Introduction to atmospheric corrosion research in China

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Received 8 July 2007; received in revised form 31 July 2007; accepted 31 August 2007
Available online 9 November 2007

Abstract
In this paper, we introduce the research on atmospheric corrosion in China. We describe the climate characteristics and the classification of atmospheric corrosivity across the whole country. We also describe the rusting evolution under simulated wet/dry cyclic conditions.

Keywords: Atmospheric corrosion; Corrosivity; Rusting evolution

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1. Introduction

The corrosion of metals exposed to the atmosphere is governed by the interplay of the resistance of the metal to corrosion and the corrosivity of the aqueous electrolyte on substances on the material surface [1]. The atmospheric corrosion of metals is usually electrochemical, involving the anodic dissolution of the metal, the cathodic reduction of an oxidant, such as oxygen or γ-FeOOH, and the transport of reactants and products to and from the surface [1–5].

In general, the surface aqueous electrolyte induces two effects, resulting in the atmospheric corrosion of a metal: (1) it connects anodic and cathodic areas to form an electrochemical circuit with electronic conduction in the solid state and (2) it is involved in the breakdown of the normally protective oxide film (passive film) and the deposition and reaction of corrosive gases on the metal. The corrosivity of trace gases such as SO2 is therefore often connected with the formation of an aqueous electrolyte on the material surface. Some other corrosive trace components, such as H+ from acidic rain, may replace oxygen as the oxidizing agent of the metal, while others, such as NaCl, tend to facilitate the dissolution of the metal. However, the resistance to atmospheric corrosion is mainly governed by the chemical activity of the metal itself and the
chemical stability of its corrosion products formed on the surface. For instance, aluminum is easily corroded because of its high chemical activity. However, the corrosion product of aluminum, alumina, is stable because of its chemical inertia. This means that aluminum is a good engineering material with high corrosion resistance. In addition, alloying elements may have a significant effect on improving the corrosion resistivity of the products formed on the metal. For example, the alloying of nickel and copper in weathering steel [6,7] may strengthen the rust structure and increase the resistance to atmospheric corrosion [8,9].

Atmospheric corrosion may cause serious damage to metallic structures and equipments. The effect is so serious that the annual cost of atmospheric corrosion is approximately half the total annual cost of all types of corrosion of metals [10]. Corrosion scientists and engineers of many countries have carried out numerous investigations on atmospheric corrosion [10–15]. In past decades, atmospheric corrosion research was mainly dominated by field studies comparing the resistance to corrosion of different materials [16–18], the corrosivity of different environments [19–24] and on empirical correlations between corrosion rate and environmental parameters [25–29]. A few studies addressed the processes occurring on the material surface that cause corrosion [30–36].

China started to establish atmospheric corrosion test stations at the end of the 1950s. Since then, 13 national atmospheric corrosion test stations have been successfully established, the sites of which are selected as being typical examples of urban, rural, coastal and industrialized environments, and some valuable results have been obtained [37]. Recently, a few simulative studies addressing the processes occurring on the material surface that cause atmospheric corrosion have been carried out, and the mechanism of the rusting process of mild and low-alloy steel was proposed [38,39]. This paper will concentrate mainly on the results of the field corrosion investigations and simulative corrosion studies of iron and steel, with references to other metals when necessary.

2. Field studies of atmospheric corrosion in China

2.1. Climate characteristics and the National Corrosion Survey Organization of China [40–44]

There are seven types of climate in China (Fig. 1). The eastern part mainly has the East Asian monsoon climate, which is warm and humid with high rainfall. However, the northwest part has a typical inland arid climate. The northern part includes frigid and frigid temperate zones. The south includes a warm temperate zone, a humid subtropical zone and a humid tropical zone. Most of the country is in the frigid temperate zone, warm temperate zone, or humid subtropical zone. The industrial development of the eastern region has resulted in serious atmospheric contamination, while the tableland in the western part is exposed to strong ultraviolet radiation and frequent sandstorms. Close to Qianghai Lake, the sand contains a lot of salt [45]. Because of the big differences in the climate and concentrations of corrosive substances in the atmosphere across the country, the corrosion rate of materials is strongly dependent on the site where the materials are located.

Since the late 1950s, under the joint leadership of the Ministry of Science and Technology (MOST) and the National Natural Science Foundation of China (NSFC), China has successfully built up the National Network for the Atmospheric Corrosion Survey of Materials (NACSM) and 13 test stations have been built across the country (Fig. 1). Among these sites, five stations were built in the 1950s, three in the 1970s, three in the 1990s and three after 2000. The sites cover the seven types of climate and represent the four atmospheric environments of urban, rural, coastal and industrialized areas. Information on these sites is given in Table 1.

2.2. Classification of atmospheric corrosivity in China

A classification of the corrosivity of the atmosphere based on surveys of time of wetness, temperature and contamination (ISO9223) at seven sites in eastern China is given in Table 2 [11,37,46–52]. It is possible to place each of these sites into one of the five categories of corrosivity. Table 2 shows that the atmosphere at the listed sites has corrosivity levels of 3 or 4.

In addition to the classification based on the surveys of wetting time, temperature and contamination (ISO9223), the corrosivity of the atmosphere was classified into seven categories on the basis of a number of surveys of the rate of corrosion of a standard specimen (ISO9223), as shown in Table 3. In the table, a category lower than C1 and a category higher than C5 have been added, and the average corrosion rate over a 10-year exposure test was used instead of the 1-year test in ISO9223. To allow a
comparison with ISO9223, we also adjusted the scale of the corrosion rate corresponding to each category in Table 3, which was different from the standard data listed in ISO9223. A number of surveys to determine the corrosion rate at various sites in China made it possible to place each of these sites into one of the seven categories. Referring to the corrosion rate of A3 mild steel, Table 4 shows that the atmosphere at the listed sites generally has corrosivity levels of 3 or 4. The category of atmospheric corrosivity is related to not only the environment but also the material and exposure period. Table 4 shows that the category for mild steel is generally different from those for zinc, copper and aluminum throughout the sites. Comparing the corrosion rate for the 1st year with the average rate over

### Table 1
The 13 NASCM test sites

| Station | Year built | Geographical position | Altitude (m) | Climate type | Average T (°C) | Radiation time (h/a) | Rainfall (mm/a) | RH (%) |
|---------|------------|-----------------------|--------------|--------------|----------------|----------------------|----------------|--------|
| Mohe    | 1991       | 122°23'01"           | 53°01'01"   | Rural frigid temperate | -3.5          | 2317.9               | 236.7          | 69.2   |
| Shenyang| 1991       | 123°26'01"           | 41°46'01"   | Urban frigid temperate  | 9.4           | 2279.3               | 408.5          | 66     |
| Beijing | 1957       | 116°16'06"           | 36°06'06"   | Urban warm temperate   | 11.9          | 2559.3               | 586.0          | 57     |
| Dunhuang| 2002       | 94°41'09"            | 40°09'09"   | Rural arid tropical    | 10.8          | 3257.8               | 35.0           | 45     |
| Qingdao | 1976       | 120°25'38"           | 30°38'38"   | Rural frigid temperate  | 11.1          | 3050.9               | 48.9           |        |
| Wuhan   | 1958       | 114°04'19"           | 29°19'19"   | Urban humid subtropical| 12.3          | 1944.0               | 561.7          | 71     |
| Jiangjin| 1974       | 106°17'23"           | 23°08'02"   | Industrial humid subtropical| 17.9          | 1317.0               | 1202.9         | 81     |
| Lhasa   | 2002       | 91°08'29"            | 29°40'29"   | Tableland frigid temperate| 9             | 3053.1               | 580.9          | 46     |
| Guangzhou| 1956     | 113°17'11°           | 113°17'11°  | Urban humid subtropical| 22.7          | 1607.0               | 1562.7         | 77     |
| Qionghai| 1956       | 110°05'19"           | 19°02'19"   | Rural humid tropical   | 24.3          | 2072.0               | 1794.0         | 86     |
| Wanning | 1974       | 110°05'18°           | 18°58'18°   | Coastal humid tropical | 24.2          | 2026.5               | 1515.0         | 86     |
| Xishuangbanna | 1958 | 100°40'21"          | 21°35'21"   | Rural tropical         | 21.6          | 1716                 | 1713           | 83     |

### Table 2
Corrosivity classification based on time of wetness, temperature and contamination for seven NACSM test stations (ISO9223)

| Station | Cl/C0 | SO2 | Time of wetness | Corrosivity categories | Environmental characteristic |
|---------|-------|-----|----------------|------------------------|-----------------------------|
| Beijing | 0.049 | S1  | 0.442          | P2                     | 2358                        | T3                          | 3 or 4 | Urban |
| Qingdao | 0.25  | S1  | 0.704          | P2                     | 4049                        | T4                          | 4      | Coastal |
| Wuhan   | 0.011 | S0  | 0.272          | P1                     | 4871                        | T4                          | 3      | Urban |
| Jiangjin| 0.006 | S0  | 0.667          | P2                     | 5304                        | T4                          | 4      | Industrial |
| Guangzhou| 0.024 | S0  | 0.107          | P1                     | 5048                        | T4                          | 3      | Urban |
| Qionghai| 0.199 | S1  | 0.15           | P1                     | 6314                        | T5                          | 3 or 4 | Rural |
| Wanning | 0.387 | S1  | 0.06           | P0                     | 6736                        | T5                          | 3 or 4 | Coastal |

### Table 3
Atmospheric corrosivity classification based on surveys of the corrosion rate at various sites in China

| Level | Atmospheric corrosivity | Calculated corrosivity | Average corrosion rate (µm/a, 10 years) |
|-------|-------------------------|------------------------|-----------------------------------------|
|       | A3                      | Low-alloy steel        | Zn                                      | Cu                                      | Al                                      |
| 1     | C0                      | Lowest                 | <1                                      | <0.1                                    | <0.05                                   | <0.005                                 | <0.002                                 |
| 2     | C1                      | Very low               | 1–10                                    | 0.1–0.5                                 | 0.05–0.1                                | 0.005–0.01                             | 0.002–0.01                             |
| 3     | C2                      | Low                    | 10–50                                   | 0.5–5                                   | 0.1–0.5                                 | 0.01–0.1                               | 0.01–0.05                              |
| 4     | C3                      | Middle                 | 50–150                                  | 5–12                                    | 0.5–2                                   | 0.1–1.5                                | 0.025–0.2                              |
| 5     | C4                      | High                   | 150–250                                 | 12–30                                   | 2–4                                     | 1.5–3                                  | 0.2–1                                  |
| 6     | C5                      | Very high              | 250–350                                 | 30–100                                  | 4–10                                    | 3–5                                    | 1–3                                    |
| 7     | C6                      | Highest                | >350                                    | >100                                    | >10                                     | >5                                     | >3                                     |
the time of wetness is lower than those of Wanning and Qionghai, \( n \) is less than 1 for both mild and Corten-A steels. Comparing the data on the mdd of chloride ions and SO\(_2\) listed in Table 2, it can be concluded that SO\(_2\) has a significant effect on the values of \( A \) and \( n \). The most typical sites are Jiangjin and Qingdao. In Jiangjin, where the mdd of SO\(_2\) is 0.667 and that of Cl\(^-\) is very low, \( n \) is 0.45. In Qingdao, where the mdd of SO\(_2\) is 0.704 and that of Cl\(^-\) is 0.25, \( n \) is 0.57. The higher value of \( n \) for Qingdao is caused by the interaction of Cl\(^-\) and SO\(_2\) in the corrosion process of steel. Because the time of wetness in Qingdao is shorter than that of Jiangjin, \( A \) for Qingdao is smaller. Data for Corten-A steel exposed to the atmosphere at Qingdao and Jiangjin shows a pattern similar to that for mild steel.

### 3. Study on rusting evolution of mild steel in a simulated atmospheric environment [38–39,62]

The field investigation of atmospheric corrosion provides actual information on the corrosion of materials; thus, it is the most important method of evaluating atmospheric corrosion. However, it usually takes about 10–20 years for one evaluation period, which makes it difficult to determine the rusting evolution induced atmospheric corrosion and to evaluate new materials designed to resist atmospheric corrosion. In previous studies, simulative experiments enabling the acceleration of corrosion have been developed. Complex cyclic corrosion tests (CCTs) based on saltwater spray followed by drying have been widely used to accelerate the corrosion of coated and noncoated steels. Such tests have been also adopted in several standards. The rusting of steel in the atmosphere includes many reaction steps at different corrosion stages. In the initial stage, the anodic dissolution of steel and the cathodic reduction of oxygen dominate the corrosion. Then, the dissolved ferrous ions are hydrolyzed into a deposit of Fe(OH)\(_2\). During the drying of the aqueous film, Fe(OH)\(_2\) is oxidized into a colloid deposit of Fe(OH)\(_3\), which can transform into an amorphous deposit of FeOOH on the dry surface of steel. The accumulated deposit on the steel surface blocks the transmission of oxygen to the steel surface. Then, the cathodic reduction is dominated by the reduction of FeOOH, and the reductive product is Fe\(_3\)O\(_4\). Meanwhile, the crystallization of the amorphous FeOOH is inhibited with the development of atmospheric corrosion, \( x \)-FeOOH, \( \beta \)-FeOOH, \( \gamma \)-FeOOH and magnetite are the main components of steel rust. The structural evolution of the rust layer of mild steel has been proposed by Dong et al. [38,39]. Using an accelerated CCT proposed by Nishimura et al. [62], the weight gain of rust on mild steel with increasing number of wet/dry cycles was determined; the results are shown in Fig. 2(a). The simulated result shows that the rusting process includes two stages, and the transition is at approximately 30 cycles. Fig. 2b shows that the rate of rust formation increases with increasing number of wet/dry cycles in the first stage but decreases after the transition. It was shown by XRD analysis that the initial rust included a large amount of amorphous

### 2.3. Atmospheric corrosion law for mild steel and weathering steel [11,26,53–61]

On the basis of the regression analysis of the atmospheric corrosion data measured at the test sites, the rusting evolution of metal satisfies the exponential equation:

\[
D = A \cdot t^n,
\]

where \( D \) is the corrosion depth, \( t \) is the exposure time of the specimen, and \( A \) and \( n \) are constants. \( A \) represents the corrosion rate of the first year and \( n \) represents the propensity of corrosion. Table 5 lists some simulative data for mild steel and weathering steel collected at various test sites in eastern China. At Qionghai and Wanning, which are located on Hainan island, \( n \) is higher than 1 for mild steel but less than 0.5 for Corten-A steel. Even though Wanning and Qionghai have almost the same humidity and temperature, the mdd (mg dm\(^{-2}\) day\(^{-1}\)) of chloride ions in Wanning is higher than that in Qionghai; thus, the values of both \( A \) and \( n \) in Wanning are higher than those in Qionghai. In the other stations listed in Table 5, because
FeOOH with exiguous $\alpha$-FeOOH and $\beta$-FeOOH. After the transition, $\gamma$-FeOOH and magnetite appear as the intergrowth in the rust. Fig. 3 shows the micromorphology evolution during the rusting of mild steel. It shows that the initial rust layer has low density but it transforms into a dense layer after the transition. A flow chart of the rusting evolution of mild steel under wet/dry cyclic corrosion conditions is shown in Fig. 4.

4. Summary

1. In this paper, we have briefly discussed the classification of the atmospheric corrosivity in the eastern region of China. The results show that the atmospheric corrosivity in the eastern region is moderate to severe, with a high incidence of rusting and corrosion. The classification is based on the corrosion rate and the weight gain of mild steel.

Fig. 2. Result of corrosion acceleration test for mild steel with 0.3% NaCl solution: (a) weight gain and (b) corrosion rate.

Fig. 3. Micromorphology evolution of the rust layer with increasing number of wet/dry cycles.

Fig. 4. Flow chart of the rusting evolution of mild steel under wet/dry cyclic-corrosion conditions.
China. The NASCM has set up a database containing a substantial amount of data from the test sites located in the eastern region. With the rapid development of the economy of China, the NASCM will collect atmospheric corrosion data from the other stations located in the north and west to extend the database, which will be used in conjunction with future construction projects.

2. The rusting evolution of mild steel in a simulated coastal atmospheric environment was discussed. The rusting process includes two stages. The corrosion rate increases with time in the initial stage, during which the rust consists of a large amount of amorphous FeOOH with exiguous crystallized α-FeOOH and β-FeOOH in a low-density layer. However, the corrosion rate decreases with time in the subsequent stage, and the rust forms a high-density layer of γ-FeOOH and magnetite.

Acknowledgement

The work is funded by NSFC Projects 5049336 and 973 plan 2004CB619101. The authors acknowledge the assistance.

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