to derive accurate models to estimate corrosion under different environmental conditions.

This paper summarizes the commonly used corrosion rate - environmental factors models for atmospheric and marine environment, and gives the parameter meaning and applicable conditions of each model. The interaction between different environmental factors is also briefly discussed.

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2. Effects of environmental factors on atmospheric corrosion

Atmospheric corrosion is simultaneously influenced by various environmental factors. In this paper, only the effects of relative humidity, temperature, sulphur dioxide, and chloride on corrosion are studied. Effects of wind and other factors on atmospheric corrosion are discussed in Ref. [1-4]. The acceleration model is a link that relates the corrosion parameters to the environmental variables. General discussions about which model is useful for different environmental factors in practice can be found in Ref. [5].

2.1. Relative humidity

The increase of relative humidity has been found to increase the corrosion rate [2, 6-8]. Studies have demonstrated that the corrosion current increases following an exponential law when RH increases from 53% to 92% [7] and from 40% to 90% [8]. However, when the relative humidity is below 80% - 85%, nearly no atmospheric corrosion of carbon steel was observed in many studies [9, 10]. This is because that the presence of a film electrolyte formed on metallic surfaces is the fundamental basis to proceed atmospheric corrosion with anodic and cathodic reactions. This threshold is denoted as the critical relative humidity (CRH). Studies have also found that the thickness of the electrolyte film can influence the corrosion rate. Corrosion rates increase with the thickness of the electrolyte film. When the electrolyte film exceeds a finite thickness, corrosion reaction will slow down due to limited oxygen diffusion [11].

In atmospheric conditions, there are many factors that can influence the critical relative humidity level and the thickness of the electrolyte film. These factors include material, corrosion products composition, pollutants concentration, and hygroscopic salts [4]. For instance, N. Van den Steen, et al. [12] have found that sample thickness, heat transfer and changing rates, and relative humidity influence the electrolyte film thickness. When metallic surfaces are contaminated by hygroscopic salts, the surface can be wetted at lower RH [4].

In most applications where relative humidity is used as an accelerating variable, the Peck accelerating model is employed, which is expressed as

$$r(RH) = A \cdot RH^{B}$$
(1)

where *RH* is a proportion denoting relative humidity and *A*, *B* are constants. An alternative relative humidity relationship suggested by Klinger [13] on the basis of a simple corrosion kinetic model, uses the term RH/(1-RH) instead of *RH* in Eq. (1). Thus, the Peck accelerating relation comes to

$$r(RH) = A \cdot \left[RH \left(1 - RH_0 \right) \right]^B$$
⁽²⁾

Note that as $RH \rightarrow 1$, Eq. (2) is singular, and so it is not valid if RH is sufficiently close to 1. The exponential relation proposed by Vernon (Eq. (3)) [14] can be introduced to correlate the corrosion rate with relative humidity, which is

$$r(RH) = A \cdot e^{B \cdot RH} \tag{3}$$

2.2. Temperature

The complicated effect of temperature on corrosion is reflected in two aspects: the influence on corrosion reaction rate directly and influence on electrolyte film formation.

Atmospheric corrosion is an electrochemical process controlled by anodic and cathodic reactions. In theory, the corrosion rate can be correlated to the ambient temperature with the Arrhenius law [5]. It has been suggested that a 2 °C increase in temperature can increase the corrosion rate by 15% [15]. C. Lin [16] studies three kinds of steel in accelerated corrosion tests and develops a corrosion model

deduced from the Arrhenius law. There is also a strong positive correlation between corrosion rate and temperature for magnesium [6, 17] and zinc [7].

In reality, the atmospheric corrosion is a complex discontinuous electrochemical process due to the evaporation and condensation of moisture in highly dynamic environments. Generally, metal surfaces undergoes daily wet-dry cycles. Electrolyte film forms on the metal surface at night when temperature decreases and RH increases, proceeding the corrosion reactions. Corrosion reactions halt after sunrise when temperature increases and the electrolyte film evaporates. In the winter, when the temperature is lower than the freezing point, corrosion reactions cannot proceed due to constrained transport of oxygen to the metal surface.

Theoretically, the effect of temperature on atmospheric corrosion rate is typically described with the Arrhenius relation [5], which follows

$$r(T) = D \cdot e^{-E/T} \tag{4}$$

In Eq. (4), r(T) is the corrosion reaction rate, *D* is a constant. *T* is the thermodynamic temperature in Kelvin. $E = E_a/K$, where E_a is the activation energy which can be estimated from experimental data, and *K* is the Boltzmann constant.

2.3. Sulfur Dioxide and Chloride

Many researchers have demonstrated the accelerating effect of sulfur dioxide on atmospheric corrosion [18-20]. The corrosion rates for metal pieces (bronze, copper, marble and steel) exposed in outdoor environment are found generally proportional to the sulfur dioxide concentration [21], while some researchers [19, 22, 23] used the power function to model the accelerating effect. G. W. Walter [24] indicated that sulfur dioxide will be oxidized to sulfate ion (SO_4^{2-}) in the water. During the process, hydrogen ions (H^+) are produced, which results in the increase of the corrosion rate and causes the dissolution of corrosion products. X. Cao [3] elucidates the reasons of the accelerating effect as following: (a) the cathodic reactant is more effective than the dissolved oxygen because the solubility of sulfur dioxide is about 1,300 times higher than oxygen in the water; (b) the CRH level reduces due to the presence of sulfur dioxide; (c) sulfur dioxide acts as a catalyst and one sulfate ion can catalyze the dissolution of more than 100 atoms of iron.

It has also been reported that the presence of chloride can obviously accelerate the atmospheric corrosion for steel [16], zinc [18], and magnesium alloys [6, 16-18]. When chloride deposits on the metal surface, the electrolyte conductivity increases [6] as well as the time of wetness of the metal surface. The power function [19, 22, 23, 25] and the quadratic function [16, 18] is used to correlate the corrosion loss rate with the chloride deposition rate by some researchers. I.S. Cole [26] has discussed that the chloride deposition is primarily controlled by the wind turbulence, the distance from the coast and also influenced by rain and surface temperature.

J Tidblad [22] and A. A. Mikhailov [23] analyzed the metal exposure investigation of the ISO CORRAG program [27] and derived the dose-response function which follows

$$r(SO_2) = F \cdot SO_2^{\ G} \tag{5}$$

$$r(Cl) = H \cdot Cl^{I} \tag{6}$$

where SO_2 is the sulphur dioxide concentration, Cl is the chloride deposition rate. F, G, H, and I are constants estimated from experimental data. However, Eqs. (5)-(6) are not appropriate because in practice, the corrosion rate does not equal zero when the sulfur dioxide concentration or the chloride deposition rate equals zero. Instead, Eqs. (5)-(6) are modified to the following Eqs. (7)-(8) [19]

$$r(SO_2) = (1 + F \cdot SO_2)^G \tag{7}$$

$$r(Cl) = (1 + H \cdot Cl)^{l} \tag{8}$$

2.4. Discussion

In the field environment, there are interactive effects between different environmental factors. For example, it is showed that the zinc corrosion rate did not show dependence on temperature in the presence of carbon dioxide [28]. Similar results were also reported for copper corrosion in the presence of nitric acid [2]. Moreover, the nitrogen oxides (NO_x) are also important factors that can promote the atmospheric corrosion. J. G. Castano [29] summarizes the effect of NO_x on atmospheric corrosion of different metals (copper, aluminum, nickel, carbon steel and zinc), but no coincident conclusion is drawn. Some authors believe to be of little influence [30, 31], some detected it an inhibitive effect [32, 33], while others consider the effect is dependent on other factors such as humidity [34, 35], the type of the metal [29], and SO₂ concentrations [20, 29]. With such complex mechanisms, the interactive effect between different factors is hard to be fully quantified. In this paper, the effect of SO₂ is included and the interactions between different pollutants are not considered.

Except from the environmental factors discussed above, carbon dioxide, ozone, solar radiation, wind, and rain are also important for different materials. For example, carbonation is the major cause for the failure of concrete structure due to the erosion of carbon dioxide [15]. The corrosion of silver can be accelerated by the presence of ozone and ultraviolet [36]. Solar radiation, wind, and rain can influence the deposition rate of chloride and the time of wetness [4]. When materials are subject to more complex ambient environmental conditions with multiple atmospheric corrosive factors, interactive effect occurs and the effect of each factor should be analyzed carefully.

3. Effects of environmental factors on marine corrosion

Marine environment contains plenty of corrosive media like seawater temperature, dissolved oxygen, water velocity, pH, oxidation reduction potential (ORP) and various dissolved salts, so the influence of marine environment on corrosion is more complex than atmosphere. When components and structures operate in such a complex marine environment, all kinds of corrosion forms are inevitable. Marine corrosion can take different forms, for example: general corrosion, pitting corrosion, stress corrosion cracking, weld corrosion, bimetallic corrosion, filiform corrosion, corrosion fatigue, fretting corrosion and bacterial corrosion [37-39, 51]. In general marine corrosion, which is the most common form of corrosion, the wastage is spread over the surface of the materials [40]. Through the different forms of corrosion, the uniform general corrosion is the type that is considered here.

3.1. Salinity

Seawater is extremely corrosive due to its high salt content. The salinity of seawater generally is 35 ppt and far higher than river water which is only 0.02 ppt. Thus, marine corrosion occurs easily and accelerates the corrosion rates. But the corrosion rates do not rise all the time with the salinity rising. Test shows that corrosion rates reach the maximum when the salinity is 32 to 35 ppt, namely the salinity of natural seawater [45, 49].

This is due to the effect of salinity on the corrosion reaction. On one hand, the transfer speed of the charge is accelerated with the increase of the salinity of the seawater. So, the corrosion rates accelerate obviously. On the other side, with the salt concentration increasing, the solubility of oxygen in the seawater is decreasing so that the corrosion rate will be reduced. When the salinity is less than the natural sea, the influence of electrical conductivity is dominated. When the salinity exceeds the natural sea water salinity, the increase of salinity causes the decrease of oxygen content to exceed the increase of electrical conductivity. In this case, the corrosion rate decreases with the increase of salinity.

The relation between the corrosion rate correction factors for salinity and salinity ratio, based on the results presented by Uhlig and Revie [42], can be modeled by a truncated log-normal function as

$$R(S) = \frac{\gamma}{\varepsilon\sqrt{2\pi}(S+\delta)} \exp\left[-\frac{\left(\ln(S+\delta)-\beta\right)^2}{2\varepsilon^2}\right]$$
(9)

In Eq. (9), R(S) is the corrosion rate correction factor for salinity (corrosion rate at actual salinity / corrosion rate at nominal conditions), S is the salinity ratio (actual salinity / nominal salinity). γ is a constant introduced as a magnification factor to adjust the values of the corrosion rate correction factor ($\gamma \ge 0$). δ is a constant introduced to adjust the truncated portion ($\delta \ge 0$). β , and ε are constants corresponding to mean value and standard deviation of the distribution. It must be stressed that this function has been chosen just to represent the form of the curve and not as a probability density function.

3.2. Temperature

Temperature is also an important parameter in seawater corrosion because it usually accelerates corrosion by increasing the temperature [43-45, 50]. However, as the temperature rises, the solubility of oxygen decreases, which also weakens the temperature effect [48].

Based on the experimental evidence, a correlation factor is proposed to adjust for the effect of temperature. It is assumed that corrosion rate is a linear function of temperature for seawater temperatures below 80 \mathbb{C}

$$R(T) = cT + d \tag{10}$$

In Eq. (10), R(T) is the corrosion rate correction factor for temperature (corrosion rate at actual temperature / corrosion rate at nominal conditions), T is the temperature ratio (actual temperature / nominal temperature), c is the constant representing the slope of the R(T)-T relationship and d is the constant represents the R(T) value at zero T.

3.3. Dissolved oxygen

Because the corrosion of most metals in seawater is oxygen depolarization corrosion, the content of dissolved oxygen in seawater is an important factor affecting the corrosivity of seawater. The solubility of oxygen in sea water mainly depends on the salinity and temperature of the sea water. With the increase of salinity or temperature, the solubility of oxygen is reduced [45].

Melchers [46] has shown that there is a linear relationship between dissolved oxygen and rate of corrosion. Fontana [43] has proposed a schematic diagram showing the effect of oxygen and oxidizers on the corrosion rate.

Based on the mentioned results, the relation between the corrosion rate correction factor for dissolved oxygen and the dissolved oxygen concentration ratio is proposed as a linear relationship:

$$R(O) = aO + b \tag{11}$$

In Eq. (11), where R(O) is the corrosion rate correction factor for dissolved oxygen concentration (corrosion rate at actual oxygen concentration / corrosion rate at nominal conditions), O is the dissolved oxygen concentration ratio (actual oxygen concentration / nominal oxygen)

concentration), *a* is a constant representing the slope of the R(O)-O relationship and *b* is a constant representing the corrosion rate correction factor R(O) at zero O.

3.4. pH

In the range of near neutral pH, the corrosion rate of metals decreases with the increase of pH. After the reduction of pH, the corrosion rate of metals increased significantly, which is not only due to the increase of hydrogen evolution, but also the metal surface dissolved by the surface oxide film has greater affinity for oxygen and is conducive to the depolarization of oxygen. However, the pH of seawater is always stabilized at 7.6 to 8.3. That is to say, the difference of corrosion rate in this range is very small.

A relation between corrosion rate and pH can be derived [37, 48] as

$$R(pH) = k \cdot 10^{-(n \cdot pH)} \tag{12}$$

In Eq. (12), R(pH) is corrosion rate correction factor for Ph (corrosion rate at actual Ph / corrosion rate at nominal conditions). k and n are constants.

3.5. Water velocity

Flowing water can result in an increase in the amount of dissolved oxygen that reaches the material surface. Meanwhile, flowing water can remove protective films over the material surface. Higher velocity of seawater particles will lead to an increase in corrosion rate. The corrosion rate may double when water moves at 1m/s [47].

These results suggest that the relation between the corrosion rate correction factor for velocity and velocity ratio can be modeled as an exponential relation:

$$R(v) = \lambda \left(1 - e^{-\eta(v+\theta)} \right)$$
(13)

In Eq. (13), R(v) is the corrosion rate correction factor for velocity, v is the flow velocity ratio,

 λ is a magnification factor to adjust the value of the corrosion rate correction factor ($\lambda \ge 0$), θ is a constant introduced to adjust the truncated portion from the distribution ($\theta \ge 0$) and η is a factor to adjust the curvature and the slop of the curve ($\eta \ge 0$).

3.6. Discussion

The marine environmental factors that mentioned above do not vary independently and they have a strong correlation. For instance, temperature can make great difference to other parameters and the increase of dissolved oxygen can rise the ORP. Therefore, it is difficult to analyze the marine environment factors and the correlation of corrosion rate.

Generally, temperature is the independent variable which is not changed by other factors. Except salinity, pH, dissolved oxygen and ORP are affected with temperature variation. In addition, dissolved oxygen is negatively correlated with temperature and salinity. And temperature, dissolved oxygen and pH have varying degrees of effect on ORP.

4. Conclusions

This paper presented a review of the influential environmental factors on atmospheric and marine corrosion processes and the accelerating models. Relative humidity, temperature, sulfur dioxide, and chloride are the major influential factors to atmospheric corrosion while in marine environment, the factors include salinity, temperature, dissolved dioxide, pH, oxidation reduction potential and water velocity. Generally, the change of these factors would change the corrosion rate. However, the

accelerating effects are different for each environmental factors. Interactive effects exist between these factors and the mechanisms are complicated. Care should been taken when these models are applied in practice for different materials and in different environments.

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